On the Synthesis of New Alkoxide and Aryloxide Clusters with Alkali, Alkaline Earth and Lanthanide Metal Ions

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William MAUDEZ

aus Paimpol, France

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Auf Antrag von

Prof. Dr. Katharina M. FROMM
Prof. Dr. Dietmar STALKE

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Prof. Dr. Hans-Jakob Wirz

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Abstract

This thesis reports some new crystal structures of alkali, alkaline earth and lanthanide metals ions in non polar aprotic solvents. First, structures of some compounds which have been used as starting materials are described. Then, this thesis reports crystal structure of cluster compounds obtained during this work using alkoxide and/or aryloxide reagents. A particular interest is related on the similar chemical behavior of alkaline earth and lanthanide(II) metal ions in non polar aprotic solvents, both in terms of starting material and cluster compounds.

Chapter A gives a brief introduction to superconductor materials and the different strategies employed in order to obtain good precursors with a particular interest on the group 1 and 2 alkoxide and aryloxide compounds reported in the literature. Chapter A also presents the general synthetic procedure used in this work.

Chapter B described the different alkali, alkaline earth and lanthanide compounds obtained during this PhD.

In a first part, it shows the importance of the coordination sphere of the alkaline earth starting materials on its reactivity. It also presents the similar chemical behavior observed between alkaline earth and lanthanide(II) metal ions in non polar aprotic solvents.

In a second part, this chapter presents some new homometallic alkali metal clusters with aryloxide ligands.

Finally some new homo and heterometallic cluster compounds are presented, highlighting the importance of the alkali earth metal, the R-group of the “alkoxide” reagents, the alkali metal and the solvent on the crystal structure of the final compounds.

Chapter C summarizes related work and put some fundamental questions. It gives the conclusion to this work and a general overview of the complexes synthesised in this thesis.

Some of these results have been reported in these publications:

- Maudez W., Vig-Slenters T., Mirolo L., Fleury A., Fromm K. M., *Main Group Chemistry*, **2006**, *5*, 41-49.

- Maudez W., Häussinger D, Fromm K. M., *Zeitschrift für anorganische und allgemeine Chemie*, **2006**, *632*, 2295-2298.

- Fromm K. M., Gueneau E. D., Robin A. Y., Maudez W., Sague J., Bergougnant R., *Zeitschrift für anorganische und allgemeine Chemie*, **2005**, *631*, 1725-1740.

- Fromm K. M., Maudez W., *European Journal of Inorganic Chemistry*, **2003**, 3440-3444.

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A - Introduction

A - I - General overview on alkali/alkaline earth metal ions

Alkali and alkaline earth metal cations form the s-block elements of the periodic table where they belong to the groups 1 and 2 respectively. They play an important role in nature, for instance alkali cations Li^+, Na^+ and K^+ have very specific functions such as the regulation of the ionic equilibrium of living cells in our body. Alkaline earth cations also have a contribution in our body, for instance calcium is the most important constituent of our organism.

They above all and always find applications in man-made materials in a wide spread of fields: catalysts, ferroelectrics, metallic conductors and superconductor materials. The latter example, superconductivity, is one of the last great frontiers of scientific discovery since its discovery in 1911 by Onnes H. K. (Nobel prize in Physics in 1913). When he cooled mercury to the temperature of liquid helium (4K), its resistance suddenly disappeared. The concept of superconductivity “was born”.

More importantly, today, not only have the limits of superconductivity not been reached, but the theories that explain superconductor behaviour seem to be constantly under review.

The middle of the 80’s was significant with the discovery of the high T_c superconductors by Bednorz J. G. and Müller A. (Nobel prize in Physics in 1987) with the synthesis of $La_{1.85}Ba_{0.15}CuO_4$ (T_c = 30 K), the first ceramic superconducting copper-oxides (cuprates). Later, by simple substitution of yttrium for lanthanum, Wu M.-K. and his graduate students reported the famous $YBa_2Cu_3O_7$ with an incredible T_c at 92 K.

The rapid succession of new high temperature superconducting materials discovered by these groups ushered in a new era in Material Science and Chemistry.

The term “high T_c” is generally used to define cuprate-perovskite ceramic materials or, in a more general way, type-II superconductors.

The current class (or "system") of ceramic superconductors with the highest transition temperatures are the mercuric-cuprates. The first synthesis of one of these compounds was achieved in 1993 by Onbasli U. and the team of Schilling A., Cantoni M., Guo J. D. and Ott H. R. The T_c record is now held by a thallium-doped, mercuric-cuprate $(Hg_{0.8}Tl_{0.2})Ba_2Ca_2Cu_3O_{8.33}$ with a T_c at 138K.

$YBa_2Cu_3O_7$ was first synthesized by mixing the metal carbonate precursors together and reacting them at temperatures between 1000 K to 1300 K, following the reaction scheme [1]:

$$4\ BaCO_3 + Y_2(CO_3)_3 + 6\ CuCO_3 \rightarrow 2\ YBa_2Cu_3O_{7-x} + 13\ CO_2$$

Unfortunately, the high temperature synthesis of such oxide materials required in the classical solid state synthesis is generally more complicated for s-block elements due to the ionic character of their oxides, and the hygroscopy of the compounds. In addition to being sensitive to the amount of oxygen, special care must be taken to sinter $YBa_2Cu_3O_7$. Numerous other methods more flexible to synthesize $YBa_2Cu_3O_7$ have been developed since its discovery by Wu and his coworkers, such as Chemical Vapor Deposition (CVD), sol-gel and aerosol processes [2, 3].

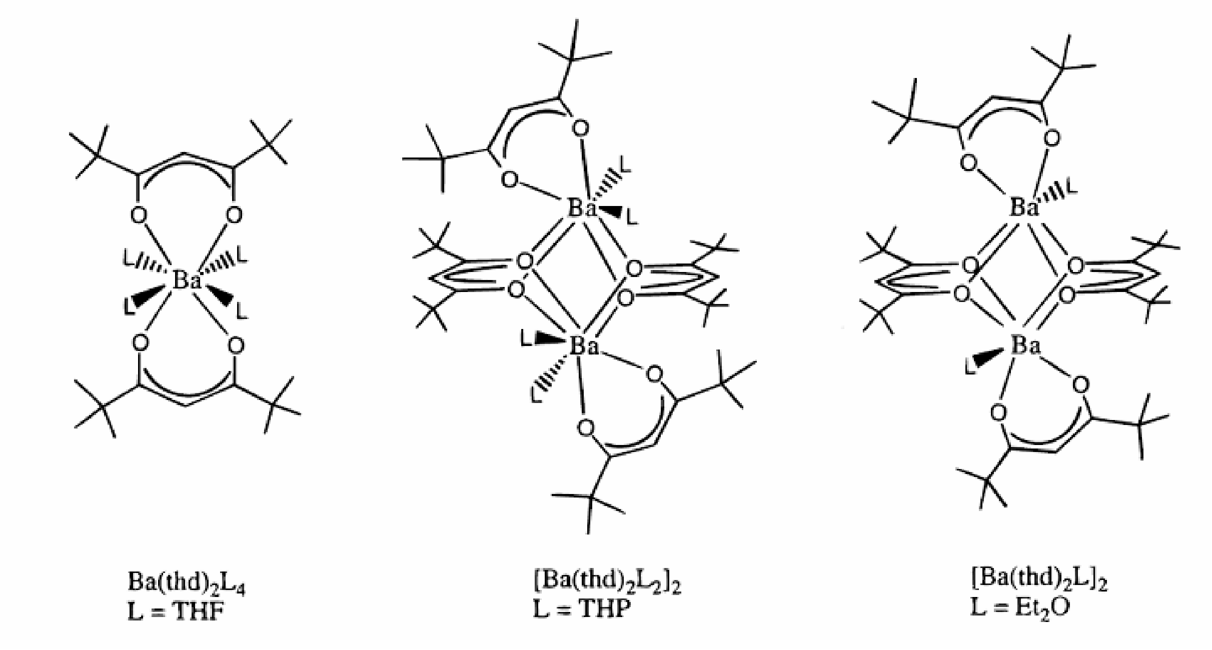
These techniques are now currently used for the preparation of oxide-ceramic systems. Nevertheless, they require molecular compounds including clusters in order to expect some volatility for MOCVD or/and solubility for sol-gel processes to generate the corresponding oxides. This lead to an unprecedented search for soluble and volatile alkaline earth metal derivatives, alkaline earth metal complexes being in a general way less soluble, volatile and thermally stable than the copper and rare earth metal precursors. Alkaline earth metals are hard cations (according the HSAB theory [4-8]). From the coordination point of view that means that they prefer hard donating atoms like oxygen. Thus, two principal kinds of O-donor ligands are in the focus of the recent development of “organometallic” compounds of s-block elements, namely β-diketonates and the organo-alkali compounds, alkoxides/aryloxides.

A - II - Strategy: O-donor ligands

A - II.1 - β-diketonates

In the quest of the “perfect” alkaline earth metal compounds for the MOCVD process, sterically encumbered multidentate ligands, such as β-diketonates, are known to be very useful [9]. In the past, however, the synthesis of homoleptic strontium and barium β-diketonates has created innumerable difficulties for scientists over a considerable period of time due to their sensitivity toward humidity and O_2 and their susceptibility to incorporate coordinating solvent (poorly reproducible stoichiometries), their tendency to decompose (poor thermal stability) and more, the MOCVD sources have proven to be little volatile.

For instance, the 2,2,6,6-tetramethyl-3,5-heptanedionate (tmhd or thd) β-diketonate ligand has been intensively studied with the group 2 metals and has shown a number of adducts with different degrees of oligomerization depending on the experimental conditions [10-15]. Some examples are presented in Figure 1.



$Ba(thd)_2L_4$
L = THF

$[Ba(thd)_2L_2]_2$
L = THP

$[Ba(thd)_2L]_2$
$L = Et_2O$

Figure 1. Some species observed for the Ba - tmhd system

To date, the best β-diketonate precursors are $[M(tmhd)_2(thf)_4]$ M = Sr, Ba (Figure 1on the left) which have a very low melting point ($[Sr(tmhd)_2(thf)_4]$ = 30°C, $[Ba(tmhd)_2(thf)_4]$ = 25°C) [14]. Such source reagent complexes of Ba and Sr are usefully employed in CVD in the formation of barium strontium titanate and other group 2 thin films [16-18].

Moreover, in a general way, fluorinated β-diketonate ligands are known to exhibit better volatility and thermal stability [19] than non fluorinated compounds but, on the other hand, deposited films are typically contaminated by fluoride BaF_2 impurities [20-23].

A - II.2 - Alkali metal precursors

A - II.2.1 - Introduction

Historically, a great number of alkali metal clusters was merely discovered by serendipity as secondary products using superbases [24] or metallation agents [25] in organic synthesis. However, many of the structures as well as the formation mechanisms for these species remain to be investigated. The so far characterized clusters possess very interesting structures, such as tetramers, hexamers, nonamers or decamers, which might explain their reactivity. Indeed, larger aggregates seem to exhibit an enhanced reactivity compared to more simple compounds. Organo-lithium compounds show some typical properties known for covalent species: solubility in non-polar solvents and volatility. Thus, the lithium clusters were among the first discovered ones, as unexpected intermediates or secondary products during metallation reactions. Some of them are now used as reagents in organic synthesis and possess fascinating structures. They are known for their formation of aggregates in solution, the gas phase, and the solid state [26]. Small alkali metal cations have been found to form cage-structures, whereas clusters of the heavier homologues are almost unknown [27].

The reactivity of organometallic compounds MR in general can be increased considerably by addition of Lewis bases, such as amines or alkoxides M'OR'. This important effect is based on the formation of mixed aggregates of for instance [(MR)(M'OR')], yielding a ''superbase''. A better solubility in organic solvents is observed, which is reflected in higher reactivity as well. Since many of these compounds are air and/or moisture sensitive, the single-crystal structure resolution is usually delicate. However, the great interest in alkoxides and enolates of alkali metals pushed forward the investigations of these compounds.

A - II.2.2 - Alkoxides and aryloxides of group 1 metals

A - II.2.2.1 - Introduction

The use of alkali alkoxide or aryloxide reagents in organometallic synthesis often depends on their solubility, a property derived from their structure [28]. The regain in interest of alkali alkoxides and aryloxides also resides in the discovery of high temperature superconducting compounds which has generated a great interest in the formation of oxide materials and other ceramics. Whereas many "alkoxides" of yttrium [20, 29, 30] and copper [20, 29-36] are common precursors for oxide materials, relatively few "alkoxides" of alkaline earth metals are reported [37]. Moreover, the synthesis of heterobimetallic alkoxides has provided a facile route for obtaining soluble, volatile, and generally monomeric species of group 2 and 12 metals of which homometallic alkoxides are generally polymeric, insoluble, and non-volatile. These heterobimetallic complexes can thus serve as valuable precursors for making metal oxides under rather mild conditions as encountered by sol-gel methods or Chemical Vapor Deposition (CVD) [2, 3].

A - II.2.2.2 - General synthesis of [M(OR)]$_n$ reagents

Alkali alkoxides and aryloxides of the type $L_xM(OR)_y$; R = alkyl or aryl; L_x = neutral ligand; y = integers) are in most cases commercially available but may be synthesized mainly by at least eight different routes [38-40], of which the most relevant are listed below. These synthetic routes are in a general way also available for the synthesis of main-group metal alkoxides. The methods of preparation are often chosen as a function of the electronegativity of the metal [41-43].
This type of direct reactions is naturally more facile with highly electropositive species like alkali metals.

Reactions of metals and alcohols:

$M + ROH \rightarrow MOR + \frac{1}{2} H_2$

Reactions of metals hydrides with alcohols:

$MH + ROH \rightarrow MOR + H_2$

Metal-carbon bond cleavage reactions:

$^nBuLi + ROH \rightarrow LiOR + {}^nBuH$

Reactions of metal dialkyl amides with alcohols:

$M\{N(SiMe_3)_2\} + ROH \rightarrow MOR + HN(SiMe_3)_2$

The interest in these reactions clearly relies on the fact that the secondary product is volatile, allowing easy purification of the product.

Reactions of metal hydroxide with alcohols:

$$MOH + ROH \rightarrow MOR + H_2O$$

The water formed during this reaction has to be eliminated by azeotropic distillation, for instance with NaOH dissolved in a mixture of ethanol/benzene under reflux. The more acidic phenols allow formation of most group 1 phenoxides more readily by simple heating of the hydroxide in dried ethanol, followed by recrystallization.

A - II.2.3 - Structural varieties

Bradley and Mehrotra [38-40] have developed some principles in which metal alkoxides/aryloxides MOR may form “cage-compounds” if two conditions are satisfied: (1) the metal M should be low valent or should bear a low charge; (2) the substituent R should be bulky.

A simple definition of the term cage is:

> *“It is first of all a polycyclic compound that contains atoms connected with one another in such a way that an enclosed volume is created. In this volume no atom or atomic group needs to be situated, and often there is no place for even a hydrogen atom.”*
>
> Michael Veith [27]

The geometry of the structure is based on the difference of electronegativity between the metal and the oxygen atom (interaction M–O) associated with the bulkiness of the R group. The main driving force for aggregation in weakly polar donor solvents is the maximization of electrostatic interactions between the alkali metal cation and the alcoholate anion. For the lighter lithium cation, aggregation generally occurs at the expense of the solvation of the ions, the process being viewed as a competition between anions and solvent for the available coordinating sites. The first organo-alkali compounds that have been crystallographically characterized possess unsolvated structures; they were generally obtained as side-products in organic reactions, in which solvents are generally non-polar hydrocarbon, and in which the competition did not occur.

The progress made during the last 15 years in the single-crystal data acquisition allowed the screening of the structures of a large number of organometallic group 1 compounds. They show a variety of possible structure types, such as chains, ladders, cycles, cubanes, …etc (Figure 2) [40, 44].

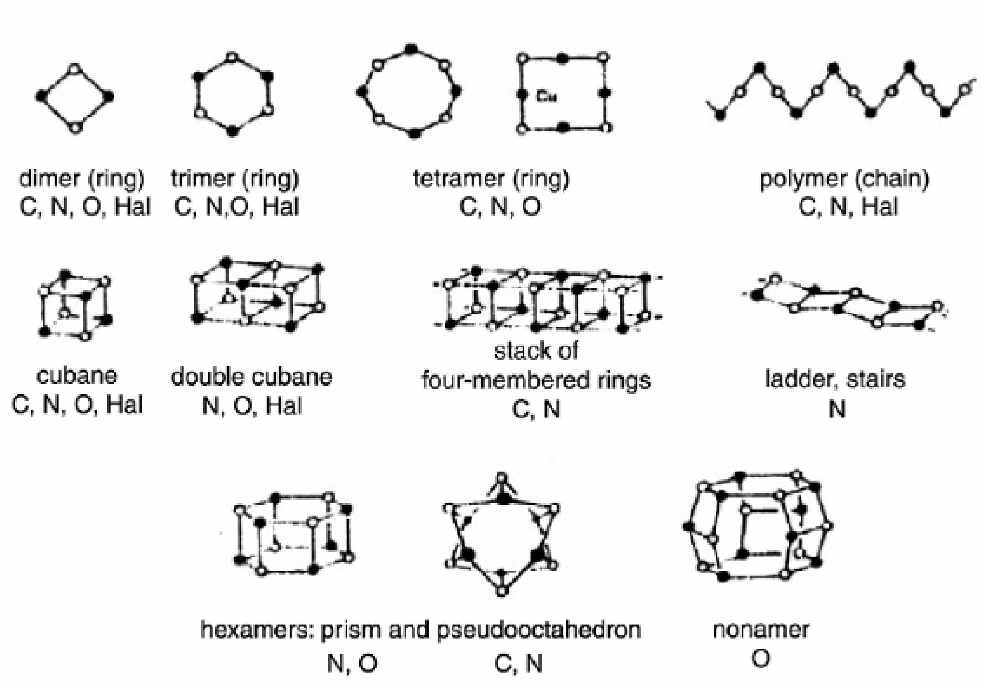


Figure 2. Important idealized coordination types for ion aggregates of the alkali metals (•) with C, N, O and the halogen anions (◦)

A - II.2.3.1 - Alkoxides of group 1 metals

Unsolvated group 1 methoxides (MOMe) and isopropyloxides (MO^iPr) (M = K-Cs) are polymeric [45-49]. From the literature data, only the lithium isopropyloxide derivative [50] possesses a non-polymeric structure, a $[LiO^iPr]_{11}$ aggregate, which is a very high degree of oligomerization. Due to their polymeric structures, these compounds are neither volatile nor soluble in organic solvents. With a more sterically demanding ligand such as *tert*-butyl, “all” alkali derivatives possess a molecular structure. The first ones to be discovered are the unsolvated $[MO^tBu]_4$ M = K-Cs [51, 52]. They are all tetrameric and build cubane structures (Figure 3), which can be interpreted as a stacking of two M_2O_2 entities in a ring.

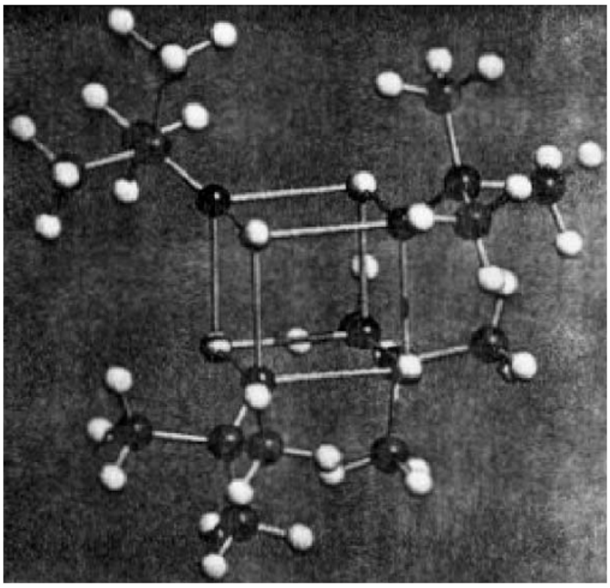


Figure 3. The cubane structure of [MO^{t}Bu]$_4$ M = K, Rb, Cs

Alkoxydes of the lighter alkali metals Li and Na present some unusual and different oligomeric structures.

For instance, the sodium *tert*-butoxide present a very interesting and surprisingly unsolvated structure with two different oligomeric species in its unit cell, one hexamer [NaO^{t}Bu]$_6$ and a much larger nonamer [NaO^{t}Bu]$_9$ [53-55] (Figure 4). The hexameric oligomer can be described as a stacking of three alternated M_2O_2 entities arranged to a ring and the nonamer as the fusion of three distorted M_3O_3 ladders connected with the outer atoms.

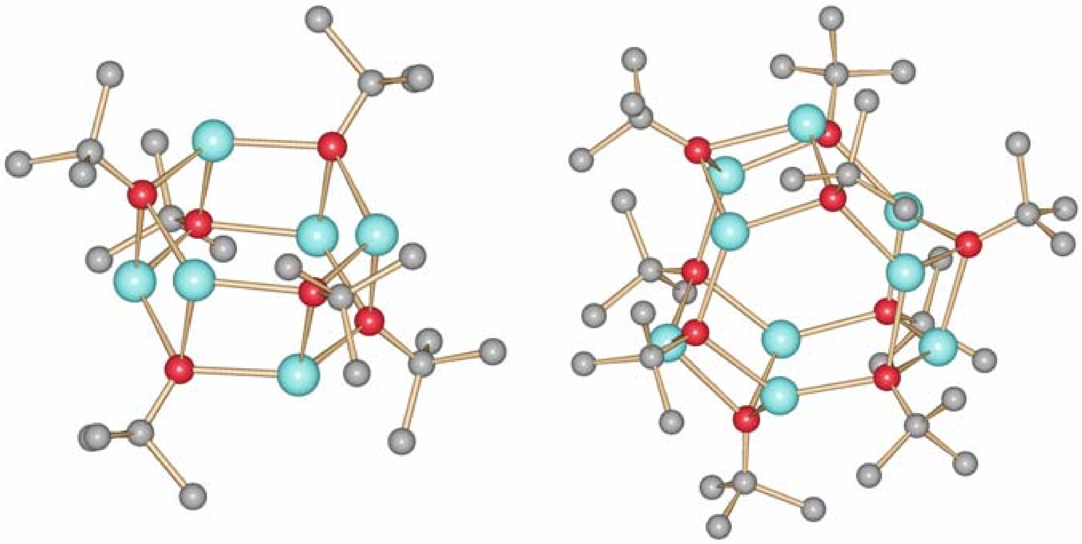


Figure 4. Schematic representation of the hexameric [NaO^{t}Bu]$_6$ (left) and nonameric [NaO^{t}Bu]$_9$ (right) species, H atoms have been omitted for clarity

The most widely used lithium *tert*-butoxide, as for itself, has posed a problem for chemist for almost 40 years. The compound was first confirmed to be hexameric in the gas phase as well as in solution [56-58]. It was only recently confirmed to be hexameric in the solid state by X-ray diffraction [55]. The structure of $[LiO^tBu]_6$ (Figure 5) shows a very high disorder of the *tert*-butyl groups and a total delocalization of the lithium atoms over the eight equivalent triangular faces of the octahedron, which allows to understand why the structure resolution was so difficult.

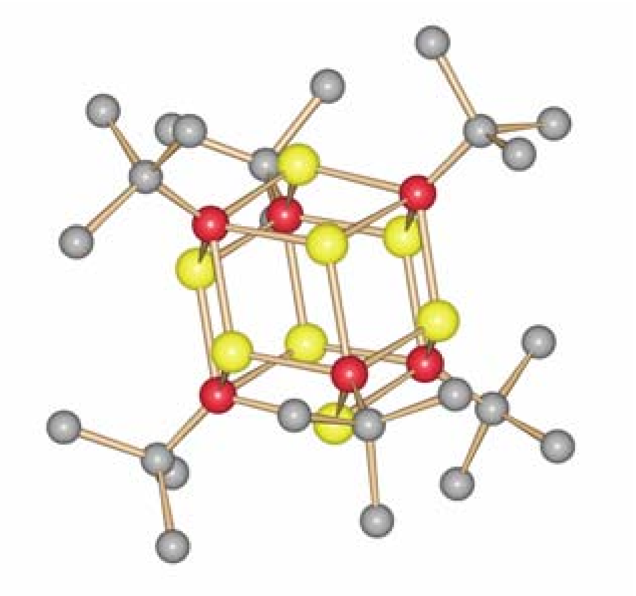


Figure 5. Schematic representation of the molecular structure of the hexameric $[LiO^tBu]_6$ species, H atoms have been omitted for clarity

Very recently, in 2004, an octameric form of lithium *tert*-butoxide was reported by Henderson *et al.* [59] (Figure 6). In contrast to the hexameric species, the $[LiO^tBu]_8$ species was easily obtained by simply cooling to -44°C of a ^tBuLi solution, the synthesis being reproducible. However, only by dissolving and recrystallizing this octameric form in toluene, the hexamer $[LiO^tBu]_6$ is obtained; this shows that the $[LiO^tBu]_8$ compound is a kinetically stable form of lithium *tert*-butoxyde $[LiO^tBu]_6$. The unusual structure can be interpreted as the fusion of one distorted cubane Li_4O_4 and one distorted hexamer Li_6O_6 sharing one Li_2O_2 face.

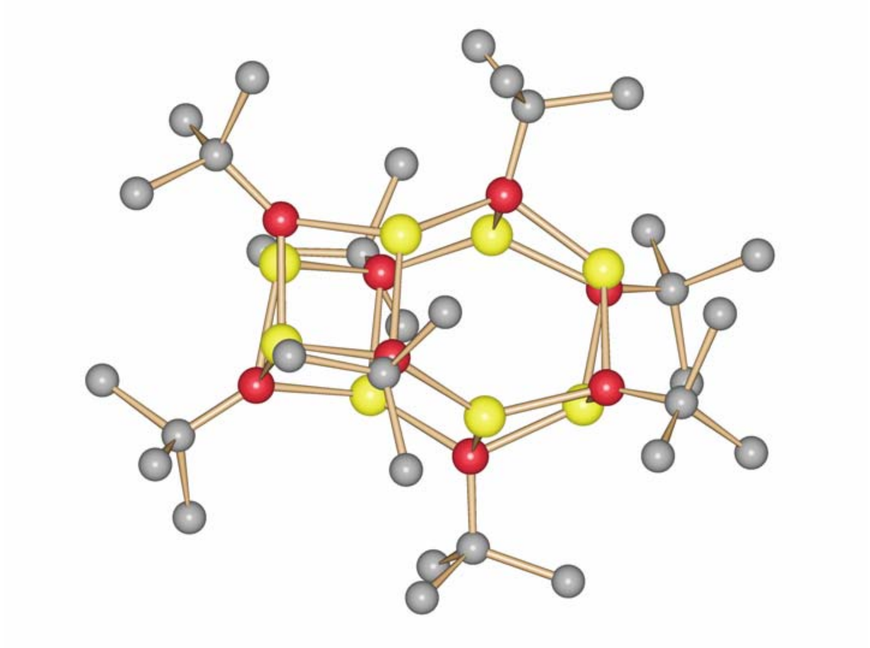


Figure 6. Schematic representation of the molecular structure of the octameric $[LiO^tBu]_8$ species, H atoms have been omitted for clarity

A - II.2.3.2 - Aryloxides of group 1 metals

Alkali aryloxides can easily be prepared in the same way with the methods cited before [60-64].

Aryloxide compounds have been less studied than alkoxide adducts for the synthesis of suitable metal-oxide precursors in MOCVD and sol-gel processes, especially for alkaline earth metals while they can offer an alternative in order to limit the formation of polymers as they are bulky ligands. In the case of aryloxide derivatives of the group 1 metals, a large number of lithium [62, 63, 65-85] and sodium [62, 67, 76, 84, 86-97] derivatives have been crystallographically characterized, fewer potassium derivatives are known [62, 64, 66, 86, 98, 99], and even less rubidium and cesium compounds are known [62, 66, 67, 100, 101]. As for alkoxide reagents, the degree of aggregation of aryloxide compounds depends on the steric demand of the aryloxide ligand and the alkali metal. The substitution in the ortho- (and also in meta-) position of the phenyl ring has shown a great influence in the overall structure of the alkali aryloxide compounds. In a general way, due to the important steric bulk of the alcoholate, oligomers usually observed are smaller than those observed with alkoxides; they are: dimers, trimers, tetramers and more rarely hexamers. Contrary to alkali alkoxides (which have been all characterized as unsolvated compounds), alkali aryloxide adducts are in most of case solvated and the nature as well as the Lewis-basicity of the solvent also show an important influence on the overall structure.

The lightest alkali metal unhindered phenoxide LiOPh, as for the *tert*-butoxide analogue, has also posed some problems to chemist this last decade. In 1991, Arnett and Moe [102] have established, using vapor osmometry, that lithium phenolate is tetrameric in THF at 37°C. However, until 2000, the only crystallographically characterized material presented a hexameric structure [69] (Figure 7) while the authors confirmed in the same time by ^{13}C and ^{7}Li NMR that the tetrameric form is the predominant species in the temperature range 30 to -70°C in THF. At temperatures below -70°C, new aggregates appear but can not be identified. The hexameric LiOPh described adopts two very similar structures, $[LiOPh(thf)]_6$ and $[(LiOPh(thf))_3]_2$, with only one hexamer respectively two independent trimers in their asymmetric unit. Only very small differences in the conformations of the phenyl and THF groups relative to the Li–O hexameric core are observed between these two structures.

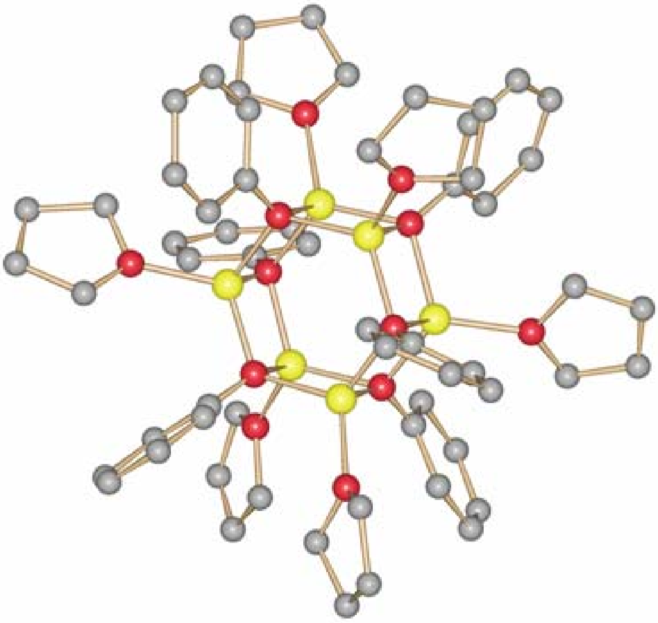


Figure 7. Schematic representation of the molecular structure of the hexameric $[LiOPh(thf)]_6$ species, H atoms have been omitted for clarity

In 2000, Boyle *et al.* [63] have reinvestigated the characterization of lithium aryloxide derivatives and have finally crystallographically characterized the tetrameric form of lithium phenolate $[LiOPh(thf)]_4$ (Figure 8).

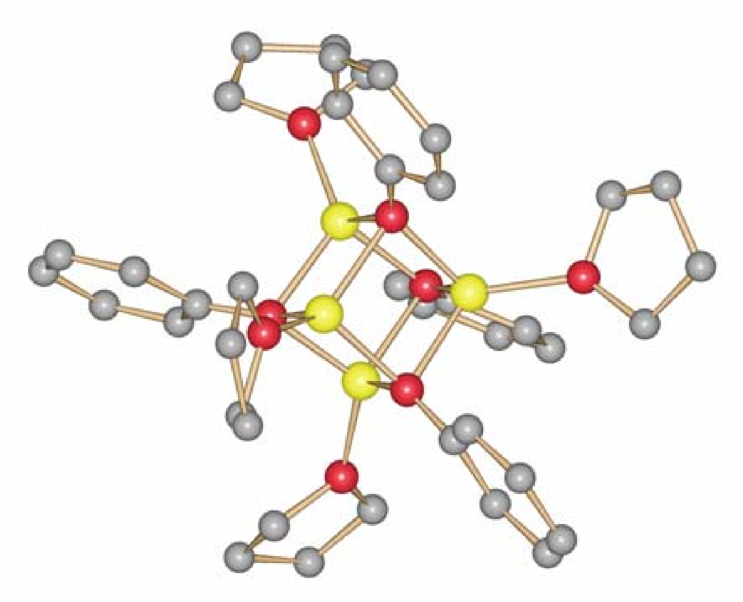


Figure 8. Schematic representation of the molecular structure of the tetrameric [LiOPh(thf)]$_4$ species, H atoms have been omitted for clarity

From the literature data, the sodium derivative possesses a polymeric structure [62, 91]. However, using THF as crystallization solvent, a hexameric structure [NaOPh(thf)]$_6$ is obtained which could be described, in this case, as two heterocubanes [NaOPh]$_4$ sharing a face [91] (Figure 9).

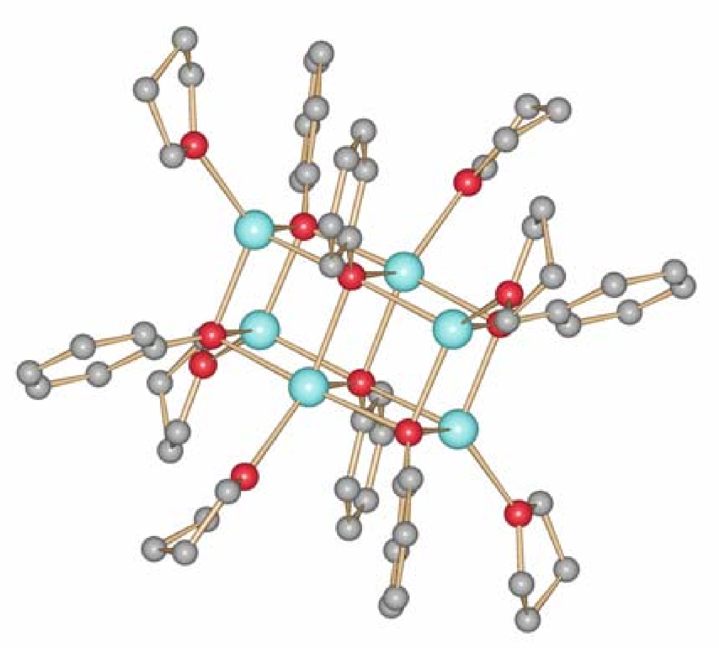


Figure 9. Schematic representation of the molecular structure of the hexameric [NaOPh(thf)]$_6$ species, H atoms have been omitted for clarity

In the literature data, only few K-, Rb-, Cs-derivatives have been crystallographically characterized. The heavier alkali unhindered phenolate compounds MOPh (M = K [62, 103, 104], Cs [62], Rb [62]) are isostructural and polymeric. Contrary to the lighter alkali phenolate compounds, they are unsolvated while the Cs and Rb phenolate derivatives were synthesized in presence of THF. For potassium, three different derivatives of formula KOPh.nPhOH n = 0, 2, 3 can be obtained; residual phenol molecules might be included in the structure. Whereas the KOPh.nPhOH compounds (n = 2, 3) present clearly structures in which π-interactions between the aryl rings of the OPh groups and the neighbouring potassium atoms are found (Figure 10), these π-interactions are less evident in the structures of the MOPh M = K, Rb, Cs derivatives (Figure 11).

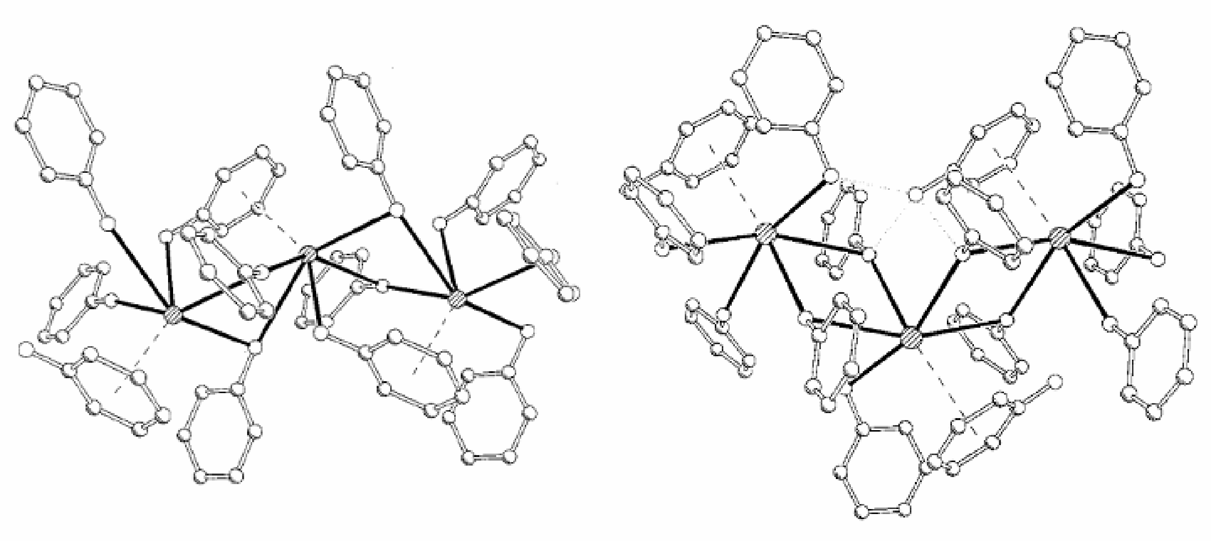


Figure 10. Schematic representation of the molecular structure of the polymeric species [KOPh].nPhOH, n =2 (left), 3 (right)

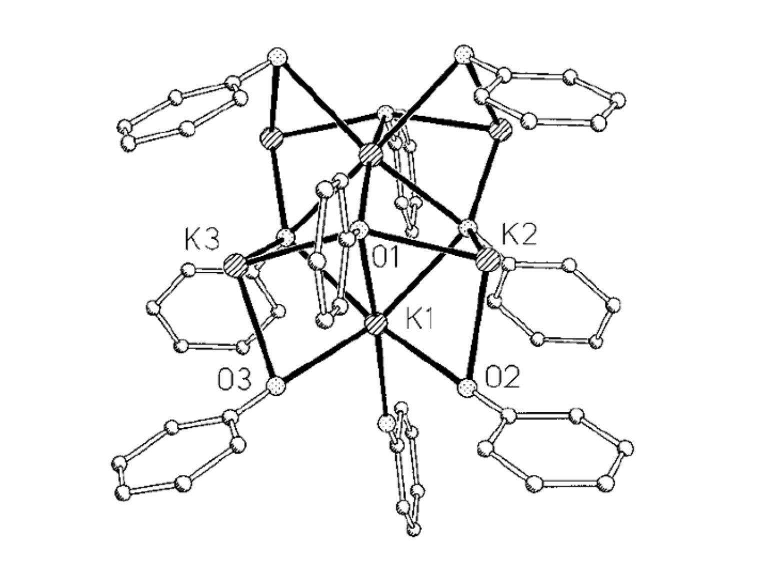


Figure 11. Schematic representation of the molecular structure of the polymeric $[MOPh]_{\infty}$ compounds M = K, Rb, Cs

A - II.2.3.3 - Alkyl-substituted aryloxides of group 1 metals

The chemistry of aryloxides is very rich due to an infinite number of possibilities of substituents on the phenyl ring. Thus, in this work and in this thesis, we were only interested in the 2 and 2,6-alkyl substituted alkali aryloxide reagents, being in a general way the predominant factor influencing the structure of the aggregates.

Boyle et *al.* have recently published articles dealing with the influence of the alkyl-substituent on the phenolate group on the overall structure of the MOR compounds M= Li [63], K [64]; R = substituted phenyl ring. In a general way, the "size" of the alkyl substituent(s) on the ortho-position(s) of the phenyl ring is a predominant factor on the degree of aggregation of the species.

As shows Figure 12, the degree of oligomerization of the "Li(OR)(thf)" adducts oscillates between dimeric and tetrameric complexes, the formation of the former occurring of course with the most bulky ^{t}Bu substituent in position 2 (Figure 12 left) or 2,6 (Figure 12 right). In both complexes, lithium cations coordinate two THF molecules reaching a tetrahedral coordination sphere except in the most hindered adducts where only one solvent molecule can bind to the lithium cation.

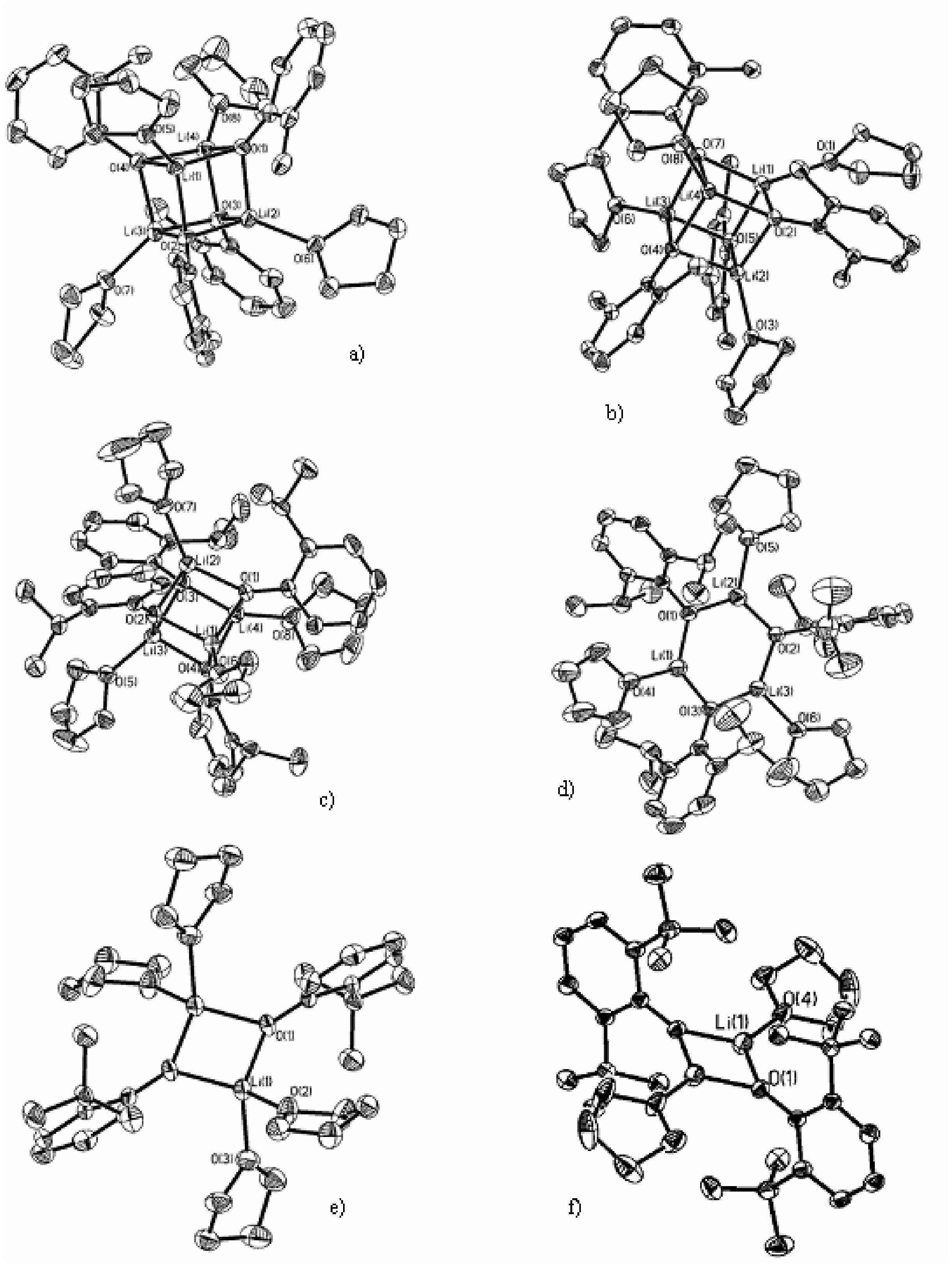


Figure 12. Representation of some [LiOAr] complexes in THF, a) [Li(2-Me-C_6H_4O)(thf)]$_4$ b) [Li(2,6-Me$_2$-C_6H_3O)(thf)]$_4$ c) [Li(2-^{i}Pr-C_6H_4O)(thf)]$_4$ d) [Li(2,6-^{i}Pr$_2$-C_6H_3O)(thf)]$_3$ e) [Li(2-^{t}Bu-C_6H_4O)(thf)$_2$]$_2$ f) [Li(2,6-^{t}Bu$_2$-C_6H_3O)(thf)]$_2$

In the two dimeric compounds, the introduction of a sterically bulky group, namely ^{t}Bu, in ortho-position (and both ortho-positions respectively) of the phenyl ring limits the amount of electron density available on the Li metal ions for solvent molecules, resulting in a stronger Li–O attraction, thus in shorter Li–O distances.

Unfortunately, only few crystallographic and analytical data concerning sodium derivatives can be found in the literature. If the para-position of the phenyl ring is substituted: i) with a fluor atom, in THF, the structure is very similar to the $[NaOPh(thf)]_6$ one, but two sodium cations coordinate one more THF molecule leading to $[(4\text{-F-}C_6H_4ONa)_6(thf)_8]$ [96] (Figure 13), ii) with a methyl-group, in DME, the compound displays a tetrameric structure $[Na(dme)(\mu_3\text{-}OC_6H_4\text{-Me-4})]_4$ [90], and finally iii) with an ethyl-group or a fluor, in dioxolane, the compound is polymeric $\{[(4\text{-R-}C_6H_4ONa)_6(dioxolane)_3]_\infty\}$ R = Et, F [96] (Figure 14). This highlights the real importance of the solvent on the overall structure of the alkali aryloxide compounds. As a general rule, sodium aryloxides preferentially crystallize as tetramers or "packing" of tetramers in aprotic solvent. However, if the ortho-positions of the phenyl ring are substituted, dimeric compounds are formed in THF, for instance $[Na(OR)(thf)_2]_2$ (ROH = $2,6\text{-}^t Bu_2\text{-}C_6H_3OH$ [97] or $2,4,6\text{-}(CF_3)_3\text{-}C_6H_2OH$ [86]) (Figure 15). This is also the case in DMSO, however, the sodium derivative presents an unusual crystal structure $[Na(2,6\text{-}^t Bu_2\text{-}OC_6H_3)(\mu\text{-}Me_2SO)(Me_2SO)]_2$ in which two solvent DMSO molecules bridge the two metal cations [89], the aryloxide ligands act as terminal groups (Figure 15).

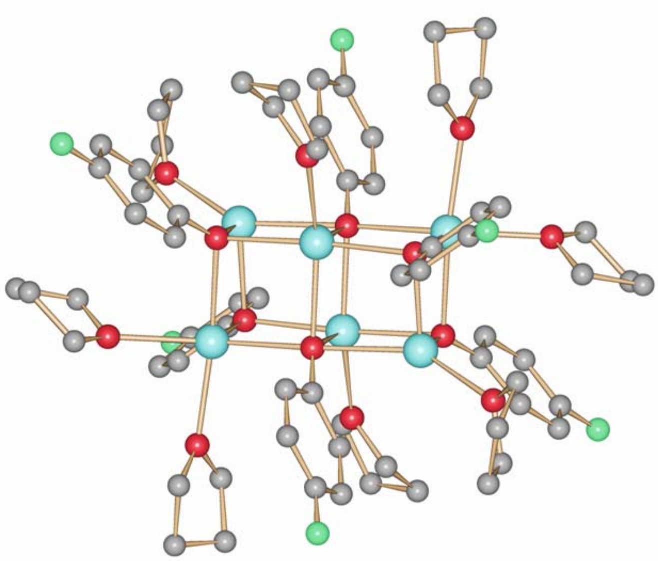


Figure 13. Schakal view of the hexameric structure of $[(4\text{-F-}C_6H_4ONa)_6(thf)_8]$, H atoms have been omitted for clarity

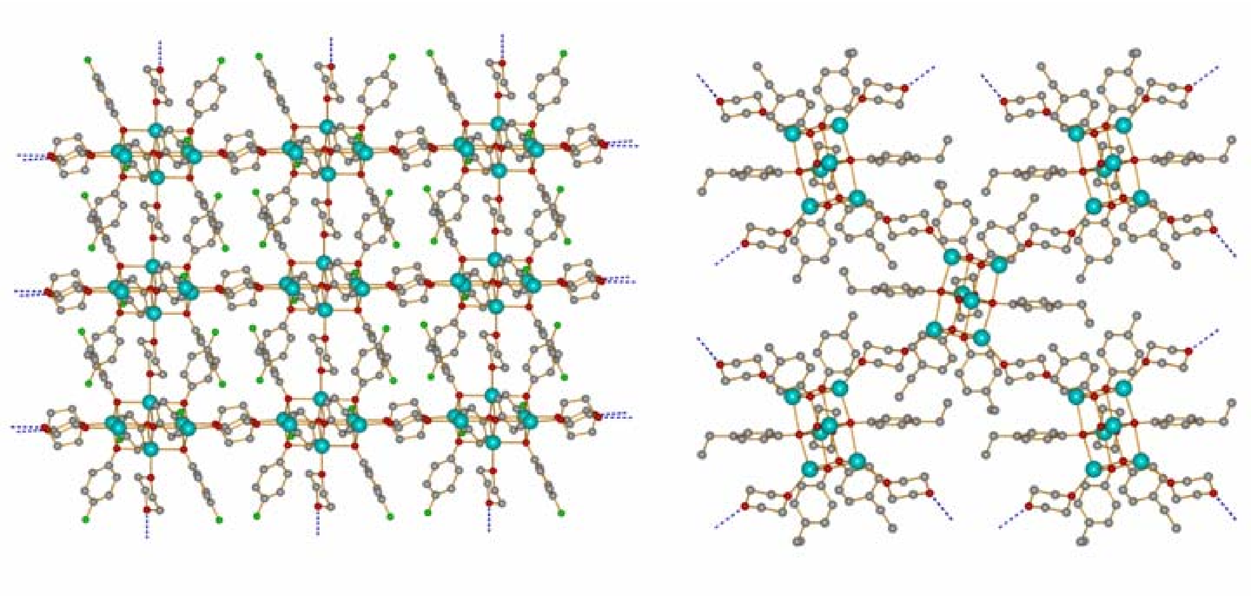


Figure 14. 3D-network formed in $\{[(4\text{-R-}C_6H_4ONa)_6(\text{dioxolane})_3]_\infty\}$ R = F (left), Et (right), H atoms have been omitted for clarity

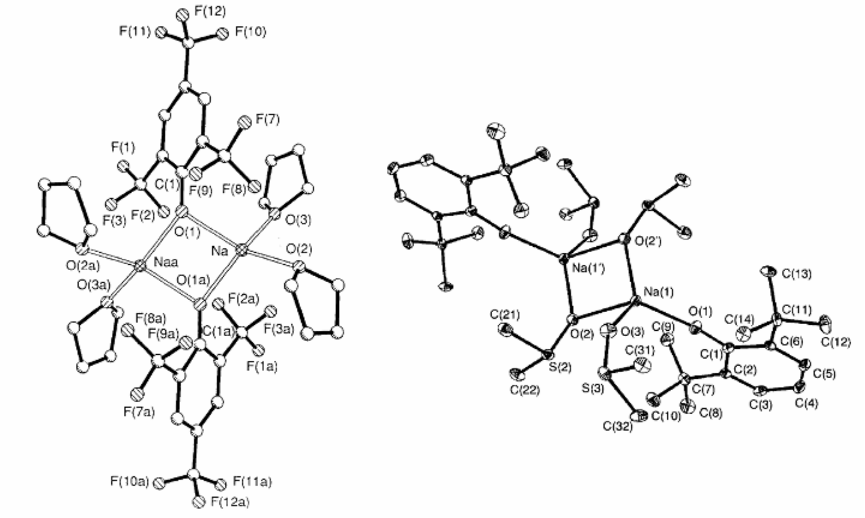


Figure 15. Molecular structure of the dimeric sodium aryloxides $[Na(2,4,6\text{-}(CF_3)_3\text{-}C_6H_2O)(thf)_2]_2$ (left) and $[Na(2,6\text{-}{}^tBu_2\text{-}C_6H_3O)(\mu\text{-}Me_2SO)(Me_2SO)]_2$ (right)

Potassium alkoxides and aryloxides KOR often possess polymeric structures due to the large ionic radius and the low charge of the potassium cation. In general, potassium adducts with the less sterically demanding ligands present solvated polymeric structures and by increasing the steric bulk, potassium complexes form unsolvated polymers. Usually, the potassium atoms are π-bonded to the aryl rings of the neighbouring derivatives to fill their unsaturated coordination sites (Figure 16).

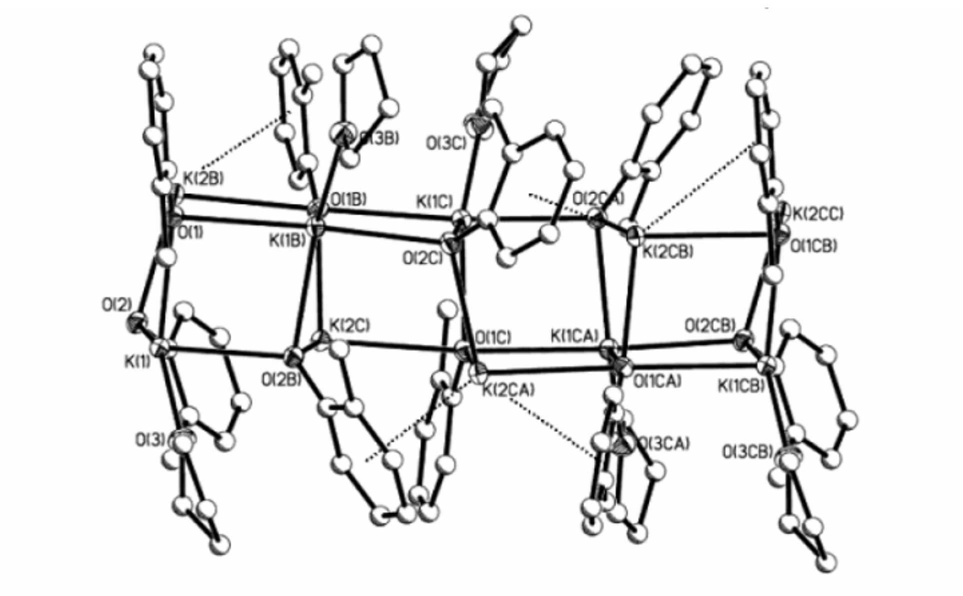


Figure 16. Example of π-K interactions generally observed in KOAr compounds

Nevertheless, in THF, two molecular compounds have been described in the solid state, a tetrameric species [K(2-^{i}Pr-C_6H_4O)]$_4$(thf)$_3$ and a hexameric species [K(2-^{t}Bu-C_6H_4O)(thf)]$_6$ [64] (Figure 17). The former compound possesses a relatively "strange" structure, two of the four K atoms are 3-coordinated without any association with the Lewis-basic THF solvent molecules. The remaining K atoms are 4- and 5-coordinated, binding one and two THF molecules, respectively, resulting in an asymmetric molecule (Figure 17 left).

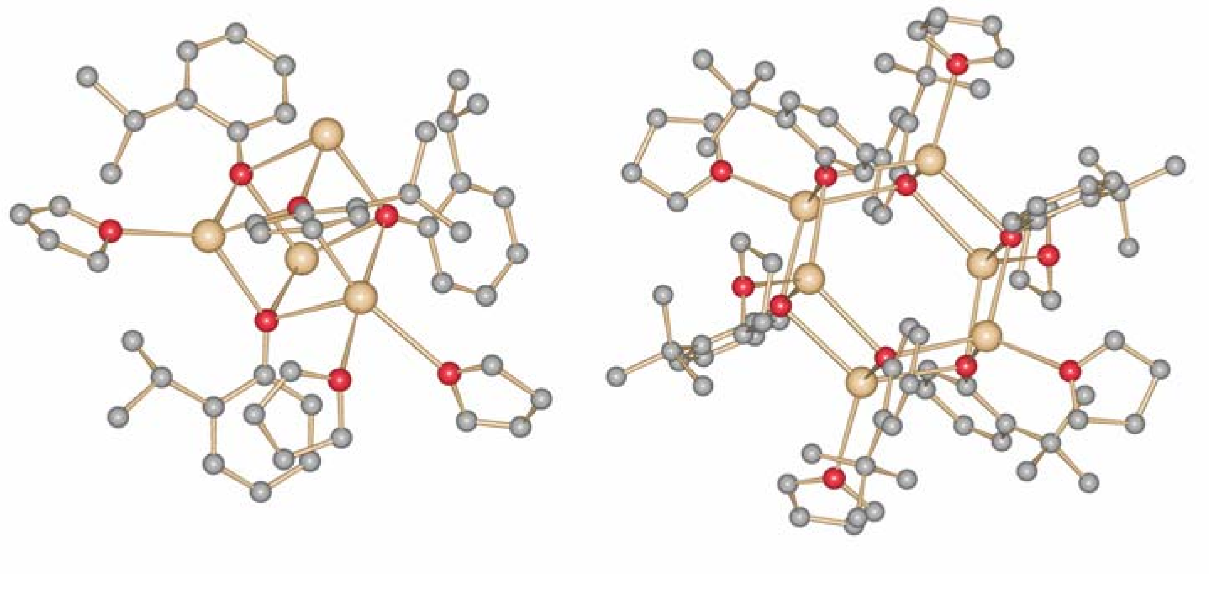


Figure 17. Molecular structures of [K(2-^{i}Pr-C_6H_4O)]$_4$(thf)$_3$ (left) and [K(2-^{t}Bu-C_6H_4O)(thf)]$_6$ (right), H atoms have been omitted for clarity

In contrast to the lithium family of compounds, additional steric bulk does not lead to compounds of lower nuclearity, but instead, by adding the oBP ligand (*tert*-butyl group in the ortho-position), a compound with a hexameric structure was isolated wherein all of the K metal ions adopt very distorted tetrahedral geometries (Figure 17 right).

A - II.2.3.4 - Aryloxides of group 2 metals

In the quest for barium precursors for the MOCVD process, the chemistry of main group 2 metals aryloxides has received a more limited attention than the alkoxide ones while the bulk of the alcoholate anion is a good omen to avoid or limit polymerization. For instance, with the lightest beryllium element, due of the high-toxicity of its compounds, only one crystal structure of aryloxide compound has been described $[Be(2,4,6\text{-}^{t}Bu_3\text{-}C_6H_2O)_2(OEt_2)]$ [105]. From the Cambridge Structural Database, only 7 calcium- [106-113], 5 strontium- [108, 110, 114-116] and 16 barium aryloxide crystal structures [108, 110, 113, 114, 117-124] are reported. Regardless the bulk of the aryloxide anions, calcium derivatives revealed structures varying between monomers and trimers whereas complexes of the heavier strontium and barium metal ions present some more complex architectures. If the ortho-positions of the phenyl rings are substituted, complexes with low degree of oligomerization, principally monomers or dimers, are obtained. However, a soluble and volatile pentamer barium aryloxide derivative, namely $[Ba_5(\mu_5\text{-}OH)(\mu_3\text{-}OAr)_4(\mu\text{-}OAr)_4(OAr)(THF)_5]$ (Ar = $3,5\text{-}^{t}Bu_2\text{-}C_6H_3$) [124] is reached if only the meta-positions are substituted with alkyl-groups. With the most unhindered phenolate ligands, higher degrees of oligomerization are found: two pseudo-isostructural trimers for calcium and strontium cations of formula $[Ca_3(OPh)_5(HMPA)_6].OPh.2PhOH$ and $[Sr_3(OPh)_6(HMPA)_5]$ [110] (Figure 18), and a tetramer with $[Sr_4(OPh)_8(PhOH)_2(thf)_6]$ for the strontium cation [115] (Figure 19). Caulton *et al.* have reported a number of larger aggregates for the barium cation using the least hindered OPh ligand such as $[HBa_5(O)(OPh)_9(thf)_8]$ [123] (Figure 20), $[Ba_6(OPh)_{12}(TMEDA)_4]$ [110] (Figure 21) or $[H_2Ba_8(\mu_5\text{-}O)_2(OPh)_{14}(HMPA)_6]$ [114] (Figure 22).

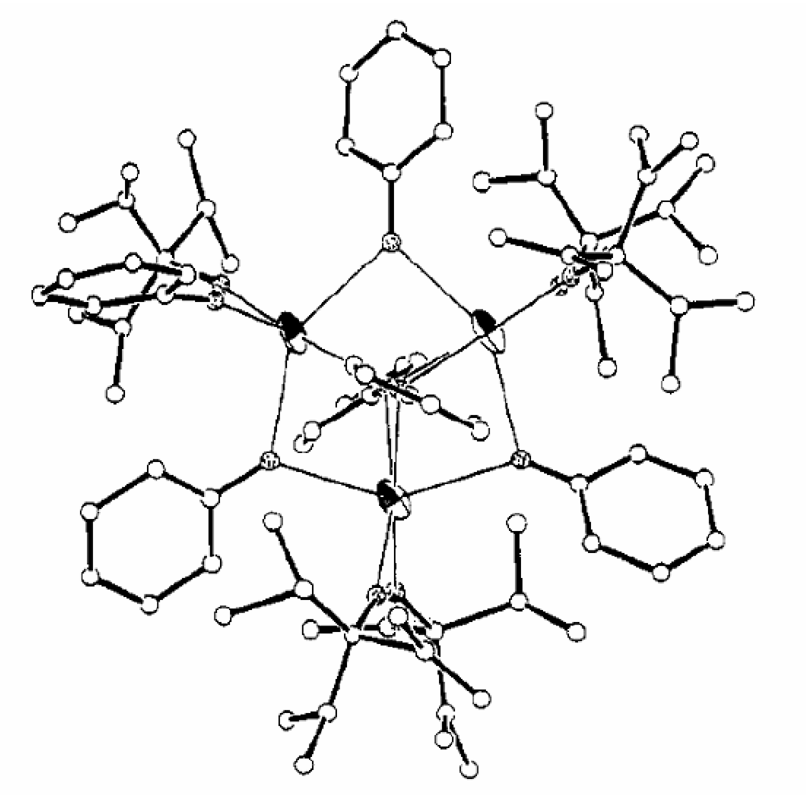


Figure 18. Schematic representation of the trimeric [$M_3(OPh)_5(HMPA)_6$] compounds (M = Ca, Sr)

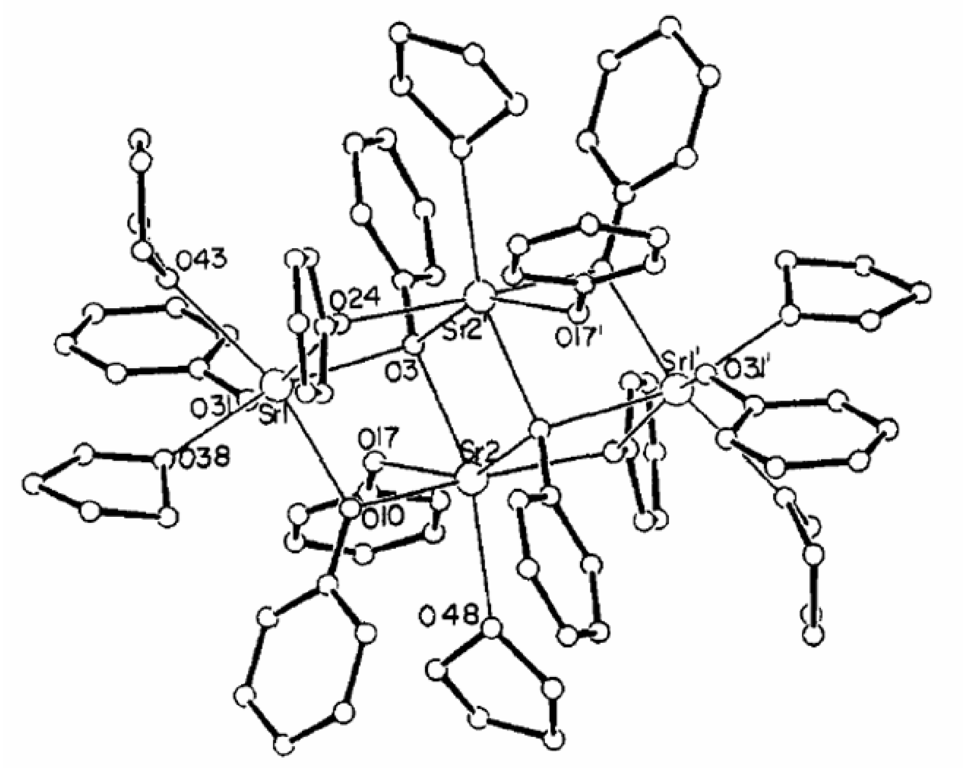


Figure 19. Molecular structure of the tetameric [$Sr_4(OPh)_8(PhOH)_2(thf)_6$] derivative

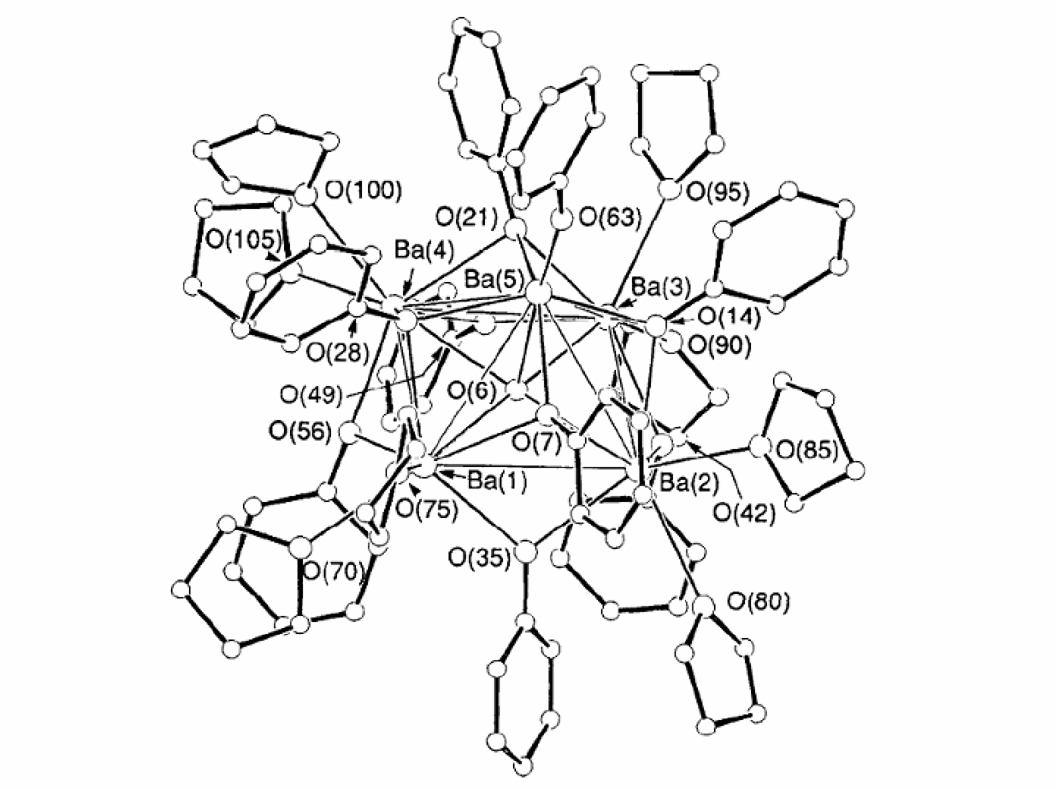


Figure 20. Molecular structure of the pentameric [$HBa_5(O)(OPh)_9(thf)_8$] species

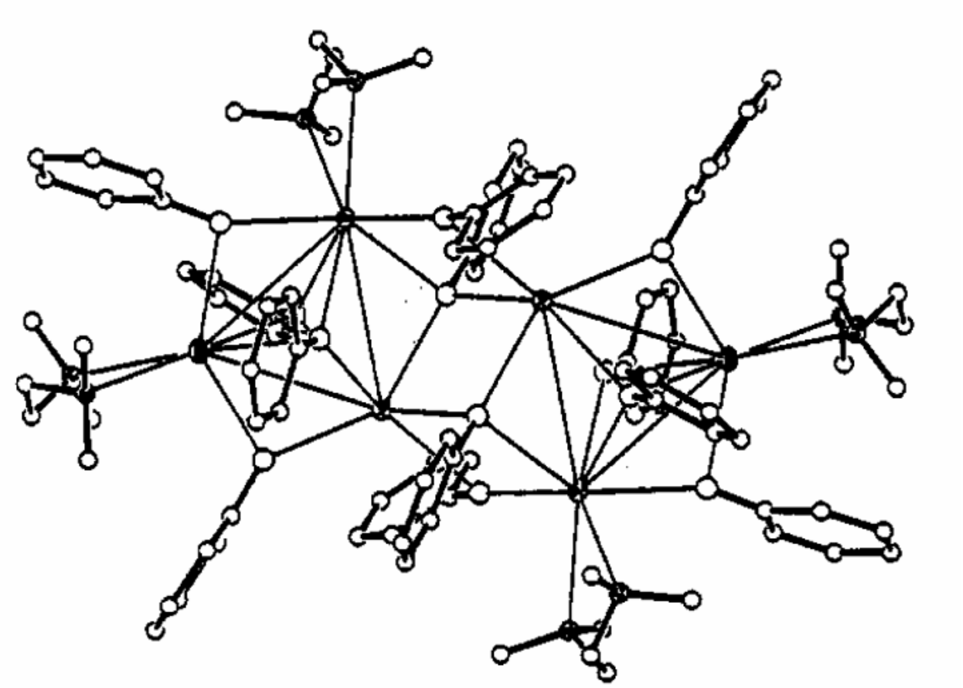


Figure 21. Molecular structure of the hexameric [$Ba_6(OPh)_{12}(TMEDA)_4$] compound

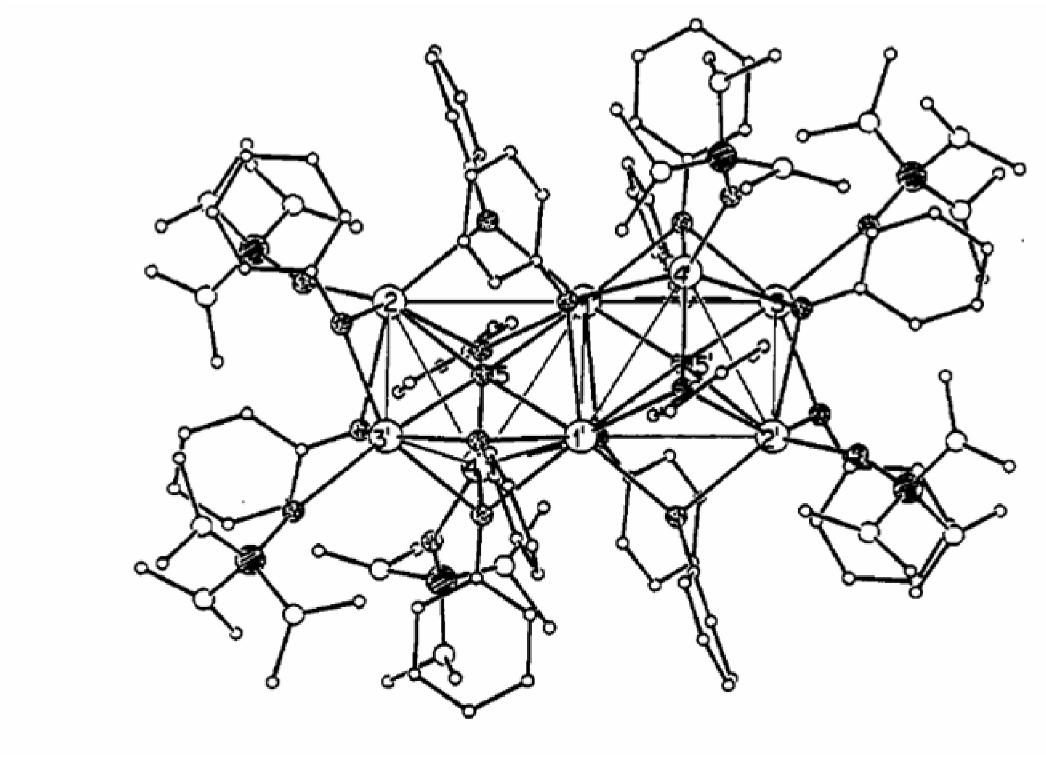


Figure 22. Molecular structure of the octameric $[H_2Ba_8(\mu_5\text{-}O)_2(OPh)_{14}(HMPA)_6]$ derivative

A heterometallic cluster of group 2 metals $[H_2Sr_6Ba_2(\mu_5\text{-}O)_2(OPh)_{14}(HMPA)_6]$ is also found and possesses an "octameric core" and could be described as two Ba_2Sr_3O-units fused along the basal Ba-Ba edge (Figure 23) [114].

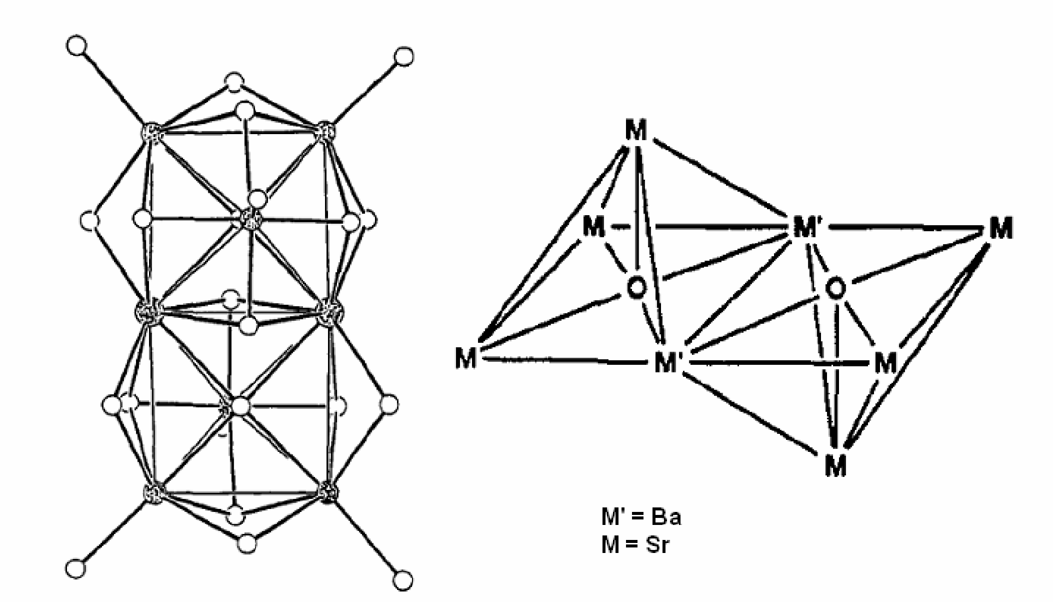


Figure 23. Schematic representation of the octameric heterometallic $[H_2Sr_6Ba_2(\mu_5\text{-}O)_2(OPh)_{14}(HMPA)_6]$ species

It has to be said that all these metal complexes have been obtained using the crude alkaline earth metal or the hydride (CaH_2) and the corresponding alcohol, no alkali aryloxide reagents were used.

Among the main group 2 metals, magnesium aryloxides have received the most attention while the coordination chemistry of these species is not exhaustive. While aggregates are generally comprised between monomers and trimers, magnesium aryloxide compounds adopt a varied form of architectures depending on the size of the anion and the influence of donor solvents. As expected, with bulky substituted phenyl ring such as 2,6-^{t}Bu$_2$-$C_6H_3O^-$ ligands, magnesium aryloxides derivatives afford monomeric species such as [Mg(2,6-^{t}Bu$_2$-$C_6H_3O)_2$(thf)$_2$] or [Mg(2,6-^{t}Bu$_2$-$C_6H_3O)_2$(TMEDA)] [125] (Figure 24). From the literature data, the largest magnesium aryloxide aggregate is a tetramer-unit to which one lithium cation is inserted, namely [$LiMg_4$(O)(2-Me-$C_6H_4O)_7$(thf)$_4$] [126]. The insertion of a lithium cation is due to the use of ^{n}BuLi solution during the preparation of the complex. Using a stronger and larger Lewis-coordinating solvent such as TMEDA (TMEDA = tetramethylethylenediamine) on this compound affords the formation of a monomer of magnesium of formula [Li_2Mg(2-Me-$C_6H_4O)_4$(TMEDA)$_2$] [126] (Figure 25).

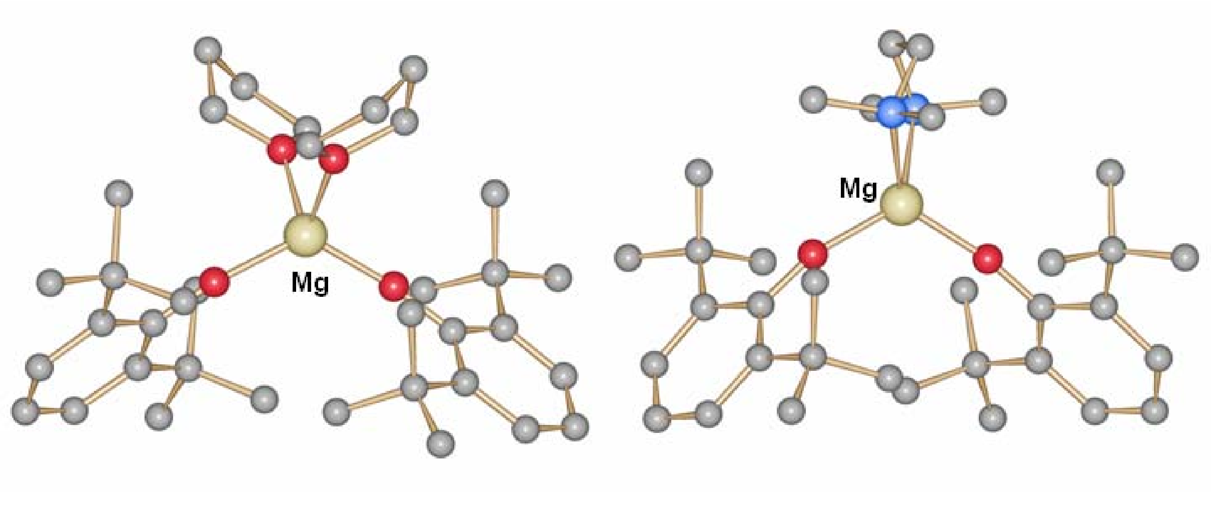


Figure 24. Molecular structures of [Mg(2,6-^{t}Bu$_2$-$C_6H_3O)_2$(thf)$_2$] (left) and [Mg(2,6-^{t}Bu$_2$-$C_6H_3O)_2$(TMEDA)] (right), H atoms are omitted for clarity

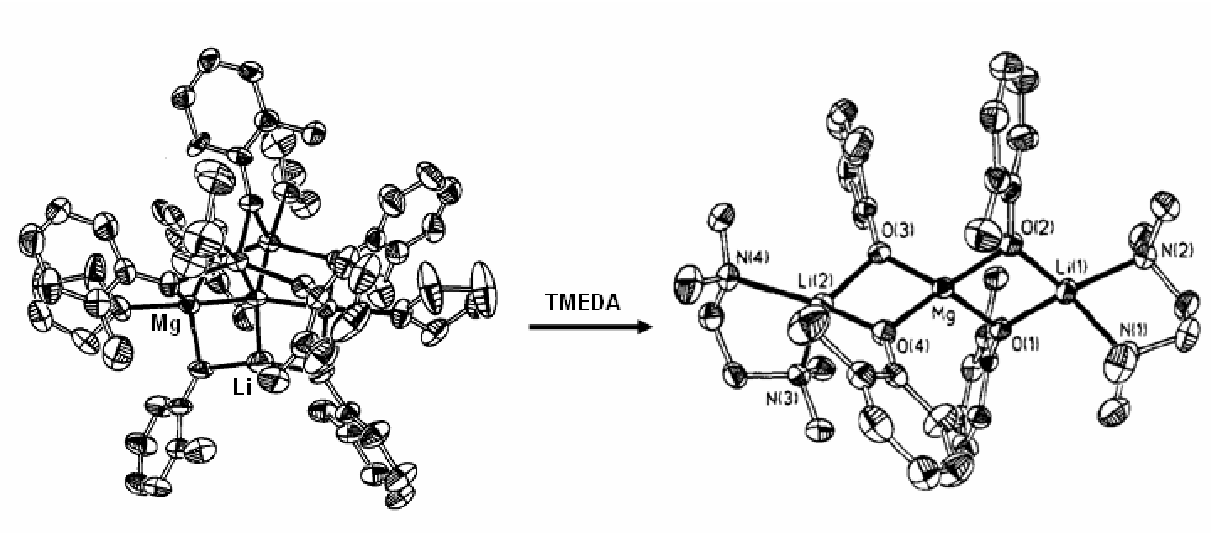


Figure 25. Schematic representation of the transformation of [$LiMg_4(O)(2\text{-}Me\text{-}C_6H_4O)_7(thf)_4$] species into [$Li_2Mg(2\text{-}Me\text{-}C_6H_4O)_4(TMEDA)_2$] species by addition of TMEDA

This underlines once again the importance of the solvent in the construction of aggregates.

A - III - Alkaline earth and divalent rare earth metal complexes: very close behaviour

The structures and chemical behaviour of heavier alkaline earth metal complexes (Ca, Sr, Ba) have been often compared to that of early d- and f-block metal complexes but in a major part with the well-developed cyclopentadienide chemistry [127-136]. Because of similarities with lanthanide(II), parallels with lanthanide(II) complexes have been observed but not pursued in other fields. The term alkaline earth comes from millennia old, due to their intermediate nature between the alkali (oxides of alkali metals) and the rare earth (oxides of rare earth metals). Moreover, lanthanides ions are d^0-species with a limited radial extension of their 4f shell. Thus, orbital factors do not affect their chemistry as much as in transition-metal chemistry. As for complexes of the heavier alkaline earth metals, their bonding and structures are mainly guided by electrostatic and steric factors.

Table 1. Ionic radii of alkaline earth and rare earth metal cations

Alkaline earth metal cations			Rare earth metal cations		
M^{2+}	CN	$r_{M^{2+}}$	M^{2+}	CN	$r_{M^{2+}}$
Ca	6	1.00	Yb	6	1.02
	7	1.06		7	1.08
	8	1.12		8	1.14
Sr			Eu	6	1.17
	6	1.18		7	1.20
	7	1.21		8	1.25
	8	1.26	Sm	7	1.22
				8	1.27
Ba	6	1.35			
	7	1.38			
	8	1.42			

The chemistry of divalent lanthanide complexes was some years ago exclusively reserved for the Eu, Sm and Yb metal cations while other lanthanide metal cations such as neodymium (Nd), dysprosium (Dy) or thulium (Tm) were known to exist in +2 oxidation state [137, 138]. The substances were unfortunately impossible to isolate due to their difficulty of preparation. However, during this last decade, some new Ln(II) complexes have been crystallographically characterized [139-141] and some of them are presented, like SmI_2/THF, as very good reducing agents in organic synthesis [142-148].

The chemistry of the common LnI_2 (Ln = Yb, Eu and Sm) in weak polar aprotic solvents has been well studied and presents similar behaviour than the alkaline earth derivatives. For instance, in presence of THF, although variable degrees of solvation have been reported depending upon the method of isolation, complexometric analysis of dry powders is consistent with the formula $LnI_2(thf)_2$, Ln = Yb, Sm, Eu [149]. In the chemistry of the alkaline earth metal iodides, some comparable results have been obtained with the heaviest barium metal ion. Indeed, under certain crystallization conditions a pseudo-analogue has been crystallographically characterized, namely the polymeric $[BaI_2(thf)_3]_{1/\infty}$ [150, 151]. However, it was improbable that these large lanthanide metal ions have a four-coordinate geometry in solution in presence of available oxygen donors since studies on polyether ligands suggested that they prefer a coordination number greater than four. Investigations on the wide spread chemistry of divalent rare earth metal iodides allowed the characterization of, often as side-products, the molecular compounds *trans*-[$YbI_2(thf)_4$] [152], *trans*-[$EuI_2(thf)_5$] [153] and *trans*-[$SmI_2(thf)_5$] [154]. Figure 26 shows their molecular structures.

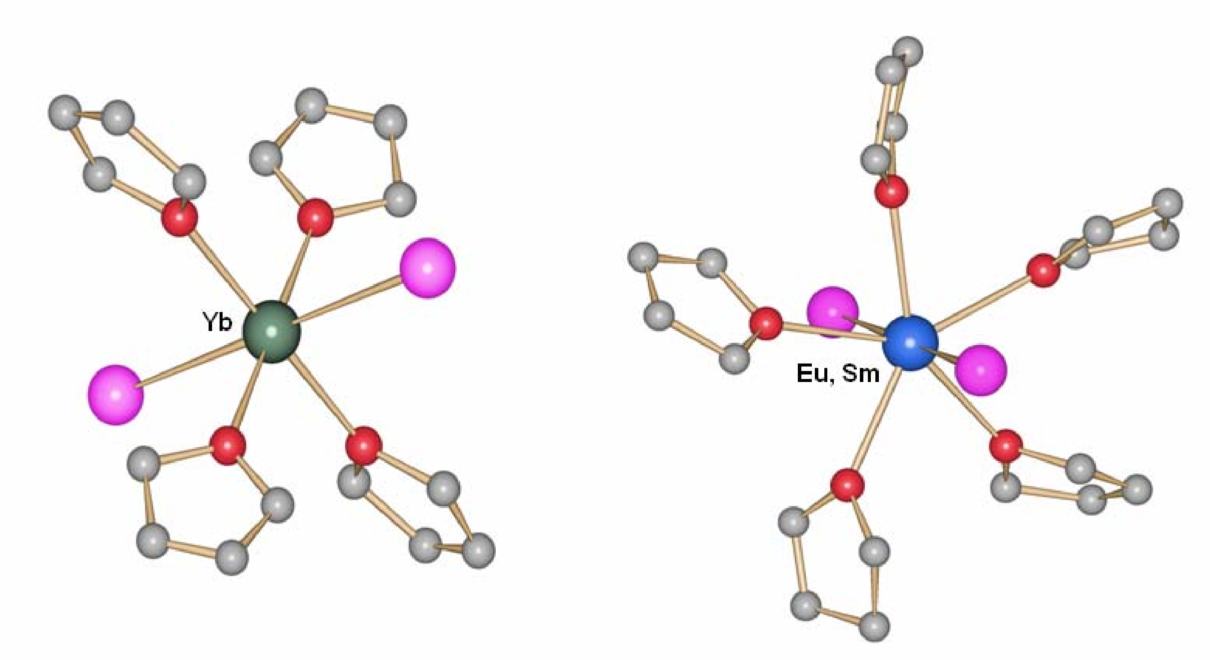


Figure 26. Molecular representation of *trans*-[$Yb(thf)_4$] (left) and *trans*-[$LnI_2(thf)_5$] Ln = Eu, Sm (right), H atoms have been omitted for clarity

Common starting materials for the synthesis of alkaline earth metal clusters are the THF-derivatives, [$MI_2(thf)_n$], M = Ca [119] with n = 4, M = Sr [155], Ba with n = 5 [150, 151], presented in Figure 27. The analogy between the THF-adducts of alkaline earth and rare earth metal iodides is striking, a similar geometry is observed depending of the ionic radii of the metals cations. The structures of *trans*-[$MI_2(thf)_4$] M = Ca, Yb present a square bipyramidal arrangement around the metal with iodide anions in axial positions. In the same way, the crystal structures of *trans*-[$MI_2(thf)_5$] M = Sr (and Ba), Eu, Sm due to a larger ionic radius accept one more THF molecule in the coordination sphere of the metal cation compared to Ca^{2+} respectively Yb^{2+}, resulting in a pentagonal bipyramidal geometry around the metal.

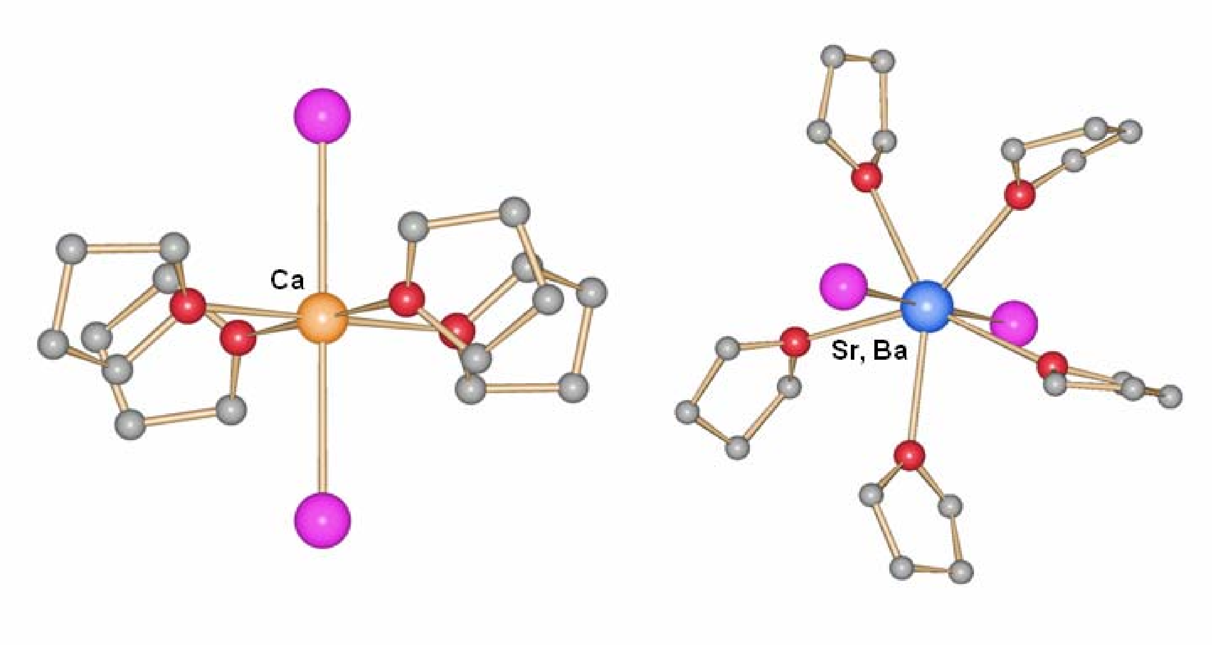


Figure 27. Schematic representation of the molecular structures *trans*-[$CaI_2(thf)_4$] (left) and *trans*-[$MI_2(thf)_5$] M = Sr, Ba (right), H atoms have been omitted for clarity

Moreover, due to similar ionic radii (Table 1) [156], the M–I and M–O bond lengths as well as the I–M–I angle are in a similar range of value than the corresponding alkaline earth metal iodide adducts (Table 2). However, these compounds are very sensitive and the crystallographic data for *trans*-[$SmI_2(thf)_5$] are just sufficient to allow the connectivity of the atoms.

Table 2. Principal parameters of the molecular compounds *trans*-[$MI_2(thf)_n$], bond lengths (Å) and angles (°)

	CN	M–I	M–O	I–M–I
[$CaI_2(thf)_4$]	6	3.106	2.340	180
[$YbI_2(thf)_4$]	6	3.103	2.373-2.399	180
[$EuI_2(thf)_5$]	7	3.222-3.254	2.546-2.653	177.38-179.10
[$SrI_2(thf)_5$]	7	3.229	2.562-2.618	176.3
[$BaI_2(thf)_5$]	7	3.374-3.382	2.696-2.741	178.6

A - IV - Aim of the thesis

The main topic research of this PhD is to explore the chemistry of alkali and alkaline earth metals in weakly polar aprotic solvents in a fundamental point of view with a particular attention on the synthesis of alkaline earth metal clusters.

Due to general similarities between clusters of group 1 and 11 metals and similar behaviours between group 2 and 12 metals, an analogue procedure for the synthesis of group 12 metal clusters will be tempted for the preparation of alkaline earth metals clusters (Equation 1). This similar reaction pathway has already shown some important results [157].

$$\text{n MI}_2 + \text{p M'OR} \xrightarrow[+\text{ Ligand L}]{-[\text{M'X}]_m} \text{Cluster}$$

M = Ca, Sr, Ba (Eu, Sm); M' = Li, Na; R = O^tBu, OPh; L = THF, DME; n ~ 1; p ≥ 2n; m ≤ 2n

Equation 1. Synthetic procedure employed during this work for the synthesis of organometallic clusters

During this thesis, a general overview on the synthetic procedure of alkaline earth metal clusters will be undertaken taking into account all the constituents of the reaction scheme (Equation 1). Alkaline earth metal iodides are chosen since they present a better solubility than their other halide analogues in organic media. Moreover, alkaline earth metal iodides dissolve readily in ethereal solvents like THF in order to form undissociated species of the type $[MI_2(thf)_n]$, M = Ca with n = 4 [119], M = Sr [155], Ba [150, 151] with n = 5. However, the chemistry of alkaline earth metal iodides still remains poorly known and even less in weakly polar aprotic solvents while the common starting materials for the preparation of alkaline earth metal clusters are synthesized using THF.

The first part of this thesis deals with the synthesis of new homo- and heteroleptic molecular alkaline earth metal iodide adducts MI_2/L using n-glyme ligands n = 1, 2, 3 (n-glyme = $CH_3(OCH_2CH_2)_nOCH_3$). We want to evaluate the influence, the reactivity of multidentate coordinating-ligands on the coordination sphere of the metal cations compared to the simple monodentate THF-adducts. We also want to contribute to the study of alkaline earth metal iodide compounds in weakly polar aprotic solvents, a chemistry much less explored than the aqueous one.

The stability of alkaline earth metal derivatives depends on a delicate balance of steric effects, metal size, ligand basicity and solubility equilibria. Thus, subsequently, a study on the organo-alkali reagents M'OR will follow, more precisely on the influence of the alkali metal M' as well as the bulk of the OR alkyl/aryl-group on the generation of metal clusters. This should lead to the preparation of new clusters of pure alkali, alkaline earth and mixed metal ions.

Thus, the second part of this thesis deals with alkali aryloxide compounds, one of the two major strategies employed for the generation of alkaline earth metal clusters. In this part, a particular attention will be carried on the influence of the solvent basicity employed during the synthesis. Alkali alkoxides and aryloxides present a very large number of possible structures in the solid state depending of the alkali metal, the bulk of the alkyl-group and of course the basicity of the solvent. In solution, however, depending of the temperature in most of case, more architectures are expected but still unknown and this makes often their interpretation very difficult to proceed or/and to understand. In the solid state, due to the progress in the single-crystal data acquisition, important results have been highlighted concerning the influence of the basicity of the solvent on the structure of the alkali alkoxide/aryloxide derivatives. However, only few data are available and show the importance of following the research on.

Finally, the third part of this thesis presents the synthesis and the crystal structure of some new alkali and alkaline earth metal clusters with original features showing mainly the importance of the different factors cited above: bulk of the alkyl-group and basicity (or size) of the solvent.

Clusters obtained during this work will be synthesized using two different techniques: i) classical schlenck-technique, and ii) microwave synthesis. The crystallization of organometallic clusters can also be achieved by different methods, but two main approaches will be used here: i) layering with a non polar solvent (hexane), and ii) varying temperature.

In parallel of these different parts, a general comparison of alkaline earth and rare earth metal complexes behaviour will be undertaken in order to explore the analogy between these two groups of metals, first in the simple system such as homo- and heteroleptic starting materials MI_2/L but also in more complex systems such as the formation of metal clusters.

B - Results and discussion

B - I - Starting materials

B - I.1 - Pure ethereal compounds

B - I.1.1 - Introduction

We are interested in molecular compounds, especially oxygen donor adducts of alkaline earth metal iodides, because they are used by us as starting materials in the synthesis of low-dimensional compounds including clusters [41, 150, 151, 158-171]. Since more than two decades, metal clusters compounds are used in the low-cost synthesis of superconductors and other oxide materials by the sol-gel technique, or as volatile precursors in MOCVD (Metal Organic Chemical Vapor Deposition) process if they present the required properties, namely solubility and/or volatility [2, 3, 38-40, 158, 166, 167].

One of the major problems of the synthesis of organo-alkaline earth metals compounds is their tendency to form insoluble polymers [40, 172-174] due on one hand to their low metal oxidation state (II) which only allows two anionic ligands, and on the other hand, their large ionic radii which demand a large coordination number. For instance, with anions of "average" size (*eg.* Et, OMe, Cp), the alkaline earth ions are coordinatively unsaturated and compensate by oligomerizing with high coordination numbers (8-12), with values found in the order $Ca^{2+}<Sr^{2+}<Ba^{2+}$ [175]. The high coordination numbers are reached by multiplying bridging anions and thus formation of oligomers or polymers occurs. A parry to prevent a high degree of oligomerization is the use of neutral Lewis-coordinating ligands such as monodentate THF or multidentate polyether ligands which avoid any further "metal-metal contacts" via bridging ligands, saturating the metal cation. However, the chemistry of alkaline earth metals with these neutral Lewis-coordinating ligands (usually non-polar aprotic solvents) is still not well known due to the expected fast exchange of ligands in solution.

Compounds that have so far been isolated in the class of molecular species are, for instance, the zero-dimensional compounds *trans*-$[MI_2(thf)_n]$ (M = Ca [119], Sr [155], Ba [150, 151]) (thf = tetrahydrofuran) or *trans*-$[SrI_2(dme)_3]$ [176] (dme = ethyleneglycoldimethylether) and *trans*-$[CaI_2(diglyme)(dme)]$ [165] (diglyme = diethyleneglycoldimethylether). In these molecular compounds, the metal cation is always surrounded in a linear or quasi-linear fashion by the two anions, whereas the THF, DME or diglyme ligands are found in the equatorial positions of a square bipyramid in *trans*-$[CaI_2(thf)_4]$, a pentagonal bipyramid in *trans*-[MI_2(thf)$_5$] M = Sr, Ba and *trans*-[CaI_2(diglyme)(dme)] or a hexagonal bipyramid in *trans*-[SrI_2(dme)$_3$] (Figure 27, Figure 28 and Table 3).

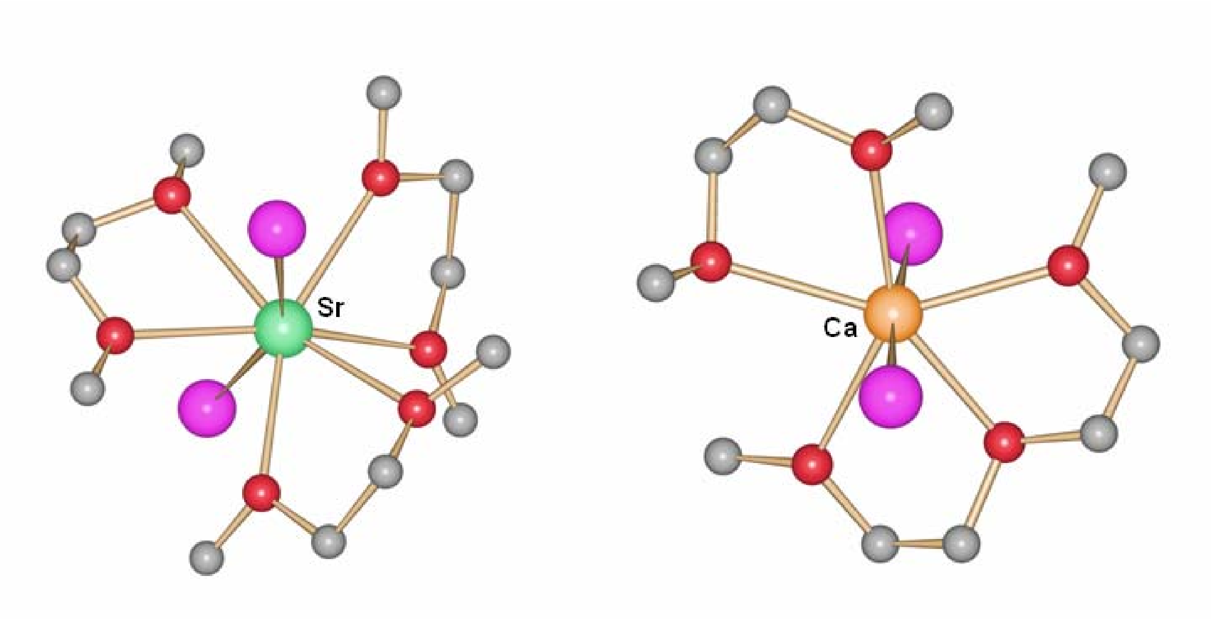


Figure 28. Schematic representation of the molecular structures *trans*-[SrI_2(dme)$_3$] (left) and *trans*-[CaI_2(diglyme)(dme)] (right), H atoms have been omitted for clarity

Table 3. Principal parameters of theses molecular compounds, bond lengths (Å) and angles (°)

	CN	M–I	M–O	I–M–I
[CaI_2(thf)$_4$]	6	3.106	2.340	180
[SrI_2(thf)$_5$]	7	3.229	2.562-2.618	176.3
[BaI_2(thf)$_5$]	7	3.374-3.382	2.696-2.741	178.6
[CaI_2(diglyme)(dme)]	7	3.089-3.139	2.415-2.467	176.5
[SrI_2(dme)$_3$]	8	3.383-3.413	2.631-2.656	158.9

THF-adducts are commonly used as starting materials for substitution reactions of at least one iodide [119, 158, 162, 167, 177]. The reactivity of these compounds in solution is undeniable. Other compounds can also be molecular, but without any direct M–I contacts left to be reactive. Instead, the halide ions are replaced in the first coordination sphere of the metal atom by neutral water or polyether oxygen donor ligands for instance, leading to compounds such as [$Ba(OH_2)$(triglyme)$_2$]I_2 (triglyme = $CH_3(OC_2H_4)_3OCH_3$) [163]. The anions are linked to the cationic complex by hydrogen bonding to the protons of the water molecules remaining in a second coordination sphere.

In this context, we have synthesized and characterized some new molecular compounds using larger neutral Lewis-coordinating ligands such as DME ($CH_3OC_2H_4OCH_3$), diglyme ($CH_3O(C_2H_4)_2OCH_3$) and triglyme (triglyme = $CH_3(OC_2H_4)_3OCH_3$) in order to, in a fundamental way, know and understand better the chemistry of alkaline earth metals in aprotic solvents. Secondly, we were interested in the study of the influence of the size of the ligand on the coordination sphere of the metal cation using monodentate (THF), bidentate (DME), tridentate (diglyme) and finally tetradentate (triglyme) O-donor ligands [150, 151, 165]. Finally, we wanted to compare the reactivity of the polydentate polyether containing molecular compounds with the THF-adduct ones.

As exposed in the general introduction, alkaline earth metal ions present also similar physical characteristics with divalent lanthanide ions (for instance hard character of the metal cation, charge and ionic radii). Although there is a high similarity between the radius/charge ratio for Eu^{2+}, Sm^{2+}/Sr^{2+} and also for Yb^{2+}/Ca^{2+}, this analogy has not been much studied from the structural point of view of adducts synthesized in the same conditions. Lanthanide and alkaline earth THF-derivatives presented in the introduction possess relatively similar behaviour. At the end of this part, a structural comparison of the divalent lanthanide and the alkaline earth iodide polyether compounds presented will be made showing the high similarity between.

B - I.1.2 - Crystallographic structure of [CaI(dme)$_3$]I 1

The first compound presented here, [CaI(dme)$_3$]I **1** [168], was obtained by crystallizing CaI_2 from freshly dried and distilled DME ($CH_3OC_2H_4OCH_3$). Compound **1** crystallizes in the monoclinic space group $P2_1/n$ (Nr. 14). The crystal structure of **1** is built up from two independent cationic molecules A and B per asymmetric unit, each consisting of a calcium cation, Ca1 and Ca2, to which one iodide and three DME ligands are bonded terminally via both oxygen atoms, with two separate iodides as counterions (Figure 29).

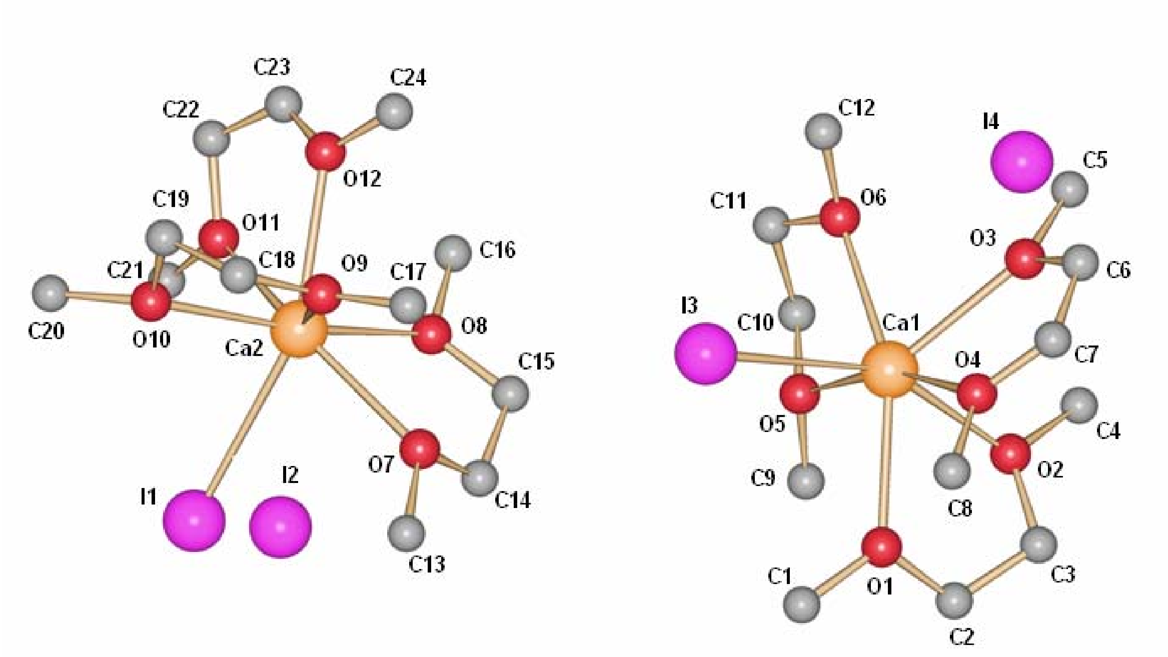


Figure 29. Schematic representation of molecules A (right) and B (left) in 1, H atoms have been omitted for clarity

Thus, the cation reaches a coordination number of seven, that is between six and eight, which are the most common coordination numbers for the calcium atom in general. The coordination geometry can roughly be described as a distorted pentagonal bipyramid with one iodide and an oxygen atom in axial positions. The corresponding I–Ca–O angle is, however, far from linear with an average value of 154.45(3)°. This is due to the bite angles of the DME ligands, which vary from 63.7(4) to 68.8(3)°. Of the five oxygen atoms in equatorial positions, one is clearly more out of the mean plane (formed by Ca and the five oxygen atoms) than the other four oxygen atoms, as has been described for a calcium compound with a similar coordination sphere [165, 178]. The Ca–O bonds vary between 2.375(1) and 2.496(1) Å, the shorter bonds on average being found in molecule A around Ca1. The Ca–I bond is 3.120(3) Å and 3.121(3) Å for Ca2 and Ca1, respectively. This gives a cationic species for each molecule, the counterions I2 and I4 not being bonded at all to the cationic unit since all further Ca···I contacts are larger than 5.8 Å. In fact, there are no H···I contacts to I2 and I4 of less than 3.7 Å. Therefore, these anions can be considered as independent and not H-bonded to the cationic units. However, some contacts can be found between two neighbouring molecules B with a O10···H20C distance of 2.800(7) Å (Figure 30), they form kind of dimers via hydrogen bonding between DME ligands. It does not occur between molecules A.

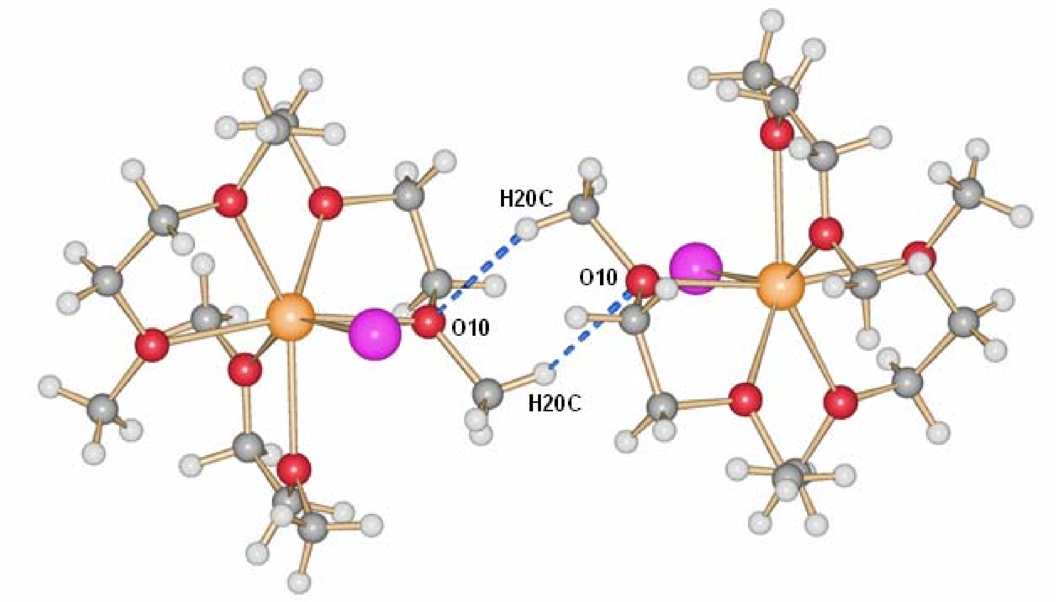


Figure 30. Schematic representation of the hydrogen bonds involved in the formation of dimers of molecule B in 1, H atoms are placed in geometrically calculated positions and refined using a ridding model

The $[CaI(dme)_3]^+$ cations of **1** possess a strong dipole moment along the Ca–I bond vector, as can be seen from Figure 31. Such polar species are scarce: among the few examples found in the literature data [179-188], only one example with calcium and iodide has been described so far to the best of our knowledge, $[CaI(thf)_5]^+$ [189], in which the cation possesses a coordination number of six, the counterion being an extremely bulky phosphonium diylide. The bond lengths in **1** are generally longer than in $[CaI(thf)_5]^+$, which is readily explained by the larger coordination number. In fact, the bond valence sums (BVS) for the calcium cations in **1** are, at 2.23 and 2.27 [190, 191], larger than the charge of the cation, indicating a more than satisfying bonding situation. The cation is indeed well wrapped up by its ligands, as shows its space-filling model (Figure 31).

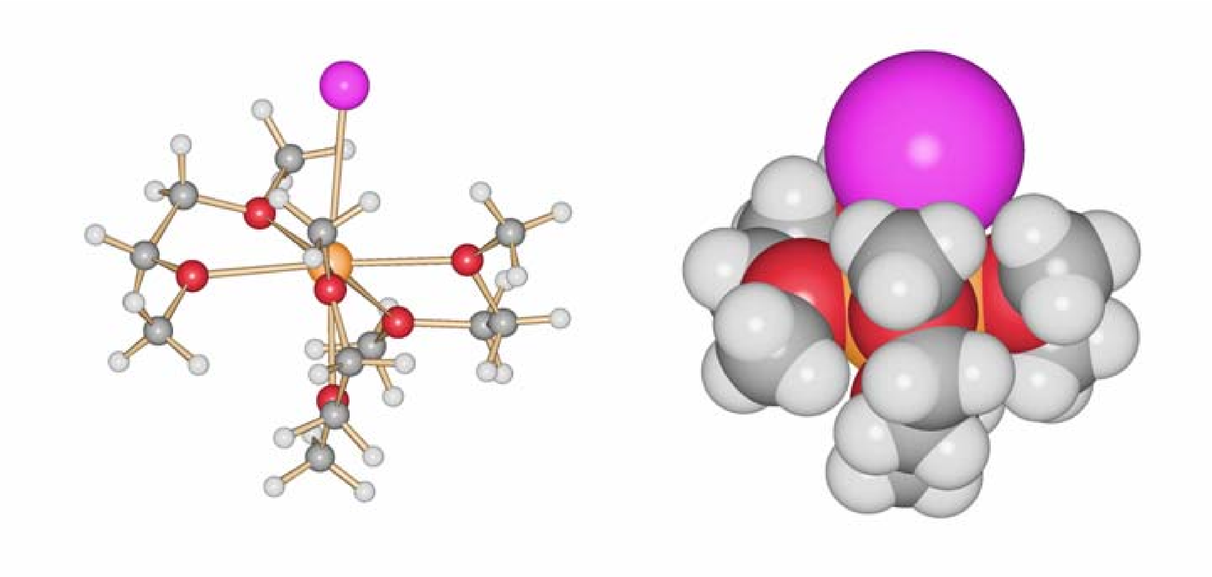


Figure 31. Schematic representation of the cationic unit [CaI(dme)$_3$]$^+$ (left) and its space-filling model (right) in 1

Other polar compounds of alkaline earth metal cations linked to one halide and other neutral ligands can only be achieved when one coordination side of the cation is efficiently shielded by a sterically bulky ligand [185, 192, 193]. In some cases, formation of dimers occurs in order to avoid single polar units [194-199] when coordination sites on the cation remain empty, whereas other complexes form infinite polymer structures via H-bonding of the neutral ligands toward both of the linked and free anions [200, 201].

The compound [CaI(dme)$_3$]I **1** is therefore the first example of a polar molecular alkaline earth metal iodide precursor. Unfortunately, the polarity of the molecules of **1** is not maintained in the overall solid state as the compound crystallizes in a centro-symmetric space group.

Syntheses of alkaline earth metal “clusters” will be described later in more detail. However, many attempts using compounds **1**-**8** failed, yielding again the starting material employed. This can be explained by a) the high bond valence sums in some cases, b) the good shielding and c) the probably slower exchange of ligands in solution when polydentate ligands are used compared to THF.

However the reaction of [CaI(dme)$_3$]I **1** and a ^{n}BuLi solution leads to the crystallization of a superstructure to **1**, namely **1a**. Compound **1a** crystallizes in the monoclinic space group $P2_1/c$ (Nr. 14) with only one molecule per asymmetric unit. The crystal structure of **1a** is very close to the one of **1**, thus the calcium cation is binding to one iodide and three DME ligands, the second iodide anion being free in the second coordination sphere of the metal center leading to a separate ion-pair (Figure 32).

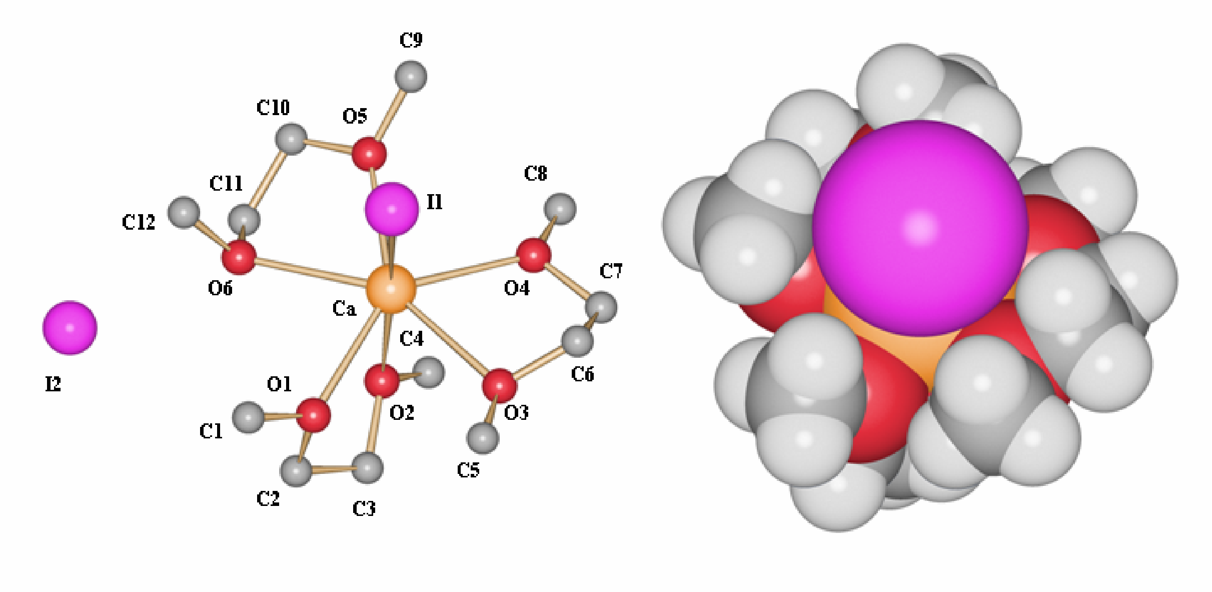


Figure 32. Schematic representation of molecule in 1a (left) and space-filling model of the cationic unit [CaI(dme)$_3$]$^+$ in 1a (right), H atoms have been omitted in the representation of the molecule for clarity

The unit cell parameters for compound **1** (a = 13.594(3) Å, b = 17.256(4) Å, c = 18.638(4) Å, β = 91.91(3)°, V = 4369.6(15) Å^3, Z = 8) and respectively for compound **1a** (a = 12.3066(7) Å, b = 10.8218(6) Å, c = 16.2620(9) Å, β = 99.733(5)°, V = 2134.6(2) Å^3, Z = 4) show truly different structures.

In **1a**, the cation also reaches a coordination number seven; the coordination sphere around the metal center can be described as a distorted pentagonal bipyramid with also one iodide atom and one oxygen atom (O2) in axial positions. The corresponding I1–Ca–O2 angle is with a value of 166.36(4)° far from linear but is 10° larger than the one observed in **1**. The bite angle of the DME ligands vary less than those observed in **1** with value from 65.98(9) and 68.48(1)°.

The Ca–O distances in the compound **1a** are comprised between 2.391(5) and 2.515(4) Å and so, are longer in average (2.443(7) Å) to the ones in **1** (average Ca1: 2.418(2) Å; Ca2:

2.428(2) Å). The Ca–I1 bond length in the cationic unit $[CaI(dme)_3]^+$ of **1a** with 3.050(7) Å is 0.07 Å shorter than the one observed in **1**, I2 is not binding at all to the calcium cation since the Ca···I2 distance is larger than 6.35 Å. The second counterion I2 is thus very far from the cationic unit compared to the Ca···I distance observed in **1** with 5.8 Å. There are no H···I contacts to I1 and I2 shorter than 3.18 Å. Therefore, the I2 anion can be considered as independent and not H-bonded to the cationic units. No H-bonds are also observed between cationic units via the ethereal ligands. The bond lengths in **1a** are one average longer than in **1**, which results in a bond valence sum smaller for the calcium cation in **1a** with a value at 2.12 [190, 191]. Nevertheless, this indicates a more than satisfying bonding situation as shows the space-filling model of **1a** (Figure 32).

The compound $[CaI(dme)_3]I$ **1a** is also polar at the molecular level but the polarity is vanished in the overall solid state due the centro-symmetricity of the space group.

B - I.1.3 - Crystallographic structure of trans-$[SrI_2(dme)_3]$ 2

The next compound *trans*-$[SrI_2(dme)_3]$ **2** was obtained by crystallizing SrI_2 from a saturated solution with dried and distilled DME, a simpler synthetic pathway than the one described for the literature known species [176]. The compound **2** crystallizes in the monoclinic space group $P2_1$ (Nr. 4) with two molecules per unit cell. Compared to calcium, the strontium cation has a larger ionic radius, and can thus accommodate three DME molecules and two iodide anions in its coordination sphere without rupturing a Sr–I bond. The structure can be described as a distorted hexagonal bipyramid with the two anions in axial positions and the three DME ligands in equatorial positions (Figure 33).

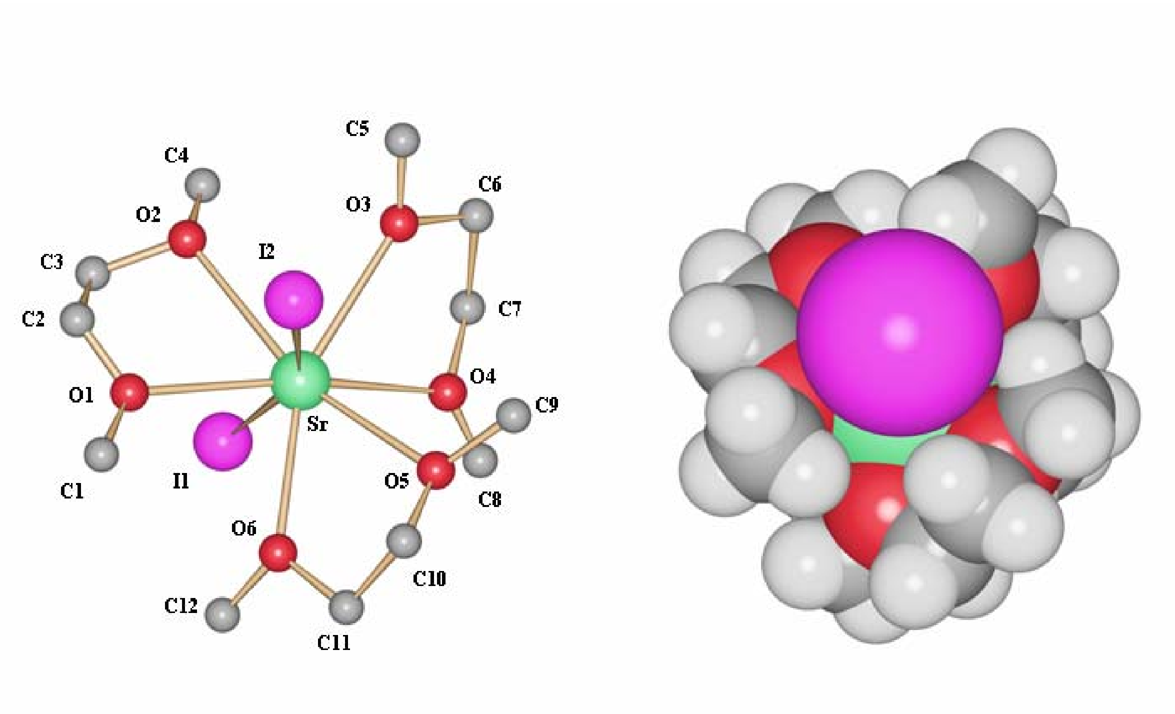


Figure 33. Schematic representation of molecule in 2 (left) and its space-filling model (right), H atoms have been omitted in the representation of the molecule for clarity

The Sr–I distances with 3.416(3) and 3.358(8) Å, and the I–Sr–I angle with a value of 158.73(3)° are drastically longer than the Sr–I bonds and respectively far from the linear I–Sr–I angle observed in other molecular strontium iodide adducts. But they can be explained with a coordination number of eight, which is larger than the coordination number of seven observed in literature compounds [155, 184, 202, 203], the repulsions between DME ligands being important in **2**.

They compare well with the values observed in the literature known species *trans*-[$SrI_2(dme)_3$] [176]. The only known molecular compound with the same coordination number and a similar coordination geometry is [$SrI_2(bipy)_3$] (bipy: 2,2'-bipyridine), described by Skelton *et al.* [185] where the Sr–I bonds with 3.443(1) and 3.468(1) Å and the I–Sr–I angle with 166.48(3)° are longer and respectively larger than those observed in **2**. The six donor atoms of the three DME ligands in **2** are arranged in a propeller-like fashion around the strontium cation, with Sr–O distances which vary between 2.570(8) and 2.729(7) Å. The average Sr–O distance of 2.631(2) Å in **2** is slightly longer than that found for seven-coordinated molecular compounds [155, 184].

The bite angles of the DME ligands vary between 61.6(2) to 62.37(2)° and are relatively smaller than those observed in **1** probably due to the interactions between ligands. The O–Sr–

O angles between adjacent DME ligands are of 64.5(3), 69.5(2) and 76.2(2)°. The coordination number of eight for the strontium cation is relatively common. Generally, the strontium cation usually behaves more like barium than calcium as far as coordination numbers are concerned. Examples are found with a coordination number of seven in the compounds *trans*-[$MI_2(thf)_5$] (M = Sr [155], Ba [150, 151]), whereas the corresponding calcium compound possesses a coordination number of six in *trans*-[$CaI_2(thf)_4$] [119].

Molecules of **2** can be considered as independent to each other since there are no H···I contacts smaller than 3 Å (H9B–I1 = 3.208(6) Å). However, some contacts can be found between neutral polyether ligands of each molecule with a O2···H1A distance of 2.907(2) Å leading to the "formation of zigzag hydrogen bonded polymeric chains" (Figure 34). The published species [176], due to a H-bonded network more important between ethereal ligands, possesses "a two dimensional structure".

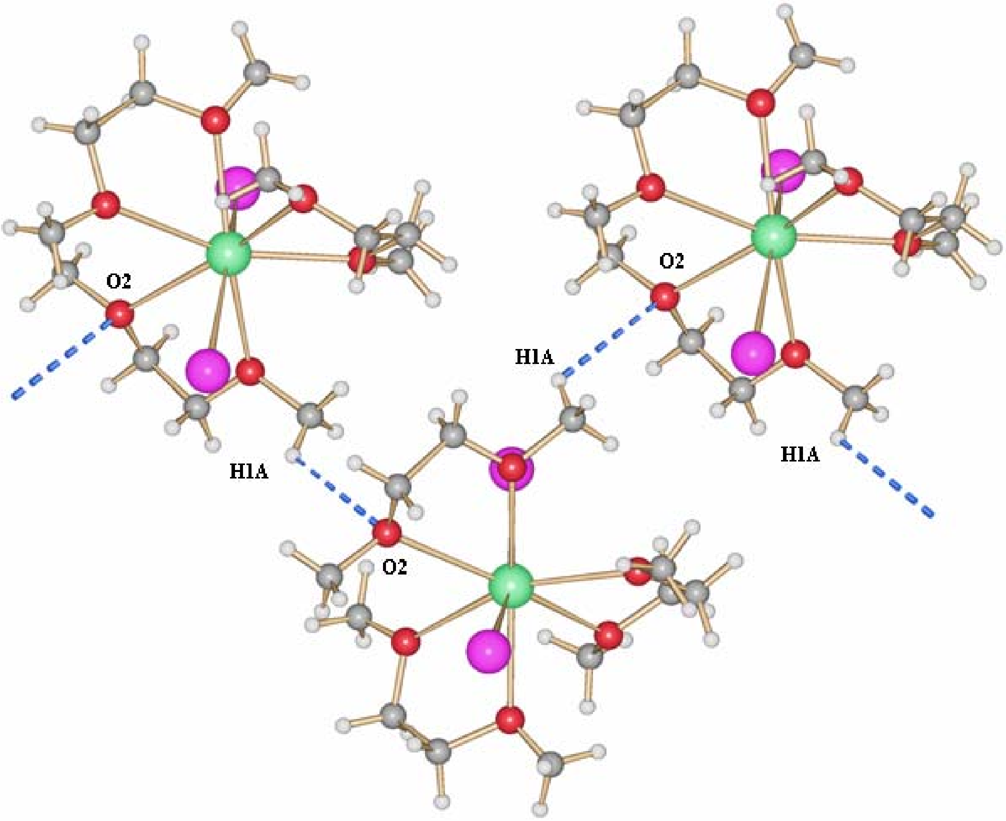


Figure 34. Schematic representation of the hydrogen bonds involved in the formation of polymeric chains in 2, H atoms are placed in geometrically calculated positions and refined using a ridding model

The bond valence sum for the strontium cation in **2** is at 1.98 [190, 191], slightly smaller than the charge of the cation, indicating a not so much satisfying bonding situation. This means that the cation is not sufficiently coordinated and would therefore be an excellent starting material for further synthesis, as it would tend to improve its coordination sphere by exchanging ligands for instance. However, the space-filling model of **2** (Figure 33) shows how well the cation is shielded by its ligands despite the bond valence sum in **2** remains below two.

B - I.1.4 - Crystallographic structure of trans-[$BaI_2(dme)_3$] 3

When the heavier alkaline earth metal iodide BaI_2 is dissolved and re-crystallized from freshly dried and distilled DME ($CH_3OC_2H_4OCH_3$), only the homoleptic compound *trans*-[BaI_2(dme)$_3$] **3** is obtained. The compound **3** crystallizes in the monoclinic space group *C*2/*c* (Nr. 15) with four molecules per unit cell. The barium cation is found on a crystallographic mirror plane with special position (1, y, ¼ (e)), so that the asymmetric unit consists of one cation, one anion and one and a half DME ligands. Thus, the molecule consists of a barium cation to which three DME ligands and two iodide anions are directly linked, reaching a coordination number eight. The structure can be described as a distorted hexagonal bipyramid with the two anions in axial positions and the three DME ligands in equatorial positions (Figure 35) as observed above in the *trans*-[SrI_2(dme)$_3$] compound **2**.

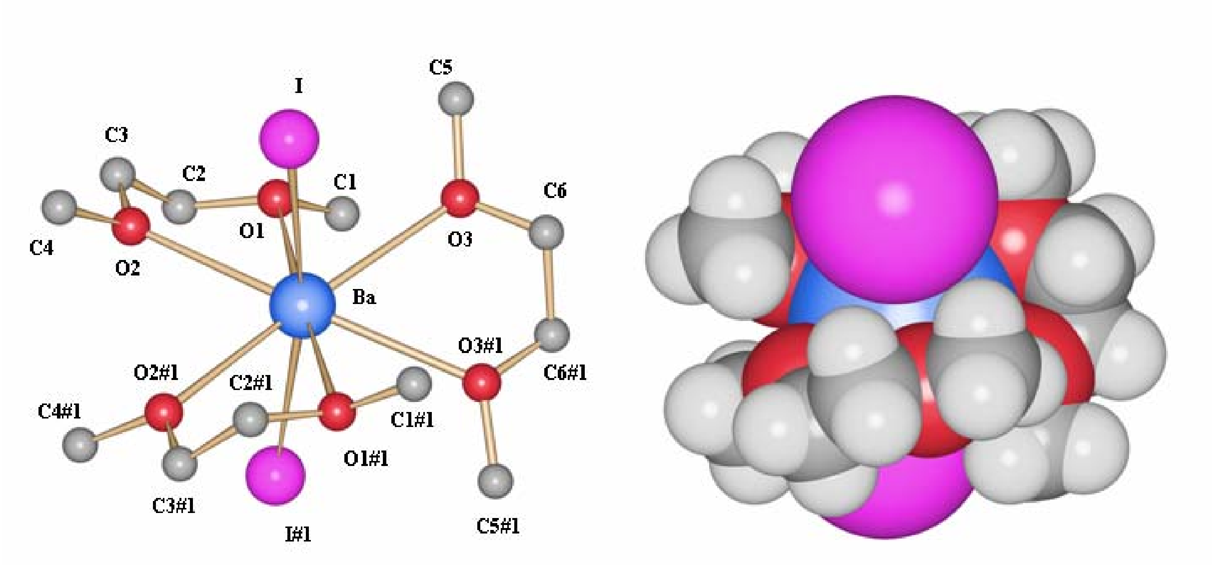


Figure 35. Schematic representation of molecule in 3 (left) and its space-filling model (right), H atoms have been omitted in the representation of the molecule for clarity

The Ba–I distances, with 3.479(1) Å, are shorter than Ba–I bonds in other molecular barium iodide adducts with the same coordination number whatever the I–Ba–I angle (*cis* or *trans*-compounds) [187, 204, 205]. However, they are longer than the Ba–I bonds in other molecular barium iodide adducts [150, 151] due to the higher coordination number in **3** (eight instead of seven) but they are shorter than the bonds in compounds where iodide plays the role of a μ-bridging ligand between two barium cations [183, 185].

The I–Ba–I angle is slightly different from linear with a value of 170.25(1)° probably due to some sterical repulsions between the three DME ligands; but it is relatively closer to linear than the one observed in **2**, barium cation being larger than strontium and thus having more space available to the ligands. Oxygen atoms of DME ligands are coordinated to the barium ion with distances ranging between 2.802(4) and 2.852(3) Å. The bite angles of the monoglyme ligands are 57.94(1), 57.94(1) and 58.25(1)°, thus smaller than those observed in **1** and **2**. The other angles between the three DME ligands are 72.31(2)° for O2–Ba–O2#1 and 68.23(9)° for O1–Ba–O3, respectively O1#1–Ba–O3#1.

3 can be considered as molecular since there are no H···I contacts shorter than 3.28 Å between adjacent molecules. The bond valence sum for the barium cation in **3** is, at 2.17 [190, 191], larger than the charge of the cation, indicating a more than satisfying bonding situation than for **2** (*trans*-[$SrI_2(dme)_3$]). Due to its larger ionic radius, repulsive interactions between DME ligands decrease in **3**, and the O-donor ligands can be more easily coordinated to the metal cation. The space-filling model of **3** (Figure 35) shows how well the cation is shielded by its ligands.

It has been shown before that small polyether molecules (such as DME) can easily be replaced by larger ones (diglyme or triglyme for instance), as long as the number of oxygen atoms remains constant, without changes in the structure except for possible higher symmetries [163]. This is confirmed in some of the following compounds.

B - I.1.5 - Crystallographic structure of [CaI(diglyme)$_2$]I 4

A similar compound to **1** and **1a** can be obtained by replacing the three DME ligands in **1** and **1a** by two larger diglyme molecules ($CH_3O(C_2H_4O)_2CH_3$). Thus, the number of oxygen atoms remains identical, and so does their arrangement around the cation. Indeed, the compound which is then obtained when CaI_2 is dissolved and re-crystallized from freshly dried and distilled diglyme, can therefore be written as [CaI(diglyme)$_2$]I **4** [201] (Figure 36).

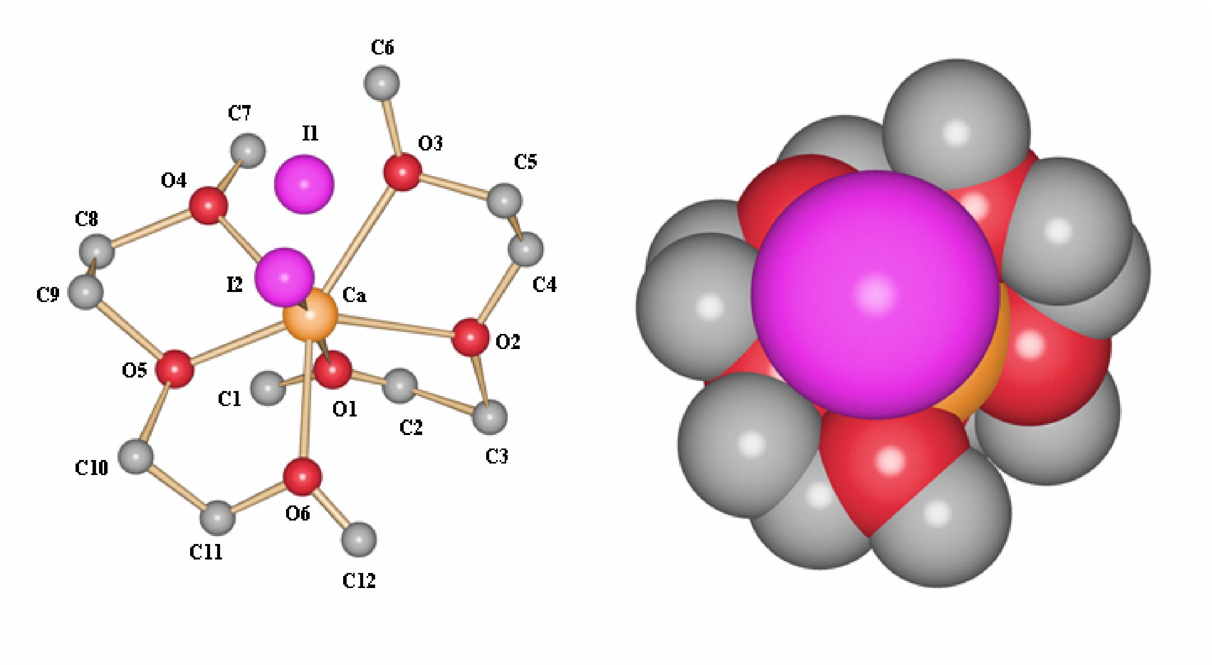


Figure 36. Schematic representation of molecules in 4 (left) and its space-filling model (right), H atoms could not be calculated due to the poor quality of the crystals

The compound **4** crystallizes in the monoclinic space group $P2_1/c$ (Nr. 14) with four molecules per unit cell. As crystals of polar compounds are difficult to grow, as mentioned by Rogers *et al.* [206], the single-crystal data of **4** are not yet of sufficient quality for publication (R1 = 0.2008) but the heavy atoms of **4** could be identified without ambiguity. In this structure, the calcium cation is surrounded by two diglyme ligands and one iodide anion, the second iodide anion being free in the second coordination sphere of the metal cation as observed for compound **1** and **1a**. In contrast to **1**, and in the same time identical to **1a**, only one molecular species exist in the unit cell of **4**, whereas two different molecules are present in **1**.

The structure can be described as a distorted pentagonal bipyramid formed by one diglyme ligand and two oxygen atoms (O2, O3) of the second diglyme ligand in equatorial positions, the iodide anion and the third oxygen atom (O1) of the second diglyme ligand being in axial positions. The corresponding I2–Ca–O1 angle is relatively close to linear with a value of 170.7(7)°. The bite angles of the diglyme ligands, 65.0(9) and 67.2(9)° for the first diglyme ligand, 65.4(8) and 66.1(8)° for the second one, are relatively different from the ideal value of 72° for this geometry.

The Ca–O bond lengths vary between 2.32(2) and 2.49(3) Å, the Ca–I distance is 3.106(7) Å. This gives a cationic species, the counterion I1 not being bonded at all to the cationic unit since all further Ca···I contacts are larger than 5.5 Å.

As for **1** and **1a**, the [CaI(diglyme)$_2$]$^+$ cation of **4** possesses a strong dipole moment along the Ca–I bond vector at the molecular level, as can be seen from Figure 36. The bond valence sum for the calcium cation in **4** is, at 2.34 [190, 191], larger than the charge of the cation, indicating a more than satisfying bonding situation. The cation is indeed well wrapped up by its ligands, as shown in the space-filling model of **4** (Figure 36).

Compound **4** is therefore the second example of a polar molecular alkaline earth metal halides, but unfortunately as for **1** and **1a**, the polarity of the molecules of **4** is not maintained in the overall solid state as the compound crystallizes in a centro-symmetric space group.

B - I.1.6 - Crystallographic structure of cis-[SrI$_2$(diglyme)$_2$] 5

When SrI$_2$ is dissolved and re-crystallized from freshly dried and distilled diglyme, only the compound *cis*-[SrI$_2$(diglyme)$_2$] **5** is obtained [168]. Compared to the compound *trans*-[SrI$_2$(dme)$_3$] **5**, the three DME molecules bound to the strontium metal cation have been replaced by two larger diglyme molecules in **5**. Compound **5** crystallizes in the monoclinic space group *P*2$_1$/*c* (Nr. 14) with two independent molecules A and B per asymmetric unit (Figure 37).

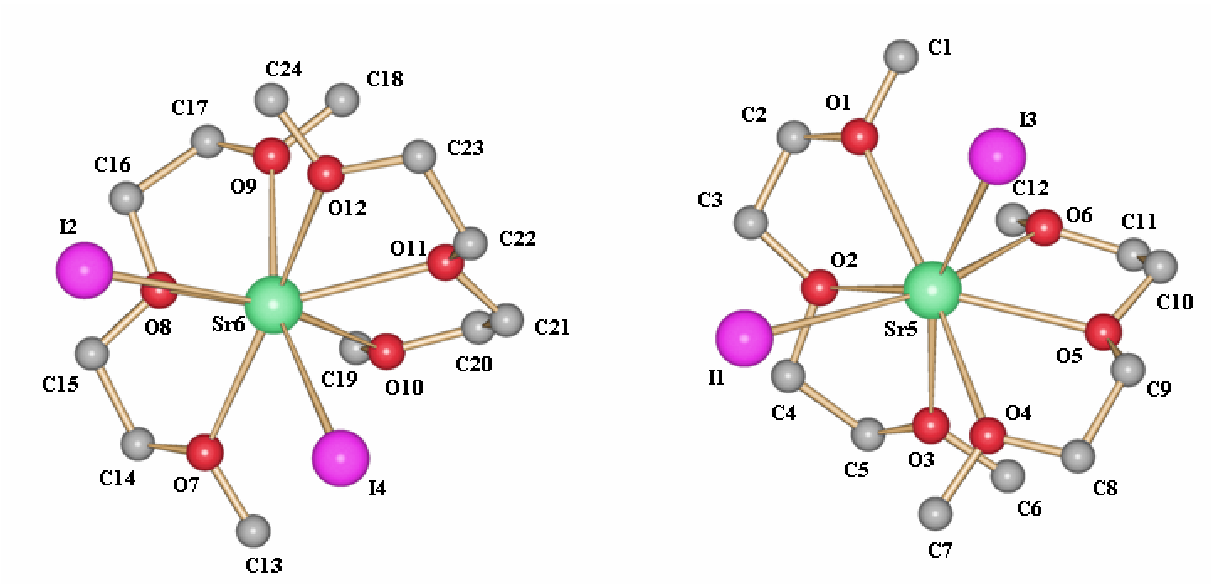


Figure 37. Schematic representation of molecules A (right) and B (left) in 5, H atoms have been omitted for clarity

Both molecules consist of a strontium cation to which two diglyme ligands and two anions are directly linked, with Sr–I distances between 3.314(3) and 3.335(3) Å, the shorter bonds being found in the first molecule A with Sr5. They are 0.11 Å longer than the Sr–I bonds in other molecular strontium iodide adducts, firstly due to the higher coordination number in **5** (eight instead of seven), and secondly due to the intra-ionic repulsion between the iodides in the *cis*-positions [155, 167]. On the other hand, they are shorter than the bonds in compounds where iodide plays the role of a μ-bridging ligand between two strontium cations [167]. Surprisingly, the Sr–I distances in **2** are 0.06 Å longer than Sr–I bond lengths in **5**, while the iodide anions are in *cis*-position in **5**. Nevertheless, this can be understood with much more interactions in **2** due to smaller ethereal ligands, repulsions of the DME ligands around the cation in **2** seem to be larger than the repulsions between diglyme ligands in **5**. The I1–Sr5–I3 angle is, at 91.25(9)°, only slightly smaller than that in the second molecule with I2–Sr6–I4 at 91.78(9)°.
In addition to the anions, each alkaline earth metal cation is surrounded by two diglyme ligands, their oxygen atoms coordinating the strontium ions with distances ranging between 2.614(7) and 2.731(8) Å. This results in a severely distorted square antiprismatic coordination sphere around the cation in each molecule. In molecule A, the bite angles of the diglyme ligand are 58.6(7) and 60.9(7)° for the first, and 58.8(6) and 60.6(6)° for the second ligand. In molecule B, the corresponding values are with 60.3(7), 61.1(7), 60.7(6) and 59.3(6)°, slightly larger than in molecule A. The O–Sr–O angles closest to linear are O1–Sr5–O4 with 166.9(7)° and O7–Sr6–O12 with 165.6(7)°. The other angles between the two diglyme ligands of each molecule are 74.2(7) and 74.3(6)° for O3–Sr5–O4 and O1–Sr5–O6, respectively, and 80.9(7)° for O3–Sr5–O6 in molecule A, and 74.1(7), 74.4(7) and 81.2(7)° for O7–Sr2–O10, O9–Sr2–O12 and O9–Sr2–O10, respectively, in molecule B. The C–O and C–C bonds are normal at 1.42 and 1.55 Å, respectively, on average, but with the general tendency of being slightly longer in molecule B than in molecule A. The molecules A and B can be considered as isolated from each other as there are no close contacts between, for instance, the iodide of one molecule and hydrogen atoms of a neighbouring unit is >3 Å. However, two weak intramolecular H-bonds can be found in molecule B, with a I2···H24B distance of 2.958(6) Å, the other with a I4···H22B distance of 3.003(2) Å. There are no contacts between the iodides of one unit and the strontium cations of another, as the cation is completely protected by the organic ligands and its own anions. Thus, the shortest distance between the anions of one molecule and the cation of another is greater than 6 Å. However, some intermolecular H-bonds can be found between two neighbouring molecules A and two

neighbouring molecules B via ethereal ligands with a O1···H1C distance of 2.997(7) Å for molecules A, and respectively a O7···H13A distance of 2.953(5) Å for molecules B. This gives a packing of dimers (Figure 38).

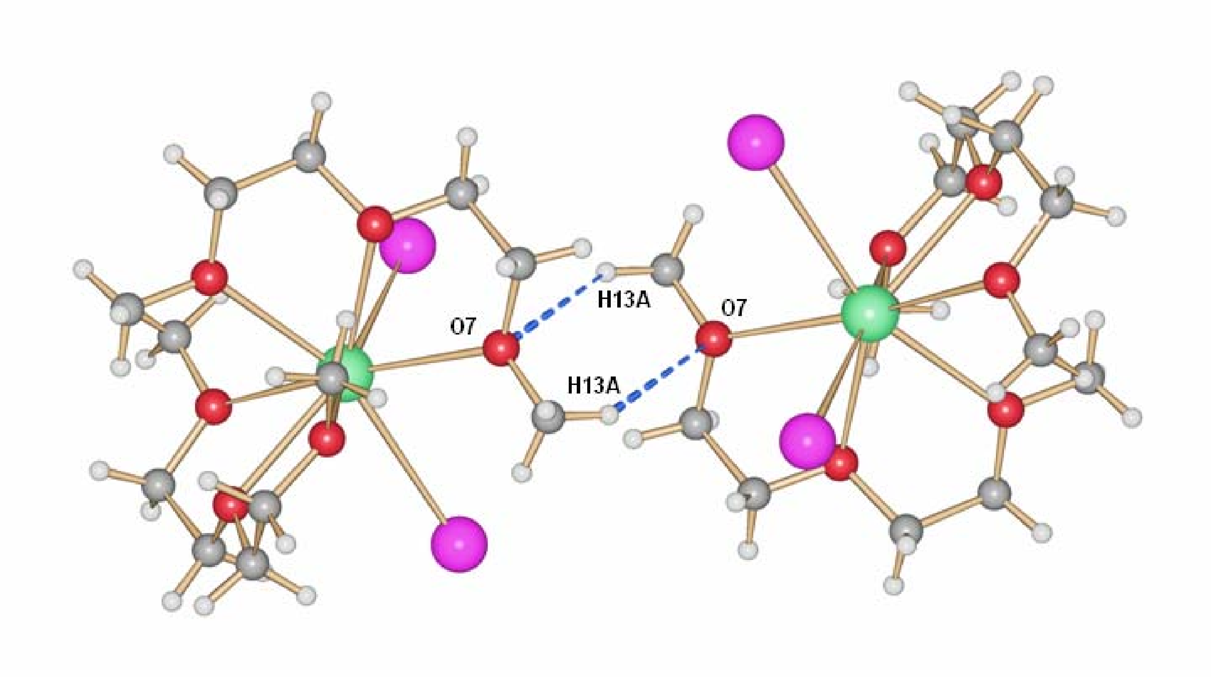


Figure 38. Schematic representation of the hydrogen bonds involved in the formation of dimeric units in 5, H atoms are placed in geometrically calculated positions and refined using a ridding model

Although there are some similarities between the two molecules A and B of **5**, no correlation matrix was found linking the two in order to indicate a higher symmetry. Furthermore, careful analysis of the X-ray data gave no hints for the presence of a higher symmetry. In **5**, however, we observe a coordination number of eight for the strontium cation, and, more importantly, a bond valence sums of 1.95 and 1.91 for Sr5 and Sr6, respectively, which is obviously less than two [190, 191]. This means that the cation is not sufficiently coordinated and would therefore be expected to be an excellent starting material for further synthesis, as it would tend to complete its coordination sphere by exchanging ligands for instance. However, the space-filling model of molecule A (Figure 39) shows how well the cation is shielded by its ligands, explaining why the bond valence sums remain below two.

The most intriguing fact about this structure is the fact that both anions occupy vicinal positions. This has never been observed before in a molecular species of the heavier alkaline earth metal halides, but only in two- or three-dimensional compounds with H-bonding involved [161, 162, 187], or forming polymers or dimers with other anions of the neighbouring units [150, 185, 197].

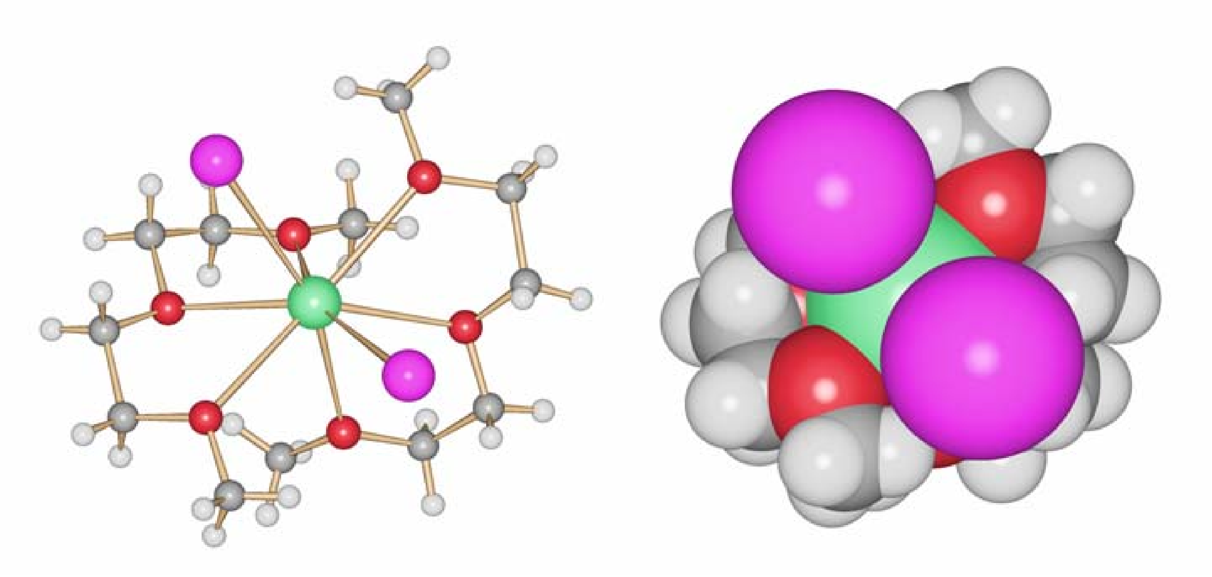


Figure 39. Schematic representation of molecule A in 5 and its space-filling representation (right)

For small alkaline earth metal cations, like Mg, with a coordination number of four, two anions are automatically in the vicinal positions, although with a larger angle between the anions than in **5** [205]. In general, to obtain such structures with the anions in *cis*-positions, a sterically important ligand, which shields one side of the cation, such as slightly too small crown ethers [187] or calixarene [207] is required. In these cases, the X–M–X angles are usually much larger and the M–X bonds are longer than in **5**, and the anions are involved in H-bonding to build up a polymeric structure. Compound **5** is the third example presented here of a polar molecular alkaline earth metal iodide precursor. The strongly bent I–Sr–I feature in this structure is reminiscent of the alkaline earth metal halides, especially the heavier ones with strontium, barium and iodide as counterions, in the gas phase. Indeed, experimental as well as theoretical data show bent structures for the molecules in the gas phase [208, 209]. So, **5** could be compared to a gas phase species stabilized by oxygen donor ligands. The bent structure is also reminiscent of the cyclopentadienyl derivatives of the alkaline earth metals. They have bent structures as well, although in the solid state they form polymers via contacts to neighbouring units. The THF-solvated cyclopentadienyl species are more similar to **5** [210-212]. More generally, other neutral complexes of alkaline earth metal cations, with coordination numbers greater than or equal to six, where two anions, such as halides or bulky amides for instance, are directly linked to the cation, preferentially show the anions organized in *trans*-positions as observed for **2**. If the anions and further coordinating ligands are sterically more demanding, a distortion from the quasi-linear arrangement is observed, although it never reaches as small angle between the anions as observed in **5** [185, 197, 205, 213, 214].

Unfortunately as for **1**, **1a** and **4**, the polarity of the molecules of **5** is not maintained in the overall solid state as the compound crystallizes in a centro-symmetric space group.

A pseudo analogue to **5** in terms of oxygen atoms with pseudo-halide is [Sr(NO_3)$_2$(EO5)] (EO5 = pentaethylene glycol) [206]. The polyether ligand, very crown ether-like, coordinates the strontium cation in an equatorial girdle. Thus, the two nitrate anions are coordinated in *trans*-positions above and below this girdle, but link molecules to each other via hydrogen bonds leading to zigzag polymeric chains.

B - I.1.7 - Crystallographic structure of trans-[BaI$_2$(diglyme)$_2$] 6

When BaI_2 is dissolved and re-crystallized from freshly dried and distilled diglyme, only the compound *trans*-[BaI$_2$(diglyme)$_2$] **6** is obtained. Compound **6** crystallizes in the triclinic space group *P*-1 (Nr. 2) with two independent molecules A and B per asymmetric unit (Figure 40). Both molecules consist of a barium cation to which two diglyme ligands and two anions are directly linked, with Ba–I distances between 3.414(3) and 3.419(4) Å, the shorter bonds being found in the first molecule A with Ba1. Compared to molecular barium iodide adducts with coordination number eight, where iodide act as terminal ligand, the Ba–I distances in **6** are shorter [187], but longer that in other barium iodide compounds with smaller coordination numbers [150, 151, 183, 215]. In compounds where iodide plays the role of a μ-bridging ligand between two barium cations and independently of the coordination number of barium cations (7-9), Ba–I distances are generally longer than in **6** [119, 150, 151, 183, 185]. The I1–Ba1–I1#1 and I2–Ba2–I2#4 angles are perfectly linear due to inversion centres on which the barium cations are located (Ba1 ½, 0, ½ (f); Ba2 0, -½, 0 (c)). In addition to the anions, each alkaline earth metal cation is surrounded by two diglyme ligands, their oxygen atoms being coordinated to the barium ion with distances ranging between 2.793(9) and 2.835(3) Å, the shorter bonds being found in molecules A.

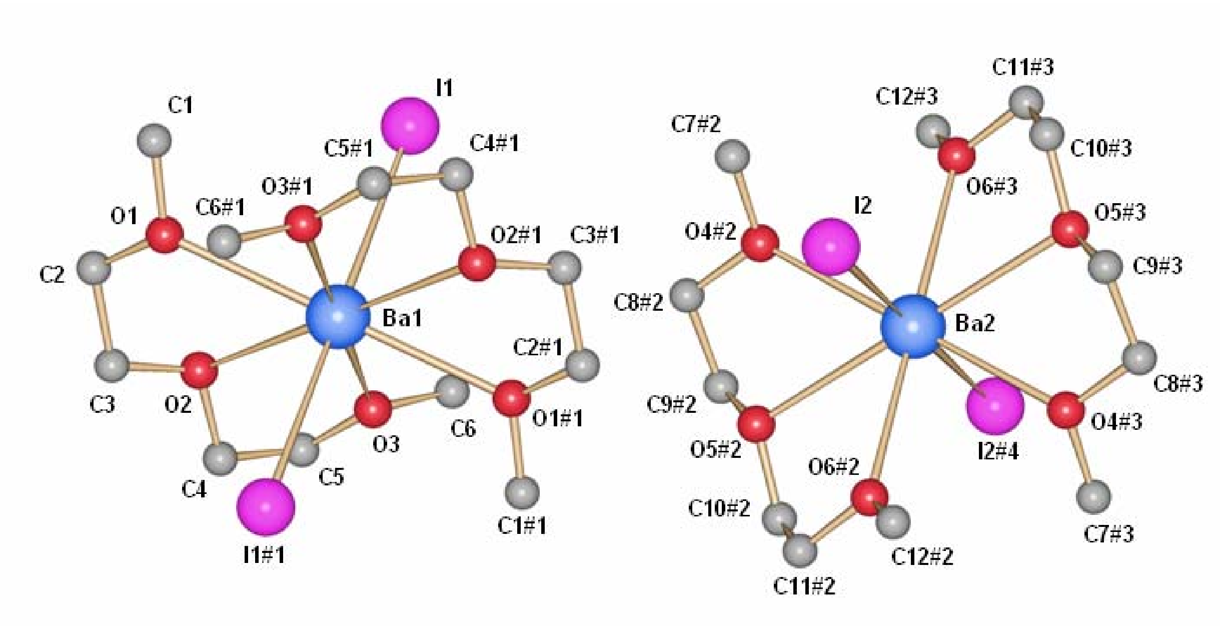


Figure 40. Schematic representation of molecules A (left) and B (right) in 6, H atoms have been omitted for clarity

In each molecule, the barium cation reaches the coordination number eight resulting in a distorted hexagonal bipyramid with the two anions in axial positions and two diglyme ligands in equatorial positions. The bite angles of diglyme ligands are 57.06(6) and 57.32(5)° in molecule A and respectively 57.56(5) and 56.89(5)° in molecule B. The other angles between the two diglyme ligands of each molecule are 68.89(6) and 68.51(6)° for O1–Ba1–O3 in molecule A and O4–Ba2–O6 in molecule B, respectively. Although there is some similarity between the two molecules A and B of **6**, no correlation matrix was found linking the two in order to indicate a higher symmetry. Furthermore, careful analysis of the X-ray data gave no hints for the presence of a higher symmetry.

In **6**, however, we observed high bond valence sums with values at 2.34 and 2.26 for Ba1 and Ba2, respectively, which is obviously larger than two [190, 191]. The cation is indeed well wrapped up by its ligands in the equatorial plane as shown in the space-filling model (Figure 41).

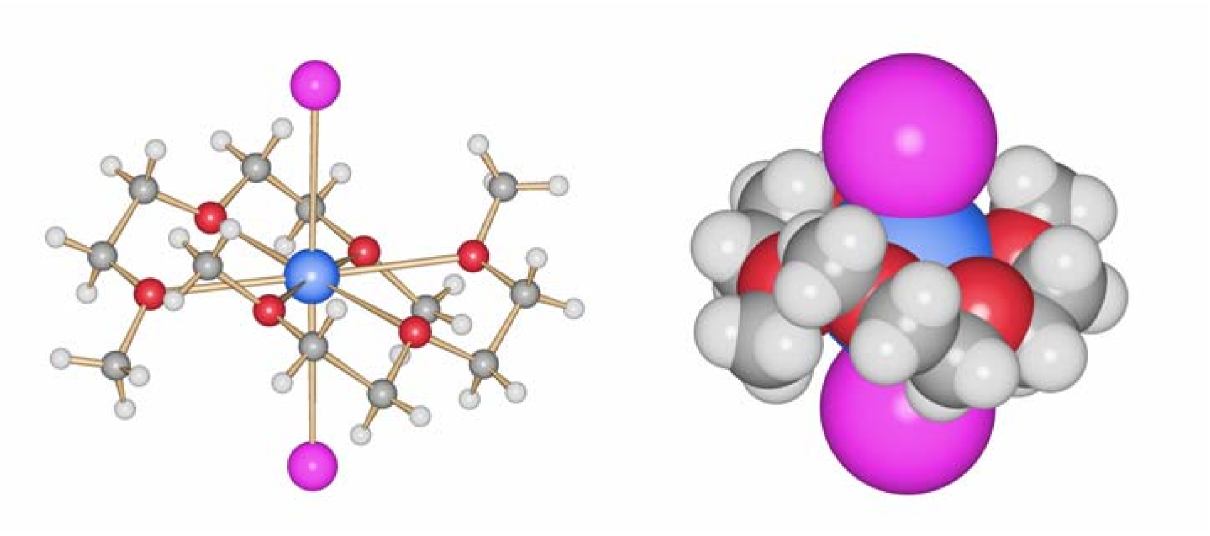


Figure 41. Schematic representation of molecule A in 6 (left) and its space-filling representation (right)

Only one hypothetic very weak intermolecular H-bond via diglyme ligands can be found between molecules A and B with a O2···H8B distance of 3.005(7) Å, leading to the formation of parallel infinite polymeric chains (Figure 42).

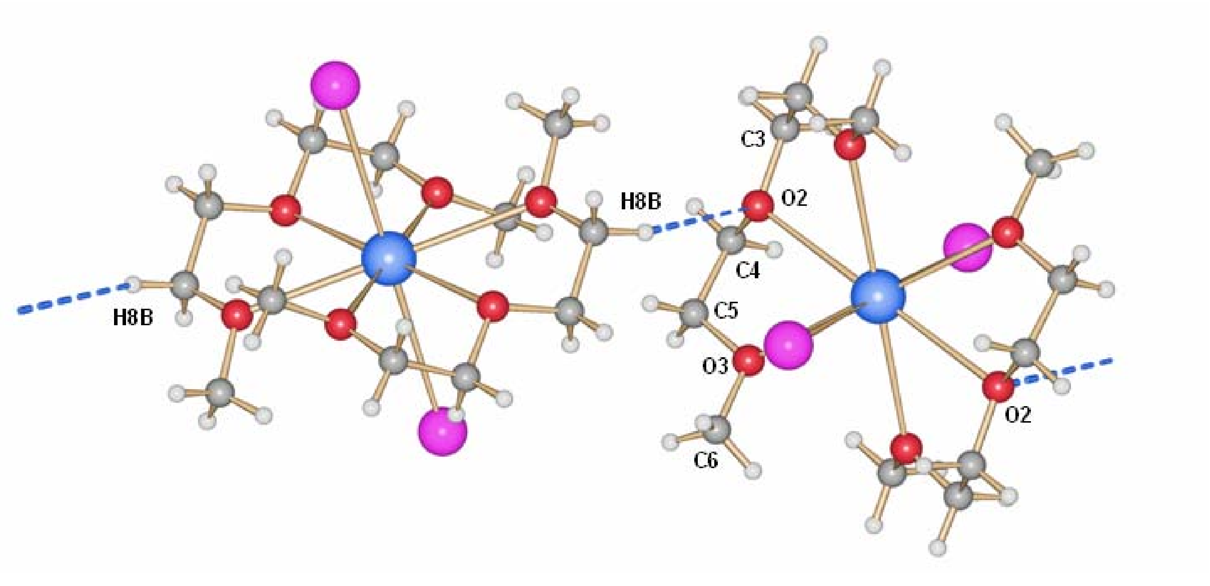


Figure 42. Schematic representation of the hydrogen bonds involved in the formation of polymeric chains in 6, H atoms are placed in geometrically calculated positions and refined using a ridding model

This O2···H8B hydrogen bond is only hypothetic. Indeed, the C3–O2–C4 and C5–O3–C6 angles are relatively similar (C3–O2–C4 = 115.0(2)°, C5–O3–C6 = 113.1(2)° respectively) indicating no or very weak interaction.

The compounds **1-6** which have been described above show that small polyether molecules can easily be replaced by larger ones, DME by diglyme for instance, as long as the number of oxygen atoms remains constant, without important changes in the structure except for higher symmetries [163]. In the case of changes in coordination numbers, "predictable" modifications occur.

B - I.1.8 - Crystallographic structure of [SrI(triglyme)$_2$]I 7

Thus, when SrI_2 is dissolved and re-crystallized from freshly dried and distilled triglyme ($CH_3O(CH_2O)_3CH_3$), only the compound [SrI(triglyme)$_2$]I **7** is obtained. The compound **7** crystallizes in the monoclinic space group $P2_1/c$ (Nr. 14) with four molecules per unit cell. The structure is built up from a cationic molecule consisting of a strontium cation to which one iodide and two triglyme ligands are bonded terminally via both oxygen atoms, with a separate iodide as counterion (Figure 43).

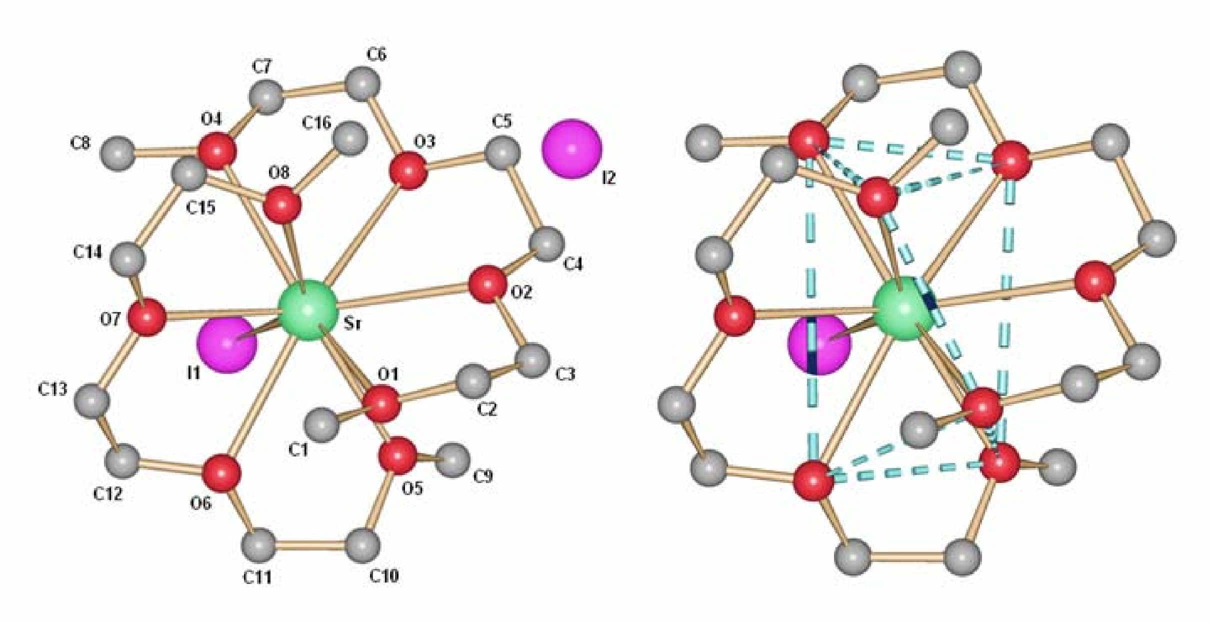


Figure 43. Schematic representation of molecule (left) and the prismatic coordination geometry of the strontium cation (right) in 7, H atoms have been omitted for clarity

As seen for calcium compounds **1**, **1a** and **4** (with DME or diglyme), triglyme ligands seem to be too large for strontium cation to accommodate also the two iodide anions in its coordination sphere. The strontium cation reaches a coordination number nine. The coordination geometry can roughly be described as a distorted tricapped trigonal prism formed by two oxygen atoms of one ligand and one oxygen atom of the other triglyme ligand in each trigonal face (O1, O2, O5 and respectively O4, O7, O8). The iodide anion and the last oxygen atom of each triglyme ligand (O3 and O6) cap the three square faces of the prism (Figure 43). The Sr–O bonds vary between 2.614(3) and 2.717(5) Å and the bite O–Sr–O angles of triglyme ligands vary between 59.98(6) and 63.91(9)°. The Sr–I bond at 3.485(4) Å in **7** is by 0.1 Å and 0.16 Å larger than the Sr–I distances observed in **2** and **5** respectively, but can be explained by a larger coordination number.

This gives a cationic species, the counterion I2 not being bonded at all to the cationic unit since all further Sr···I contacts are larger than 6.43 Å. In fact, there is no H···I contact to I2 of less than 3.13 Å (H8A···I2 = 3.139(7) Å). Therefore, these anions I2 can be considered as independent and not H-bonded to the cationic units. Only very weak intermolecular H-bonds can be found between molecules of **7** via the ethereal ligands with a O2···H12A distance at 3.095(2) Å leading to the formation of parallel zigzag polymeric chains (Figure 44).

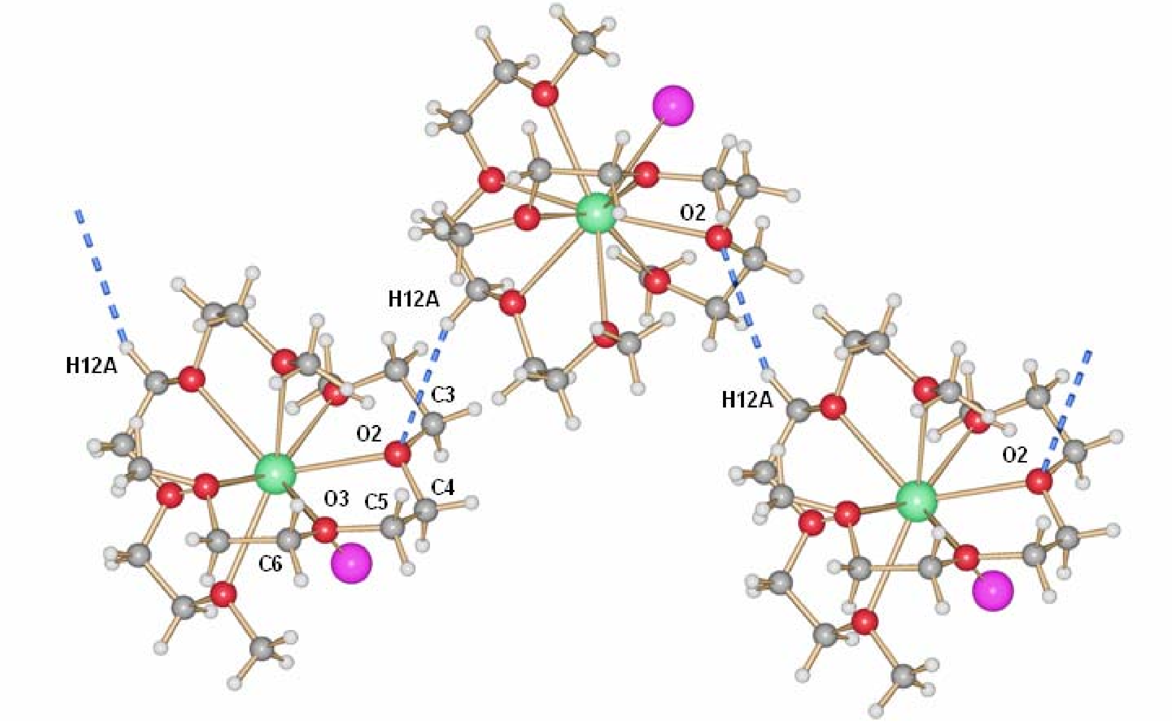


Figure 44. Schematic representation of the hydrogen bonds involved in the formation of polymeric chains in 7, H atoms are placed in geometrically calculated positions and refined using a ridding model

However, the C3–O2–C4 and C5–O3–C6 angles are relatively similar (C3–O2–C4 = 114.86(3)°, C5–O3–C6 = 112.45(3)° respectively) indicating no or at least very weak interaction.

The bond valence sum for the strontium cation in **7** is with 2.01 [190, 191] slightly larger than the charge of the cation, indicating a satisfying bonding situation. The cation is indeed well wrapped by its ligands, as shown in the space-filling model (Figure 45). The $[SrI(triglyme)_2]^+$ cations of **7** possess a strong dipole moment along the Sr–I bond vector at the molecular level, as can be seen from Figure 45. Compound **7** is therefore the fourth example presented here of a polar molecular alkaline earth metal halide, but unfortunately as for **1**, **1a**, **4** and **5**, the polarity of the molecules of **7** is not maintained in the overall solid state as the compound crystallizes in a centro-symmetric space group.

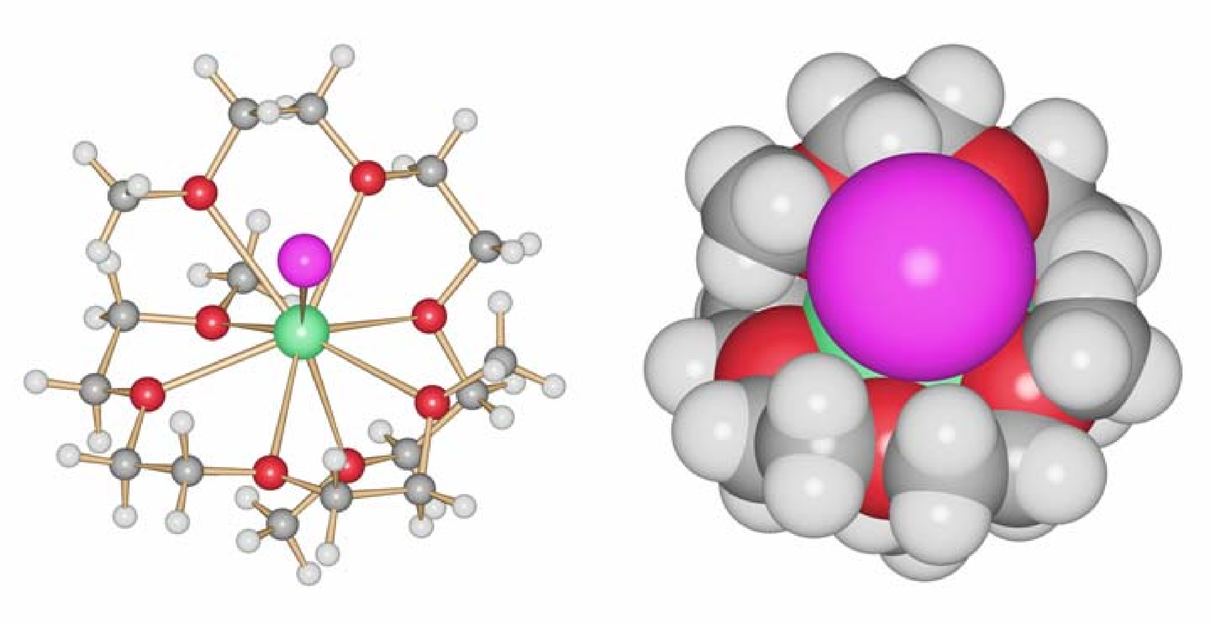


Figure 45. Schematic representation of the cationic unit $[SrI(triglyme)_2]^+$ and its space-filling representation in 7

An analogue to **7** with pseudo-halides is $[Sr(NO_3)(EO3)_2](NO_3)$ (EO3 = triethylene glycol) [206], where one anion is directly bonded to the cation whereas the other is weakly linked via H-bonds to an OH group of one of the polyglycols. In contrast to **7**, the H-bonding allows connections between anions and cationic units to form an overall three dimensional network. This is not observed in **7**. From the same reference [206], another complex with halide is described, namely $[Sr(EO3)_2]Cl_2$. The ligands form equatorial girdles resulting in pseudo cyclic, crown ether-like equatorial arrays. The chloride counterions are not directly bonded to the metal cation but via H-bonding to terminal alcoholic oxygen atoms, they act as μ-bridging group resulting in overall two dimensional sheets of zigzag polymeric chains.

B - I.1.9 - Crystallographic structure of [BaI(triglyme)$_2$]I 8

Finally, when BaI_2 is dissolved and re-crystallized from freshly dried and distilled triglyme ($CH_3O(CH_2O)_3CH_3$), only the compound [BaI(triglyme)$_2$]I **8** is obtained. The compound **8** crystallizes in the monoclinic space group $P2_1/n$ (Nr. 14) with four molecules per unit cell. Although barium possesses a larger ionic radius than strontium, the coordination of two triglyme ligands around the barium cation leads to the separate ion-pairs, as described above for [CaI(dme)$_3$]I **1** and **1a**, [CaI(diglyme)$_2$]I **4** and [SrI(triglyme)$_2$]I **7** (Figure 46).

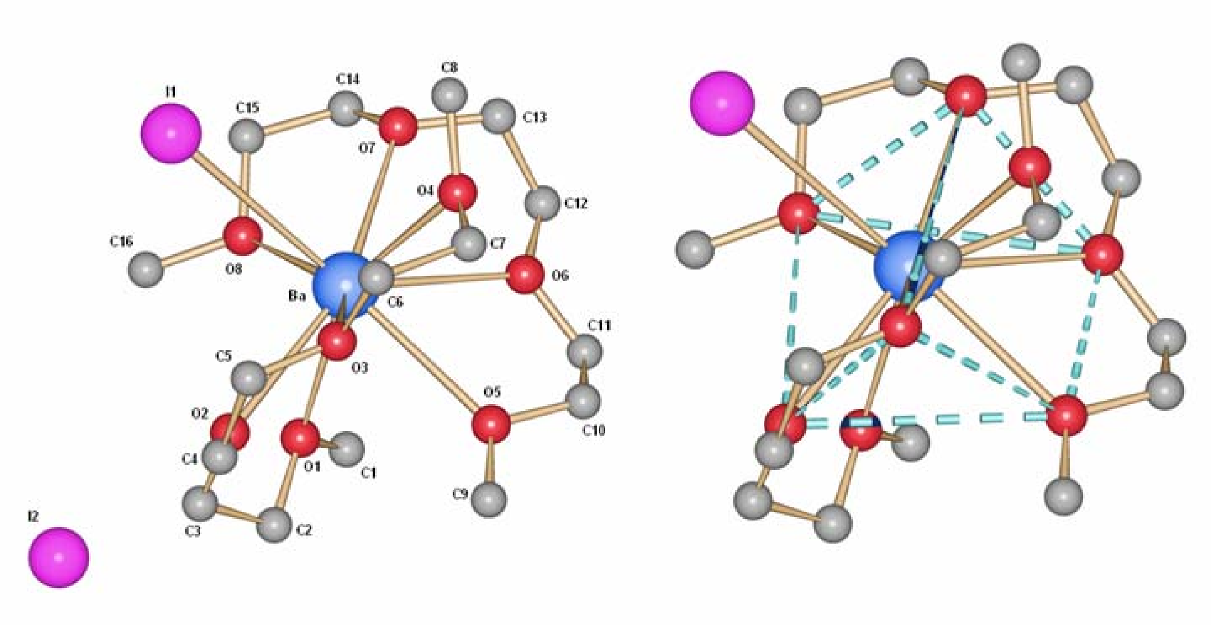


Figure 46. Schematic representation of molecule (left) and the prismatic coordination geometry of the barium cation (right) in 8, H atoms have been omitted for clarity

The barium reaches a coordination number nine and the coordination geometry can roughly be described as for the strontium adduct **7** as a distorted tricapped trigonal prism. The first trigonal face is formed by three oxygen atoms of one triglyme ligand (O6, O7, O8), the second one by the last oxygen atom of this ligand and two oxygen atoms of the other triglyme ligand (O2, O3, O5). The first and the last oxygen atoms of the second triglyme ligand (O1 and O4) and the iodide anion cap the three square faces of the prism.

The Ba–O bonds vary between 2.777(7) and 2.867(5) Å and the bite O–Ba–O angles of triglyme ligands vary between 56.92(3) and 60.56(2)°. The Ba–I bond length at 3.534(3) Å is much longer than the Ba–I distances observed in **3** and **6** but can be explained by a larger coordination number. This Ba–I distance bond length is generally observed for μ-bridging iodide anion, not for terminal ligand.

This gives a cationic species, the counterion I2 not being bonded at all to the cationic unit since all further Ba···I contacts are larger than 6.60 Å. In fact, there are no H···I contacts to I2 of less than 3.18 Å (H13B···I2 = 3.184(7) Å). Therefore, the anion can be considered as independent and not H-bonded to the cationic units.

The $[BaI(triglyme)_2]^+$ cations of **8** possess a strong dipole moment along the Ba–I bond vector, as can be seen from Figure 47. The bond valence sums for the barium cation in **8** is at 2.36 [190, 191], much larger than the charge of the cation, indicating a more than satisfying bonding situation. The cation is indeed well wrapped by its ligands, as shows the space-filling model of **8** in Figure 47, and this is the probably cause of the so long Ba–I bond.

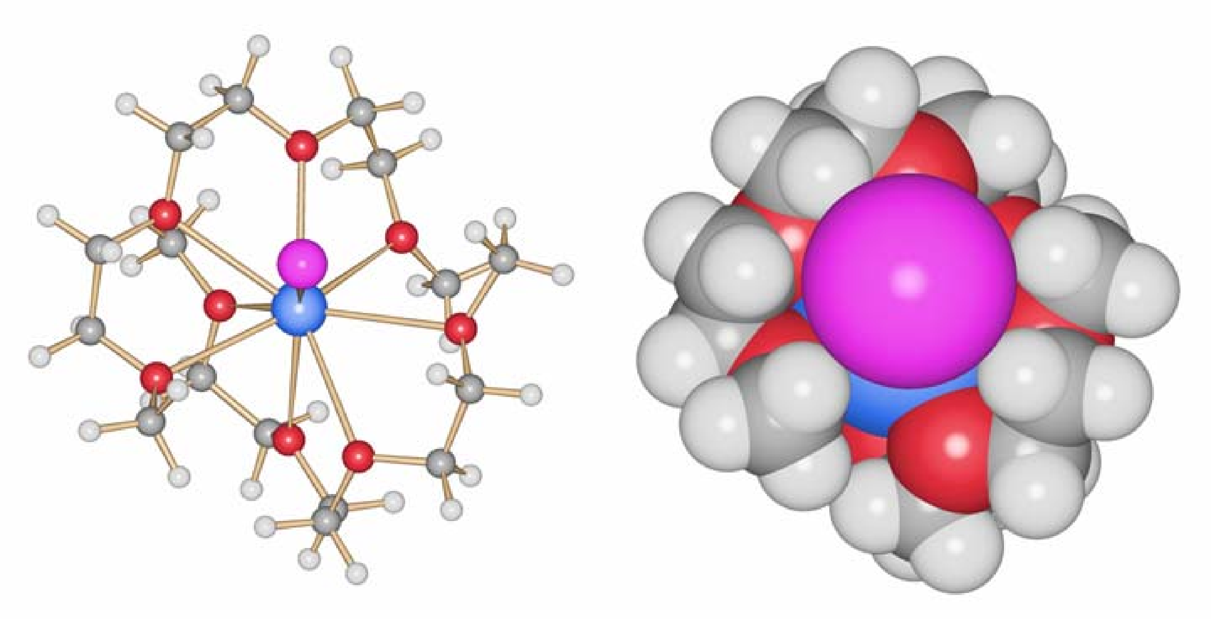


Figure 47. Schematic representation of the cationic unit $[BaI(triglyme)_2]^+$ and its space-filling representation in 8

Compound **8** is therefore the fifth example of polar molecular alkaline earth metal halides, but unfortunately as for **1**, **1a**, **4**, **5** and **7** the polarity of the molecules of **8** is not maintained in the overall solid state as the compound crystallizes in a centro-symmetric space group.

A molecular pseudo-analogue to **8** is $[Ba(heptaglyme)(NCS)_2]$ [216]. The larger heptaglyme ligand ($CH_3(OC_2H_4)_7OCH_3$) is equivalent in terms of oxygen atoms to two triglyme ligands and can be compared to a 14C8 crown-ether molecule which wraps helically very well the barium cation. Two isothiocyanate counterions are coordinated to the metal atom in *trans*-

position, these two opposites coordination sites not being occupied at all by the heptaglyme ligand.

B - I.1.10 - Comparison of the pure ethereal compounds 1-8

A comparison of the most important structural parameters of the molecular compounds **1** to **8** is given in Table 4.

Table 4. Principal parameters of the molecular compounds **1-8**, bond lengths (Å) and angles (°)

	CN	M–I (Å)	M–O (Å)	I–M–I (°)	V_M^{2+}
[CaI(dme)$_3$]I **1**	7	3.120(3)-3.121(3)	2.375(1)-2.497(1)	/	2.23-2.27
[CaI(dme)$_3$]I **1a**	7	3.050(7)	2.391(5)-2.515(4)	/	2.12
Trans-[SrI$_2$(dme)$_3$] **2**	8	3.416(3)-3.358(8)	2.570(8)-2.729(7)	158.73(3)	1.98
Trans-[BaI$_2$(dme)$_3$] **3**	8	3.479(1)	2.802(4)-2.852(3)	170.25(1)	2.17
[CaI(diglyme)$_2$]I **4**	7	3.106(7)	2.32(2)-2.49(3)	/	2.34
Cis-[SrI$_2$(diglyme)$_2$] **5**	8	3.314(3)-3.335(3)	2.61(2)-2.73(2)	91.25(9)-91.78(9)	1.91-1.95
Trans-[BaI$_2$(diglyme)$_2$] **6**	8	3.414(3)-3.419(4)	2.793(9)-2.835(3)	180	2.34-2.26
[SrI(triglyme)$_2$]I **7**	9	3.485(4)	2.614(3)-2.728(3)	/	2.01
[BaI(triglyme)$_2$]I **8**	9	3.534(3)	2.777(7)-2.867(5)	/	2.36

As described above, as far as the number of oxygen atoms in the coordination sphere of the alkaline earth metal cation remains constant, small polyether molecules can easily be replaced by larger one, mostly, without important changes in the structure. This is confirmed by comparing the crystal structures of **1** (respectively **1a**) and **4** for calcium compounds, **2** and **5** for strontium adducts and **3** and **6** for molecular barium compounds. In each case, the coordination number as well as the coordination sphere of the alkaline earth metal cation is maintained. The bond lengths vary as expected when going from the smaller calcium to the larger barium cation for the M–I and the M–O distances in all compounds. For instance, for molecular calcium adducts **1**, **1a** and **4**, with a coordination number seven, the coordination sphere of the cation can be described as a distorted pentagonal bipyramid built up by six oxygen atoms (three DME molecules in **1** and **1a,** two diglyme molecules in **4**) and only one iodide anion, the second iodide ion being free in the second coordination sphere of the alkaline earth metal cation. In fact, the calcium ion seems to be too small to accommodate either three small DME molecules or two larger diglyme ligands and two iodide anions.

From the Table 2, the Ca–O as well as the Ca–I bond lengths are slightly shorter in **4** than in **1** and **1a** but this can be easily understood by comparing the “size” of DME and diglyme molecules. DME is by nature clearly smaller than diglyme and in terms of oxygen atoms three DME ligands are equivalent to two diglyme ligands. By replacing three DME with two diglyme solvent molecules in the coordination sphere of the metal cation, the two terminal methyl-groups of the DME ligands are formally replaced by one smaller ethyl-group in diglyme. Larger ligands such as diglyme have less degree of freedom than DME but steric repulsions imposed between the three “smaller” DME ligands are stronger than those with two larger diglyme ligands around the calcium atom. This results in longer Ca–X (X = O, I) bond lengths in **1** and **1a**.

No important structural changes are also observed in the heavier homologue molecular adducts **3** and **6**. In both structures, the barium cation is surrounded by six oxygen atoms provided from three DME molecules in **3** or two diglyme molecules in **6**, and two iodide anions in *trans*-positions resulting in a hexagonal bipyramidal geometry. Each barium cation possesses thus its common coordination number eight. Although the barium cation is larger than the lighter alkaline earth metals, calcium or strontium cations, the phenomena observed between **1** and **4**, are also observed between **3** and **6**. All bond lengths, Ba–O and Ba–I respectively, are longer in **3**. Because of the higher degree of freedom of DME ligands around the barium cation in **3**, the I–Ba–I angle in **3** is by 10° smaller than the one observed in **6**, a direct consequence of the steric repulsions of the three DME ligands in the coordination sphere of the barium cation in **3**.

Two compounds obtained with larger glyme ligands (pentaglyme ($CH_3(OC_2H_4O)_5OCH_3$) and hexaglyme ($CH_3(OC_2H_4O)_6OCH_3$)), namely [Ba(pentaethyleneglycol)$(NCS)_2(H_2O)$] [217] and [Ba(hexaethyleneglycol)$(NCS)_2$] [218] are described in the literature. Larger glyme ligands such as hexaglyme can be compared to a 12C6 crown-ether molecule. In these complexes, the metal cation can easily accommodate the two anions in its coordination sphere, two opposite sides not being shielded at all by polyether ligands. In the hexaglyme compound, the two counterions are in *cis*-position (N–M–N = 74.99(9)°) and shield one face, one of the two anions being also bonded to the barium cation of a neighbouring molecule via the non occupied face, leading thus to a polymeric chain. The second compound possesses a smaller ligand, a pentaglyme molecule. The barium cation completes its coordination sphere with one water molecule and thus reaches an equal number of oxygen atoms. This water molecule shields the empty side described in the hexaglyme adduct; interactions between the counterion and the barium cation of adjacent molecules can thus not be observed any more, the water molecule blocking.

In **2** and **5**, in contrast to **1** and **4**, respectively **3** and **6**, and although the coordination number eight and the coordination sphere of the metal cation are respected, structural changes can be found. As for **1** and **4**, respectively **3** and **6**, the Sr–I bond lengths in **2** are longer than in **5**, but the Sr–O distances are slightly shorter in **2**. The most important difference between both compounds is the I–M–I angle with 158.73(3)° in **2** and a very acute angle with 91.25(9)-91.78(9)° in **5**. Contrary to **6**, due to a smaller ionic radius for strontium cation, the two larger diglyme ligands in **5** can not be accommodated in an equatorial fashion but can only shield one side of the strontium cation, as shown in Figure 39. The two iodide anions are forced to be in vicinal position with a surprisingly small I–Sr–I angle of 91.5° on average.

The two last compounds, **7** and **8**, have been obtained with a larger polyether ligand, namely triglyme, which affects consequently the coordination sphere of both alkaline earth metal cations strontium and barium. First, compared to compounds obtained with smaller polyether ligands, DME and diglyme, the coordination number of cations increases from eight to nine, the coordination sphere of cations changes from a hexagonal bipyramid (CN8) to a tricapped trigonal prism (CN9). In both cases, the alkaline earth metal cation seems to be too small, as for calcium with DME or diglyme, to accommodate the two anions in their coordination sphere yielding a separated ion-pair. The fact that the coordination number becomes larger in **7** and **8**, makes that the M–X (X = O, I) bond lengths logically get longer on average compared to distances observed in previous molecular compounds **2** and **5** for strontium and **3** and **6** for barium.

Five compounds described above, namely **1**, **4**, **5**, **7** and **8**, present some interactions (H-bonds) between molecules via the ethereal ligands, their packing leading only to the formation of dimers or polymeric chains. These interactions provided only from ligands can be expected as negligible, or at least very weak, heavier neighbouring atoms (metal and counterion) being independent from each other. In this way, all compounds can be regarded as molecular in the solid state.

Five of the eight compounds presented above present a dipole moment (**1** (**1a**), **4**, **5**, **7** and **8**), but unfortunately this is only a local phenomenon at the molecular level; these compounds crystallizing in centro-symmetric space groups, the dipole moment is vanished in the overall solid state structure. These compounds are interesting for possible applications in NLO (Non Linear Optic), for instance second harmonic generation, but the way to understand how these polar molecules can be forced to crystallize in polar space groups is still obscure and requires further investigation. Thus, crystallization of polar molecules in polar porous materials or on polar surfaces can be envisaged.

B - I.2 - Mixed ethereal compounds

B - I.2.1 - Introduction

THF-adducts *trans*-[$MX_n(thf)_m$] (M = main group metal; X = halide or pseudo-halide; n, m = integers) are common starting materials for the construction of homo or heterometallic clusters [158, 162, 167, 219-221].

The compounds **1**-**8** described in the last part are or seem to be much less reactive toward any organo-alkali compounds used during this work. The chelating nature of the glyme ligands tends to shield very well and saturate the metal cation although the bond valence sums for the strontium compounds **2** and **5** is <2, [190, 191] blocking the metal cation to any further "approach" of organo-alkali reagents. Moreover, these ligands are also less labile than monodentate ligands such as THF. In order to induce some reactivity in the compounds described above, introduction of THF seemed to be a good idea in order to "open", more or less, the coordination sphere of the metal complex to organo-alkali reagents. Mixtures of dried and distilled THF and ethereal ligands (for instance DME and diglyme) in different ratio were prepared and added to MI_2 (M = Ca, Sr, Ba) in order to obtain heteroleptic compounds. Some have been obtained and characterized, their solid state structures are described below and their reactivity is discussed.

B - I.2.2 - Crystallographic structure of trans-[$CaI_2(dme)_2(thf)$] 9

The reaction of CaI_2 and a 1:1 mixture of freshly dried and distilled DME and THF, leads to the crystallization of the compound *trans*-[$CaI_2(dme)_2(thf)$] **9**. The compound **9** crystallizes in the monoclinic space group *C*2/*c* (Nr. 15) with four molecules in its unit cell. The calcium cation is found on a crystallographic mirror plane with special position (0, y, ¼ (e)), so the asymmetric unit of **9** is composed with one calcium cation, one iodide anion, one DME ligand and half a molecule of THF. The Ca–I bond lengths of 3.137(9) Å compare well with the Ca–I distances in [CaI_2(diglyme)(dme)] [165], but are slightly longer than observed in **1** (**1a**) and [$CaI_2(thf)_4$] [119] due to a larger coordination number (seven instead of six) (Figure 48).

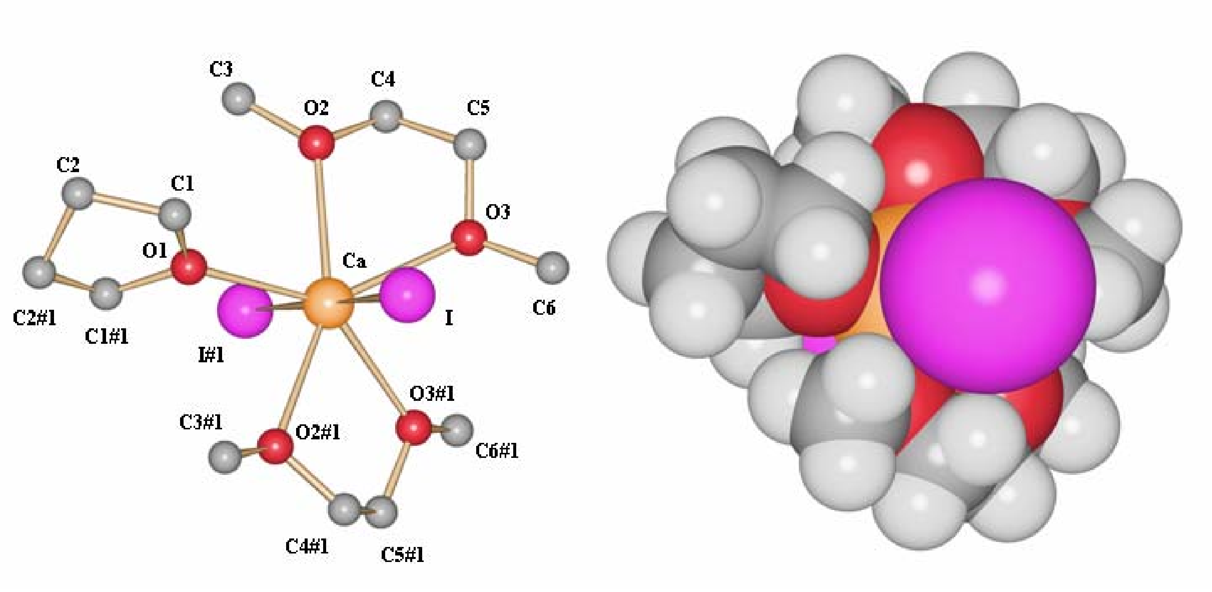


Figure 48. Schematic representation of molecule (left) and its space-filling representation (right) in 9, H atoms have been omitted in the representation of the molecule for clarity

The I–Ca–I angle (178.60(2)°) agrees with the one observed in [$BaI_2(thf)_5$] [150, 151]. In fact, the same coordination number and geometry as for the *trans*-[$MI_2(thf)_5$] adducts (M = Sr [155], Ba [150, 151]) and [CaI_2(diglyme)(dme)] [165] are observed: seven and a pentagonal bipyramid. However, due to the smaller coordination sphere around calcium however, the geometry does not fit that well the almost perfect pentagonal bipyramid of the THF-compounds any more, but resembles more a very distorted one as observed in the [CaI_2(diglyme)(dme)] adduct. The Ca–O bonds vary from 2.391(3) to 2.510(5) Å, the shortest being the Ca–O(THF). The Ca–O(DME) distances correspond well with those observed in **1** and **1a**, while the Ca–O(THF) bond length is relatively longer than the Ca–O(THF) observed in the compound trans-[$CaI_2(thf)_4$] [119].

The O–Ca–O angles of neighbouring oxygen atoms vary considerably from the ideal value of 72° with values at 67.38(7)° (bite angle of DME ligands), 76.39(9)° (angle between DME molecules) and 77.19(5)° (angles between DME and THF). Compared to the pure DME-adduct [CaI$(dme)_3$]I **1** [168], one of the three bidentate DME ligands has been replaced by one monodentate THF molecule, the missing oxygen being replaced by the second iodide anion leading no more to a separate ion-pair compound.

The bond valence sum for the calcium cation in **9** is at 1.98 [190, 191], slightly smaller than the charge of the cation, indicating a “not so much” satisfying bonding situation. This means that the cation is just sufficiently coordinated as shows the space-filling model of **9** in the (Figure 48). However, **9** is an excellent starting material for further synthesis, as it would tend to complete its coordination sphere by exchanging ligands for instance.

Molecules of **9** can be considered as independent since there is no H···I contact shorter than 3.10 Å (H4B···I = 3.101(4) Å) and no H···O interactions between molecules.

B - I.2.3 - Crystallographic structure of trans-[$SrI_2(dme)_2(thf)$] 10

When SrI_2 is dissolved and re-crystallized from a freshly dried and distilled 1:3 mixture of DME and THF, only the compound *trans*-[$SrI_2(dme)_2(thf)$] **10** is obtained. Compound **10** crystallizes in the monoclinic space group *C*2/*c* (Nr. 15) with four molecules in its unit cell. The strontium cation lays on a crystallographic mirror plane with special position (0, y, ¼ (e)), so the asymmetric unit of **10** is also constituted of one strontium cation, one iodide anion, one DME ligand and half a molecule of THF. In this structure, the strontium cation is surrounded, as for [$CaI_2(dme)_2(thf)$] **9**, by two DME ligands and one THF molecule as O-donor ligands and two iodide anions (Figure 49).

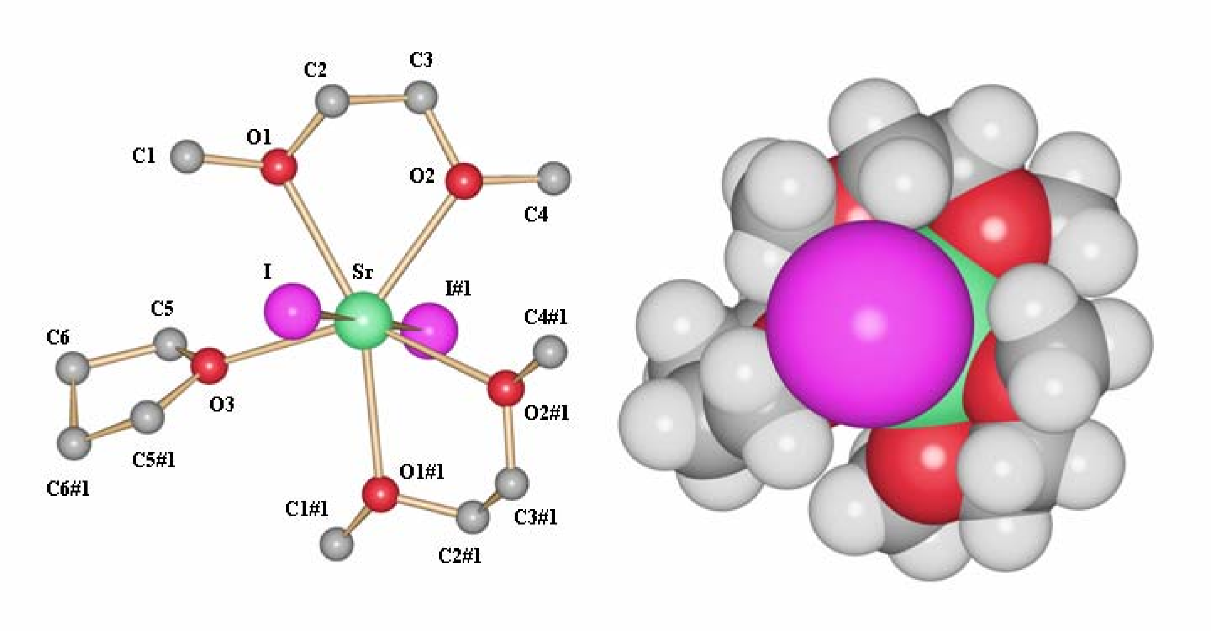


Figure 49. Schematic representation of molecule (left) and its space-filling representation (right) in 10, H atoms have been omitted in the representation of the molecule for clarity

The structure can also be described as a distorted pentagonal bipyramid, the two iodide anions being in axial positions with Sr–I bond lengths of 3.253(5) Å. These distances are slightly longer than those observed in [$SrI_2(thf)_5$] [155], but shorter than the ones observed in [$SrI_2(HOCH_3)_3$(TMEDA)] (TMEDA = $Me_2NCH_2CH_2NMe_2$) [184], compounds with the same coordination number seven. They are relatively smaller than those observed in **2**, due to its inferior coordination number (eight in **2**). The Sr–O bond lengths vary between 2.515(5) and 2.634(5) Å, the shortest being the Sr–O(THF), and are smaller than the Sr–O distances observed in **2**, **5**, **7** due to a smaller coordination number (CN7), but correspond well with those in [$SrI_2(thf)_5$] [155]. Although **10** has the same coordination sphere than [$SrI_2(thf)_5$], the geometry does not fit that well the almost perfect pentagonal bipyramid of the pure THF-compounds any more [$SrI_2(thf)_5$] [155] and [$BaI_2(thf)_5$] [150, 151], but resembles more a very distorted one as observed in **9** and [CaI_2(diglyme)(dme)] [165]. The O–Sr–O angles of neighbouring oxygen atoms vary considerably from the ideal value of 72° with values at 64.66(5)° (bite angle of DME ligands), 77.95(6)° (angle between DME and THF ligands) and 79.49(1)° (angle between DME ligands). Compared to *trans*-[$SrI_2(dme)_3$] **2**, the I–Sr–I angle in **10** is much more linear with a value of 178.64(4)°, probably due to the decrease of the sterical repulsions between the O-donor ligands with a smaller coordination number (seven in **10** instead of eight in **2**). This I–Sr–I angle is very similar to those observed in *trans*-[$MI_2(thf)_5$] (M = Sr [155], Ba [150, 151]), [CaI_2(diglyme)(dme)] [165] and **9**.

The bond valence sum for the strontium cation in **10** is at 2.07 [190, 191], slightly larger than the charge of the cation, indicating a satisfying bonding situation. This means that the cation is sufficiently coordinated as shows the space-filling model of **10** in Figure 49. **10** is indeed well wrapped by its ligands.

Molecules of **10** can be considered as independent since there is no H···I contact shorter than 3.12 Å (H2B···I = 3.123(4) Å) and no H···O interactions between molecules.

B - I.2.4 - Crystallographic structure of trans-[$BaI_2(dme)_2(thf)_2$] 11

Following the same procedure using BaI_2, the *trans*-[$BaI_2(dme)_2(thf)_2$] **11** is obtained (Figure 42). Compound **11** crystallizes in the monoclinic space group *C*2/*c* (Nr. 15) with four molecules in its unit cell. In **11**, the barium cation is located on a crystallographic mirror plane with special position (0, y, ¼ (e)), so the asymmetric unit of **11** is only composed of one barium, one iodide, one DME and one THF ligands. With a coordination number of eight, the coordination sphere of the barium cation in the complex **11** can be described as a very distorted hexagonal bipyramid (Figure 50).

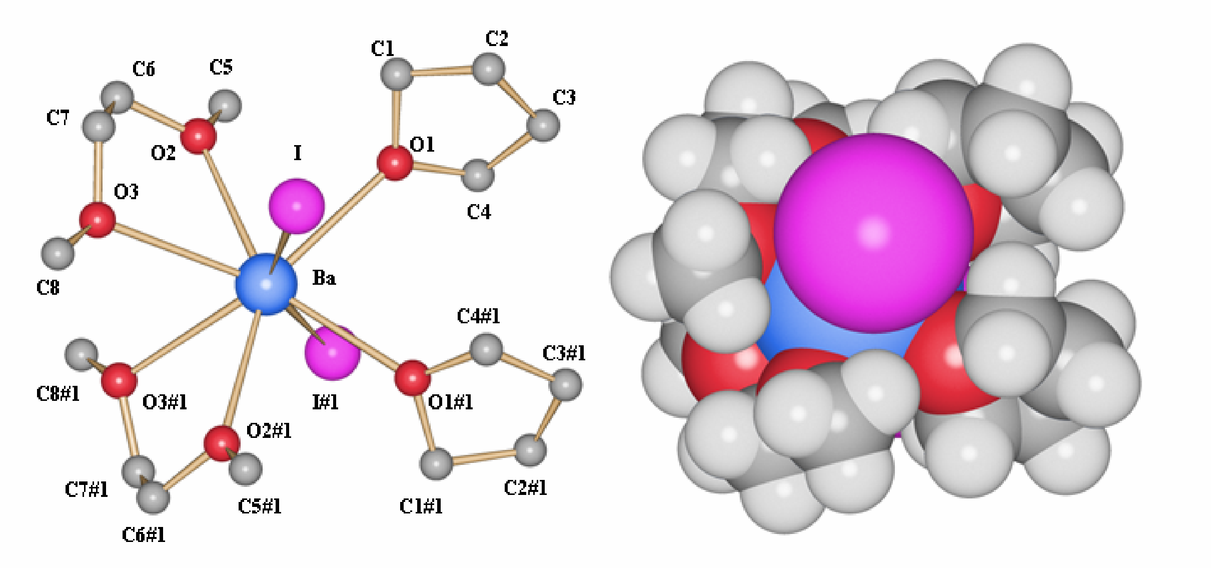


Figure 50. Schematic representation of molecule (left) and its space-filling representation (right) in 11, H atoms have been omitted in the representation of the molecule for clarity

The Ba–I bond lengths with 3.448(3) Å are smaller than those observed in other eight-coordinated molecular barium adducts [204, 205] including **3**. They are however longer than the Ba–I distances in **6**, due to the entropic effect of smaller ligands, diglyme ligands in **6** have less degrees of freedom as cited before and thus, repulsions between these ligands are smaller. They are also longer than Ba–I distances in [$BaI_2(thf)_5$] [150, 151] due to a larger coordination number.

The I–Ba–I angle, with a value of 154.90(1)°, is very far from linear as observed in the *trans*-[$BaI_2(dme)_3$] compound **3** and the *trans*-[$BaI_2(diglyme)_2$] compound **6**, but is similar to the one observed in the *trans*-[$SrI_2(dme)_3$] compound **2**. This is probably due to steric repulsions between the four ethereal ligands, the two DME ligands shielding one side of the barium cation, the other side being shielded by the two THF molecules.

As discussed in the last part, for an equal number of oxygen atoms, larger ligands are less sterically demanding than smaller one. These O-donor ligands are coordinated to the barium cation with Ba–O distances ranging between 2.755(3) and 2.852(3) Å. In **11**, contrary to the other mixed-ethereal ligand adducts **9** and **10**, the Ba–O(thf) bond lengths are not the shortest ones with Ba–O(thf) = 2.763(3) Å on average. These distances are longer than those observed in the compound *trans*-[$BaI_2(thf)_5$] [150, 151] and correspond well with Ba–O bonds lengths in **3** and **6**. The O–Ba–O angles in **11** vary from 58.33(9)° (bite angle of the DME ligands), 68.77(1) ° (angle between DME and THF ligands) to a very large angle of 79.43(1)° for the O(THF)–Ba–O(OTHF).

The bond valence sum for the barium cation in **11** is with 2.37 [190, 191], much larger than the charge of the cation, indicating a very satisfying bonding situation. This means that the cation is well coordinated as shows the space-filling model of **11** in Figure 50.

Molecules of **11** can be considered as independent to each other since there is no H···I contact less than 3.19 Å (H3A···I = 3.200(4) Å). However, some very weak intermolecular H-bonds can be found between one oxygen atom of each DME ligand and one hydrogen atom of each THF molecule of a neighbouring molecule with a H3B···O3 distance of 3.013(9) Å, leading to parallel polymeric chains (Figure 51). Whereas in complex *trans*-[$BaI_2(dme)_3$] **3**, the C–O–C angles are almost similar and no H-bonds are observed between DME ligands, the angles C5–O2–C6 = 111.6(4)° and C7–O3–C8 = 114.2(4)° in **11** are slightly different. However, this difference is relatively small and might only indicates very weak interactions between molecules of **11** via THF and DME ligands.

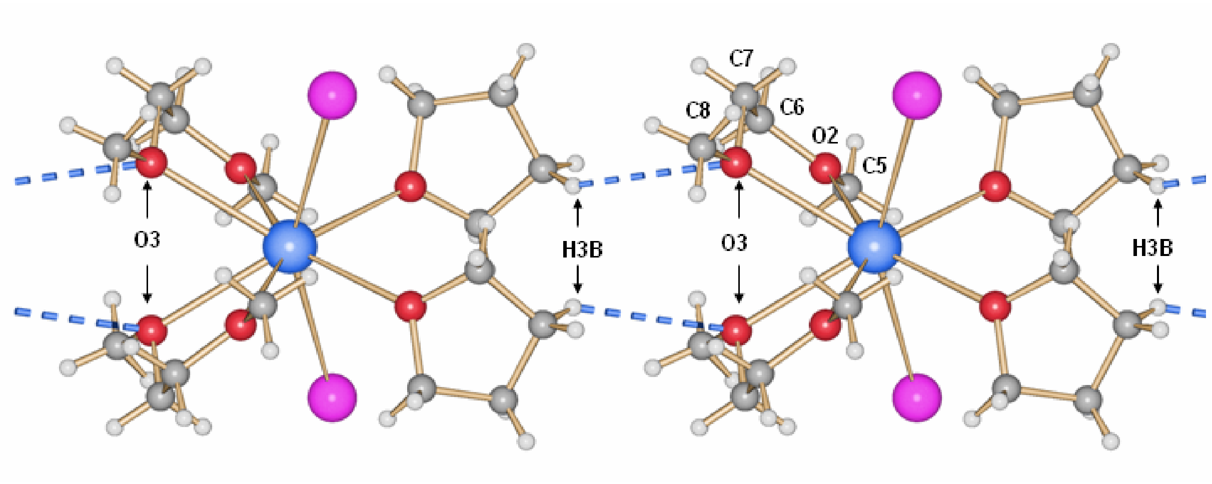


Figure 51. Schematic representation of the hydrogen bonds involved in the formation of polymeric chains in 11, H atoms are placed in geometrically calculated positions and refined using a riding model

B - I.2.5 - Crystallographic structure of trans-[CaI$_2$(diglyme)(thf)$_2$] 12

The reaction of CaI$_2$ in a 1:1 mixture of freshly dried and distilled diglyme and THF, leads to the crystallization of the compound *trans*-[CaI$_2$(diglyme)(thf)$_2$] **12** (Figure 52). It crystallizes in the orthorhombic space group *P*bca (Nr. 61) with eight molecules in the unit cell. In **12**, the Ca–I bond lengths are 3.110(8) and 3.112(3) Å, and compare well with Ca–I distances in [CaI$_2$(diglyme)(dme)] [165], but are slightly longer than in [CaI$_2$(thf)$_4$] [119] due to a larger coordination number (seven instead of six) and are slightly shorter than the Ca–I bond lengths in **9**.

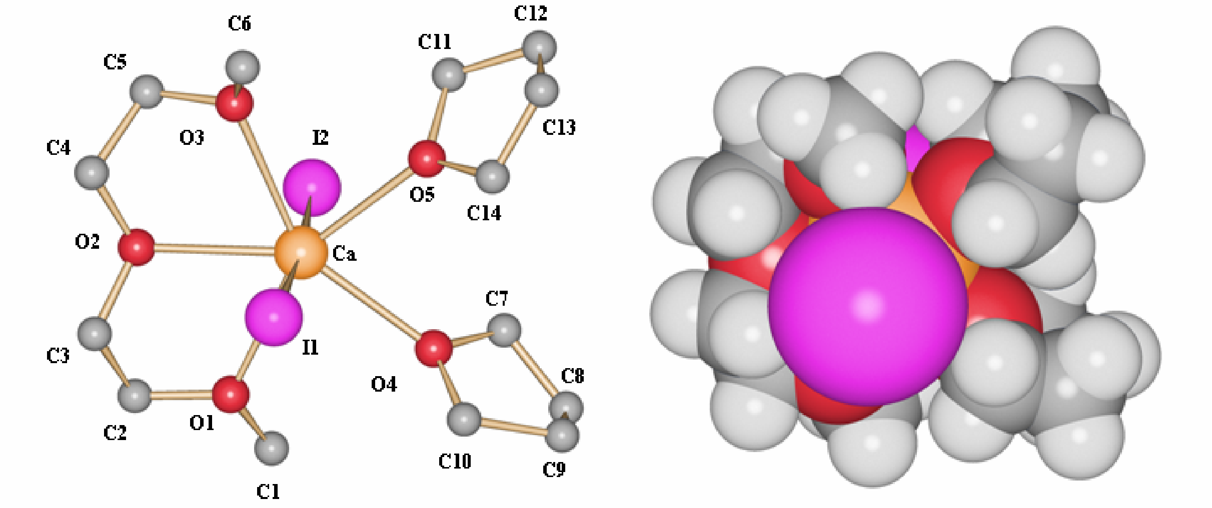


Figure 52. Schematic representation of molecule (left) and its space-filling representation (right) in 12, H atoms have been omitted in the representation of the molecule for clarity

The I–Ca–I angle with 175.48(1)° agrees with the one observed in [CaI_2(diglyme)(dme)] [165] but is slightly smaller than in *trans*-[CaI_2(thf)$_4$]. As described above for **1** (**1a**) and **4** (and respectively **2** and **5**, **3** and **7**), small polyether molecules (such as THF) can easily be replaced by larger ones, DME for instance, as long as the number of oxygen atoms remains constant, without changes in the structure except for higher symmetries [163]. But what happened when larger ligands are replaced by smaller one? The coordination spheres of **12** and [CaI_2(diglyme)(dme)] are very similar with only the formal substitution of the two THF molecules in **12** by one larger DME ligand in [CaI_2(diglyme)(dme)]. In both compounds, the Ca–O bonds in average are similar (Ca–O = 2.460(1) Å in **12**).

Usually, the coordination number of seven in the form of a pentagonal bipyramid is observed with distortion, at least one oxygen atom being out of the mean plane formed by the oxygen atoms of the ligands. This is observed in compounds *trans*-[CaI_2(diglyme)(dme)] [165] and **9** but not in **12**. In **12**, all oxygen atoms of the ligands, as well as the calcium cation, are in the same plane, no distortion is observed probably due to higher degrees of freedom for THF ligands. On the other hand, the O–Ca–O angle in **12** varies considerably from the ideal value of 72° with values comprised between 65.21(7) (one of the bite angles of the diglyme ligand) and 78.94(6)° (angle between O4(thf) and O1(diglyme)).

The bond valence sum for the calcium cation in **12** is at 2.05 [190, 191], slightly higher than the charge of the cation, indicating a satisfying bonding situation. This means that the cation is sufficiently coordinated as shows the space-filling model of **12** in Figure 52.

Molecules of **12** can also be considered as independent to each other since there is no H···I contact shorter than 3.22 Å (H1A···I2 = 3.225(8) Å).

B - I.2.6 - Comparison of the mixed-ethereal ligand compounds 9-12

A comparison of the most important structural parameters of the starting materials **9** to **12** is given in Table 5.

In each compound from **9**-**12**, the alkaline earth metal cation reaches a common coordination number: seven for the smaller calcium and strontium cations and eight for the larger barium cation. As can be seen from Table 3, the bond lengths vary as expected when going from the smaller calcium to the larger barium cation, as observed with the compounds **1**-**8**. Compared to the pure ethereal compounds **1** (**1a**) and **4**, mixed-ethereal compounds **9** and **12** have the same coordination number (CN7), but not the same coordination sphere. One of the three DME ligands of **1**, respectively **1a** is formally replaced by one THF and one iodide anion in **9**, the two iodide anions in **9** are now in *trans*-positions. The same process occurs in **12**, one diglyme ligand of **4** is formally replaced by two THF molecules and one iodide anion. The two iodide anions are in *trans*-positions in both compounds **9** and **12** and lead to a non-polar molecule.

Table 5. Principal parameters of **9-12**, bond lengths (Å)and angles (°)

	CN	M–I	M–O	I–M–I	V_M^{2+}
[$CaI_2(dme)_2(thf)$] **9**	7	3.137(9)	2.391(3)-2.510(5)	178.60(2)	1.98
[$SrI_2(dme)_2(thf)$] **10**	7	3.253(5)	2.515(5)-2.634(5)	178.64(4)	2.07
[$BaI_2(dme)_2(thf)_2$] **11**	8	3.448(3)	2.756(1)-2.852(3)	154.90(1)	2.37
[$CaI_2(diglyme)(thf)_2$] **12**	7	3.112(3)-3.110(8)	2.405(7)-2.519(6)	175.48(1)	2.05

Some formal substitutions also occur in the coordination sphere of **11** with respect to **3** while its coordination number did not change. One DME molecule of **3** has been formally replaced by two THF molecules in **11**. However, this substitution generates some changes, the most important being the I–Ba–I angle, which is relatively far from linear in **11** (I–Ba–I = 154.90(1)°). This can be understood comparing the two crystal structures of **3** and **11**, monodentate ligands such as THF (compound **11**) are more flexible than polydentate ligands such as DME (compound **3**), thus they occupied more space due to less constraint in the coordination sphere of the metal cation in **11** compared to **3**.

The opposite fact is observed for **10**, where one DME molecule of **2** has been formally replaced by only one THF molecule in **10** probably due to a smaller ionic radius for the strontium cation. Thus, the coordination number decreases from eight in **2** to seven in **10**, the steric repulsions between ethereal ligands observed in **2** decreased in **10**, the I–Sr–I angle in **10** is now much more close to linear with a value of 178.64(4)° (158.73(3)° in **2**).

Only one mixed ethereal compound, namely *trans*-[$BaI_2(dme)_2(thf)_2$] **11**, has some interactions between molecules in its packing. These interactions, hydrogen bonds between ethereal ligands (as observed in the pure molecular compounds **1**, **2**, **5**, **6**, **7** described above), are very weak and can be assumed as negligible. Thus, the compounds **9-12** can be considered as molecular in the solid state.

Similar to the pure ethereal compounds, several attempts were made to synthesize alkaline earth metal “clusters” with these mixed-ethereal molecular and organo-alkali compounds. Most of them were successful, but the introduction of different ligands (DME and THF) via the starting material did not have any influence on the structure and the formula of the final clusters. Same clusters were obtained using THF- as well as mixed THF/polyether starting materials.

B - I.3 - Comparison of molecular alkaline earth and rare earth metal iodide adducts

Lanthanide cations are generally described as very electropositive spheres. The 4f orbitals are often described as “diffuse” and are confined to the inner region of the ion, rare earth ions are not affected with the crystal field effects. Thus, steric rather than bonding requirements usually govern the arrangement of ligands in the coordination sphere of the metal ions.

The chemistry of the alkaline earth metal ions calcium, strontium and barium can be compared with that of divalent rare earth metals ytterbium, europium and samarium due to close similarities in the size/charge ratio for Yb^{2+}/Ca^{2+} and Eu^{2+}, Sm^{2+}/Sr^{2+} (Table 1) [156].

The alkaline earth metal cation Ba^{2+} does not have any divalent lanthanide analogue, except La^{2+}, the largest “possible” divalent lanthanoid. Indeed, the ionic radii of eight and ten coordinated Ba^{2+} ions are 1.42 Å and 1.52 Å respectively, while from an extrapolation of Shannon radii [156], the radii of La^{2+} is approximately 0.07 Å smaller.

While the chemistry of divalent lanthanide metal iodides recently rapidly expanded due to wide applicability to both organic [146] and organometallic [222] synthesis (especially with the well known selective one-electron reducing reagents SmI_2/THF [142-144, 223]), the analogy between alkaline earth and divalent rare earth metals has been little pursued. Apart from the well-developed cyclopendienide chemistry [135, 136], few other molecular compounds have been prepared with identical ligand and donor sets to allow the direct comparison of their synthetic and structural chemistry [130].

Amongst the reported molecular adducts, some examples of LnI_2 Ln = Yb, Sm, Eu compounds synthesized with polyether ligands (THF, DME, diglyme, triglyme and tetraglyme) and also mixtures of them present a similar behaviour with alkaline earth metal iodide adducts. Because of that, a direct comparison between the two groups of metals, in particular between the Yb^{2+}/Ca^{2+} and respectively Sm^{2+}, Eu^{2+}/Sr^{2+} adducts, both in terms of synthetic methods and structural features can be undertaken in order to establish some correlation between them.

The structures of the THF-derivatives of the alkaline earth MI_2 (M = Ca, Sr, Ba) as well as the divalent lanthanides EuI_2 and SmI_2 presented in the introduction show a very high degree of similarity both in terms of structures, bond length, angle as well as synthetic part.

Just from a structural point of view, the chemistry of the trivalent LnX_3 (X = Cl, I) is richer while the chemistry of lanthanide triiodide is not so explored. For instance, many types of ionic complexes with homoleptic environment but heteroleptic coordination have been characterized [224-226]. Among of them, two THF adducts of ytterbium(III) present very interesting and amazing structures, $[YbI_2(thf)_5]I_3$ [227] (Figure 53) and $[YbI_2(thf)_5][YbI_4(thf)_2]$ [228] (Figure 54), the former compound possess a lanthanum(III) analogue [229] and the latter compound possess an yttrium(III), a neodymium(III), a samarium(III) and a gadolinium(III) analogues of formula $[MI_2(thf)_5][MI_4(thf)_2]$ (M = Y [230], Nd [230], Sm [231], Gd [230]).

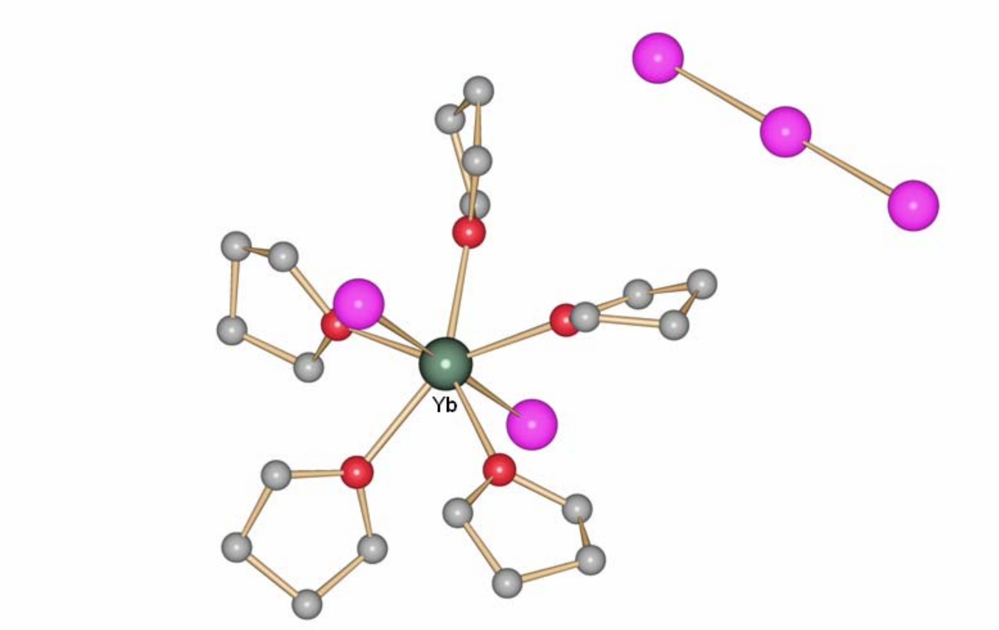


Figure 53. Molecular representation of the compound $[YbI_2(thf)_5]I_3$, H atoms have been omitted for clarity

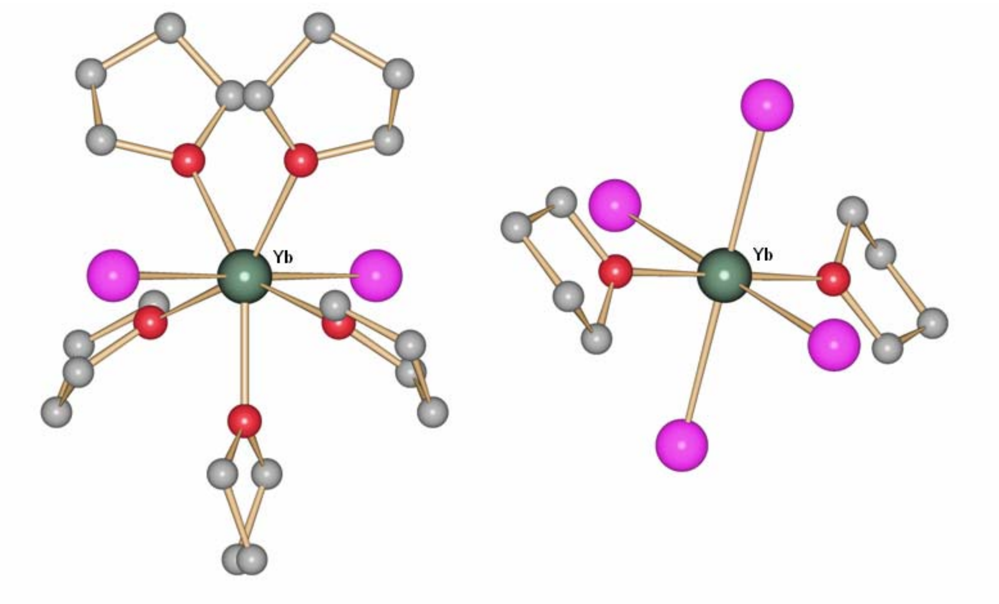


Figure 54. Molecular representation of the compound [$YbI_2(thf)_5$][$YbI_4(thf)_2$], H atoms have been omitted for clarity

In presence of the bidentate DME ligand, isomorphic structures have been characterized for Eu(II) and Sm(II) iodide with *trans*-[$LnI_2(dme)_3$] M = Eu [232], Sm [233, 234] (Figure 55). These two compounds possess an analogue structure than *trans*-[$SrI_2(dme)_3$] **2** [176] (and *trans*-[$BaI_2(dme)_3$] **3**) with three chelating equatorial DME ligands and two iodide ligands in apical positions of a distorted hexagonal bypiramid. However, different chiral crystal structure can be obtained as a function of the crystallization conditions (temperature). At ambient temperature two configurationally chiral *Δ* and *Λ* adducts are produced in the same ratio whereas at -20°C a different phase is obtained. For the former compounds only the arrangement of the DME ligands in the coordination sphere of the Sm^{2+} change leading to enantiomers, the I–Sm–I angle in both compounds is similar. However, at -20°C a racemic phase with two geometrical isomers are produced in the same crystal which is really scarce. One closely resembles to *Δ* and *Λ*, but the other differs with a I–Sm–I angle at 180°.

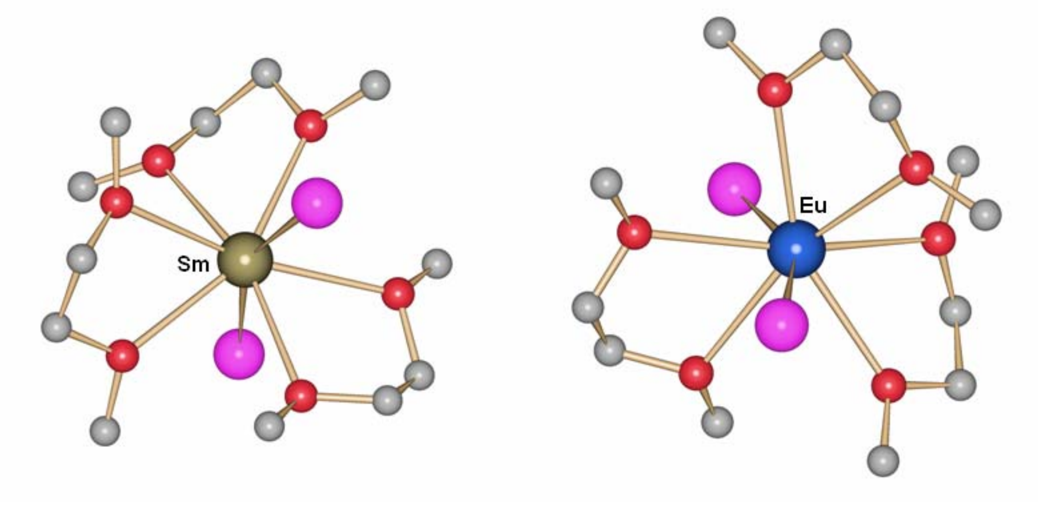


Figure 55. Molecular representation of *trans*-[$SmI_2(dme)_3$] (left) and *trans*-[$EuI_2(dme)_3$] (right), H atoms have been omitted for clarity

Unlike calcium, which only accommodates three DME and one iodide ligands in its coordination sphere resulting in [CaI(dme)$_3$]I **1** [168] or **1a**, the divalent ytterbium Yb^{2+} accepts the two iodide anions but not the three DME ligands. Due to a higher electroposivity and a larger ionic radius (Table 1) than Ca^{2+} [156], the Yb^{2+} metal ion may prefer forming a neutral complex. Two YbI_2/DME adducts have been cristallographically characterized (Figure 56), one monomer *trans*-[$YbI_2(dme)_3$] [235] and one dimer *trans*-{(μ-dme)[$YbI_2(dme)_2$]$_2$} [236], the formation of the latter might be a logical consequence of a non-coordinated oxygen atom of one DME ligand in the former compound.

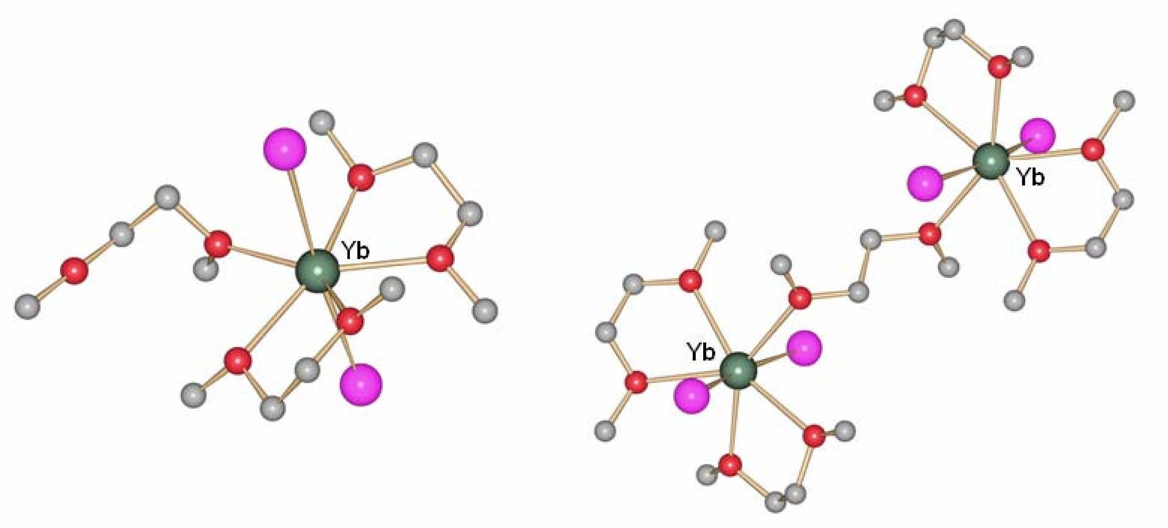


Figure 56. Molecular representation of *trans*-[$YbI_2(dme)_3$] (left) and *trans*-{(μ-dme)[$YbI_2(dme)_2$]$_2$} (right), H atoms have been omitted for clarity

With the larger tridendate diglyme ligand, some interesting results have been obtained with Sm^{2+} with the characterization of the two diastereoisomers *cis* and *trans*-[SmI_2(diglyme)$_2$] [237, 238] (Figure 57). Nevertheless, while the *trans*-isomer is easily obtained by addition of diglyme to $SmI_2(thf)_2$, the *cis* isomer was obtained in low yield as a byproduct. Only few structurally characterized geometrical isomers have been reported for eight-coordinate complexes, such as [SmI_2(dme)$_3$] [233, 234], but they should exist [239]. The *cis*-isomer is very similar to [SrI_2(diglyme)$_2$] **5** both in terms of general arrangement and bond lengths as well as angles. The I–M–I angle in the *cis*-[SmI_2(diglyme)$_2$] is comparable to the one in **5** with a value at 92.0(1)° (91.52(9)° in **5**). However, the *trans*-[SmI_2(diglyme)$_2$] looks more like **6**, *trans*-[BaI_2(diglyme)$_2$], although the Ba^{2+} cation is larger than Sm^{2+}. Nevertheless, the ionic radius of Sm^{2+} is slightly larger than the Sr^{2+} one (for a CN8: $r_{Sr}{}^{2+} = 1.26$ Å, $r_{Sm}{}^{2+} = 1.27$ Å [156]), and should explain why the samarium cation allows the two isomeric forms, *cis*- and *trans*- whereas in our results the strontium ion only adopts the *cis*-arrangement.

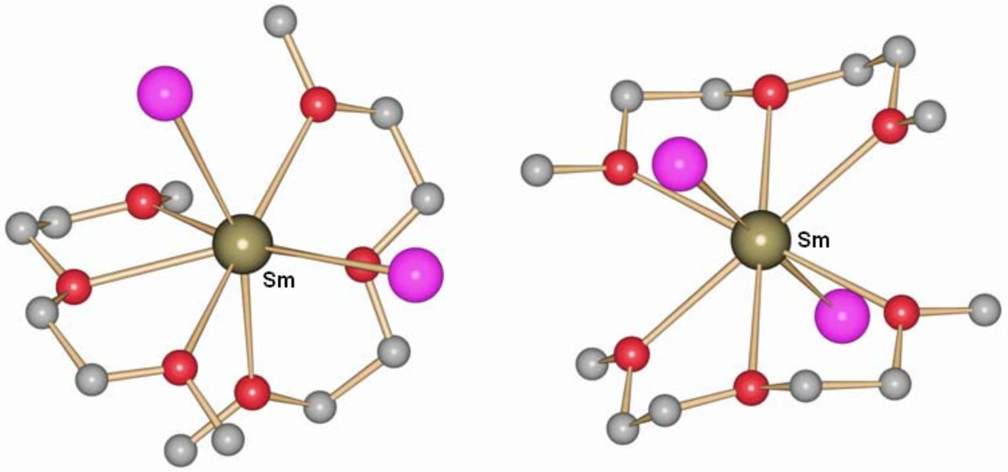


Figure 57. Molecular representation of the two geometrical isomers of [SmI_2(diglyme)$_2$]: cis-[SmI_2(diglyme)$_2$] (left) and *trans*-[SmI_2(diglyme)$_2$] (right), H atoms have been omitted for clarity

Whereas it was impossible in this work to obtain homoleptic calcium iodide adducts with larger polyether ligand than diglyme, a seven-coordinated ytterbium iodide compound was isolated with tetraglyme ($CH_3(OC_2H_4)_4OCH_3$), namely *trans*-[YbI_2(tetraglyme)] [240] (Figure 58). Larger ligands such as tetraglyme are very crown-ether like, they loose in entropy but de facto, the steric repulsions decrease. Compared to the previously described compounds *trans*-[YbI_2(dme)$_3$] [235] and *trans*-{(μ-dme)[YbI_2(dme)$_2$]$_2$} [236], the cited phenomenon with alkaline earth metal ions also occurs here, the tetraglyme ligand replaces the two and half

DME molecules without changes in the structure, the number of oxygen atoms being equivalent.

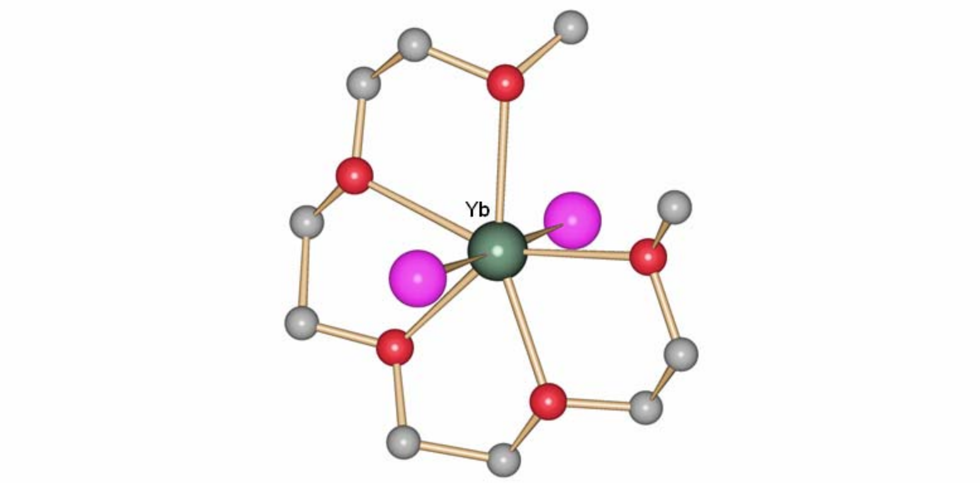


Figure 58. Molecular representation of the compound *trans*-[YbI_2(tetraglyme)], H atoms have been omitted for clarity

An amazing Sm^{2+} compound was obtained by mixing SmI_2 to a tetraglyme solution; the complex is composed of three ionic species in the form of [Sm(tetraglyme)$_2$][SmI_3(tetragyme)]I [240]. In the cationic species [Sm(tetraglyme)$_2$]$^{2+}$, the samarium cation is surrounded by two tetraglyme ligands, and thus presents an unusual ten-coordinated complex. The +2 charge is counterbalanced by two separate anionic species: a seven-coordinated [SmI_3(tetraglyme)]$^-$ and one free I^- (Figure 59). This shows the rich structural chemistry with the high potential coordination numbers for lanthanide metal ions.

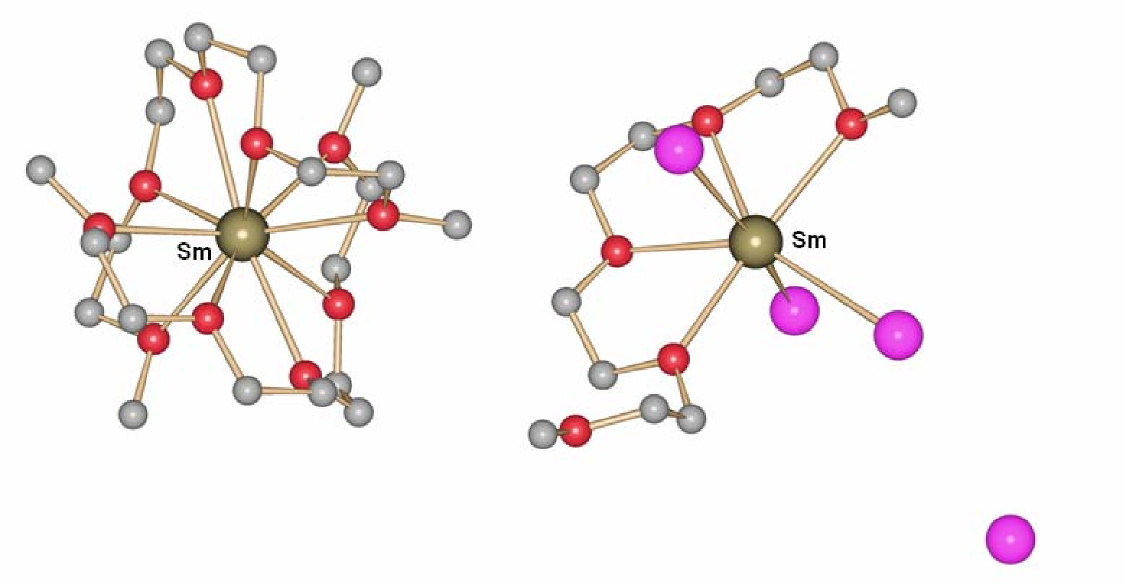


Figure 59. Molecular representation of the amazing compound [Sm(tetraglyme)$_2$][SmI$_3$(tetragyme)]I, H atoms have been omitted for clarity

Some divalent rare earth metal complexes with mixture of ethereal ligands, namely THF and DME have been reported, among of them *trans*-[SmI$_2$(dme)$_2$(thf)] [154] and *trans*-[SmI$_2$(dme)(thf)$_3$] [154] (Figure 60). The former compound possesses an isomorphic structure to the one described for [SrI$_2$(dme)$_2$(thf)] **10** as well as a similar synthetic procedure. Both compounds present a seven-coordinated pentagonal bipyramidal structure with iodide anions in apical positions. However, in the preparation of *trans*-[SrI$_2$(dme)$_2$(thf)] **10**, it is not possible to isolate the strontium analogue with three THF-coordinated molecules, **10** is the only compound characterized so far.

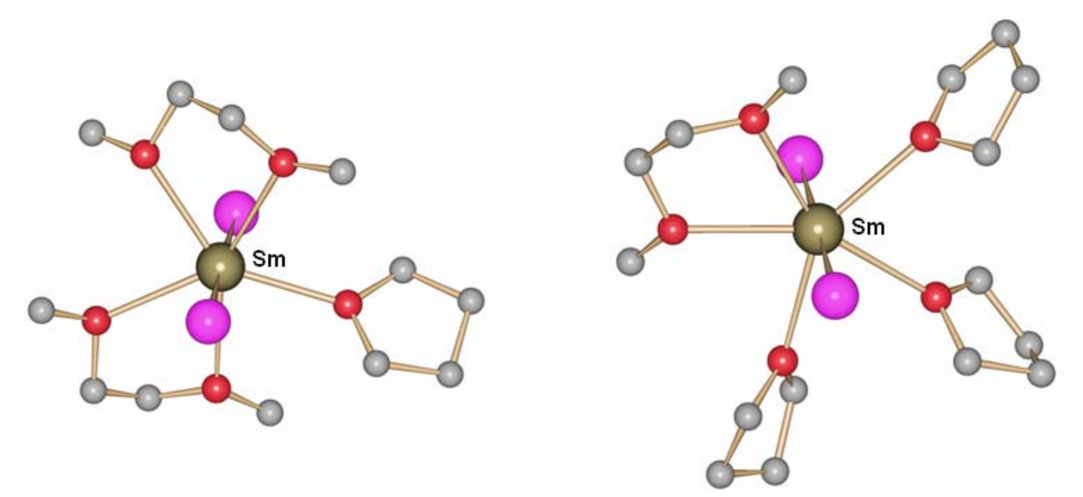


Figure 60. Molecular representation of the compounds *trans*-[SmI$_2$(dme)$_2$(thf)] (left) and *trans*-[SmI$_2$(dme)(thf)$_3$] (right), H atoms have been omitted for clarity

Figure 61 shows some others heteroleptic divalent rare earth metal iodide adducts, namely *trans*-[YbI$_2$(triglyme)(thf)], *cis*-[SmI$_2$(triglyme)(thf)], *trans*-[SmI$_2$(triglyme)(dme)] and *trans*-[EuI$_2$(tetraglyme)(thf)] [240]. What is very interesting in the two former complexes is that the smaller Yb^{2+} cation coordinates the two iodide anions in *trans*-position while the larger Sm^{2+} prefers the *cis*-arrangement. When the THF molecule is formally replaced by a larger DME ligand, the compound *trans*-[SmI$_2$(triglyme)(dme)] is isolated and presents now the iodide anions in *trans*-position.

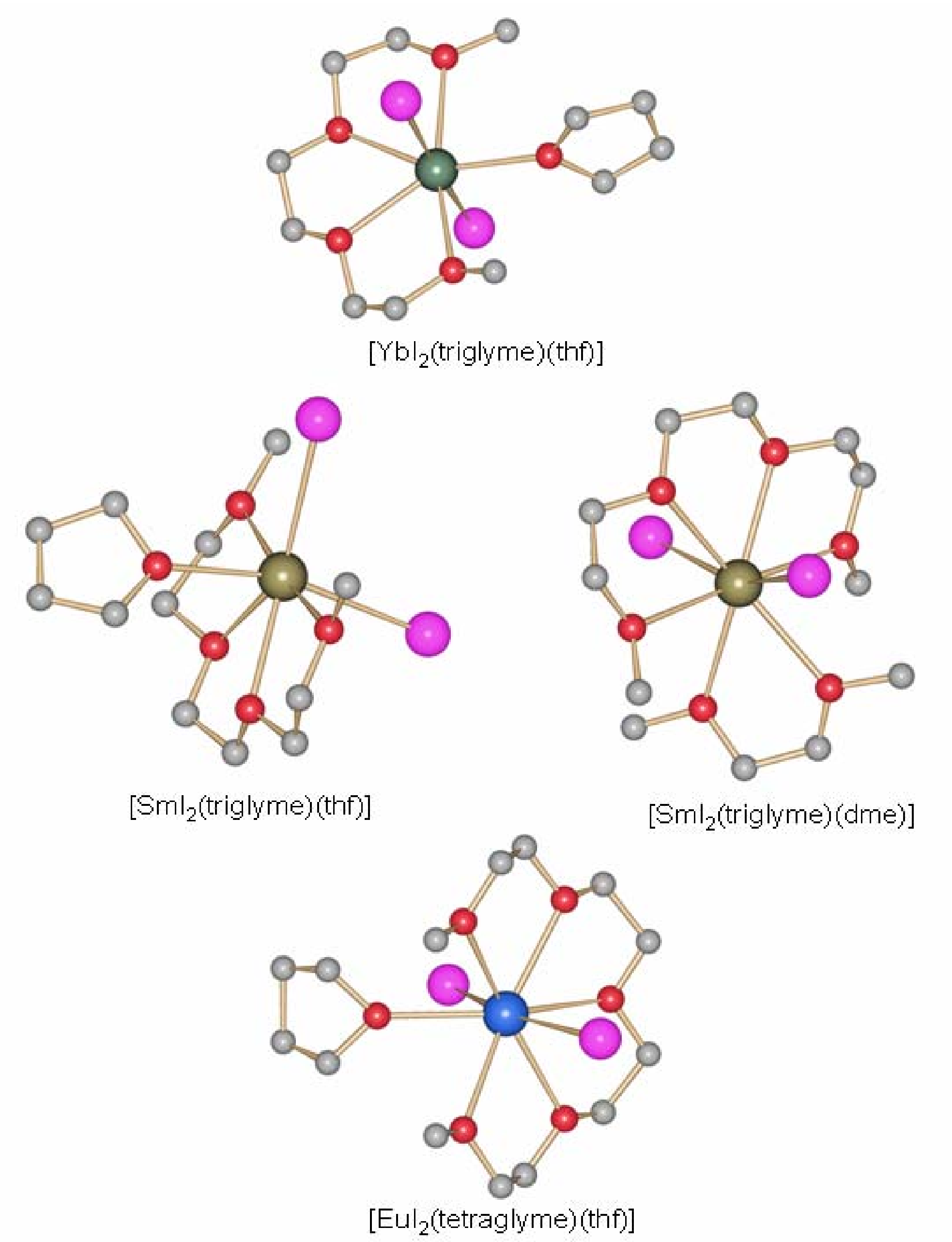


Figure 61. Molecular structure of *trans*-[YbI$_2$(triglyme)(thf)], *cis*-[SmI$_2$(triglyme)(thf)], *trans*-[SmI$_2$(triglyme)(dme)] and *trans*-[EuI$_2$(tetraglyme)(thf)], H atoms have been omitted for clarity

B - I.4 - Conclusion

Whereas the chemistry of alkaline earth metals in aqueous solution is well known since a number of years, the chemistry of alkaline earth metals in less polar aprotic solvents is not very well studied. However, it shows several interesting points such as the formation of a number of polar compounds. Further studies should be carried out in order to be able to understand how the molecular compounds **1**, **4**, **5**, **7**, **8** could crystallize in non-centro-symmetric space groups in order to have some possible applications in NLO, this also with respect to the used ligand type.

This study has also shown that the reactivity of these molecular compounds is related to their coordination sphere. Monodentate ligands are more labile than polydentate ligands, which could be an explanation for the low reactivity of compounds **1** to **8** towards organo-alkali compounds. However, compounds formed with a mix of these kind of ligands (for instance compounds **9** and **10**) are able to be as reactive as those formed with monodentate ligands, for instance THF-adducts [119, 150, 151, 155]. Introduction of polydentate ligands in the starting materials do not influence the overall structure of clusters obtained, polyether ligands being not at all found in the coordination of the latter. In a formal way, the reactivity of these molecular compounds can thus be translated as THF- ≥ THF/ other ethereal ligands- > other ethereal ligands-adducts.

The comparison of the alkaline earth metal iodide adducts **1-12** with their rare earth iodide homologues shows the high similarities between them, both in the synthetic procedure and structural behaviour, but until now only with simple ethereal ligands. Most of the lanthanide adducts presented here, present the same general arrangement of ligands in their coordination sphere than alkaline earth metal compounds. However, rare earth elements show a richer chemistry with the characterization of more adducts, the chemistry of alkaline earth metal iodides in non-polar aprotic solvents should be carry on.

B - II - Alkali metal clusters: Influence of the solvent

B - II.1 - Introduction

As cited in the introduction, the regain in interest of alkali alkoxides and aryloxides resides in the generation of single source or heterometallic precursors for the formation of oxide materials and other ceramics. Alkali alkoxides and aryloxides are thus usually used to introduce alcoholate-groups via elimination of a salt. Unfortunately, retention of the alkali metal or halide is often observed showing the complexity of the "simplistically" written "A(OR)" [3]. Because of that, alkali alkoxides and aryloxides were the focus of research in order to understand this phenomenon, and lead to a great number of papers on their structural characterization both in solution and the solid state. Alkali alkoxides and aryloxides described in the general introduction show how the alkali metal as well as the bulk of the R-group of the OR alcoholate are important factors on the degree of aggregation of the corresponding MOR compound.

However, on top of these parameters, the Lewis-basicity as well as the bonding nature of the solvent employed during the reaction have a strong influence on the overall structure of the MOR compounds. For instance, Boyle *et al.* have studied the structural diversity of solvated lithium [63] and potassium [64] aryloxides in THF and pyridine taking in account the strength of the Lewis-base solvent. Tombul *et al.* have also reported the structure of the lithium phenolate in acetonitrile [241].

First results show important variations in structure of the most unhindered LiOPh depending of the solvents of crystallization $[Li(OPh)(thf)]_4$, $[Li(OPh)(CH_3CN)]_4$ and $[Li(OPh)(Py)_2]_2$. Figure 62 shows the solid state structures of both compounds. Contrary to the most unhindered compound LiOPh which adopts a tretrameric structure in presence of the weakly polar THF solvent, in a more polar but smaller Lewis-coordinating solvent such as acetonitrile, the pyridine analogue (pyridine being the most polar as well as the bulkiest) crystallizes as a dimeric compound. In both structures, the lithium ions reach a tetrahedral coordination sphere by coordinating one solvent molecule in THF and CH_3CN, two solvent molecules per metal ion in pyridine.

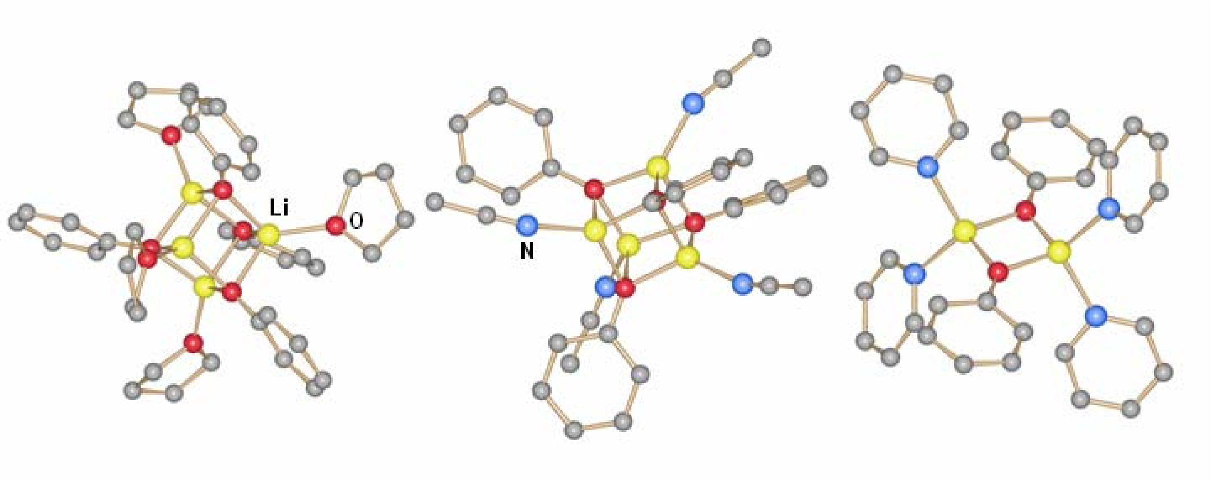


Figure 62. Representation of the influence of the solvent on the LiOPh compound: $[Li(OPh)(thf)]_4$ (left), $[Li(OPh)(CH_3CN)]_4$ (center), $[Li(OPh)(py)_2]_2$ (right), H atoms have been omitted for clarity

Unfortunately, only one lithium derivative, namely $[Li(OPh)(CH_3CN)]_4$ have been reported using acetonitrile as solvent which makes the comparison difficult. Nevertheless, in presence of a stronger and larger Lewis-basic solvent than THF such as pyridine, the degree of oligomerization of the corresponding substituted adducts "Li(OAr)(py)" is smaller and less varied as shows Figure 63. All py-compounds adopt a dimeric arrangement, which can be described as an edge-shared fused tetrahedron.

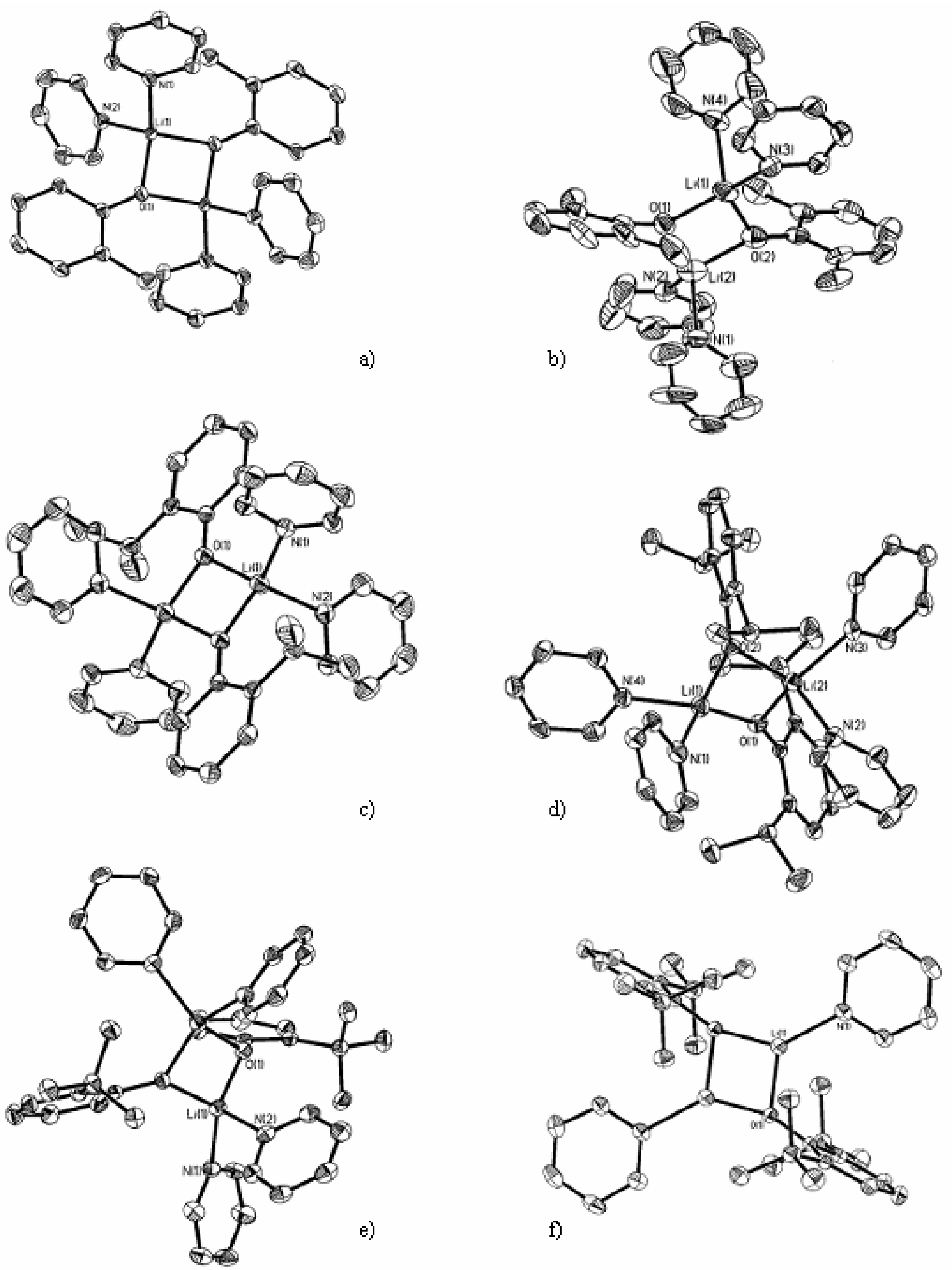


Figure 63. Representation of some [LiOAr] complexes in pyridine a) [Li(2-Me-C_6H_4O)$(py)_2$]$_2$ b) [Li(2,6-Me_2-C_6H_3O)$(py)_2$]$_2$ c) [Li(2-^{i}Pr-C_6H_4O)$(py)_2$]$_2$ d) [Li(2,6-$^iPr_2$-C_6H_3O)$(py)_2$]$_2$ e) [Li(2-^{t}Bu-C_6H_4O)$(py)_2$]$_2$ f) [Li(2,6-$^tBu_2$-C_6H_3O)(py)]$_2$

The lithium cations reach a traditional tetrahedral coordination sphere by coordinating two more pyridine molecules. As for the THF-adducts, the introduction of the very sterically demanding ^{t}Bu-groups on the ortho-positions of the phenyl ring leads to the loss of one solvent molecule per lithium ion.

It is also very interesting to understand what happens in solution, the degree of aggregation influencing reactivity. Indeed, the structures of the MOAr complexes shown on the Figure 12 and Figure 63 have been obtained in the solid state. However, in solution, it is relatively more difficult to know exactly which species are present. Due to a more entropic effect in solution depending of course of the Lewis-basicity of the solvent but also on the temperature and the hindering of the anion, some equilibrium may be induced.

A series of investigation leads by Boyle *et al.* were made using ^{7}Li NMR, which is a very sensitive method for determining the environment of the Li cations. It reveals some interesting results and confirms others already known. First, in THF at low temperature, the LiOPh compound exists as a mixture of tetrameric and hexameric species. This result had already been reported by Jackman *et al.* [69]. Secondly, the LiOAr (Ar = 2-^{i}Pr-C_6H_4) adduct, with a second resonance, seems also to exhibit a mixture of tetrameric and hexameric species in solution. However, it seems that the favorable species in THF-solution is the tetrameric one. All the disubstitued complexes as well as the LiOAr (Ar = 2-Me-C_6H_4) compound show only one resonance leading to the conclusion that these species exist only as a tetramer in solution as well as in the solid state.

Concerning the pyridine-solvated LiOAr compounds, only one ^{7}Li NMR resonance is observed in solution for all experiments meaning (with caution) that all species exist in solution as in the solid state as cubane compounds.

Besides this important work lead by Boyle *et al.*, which allows to have an idea of the species present in solution, Jackman *et al.* [242-246] have reported a series of papers regarding the nuclearity of LiOAr compounds in solution in a variety of different solvents (dioxolane, DME and pyridine). Some of this conclusion may be taken carefully as it is sometimes in “contradiction” with results set out above. In these reports, Jackman *et al.* exposed that in all three solvents, LiOAr (Ar = 2,6-Me_2-C_6H_3O) appears to be dimeric even at low temperature. In the same time, he also exposed that up to -40°C, LiOPh is tetrameric in all these three solvents while investigations carried out by Boyle *et al.* reveal that LiOPh is dimeric in pyridine and a communication by Henderson *et al.* shows that in dioxolane solution, LiOPh forms a three-dimensional network but in the solid state [85].

This shows the difficulty to expect or confirm what is really in solution and why it is important to follow up with this research.

Although sodium aryloxides are useful reagents for salt elimination syntheses as their lithium analogues and find application in the Kolbe-Schmitt synthesis [91, 247-252], only few derivatives have been crystallographically characterized. They generally display polymeric or high nuclearity structures: For instance the least hindered phenolate derivative presents a hexameric structure in THF which can be described as a two face-fused cubic tetramers $[Na(OPh)(thf)]_6$ [62, 91] (Figure 9). In presence of a stronger Lewis-base solvent such as acetonitrile, the sodium derivative exist in form of a polymeric species $[Na(OPh)(CH_3CN)]_\infty$ [253] (Figure 64 and Figure 65). Nevertheless, with a more stronger and larger Lewis-base solvent namely tetramethylurea ($C_5H_{12}N_2O$), a tetrameric oligomer could be obtained $[Na(OPh)(ON_2C_5H_{12})]_4$ [91] (Figure 66).

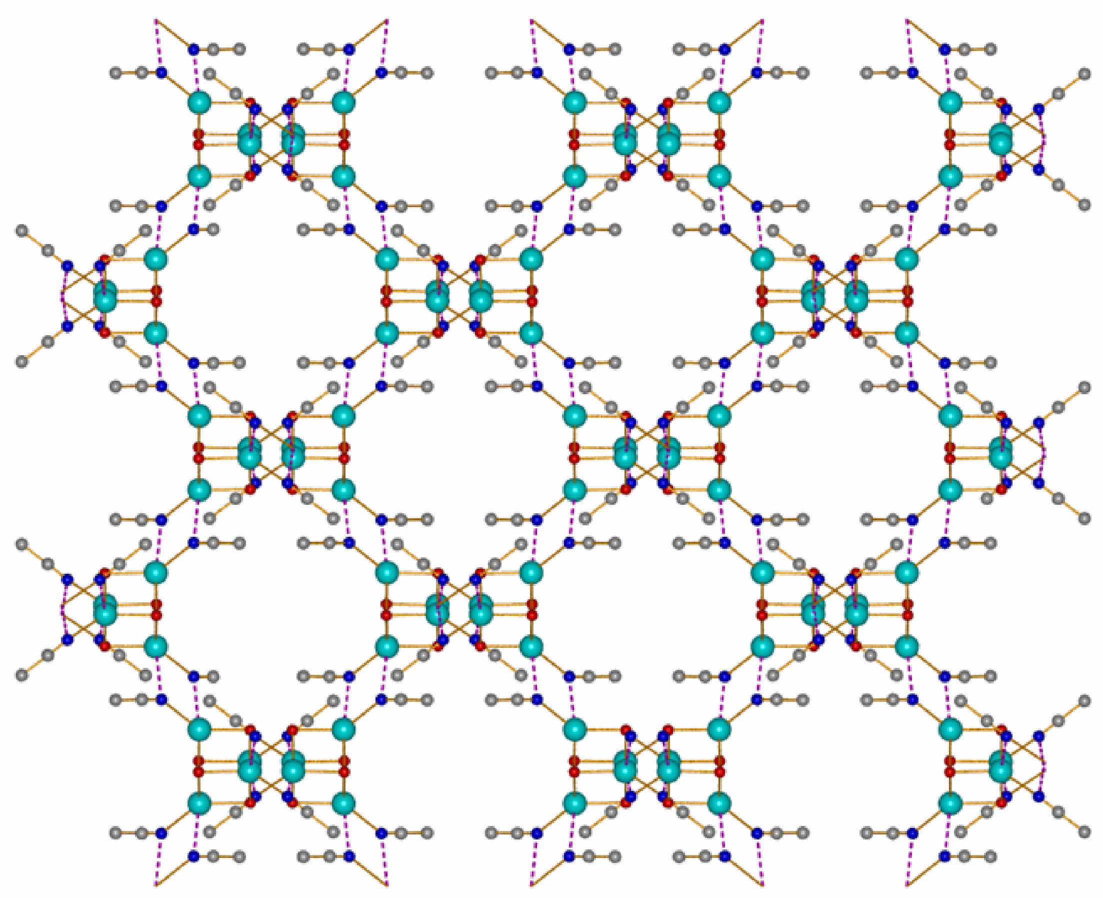


Figure 64. Representation of the 3D-network in $[Na(OPh)(CH_3CN)]$ along the a-axis, H atoms have been omitted for clarity

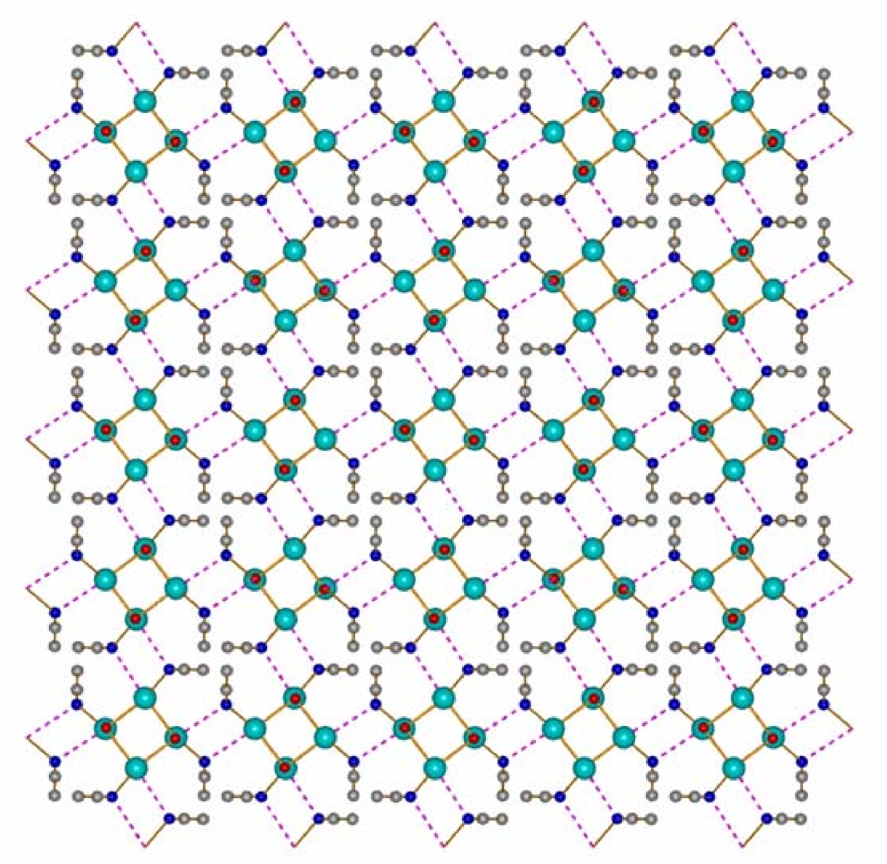


Figure 65. Representation of the 3D-network in [Na(OPh)(CH_3CN)] along the c-axis, H atoms have been omitted for clarity

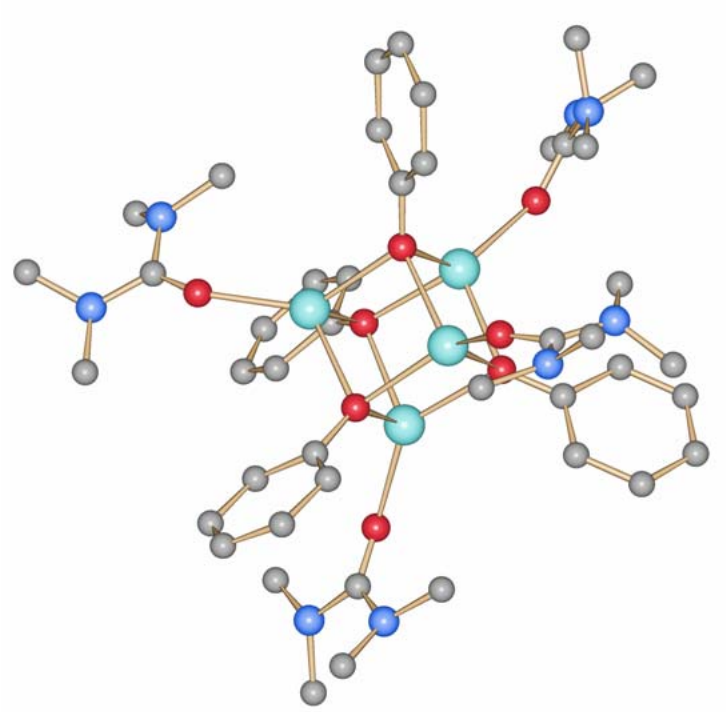


Figure 66. Molecular representation of the tetrameric [Na(OPh)($ON_2C_5H_{12}$)]$_4$ species, H atoms have been omitted for clarity

As described in the introduction, potassium aryloxide are generally polymeric species while two molecular THF-derivatives have been characterized in the solid state. In Pyridine, all substituted potassium aryloxides as well as the most unhindered potassium phenoxide form polymeric structures. However, the solid state structures of the K(OAr) compounds do not appear to be retained in solution due to the simplicity of the NMR spectra. Different possible structures might be expected depending of the temperature and concentration, as well as variations in handling techniques.

Table 6 presents the degree of aggregation of some (simple phenoxide, 2- and 2,6-alkyl substituted phenyl rings) lithium-, sodium- and potassium-aryloxide derivatives in the most commonly used solvents: THF and pyridine.

A part from the family of lithium and potassium aryloxides that have been well studied by Boyle *et al.* in the solid state as well as in solution [63, 64] even if more analysis are required to confirm these data, the structure of most sodium derivatives is still nowadays unknown.

It is clear that the size of the alkali metal as well as the bulk of the aryloxide are predominant factors, but the solvent has also an important contribution in the construction of the aggregate with regard to the lithium-derivatives family.

Table 6. Degree of aggregation of some A(OAr) in common solvents, THF and Pyridine

MOAr	solvent	OPh	oMP	DMP	oPP	DIP	oBP	DBP
Li	THF	4	4	4	4	4	2	2
Li	Py	2	2	2	2	2	2	2
Na	THF	6	?	?	?	?	?	2
K	THF	∞	∞	∞	4	∞	6	∞
K	Py	∞	∞	∞	∞	∞	∞	∞

oMP: 2-Me-$C_6H_4O^-$; DMP: 2,6-Me_2-$C_6H_3O^-$; oPP: 2-^{i}Pr-$C_6H_4O^-$; DIP: 2,6-$^iPr_2$-$C_6H_3O^-$; oBP: 2-^{t}Bu-$C_6H_4O^-$: DBP: 2,6-$^tBu_2$-$C_6H_3O^-$

This table only presents differences in derivatives aggregation due to the strength of the solvent (pyridine being a more polar solvent than THF), but they are both as simple monodentate ligands as each other. Only little is known about polydentate ligands such as DME; to our knowledge only one sodium derivative, namely [Na(dme)(4-Me-C_6H_4O)]$_4$ [90], has been crystallographically characterized while DME is a good neutral Lewis-coordinating ligand to saturate the alkali metal cations and thus hinders high degrees of aggregation or even polymerization.

B - II.2 - Crystallographic structure of [Na(OPh)(dme)]$_4$ 13

The reaction of [SrI$_2$(thf)$_5$] and an excess of [Na(OPh)(thf)]$_6$ in THF, followed by the recrystallization in DME of the solid formed after evaporation to dryness of the light brown solution leads to the formation at low temperature (-25°C) of very nice crystals within one week of the formula [NaOPh(dme)]$_4$ **13**, as demonstrated by a X-ray diffraction analysis (Figure 67).

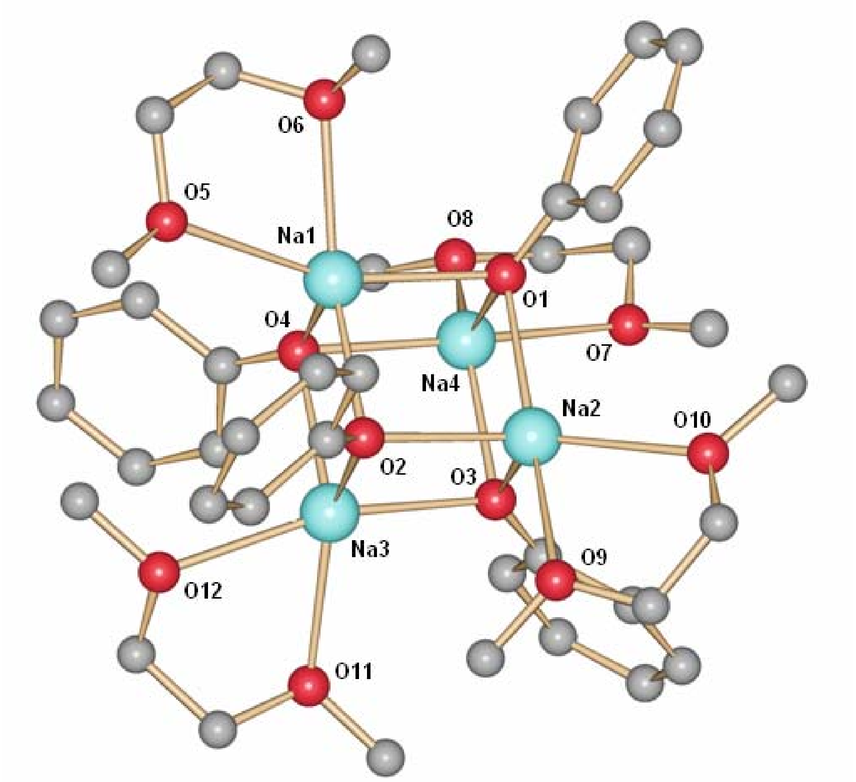


Figure 67. Schakal view of the partially labelled asymmetric unit of 13, H atoms have been omitted for clarity

The formation of the compound **13** can be interpreted as the result of the crystallization of the excess of the compound [NaOPh(thf)]$_6$ in DME, cluster compounds being generally not the most thermodynamically stable compound during a reaction. The structure of compound **13** is very similar to the [Na(4-Me-C$_6$H$_4$O)(dme)]$_4$ one [90] probably due to the non-substituted 2-

or 2,6- position(s) of the phenyl ring of the phenolate ligands, there is no interaction between neighbouring phenyl rings.

Compound **13** crystallizes in the triclinic space group *P*-1 (Nr. 2) with two molecules in its unit cell. As can be seen from Figure 67, compound **13** is tetrameric and its structure can be described as two fused Na_2O_2-rings or two interpenetrating tetrahedra of four sodium atoms and four oxygen atoms. Each sodium atom has the same coordination sphere (CN5) in form of a trigonal bipyramid with three μ_3-bridging phenolate groups and one terminal bidentate DME molecule, which saturate the sodium cations avoiding polymerization.

The most important bond lengths and angle for the compound **13** is given in Table 7.

Table 7. Most important parameters in **13**, bond (Å) and angles (°)

Na1–μ_3-OPh	2.338(7)	OPh–Na1–OPh	90.08(3)
Na2–μ_3-OPh	2.305(1)	OPh–Na2–OPh	91.29(4)
Na3–μ_3-OPh	2.328(2)	OPh–Na3–OPh	89.03(3)
Na4–μ_3-OPh	2.334(7)	OPh–Na4–OPh	89.49(3)
Na–O(dme)	2.456(1)	O(dme)–Na–O(dme)	67.93(3)
Na1···Na2	3.300(6)	Na1–OPh–Na2	89.75(4)
Na1···Na3	3.216(5)	Na1–OPh–Na3	88.28(5)
Na1···Na4	3.297(9)	Na1–OPh–Na4	89.79(5)
Na2···Na3	3.295(4)	Na2–OPh–Na3	90.73(5)
Na2···Na4	3.216(5)	Na2–OPh–Na4	88.15(5)
Na3···Na4	3.411(4)	Na3–OPh–Na4	93.07(5)

The Na–O(μ_3-OR) distances range between 2.285(4) and 2.407(9) Å with an average value of 2.326(7) Å. They compare well with the ones observed in $[Na(4\text{-}Me\text{-}C_6H_4O)(dme)]_4$ [90] and other Na-OR complexes, even hexameric ones such as $[Na(OPh)(thf)]_6$ [91] or dimeric ones with $[Na(OR)(thf)_2]_2$ (OR = $2,4,6\text{-}(CF_3)_3\text{-}C_6H_2O$) [86] although the bridging mode of the OR anion is different. They are also longer as expected than the μ-OR distances observed in $[Na(2,6\text{-}{}^tBu_2\text{-}C_6H_3O)(\mu\text{-}Me_2SO)(Me_2SO)]_2$ [93] and $[(2,6\text{-}Me_2\text{-}C_6H_3O)_4Cr][Na(TMEDA)]_2.C_6H_5CH_3$ [254] but relatively shorter than the Na–μ_3-OPh bond lengths observed in $[(PhO)_8Cr_2][Na(Py)]_4.C_6H_5CH_3$ [254]. The Na–O(dme) average distance of 2.456(1) Å (variation from 2.401(6) to 2.578(4) Å) is common [255, 256] but is slightly longer than those observed in [Na_4(salphen)$_2$(dme)$_2$] (H_2salphen = N,N'-o-phenylenebis(salicylideneimine)), [Na_4(salen)$_2$(dme)$_2$] (H_2salen = N,N'-ethylenebis(salicylideneimine)) [92] and [Na(4-Me-C_6H_4O)(dme)]$_4$ [90]. The OR–Na–OR angles which vary from 86.59(4) to 92.48(5)° (average 89.97(8)°) as well as the Na–OR–Na which vary from 87.58(4)° to 93.44(4) (average 89.96(6)°) reflect well the regularity of the four-membered ring (ideal bond angles of 90°). Nevertheless, the Na···Na distances are ranged in a quite large gap of distances, from 3.216(5) to 3.411(4) Å (average 3.289(2) Å) and reveal a distortion of the cube. Some intermolecular H-bonds can be found between ethereal ligands and also between aryl-groups and ethereal ligands. The shortest contacts are O11···H38A = 2.818(5) Å and O7···H38B = 2.914(7) Å, they are DME-DME interactions and lead to the formation of dimers (Figure 68 and Figure 69). However, the values of the C29–O7–C30 = 112.2(2)° and C37–O11–C38 = 113.80(2)° angles are in similar range of values compared to the C–O–C angles of atoms not involved in H-bond. This means that these interactions can be considered as very weak.

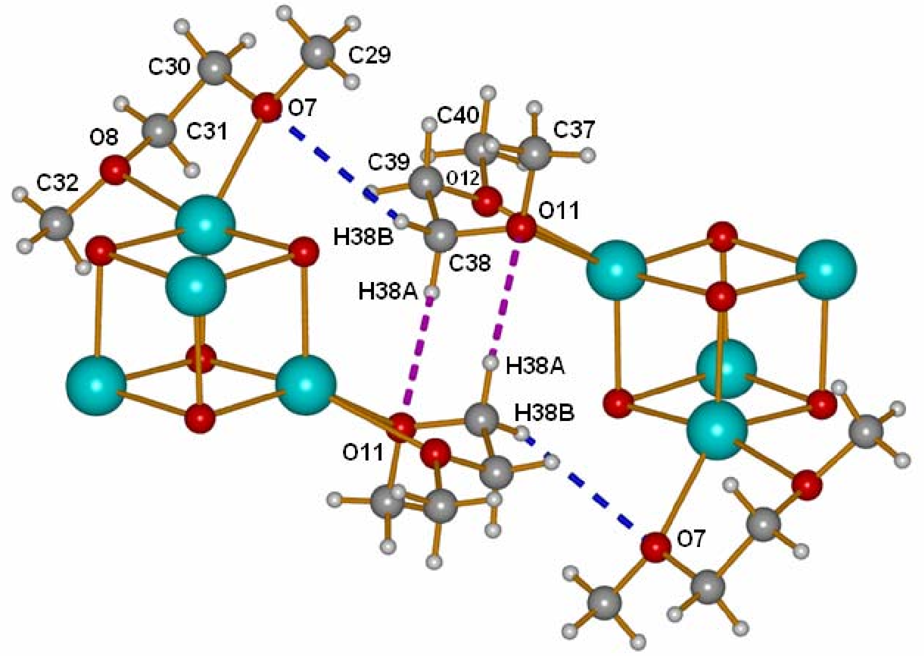


Figure 68. DME-DME interactions in 13, O11···H38A (purple) and O7···H38B (blue), leading to the formation of dimers

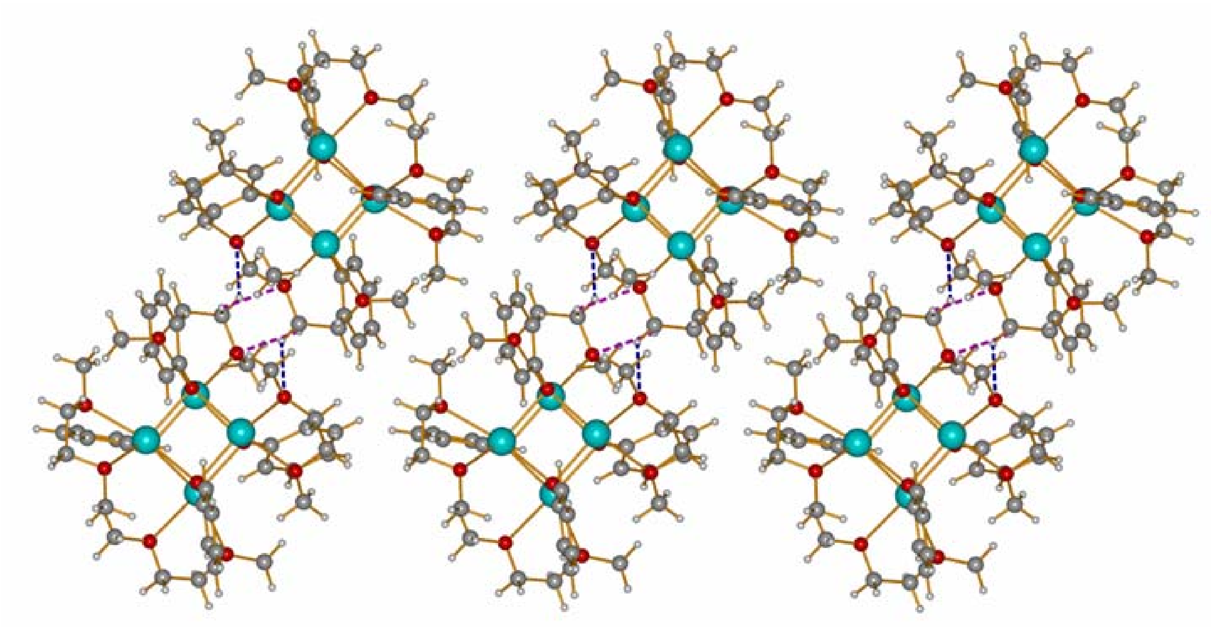


Figure 69. Schematic representation of the packing of dimers due to the O11···H38A and O7···H38B interactions in 13

Longer contacts are found between phenyl-rings and DME ligands with O5···H17 = 2.941(6) Å, and form chains of these dimers along the a-axis (Figure 70). Finally two longer interactions >3 Å lead to the formation of ladders, one between aryl-rings and DME with O6···H23 = 3.003(6) Å along the a-axis, the other one between DME ligands with O8···H33C = 3.014(8) Å along the c-axis. These two contacts, additionally to the shorter one, form finally a three dimensional structure (Figure 71 and Figure 72).

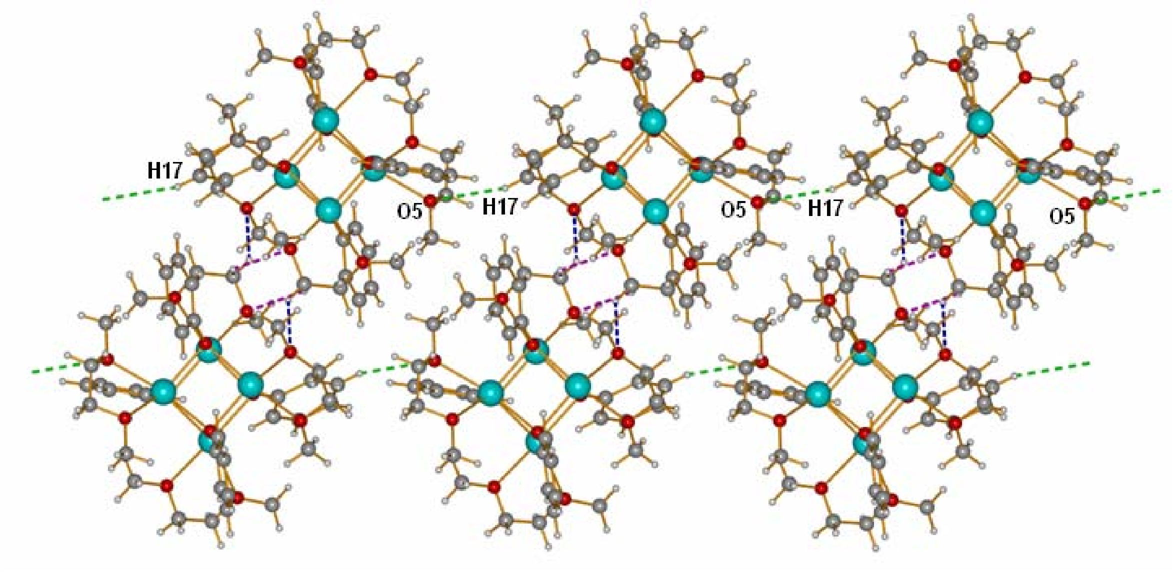


Figure 70. Schematic representation of the formation of double chains with O5···H17 interactions in 13

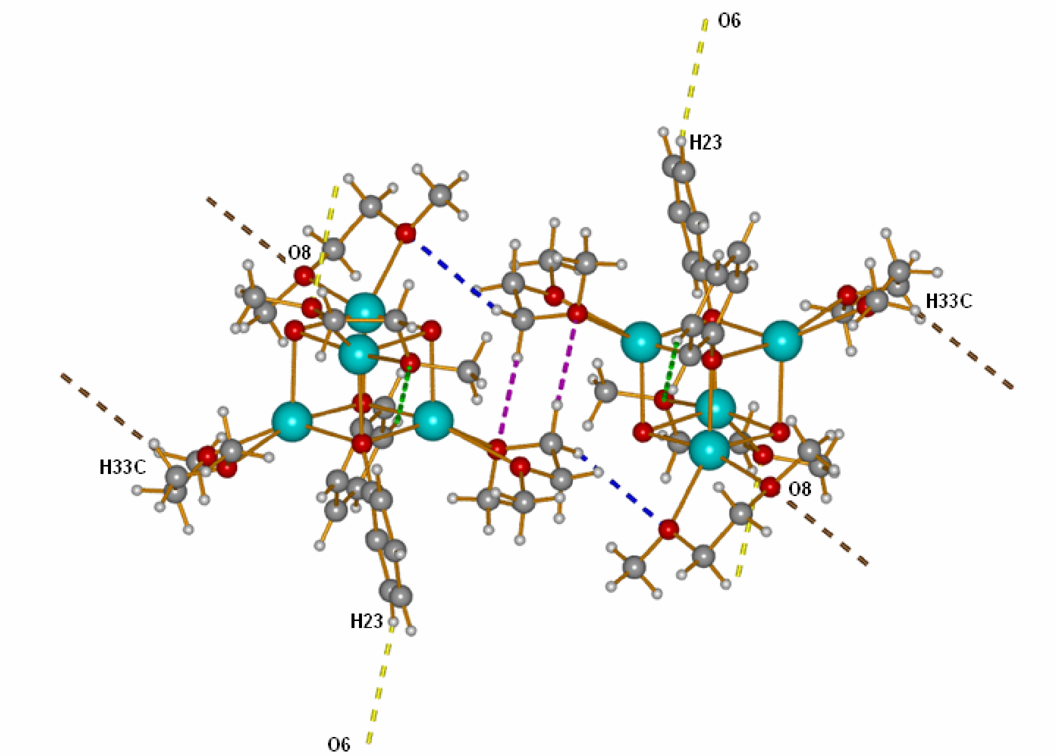


Figure 71. Schematic representation of the two interactions >3 Å leading to the formation of a 3D-network in 13: O6···H23 = 3.003(6) Å (yellow) and O8···H33C = 3.014(8) Å (brown)

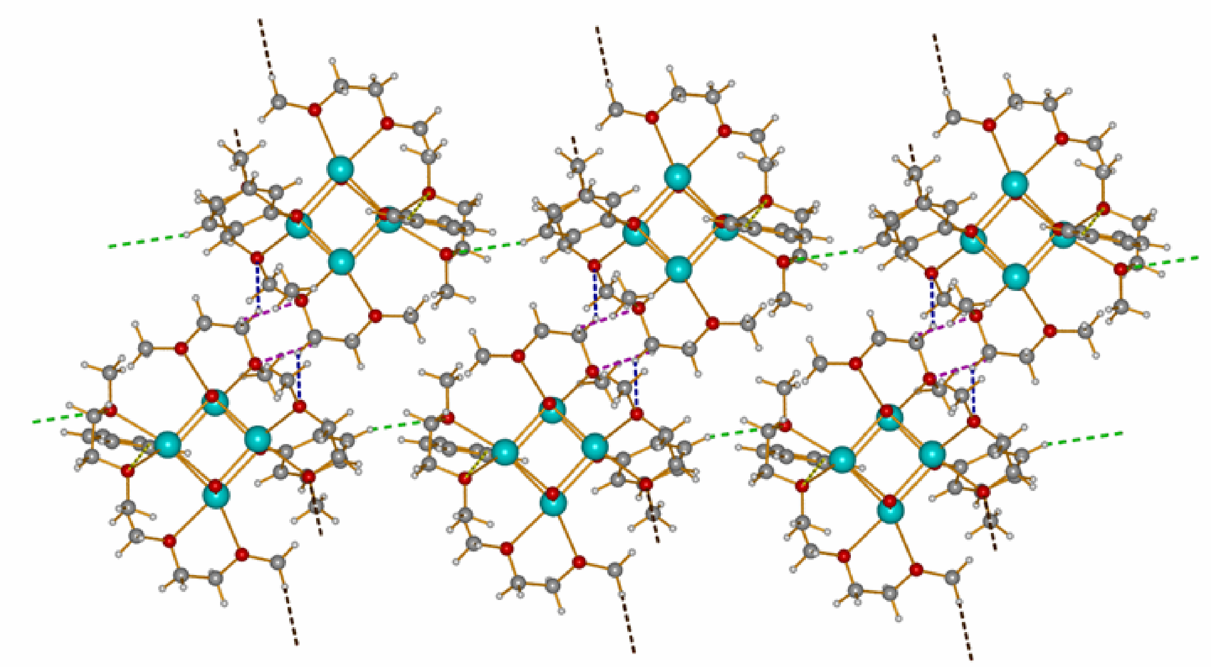


Figure 72. Schematic representation of all H-bonds involved in the formation of the 3D-network: O11···H38A (purple), O7···H38B (blue), O6···H23 (yellow) and O8···H33C (brown)

The compounds $[NaOPh(thf)]_6$, $[Na(OPh)(ON_2C_5H_{12})]_4$ [91] and $[NaOPh(dme)]_4$ **13** possess relatively "similar" structures (Figure 73), $[NaOPh(L)]_6$ being described in a general way as the fusion of two $[NaOPh(L)]_4$-units sharing a face.

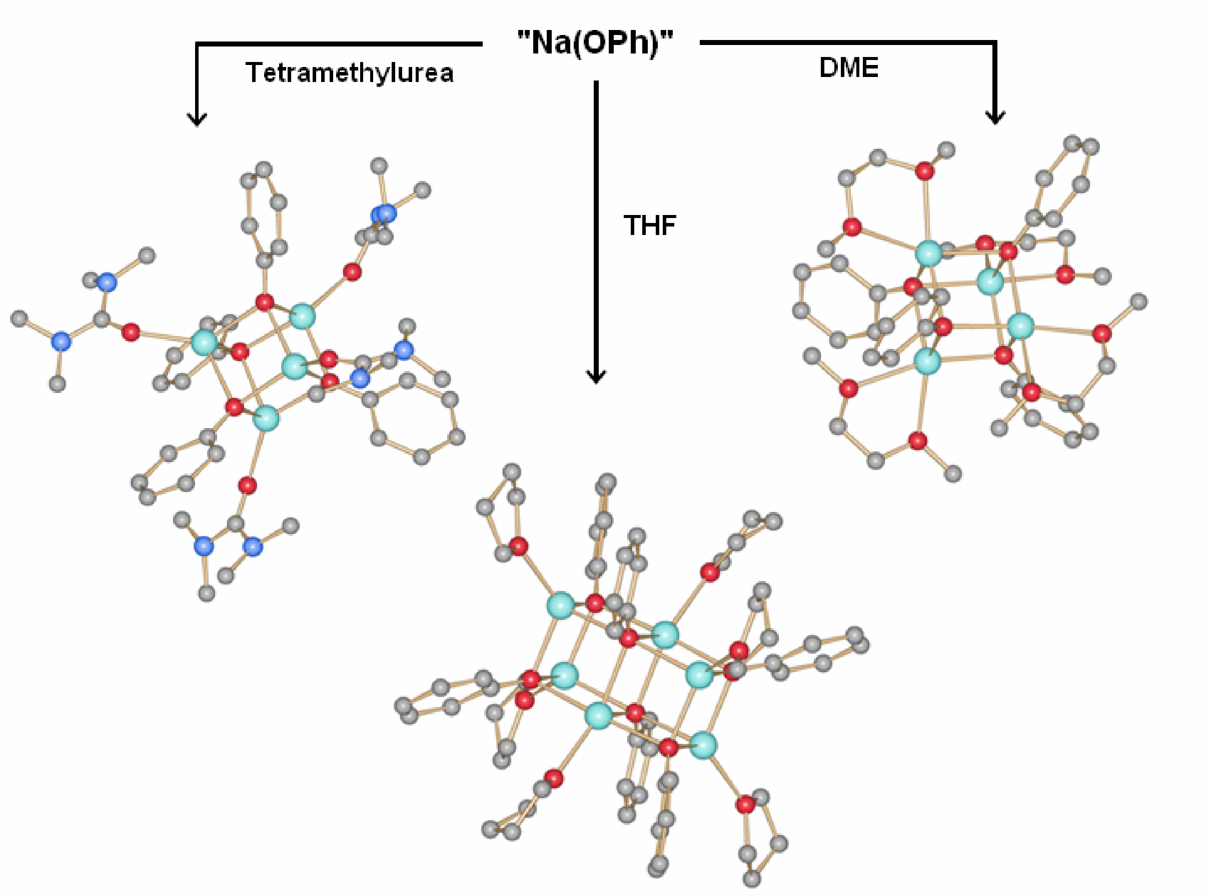


Figure 73. Representation of the solvent-influence on the degree of aggregation of NaOPh in THF (center), tetramethylurea (left) and DME (right)

More importantly, this shows the importance of the Lewis-base coordinating ligand. As expected, using a stronger Lewis-base solvent than THF such as tetramethylurea, the degree of aggregation of the oligomer decreases. The same effect is observed with DME while it is presumably a somewhat less basic solvent than THF. Its ability to coordinate bidentately a metal cation is a force to promote lower aggregates by coordination to the metal cation in preference to bridging phenolates [83, 257]. Indeed, in addition of the three phenolate-groups, a DME molecule coordinates each sodium cation saturating the latter, the ubiquitous coordination number of five for sodium atoms being reached, a higher degree of oligomerization for saturating the latter is thus unnecessary.

B - II.3 - Crystallographic structure of [Li(2,6-Me$_2$-C$_6$H$_3$O)(dme)]$_2$ 14

During this work, a particular attention was given to the least hindered aryloxides, namely phenoxides. However, in order to study the influence on the structures of alkaline earth metal clusters or at least to have an idea of the impact of bulky alcoholate ligands, some syntheses were undertaken using more sterically demanding aryloxides, namely (2,6-R$_2$-C$_6$H$_3$O)Li R = Me, ^{i}Pr, ^{t}Bu. Unfortunately, all these syntheses failed resulting most of the time in the crystallization of the alkali aryloxide. Nevertheless, attempts with DME as solvent of crystallization lead to the characterization of an unknown solvated alkali-aryloxide compound until now. This characterization confirm the prediction of Jackman *et al.* concerning the formation of the dimeric [(2,6-Me$_2$-C$_6$H$_3$OLi)(dme)]$_2$ species [243].

The reaction of [CaI$_2$(thf)$_4$] and an excess of [(2,6-Me$_2$-C$_6$H$_3$O)Li(thf)]$_4$ in THF, followed by the recrystallization in DME of the solid formed after evaporation to dryness of the purple solution leads to the formation at low temperature (-25°C) of very nice crystals within four days of the formula [Li(2,6-Me$_2$-C$_6$H$_3$O)(dme)]$_2$ **14**, as shown by a X-ray diffraction analysis (Figure 74).

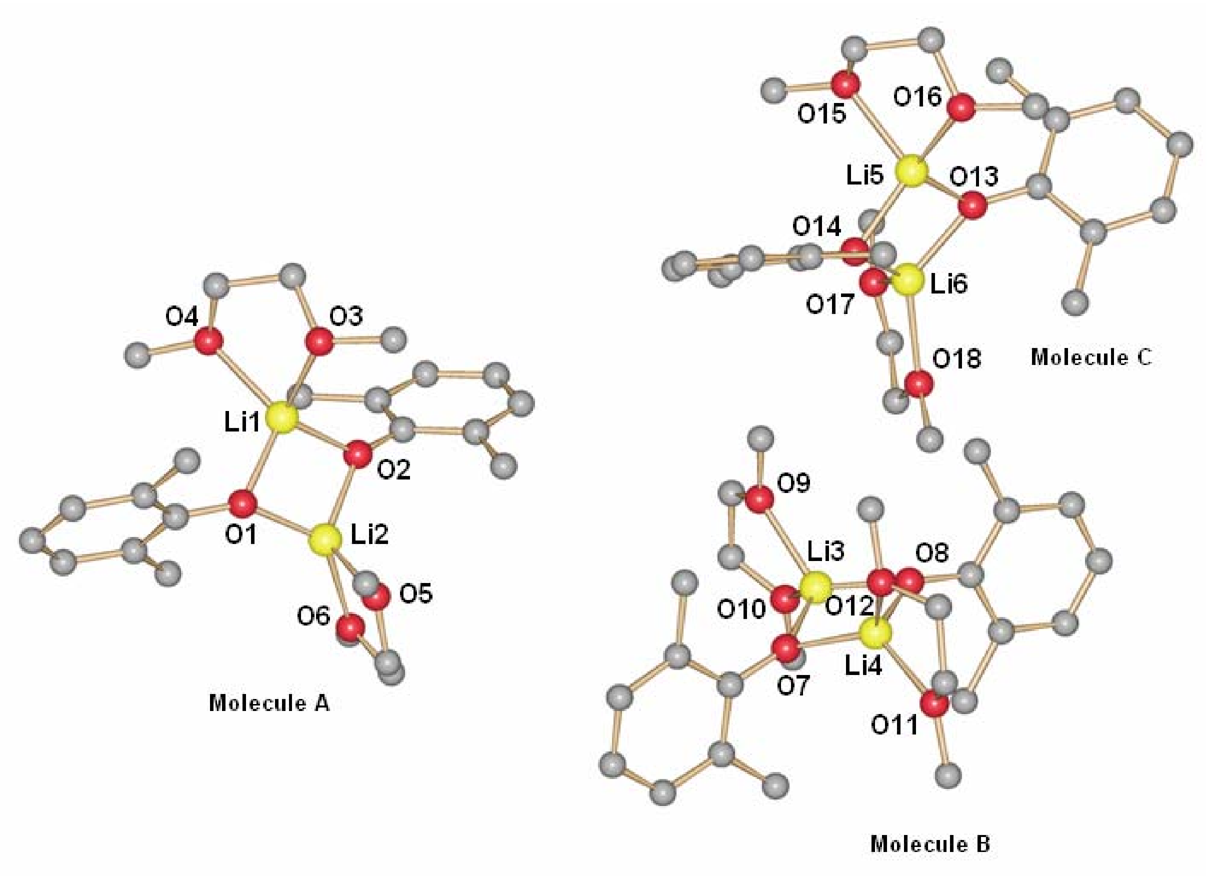


Figure 74. Schackal view of the partially labelled asymmetric unit of 14, H atoms have been omitted for clarity

As for the synthesis of the compound [NaOPh(dme)]$_4$ **13**, the formation of **14** can be interpreted as the result of the crystallization of the excess of the compound [(2,6-Me$_2$-C$_6$H$_3$O)Li(thf)]$_4$ in DME.

Compound **13** crystallizes in the monoclinic space group *P*2$_1$/*c* (Nr. 14) with three molecules in its asymmetric unit. As can be seen from the Figure 74, molecules of the compound **13** possess dimeric fragments which can be described as a four-membered Li$_2$O$_2$-ring.

In each molecule, aryloxo-groups act as μ-briging ligands linking two lithium cations in a Li$_2$O$_2$-unit. Li–O(μ-OR) distances vary between 1.846(3) and 1.885(3) Å (average 1.867(4) Å) are consistent and in agreement with literature data [63, 258-262]. As expected they are relatively shorter than Li–O(μ$_3$-OR) bond lengths in [Li(2,6-Me$_2$-C$_6$H$_3$O)(thf)]$_4$ (average 2.00 Å) [63]. In each molecule, the Li$_2$O$_2$-unit is almost planar although [Li–O]-subunits are slightly asymmetrical as indicated by the difference in Li–O(μ-OR) bond lengths. The bulky phenyl rings in molecule A (Li1 and Li2) are almost situated above (or below) the Li$_2$O$_2$-

plane (Figure 75) and are inverted to each other. This is reflected by the angle they form with the Li_2O_2-rhombus. In molecule A, the angles of the phenyl rings to the Li_2O_2-plane are 66.28(2) and 65.57(4)°, and the angle between the phenyl rings is 51.33(1)°.

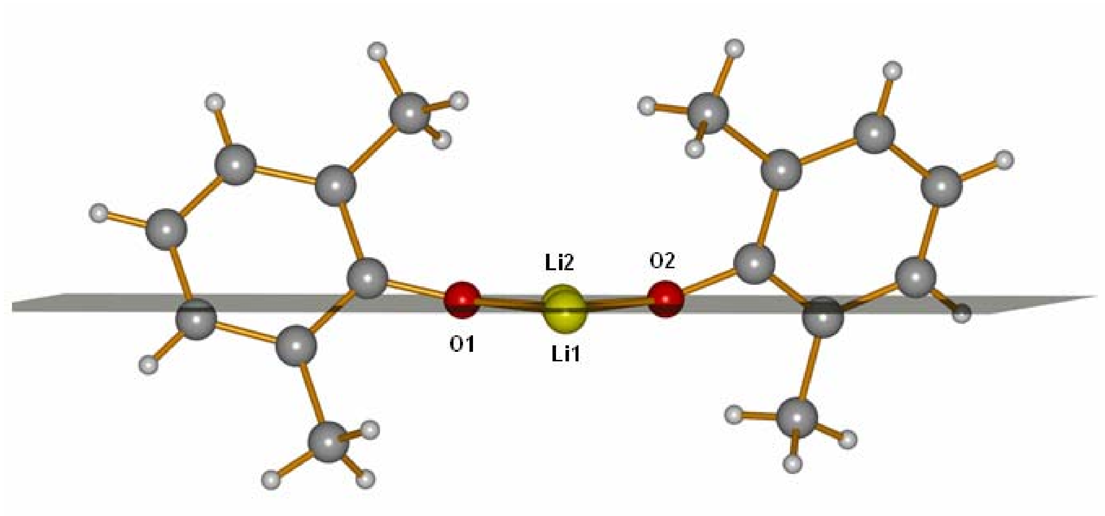


Figure 75. Schematic representation of the asymmetrical phenyl rings versus the Li_2O_2-plane in molecules

In the molecule C (Li5 and Li6), the phenyl rings adopt another conformation, one is clearly centered on the Li_2O_2-plane, the other one almost above (Figure 76). The phenyl rings are also inverted to each other (70.08(1°)) and form an angle of 57.10°, respectively 65.45(9)° to the Li_2O_2-plane. Finally, in the molecule B (Li3 and Li4) the two phenyl rings are co-planar (deviation of 3.18(2)°) and are almost perpendicular to the Li_2O_2-plane with angle of 87.20(1) and 89.65(1)° for the first phenyl ring, respectively the second one while it is almost below the Li_2O_2-rhombus (Figure 77).

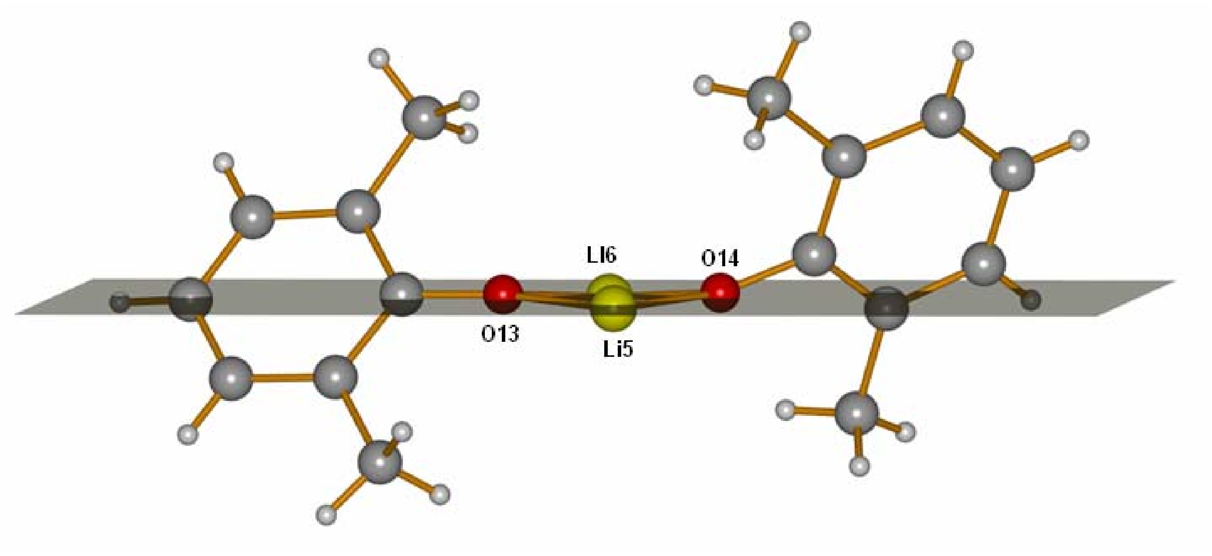


Figure 76. Schematic representation of the asymmetrical phenyl rings versus the Li_2O_2-plane in molecules B

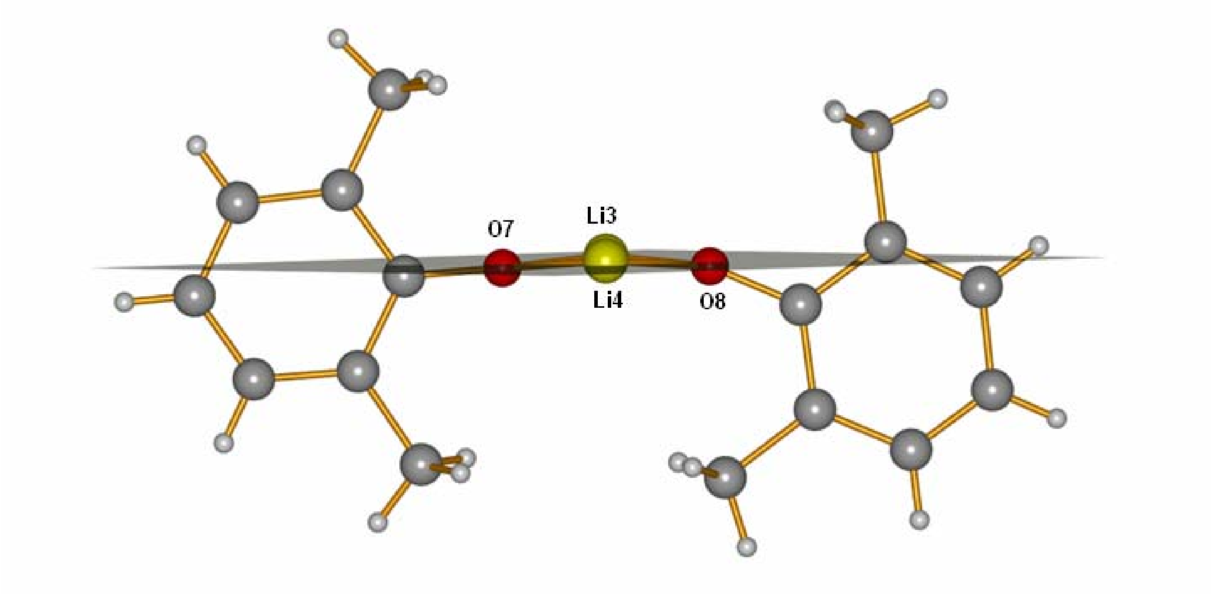


Figure 77. Schematic representation of the asymmetrical phenyl rings versus the Li_2O_2-plane in molecules C

The most important bond lengths and angles for the compound **13** is given in Table 8.

Each lithium cation reaches its traditional distorted tetrahedral coordination sphere with one coordinating DME solvent molecule in addition to the two bridging phenoxo-ligands. The Li–O(dme) disatnces vary between 2.016(3) and 2.076(3) Å (average 2.047(3) Å) as well as the O(dme)–Li–O(dme) angle (average 79.96(2)°) are in accordance with those observed in the literature [219, 258, 263]. The regularity of the four-membered rings is not so much reflected in the approximate ideal bond angles of 90° for **14** with average OPh–Li–OPh angles of 95.11(7)° and Li–OPh–Li angles of 84.24(1)°, respectively.

Table 8. Most important parameters in **14**, bond (Å) and angles (°)

Li1–µ-OPh	1.863(5)	OPh–Li1–OPh	95.46(1)
Li2–µ-OPh	1.865(3)	OPh–Li2–OPh	95.36(1)
Li3–µ-OPh	1.872(5)	OPh–Li3–OPh	94.92(2)
Li4–µ-OPh	1.867(5)	OPh–Li4–OPh	95.24(1)
Li5–µ-OPh	1.874(3)	OPh–Li5–OPh	94.95(1)
Li6–µ-OPh	1.862(3)	OPh–Li6–OPh	94.77(1)
Li–O(dme)	2.047(3)	O(dme)–Li–O(dme)	79.96(2)
Li1···Li2	2.496(4)	Li1–OPh–Li2	84.05(1)
Li3···Li4	2.515(4)	Li3–OPh–Li4	84.48(5)
Li5···Li6	2.504(4)	Li5–OPh–Li6	84.18(5)

The Li···Li distances in **14** (average 2.505(4) Å) are relatively shorter than those observed in tetrameric compounds such as $[2,6\text{-}Me_2\text{-}C_6H_3O)Li(thf)]_4$ [63]; they are however in accordance with other dimeric $[Li(OR)]_2$ aryloxide adducts [63].

Some very weak interactions can be observed in **14** between molecular species. The two shortest ones are: the first one between molecules B via DME ligands with O11···H42A = 2.933(2) Å (in blue) leading to the formation of polymeric chains of molecules B (in pink on Figure 78). The second one between molecules C via the methyl group of one phenyl ring and one DME ligand with O16···H63A = 2.953(5) Å (in green) leading to the formation of dimers (in different blue on Figure 78 and Figure 79). Molecules A are represented in yellow and orange on both Figures. But there is no contact between the different molecules A, B and C less than 3Å.

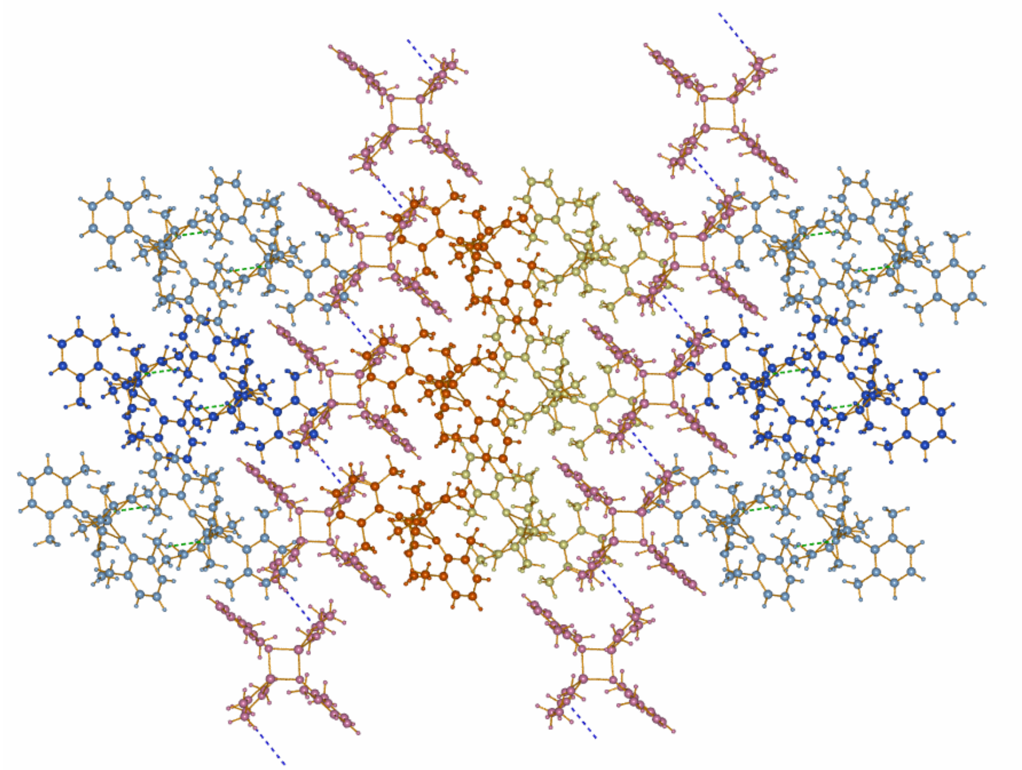


Figure 78. Schematic representation of the packing of molecules A (yellow and orange), B (pink) and C (blue and cyan) in 14 along the b-axis

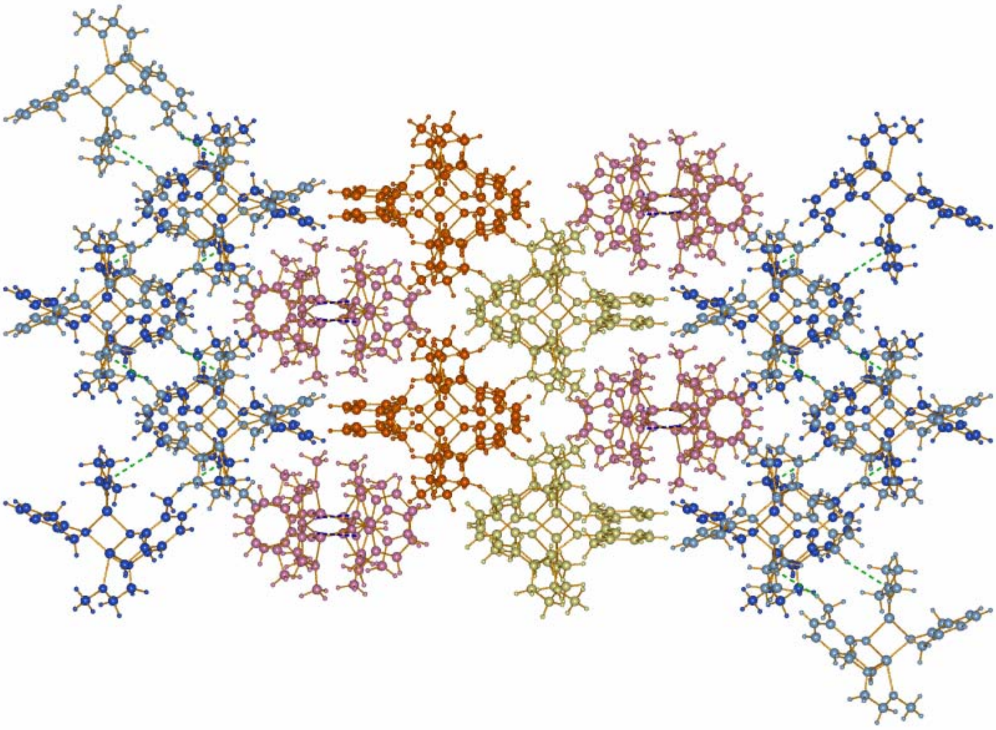


Figure 79. Schematic representation of the packing of molecules A (yellow and orange), B (pink) and C (blue and cyan) in 14 along the c-axis

The compound $[(2,6\text{-}Me_2\text{-}C_6H_3O)Li(dme)]_2$ **14** is one of the rare alkali aryloxide which have been characterized in more than two different solvents: THF [63], pyridine [63] and now DME. Only the Li(OAr) (Ar = $2,6\text{-}^tBu_2\text{-}C_6H_3$)) compound has been characterized in four different solvents: THF and pyridine [63], Et_2O [80] and DMSO [65]. In all these solvents, the compound presents a dimeric structure, the very bulky ^{t}Bu-groups in ortho-position of the phenyl ring justifying on their own the low degree of oligomerization. As shows Figure 80, the solvents used have an important effect on the overall structure of the solvated compound. In the less strong Lewis-basic solvent THF, the structure is tetrameric while in the other two, more basic or chelating, pyridine and DME, the degree of aggregation is lower and yield dimeric structures. However, in all compounds the lithium cations adopt a distorted tetrahedral coordination sphere.

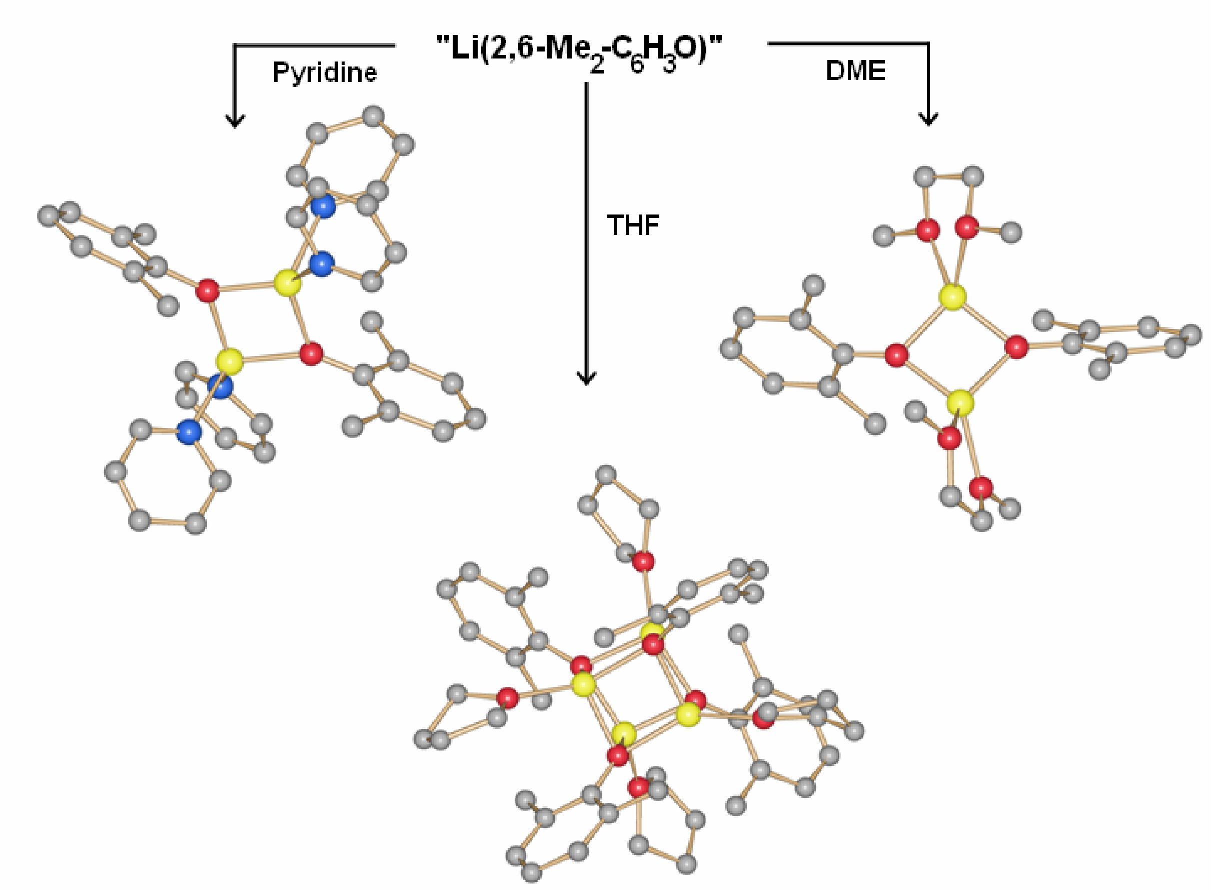


Figure 80. Representation of the solvent-influence on the degree of aggregation of $[Li(2,6\text{-}Me_2\text{-}C_6H_3O)]$ in THF (center), pyridine (left) and DME (right)

B - II.4 - Conclusion

Compare to the THF-aryloxide adducts, their analogues in DME possess a lower degree of aggregation. This can be easily understood with the bidentate function of the DME ligand. They saturate each alkali metal cation, sodium in **13** and, respectively lithium in **14**, easier than in THF resulting in a tetrameric structure in DME for the sodium derivative instead of a hexamer in THF, and respectively a dimer in DME instead of a tetramer in THF for the lithium cluster.

DME acts somewhat as pyridine compared to THF. Pyridine is more basic than THF as well as DME, and THF is more basic than DME but the functionality of the two oxygen atoms of DME make it stronger. However, as no sodium aryloxide compound has been obtained in pyridine, the comparison of the influence of these two solvents, DME and pyridine, is thus impossible for the time being, but nevertheless it seems that strong as well as polyfunctional Lewis-base coordinating solvents act in the same way: decrease of the aggregation.

B - III - Heterometallic alkoxide clusters

B - III.1 - Introduction

Alkali and alkaline earth metal ions show similarities with groups 11 and 12 transition metal ions, mostly in the reactivity and structure of organo-lithium and organo-copper compounds [25, 264, 265]. While the synthesis of group 11 metal clusters is well established [266], no systematic approach for alkaline earth metal clusters is known. Due to these similarities, a synthetic procedure was tempted similar to the ones for transition metals in order to generate alkaline earth metal aggregates or clusters (Equation 1).

It is well known that volatility should be the principal characteristic of metal-organic compounds in order to be useful as precursors in chemical vapor deposition, respectively solubility for sol-gel techniques. These properties are undoubtedly related to the molecular structure of these compounds. By using “weak” sterically demanding alkoxide ligands, organo-alkaline earth metals compounds form generally insoluble polymers [40, 172-174]. The volatility and solubility of lithium *tert*-butoxide in organic solvent, due to its structure and more covalent character, is one important asset of its use on the preparation of metal clusters in the field of oxide-ceramic materials. A large number of publications deal with structures and properties of homo- and heterometallic clusters.

Previous works in our group carried out by Dr. Estelle Gueneau [157] have shown some interesting results by the use of lithium *tert*-butoxide with alkaline earth metal iodides. Two heterometallic clusters, namely $[IM(O^tBu)_4\{Li(thf)\}_4(OH)]$ (M = Sr [167], Ba [162, 167]), have been characterized and show properties such as volatility. The formation of these two alkaline earth metal clusters can be understood in terms of a Lewis acid-base reaction [3]. The formation of the "pure" alkaline earth metal alkoxide compounds failed probably due to their too high Lewis-acidity resulting in the retention of a halide and lithium cations [177, 267-269].

In order to study the chemical behaviour of the common alkaline earth calcium-, strontium- and barium- metal iodides in its totality with the lithium *tert*-butoxide reagent, some attempts were undertaken with CaI_2. Due to the difference in ionic radius of the common alkaline earth metal ions, some structural changes might be expected.

More, in order to follow the comparison between alkaline earth and rare earth metal iodide in terms of arrangement of anionic ligands in the coordination sphere of the metal cation and thus in the overall structure of the metal cluster, syntheses with the divalent LnI_2 Ln = Eu, Sm were carried out using the same general pathway (Equation 1).

First attempts of reactions with $[CaI_2(thf)_4]$ as starting material and LiO^tBu leads to the crystallization of the homometallic cluster of lithium $[(thf)_4Li_4(O^tBu)_3I]$ [157, 270] as shown in the Equation 2:

$$CaI_2 + 4\ LiO^tBu \xrightarrow[\textit{Via}\ [CaI_2(thf)_4]]{THF} [(thf)_4Li_4(O^tBu)_3I] + \text{"}[ICa(O^tBu)(thf)_n]\text{"}$$

Equation 2. Reaction pathway tempted for the synthesis of the calcium-analogue cluster

Although the reaction should be possible as it is an analogy with the synthesis of alkaline earth metal alkoxides described by Hanusa *et al.* [119] and our first results with Sr [167] and Ba [162, 167] metal ions, the calcium compound could not be isolated and characterized. However, the ^1H NMR spectrum of the reaction solution gives hints for two more species containing O^tBu-groups in some form, one of them being very probably ^tBuOH, the product obtained from partial hydrolysis of either the final compound $[(thf)_4Li_4(O^tBu)_3I]$ [157, 270] or the initial compound LiO^tBu.

B - III.2 - Synthesis and crystallographic structure of $[ICa(O^tBu)_4\{Li(thf)\}_4(OH)].THF$ 15

The reaction carried out with $[CaI_2(thf)_4]$ under inert atmosphere with a very large excess of a 1M LiO^tBu solution in THF in the presence of LiOH leads to the isolation of the uncharged, mixed-metal cluster compound $[ICa(O^tBu)_4\{Li(thf)\}_4(OH)].THF$ **15**. Compound **15** can also be obtained with a better yield by reaction of the compound $[CaI_2(dme)_2(thf)]$ **9** with four equivalents of a 1M LiO^tBu solution in THF. In both cases, LiOH is introduced by partial hydrolysis of the LiO^tBu solution.

Compound **15** crystallizes from the mother liquor at low temperature (-25°C) after several days in the form of colourless cubic crystals in the tetragonal space group *P*4/nmm (Nr. 129). The structure can be described as a square antiprism formed by four Li-atoms in one square plane and four O-atoms of the O^tBu-ligands in the other square plane, the Li-face being capped by an OH-group, the O-face by a Ca–I-unit, leading to an overall almost spherical entity. Its formation can be formally explained by the successful substitution of one iodide and the O-donor THF molecules of $[CaI_2(thf)_4]$ for instance, by a $[LiO^tBu]_4$-unit and a μ_5-capping OH-group (Figure 81).

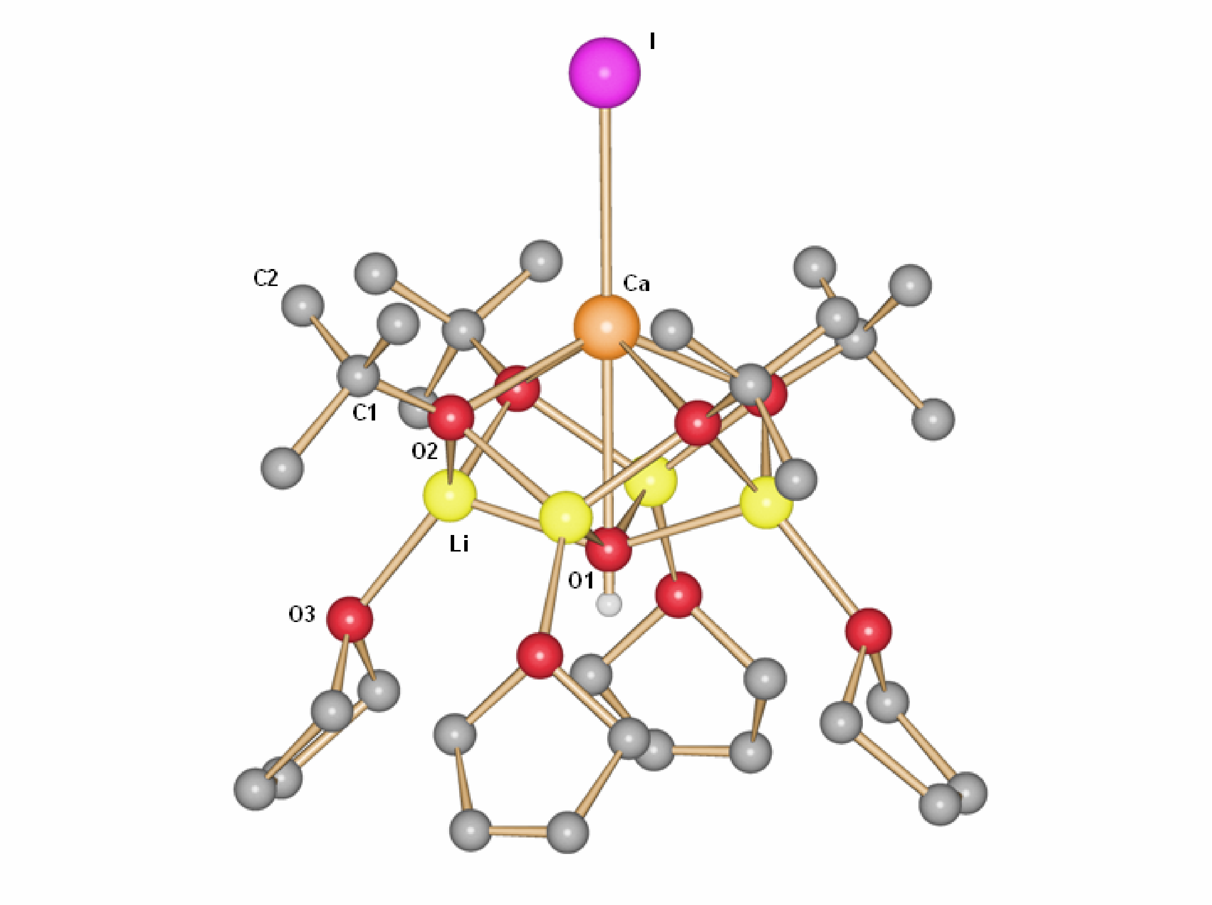


Figure 81. Schakal representation of the crystal structure of 15

The coordination sphere of calcium is built up by one remaining iodide, four O^tBu-groups and one OH-group to give an octahedral geometry. Calcium has thus its common coordination number six, and the lithium cations reach their common distorted tetrahedral coordination sphere with two O^tBu-groups, the OH^- anion and one terminal THF molecule.

The most important bond lengths and angles in **15** are summarized in Table 9.

The Ca–I distance is with 3.072(2) Å by 0.03 Å shorter than in $[CaI_2(thf)_4]$ (Ca–I 3.106(2) Å) or $[ICa(clox)(THF)_4]$ (Ca–I 3.108(3) Å; clox = $OCPh_2CH_2C_6H_4Cl_4$) [119] while the coordination number and geometry are still the same, but corresponds to the sum of the Shannon ionic radii (for a CN6: Ca^{2+} 1.00 Å, I^- 2.20 Å) [156]. It is also shorter by 0.06 Å than in the other possible starting material [$CaI_2(dme)_2(thf)$] **9** (Ca–I 3.137(9) Å), but probably due here to a lower coordination number.

Table 9. Most important bond lengths (Å)and angles (°) in **15**

Ca–I	3.072(2)	O2–Ca–I	113.67(10)
Ca–O1(OH)	2.696(7)	O2–Ca–O2 (*trans*)	132.65(19)
Ca–O2(O^{t}Bu)	2.352(4)	O2–Ca–O2 (*cis*)	80.72(7)
OH···I	3.612(5)	O1–Ca–O2	66.33(1)
Li–O1(OH)	2.024(1)	O1–Li–O2	89.1(4)
Li–O2(O^{t}Bu)	1.933(6)	O1–Li–O3	113.4(5)
Ca···Li	2.822(1)	O2–Li–O3	124.8(3)
Li···Li	2.719(1)	Li–O1–Li (*trans*)	143.7(7)
		Li–O1–Li (*cis*)	84.4(2)

The Ca–O(O^{t}Bu) distances in **16** are 2.352(4) Å long, and correspond well to those observed in the heterometallic compounds [$CaGe_2(O^tBu)_6$] [271] (average Ca–O(O^{t}Bu) = 2.360 Å) and [$CaSn_2(O^tBu)_6$] [271] (average Ca–O(O^{t}Bu) = 2.368 Å) although the bridging mode of the O^{t}Bu-groups in these compounds differs. The Ca–O(OH) distance in **15** is with 2.696(7) Å longer than the Ca–O(OH) distances in Li[$\{Ca_7(\mu_3\text{-}OH)_8I_6(thf)_{12}\}_2(\mu\text{-}I)$].3THF (average Ca–O(OH) = 2.323(2) Å) [158, 167], probably due to the bridging mode of the OH-group with five bonding partners.

The Li···Li contacts at 2.719(1) Å are shorter than in elemental lithium (3.0390 Å), but longer than in similar compounds like [$Ph_2P(NSiMe_3)]_2CLi_2$ [272] with 2.393-2.410 Å. The enlargement relative to the literature data is probably due to the short Ca–OH bond of 2.696(7) Å in which the alkaline earth cation strongly attracts the OH^- anion which caps the Li_4-square. This leads to the formation of the very flat square antiprism in which the plane containing the four Li atoms is only 1.12 Å apart from the plane containing the oxygen atoms of the O^{t}Bu-groups. Thus, the OH group is 0.63 Å below the Li_4-plane, and the Ca atom is 0.94 Å above the O_4-plane (Figure 81). The structure can thus be interpreted as insertion of a [(thf)LiO^{t}Bu]$_4$-unit into the Ca–OH bond of a linear I–Ca–OH fragment. This confirms the data derived from NMR data of the mother solution from which **15** can be obtained [157], and the complete reaction equation can thus be written as (Equation 3):

$$\mathrm{CaI_2 + 7\ LiO^{\mathit{t}}Bu} \xrightarrow[\textit{Via}\ \mathrm{[CaI_2(thf)_4]}]{\mathrm{THF}} \mathrm{[(thf)_4Li_4(O^{\mathit{t}}Bu)_3I] + \underset{\mathbf{15}}{[ICa(O^{\mathit{t}}Bu)_4\{Li(thf)\}_4(OH)]}}$$

Equation 3. Complete reaction equation for the formation of the cluster 15

The alkaline earth metal Ca^{2+} lays on a crystallographic 4mm site (¼, ¼, z (c)) just as well as do the halide I and the O1-hydroxy group. The Li-atom is found on a crystallographic mirror plane m (¼, y, z (i)) together with the attached C1-atom and one of the three methyl groups C2. The main symmetric feature of the molecule are thus the four-fold axes through I, Ca and O1 as well as the two mirror planes through Li and O2. In the crystal, the neutral clusters are arranged along the C_4-axis with rather long I···O1(H) hydrogen bonds of 3.612(5) Å (Figure 82).

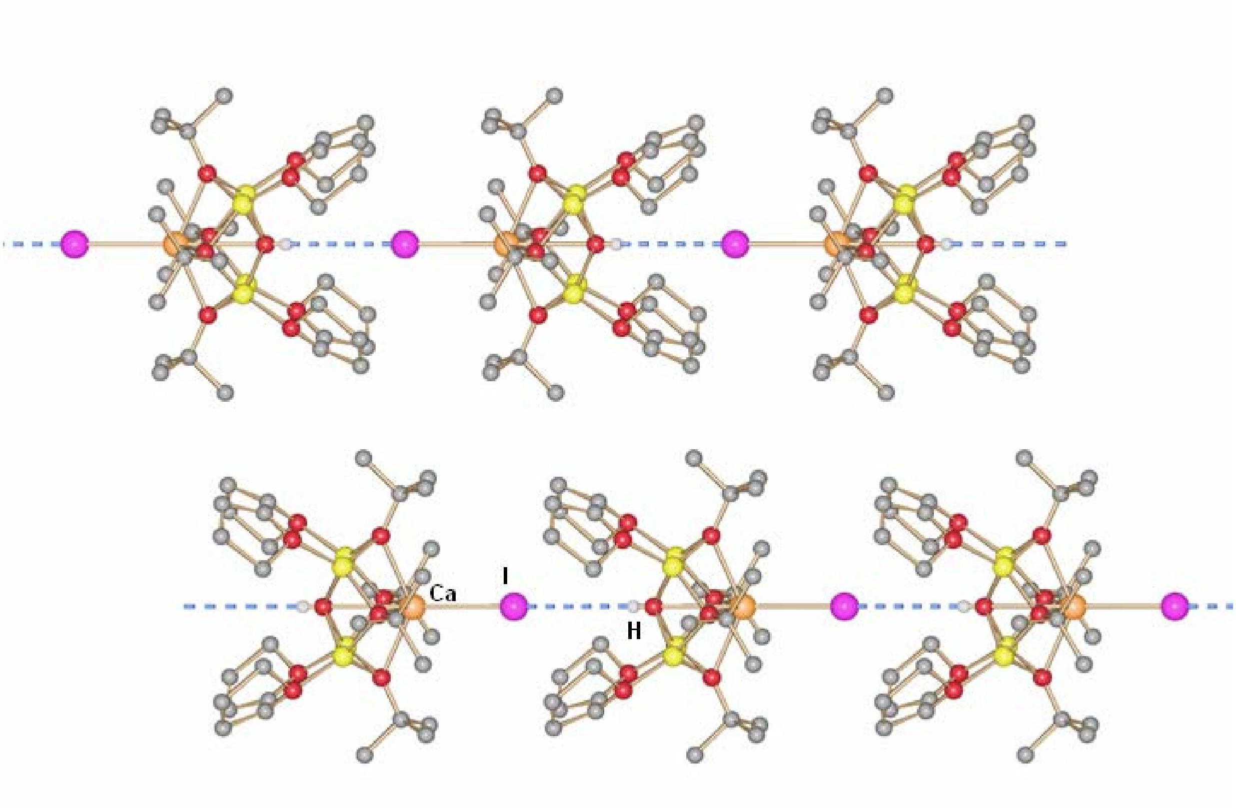


Figure 82. Stacking of clusters 15 in the crystal

B - III.3 - Synthesis and crystallographic structure of [IEu(O^{t}Bu)$_4${Li(thf)}$_4$(OH)].THF 16

The reaction of [EuI$_2$(thf)$_5$] [153] obtained via dissolution of EuI$_2$ in THF under inert atmosphere with five equivalents of a 1M LiO^{t}Bu solution in THF in the presence of LiOH leads to the isolation of the uncharged, mixed-metal cluster compound [IEu(O^{t}Bu)$_4${Li(thf)}$_4$(OH)].THF **16**.

Compound **16** crystallizes from the mother liquor at low temperature (-25°C) after a long period (several months) in a very low yield (which can not be estimated) in the form of colourless cubic crystals in the tetragonal space group *P*4/nmm (Nr. 129) with two molecules per unit cell (Figure 83). Unfortunately, attempts to reproduce the mixed-metal cluster **16** failed, and the full characterization of this complex could not be achieved. Nevertheless, single-crystal X-ray diffraction data were sufficient to obtain the crystal structure of **16**.

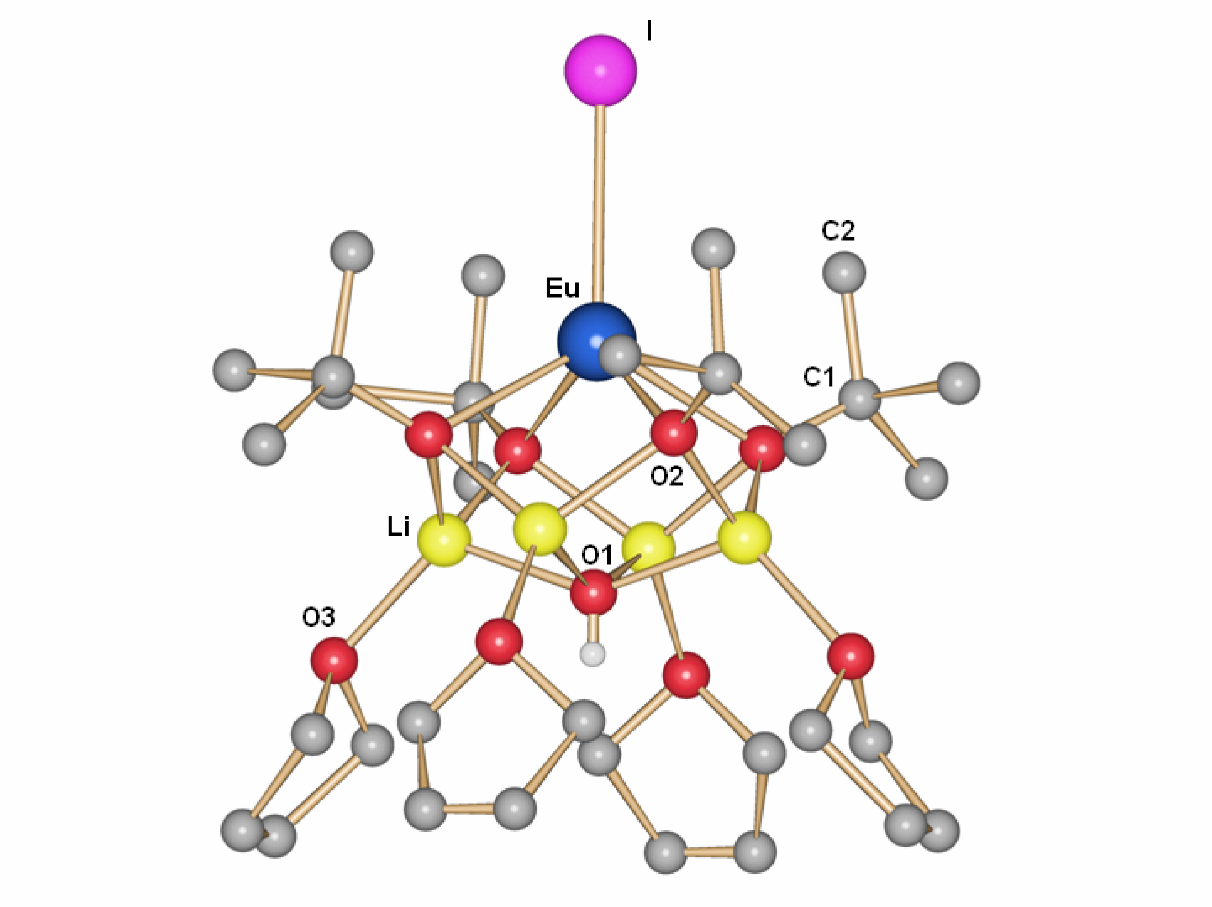


Figure 83. Schakal representation of the crystal structure of 16

The structure of **16** is isomorphic with the one of **15** and those of previously described by Dr. Estelle Gueneau [157], with general formula [IM(O^{t}Bu)$_4${Li(thf)}$_4$(OH)] (M = Ca **15**, Sr [167], Ba [162, 167]). Thus, the structure can be described as a square antiprism formed by four Li-atoms in one plane and four O-atoms of the O^{t}Bu-ligands in the other square plane, the Li-face being capped by an OH-group, the O-face by a Eu–I-unit. As for the other mixed-metal clusters [IM(O^{t}Bu)$_4${Li(thf)}$_4$(OH)] (M = Ca **15**, Sr, Ba), the formation of **16** can be formally explained by the successful substitution of one iodide and five THF molecules of [EuI$_2$(thf)$_5$] by a [LiO^{t}Bu]$_4$-unit and a μ_4-capping OH-group, the latter being introduced by partial hydrolysis of the THF solution of LiO^{t}Bu.

One remaining iodide and four O^{t}Bu-groups provide for the europium cation a square pyramidal geometry. Europium has thus a coordination number five which is relatively low for such a big cation (r_{Eu}^{2+} = 1.17 Å for a coordination number 6) [156]; the coordination number observed for divalent europium cation is usually greater than five. This low coordination number can be understood with the steric protection of the four *tert*-butyl-groups. Lithium cations reach their ubiquitous coordination number four with two O^{t}Bu-groups, the OH$^-$ anion and one terminal THF molecule in form of a distorted tetrahedral geometry.

The most important bond lengths and angles in **16** are summarized in Table 10.

Table 10. Most important bond lengths (Å)and angles (°) in **16**

Eu–I	3.210(2)	O2–Eu–I	118.50(9)
Eu–O1(OH)	2.974(7)	O2–Eu–O2 (*trans*)	123.01(2)
Eu–O2(O^{t}Bu)	2.485(4)	O2–Eu–O2 (*cis*)	76.84(8)
OH···I	3.286(1)	O1–Eu–O2	61.50(9)
Li–O1(OH)	1.995(1)	O1–Li–O2	91.2(4)
Li–O2(O^{t}Bu)	1.957(7)	O1–Li–O3	115.2(5)
Eu···Li	3.005(9)	O2–Li–O3	123.1(3)
Li···Li	2.673(1)	Li–O1–Li (*trans*)	142.7(6)
		Li–O1–Li (*cis*)	84.1(2)

Only few compounds of divalent lanthanides (Sm, Eu and Yb) with the O^{t}Bu-anion are known. For instance with the europium cation are reported: only one homometallic compound

$[(C_5Me_5)Eu^{III}(O^tBu)(\mu\text{-}O^tBu)]_2$ [273] and two heterometallic complexes $[Eu^{II}Ge_2(\mu\text{-}O^tBu)_6]$ [271] , $[Eu^{III}Na_8(O^tBu)_{10}Cl]$ [274].

The terminal Eu–I distance at 3.210(2) Å is relatively short due to the low coordination number of the Eu^{2+} cation. For instance, in $[EuI_2(thf)_5]$ [153], the terminal Eu–I distances are 3.222(2) and 3.254(2) Å (average 3.235 Å) for a coordination number of seven. For compounds where iodine act as μ-bridging ligand [275-277], the Eu–I bond lengths are longer than the one observed in **16**. This is also the case where iodine act as terminal ligand, but the europium metal ion possesses generally a higher coordination number [232, 240, 278].
The $Eu–O(O^tBu)$ distances in **16** are 2.485(4) Å long, and are curiously slightly shorter than the $Eu–O(O^tBu)$ bond lengths observed in $[Eu^{II}Ge_2(\mu\text{-}O^tBu)_6]$ (average 2.496 Å) [271] where the O^tBu-groups act as μ-bridging ligands. From the literature, this is the only compound with $Eu^{2+}–O^tBu$ bonds. Surprisingly, with the most widely used Eu^{3+} cation, only two compounds with $Eu^{3+}–O^tBu$ bonds are found, namely $[Eu^{III}Na_8(O^tBu)_{10}Cl]$ [274] and $[(C_5Me_5)Eu^{III}(O^tBu)(\mu\text{-}O^tBu)]_2$ [273]. The first compound possesses terminal and μ_3-bridging O^tBu-groups, the second compound terminal and μ-bridging O^tBu-anions. The corresponding distances $Eu^{3+}–O^tBu$ are as expected in both cases shorter than those observed in **16**. While there is no direct bond between the europium cation and the hydroxo-group, the Eu···O1(OH) distance in **16** is relatively short with 2.974(7) Å. The Li···Li contacts at 2.673(1) Å are shorter than in **15** (2.719(1) Å) and elemental lithium (3.0390 Å), but longer than in similar compounds like $[Ph_2P(NSiMe_3)]_2CLi_2$ with 2.393-2.410 Å. As for the mixed-metal cluster **15**, the enlargement relative to the literature data is probably due to the short Eu–OH bond Å in which the rare earth cation strongly attracts the OH^- anion which caps the Li_4-square. This leads also to the formation of the very flat square antiprism in which the plane containing the four Li atoms is only 1.15 Å apart from the plane containing the oxygen atoms of the O^tBu-groups. Thus, the OH-group is 0.64 Å below the Li_4-plane, and the Eu atom is 1.18 Å above the O_4-plane (Figure 83). The structure can thus be interpreted as insertion of a $[(thf)LiO^tBu]_4$-unit into the Eu–OH bond of a linear I–Eu–OH fragment.

The rare earth metal cation Eu^{2+} also lays on a crystallographic 4mm site (¼, ¼, z (c)) just as well as the halide I and the O1-hydroxy group. The Li atom is found on a crystallographic mirror plane m (x, ¼, z (i)) together with the attached C1-atom and one of the three methyl groups C2. The main symmetric feature of the molecule are thus the four-fold axes through I, Ca and O1 as well as the two mirror planes through Li and O2. In the crystal, the neutral clusters are arranged along the C_4-axis with rather short $I\cdots O1(H)$ hydrogen bonds of 3.286(1) Å (Figure 84).

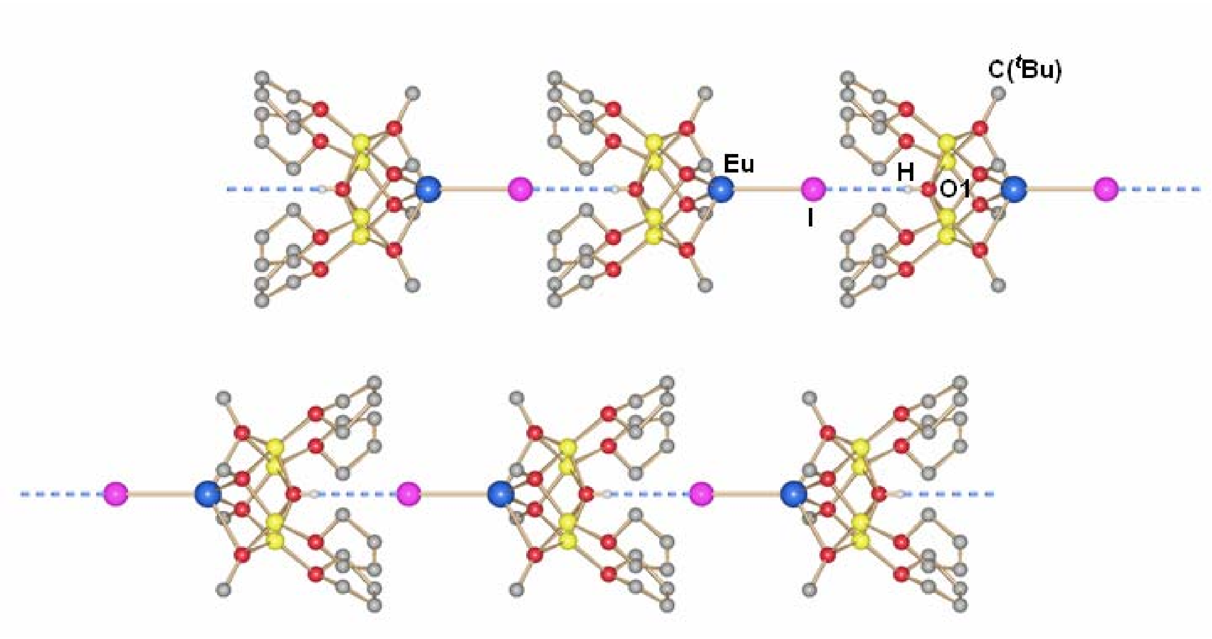


Figure 84. Stacking of clusters 16 in the crystal

Structures containing a similar square arrangement of four alkali metals as observed for $[IM(O^tBu)_4\{Li(thf)\}_4(OH)]$ (M = Ca **15**, Eu **16**, Sr [167], Ba [162, 167]) are : $[(OR)_8Cr_2Na_4(thf)_4]$ (R = ^{i}Pr, Ph) [221], $[Ph_2P(NSiMe_3)]_2CLi_2$ [272], $[Li_4Na_4(O^tBu)_4\{PhN(H)\}_4(NaOH)(4\text{-}Me\text{-}py)_4]$ [279], $[Li_4K_4(O^tBu)_4(C_6H_{11}O)_4(KOH)(thf)_5]$ [280], $[Na_4][P\{Si(F)R_2\}(SiPr^i_3)]_2$ (R = 2,4,6-$Pr^i_3C_6H_2$) [281], $[(LiO^tBu)_{10}(LiOH)_6]$ [282], $[Me_2C(CH_2)_3CMe_2NLi]_4$ [283], $[\{Li(N^tBu)_3S\}_2]$ [284] or $[Li_4L\cdot LiOH\cdot 4HMPA]$ (H_4L = *tert*-butylcalix[4]arene; HMPA = $(Me_2N)_3P{=}O$) [285] as well as $[(^tBuO)_8Li_4K_4]$ [286]. In the structures of $[(LiO^tBu)_{10}(LiOH)_6]$, $[Li_4Na_4(O^tBu)_4\{PhN(H)\}_4(NaOH)(4\text{-}Me\text{-}py)_4]$ and $[Li_4K_4(O^tBu)_4(C_6H_{11}O)_4(KOH)(thf)_5]$, the square Li_4O_4-antiprism can be found. It is capped on one side by an HO^- ligand. These fragments show similar Li–O^{t}Bu and Li–OH bond lengths as found in **15** and **16**.

B - III.4 - Comparison of clusters with general formula [IM(O^{t}Bu)$_4${Li(thf)}$_4$(OH)]

As written before, using THF-adducts of SrI_2 or BaI_2 as starting materials, we were able to isolate mixed-metal cluster compounds of the same composition [IM(O^{t}Bu)$_4${Li(thf)}$_4$(OH)] (M = Sr [167]**,** Ba [162, 167]). Their structures, abbreviated $SrLi_4$ and $BaLi_4$, were communicated before so that we here refer to a short resumed description. Both structures are analogue to the calcium and europium ones with all bonds involving strontium or barium elongated compared to **15**, which is in accordance with the larger ionic radius of the heavier alkaline earth cation compared to calcium (Figure 85).

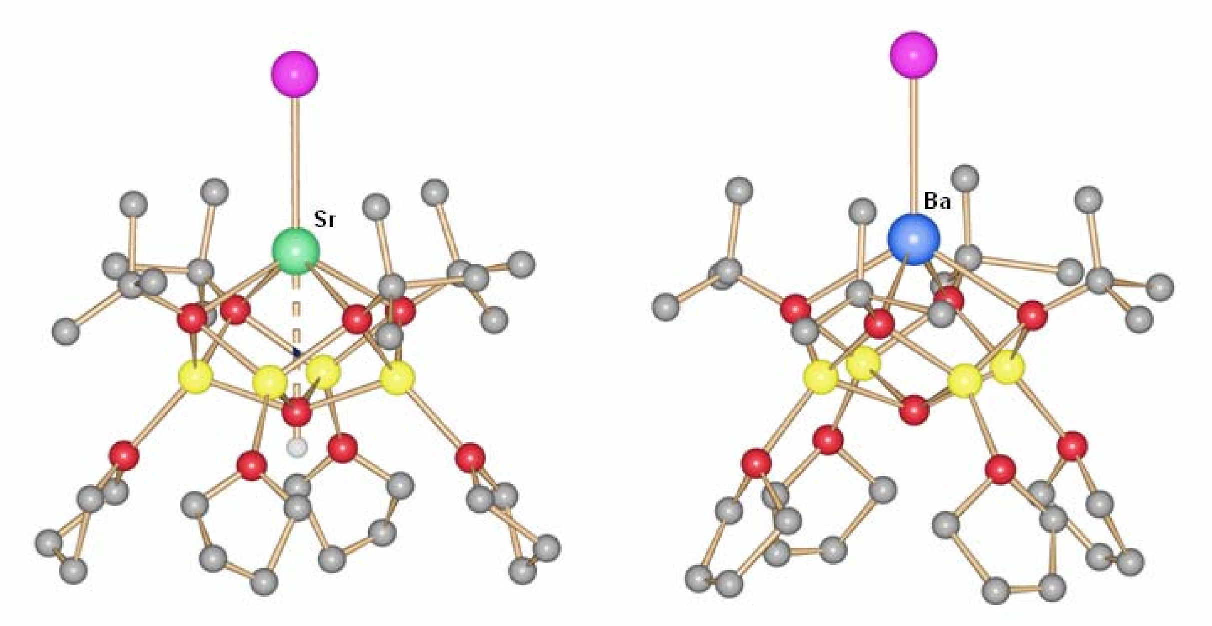


Figure 85. Schakal representation of the [IM(O^{t}Bu)4{Li(thf)}4(OH)] clusters, M = Sr (left), Ba (right)

With the series of compounds [IM(O^{t}Bu)$_4${Li(thf)}$_4$(OH)] (M = Ca **15**, Eu **16**, Sr, Ba) the most important structural differences can be discussed. The most relevant bond lengths are given in Table 11, together with literature data on the molecular precursors for these cluster compounds [CaI$_2$(dme)$_2$(thf)] **9**, [CaI$_2$(thf)$_4$], [MI$_2$(thf)$_5$] (M = Eu, Sr, Ba).

As shown in Figures 81, 83 and 85 presenting the crystal structure of each mixed-metal cluster, the latter are isostructural. Only the M^{2+}–X (X = I, O) distances are different which can easily be understood with the difference in radii between the alkaline earth and rare earth metal cations.

Table 11. Comparison of the most important structural parameters between $[CaI_2(thf)_4]$, **9** and **15**, $[EuI_2(thf)_5]$ and **16**, $[SrI_2(thf)_5]$ and $[ISr(O^tBu)_4\{Li(thf)\}_4(OH)]$ and $[BaI_2(thf)_5]$ and $[IBa(O^tBu)_4\{Li(thf)\}_4(OH)]$

	Ca–thf	**9**	**15**	Eu–thf	**16**	Sr–thf	$SrLi_4$	Ba–thf	$BaLi_4$
CN	6	7	6	7	5	7	6	7	5
M^{2+}–I	3.106	3.137	3.072	3.235	3.210	3.228	3.223	3.378	3.344
M^{2+}–O(thf)	2.34	2.391	/	2.587	/	2.586	/	2.728	/
M^{2+}–O^tBu	/	/	2.352	/	2.485	/	2.482	/	2.597
M–OH	/	/	2.696	/	2.974	/	2.935	/	3.115
I–M^{2+}–I	180	178.60	/	178.00	/	176.34	/	178.61	/
I···O(H)	/	/	3.612	/	3.286	/	3.241	/	3.935
$M^{2+}\cdots Li^+$	/	/	2.822	/	3.005	/	2.972	/	3.108

MLi_4 : $[IM(O^tBu)_4\{Li(thf)\}_4(OH)]$ M = Sr, Ba

M–thf : $[MI_2(thf)_n]$ M = Ca, n = 4; M = Eu, Sr, Ba, n = 5

Due to similar ionic radii (for a CN 6; $r_{Eu}{}^{2+}$ = 1.17 Å, $r_{Sr}{}^{2+}$ = 1.18 Å), the bond lengths in the clusters **16** and the strontium analogue $[ISr(O^tBu)_4\{Li(thf)\}_4(OH)]$ are very similar.

The M^{2+}–I distances get shorter when passing from the monomer to the cluster compounds, decreasing from 3.106(2) Å in $[CaI_2(thf)_4]$ (and 3.137(9) Å respectively for **9**) to 3.072(2) Å in average in **15**, from 3.235 Å in $[EuI_2(thf)_5]$ [153] to 3.210(2) Å in **16** and from 3.228(8) and 3.378(8) Å in $[MI_2(thf)_5]$ for Sr and Ba, respectively to 3.223(2) and 3.344(2)Å in the corresponding compound $[IM(O^tBu)_4\{Li(thf)\}_4(OH)]$ (M = Sr, Ba). This can be explained by the lower coordination number of six for strontium, respectively five for europium and barium in $[IM(O^tBu)_4\{Li(thf)\}_4(OH)]$ M = Sr, Ba compared to seven in $[MI_2(thf)_5]$ (M = Eu, Sr, Ba) due to sterical protection by the *tert*-butyl groups of the cluster. A similar effect is observed for the corresponding calcium-starting materials ($[CaI_2(thf)_4]$ and **9**) and **15**, and it is probably due to the fact that the metal ion is only linked to two anions in $[CaI_2(thf)_4]$ and **9**, but to five anions in **15**.

The insertion of the four LiO^tBu-unit changes the coordination geometry around the europium, strontium and barium ions, from a pentagonal bipyramid to a square pyramid.

The Ca–OH, Eu···OH and Sr···OH bonds in $[IM(O^tBu)_4\{Li(thf)\}_4(OH)]$ (M = Ca **15**, Eu **16**, Sr) are shorter than the Ca/Eu/Sr···Li distances, whereas in $[IBa(O^tBu)_4\{Li(thf)\}_4(OH)]$, the Ba···OH bond is longer than the intermetallic Ba···Li distance. This can be explained by the higher charge concentration on Ca^{2+}, Eu^{2+} and Sr^{2+} compared to Ba^{2+}, leading to a stronger attraction of the anion OH^- and a stronger repulsion of the Li^+ ions for calcium, europium and strontium than for barium cations.

At the same time, the heavier alkaline earth metal barium cluster is volatile, the ^{t}Bu-groups and THF ligands protect almost completely the metal core, this is the only mixed-metal cluster in which no Ba···OH interaction is observed.

B - III.5 - Theoretical calculations on $[IM(O^tBu)_4\{Li(thf)\}_4(OH)]$ clusters

Also, bond valence sums for the M^{2+} ions in $[IM(O^tBu)_4\{Li(thf)\}_4(OH)]$ (M = Ca **15**, Eu **16**, Sr, Ba) (Table 12) reveal that for Ca^{2+} and Sr^{2+}, the M–OH has to be taken into account in order to compensate the positive charge on the cation, whereas for $[IEu(O^tBu)_4\{Li(thf)\}_4(OH)]$ **16** and $[IBa(O^tBu)_4\{Li(thf)\}_4(OH)]$, the bond valence sums are reached with the five closest contacts, M–I and M–O^tBu.

Table 12. Bond valence sums for the M^{2+} ions in $[IM(O^tBu)_4\{Li(thf)\}_4(OH)]$ (M = Ca **15**, Eu **16**, Sr, Ba)

MLi_4	$CaLi_4$		$EuLi_4$		$SrLi_4$		$BaLi_4$	
V_{Li^+}	1.12 (CN = 4)		1.12 (CN = 4)		1.1 (CN = 4)		1 (CN = 4)	
$V_{M^{2+}}$	1.84 (CN = 5) (OH excluded)	1.98 (CN = 6) (OH included)	2.00 (CN = 5) (OH excluded)	2.11 (CN = 6) (OH included)	1.80 (CN = 5) (OH excluded)	1.96 (CN = 6) (OH included)	2.30 (CN = 5) (OH excluded)	2.44 (CN = 6) (OH included)

MLi_4 : $[IM(O^tBu)_4\{Li(thf)\}_4(OH)]$ M = Ca **15**, Eu **16**, Sr, Ba; V_i = bond valence sums

Compared to the increasing ionic radius of the cations, the M–OH bonds increase more importantly than by just the radii difference. To corroborate these experimental results and provide further insight into the observed differences between the complexes, electronic structure calculations were carried using density functional theory, in collaboration with Prof. Markus Meuwly, University of Basel. The calculations were carried out with the B3LYP functional and the LANL2DZ basis for I, Ba, Sr, Ca, the 6-31G* basis set for O, Li, and H, and the 3-21G* basis for C. Starting from the X-ray geometry, the M–I, M–O, O–H and Li–O distances were allowed to relax. The remaining internal coordinates were fixed at the crystallographic values. The M–O bond lengths vary between 2.80 and 3.23 Å while the I–M distances are between 3.30 and 3.60 Å. The diameter of the Li_4-ring increases from 3.79 for the Ba-containing species to 3.85 Å for $[ICa(O^tBu)_4\{Li(thf)\}_4(OH)]$ **15**.

It is also of interest to compare the nuclear charges on the most relevant atoms. While the charge on the M-atom increases from 1.81 for Ca to 1.90 for Ba, the charge on the I-atom partially counteracts this: it changes from -0.88 to -0.92. The fact that the Ba–OH bond increases so much compared to the real value seems indeed to confirm that the barium cation does not see the OH-group, its charge being compensated by the other anions. One can therefore approve the coordination number of 5 to the barium cation, whereas the M–OH bond has to be considered in the other compounds of this series. Further calculations are on the way to also include the lanthanide results.

B - IV - Heterometallic phenoxide clusters

B - IV.1 - Influence of the alkali metal

B - IV.1.1 - LiOPh as alkali reagent

B - IV.1.1.1 - Introduction

LiO^{t}Bu has been the alkoxide compound the most studied the last two decades because of its properties (solubility and volatility). This is the first lithium-alkoxide compound which presents a cage-like structure, *tert*-butyl-groups shielding the hexameric metal-core [55]. Moreover, it has been shown that the alkyl-group is one of the principal factors (see introduction) controlling the degree of oligomerization of the MOR alkoxides and these fundamental properties (solubility and volatility) are directly linked to the structure. Although lithium aryloxide compounds also present cage-like structures (see introduction), only rare synthetic approaches have been reported with this reagent in the literature [220, 258, 260]. The only rare examples of aryloxides of alkaline earth metals described have been obtained by direct reaction of the crude metal with the corresponding alcohol [114, 115, 123].

In order to study the influence of the R-group of the MOR compound on the structure of the alkaline earth metal cluster and in view of the results obtained with LiO^{t}Bu in the previous part of this manuscript, some attempts were undertaken with the sterically unhindered LiOPh. Analogies between alkaline earth and rare earth metals were also pursued by synthesis attempts under the same condition with the divalent rare earth reagents EuI_2 and SmI_2.

B - IV.1.1.2 - Crystallographic structure of [CaLi$_6$(OPh)$_8$(thf)$_6$] 17

The heterometallic [CaLi$_6$(OPh)$_8$(thf)$_6$] cluster **17** can be prepared using three different synthetic routes. i) The reaction of CaI_2 in THF via [CaI_2(thf)$_4$] with an excess of a 1M LiOPh-solution in THF, under dry and inert conditions at room temperature, yields small crystals of [CaLi$_6$(OPh)$_8$(thf)$_6$] **17** within one week after recrystallization in a THF/hexane mixture. ii) Following the same procedure, replacing formally [CaI_2(thf)$_4$] by the starting material [CaI_2(dme)$_2$(thf)] **9**, the reaction affords crystals of **17** in a similar yield.

iii) Larger crystals of **17** can also be obtained quickly (one night) by a microwave-assisted reaction (500 W during two minutes).

Compound **17** crystallizes in the monoclinic space group $P2_1/n$ (Nr. 14) with two molecules in the unit cell. The structure consists of two $CaLi_3$-tetrahedra linked via the Ca-vertex (Figure 86). The structure can alternatively be described as two vertex-sharing $CaLi_3O_4$-heterocubanes and can thus be viewed as a substitution of each iodide of CaI_2 by a Li_3O_4-group provided from the $[LiOPh(thf)]_4$ reagent; the driving force of the reaction being the elimination of LiI salts. By consequence, all triangular faces of these two tetrahedra are μ_3-bridged by PhO-groups.

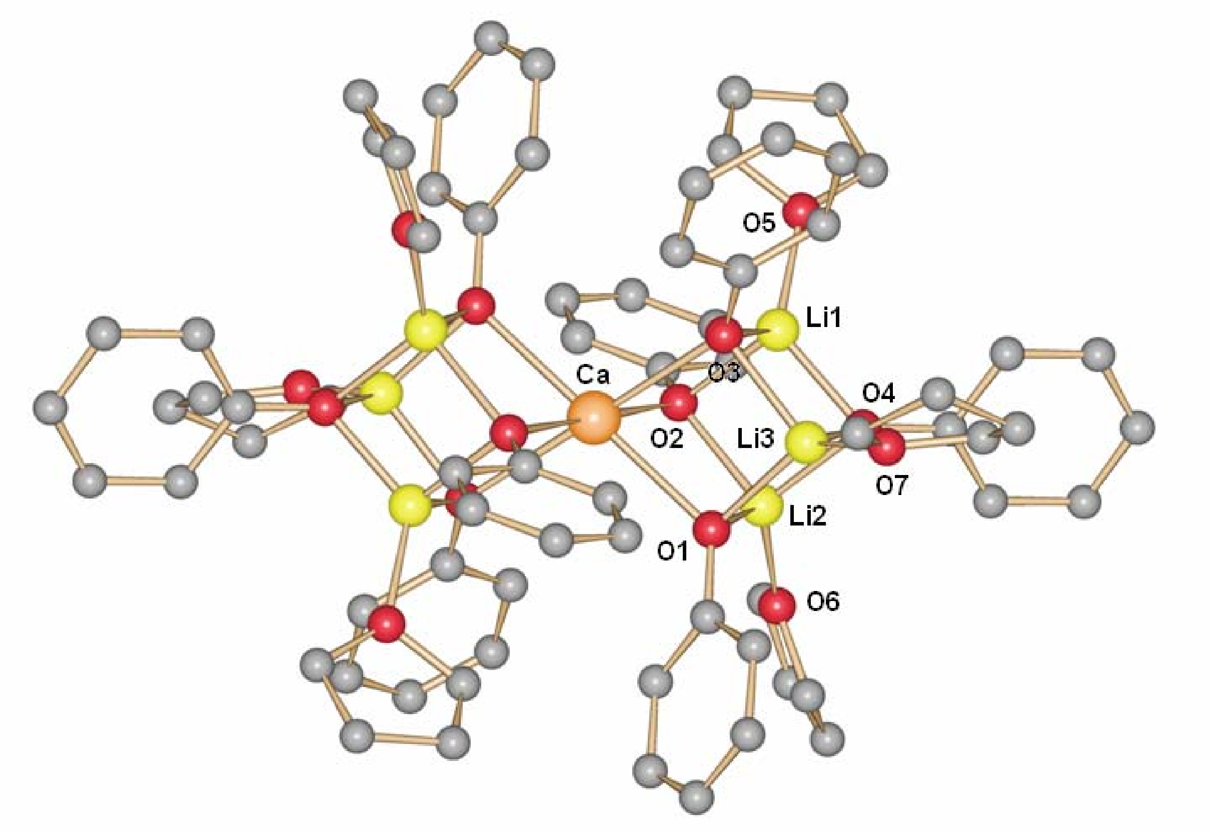


Figure 86. Schakal view of the partially labelled molecular structure of 17, H atoms have been omitted for clarity

This motif (with other ligands) has already been described in some homometallic clusters. One was characterized in our group with calcium [158, 167] but it is more frequently observed in transition metal compounds with for instance zinc [287-289] or copper [290]. Such motif can also be observed in heterometallic clusters, with mixed transition metals [291] but also as **17**, with mixed alkali-transition metals [220].

The most important bond lengths and angles in **17** are summarized in Table 13.

Table 13. Bond lengths (Å) and angles (°) in **17**

Ca–OPh	2.375(9)	OPh–Ca–OPh (*trans*)	180
Li–OPh	1.973(2)	OPh–Ca–OPh (same cubane)	76.11(7)
Li–O(thf)	1.935(6)	OPh–Ca–OPh (other cubane)	103.88(3)
Li···Li	2.613(3)	Ca–OPh–Li	94.35(7)
Ca···Li	3.211(3)	Li–OPh–Li	83.31(7)

Only few references are reported in the literature with calcium and aryloxides; only one with C_6H_6O- [110], one with 2,6-Me_2-C_6H_3O- [109], two with 2,6-$^iPr_2$-C_6H_3O- [106, 107] and one with the 2,6-Ph_2-C_6H_3O-anion [108]. Among the alkaline earth aryloxide compounds known, magnesium is the metal which has been the most studied [125, 126, 292-300].

In **17**, the calcium cation reaches a coordination number of six with an average Ca–μ_3-OPh distance of 2.375(6) Å. These bond lengths are slightly shorter than in the literature data compound $[Ca_3(OPh)_5(HMPA)_6]$.OPh.2PHOH [110]. In the same reference, the Ca–μ-OPh bond lengths (average 2.343(8) Å) are shorter than the Ca–μ_3-OPh average distance in **17**. Compared to the other calcium aryloxide compounds from the literature [106-109], the mean Ca–μ_3-OPh in **17** is relatively longer than the terminal Ca–OAr or Ca–μ-OAr distances cited. The Li–O(OPh) bond lengths (average Li–O(OPh) = 1.973(2) Å) are slightly longer than those observed in the literature [77, 82, 83, 220, 258, 301, 302]. Each lithium cation finds its tetrahedral coordination sphere completed with a terminally bonded THF ligand. The Li–O(thf) bond lengths of **17** (average Li–O(thf) = 1.935(3) Å) compare well with those described [63, 69, 162, 220, 302].

Neither π–π nor C–H···π interactions between phenyl rings of the phenolate groups are observed in **17**, meaning the $[CaLi_6(OPh)_8(thf)_6]$ cluster **17** may be molecular in the solid state. Indeed, no intermolecular even weak H-bonds between ethereal ligands or phenyl/ethereal ligands are listed in **17**. The heterometallic cluster **17** is thus molecular in the solid state, no intermolecular interactions of any kind are observed between molecules of **17**.

An inversion centre is situated at the position of the calcium cation which lies on the crystallographic position (0, ½, ½ (d)). The so obtained compound possesses a quasi spherical structure with the core of the cluster well protected by hydrophobic phenyl-groups and THF.

B - IV.1.1.3 - Crystallographic structure of [$SrLi_6(OPh)_8(thf)_6$] 18

Working under the same conditions as for the synthesis of **17**, the reactions (i), ii) and iii)) of SrI_2 with an excess of LiOPh in THF yield crystals of [$SrLi_6(OPh)_8(thf)_6$] **18**. Compound **18** crystallizes in the monoclinic space group *P*2_1/*n* (Nr. 14) with two molecules in the unit cell. The structure is isomorphic to the one described for [$CaLi_6(OPh)_8(thf)_6$] **17**, the calcium cation being formally replaced by a strontium cation. An inversion centre is situated at the position of the strontium cation which lays on the crystallographic position (1, 0, 1 (a)). Thus, the asymmetric unit is only composed of a strontium cation to which three lithium cations via four μ_3-bridging phenolate-groups in form of a tetrahedron are bonded. Finally, the structure consists of two $SrLi_3$-tetrahedra linked via the Sr-vertex (Figure 87). All triangular faces of these two tetrahedra are μ_3-bridged by phenolate-groups.

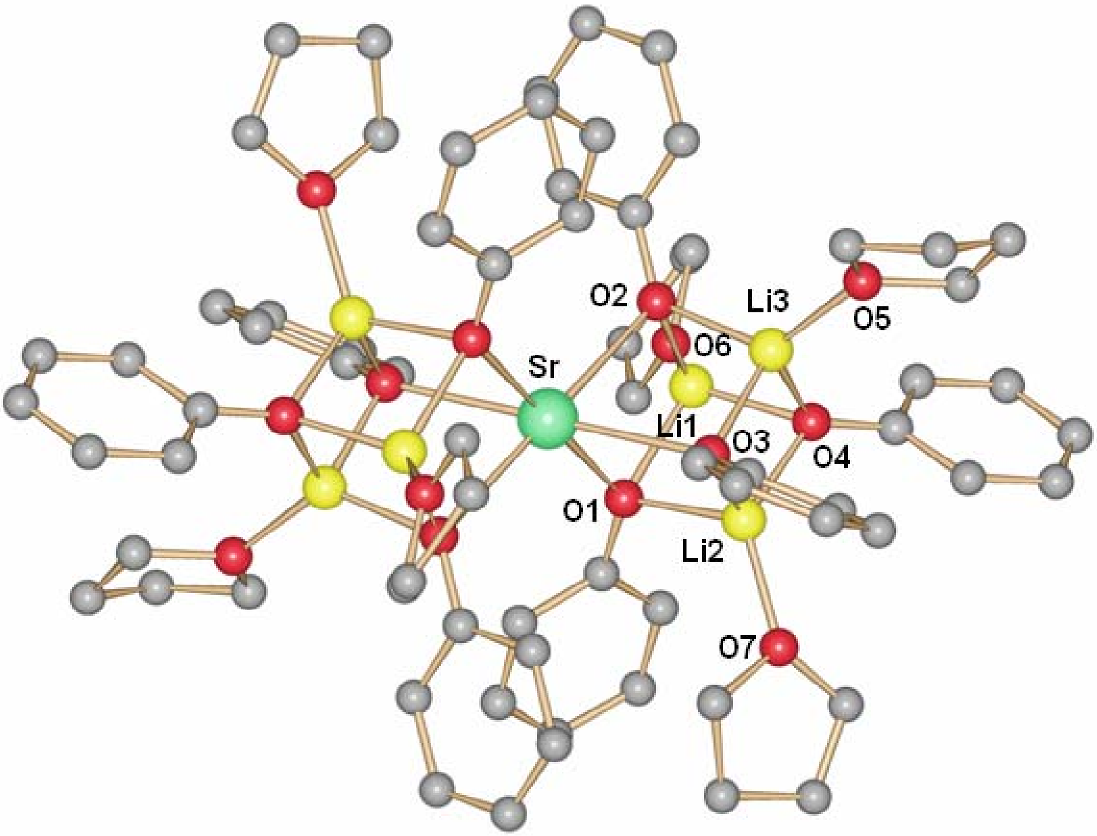


Figure 87. Schakal view of the partially labelled molecular structure of 18, H atoms have been omitted for clarity

The most important bond lengths and angles in **18** are summarized in Table 14.

Table 14. Bond lengths (Å) and angles (°) in **18**

Sr–OPh	2.516(1)	OPh–Sr–OPh (*trans*)	180
Li–OPh	1.970(6)	OPh–Sr–OPh (same cubane)	72.78(8)
Li–O(thf)	1.937(5)	OPh–Sr–OPh (other cubane)	107.21(3)
Li···Li	2.605(6)	Sr–OPh–Li	94.70(9)
Sr···Li	3.229 (6)	Li–OPh–Li	83.21(2)

In **18**, the strontium cation also reaches a coordination number of six with an average Sr–μ$_3$-OPh distance of 2.516(2) Å. This average distance is shorter than the Sr–μ$_3$-OPh bond lengths in [$Sr_4(OPh)_8(PhOH)_2(THF)_6$] [115] and [$Sr_3(OPh)_6$][$OP(NMe_2)_3$]$_5$ [110] but longer than Sr–μ-OPh distances in the same references. The Li–O(OPh) bond lengths (average Li–O(OPh) = 1.970(6) Å) are slightly longer than those observed in the literature [77, 82, 83, 220, 258, 301, 302]. Each lithium cation finds its tetrahedral coordination sphere completed with a terminally bonded THF ligand. The Li–O(thf) bond lengths of **18** (average Li–O(thf) = 1.937(5) Å) compare well with those described [63, 69, 162, 220, 302].

As **17**, no π–π and no C–H···π interactions between phenyl rings of the phenolate groups are observed in **18**. Moreover, no intermolecular, even weak H-bonds are observed since all H···O distances are >3.07 Å, the [$SrLi_6(OPh)_8(thf)_6$] cluster **18** is therefore molecular in the solid state.

The so obtained compound possesses also a quasi spherical structure with the core of the cluster well protected by hydrophobic groups of phenyl and THF.

B - IV.1.1.4 - Crystallographic structure of [$BaLi_6(OPh)_8(thf)_6$] 19

Finally, following the same reaction pathways (i) and ii)) used for the synthesis of **17** and **18**, the reaction of BaI_2 in THF with an excess of a 1M LiOPh-solution in THF under inert atmosphere, yields crystals of [$BaLi_6(OPh)_8(thf)_6$] **19**.

The microwave-assisted reaction did not afford the crystallization of **19**. Compound **19** crystallizes in the triclinic space group *P*-1 (Nr. 2) with one molecule in the unit cell. The structure is isostructural to [$CaLi_6(OPh)_8(thf)_6$] **17** and [$SrLi_6(OPh)_8(thf)_6$] **18**. An inversion centre is situated at the position of the barium cation which lays on the crystallographic position (0, ½, ½ (g)). Therefore, the structure consists of two identical $BaLi_3$-tetrahedra linked via the Ba-vertex (Figure 88). All triangular faces of these two tetrahedra are μ_3-bridged by phenolate-groups.

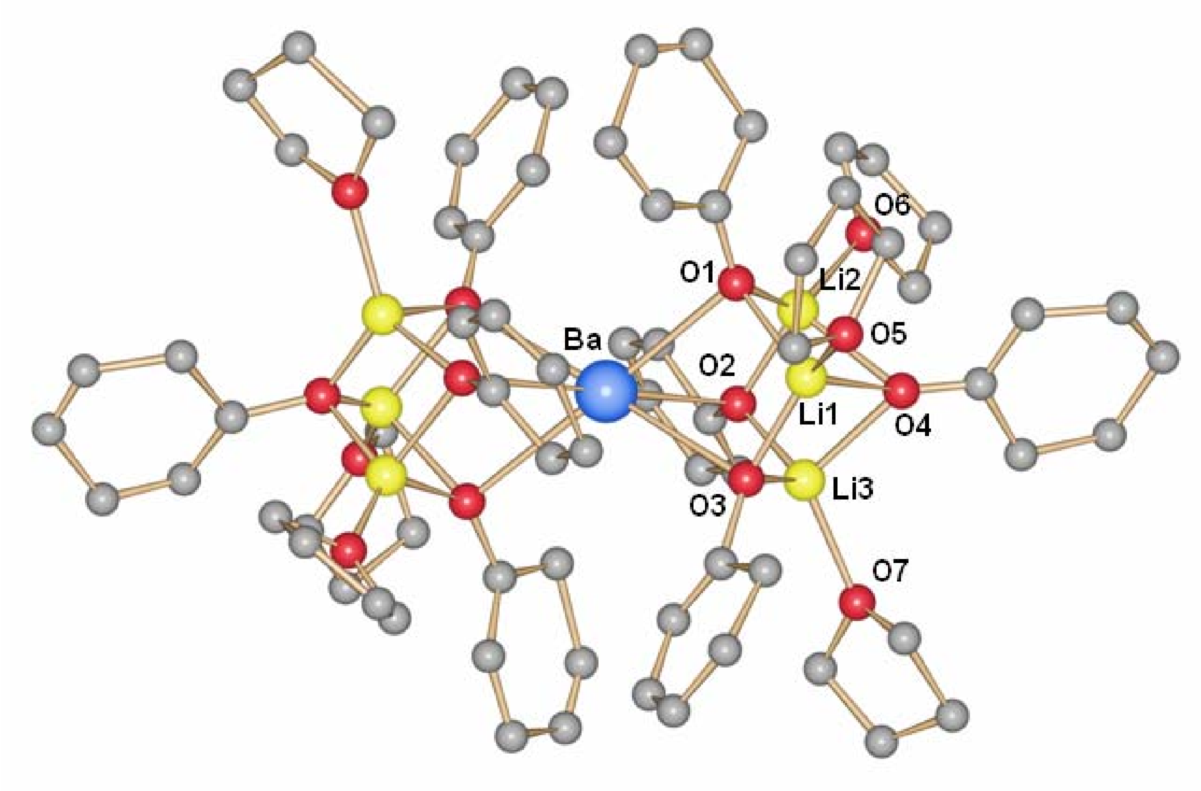


Figure 88. Schakal view of the partially labelled molecular structure of 19, H atoms have been omitted for clarity

The most important bond lengths and angles in **19** are summarized in Table 15.

Table 15. Bond lengths (Å) and angles (°) in **19**

Ba–OPh	2.718(2)	OPh–Ba–OPh (*trans*)	180
Li–OPh	1.925(6)	OPh–Ba–OPh (same cubane)	66.06(7)
Li–O(thf)	1.963(3)	OPh–Ba–OPh (other cubane)	113.93(3)
Li···Li	2.580(8)	Ba–OPh–Li	96.43(3)
Ba···Li	3.500(4)	Li–OPh–Li	84.07(9)

The barium cation reaches a coordination number of six with a mean value of Ba–μ_3-OPh distance at 2.718(2) Å. They compare well with those found in $[Ba_6(OPh)_{12}(TMEDA)_4]$ [110]

(average 2.730(2) Å) and are slightly longer than those in $[HBa_5(O)(OPh)_9(thf)_8]$ [123] (average 2.686 Å) but are slightly shorter than the average Ba–μ_3-OPh distances in $[H_2Ba_8(\mu_5\text{-}O)_2(OPh)_{14}(HMPA)]_6$ [114] (average 2.762 Å) and relatively much shorter than the Ba–μ_3-OPh bond lengths in $BaTi(OC_6H_5)_6.2DMF$ (average 2.815 Å) [120]. The Li–O(OPh) bond lengths (average Li–O(OPh) = 1.925(6) Å) are shorter than observed in literature compounds [77, 82, 83, 220, 258, 301, 302] but they are ranged in a quite large gap of values (1.86(5) to 2.01(7) Å) which induces a slight distortion of the cubane-units. However, they correspond well to Li–O(OPh) distances in the expected reagent $[Li(OPh)(thf)]_4$ [63] (average 1.93 Å). Each lithium cation finds its tetrahedral coordination sphere completed with a terminal THF molecule with a Li–O(thf) average distance at 1.963(3) Å which is longer than those observed in **17** and **18**, but are in the range of analogous bond lengths in the literature [302]. But this enlargement compared to **17** and **18** is probably due to the shorter Li–O(OPh) distances in **19**.

Neither π–π nor no C–H···π interactions between phenyl rings of the phenolate groups are found in **19**. No intermolecular H-bonds can be found between molecules of neighbouring of **19** for less than 3.67 Å (O4···H28B = 3.679(8) Å).

The cluster compound $[BaLi_6(OPh)_8(thf)_6]$ **19** is therefore molecular in the solid state.

From the last results, divalent lanthanides (Sm^{2+}, Eu^{2+}, Yb^{2+}) seem to have similar synthetic and structural chemistry than alkaline earth metals, both in terms of O-donor Lewis-coordinating solvents (B - I.3) with similar synthetic and structural complexes but also in terms of clusters with the similar arrangement of anionic ligands in their coordination sphere. (B - III.3).

In order to carry on this study, some attempts of synthesis were undertaken with a larger alkoxide reagent than LiO^tBu, namely LiOPh. Results presented above (complexes **17-19**) show completely different arrangements of anionic ligands in the coordination sphere of the alkaline earth metal ions. We wanted to verify that the same changes occur with divalent lanthanide ions.

From the literature, numbers of crystallographically characterized lanthanide aryloxide compounds are described, but only one with the least unhindered phenolate anion $[Sm(Cp^*)_2(OPh)(thf)]$ ($Cp^* = C_5Me_5$) [303]! Moreover, among these reported compounds, rare are those with divalent lanthanide metals.

B - IV.1.1.5 - Crystallographic structure of [$EuLi_6(OPh)_8(thf)_6$] 20

The reaction, under dry and inert atmosphere, of EuI_2 in THF via [$EuI_2(thf)_5$] [153] with an excess of LiOPh in THF, leads in a low yield (24%) after recrystallization in a hexane/THF mixture solution within one week at low temperature (-25°C) of the formation of crystals with formula [$EuLi_6(OPh)_8(thf)_6$] **20**.

Compound **20** crystallizes in the monoclinic space group $P2_1/n$ (Nr. 14) with two molecules in the unit cell. The structure is very similar to the ones of [$MLi_6(OPh)_8(thf)_6$] compounds (M = Ca **17**, Sr **18**, Ba **19**). Thus, the structure consists of two cubanes $EuLi_3O_4$ linked via a vertex, the Eu^{2+} cation (Figure 89).

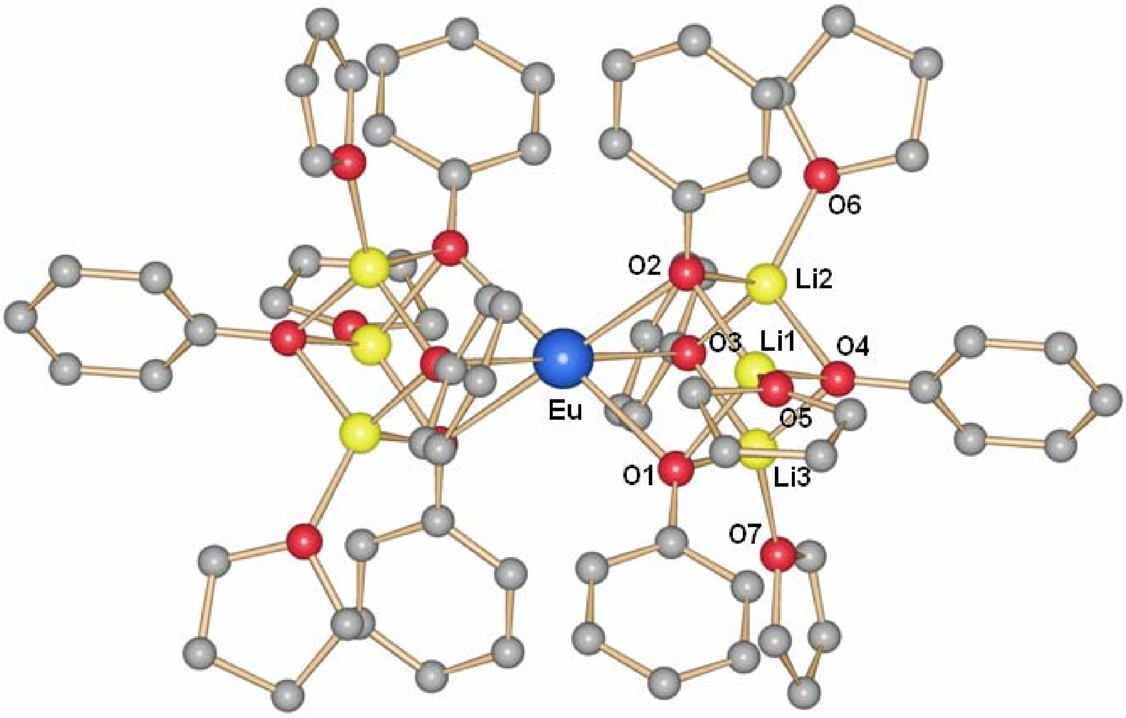


Figure 89. Schakal view of the partially labelled molecular structure of 20, H atoms have been omitted for clarity

The most important bond lengths and angles in **20** are summarized in Table 16.

Table 16. Bond lengths (Å) and angles (°) in **20**

Eu–OPh	2.540(7)	OPh–Eu–OPh (*trans*)	180
Li–OPh	1.97(3)	OPh–Eu–OPh (same cubane)	72.56(7)
Li–O(thf)	1.956(7)	OPh–Eu–OPh (other cubane)	107.43(3)
Li···Li	2.563(3)	Eu–OPh–Li	94.86(7)
Eu···Li	3.36(2)	Li–OPh–Li	81.85(2)

From the literature, only few compounds of divalent lanthanides with aryloxides are described and none with the sterically unhindered phenoxide ligand. However, Sr^{2+} and Eu^{2+}, Sm^{2+} cations have approximately the same ionic radii (for a CN6: $r_{Sr}{}^{2+}$ = 1.18 Å, $r_{Eu}{}^{2+}$ = 1.17 Å, for a CN7: $r_{Sm}{}^{2+}$ = 1.22 Å), thus the Ln^{2+}–OPh bonds should be in the same order of length than the Sr^{2+}–OPh distances.

The europium cation is situated on an inversion centre at the crystallographic position (0, ½, 0 (c)) and reaches a coordination number of six with an average Eu–μ_3-OPh distance of 2.540(7) Å. They are slightly longer than the Sr–μ_3-OPh distances in **18** but they are relatively longer on average than Eu–μ-OAr bond lengths in other aryloxide compounds, for instance $[Eu_4(\mu\text{-}OC_6H_3\text{-}^{i}Pr_2\text{-}2,6)_4(OC_6H_3\text{-}^{i}Pr_2\text{-}2,6)_2(\mu_3\text{-}OH)_2(NCMe)_6]$ (2.403-2.543 Å) [304], $[Eu_2(\mu\text{-}OC_6H_3\text{-}^{i}Pr_2\text{-}2,6)_4(NCMe)_5]$ (2.438(6)-2.494(6) Å) [305], $[Eu(\mu\text{-}OC_6H_3\text{-}Me_2\text{-}2,6)_2(thf)_2]_3$ (2.444(13)-2.581(12) Å) [306]. As expected, the Eu–μ_3-OPh distances in **20** are longer than the terminal Eu–OAr bonds in divalent europium aryloxide adducts: $[Eu(2,6\text{-}Me_2\text{-}C_6H_3O)_2(thf)_3].0.75THF$ (2.309(14)-2.313(12) Å) [307], $[Eu_4(\mu\text{-}OC_6H_3\text{-}^{i}Pr_2\text{-}2,6)_4(OC_6H_3\text{-}^{i}Pr_2\text{-}2,6)_2(\mu_3\text{-}OH)_2(NCMe)_6]$ (2.284(6)-2.299(6) Å) and $[Eu(OC_6H_3\text{-}^{t}Bu_2\text{-}2,6)_2(NCMe)_4]$ (2.313(12)-2.35(2) Å) [304].

The Li–O(OPh) bond lengths (average Li–O(OPh) = 1.97(3) Å) are slightly longer than those observed in the literature [77, 82, 83, 220, 258, 301, 302] but correspond very well to those in **18**.

In both cubane-subunits, the lithium cations reach their common tetrahedral coordination sphere, completed with a terminally coordinated THF molecule. The Li–O(thf) bond lengths of **20** (average Li–O(thf) = 1.956(7) Å) are in the range of analogous bond lengths in the literature [63, 69, 162, 220, 302].

Again, no π–π and no C–H···π interactions between phenyl rings of the phenolate groups are observed in **20**. However, very weak intermolecular H-bonds can be found between THF molecules of neighbouring $[EuLi_6(OPh)_8(thf)_6]$ clusters with a O6···H32B distance at 2.993(3)

Å. This leads to the formation of infinite polymeric chains of molecules of **20** along the c-axis (Figure 90).

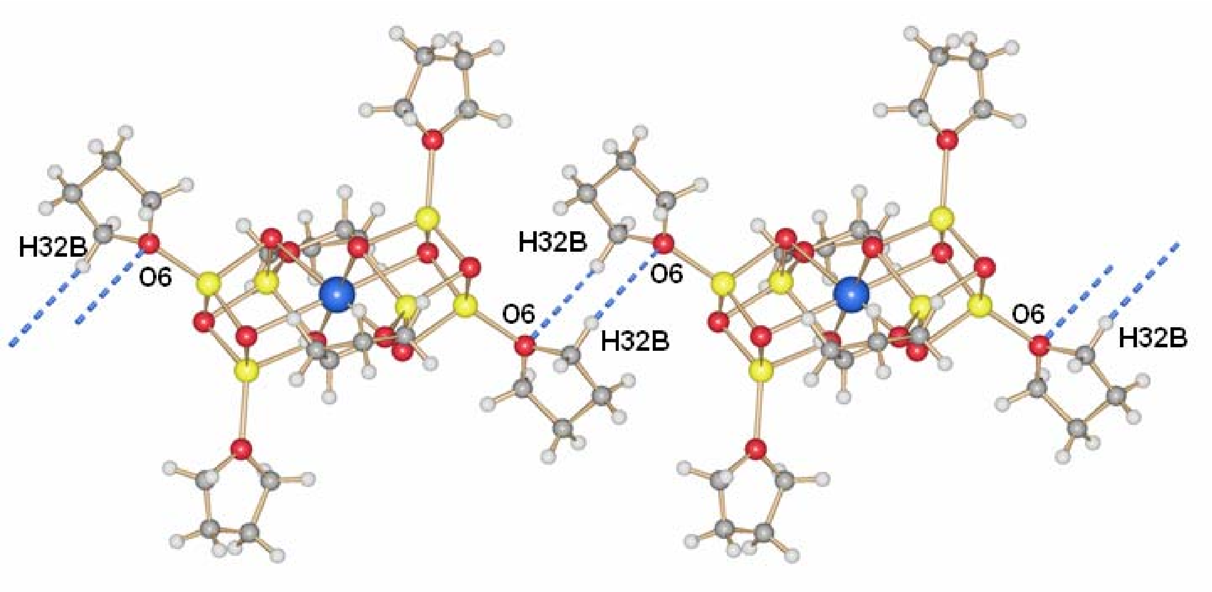


Figure 90. H-bonds involved in the formation of polymeric chains in 20, O6···H32B = 2.993(3) Å, phenyl rings are omitted for clarity

At the molecular level, the $[EuLi_6(OPh)_8(thf)_6]$ cluster compound **20** possesses a quasi spherical structure with the core of the cluster well protected by hydrophobic groups of phenyl and THF.

B - IV.1.1.6 - Crystallographic structure of $[SmLi_6(OPh)_8(thf)_6]$ 21

The heterometallic $[SmLi_6(OPh)_8(thf)_6]$ cluster **21** can be prepared as for $[MLi_6(OPh)_8(thf)_6]$ (M = Ca **17**, Sr **18**) with two different synthetic routes. i) The reaction of $[SmI_2(thf)_5]$ [154] with an excess of LiOPh in THF. This reaction was performed under dry and inert atmosphere in a glovebox at room temperature. After recrystallization in a THF/hexane mixture, single-crystals of $[SmLi_6(OPh)_8(thf)_6]$ **21** grown within one week at low temperature (-25°C). ii) **21** can also be obtained more quickly (two days) by a microwave-assisted reaction (500 W during two minutes).

Compound **21** crystallizes in the monoclinic space group $P2_1/n$ (Nr. 14) with two molecules in the unit cell. As for **17**, **18**, **19** and **20**, the structure of **21** consists of two $SmLi_3$-tetrahedra linked via the Sm-vertex (Figure 91).

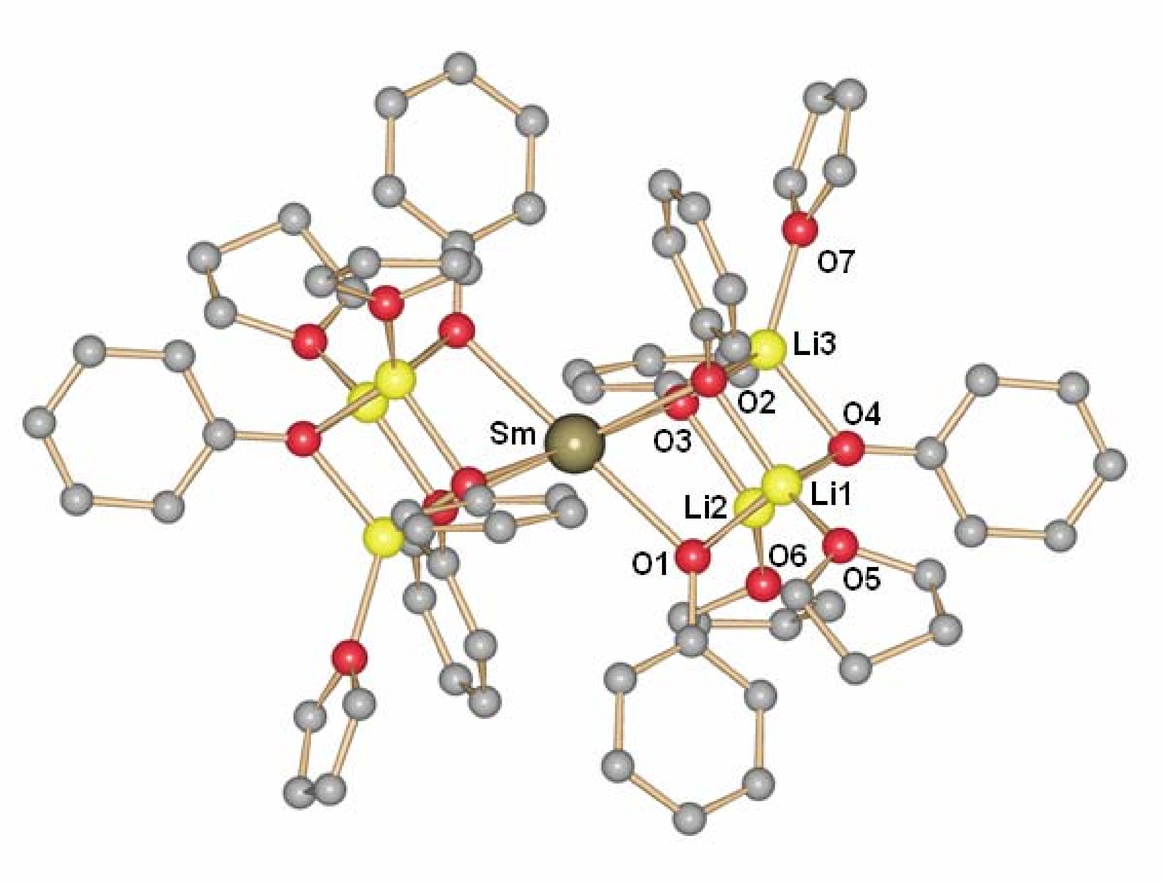


Figure 91. Schakal view of the partially labelled molecular structure of 21, H atoms have been omitted for clarity

The most important bond lengths and angles in **21** are summarized in Table 17.

Table 17. Bond lengths (Å) and angles (°) in **21**

Sm–OPh	2.530(2)	OPh–Sm–OPh (*trans*)	180
Li–OPh	1.970(7)	OPh–Sm–OPh (same cubane)	72.14(6)
Li–O(thf)	1.927(7)	OPh–Sm–OPh (other cubane)	107.85(7)
Li···Li	2.611(8)	Sm–OPh–Li	95.07(7)
Sm···Li	3.348(3)	Li–OPh–Li	83.25(2)

The samarium cation is situated on an inversion centre at the crystallographic position (1, 0, 1 (a)) and reaches a coordination number of six with an average Sm–μ_3-OPh distance of 2.530(2) Å, which compares well with those found [$Sr_4(OPh)_8(PhOH)_2(THF)_6$] [115] and [$Sr_3(OPh)_6$][$OP(NMe_2)_3$]$_5$ [110]. They are much longer compared to the terminal Sm–OPh found in [Sm(Cp*)$_2$(OPh)(thf)] (Cp* = C_5Me_5) [303] (Sm–OPh = 2.1645(14) Å). The Li–

O(OPh) bond lengths (average Li–O(OPh) = 1.970(7) Å) are slightly longer than those observed in the literature [77, 82, 83, 220, 258, 301, 302]. Each lithium cation is satisfied with its ubiquitous tetrahedral coordination sphere completed with a terminally bonded THF ligand. The Li–O(thf) bond lengths of **21** (average Li–O(thf) = 1.927(7) Å) are common and correspond well with those described in literature compounds [63, 69, 162, 220, 302].

No π–π as well as no C–H···π interactions between phenyl rings of the phenolate groups are observed in **21**. However as in **20**, very weak intermolecular H-bonds can be found between THF molecules of neighbouring [$\mathrm{SmLi_6(OPh)_8(thf)_6}$] clusters with a O5···H25A distance at 2.962(4) Å. This leads to the formation of infinite chains of cluster **21** (Figure 92).

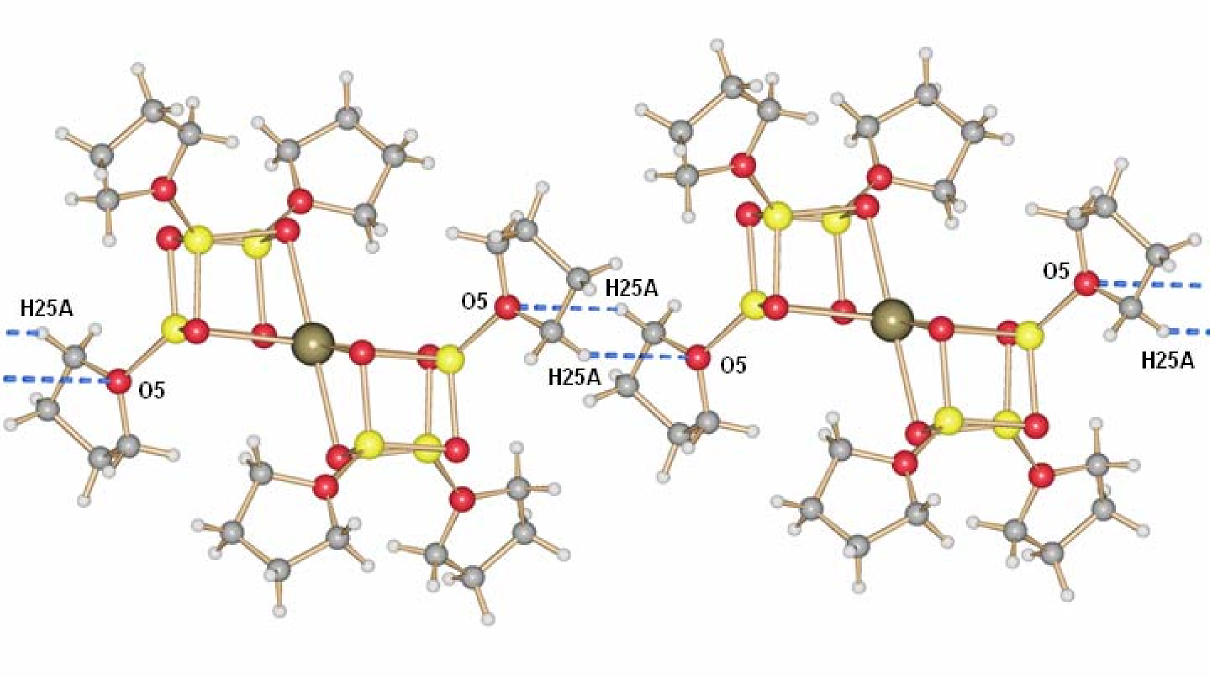


Figure 92. H-bonds involved in the formation of polymeric chains in 21, O5···H25A = 2.962(4) Å, phenyl rings are omitted for clarity

At the molecular level, the cluster compound [$\mathrm{SmLi_6(OPh)_8(thf)_6}$] **21** also possesses a quasi spherical structure with the core of the cluster well protected by hydrophobic groups of phenyl and THF.

Unfortunately, on top of being very sensitive towards air and moisture, the mixed-metal clusters [$\mathrm{MLi_6(OPh)_8(thf)_6}$] **20** and **21** melt within a minute even though working under argon out of the mother solution. The analyses were thus very difficult to perform.

B - IV.1.1.7 - General comparison of the [MLi$_6$(OPh)$_8$(thf)$_6$] clusters

A comparison of the most important structural parameters of the isostructural clusters [MLi$_6$(OPh)$_8$(thf)$_6$] M = Ca **17**, Sr **18**, Ba **19**, Eu **20** and Sm **21** clusters is given in Table 18.

All the compounds can be prepared using the same reaction pathway and present the same general formula as well as structural features. In both case, the formation of this motif can be interpreted as the substitution of each iodide and THF molecules of the [MI$_2$(thf)$_n$] starting materials by a Li$_3$O$_4$-group provided from the [LiOPh(thf)]$_4$ reagent resulting in the elimination of LiI salts.

Table 18. Comparison of the principal parameters (bond lengths (Å)) in **17**, **18**, **19**, **20** and **21**

	[Li(OPh)(thf)]$_6$ [69]	[Li(OPh)(thf)]$_4$ [63]	**17**	**20**	**18**	**21**	**19**
$r_{M^{2+}}$(CN6)	/	/	1	1.17	1.18	1.22(CN7)	1.35
M–OPh	/	/	2.375(9)	2.540(7)	2.516(1)	2.530(2)	2.718(9)
Li–OPh	1.957	1.93	1.973(2)	1.97(3)	1.970(6)	1.970(7)	1.930(8)
Li···Li	2.619	2.62	2.613(3)	2.563(3)	2.605(6)	2.611(8)	2.577(8)
Li–O(thf)	1.978	1.92	1.935(3)	1.956(7)	1.937(5)	1.927(7)	1.964(6)

The use of a sterically more demanding ligand such as OPh compared to O^{t}Bu changes completely the environment around the metal cation; the coordination geometry vary from square bipyramidal in [IM(O^{t}Bu)$_4${Li(thf)}$_4$(OH)] M = Ca **15**, Eu **16**, Sr [167], Ba [162, 167]) to octahedral in **17**-**21**. One important thing by the use of a very bulky ligand is that the coordinating ligands of the starting materials [MI$_2$(thf)$_n$] have totally been completely exchanged while with the use of the less steric O^{t}Bu anion, all alkaline earth metal ions help one remaining iodide anion.

The M–OPh bond lengths vary as expected when going from the smaller calcium to the larger barium cation. By way of consequence, this influences the geometry of the tetrahedron around the alkaline earth metal cations. From the Table 18, the Li–OPh as well as the Li···Li distances decrease along the series of metal cations reflecting a contraction of the "Li$_3$O$_4$"-core (Figure 93) with the stretching of the morphology of the tetrahedron for the heavier barium cation, reflected with the M–OPh bond lengths, the slight increase of the M–OPh–Li angle and the decrease of the OPh–M–OPh angle on the cubane-units along the series. However, the "structure" of the cubane is not so distorted as the Li–OPh–Li and OPh–Li–OPh angles are more or less identical in both compounds (in **17** 83.31(7) and 95.93(8)°; in **18** 83.21(2) and 96.78(1)°; in **19** 84.02(8) and 97.09(9)°).

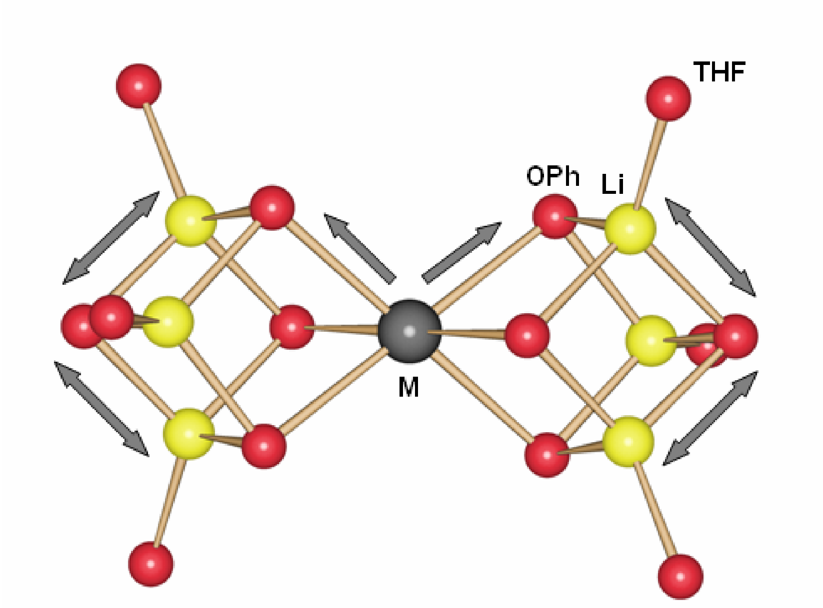


Figure 93. Schematic representation of the stretching in the $[MLi_6(OPh)_8(thf)_6]$ clusters

Rare earth metal cations Eu^{2+} and Sm^{2+} allow the same packing of OPh-ligands in their coordination sphere than the alkaline earth metal cations. Although Eu^{2+} is smaller and Sm^{2+} larger than Sr^{2+}, they possess in **20** and **21** relatively similar Ln^{2+}–OPh bond lengths which are slightly longer in both compounds than the Sr^{2+}–OPh distances in **18**. This notably difference in Ln^{2+}–OPh bond lengths compared to the Sr^{2+}–OPh distances, especially for Eu^{2+} show the difficulty on the determination of ionic radii of elements for a given coordination number.

Usually, metal radii are thought to play a key role in fixing metal-ligand distances resulting in an increase of coordination of ligand for larger metal. This is reflected for instance with the starting materials $[MI_2(thf)_n]$ (n = 4 for Ca [119], n = 5 for Eu [153], Sr [155], Sm [154], Ba [150, 151]) with a difference of radii of 0.35 Å between the smallest Ca^{2+} to the biggest Ba^{2+} for a coordination number six [156]. However, it also appears that the packing of ligands around the metal may be just as critical, and can lead to isostructural compounds even with large changes in radii, as for the $[MLi_6(OPh)_8(thf)_6]$ compounds **17-21** but also with the

[IM(O^{t}Bu)$_4${Li(thf)}$_4$(OH)] clusters described above. This has already been observed in other molecules, for instance [M(BHT)$_2$(thf)$_3$] (M = alkaline earth metals; BHT = OC$_6$H$_2$-^{t}Bu$_2$-2,6-Me-4) [113].

In order to verify if the metal cations, and particularly the heavier barium metal ion, are satisfied with their environment, calculations of the bond valence sum (BVS) for the alkaline earth as well the alkali metal cations in each cluster gives some more insight (Table 19).

Table 19. Bond valence sums (BVS) for M^{2+} and M^+ in **17-21**

	17	**20**	**18**	**21**	**19**
V_M^{2+}	2.05	2.07	2.03	1.96	2.02
V_{Li}^{+}	1.14	1.14	1.14	1.15	1.22

As shows the Table 19, the lithium cations in both complexes are rather more than satisfied, their bond valence sum being greater than their +1 charge. The alkaline earth metal cations, however, are just satisfied with a BVS ~ 2 for each. Phenolate ligands are bulky groups and, in order to minimize the interactions between the phenyl rings and in the same time to compensate the +2 charge of the alkaline earth metal, the M–OPh bond lengths are just limit or critical as mentioned above.

The same observation can be made for the smaller rare earth metal cations Eu^{2+} (BVS = 2.07) while the packing of phenolate-ligands in the coordination sphere of the Sm^{2+} seems a little bit insufficient, this is revealed with its BVS value at 1.96.

B - IV.1.2 - NaOPh as alkali reagent

B - IV.1.2.1 - Introduction

The clusters **17-21** possess all the same general formula and structure. They have been prepared by direct reaction of [LiOPh(thf)]$_4$ and MI$_2$ in THF. The difference in radii do not influence a lot on the structure of the clusters. In order to study if the alkali metal of the MOR compound might have a more important effect on the structure of the alkaline earth metal clusters, some attempts were undertaken with the sodium-analogue NaOPh.

B - IV.1.2.2 - Crystallographic structure of [CaNa$_6$(OPh)$_8$(thf)$_6$] 22

The reaction of CaI_2 with an excess of NaOPh in THF, under dry and inert atmosphere at room temperature, yields crystals of [CaNa$_6$(OPh)$_8$(thf)$_6$] **22** within one week at low temperature (-25°C), after recrystallization in a THF/hexane mixture.

Compound **22** crystallizes in the monoclinic space group $P2_1/n$ (Nr. 14) with two molecules in the unit cell. The structure of **22** is very similar to the one of compound **17** except that the lithium atoms are formally replaced by sodium cations. In **22**, the calcium cation is situated on an inversion centre which lies on the crystallographic position (0, ½, ½ (d)). Thus, the asymmetric unit of **22** is built up with a calcium cation to which are bonded three sodium cations via four μ_3-bridging phenolate-groups in form of a tetrahedron. The structure consists of two $CaNa_3$-tetrahedra linked via the Ca-vertex. Thus, the structure can also alternatively be described as two vertex-sharing $CaNa_3O_4$-hetero-cubanes (Figure 94). All triangular faces of these two tetrahedra are μ_3-bridged by phenolate groups.

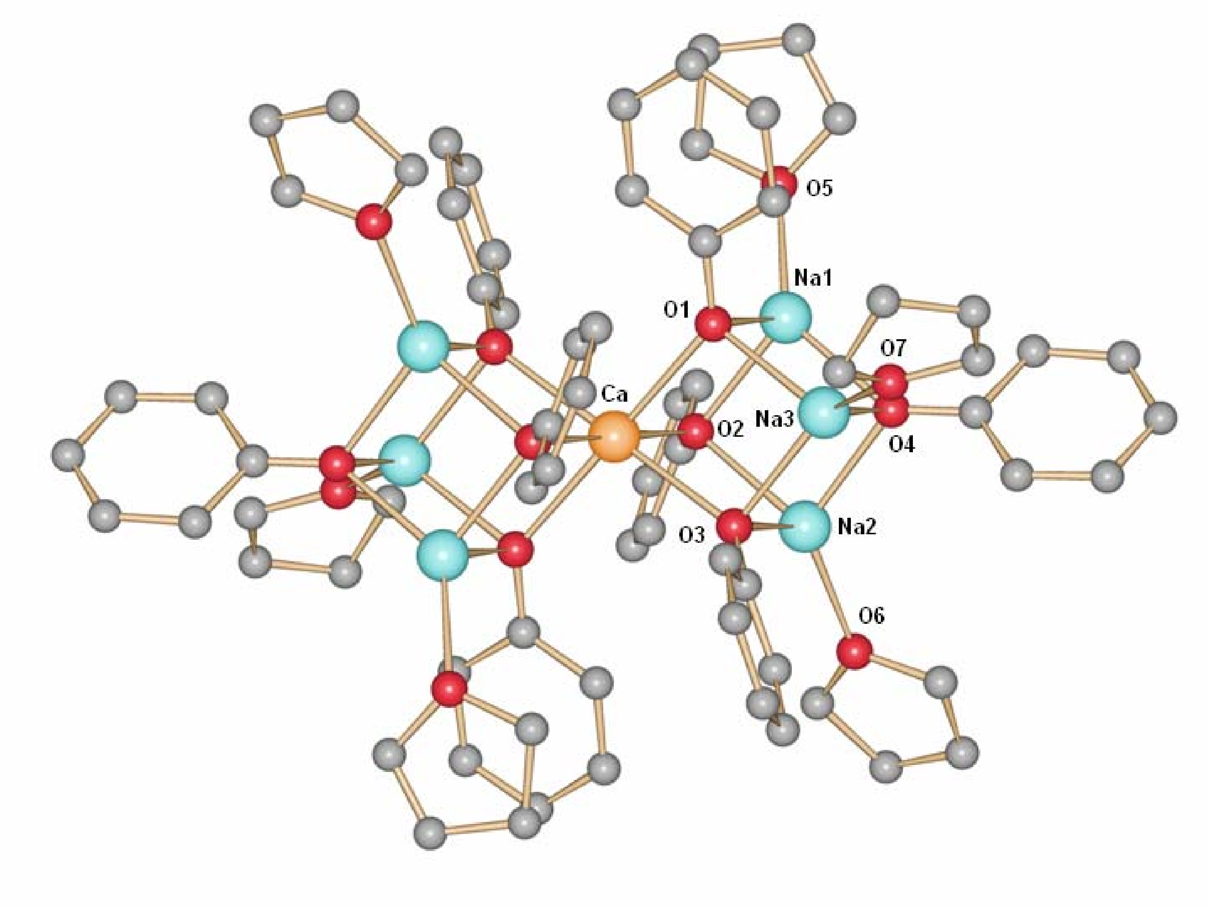


Figure 94. Schakal view of the partially labelled molecular structure of 22, H atoms have been omitted for clarity

The most important bond lengths and angles in **22** are summarized in Table 20.

Table 20. Bond lengths (Å) and angles (°) in **22**

Ca–OPh	2.365(7)	OPh–Ca–OPh (*trans*)	180
Na–OPh	2.295(1)	OPh–Ca–OPh (same cubane)	81.91(7)
Na–O(thf)	2.270(3)	OPh–Ca–OPh (other cubane)	98.08(3)
Na···Na	3.211(5)	Ca–OPh–Na	96.47(4)
Ca···Na	3.477(4)	Na–OPh–Na	88.92(5)

The calcium cation reaches a coordination number of six with an average Ca–μ_3-OPh distance of 2.365(7) Å corresponding well to the Ca–μ_3-OPh bond lengths observed in **17**. The Na–O(OPh) bond lengths (average 2.295(1) Å) are slightly shorter than those observed in the starting material $[Na(OPh)(thf)]_6$ (average 2.327(2) Å) [91] and in **13** (average 2.326(7) Å) but they are relatively shorter than those in other literature described species such as $[(PhO)_8Cr_2\{Na(thf)\}_4]$ [308]. Each sodium cation reaches a low coordination number of four and possesses a tetrahedral coordination sphere completed with a terminally bonded THF ligand. The Na–O(thf) bond lengths of **22** (average Na–O(thf) = 2.270(3) Å) are slightly shorter than those observed in compounds in the literature data [91, 309] but slightly longer than in the compound $[(PhO)_8Cr_2\{Na(thf)\}_4]$ [308].

The so obtained compound possesses a quasi spherical structure with the core of the cluster well protected by hydrophobic groups of phenyl and THF.

In **22**, no π–π as well as no C–H···π interactions between phenyl rings of the phenolate-groups are observed. Moreover, no intermolecular even weak H-bonds are listed since all H···O distances are >3.03 Å. In spite of a low coordination number for sodium cations, no Na···π interactions are noticed as usually observed for the heavier potassium cation. The $[CaNa_6(OPh)_8(thf)_6]$ cluster **22** is therefore molecular in the solid state and present a quasi-spherical structure with phenyl and THF molecules which protect well the core of the cluster **22**.

B - IV.1.2.3 - Crystallographic structure of [SrNa$_6$(OPh)$_8$(thf)$_6$] 23

The reaction under the same conditions of SrI_2 with an excess of NaOPh in THF, under dry and inert atmosphere at room temperature, yields crystals of [SrNa$_6$(OPh)$_8$(thf)$_6$] **23** within one week at low temperature (-25°C), after recrystallization in a THF/hexane mixture.
23 crystallizes in the monoclinic space group $P2_1/n$ (Nr. 14) with two units in the unit cell. The compound **23** is isostructural to the calcium analogue **22** and possesses a very similar structure to the one of compound **18** except that the lithium cations are formally replaced by sodium cations (Figure 95).

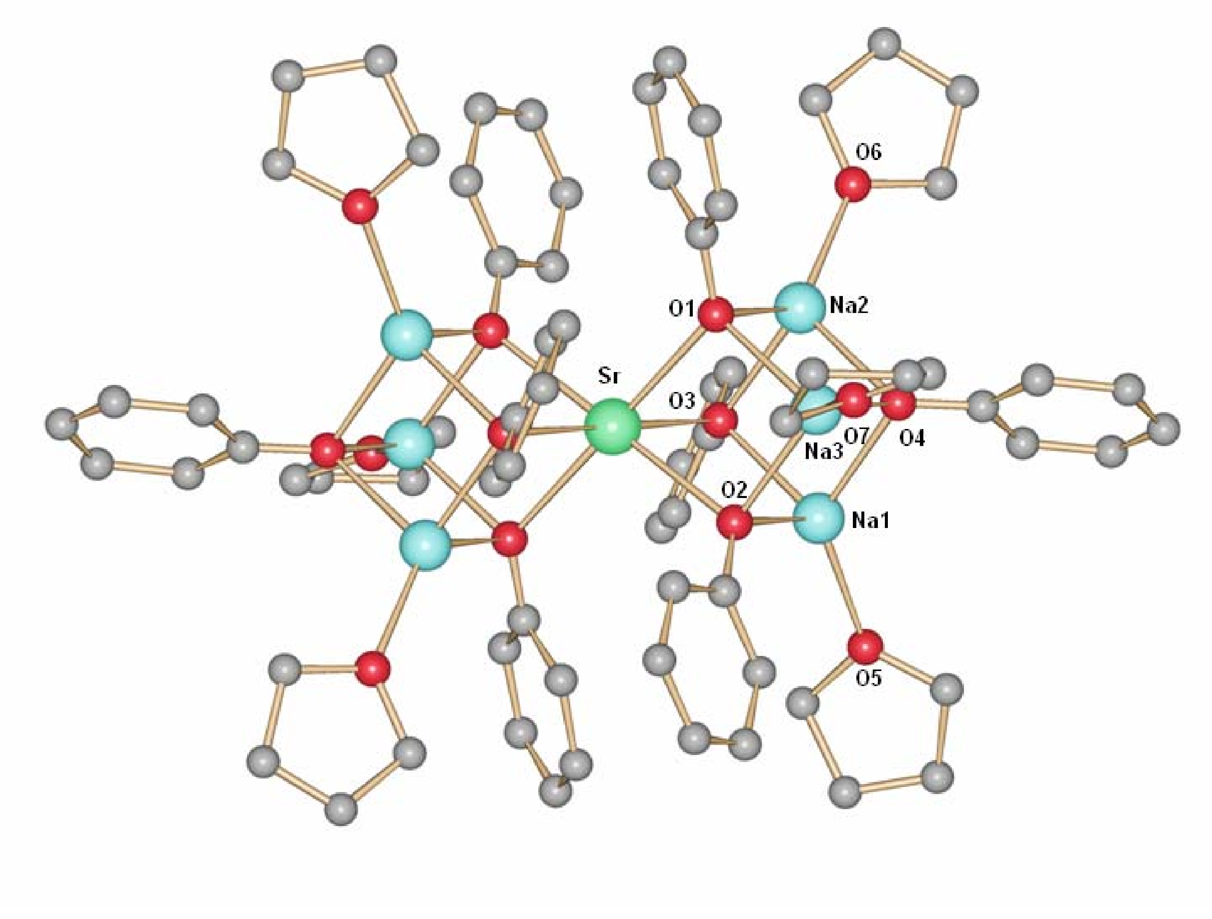


Figure 95. Schakal view of the partially labelled molecular structure of 23, H atoms have been omitted for clarity

The most important bond lengths and angles in **23** are given in Table 21.

Table 21. Bond lengths (Å) and angles (°) in **23**

Sr–OPh	2.525(7)	OPh–Sr–OPh (*trans*)	180
Na–OPh	2.303(2)	OPh–Sr–OPh (same cubane)	79.16(3)
Na–O(thf)	2.281(2)	OPh–Sr–OPh (other cubane)	100.84(4)
Na···Na	3.231(1)	Sr–OPh–Na	96.00(3)
Sr···Na	3.594(3)	Na–OPh–Na	89.17(3)

An inversion centre is situated at the position of the strontium cation which lies on the crystallographic position (0, ½, 0 (c)). In [$SrNa_6(OPh)_8(thf)_6$], the strontium cation is surrounded with six phenolate anions. The average Sr–μ_3-OPh distance of 2.525(7) Å is comparable to **18**. The Na–O(OPh) bond lengths (average Na–O(OPh) = 2.303(2) Å) are slightly shorter than those observed in the starting material [$Na(OPh)(thf)]_6$ (average 2.327(2) Å) [91] and in [$Na(OPh)(dme)]_4$ **13** (average 2.326(7) Å). Each sodium cation reaches a low coordination number four and possesses tetrahedral coordination sphere completed with a terminally bonded THF ligand. The Na–O(thf) bond lengths of **23** (average Na–O(thf) = 2.2810(2) Å) are slightly shorter than those observed in compounds in the literature data [91, 309] but slightly longer than in the compound [$(PhO)_8Cr_2\{Na(thf)\}_4$] [308].

As for the cluster **22**, the compound **23** present no π–π as well as no C–H···π interactions between phenyl rings of the phenolate-groups. More, no intermolecular even weak H-bonds are listed since all H···O distances are >3.02 Å. As for **23**, even a low coordination number for sodium cations, no Na···π interactions are noticed to saturate the alkali metal sodium. The [$SrNa_6(OPh)_8(thf)_6$] cluster **23** is therefore molecular in the solid state. The so obtained compound possesses a quasi-spherical structure with the core of the cluster well protected by hydrophobic groups of phenyl and THF.

B - IV.1.2.4 - Crystallographic structure of [$BaNa_6(OPh)_8(thf)_6$] 24

The reaction of the heaviest alkaline earth metal iodide BaI_2 with an excess of NaOPh in THF, under dry and inert atmosphere at room temperature, yields crystals of [$BaNa_6(OPh)_8(thf)_6$] **24** within one week at low temperature (-25°C), after recrystallization in a THF/hexane mixture . Compound **24** crystallizes in the monoclinic space group *P*2$_1$/*n* (Nr. 14) with two molecules in the unit cell. The structure of **24** is very similar to the one of compound **19** except that the lithium atoms are formally replaced by sodium cation. The structure of **24** is also isostructural with the one of the lighter alkaline earth metal Ca and Sr-analogues, respectively compounds **22** and **23**.

The structure consists of two $BaNa_3$-tetrahedra linked via the Ba-vertex, all triangular faces of these two tetrahedra being μ_3-bridged by phenolate groups (Figure 96).

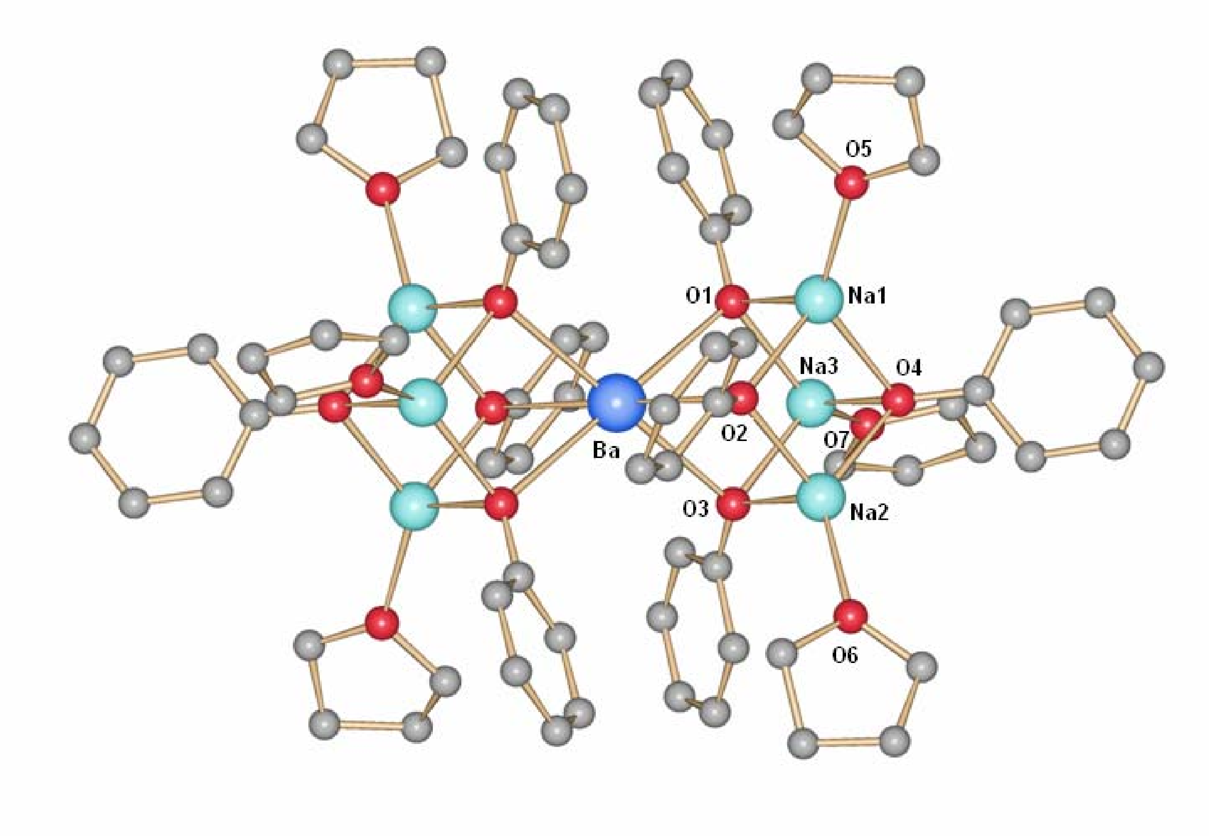


Figure 96. Schakal view of the partially labelled molecular structure of 24, H atoms have been omitted for clarity

The most important bond lengths and angles in **24** are summarized in Table 22.

Table 22. Bond lengths (Å) and angles (°) in **24**

Ba–OPh	2.698(7)	OPh–Ba–OPh (*trans*)	180
Na–OPh	2.284(7)	OPh–Ba–OPh (same cubane)	74.40(8)
Na–O(thf)	2.279(8)	OPh–Ba–OPh (other cubane)	105.59(2)
Na···Na	3.205(1)	Ba–OPh–Na	97.92(7)
Ba···Na	3.742(1)	Na–OPh–Na	89.09(7)

An inversion centre is situated at the position of the barium cation which lies on the crystallographic position (½, ½, ½ (a)). In **24**, the barium cation reaches as the calcium cation in **22** and the strontium cation in **23** a coordination number of six with six phenolate anion. The average Ba–μ_3-OPh distance of 2.698(7) Å compares well with the one in [$BaLi_6(OPh)_8(thf)_6$] 18 (average 2.718(9) Å). The Na–O(OPh) bond lengths (average Na–O(OPh) = 2.284(7) Å) are slightly shorter than those observed in the starting material [$Na(OPh)(thf)]_6$ (average 2.327(2) Å) [91] and in **13** (average 2.326(7) Å). As for **22** and **23**, each sodium cation reaches a low coordination number four and possess tetrahedral coordination sphere completed with a terminally bonded THF ligand with a mean value Na–O(thf) of 2.279(8) Å)

As for the clusters **22** and **23**, the compound **24** present neither π–π nor C–H···π interactions between phenyl rings of the phenolate-groups. No intermolecular even weak H-bonds are listed since all H···O distances are >3.04 Å. No Na···π interactions are noticed in **24**. The [$BaNa_6(OPh)_8(thf)_6$] cluster **24** is therefore molecular in the solid state and possesses a quasi-spherical structure with the core of the cluster well protected by hydrophobic groups of phenyl and THF.

B - IV.1.2.4 - General comparison of [$MNa_6(OPh)_8(thf)_6$] clusters

All the compounds **22**-**24** have been prepared using the same reaction pathway and present the same general formula as well as structural features. Surprisingly, the three [$MNa_6(OPh)_8(thf)_6$] clusters M = Ca, Sr, Ba adopt the same motif as already observed with the lithium analogues **17**-**21**. The use of a larger alkali metal do not influence at all the general geometry of the clusters and the conformation of the anions in the coordination sphere of the alkaline earth metal ions. Moreover, the sodium cations are satisfied with a distorted tetrahedral coordination sphere while they prefer usually the higher coordination number five. From the solid state structure of the sodium reagent [$Na(OPh)(thf)]_6$ [91], although some cations possess a coordination number four, the formation of this motif can not be easily interpreted. However, in solution no data are available concerning the structure or at least the degree of aggregation of the “Na(OPh)” reagent.

A comparison of the most important structural parameters of the isomorphic clusters [$MNa_6(OPh)_8(thf)_6$] M = Ca **22**, Sr **23**, Ba **24** clusters is given in Table 23.

Table 23. Comparison of the principal parameters (bond lengths (Å)and angles (°)) in **22**, **23** and **24**

	$[Na(OPh)(thf)]_6$ [91]	**22**	**23**	**24**
M–OPh	/	2.365(7)	2.525(7)	2.698(7)
Na–OPh	2.312(2)	2.295(1)	2.303(2)	2.284(7)
Na···Na	3.275(4)	3.211(5)	3.231(1)	3.205(1)
Na–O(thf)	2.293(1)	2.270(3)	2.281(2)	2.279(8)

The M–OPh bond lengths vary as expected when going from the smaller calcium to the larger barium cation. All the distances (Na–OPh, Na···Na and Na–O(thf)) in both cubane-units of the heterometallic compounds **22-24** are slightly smaller than those observed in the $[Na(OPh)(thf)]_6$ reagent. This is probably due to the introduction of a larger cation in the core of the compound $[Na(OPh)(thf)]_6$, the loss of the electron density available for sodium cations involves a slight distortion of the cubane sub-units. This is also observed with clusters **17**, **18** and **19** involving LiOPh. Indeed, due to the increase of the M–OPh bond lengths, the OPh–M–OPh angles decrease (81.91(7)° in **22**, 79.16(3)° in **23** and 74.40(8)° in **24**) and the M–OPh–Na angles increase (94.47(4)° in **22**, 96.00(3)° in **23** and 97.92(7)° in **24**) along the series of clusters **22-24**.

Nevertheless from the Table 23, the distances Na–OPh, Na···Na and Na–O(thf) in the strontium complex **23** are slightly longer than in the other two, calcium **22** and barium **24**, analogues which is difficult to understand.

In order to verify if alkali and alkaline earth metal cations and particularly the heavier strontium and barium metal cations are satisfied with their coordination sphere, their bond valence sums (BVS) were calculated (Table 24).

Table 24. Bond valence sums (BVS) for M^{2+} and M^+ in **22-24**

	22	**23**	**24**
$V_{Na}{}^{+}$	1.19	1.16	1.20
$V_M{}^{2+}$	2.10	1.98	2.14

As shows the Table 24, sodium cations in each heterometallic clusters $[MNa_6(OPh)_8(thf)_6]$ M = Ca **22**, Sr **23**, Ba **24** are more than satisfied, their bond valence sums being greater than their +1 charge. However, although the BVS for Na^+ is greater than +1 in **23**, it is smaller than the

BVS of Na^+ in the other metal clusters. This could be explained with longer bond lengths observed in the core of the cubane-subunits in **23**. The alkaline earth metal cations, calcium in **22** and barium in **24** are also satisfied with a BVS value superior to their +2 charge. However, the strontium cation in **23** possesses a BVS value slightly smaller than 2.

B - IV.2 - Influence of the solvent

B - IV.2.1 - Introduction

As discussed before, the structural motif of the alkoxide or aryloxide MOR reagents is influenced by three factors: the nature of the alkali metal M, the bulk of the R-group and also the nature of the Lewis-base used for the crystallization. But it might be also the case for metal-organic compounds, namely alkaline earth metal clusters. The two first parts of this thesis dealing with alkaline earth metal clusters and the nature of the alkali metal as well the "size" of the R-group have shown some important results. First, by introducing a larger R-group in the coordination sphere of the alkaline earth metal cation, the coordination sphere of the latter is totally rearranged, no remaining ligands, iodide or THF molecules are present. Secondly, the packing of these OR-groups on the coordination sphere of the metal cation is more important than the nature of the alkali metal. Indeed, with either the smaller lithium or the larger sodium cation, the packing of the ligands around the alkaline earth metal is still the same. Each alkali metal cation completes its coordination sphere with only one coordinating THF-molecule.

In order to consider if the use of different Lewis-coordinating solvents can have an important impact on the structure or even lead to a total rearrangement of the structure, some attempts of recrystallization with DME, a polydentate ligand, were undertaken.

B - IV.2.2 - Crystallographic structure of $[\{Ca(dme)\}_2(OPh)_6\{Li(dme)\}_2]$ 25

The reaction of an excess of LiOPh in THF with CaI_2 forms a deep brown solution which was evaporated to dryness. At room temperature, the solid residue was recrystallized in DME and affords single-crystals of $[\{Ca(dme)\}_2(OPh)_6\{Li(dme)\}_2]$ **25** within one night (Figure 97). Compound **25** crystallizes in the triclinic space group *P*-1 (Nr. 2) with one molecule per unit cell.

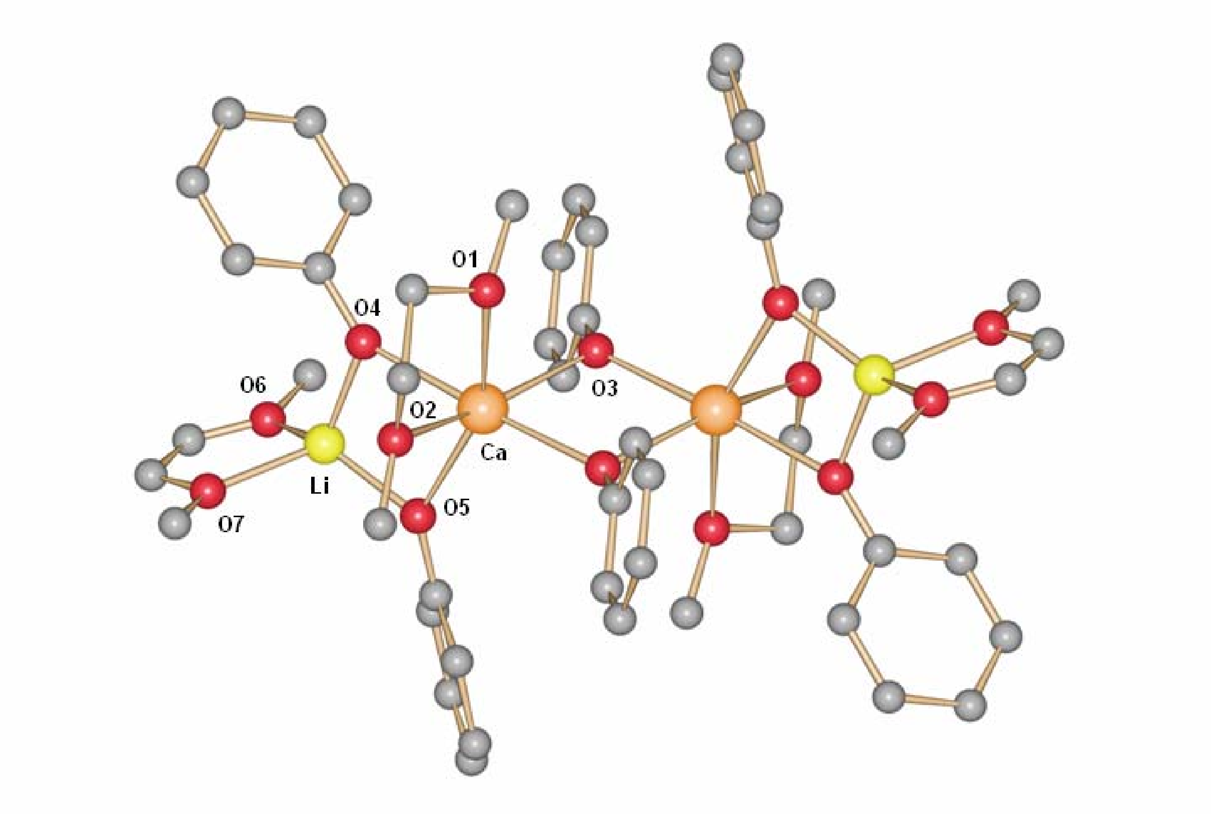


Figure 97. Schakal view of the partially labelled molecular structure of 25, H atoms have been omitted for clarity

This molecule consists of a bent chain arrangement of Li–Ca–Ca–Li in which the metal ions are pair-wise bridged by two phenolate groups each and symmetric Li–Ca–Ca angles of 141.83(6)°.

The structure of **25** can therefore also be described as a chain of two $LiCaO_2$-rhombi, linked to a Ca_2O_2-rhombus via a calcium cation. The aforementioned rhombi are all quasi planar, and the mean $LiCaO_2$ plane forms an angle of 72.88(2)° to the Ca_2O_2 rhombus. The latter is planar due to an inversion center found in the geometrical middle of this part of the structure. Each cation is furthermore coordinated by a terminal DME ligand, so that the calcium cation reaches a distorted octahedral coordination sphere whereas lithium is surrounded by four oxygen atoms in form of a distorted tetrahedron.

This linear motif has already been observed in different compounds with lithium [126, 220, 260, 310], sodium [308] and even potassium [311] as external metals, and alkaline earth or transition metal ions as central cations. The most unexpectedly is that, in all these compounds, the metal ions are pair-wise bridged by μ-bridging aryloxo-groups.

The most important bond lengths and angles in **25** are summarized in Table 25.

Table 25. Bond lengths (Å) and angles (°) in **25**

Ca–OPh	2.281(1)	Ca–OPh–Ca	102.96(4)
Li–OPh	1.864(3)	OPh–Ca–OPh (Ca_2O_2)	77.04(4)
Ca–O(dme)	2.440(2)	OPh–Ca–OPh ($LiCaO_2$)	76.81(4)
Li–O(dme)	1.986(3)	Li–O(OPh)–Ca	92.35(5)
Ca···Ca	3.588(3)	(dme)O–Ca–O(dme)	67.85(7)
Ca···Li	2.993(9)	(dme)O–Li–O(dme)	82.74(1)

The values of the Ca–O distances formed by the four bridging aryloxide groups (average Ca–O(OPh) = 2.281(1) Å) compare well with the ones observed in the literature, and the Li-O bond lengths (average Li–O(OPh) = 1.864(3) Å) are slightly shorter than literature data [77, 82, 83, 110, 220, 258, 301, 302]. The Ca–O distances to the DME ligands (average Ca–O(dme) = 2.440(2) Å) are slightly longer than those observed in [CaI(dme)$_3$]I **1** and **1a** (average Ca–O(dme) = 2.423 Å in **1** [168]) but correspond well with those observed in the literature [109, 312-314] and **1a** (average Ca-O(dme) = 2.443(7) Å). The Li–O bond lengths to the DME groups (average Li–O(dme) = 1.986(3) Å) compare well with those observed in the literature [258, 263]. The bite angle of the DME ligands at the lithium cations is with 82.76(1)° by ca. 15° larger than the one at the calcium cations (67.86(3)°), this difference revealing the flexibility of coordination of this DME ligand. Such angles are also observed in the literature [219, 258, 312-316]. Whereas the phenyl rings of the OPh-groups bridging the two calcium cations are parallel due to symmetry, the ones bridging calcium and lithium form an angle of 65.16(4)° to each other. The Ca–O(OPh)–Ca angle (102.96(4)°) is by ca. 10° wider than the Li–O(OPh)–Ca angle (92.47(1)°, and 92.24(1)°), but are among possible angles at which the OPh-groups may act as μ_2-bridging ligands [114, 309, 317-323]. However, the O(OPh)–Ca–O(OPh) angles within the two different rhombi are almost identical with 77.04(4)° for the Ca_2O_2 rhombus and 76.81(4)° for the $LiCaO_2$ rhombus. The angle sum inside the latter rhombus adds to 359.75(10)°, and shows the planarity of the system.

The compound **25** presents neither π–π nor C–H···π interactions between phenyl rings of the phenolate groups. No intermolecular even weak H-bonds are listed since all H···O distances are >3.46 Å. The [{Ca(dme)}$_2$(OPh)$_6${Li(dme)}$_2$] cluster **25** is therefore molecular in the solid state and possesses a quasi-spherical structure with the core of the cluster well protected by hydrophobic groups of phenyl and DME.

Even though the two compounds **17** and **25** are very different in stoichiometry and structure, the only difference in the synthesis is the use of another solvent. We were thus interested in studying a possible transformation of **17** into **25** and vice versa in solution (Figure 98).

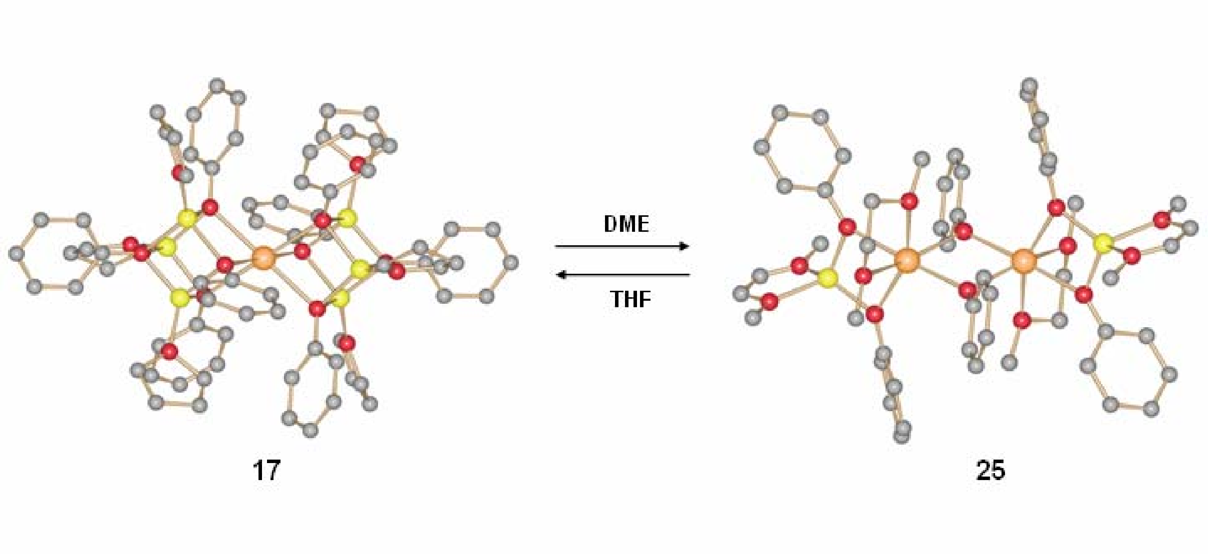


Figure 98. Representation of the possible transformation of 17 in 25 and vice-versa via exchange of solvents

To do so, a series of ^{7}Li-NMR spectra were taken in d^8-THF and d^{10}-DME as well as in varying proportions of the two solvents. Pure LiOPh which we used for the above reaction gives a sharp signal at 0.82 ppm in d^8-THF, and a signal at 0.98 ppm in d^{10}-DME.

The ^{7}Li-NMR for crystals of **17** dissolved in d^8-THF gives two signals, a major broad peak at 0.79 ppm very close to the one obtained for LiOPh, and a smaller peak at 1.07 ppm representing ca. 10% of the large one whereas crystals of **25** dissolved in d^{10}-DME give only one relatively sharp peak at 1.01 ppm (Figure 99).

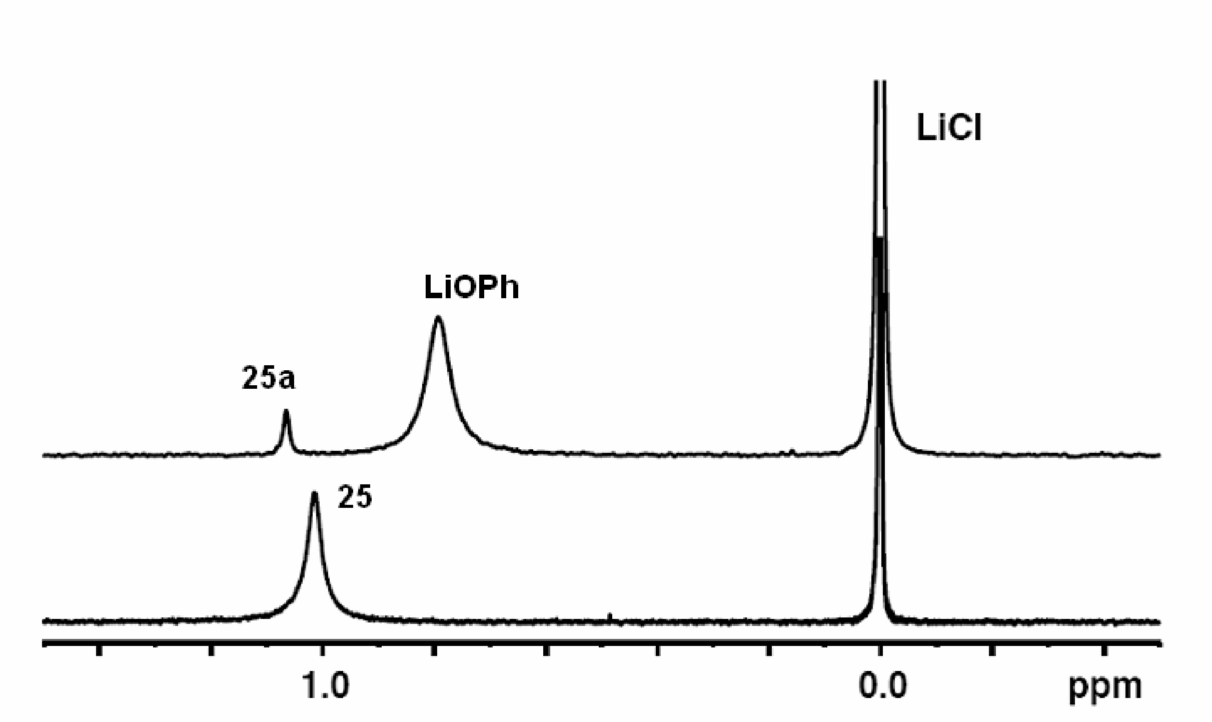


Figure 99. ^{7}Li NMR spectra of 17 (top) and 25 (bottom), reference: capillar with 1M LiCl in D_2O

The spectrum of **17** can thus be interpreted as spontaneous decomposition of **17** in solution, following the proposed reaction:

$$2\ [CaLi_6(OPh)_8(thf)_6]\ (\mathbf{17}) \longrightarrow [Ca_2Li_2(OPh)_6(thf)_n]\ (\mathbf{25a})\ +\ 10\ LiOPh$$

This would approve the ca. 1:10 relation in size for the two species. Crystals of **25** dissolved in d^{10}-DME give only one relatively sharp peak at 1.01 ppm, which is close in aspect and shift to the small peak obtained in the spectrum of **17** (Figure 99). Addition of DME to the solution of **17** leads to a broadening of the peaks.

Supposing that the THF-analogue of **25**, namely **25a**, exists in solution, the equation of the reaction should be written (Equation 4):

$$2\ CaI_2 + 6\ LiOPh \longrightarrow [Ca_2(thf)_n(OPh)_6\{Li(thf)_n\}_2]\ (\mathbf{25a})$$

Equation 4. Proposed reaction pathway for the synthesis of the THF-analogue 25a

However, while **17** have always been prepared with a large excess of the reagent LiOPh, attempts following the right ratio of the reagents CaI_2/LiOPh = $^{1}/_{3}$ leads also to the crystallization of **17**. Even with larger ratio such as ½, we always observed the formation of the compounds $[CaLi_6(OPh)_8(thf)_6]$ **17**. It was impossible to generate or more exactly to crystallize the THF-analogue of **25**.

Compound **17** resembles in its geometry very much the monomeric Ca_7-moiety of $[Li(thf)_4][Ca_7I_6(OH)_8(thf)_{12}]_2(\mu\text{-}I)$ in which two Ca_4O_4-heterocubanes are also fused via a calcium cation [158, 167]. Indeed, it seems that by formally replacing the structural $[CaI(thf)_2]^+$-fragments and the ^-OH-groups of this literature compound by $[Li(thf)]^+$- and ^-OPh-groups, compound **17** is obtained. Obviously, iso-electronic substitution can here be observed between the two compounds. Also, the compound can be interpreted as derived from the predominant tetrameric structure of LiOPh in solution [63], so that two such tetrameric moieties have been fused via one calcium cation, replacing two [Li(thf)]-fragments. **17** can also be compared to the Cr^{2+} compound $[\{Li(thf)\}_3(\mu_3\text{-}OPh)_4Cr(\mu_2\text{-}OPh)]_2$ [220]. The latter consists also of $[Li_3(M^{2+})]$-tetrahedra (or $[Li_3(M^{2+})O_4]$-hetero-cubanes), but they are not fused at the M^{2+} cation, but bridged by two ^-OPh-groups, which is a structural element in **25**. An analogue compound with Ca^{2+} was not observed so far in our system, but could be a possible intermediate during the transformation of **17** into **25** and vice versa. However, ^1H- and ^{13}C-NMR showed no indication of two different OPh-ligands in solution. Also with Cr^{2+}, a similar structure to **25** can only be obtained with a sterically more important aryloxide, $2,6\text{-}Me_2\text{-}C_6H_3O^-$, which is stabilized by THF-ligands, but has chromium in a tetra-coordination. Indeed, the small ^7Li-NMR signal in the spectrum of **17** could be the THF-substituted analogue to **25**. The use of a bidentate ligand, TMEDA, leads to breakdown of larger cluster and a smaller entity than **25**, $[\{(TMEDA)Li\}(\mu\text{-}OR)_2Cr]$, is observed [220].

B - IV.2.2 - Crystallographic structure of $[\{Ca(dme)\}_2(OPh)_6\{Na(dme)\}_2]$ 26

The reaction of an excess of NaOPh in THF with CaI_2 forms a light brown solution which was evaporated to dryness. At room temperature, the solid residue was recrystallized in DME and affords single-crystals of $[\{Ca(dme)\}_2(OPh)_6\{Na(dme)\}_2]$ **26** within one week at low temperature (-25°C). Compound **26** crystallizes in the monoclinic space group $P2_1/n$ (Nr. 14) with two molecules per unit cell.

The structure which **26** adopts (Figure 100) is common for 1:1 M:M’ stoichiometry in heterometallic alkoxides [324-329], aryloxides [64, 90, 115, 120, 304, 309, 318, 330, 331] and other [332-338] compounds (this is also true for M’ = M). For metals with a higher oxidation state, usually with transition metals, the Lewis-coordinating molecules are formally replaced by other anionic ligands in order to neutralize the clusters. This motif can formally be described as two connected face-sharing cubes, each with one vertex missing.

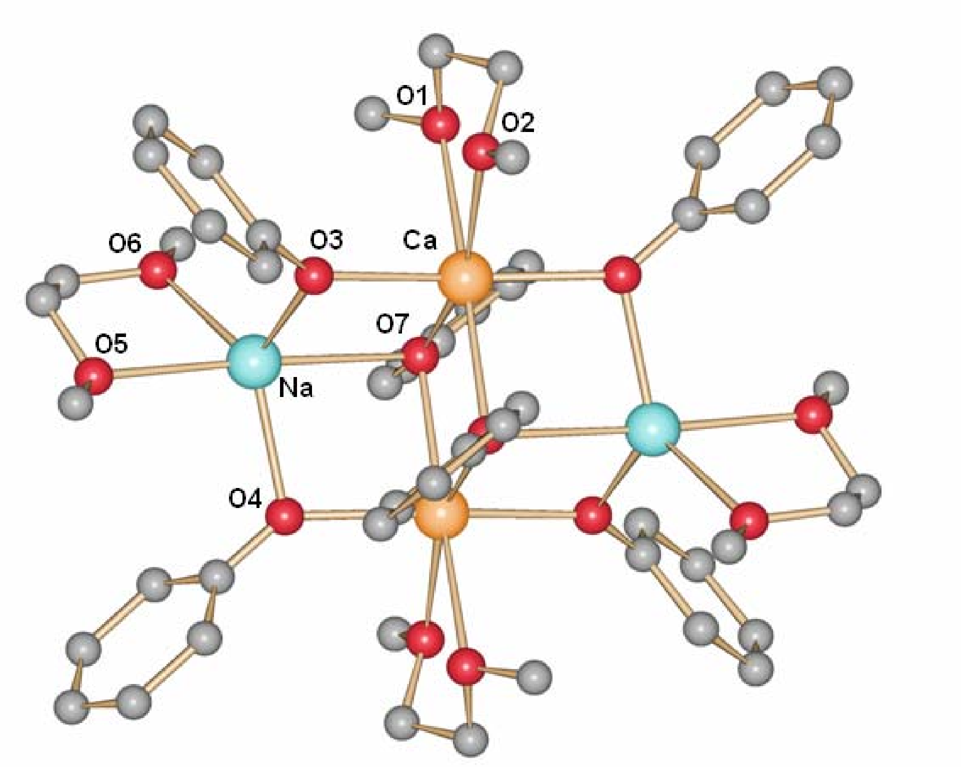


Figure 100. Schakal view of the partially labelled molecular structure of 26, H atoms have been omitted for clarity

This structure of the molecule **26** consists of a distorted square of metal cations with calcium respectively sodium metals on opposite vertices. The metal ions of the rectangle, calcium and sodium, are pair-wise linked by one μ-phenolate group over each edge, and both calcium cations are linked to each sodium cation with one μ_3-phenolate group. Metal cations are coplanar due to an inversion center found in the geometrical middle of the rhombus $Ca_2(O7)_2$. Each cation is furthermore coordinated by a terminal DME ligand, so calcium cations reach a coordination number of six with a distorted octahedral geometry whereas sodium cations have distorted trigonal bipyramidal geometry with a common coordination number five.

The most important bond lengths and angles in **26** are summarized in Table 26.

Table 26. Bond lengths (Å) and angles (°) in **26**

Ca–OPh	2.299(1)	Ca–OPh–Ca	102.97(4)
Na–OPh	2.356(4)	OPh–Ca–OPh	77.02(6)
Ca–O(dme)	2.481(4)	OPh–Na–OPh	119.22(1)
Na–O(dme)	2.408(4)	Na–O(OPh)–Ca	97.50(1)
Ca···Ca	3.681(6)	(dme)O–Ca–O(dme)	68.05(9)
Ca···Na	3.477(2)	(dme)O–Na–O(dme)	69.48(8)

In **26**, the Ca–μ-OPh distances are shorter than those found in the literature data [108, 110] and the Ca–μ_3-OPh bonds lengths are slightly shorter than those in **17** and **21**. The Na–μ-OPh bond lengths (average 2.281(7) Å) are shorter those found in $[(THF)_2Na\{B(OPh)(OH)_2H\}]_2$ [309], $[(RO)_4Cr][Na(TMEDA)]_2$ (R = 2,6-Me_2-C_6H_4) and $[(RO)_8Cr_2][NaL]_4$ (R = Ph; L = THF, Pyridine) [254]. They are also as expected shorter than the Na–μ_3-OPh distances observed for instance in the starting material $[Na(OPh)(thf)]_6$ [91], the compound $[Na(OPh)(dme)]_4$ 13 and $[(PhO)_8Cr_2\{Na(thf)\}_4]$ [308]. However, the Na–μ_3-OPh distances in **26** (average 2.506(1) Å) are relatively longer than the distances found in the compounds cited above and compounds **22**, **23** and **24** probably due to different binding partners and also change in coordination numbers.

Each metal cation completes its coordination sphere with one DME molecule. The Ca–O distances to the DME ligands (average Ca–O(dme) = 2.481(3) Å) are slightly longer than those observed in $[CaI(dme)_3]I$ **1** and **1a** (average Ca-O(dme) = 2.423 Å in **1** [168] and 2.443(7) Å in **1a**) but correspond well with those observed in the literature [109, 312-314]. The Na–O bond lengths to the DME groups (average Na–O(dme) = 2.408(4) Å) compare well with those observed in the literature [90, 92, 255, 256].

The bite angle of the DME ligands at the sodium and calcium cations are comparable with (dme)O–Ca–O(dme) = 68.05(9)° and (dme)O–Na–O(dme) = 69.48(8)° due similar ionic radii ($r_{Ca^{2+},Na^{+}}$ = 1 Å for coordination number six respectively five) and close coordination number. Such angles are also observed in the compounds **1**, **1a** and **9** but also in literature compounds [160, 314] for the calcium cation, respectively in **13** and the literature compound [92] for the sodium cation.

Due to symmetry, the phenyl rings of the OPh-groups bridging the two calcium and sodium cations are parallel as well as phenyl rings of the OPh-groups of opposite vertices.

Two intramolecular π–π interactions due to the symmetry can be noticed between phenyl rings of μ-OPh and μ_3-OPh phenolate-groups in a T-shape conformation (Figure 101), these are more precisely C–H···π interactions. Moreover, one very weak intermolecular H-bond can be found between molecules via one phenyl ring and one DME molecule with a H3···O1 distance at 3.011(1) Å leading to the formation of sheet (Figure 102) (each molecule is linked to four neighbouring molecules in a plane).

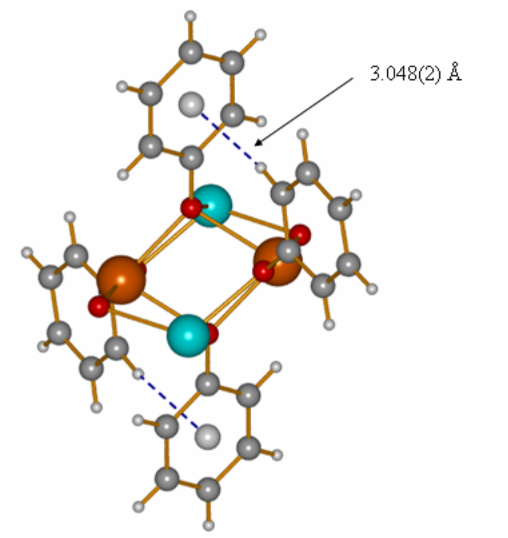


Figure 101. Intramolecular C–H···π interactions observed in 26

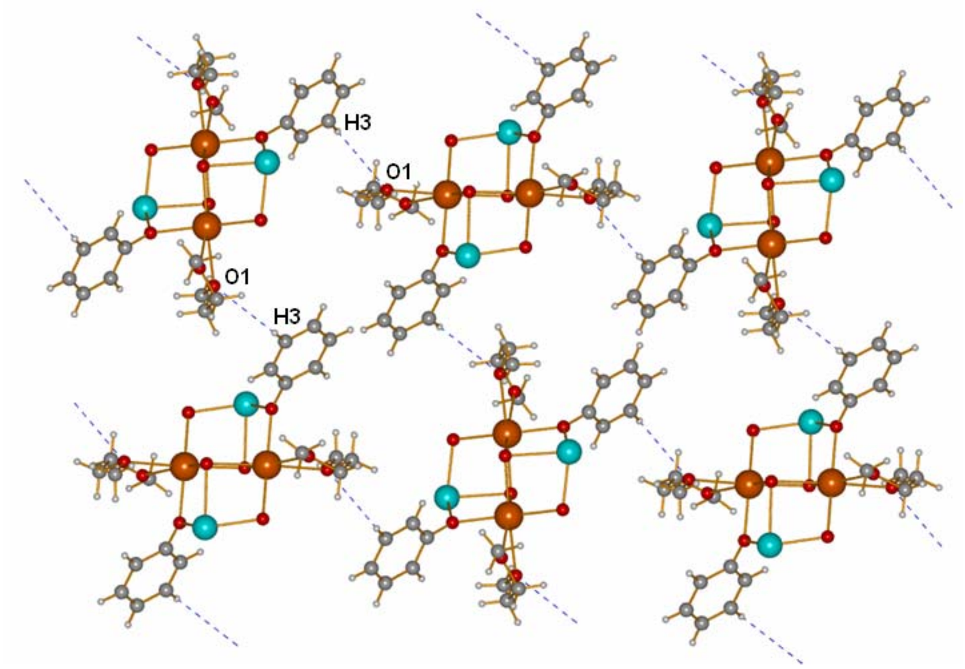


Figure 102. Intermolecular H-bonds (H3···O1) observed in 26

As for compounds **17** and **25**, the use of a different solvent in the synthesis leads to the formation of compounds with very different stoichiometry and structure, **22** and **26**. We were also here interested in studying a possible transformation of **22** into **26** and vice versa in solution. Unfortunately, ^{23}Na-NMR measurements were difficult to perform and each species, **22** and **26**, gives in d^{8}-THF respectively in d^{10}-DME a very broad signal. Further studies should be carried out.

Although compounds **25** and **26** are structurally very different, they possess the same general formula $[\{Ca(dme)\}_2(OPh)_6\{M'(dme)\}_2]$ M' = Li **25**, Na **26**. The cluster compounds $[CaM'_6(OPh)_8(thf)_6]$ M' = Li **17**, Na **22** obtained in THF possess the same general formula but also the same general structure. The only difference between **17**, **25** and **22**, **26** is the nature of the alkali metal. Thus, we can expect than the packing of the phenyl rings of the phenolate anions in the compounds **17** and **22** forces the sodium cations in compound **22** to only allow a low coordination number four, with one terminal THF molecule whereas smaller lithium cations in compound **17** adopt their usual coordination number. The bond valence sum for the sodium cation in **22** is nevertheless greater than its +1 charge, the alkali metal cation is satisfied. However, in presence of DME, the structure of **25** and **26** are presumably less compact than their “THF-analogues” **17** respectively **22**, meaning a less strong packing of phenolate ligands around the metal cations. This can be reflected by the coordination of one DME molecule to each metal cation in **25** and **26** whereas in **17** and **22**, alkali cations accept one THF molecule to complete its coordination sphere. In **25** and **26**, both alkali cations adopt their usual coordination geometry, a distorted tetrahedral for lithium atoms in **25** and respectively a trigonal bipyramidal arrangement for sodium cations in **26**. Thus, these four compounds **17**, **22**, **25** and **26** show how the bulk of the R-group, the nature of the alkali metal and the solvent are important factors influencing the structure of these heterometallic compounds.

From Table 27, it is clear that both cations, calcium and lithium in **25**, respectively calcium and sodium in **26**, are satisfied with their coordination sphere with a bond valence sum rather larger than their respective charge, +2 for the alkaline earth metal cation calcium and +1 for the alkali metal cations lithium or sodium.

Table 27. Bond Valence Sums (BVS) of the metal cations in **25** and **26**		
	25 (Li, Ca)	**26** (Na, Ca)
M^+	1.28	1.20
Ca^{2+}	2.34	2.21

B - IV.2.3 - Crystallographic structure of (μ-dme)[SrLi$_6$(OPh)$_8$(thf)$_4$] 27 and (μ-dme)[SrLi$_6$(OPh)$_8$(thf)$_2$(dme)$_2$] 28

After results obtained with these calcium clusters, we were interested to study the influence of the Lewis-coordinating DME solvent on clusters [MLi$_6$(OPh)$_8$(thf)$_6$] M = Sr **18**, Ba **19**. Indeed, does the size of the alkaline earth metal also have an influence on the structure after addition of DME? Previous results described here show that strontium and barium are similar toward LiOPh/THF with the formation of clusters of the same composition [MLi$_6$(OPh)$_8$(thf)$_6$] M = Sr **18**, Ba **19** but also toward DME with the characterization of [MI$_2$(dme)$_3$] M = Sr **2**, Ba **3**. However, the alkaline earth metal Sr^{2+} and Ba^{2+} are different from calcium toward DME due to their larger size.

Whereas it was impossible to recrystallize the cluster [BaLi$_6$(OPh)$_8$(thf)$_6$] **19** in DME, the same procedure for the [SrLi$_6$(OPh)$_8$(thf)$_6$] cluster **18** lead to the crystallization of two new metal clusters.

Working under inert conditions, the reaction of SrI_2 with an excess of LiOPh in THF forms a deep brown solution which was evaporate to dryness. At room temperature, the solid residue was recrystallized in DME and affords single-crystals of (μ-dme)[SrLi$_6$(OPh)$_8$(thf)$_4$] **27** within two weeks at low temperature (-25°C) (Figure 103).

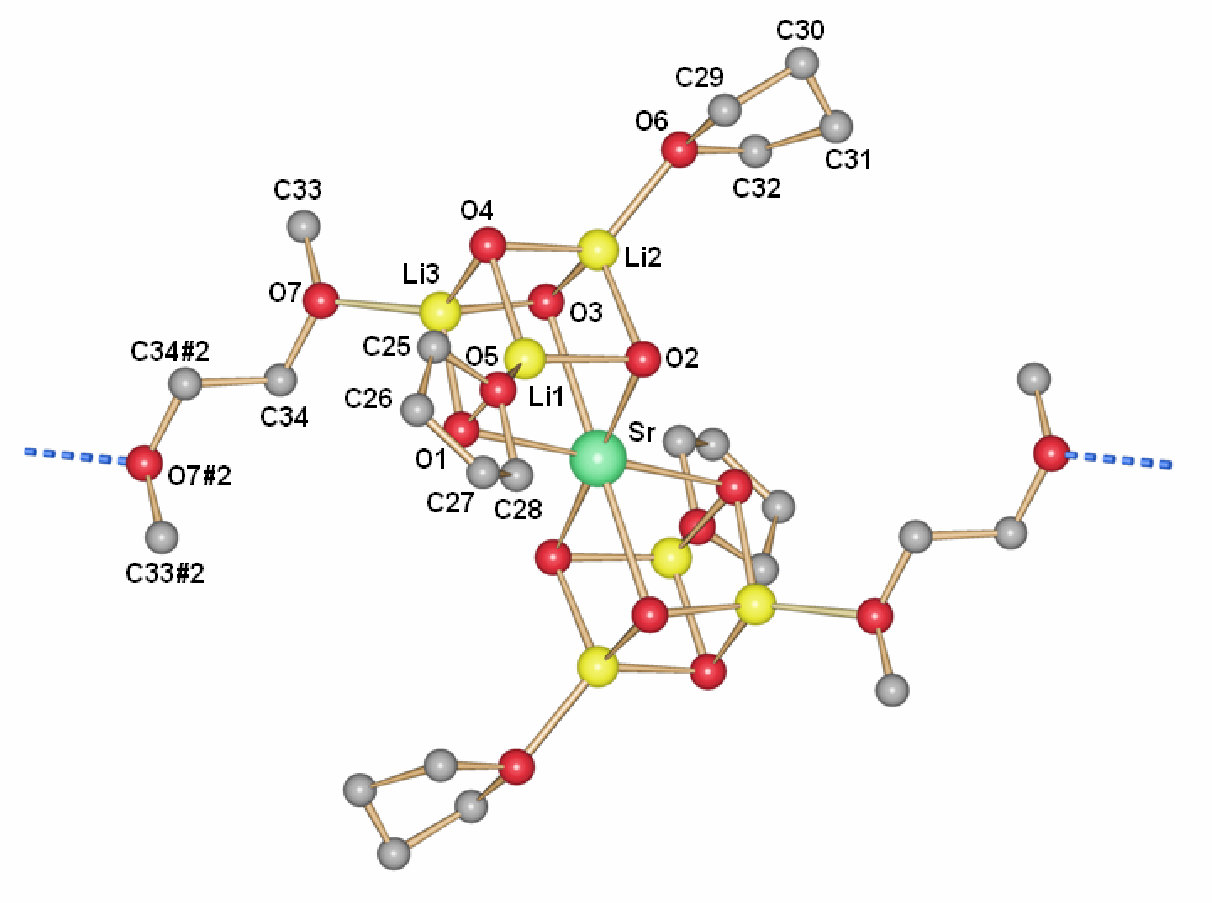


Figure 103. Schakal view of the partially labelled molecular structure of 27, phenyl rings and H atoms have been omitted for clarity

Compound **27** crystallizes in the monoclinic space group *P*2$_1$/*n* (Nr. 14) with two molecules per unit cell.

In order to obtain a better resolution factor R1 due to high disorder in one terminal coordinating THF molecule, another single-crystal was measured three months later and surprisingly, a new crystal structure was obtained with formula (μ-dme)[$SrLi_6(OPh)_8(thf)_2(dme)_2$] **28** (Figure 104).

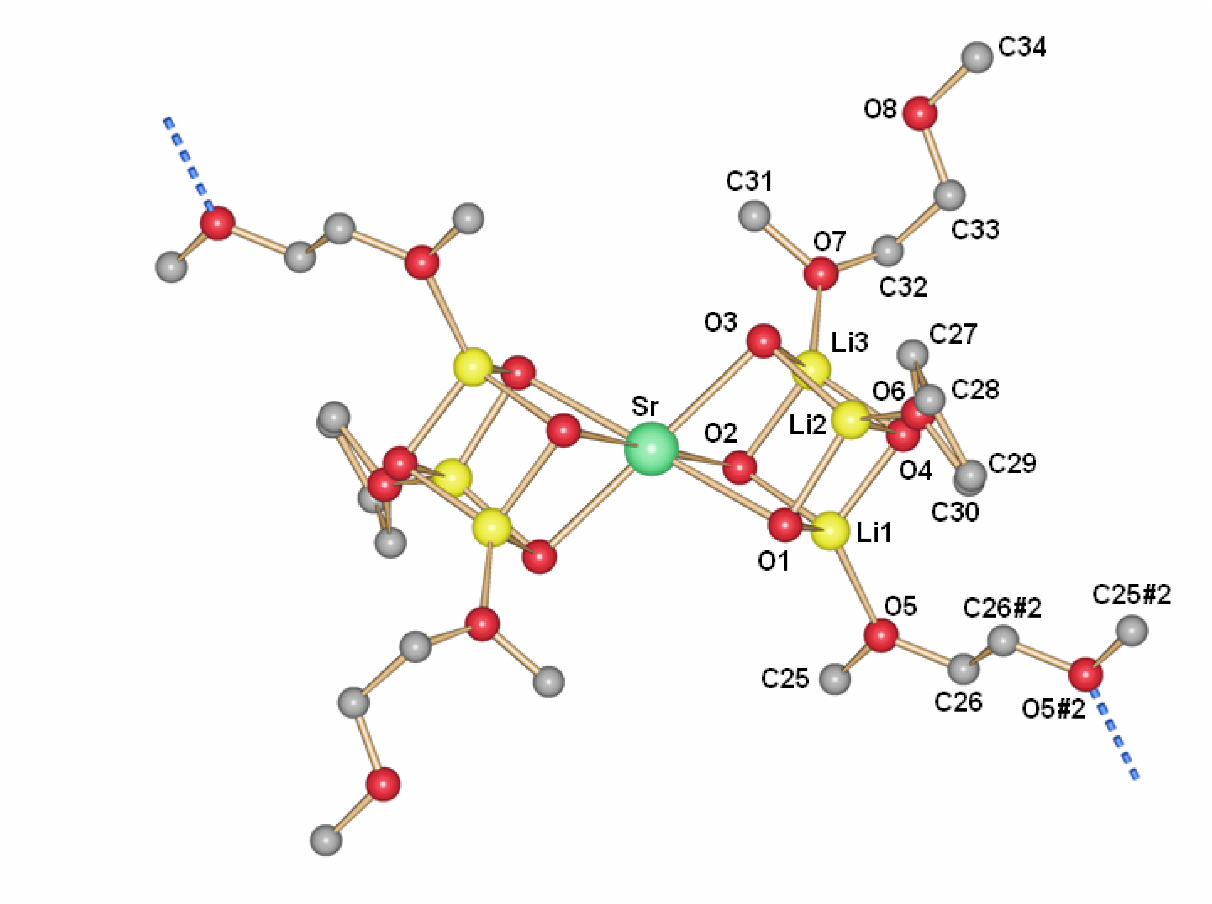


Figure 104. Schakal view of the partially labelled molecular structure of 28, phenyl rings and H atoms have been omitted for clarity

Compound **28** also crystallizes in the monoclinic space group $P2_1/n$ (Nr. 14) with two molecules per unit cell.

These two compounds present very similar structures, also compared to the initial compound **18** [$SrLi_6(OPh)_8(thf)_6$]. Indeed the "$SrLi_6(OPh)_8$"-core of **18** remains in both compounds **27** and **28**. In the structure of **27**, one terminal THF-molecule binding to a lithium cation in **18** has been replaced by one DME molecule which acts as a μ-bridge between two clusters-units. The two other lithium cations are still terminally bonded to a THF molecule. In the structure of **28**, the bridge between molecules via the DME ligand is present as in **27**, and another DME molecule has formally replaced one terminally coordinating THF molecule and acts as a terminal DME ligand. In both compounds **27** and **28**, DME act as monodentate ligands, one behaves as a bridging ligand through the oxygen atoms giving rise to an infinite polymer whereas the second one, in **28**, acts as a terminal monodentate DME ligand.

In both structures, a crystallographic centre of symmetry is located between the two methylene carbon atoms of the bridging DME and relates cluster-units into formation of a one-dimensional polymeric chain (Figure 105 and Figure 106).

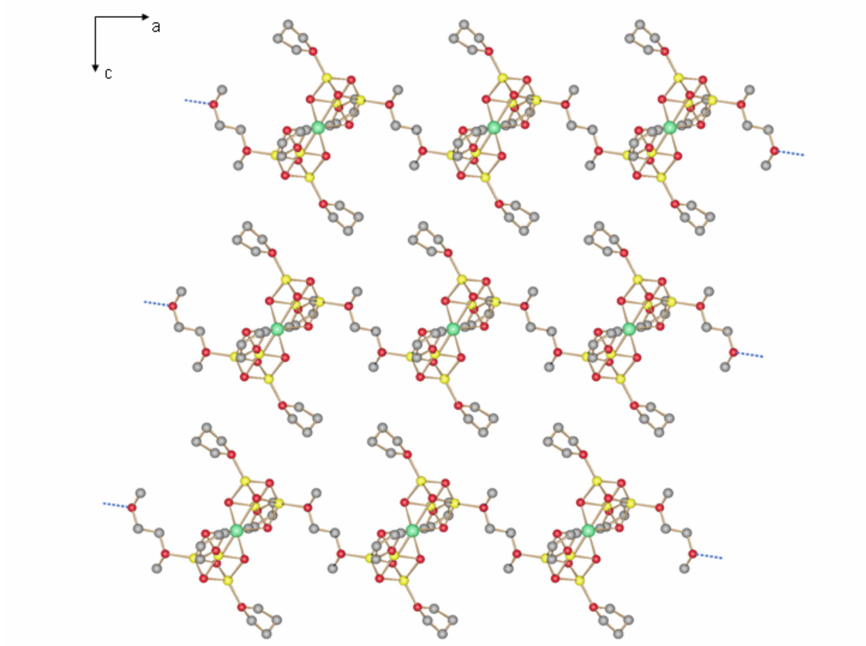


Figure 105. Packing of the polymeric chains of 27 along the b-axis, phenyl rings and H atoms have been omitted for clarity

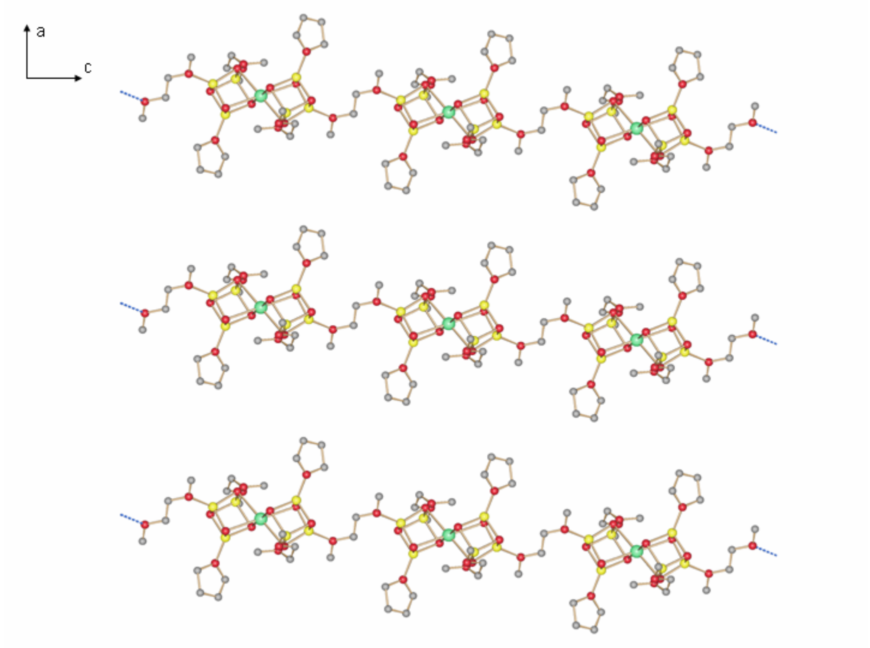


Figure 106. Packing of the polymeric chains of 28 along the b-axis, phenyl rings and H atoms have been omitted for clarity

Compounds with bridging DME molecules have already been reported [236, 339-345] although this is not a common phenomenon for bidentate molecules which often prefer to act as chelating ligand.

The Tables 28 and 29 summarize the most important distances and angles in the compounds **27**, respectively **28**.

Table 28. Bond lengths (Å) and angles (°) in **27**

Sr–OPh	2.556(5)	OPh–Sr–OPh (*trans*)	180
Li–OPh	1.972(6)	OPh–Sr–OPh (same cubane)	71.91(7)
Li–O(thf)	1.958(5)	OPh–Sr–OPh (other cubane)	108.08(3)
Li–O(dme)	2.019(1)	Sr–OPh–Li	94.80(4)
Li···Li	2.620(2)	Li–OPh–Li	83.51(7)
Sr···Li	3.363(9)		

Table 29. Bond lengths (Å) and angles (°) in **28**

Sr–OPh	2.532(3)	OPh–Sr–OPh (*trans*)	180
Li–OPh	1.968(6)	OPh–Sr–OPh (same cubane)	72.39(7)
Li–O(thf)	1.920(4)	OPh–Sr–OPh (other cubane)	107.60(3)
Li–O(dme)	1.970(4)	Sr–OPh–Li	94.76(1)
Li···Li	2.634(3)	Li–OPh–Li	84.42(7)
Sr···Li	3.343(4)		

Inversion centres are situated at the position of the strontium cation in both structures which lay on the crystallographic positions (½, ½, ½ (a)) in **27** and (½, 0, ½ (c)) in **28**.

The strontium cations reach in both compounds a coordination number six with a similar average Sr–μ_3-OPh distance of 2.556(5) Å in **27** and 2.532(3) Å in **28**. These average distances are relatively longer than the one observed in $[SrLi_6(OPh)_8(thf)_6]$ **18** (average Sr–μ_3-OPh = 2.516(1) Å). The Li–O(OPh) bond lengths (average Li–O(OPh) = 1.972(6) Å in **27**, 1.968(6) Å in **28**) are slightly longer than those observed in the literature [77, 82, 83, 220, 258, 301, 302] but correspond with the average the Li–O(OPh) distance in **18**. In **27**, Li1 and Li2 complete their coordination sphere with one terminally bonded THF ligand. The Li–

O(thf) bond lengths of **27** (average Li–O(thf) = 1.958(5) Å) compare well with the those observed in **18** and the ones described in the literature [63, 69, 162, 220, 302]. Li3 is bonded to one oxygen atom of the DME-bridging ligand with Li3–O7 of 2.019(1) Å, a common distance for "Li–O monodentate DME" distances [340, 341]. In **28**, the lithium cations have different terminal O-donor ligands. Li2 is coordinated to a THF molecule with a Li2–O6 distance of 1.968(6) Å, which compares well with those described in the literature [63, 69, 162, 220, 302]. Li3 is bonded to only one oxygen atom of a DME molecule, the latter molecule acting as terminal ligand. The Li3–O7 distance in **27** is at 1.938(4) Å relatively shorter than the Li1–O5 (2.002(5) Å), bonds involving DME as bridges between cluster-units. Concerning the core of the clusters in **27** and **28**, no distortion is observed compared to **18**: the bond lengths Li–O and angles Li–O–Li as well O–Li–O are in similar range.

In both compounds **27** and **28**, no π–π as well as no C–H···π interactions between phenyl rings of the phenolate groups are observed. In **27**, only weak intermolecular H-bonds are listed in the polymeric chain with H12···O5 = 2.601(8) Å and H9···O7 = 2.937(8) Å, but not between chains. On the other hand, in **28**, the presence of a non-coordinated oxygen atom in the DME terminal ligand leads to weak intermolecular H-bonds between polymeric chains; with the THF molecule via H29B···O8 = 2.868(1) Å and with the DME-bridging molecule via H25A···O8 = 2.911(6) Å. This leads to the formation of a three-dimensional network: Figure 107: view along b axis, Figure 108: view along c axis, Figure 109: view along the [53.280 -3.125 -0.750] direction.

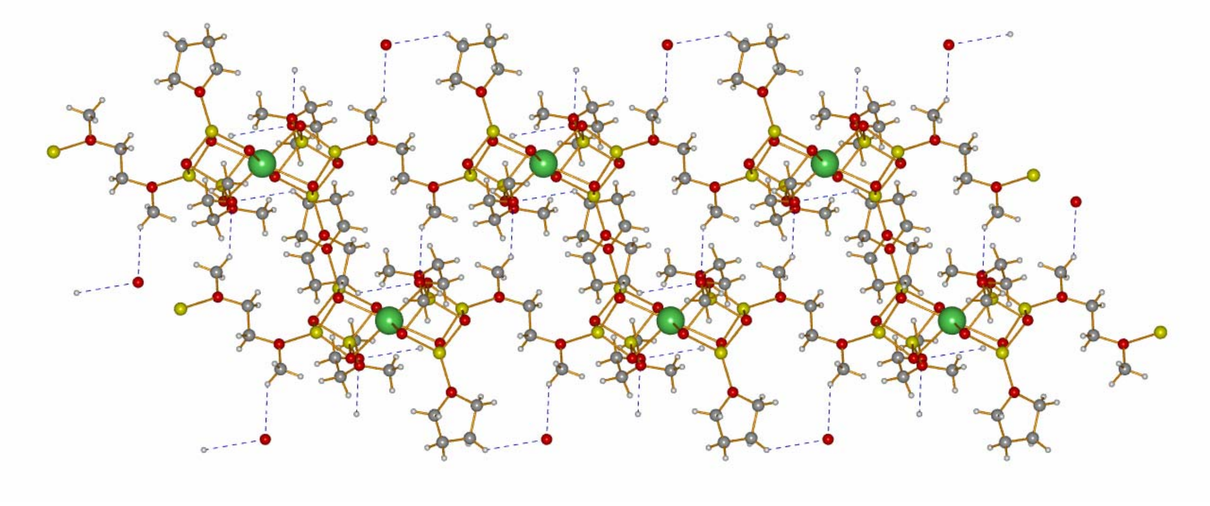


Figure 107. View of the 3D-network observed in 28 along the b-axis, phenyl rings have been omitted for clarity

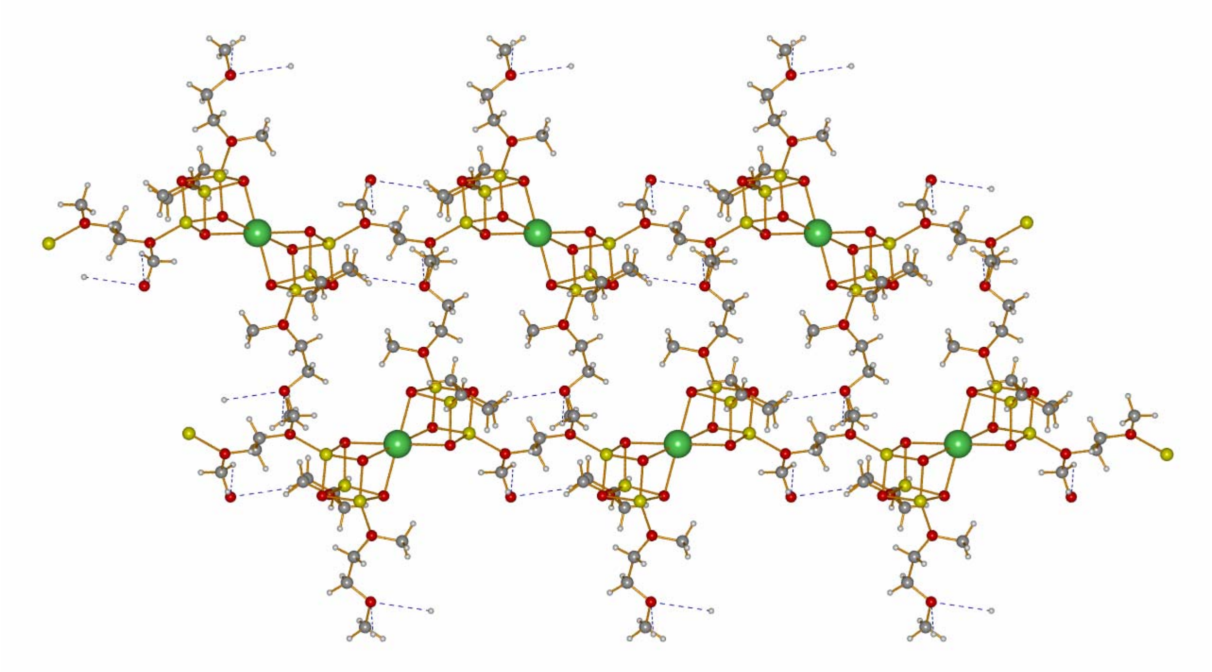


Figure 108. View of the 3D-network observed in 28 along the c-axis, phenyl rings have been omitted for clarity

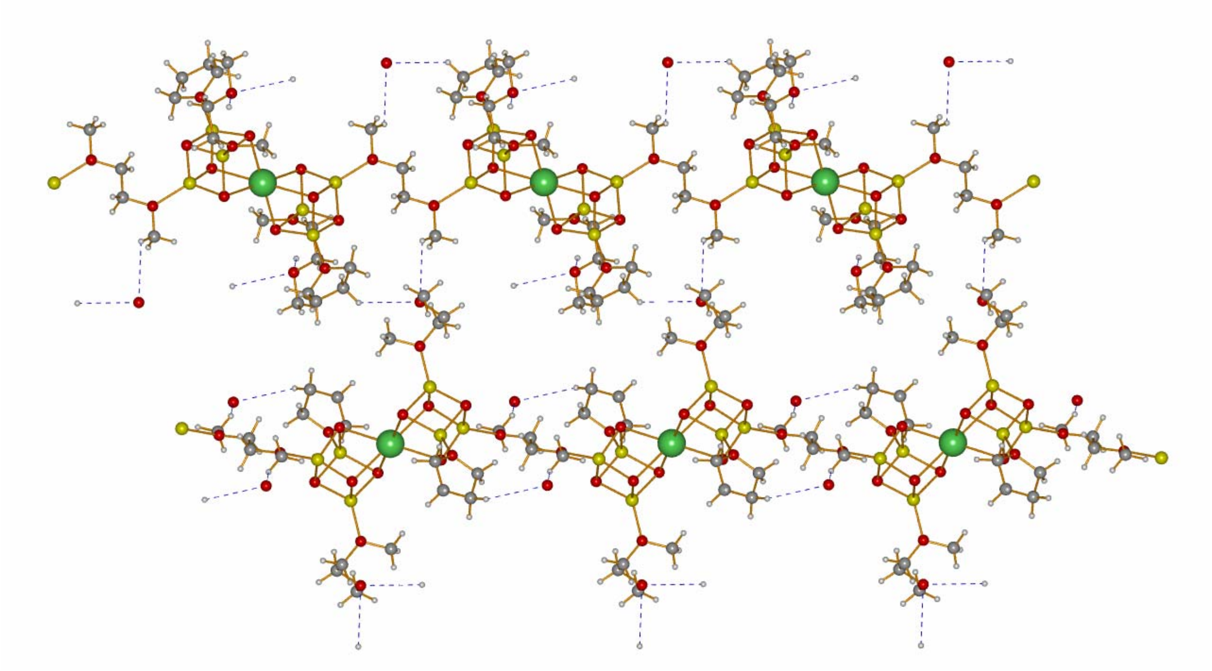


Figure 109. View of the 3D-network observed in 28 along the [53.280 -3.125 -0.750] direction, phenyl rings have been omitted for clarity

B - V - Heterometallic phenoxide/alkoxide clusters

B - IV.1 - Introduction

In this chapter, some *tert*-butoxyde and phenoxide lithium-alkaline earth metal clusters have been crystallographically characterized in the solid state. They present for each kind of OR ligand (R = ^{t}Bu, Ph), the same overall structure independently of the alkaline earth cation Ca^{2+}, Sr^{2+} or Ba^{2+}. These two type of structures are completely different with a square bipyramid in $[IM(O^tBu)_4\{Li(thf)\}_4(OH)]$ and respectively a double-cubane sharing a vertex in $[MLi_6(OPh)_8(thf)_6]$. In order to verify if a third arrangement is possible, some syntheses with both, lithium alkoxide LiO^tBu and aryloxide LiOPh, were attempted.

B - IV.2 - Synthesis and crystal structure of $[CaLi_6(OPh)_6(O^tBu)_2(THF)_6]$ 29

The reaction of CaI_2 with an equal amount of LiOPh in THF (5eq) and LiO^tBu in THF (5eq), under dry and inert atmosphere at room temperature, affords single-crystals of $[CaLi_6(OPh)_6(O^tBu)_2(thf)_6]$ **29** (Figure 110) within one week at low temperature (-25°C), after recrystallization in a THF/hexane mixture.

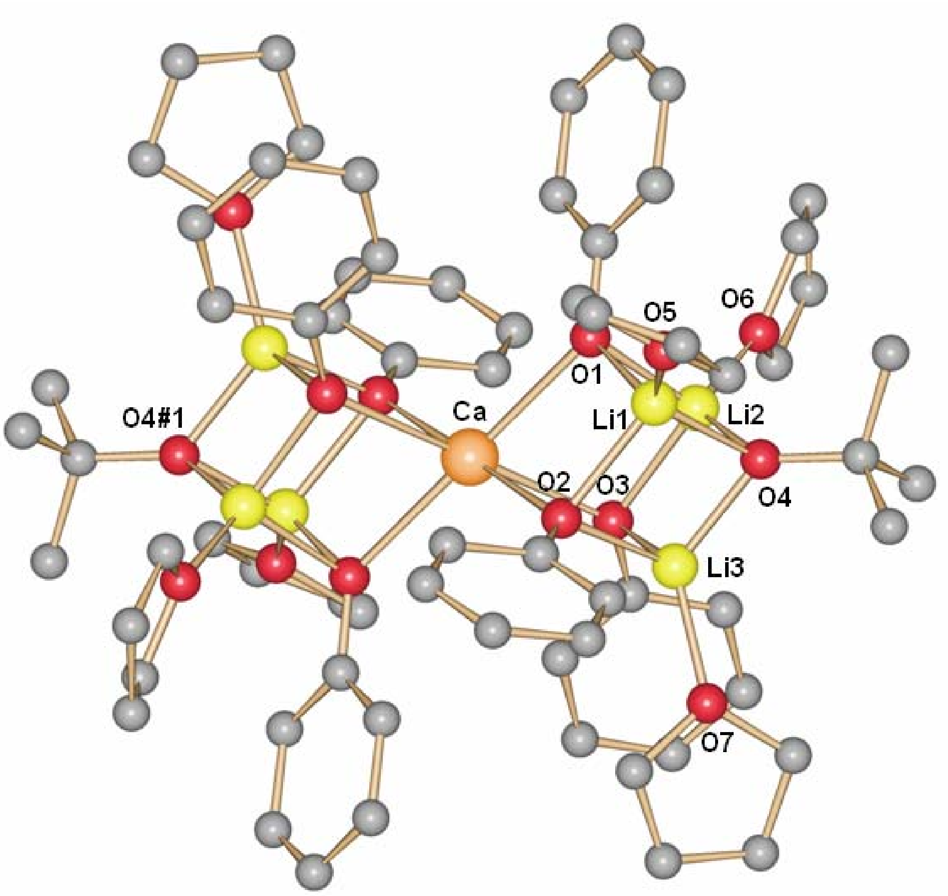


Figure 110. Schakal view of the partially labelled molecular structure of 29, H atoms have been omitted for clarity

Compound **29** crystallizes in the monoclinic space group *P*-1 (Nr. 2) with one molecule per unit cell. Unexpectedly, the structure consists as for the [$MLi_6(OPh)_8(thf)_6$] clusters (M = Ca **17**, Sr **18**, Eu **20**, Sm **21**, Ba **19**) as two $CaLi_3$-tetrahedra linked via the Ca-vertex due to an inversion centre on which is situated calcium cation which lies on the crystallographic position (0, ½, ½ (g)).
Although different symmetry operations might be expected analyzing the crystal structure of **29** (such as a C_3-axis along the O4-Ca-O4#1 (#1: 2-x, 1-y, 1-z), or other symmetry operations) no correlation matrix was found indicating a higher symmetry. Furthermore, careful analysis of the X-ray data gave no hints for the presence of a higher symmetry.

The four triangular faces of these two equivalent tetrahedra are μ_3-bridged by alcoholate anions: three phenolates- and one *tert*-butanolate-groups. In a previous article, Gagné *et al.* [346] described the synthesis of a mixed sodium alkoxide/phenoxide catalyst, namely [$Na_4(OPh)_3(O^tBu)$], obtained by simple mixing of the NaO^tBu and NaOPh salts in THF. It is possible to expect that the formation of an analogue heteroleptic alkali cluster is also possible with lithium salts resulting in [$Li_x(OPh)_y(O^tBu)_z$] (maybe [$Li_4(OPh)_3(O^tBu)$] considering the structure of **29**).

In **29**, the calcium cation reaches a coordination number of six with an average Ca–μ_3-OPh distance of 2.384(8) Å. These bond lengths correspond well with those observed in [$CaM'_6(OPh)_8(thf)_6$] M' = Li **17**, Na **22** due to the similar arrangement of ligands around the calcium cation. They are however slightly shorter than in the literature data compound [$Ca_3(OPh)_5(HMPA)_6$][OPh.2POH] [110].

The most important bond lengths and angles in **29** are summarized in Table 30.

Table 30. Bond lengths (Å) and angles (°) in **29**

Ca–OPh	2.384(8)	Ca–OPh–Ca (trans)	180
Li–OPh	2.012(7)	OPh–Ca–OPh (same cubane)	75.71(3)
Li–O^tBu	1.908(4)	OPh–Ca–OPh (other cubane)	104.28(7)
Li–O(THF)	1.977(3)	Ca–O(OPh)–Li	95.48(7)
Li···Li	2.564(3)	OR–Li–OR	96.42(7)
Ca···Li	3.264(3)	Li–OR–Li	81.80(1)

The Li–O(OPh) bond lengths, with a mean value of 2.012(7) Å are however slightly longer than those observed in the literature data [77, 82, 83, 220, 258, 301, 302] as well as in **17** (Li–O(OPh) = 1.973(2) Å), the Li–O(O^tBu) distances at 1.908(4) Å are common [55, 59].

Each lithium cation finds its tetrahedral coordination sphere completed with a terminally bonded THF molecule. The Li–O(thf) bond lengths of **29** (average Li–O(thf) = 1.977(3) Å) compare well with those described [63, 69, 162, 220, 302]. The so obtained compound possesses a quasi spherical structure with the core of the cluster well protected by hydrophobic groups of phenyl, *tert*-butyl and THF.

No π–π as well as no C–H···π interactions between phenyl rings of the phenolate-groups are observed in **29**. More, no intermolecular even weak H-bonds are listed since all H···O distances are >3.65 Å, the [$CaLi_6(OPh)_6(O^tBu)_2(thf)_6$] cluster **29** is therefore molecular in the solid state.

B - VI - Homometallic alkoxide cluster

B - VI.1 - Introduction

Alkaline earth metals are involved in a wide range of oxide-based ceramic materials. However, their formulation in a large part require at least three different metallic precursors as for the high T_c superconductor material $YBa_2Cu_3O_7$, but even more source precursors are needed for other systems such as the $Ti_2Ca_2Ba_2Cu_3O_{10}$ and $Bi_2Sr_2Ca_2Cu_3O_{10}$ (or $Bi_2Sr_2CaCu_2O_8$). It is well establish that, for obtaining semiconductors by MOCVD techniques, use of single source precursor (in which the different elements are incorporated in a single precursor molecule) increases the quality of the final material, but such precursors are really scarce [347]. A number of compounds with two elements combined, for instance Y and Cu [348-352], Ba and Cu [31-33, 348, 350, 352-359] or Y and Ba [350, 353, 357, 360-364] are also known. They are more or less volatile or possess high sublimation temperatures and show tendency to decompose. Whereas satisfying volatile homometallic “alkoxides” for yttrium [20, 29, 30] and copper [20, 29-36] exist, the perfect volatile precursors for barium can still be improved [10, 20, 29, 30, 32, 365-368].

The search for new volatile alkaline earth metal compounds in the context of CVD, and sol-gel precursors for synthesizing oxide materials, has led to a number of higher aggregates in aprotic organic solvents. For instance, a calcium cluster with nine metal centres $[Ca_9(OCH_2CH_2OMe)_{18}(HOCH_2CH_2OMe)_2]$ was reported to possess CdI_2-core geometry [369], whereas $[Ca_6(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_4(OEt)_4].14EtOH$ consists of two hetero-cubanes fused via one face [370, 371]. In our group [157], some homometallic clusters of alkaline earth metals have already been obtained with very interesting structures, namely $[Sr_3I_3(OH)_2(thf)_9]I$ [167] and $Li[\{Ca_7(\mu_3\text{-}OH)_8I_6(thf)_{12}\}_2(\mu\text{-}I)].3THF$ [158, 167]. However, some observations (intra- and intermolecular interactions observed in the crystal structures) as well as theoretical calculations showed the ionic behaviour of the clusters. Therefore, they can not be useful as precursors for MOCVD process. Nevertheless, they may act as sol-gel precursors.

B - VI.2 - Synthesis and crystallographic structure of $[Li(thf)_4]^+[\{Sr_6(O)(\mu_3\text{-}I)(I)_2(O^tBu)_7(thf)_3\}_2(\mu\text{-}I)]^-(THF)_n$ 30

Treating the starting material *trans*-$[SrI_2(thf)_5]$ with the lithium primary amide PhN(H)Li [372], freshly prepared from equimolar amounts of ^{n}BuLi and aniline ($PhNH_2$), and sodium *tert*-butoxide result in dark coloured solutions which produces large crystals in good yield of the homometallic cluster $[Li(thf)_4][\{Sr_6(O)(\mu_3\text{-}I)(I)_2(O^tBu)_7(thf)_3\}_2(\mu_2\text{-}I)](THF)_n$ **30** [170] as shown by an X-ray diffraction and further analysis. The compound **30** crystallizes in the monoclinic space group *C*2/*m* (Nr. 12) with two molecules per unit cell.

One cluster anion is formed of a centro-symmetric Sr_{12}-cluster consisting of two neutral Sr_6-units of composition $[Sr_6(O)(\mu_3\text{-}I)(I)_2(O^tBu)_7(thf)_3]$, linked together by a μ-bridging iodide ion. The core of each cluster contains an interstitial oxo-group, which is octahedrally coordinated to six strontium cations. This $Sr_6(\mu_6\text{-}O)$-unit is located within a roughly cubic arrangement of seven O^tBu anions and one iodide anion, each of which caps a triangular face of the octahedron and is coordinated to each of the three Sr^{2+} cation that define the face (Figure 111).

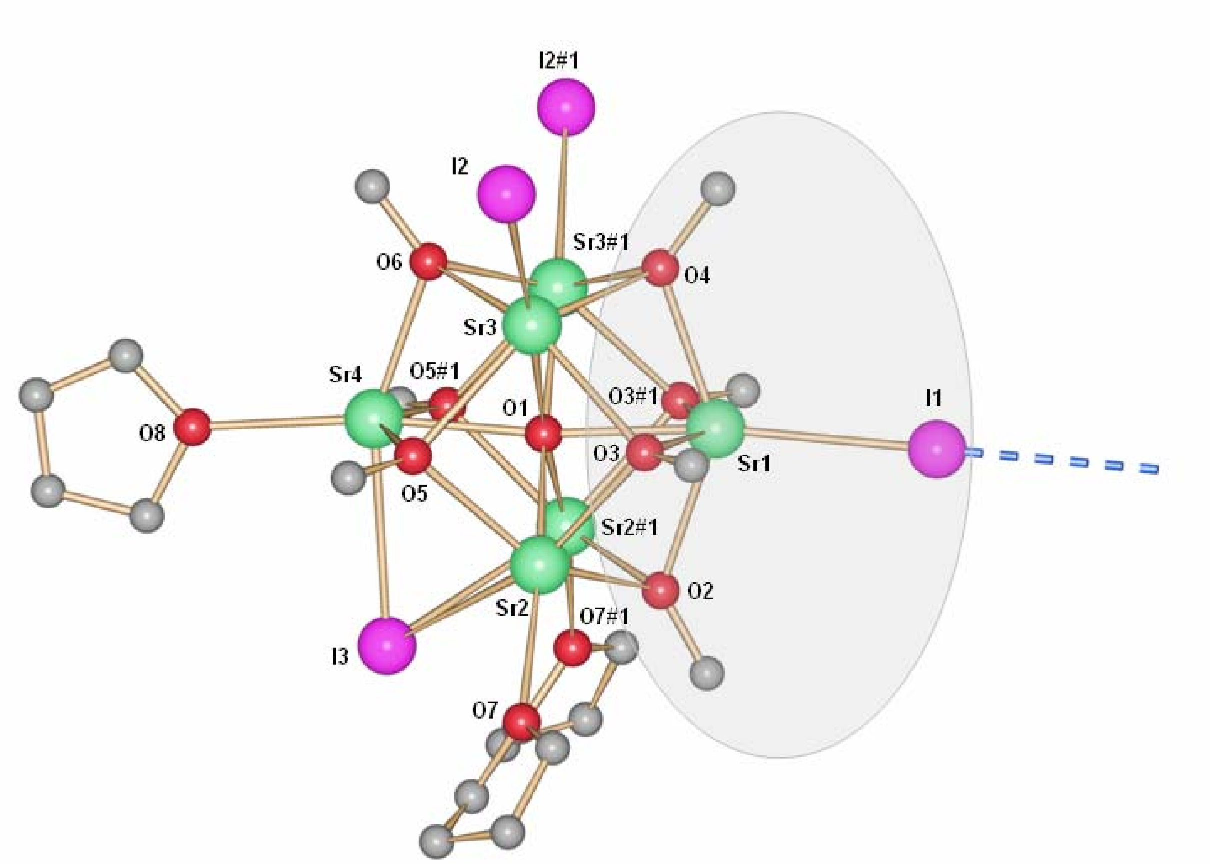


Figure 111. Schakal view of the partially labelled of the Sr_6-subunit in 30

The coordination number for all strontium ions is six. Three facially arranged Sr cations of the Sr_6-octahedron complete their distorted octahedral coordination sphere with terminal-THF ligands. Two of the remaining alkaline earth metal carry a terminal iodide anion, the sixth Sr cation features also iodide to complete its coordination sphere, but this iodide acts as bridging ligand to another strontium cation of the second Sr_6-unit of the structure.

Both Sr_6-units are related to each other through an inversion center at the position of the μ-bridging iodide ligand I1 (0, 0, 0 (a)), which gives the anionic cluster a dumb-bell shape (Figure 112). Additionally, a mirror plane passes through the ions I3, Sr1, Sr4, O1, O2, O4, and O6 (of crystallographic positions x, 0, z (i)) of a Sr_6-cluster unit. Thus, for Sr2, Sr3, I2, O3, O5 and O7 (and the attached atoms), symmetry equivalents are generated.

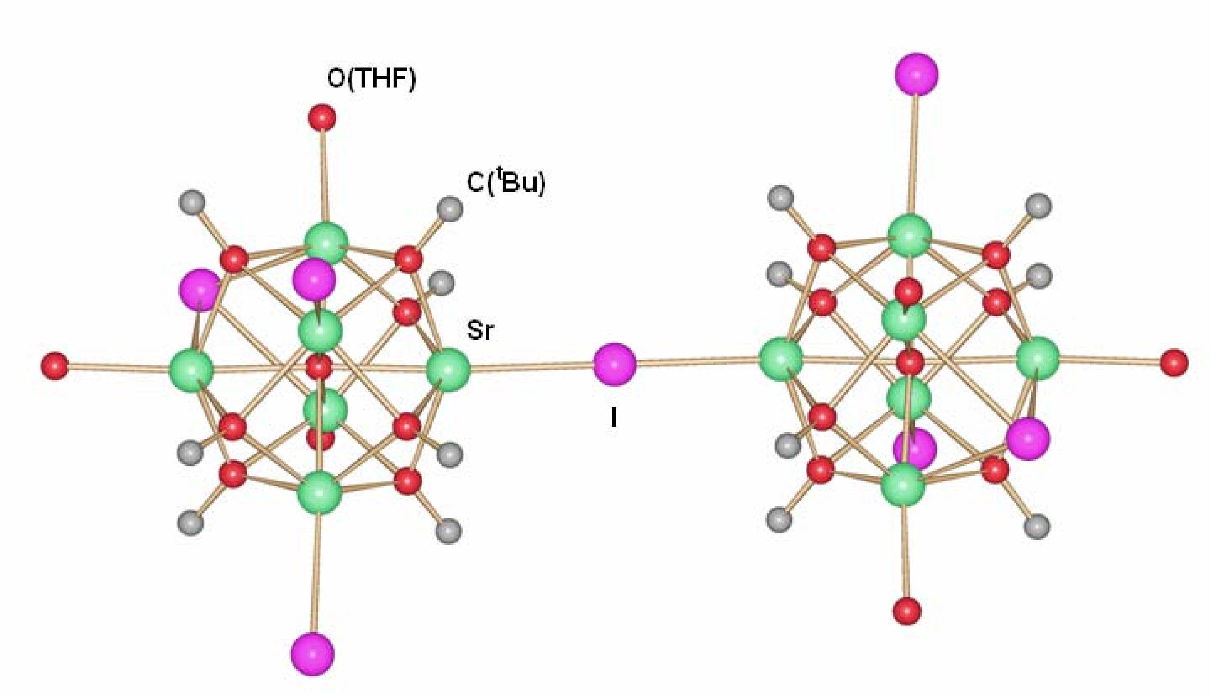


Figure 112. Schakal view of the partially labelled molecular structure of 30

The most interesting effect is observed for Sr–I bond lengths. From the literature, this is the first compound where iodide anions play three different roles. In **30**, two iodide anions act as terminal ligands (I2 and its I2#1), one acts as capping ligand (I3), and the last one (I1) acts as a μ-bridging ligand linking the two Sr_6 cores.

The Sr–I bond lengths are 3.277(9) Å (Sr1–μ-I1), 3.307(2) Å (Sr3–I2) and 3.406(9) Å (Sr–μ_3-I on average) with a total average of 3.352(1) Å which is slightly shorter than the sum of their ionic radii by Shannon [156], but 0.12 Å longer than those in [$SrI_2(thf)_5$] [155].

As expected, the μ_3-bridging iodide I3 forms the longest bonds to the cations with 3.371(1) Å (Sr4), and 3.4249(8) Å (Sr2 and its symmetry equivalent). The Sr–I bond involved in the dimer formation is shorter than those with the anion acting as terminal ligands even though terminal bonds to ligands are usually described in the literature as being the shortest compared to the same ligand in bridging position. This can be explained by the fact that the two terminally bonded iodide ligands of one Sr_6-unit are linked to vicinal Sr cations and therefore a strong repulsion occurs, pushing the soft and easily polarizable anions further apart and away from the cations and the vicinal O^{t}Bu anions. Moreover, the Sr1–μ-I1 distance in **30** (3.307(2) Å) is shorter than the Sr–μ-I bond length observed in $[Sr_3I_3(OH)_2(thf)_9]I$ [167] (average Sr–μ-I = 3.351(2) Å) probably due to its very acute Sr–I–Sr angle (67.70(6)°) compared to the linear Sr1–I1–Sr1 angle in **30**.

The oxo-anion is not perfectly in the center of the octahedron, probably due to the difference in coordination sphere of each strontium cation. The $Sr–O^{2-}$ distances are ranging from 2.492(5) Å (Sr1–O1) to 2.610(6) Å (Sr2–O1) (average Sr–O1 = 2.543(2) Å). The Sr–O1–Sr angle for Sr cations in *trans*-position is 174.13(7)° on average, the other Sr–O1–Sr vary from 87.35(5)° for Sr3–O1–Sr3#1 to 95.75(4)° for Sr2–O1–Sr4 with an average of 90.14(4)°.

The most important bond lengths and angles in **30** are summarized in Table 31.

Table 31. Bond lengths (Å) and angles (°) in average **30**

Sr–I	3.352(1)	Sr1–I1–Sr1 (dimer)	180
Sr–Sr	3.596(1)	O1–Sr1–I1	172.94(4)
$Sr–O^{2-}$	2.543(2)	O1–Sr3–I2	176.61(3)
Sr–O(^{t}Bu)	2.543(4)	Sr–O–Sr (*trans*)	174.13(7)
Sr–O(thf)	2.675(5)	Sr–O–Sr (*cis*)	90.14(4)

The Sr–O(thf) distances vary between 2.673(3) and 2.680(4) Å, and are longer than the Sr–O(thf) bonds in $[SrI_2(thf)_5]$ [155] (Sr–O(thf) 2.562(2)-2.618(9) Å) and the homometallic cluster $[Sr_3I_3(OH)_2(thf)_9]I$ [167] (Sr–O(thf) 2.57(2)-2.61(2) Å) while the coordination number for the strontium cation in **30** is lower (six in **30** and seven in the two other compounds).

The Sr–O(O^{t}Bu) distances (average Sr–O(O^{t}Bu) = 2.543(4) Å) in **30** are shorter than those in $[ISr(O^tBu)_4(OH)\{Li(thf)\}_4]$ [167] (Sr–O(O^{t}Bu) = 2.597(6) Å), and compare well with those in the heterometallic compound $[SrSn_2(O^tBu)_6\{Fe(CO)_4\}_2]$ [373] (average Sr–O(O^{t}Bu) = 2.550

Å). They are longer than the Sr–O(O^{t}Bu) distances in the heterometallic compounds [$SrSn_2(O^tBu)_6$] [374] (average Sr–O(O^{t}Bu) = 2.523 Å) and [$SrPb_2(O^tBu)_6$] [271] (average Sr–O(O^{t}Bu) = 2.474 Å). It has to be said that in these two references, O^{t}Bu groups act as μ-bridging ligand while in **30**, they act as μ_3-bridging ligands.

In addition to the anionic cluster, a THF-coordinated cation is present in the solid state structure, as can be roughly seen in the Fourier Transform Map, but not be refined properly. The experimental conditions would allow lithium and sodium to be present. Due to the high symmetry of sites where this cation is located (0, 0.5, 0.5 (d)), it was however difficult to identify the cation unambiguously. Additionally, the coordinated THF molecules are disordered around several positions, just as the free solvent molecules and many of the terminally linked THF and ^{t}Bu-groups on the anionic cluster. This made an unambiguous identification of the cation via the single-crystal structure impossible even though three different crystals were measured from different batches. Two attempts were therefore undertaken to find out more about the cation. The first one was to calculate the free space available in the solid state with only the anionic cluster in the structure. Cations like [$Li(thf)_4$]$^+$ and [$Na(thf)_6$]$^+$ were modeled (Gaussian03, Hartree-Fock method with 6-31G basis sets) in a tetrahedral, respectively octahedral arrangement, and their respective volumes compared with the amount of free space, giving ionic radii of 5.1 and 5.8 Å respectively. The cavities in the solid state structure were analyzed with the program PLATON [375, 376] and indicate one large ellipsoid cavity per cluster of ca. 4.5 x 4.5 x 11 Å. Also, the fact that the cations could not be localized, and that they are heavily disordered, means that they probably have enough space to rotate on their crystallographic position. From this comparison, the size of the cavity and with these hints, we were able to attribute more likely the lithium ion as counterion to the cluster anion (Figure 113).

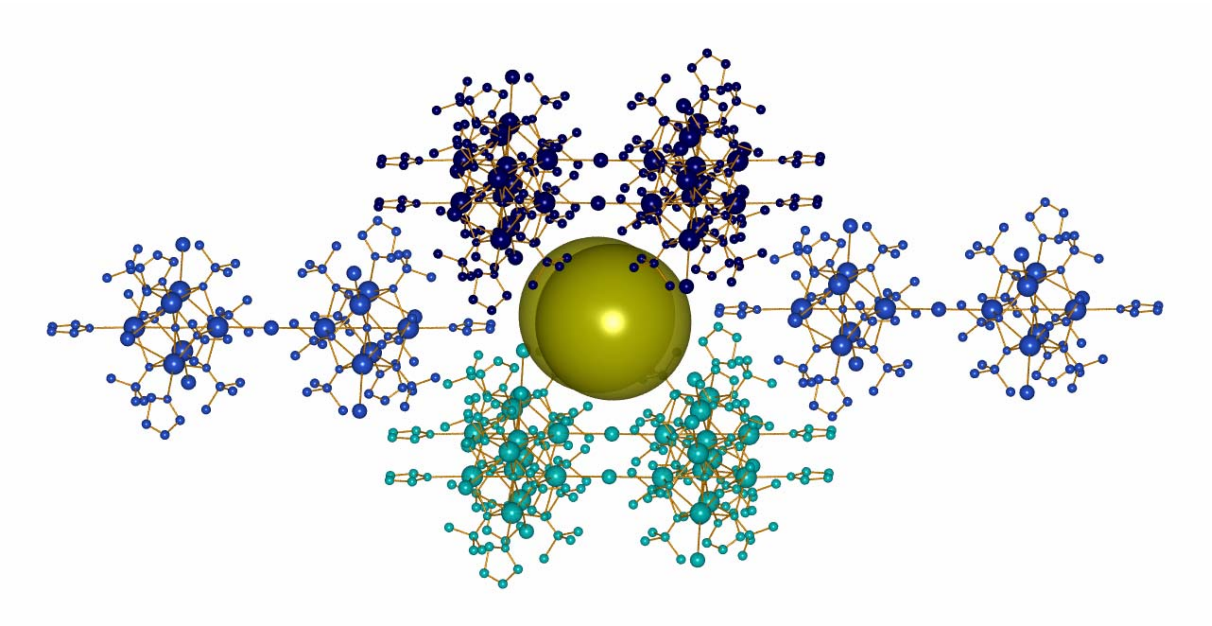


Figure 113. POVRAY view of the free ellipsoid cavity (yellow) observed between clusters 30, calculated with the program PLATON

In order to verify this experimentally, a second method was applied, using AAS (AAS = Atomic Absorption Spectrophotometry). For this, a solution of **30** was generated in water, and the results were compared with a standard curve obtained from several samples of solutions with a known concentration of lithium chloride. The obtained result proves the presence of lithium in the sample, corresponding to the 1:1 ratio of cation to anion. Presence of sodium was also detected, but in much lower concentrations. Therefore, compound **30** is likely to be written as $[Li(thf)_4]^+[\{Sr_6(O)(\mu_3\text{-}I)(I)_2(O^tBu)_7(thf)_3\}_2(\mu\text{-}I)]^-(THF)_n$. The number of THF molecules present in the solid state were difficult to determine due to fast loss of solvent as soon as taken our of the mother liquor.

Interestingly, the fragment highlighted in grey Figure 111 resembles a fragment from our series of cluster compounds of the composition $[IM(O^tBu)_4\{Li(thf)\}_4(OH)]$ (M = Ca **15**, Eu **16**, Sr [167] and Ba [162, 167]). The part "$[\{Li(thf)\}_4(OH)]^{3+}$" has been formally replaced by $[\{Sr_5(O)(\mu_3\text{-}I)(I)_2(O^tBu)_3(thf)_3\}]^{2+}$. The presence of the oxide anion in the centre of each Sr_6-unit of **30** is attributed to the presence of humidity or, more probably, hydroxide in the solutions of the starting materials. The central oxide anion in **30** must be present to compensate the high concentration of charge on the six cations. This is similar as in the mixed-metal cluster "Ba_6Li_3" in which an oxide-centered Ba_6-octahedron is present, which itself is fused to three Li-ions over a Ba_3-face to yield a second octahedron, also oxide-centered [377]. O^{t}Bu-groups are, similar as in **30**, bridging the triangular faces of the octahedron. However, in contrast to **30**, no other anions are involved in the formation of this aggregate.

A great number of papers described such large homometallic or heterometallic aggregates which present a M$_n$ core (n ≥ 4) with central oxo- or hydroxo-ligands, among of which some homometallic alkaline earth metal clusters, especially with barium: $[Ba_5(\mu_5\text{-}OH)(\mu_3\text{-}OAr)_4(\mu\text{-}OAr)_4(OAr)(THF)_5]$ (Ar = $C_6H_3Bu^t{}_2$-3,5) [124], $[HBa_5(O)(OPh)_9(thf)_8]$ [123] (Figure 20), $[H_2Ba_8(O)_2(OPh)_{14}(HMPA)_6]$ [114] (Figure 22), $[Ba_5(\mu_5\text{-}OH)(\mu_3\text{-}OCH(CF_3)_2)_4(\mu\text{-}OCH(CF_3)_2)_4(OCH(CF_3)_2)(THF)_4(H_2O)]$.THF [378], $[H_4Ba_6(O)(OCH_2CH_2OCH_3)_{14}]$ and $[Ba_6(O)(OCH_2CH_2OMe)_{10}(HOCH_2CH_2OMe)_4]$ [37, 123, 379, 380], $[H_3Ba_6(O)(O^tBu)_{11}(OCEt_2CH_2O)(thf)_3]$ and $[Ba_4(O)(2,4,6\text{-}(CH_2NMe_2)_3\text{-}C_6H_2O)_6]$ [110, 381]. Relatively less oxo-strontium compounds are known. To our knowledge, only three Sr$_n$ clusters have been so far characterized, $[Sr_4(O)(P(SiMe_2{}^iPr)_2)_6]$ [382], and $[Sr_5(\mu_4\text{-}O)(\mu_3\text{-}ONep)_4(\mu\text{-}ONep)_4(HONep)(L)_4]$ (Nep = CH_2CMe_3, L = THF, 1-methylimidazole) [383]. They possess a lower degree of nuclearity than **30** (n = 4, 5). Thus, $[Li(thf)_4][\{Sr_6(O)(\mu_3\text{-}I)(I)_2(O^tBu)_7(thf)_3\}_2(\mu\text{-}I)](THF)_n$ **30** is the first strontium compound with such a high degree of nuclearity. However such species with high nuclearity are expected to be non volatile also due to their ionic character, and can't therefore be useful as precursors in MOCVD [33]. They might be however serve in sol-gel processes.

B - VII - Heterometallic clusters of trivalent rare earth metals

B - VII.1 - Crystallographic structures of [Ln(OPh)$_6${Li(dme)}$_3$] Ln = Eu 31, Sm 32

The use of larger Lewis-coordinating solvent such as DME has shown some interesting results with complexes of the type [MLi$_6$(OPh)$_8$(thf)$_6$] (M = Ca **17**, Sr **18**). Indeed, on one hand, a total structural rearrangement is observed with [CaLi$_6$(OPh)$_8$(thf)$_6$] **17** resulting in [{Ca(dme)}$_2$(OPh)$_6${Li(dme)}$_2$] **25**. On the other hand, only a solvent-ligand exchange occurred with [SrLi$_6$(OPh)$_8$(thf)$_6$] **18**, with the characterization of two new compounds **27** (μ-dme)[SrLi$_6$(OPh)$_8$(thf)$_4$(dme)$_2$] and **28** (μ-dme)[SrLi$_6$(OPh)$_8$(thf)$_2$(dme)$_4$]. In both compounds **27** and **28**, the cluster-core of **18** "SrLi$_6$(OPh)$_8$" is maintained. In order to see the influence of the Lewis-coordinating O-donor solvent DME on the crystal structure of **20** and **21**, the former compounds were re-crystallized from DME.

However, divalent lanthanide complexes are inherently sensitive towards oxidation and during attempts of crystallization of compounds [EuLi$_6$(OPh)$_8$(thf)$_6$] **20** and [SmLi$_6$(OPh)$_8$(thf)$_6$] **21** in DME solution, two isostructural complexes with Eu^{3+} and Sm^{3+} metal cations have been produced, namely [Eu(μ-OPh)$_6${Li(dme)}$_3$] **31** and [Sm(μ-OPh)$_6${Li(dme)}$_3$] **32**.

The two clusters **31** and **32** crystallize in the trigonal space group *R*-3 (Nr. 148) with six molecules per unit cell. Their crystal structures are presented in Figure 114, respectively Figure 115.

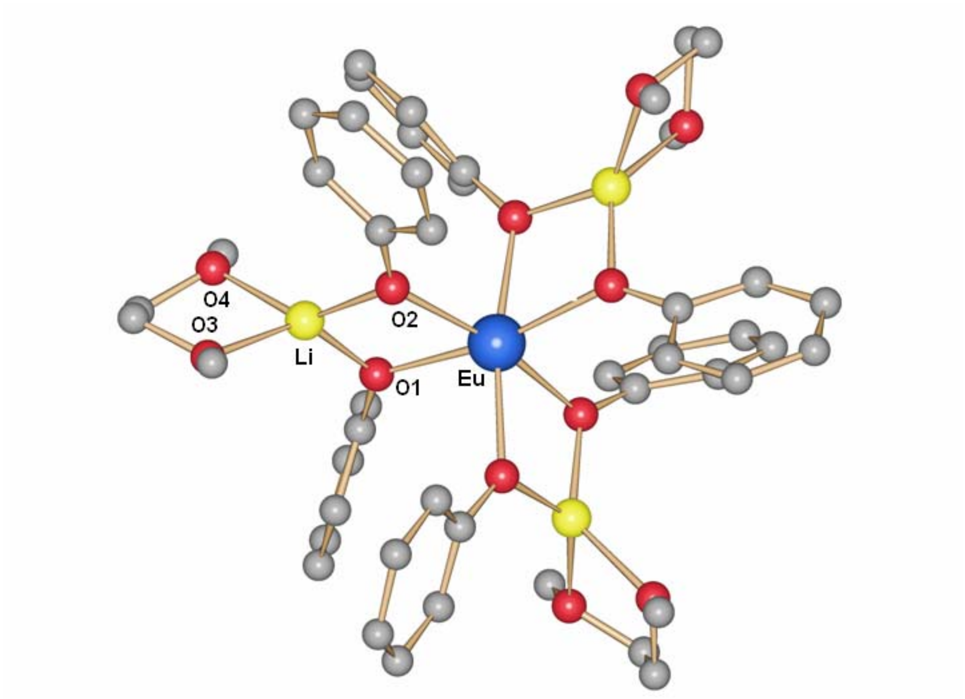


Figure 114. Schakal view of the partially labelled molecular structure of 31, H atoms have been omitted for clarity

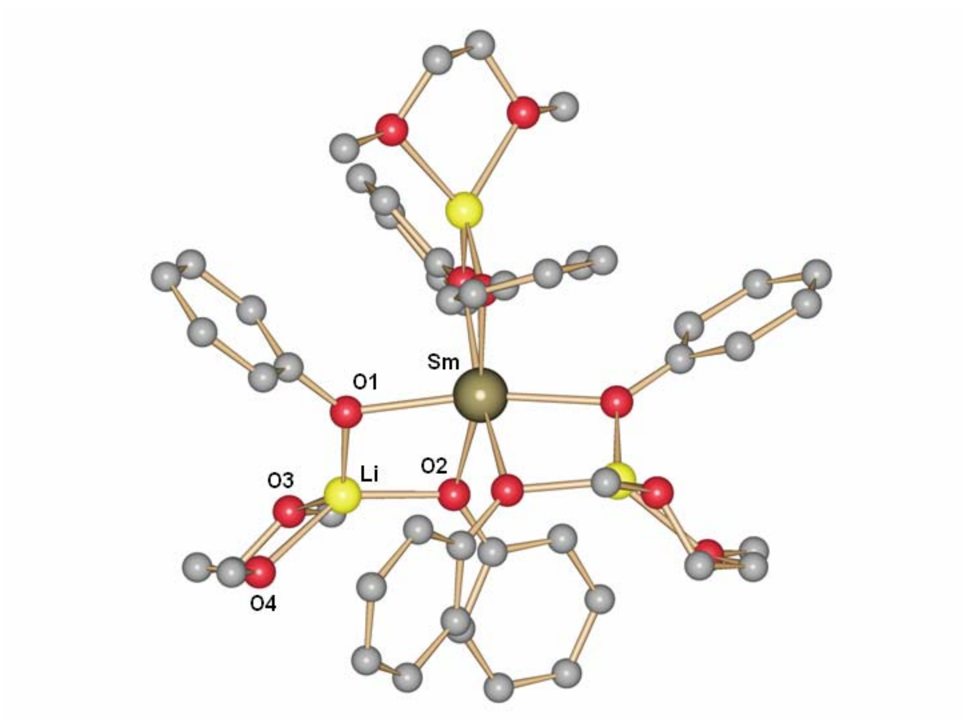


Figure 115. Schakal view of the partially labelled molecular structure of 32, H atoms have been omitted for clarity

These two complexes join the few structurally characterized homoleptic six-coordinated phenolate complexes. They are usually obtained with early-transition metals which possess different possible oxidation states. For instance for W(V), two compounds are reported: $[W(OPh)_6][N(Et)_4]$ and $[W(OPh)_6\{Li(thf)_2\}]$ [302] and for W(VI), only the compound $[W(OPh)_6]$ [384] is known.

From the literature, an isostructural complex has been characterized with V(III) namely $[V(\mu\text{-}OPh)_6\{Li(dme)\}_3]$ [258].

However, If the two bridging phenolate-groups are replaced by a binaphtolate- (binaphtol = $(C_{10}H_6OH)_2$) or catecholate-group (catechol = $C_6H_6O_2$), a rich structural database for trivalent lanthanide as well as transition metals complexes, with general formula $M'_3[M(X)_3]$ (M' = alkali metal, M = lanthanide or transition metals, X = binaphtol [385-396] (Figure 116) or catechol [397-399]) is reported. In the binaphtol complexes, the two naphtol-groups can rotate around the C–C bond, and thus, chirality is induced. The $M'_3[M(binol)_3]$ (M' = alkali metal, M = lanthanide) are very efficient catalysts in enantioselective organic reactions following a Lewis-acid mechanism.

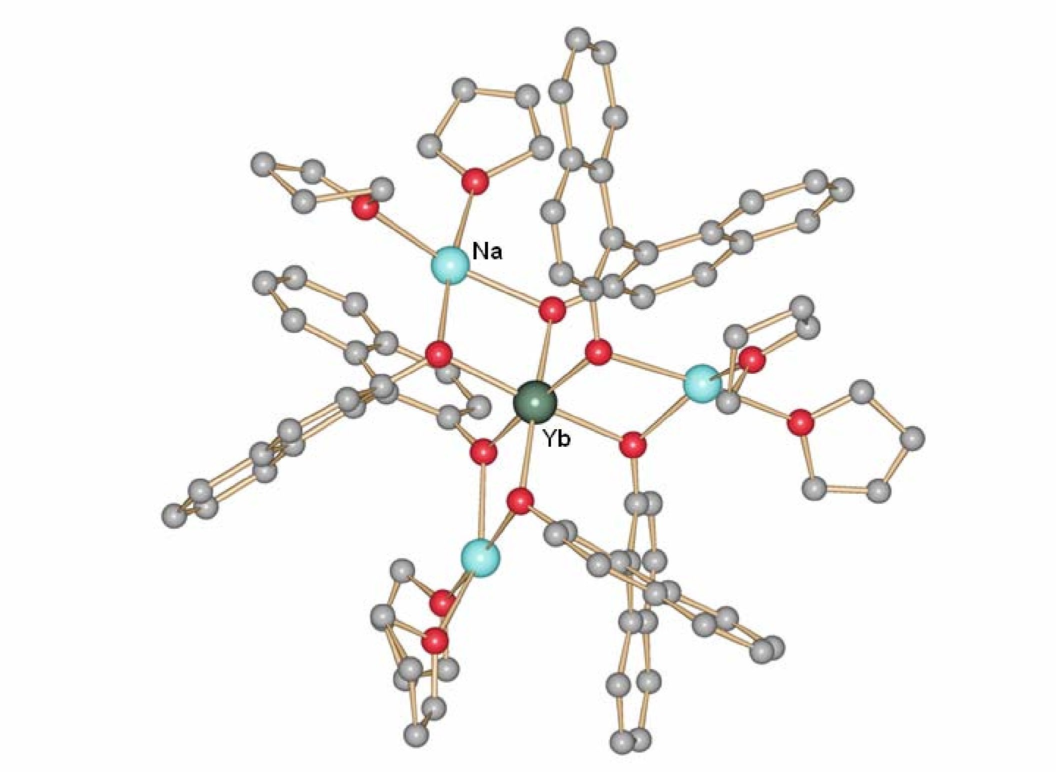


Figure 116. Molecular structure of $[Yb(BINOL)_3\{Na(thf)_2\}_3]$, H atoms are omitted for clarity

The most important bond lengths and angles in **31** and **32** are summarized in Table 32 and 33.

Table 32. Most important bond lengths (Å) and angles (°) in **31**

Eu–O1(OPh)	2.294(1)	O1–Eu–O2 (bridge)	74.01(5)
Eu–O2(OPh)	2.279(7)	O1–Eu–O2 (same plane)	89.56(6)
Li–O1(OPh)	1.909(4)	O1–Eu–O1	101.32(5)
Li–O2(OPh)	1.875(4)	O2–Eu–O2 (same plane)	95.67(5)
Li–O3(dme)	2.024(4)	O1–Eu–O2 (trans)	168.89(5)
Li–O4(dme)	2.029(4)	O3–Li–O4	81.75(2)
Eu···Li	3.124(4)	Li···Eu···Li	119.66(4)

In both complexes **31** and **32**, the lanthanide metal cation lies on 3-fold axis (Ln^{3+} : $^{1}/_{3}$, $^{2}/_{3}$, z (c)). The coordination geometry of each cation can be considered as a trigonal antiprism derived by trigonal compression of an octahedron. Indeed, the distortion from octahedral geometry is induced by the presence of three bridging lithium atoms between pairs of phenolate ligands. For instance, the bite angles O1–Ln^{3+}–O2 are 74.01(5)° in **31**, respectively 73.29(2)° in **32**. In **31** and **32**, the rhombi $LnLiO_2$ are very similar in distances and angles.

Table 33. Most important bond lengths (Å) and angles (°) in **32**

Sm–O1(OPh)	2.318(4)	O1–Sm–O2 (bridge)	73.29(2)
Sm–O2(OPh)	2.294(4)	O1–Sm–O2 (same plane)	88.67(2)
Li–O1(OPh)	1.907(2)	O1–Sm–O1	102.21(2)
Li–O2(OPh)	1.874(2)	O2–Sm–O2 (same plane)	96.32(2)
Li–O3(dme)	2.015(2)	O1–Sm–O2 (trans)	168.97(2)
Li–O4(dme)	2.020(2)	O3–Li–O4	81.9(4)
Sm···Li	3.145(1)	Li···Sm···Li	119.63(5)

The Ln^{3+}–μ-OPh distances are slightly shorter in **31** compared to **32** probably due the smaller ionic radius of Eu^{3+} and thus the O1–Ln^{3+}–O2 angle is smaller in **32**. For **31**, the Eu^{3+}–μ-OPh bond lengths average is 2.285(5) Å) and with an average distance of 2.306(4) Å in **32**, the Sm^{3+}–μ-OPh bond lengths are in **32** longer than the only Sm–OPh distance found in the literature with [Sm(Cp*)$_2$(OPh)(thf)] (2.1645(14) Å) [303], the latter being terminal. Thus, as expected, they are also longer than other terminal Sm^{3+}–OR bonds [400-402], even with very bulky alkyl-group such as either ^{i}Pr- or ^{t}Bu-groups in ortho-positions of the phenyl ring as found in [Sm(Cp*)(2,6-$^i Pr_2$-$C_6H_3O)_3$Li(thf)] (2.144(6) Å) or [Sm(Cp*)(2,6-$^t Bu_2$-$C_6H_3O)_2$(thf)] (average 2.160(5) Å) [403]. This is an effect of the loss of electron density at oxygen upon forming the Sm–O–Li bridges. However, they are slightly shorter than the rare Sm^{3+}–μ-OAr bond lengths found in the literature. In [Li(thf)]$_2$[Sm(2,6-$^i Pr_2$-$C_6H_3O)_3(CH_2SiMe_3)_2$] (CN5) [404] and [Sm(Cp*)(2,6-$^i Pr_2$-$C_6H_3O)_3$Li(thf)] (CN4) [403], the two phenolate anions also bridge a samarium(III) metal ion to a lithium cation with relatively shorter μ-OAr bonds lengths (average 2.265(7) Å in the former, 2.248(5) Å in the latter) than found in **32**. Nevertheless, this can be understood with the lower coordination number of the samarium cation in both complexes. The Li–μ-OPh bond lengths in **31** and **32** are similar with 1.892(4) Å in **31**, respectively 1.890(5) Å in **32**. As expected they are shorter than the Li–μ_3-OPh observed in the clusters **20** and **21** due to the bridging mode of the OPh-anions. They correspond well with those found in [Sm(Cp*)(2,6-$^i Pr_2$-$C_6H_3O)_3$Li(thf)] (Li–OAr = 1.910(5) Å) [403] or [Li(thf)]$_2$[Sm(2,6-$^i Pr_2$-$C_6H_3O)_3(CH_2SiMe_3)_2$] (average 1.874(5) Å) [404], although the lithium cation possesses a lower coordination number three in both complexes, but the aryloxide-groups are bulkier.

As cited above, on the one hand due to longer Ln-OPh distances in **32** compared to **31**, the O1–Sm–O2 angle is with 73.29(16)° in **32** slightly smaller than the one observed in **31** (O1–Eu–O2 = 74.01(6)°), the Ln–OAr–Li angles are on the other hand similar (96.29(5)° in **31**, 96.6(4)° in **32**) which are in the same range of values than found in [Li(thf)]$_2$[Sm(2,6-$^i Pr_2$-$C_6H_3O)_3(CH_2SiMe_3)_2$] (average OAr–Sm–OAr = 73.81(22)°, Sm–OAr–Li = 96.2(6)°) [404] and [Sm(Cp*)(2,6-$^i Pr_2$-$C_6H_3O)_3$Li(thf)] (average OAr–Sm–OAr = 76.9(2)°, Ln–OAr–Li = 94.6(6)°) [403].

In both complexes, the lithium atoms complete their traditional tetrahedral coordination sphere with a coordinating-DME molecule with Li–O(dme) distances of 2.026(5) Å in **31** and of 2.017(5) Å in **32**. The Li–O(dme) bond lengths are slightly longer in **31** due to the shorter Eu–μ-OPh distances. These values are common [340, 341], so are the O(dme)–Li–O(dme) angles with 81.75(2)° in **31**, respectively 81.9(4)° in **32** [219, 258, 263].

In each cluster, **31** and **32**, only weak intermolecular H-bonds can be considered. For instance two kind of H-bonds are noticed, one between ethereal ligands DME, the other one between phenyl rings and DME ligands. Due to high symmetry of both clusters, these interactions lead to the formation of three-dimensional networks.

In **31**, these H-bonds are, between DME ligands: O4···H16C = 2.725(3) Å and between phenyl rings and DME ligands, a shorter contact with O3···H9 = 2.657(1) Å (Figure 117 and Figure 118).

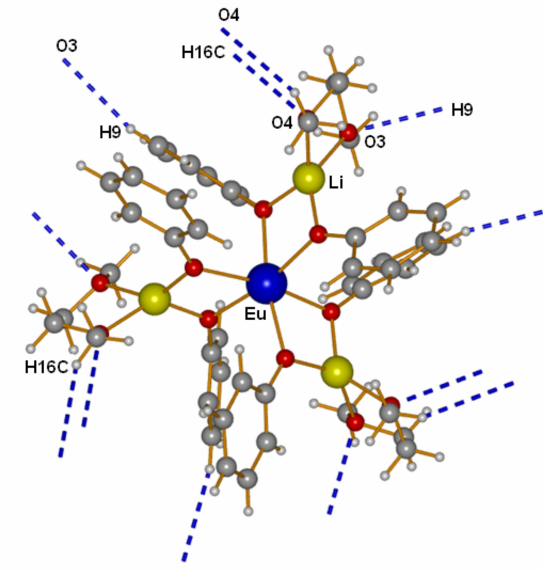


Figure 117. View of the H-bonds involved in the formation of the 3D-network in 31

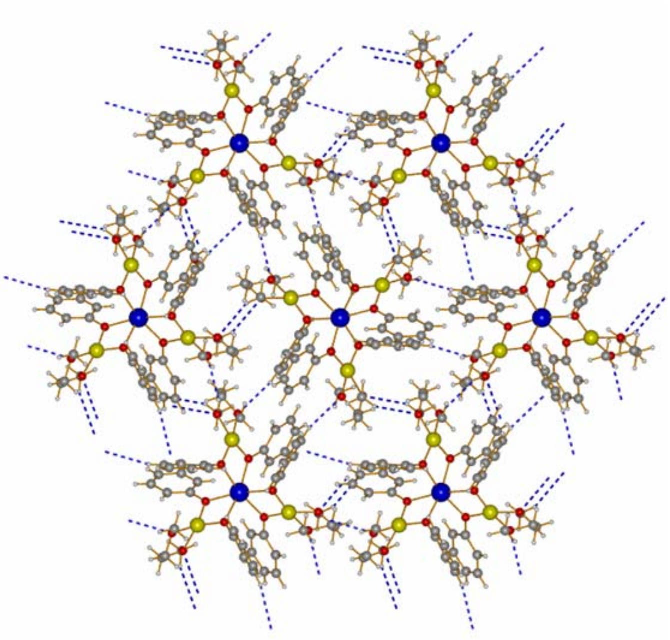


Figure 118. 3D-network of 31

The same interactions are observed in **32** with, between DME ligands, O4···H16A = 2.754(5) Å, and between phenyl rings and DME ligands, also a shorter contact with O3···H9 = 2.659(6) Å (Figure 119 and Figure 120).

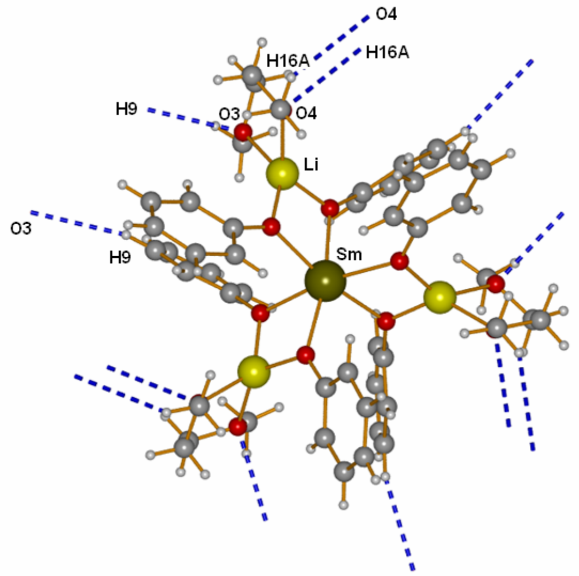


Figure 119. View of the H-bonds involved in the formation of the 3D-network in 32

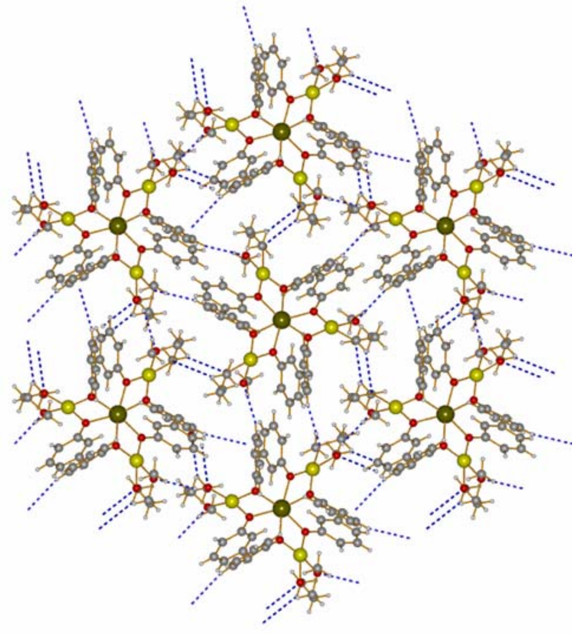


Figure 120. 3D-network of 32

C - Conclusion

Whereas the chemistry of alkali and alkaline earth metals was, some years ago, dominated by their carbanionic derivatives (compounds with M–C bonds), since the two last decades, organometallic compounds involving M–O bonds are in the current focus of research.

These species generally form molecular aggregates presenting cage-like structures also called clusters. Whereas alkali metal clusters tend to find applications more as superbasic compounds, alkaline earth metal clusters are more attractive in the field of oxide precursors. This is particularly due to the poor number of good alkaline earth metal candidates for the synthesis of mixed oxide-ceramic compounds and the difficulty to synthesize them.

This is one of the principal reason which encouraged us to study the different components involved in the general synthetic pathway described in the introduction (Equation 1).

C - I - Starting materials 1-12

This thesis reports the synthesis and characterization of twelve new molecular alkaline earth metal iodides compounds (**1**-**12**). Among these starting materials, eight homoleptic (**1**-**8**) and four heteroleptic (**9**-**12**) adducts are presented. These two groups of compounds show different behaviour and reactivity. In a general way, whereas homoleptic derivatives are not reactive towards any organo-alkali reagents, heteroleptic compounds, obtained by the simple introduction of THF molecule(s), present a very good reactivity or even as well as the common THF-adducts.

Moreover, homoleptic adducts show the importance of the ionic radii of the metal cation versus the size of the O-donor Lewis-coordinating ligand. In order to saturate the alkaline earth metal cation, a competition generally occurs between the iodide counter anions and the O-donor ligands, alkaline earth metals being hard cations. This leads in some case to the formation of separate ion-pairs. Figure 121 shows examples of the effect of the increase in size of the O-donor ligands on the overall structure of homoleptic strontium derivatives.

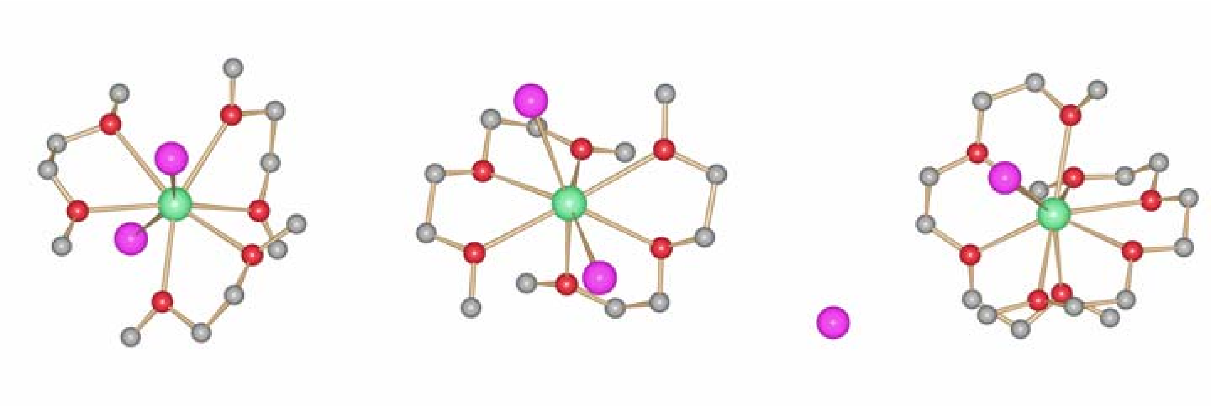


Figure 121. Schematic representation of *trans*-[$SrI_2(dme)_3$] 2 (left), *cis*-[$SrI_2(diglyme)_2$] 5 (center) and [$SrI(triglyme)_2$]I 7 (right) showing the influence of the size of the O-donor ligands on the overall structure of strontium derivatives, H atoms are omitted for clarity

C - II - Alkali and alkaline earth metal clusters

We are interested in synthesizing alkaline earth metal alkoxides and aryloxides starting from the parent iodides in order to i) have a new possible access to alkoxides and aryloxides, ii) show that alkaline earth metal iodides can react in a similar way as transition metal halides, and iii) allow the formation of new group 2 metal cage-compounds.
During this work, two new alkali aryloxide derivatives (**13**-**14**) and thirteen new alkaline earth metal clusters (**15**, **17**-**19**, **22**-**30**) have been synthesized and characterized. The results obtained lead to some remarks and outlines which are here presented.

C - II.1 - Influence of the alkaline earth metal

Whereas the first part of this thesis shows the influence of the ionic radius of the alkaline earth metal cation on the final structure of the compound in simple systems, in more complex systems, so in the formation of aggregates, the ionic radius of the metal cation does not have the same importance. Indeed, all cluster compounds have been obtained following the same procedure and present the same general packing of ligands in the coordination sphere of the metal cations resulting in very similar or even isostructural clusters, for instance [$IM(O^tBu)_4\{(Li(thf)\}_4(OH)$] and [$MM'_6(OPh)_8(thf)_6$] M = Ca, Sr, Ba; M'= Li, Na.

C - II.2 - Influence of the bulk of the alkyl-group R of the MOR compounds

Up to now, reacting the THF-species with LiOR, R = H, ^{t}Bu, yielded homo- [158] and heterometallic [162, 167] cage-compounds in which 50% of the initial iodide ligands was substituted by OR, whereas the other half remained linked to the cations in the newly formed cage-compound. Even with excess LiOR, R = H [158, 167], ^{t}Bu, we were unable to take off more than 50% of initial iodide under the commonly used reaction conditions (Figure 122).

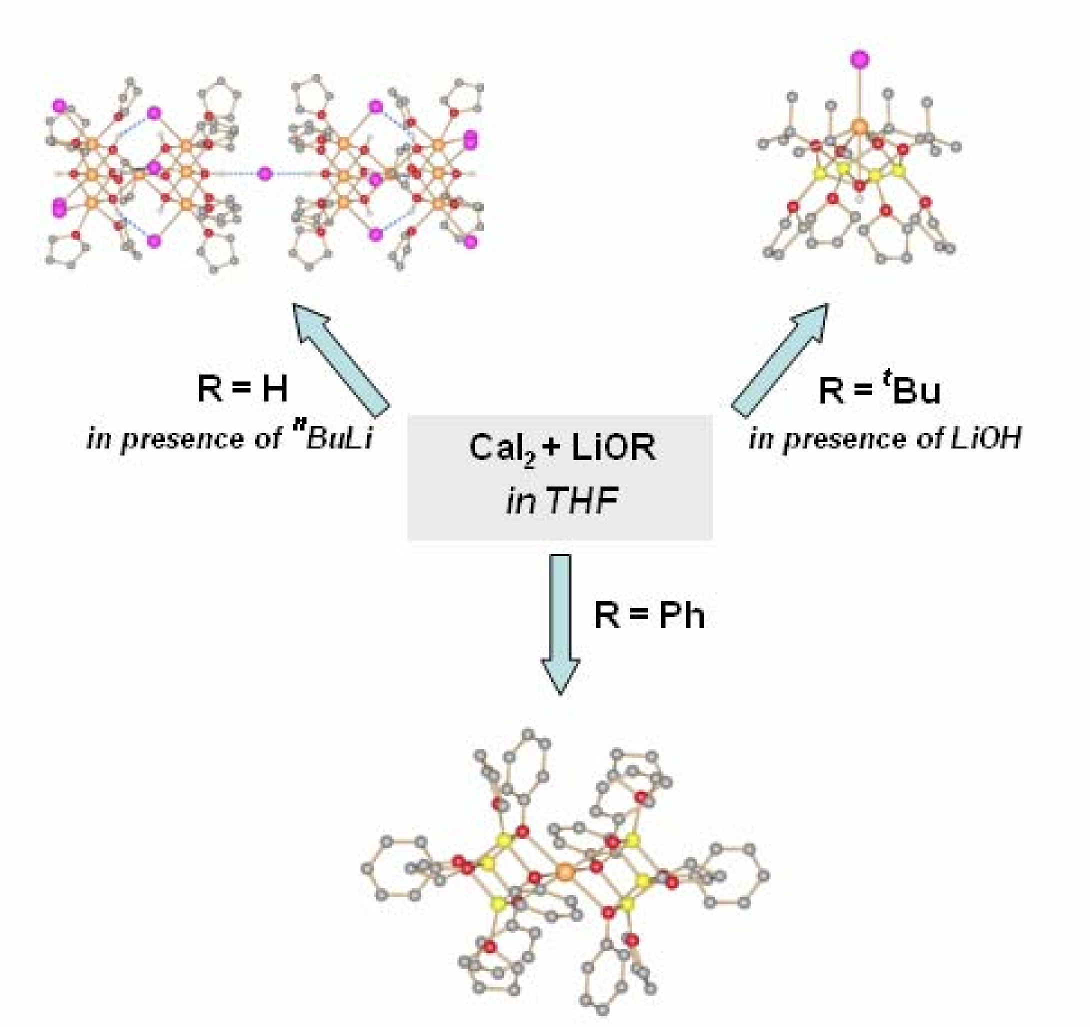


Figure 122. Examples of calcium clusters formation depending of the R-group of the "alkoxide" reagents

Following the same synthetic approach using a larger LiOR reagent such as “MOPh” (M = Li, Na) allows the complete substitution of iodide (Figure 122).

C - II.3 - Influence of the alkali metal

Two alkali metals have been studied during this work, lithium and respectively sodium cations. Among the different clusters described in this work some of them present interesting results. For instance, the use of a strongly basic mixture of NaO^{t}Bu and PhN(H)Li [372] is more efficient than LiO^{t}Bu or NaO^{t}Bu alone, and abstracts more than one iodide of each initial [SrI$_2$(thf)$_5$]-unit in the synthesis of **30**, [Li(thf)$_4$]$^+$[{Sr$_6$(O)(μ$_3$-I)(I)$_2$(O^{t}Bu)$_7$(thf)$_3$}$_2$(μ-I)]$^-$ (THF)$_n$ [170]. The more ionic, and thus more basic, sodium compound with respect to LiO^{t}Bu allows the substitution of more than half of the initially present iodide, without however complete ligand exchange. The substitution reaction however is not complete with respect to iodide, even if an excess of reagent is used. Also, no mixed alkali species as described by Mulvey *et al.* have been observed [405]. So, for the first time, we were able to replace ca 75% of initial iodide by O^{t}Bu-groups, this leading to the new type of aggregate.

On the other hand, the use of the "NaOPh" reagent in the synthesis of the clusters **22-24** does not lead to the characterization of new type of aggregates, clusters **22-24** possess the same general structure than the lithium clusters **17-19**. However, as cited in the introduction, the stability of alkaline earth metal clusters depends on a delicate balance of steric effects, metal size, ligand basicity and solubility equilibria. Thus, the formation of cage-compounds could be described as an equilibrium between a certain number of interdependent factors.

C - II.4 - Influence of the solvent

As outlined in different parts of this work, the solvent employed during the crystallization process also has a consequence on the overall structure of the derivatives as show the solid state structures of [CaM'$_6$(OPh)$_8$(thf)$_6$] (M' = Li **17**, Na **22**) and [{Ca(dme)}$_2$(OPh)$_6${M'(dme)}$_2$] (M' = Li **25**, Na **26**), the nature of the solvent can reorganized totally the coordination sphere of the metal cations.

C - III - Rare earth metal compounds

With regard to the results obtained for both, simple starting materials and more complex clusters, lanthanide(II) and alkaline earth metal cations exhibit very similar behaviour. More precisely, due to similar ionic radii and charge, the cation Ca^{2+} and Yb^{2+} as well as Sr^{2+} and Eu^{2+}/Sm^{2+} adopt in most cases similar coordination spheres and arrangements of ligands.

C - IV - Perspectives

The synthesis of these organometallic compounds based on alkali and alkaline earth metals is a further step in the preliminary work performed by Dr. Gueneau in our group. It allows the recognition of the importance of all the components involved in the reaction scheme tempted (Equation 1) and opened up a vast new field of main group metal chemistry in non-aqueous solvents.

The results obtained during this work allowed insight in some very fundamental questions of chemistry, such as the nature of the chemical bonding in such systems or why some clusters are volatile and others not? Theoretical calculations should be undertaken in order to elucidate the mechanism of formation of these clusters and the nature of the forces involved with the final aim to predict the geometry of these structures.

Further studies in solution (such as ^{7}Li- and ^{23}Na-NMR measurements) will allow to study the formation and reactivity of such clusters in more detail.

The obtained clusters are all new and allow new ideas about how to better access to new low-dimensional materials.

D - Experimental section

D - I - Materials and solvents

The hydrated and non-hydrated alkaline earth metal iodides CaI_2, SrI_2 and BaI_2 were purchased from Aldrich. The non hydrated compounds were stored under an inert atmosphere of nitrogen in a Labmaster glovebox by Braun.
All alkaline earth metal iodides (hydrated or not) were dried at 300°C under vacuum before use, to remove residual amounts of free iodine and water.

^{n}BuLi solutions, 1.6M/hexane or 2.5M/hexane, were purchased from Aldrich or Fluka and stored under nitrogen in a freezer.
LiO^{t}Bu 1M/THF and LiOPh 1M/THF were purchased from Aldrich.
Aniline ($PhNH_2$) was purchased from ACROS ORGANICS and was used with any further treatment.
NaO^{t}Bu and $NaOPh.3H_2O$ were purchased from Aldrich and were dried at 300°C under vacuum before use, to remove residual amounts of water.
Substituted alcohol 2,6-dimethylphenol was purchased from ACROS ORGANICS and used with any further treatment.

All ether and hydrocarbon solvents (tetrahydrofuran (THF), 1,2-dimetoxyethane (DME), diethyleneglycoldimethylether (diglyme), triethyleneglycoldimethylether (triglyme) and hexane) were purchased from ACROS ORGANICS. They were dried over sodium benzophenon ketyl and freshly distilled under nitrogen atmosphere at 760 mm Hg prior to use.

The starting materials $[CaI_2(thf)_4]$ [119], $[SrI_2(thf)_5]$ [155] and $[BaI_2(thf)_5]$ [150, 151] have been synthesized as described in the literature.

All reactions were handled under inert atmosphere of nitrogen or argon using schlenk techniques or in a Labmaster glovebox by Braun. For reactions in the microwave, reaction mixtures were stored under an atmosphere of argon.

D - II - Spectroscopic and analytical measurements

D - II.1 - Infrared spectroscopy

Fourier transform infrared (FTIR) spectra were acquired on a Shimazu FTIR-8400S spectrometer equipped with Golden Gate ATR (attenuated total reflection) system at the University of Basle or on a Perkin Elmer Spectrum One FT-IR spectrometer on CsI plates in Nujol at the University of Karlsruhe.

Spectra were recorded over a range of 4000-400 cm^{-1} with a resolution of 0.01 cm^{-1} (16 number of scans).

Abbreviations used are: s, strong; m, medium and w, weak.

D - II.2 - ^{1}H-NMR, ^{13}C-NMR, ^{7}Li-NMR and ^{23}Na-NMR measurements

High resolution ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker AV 400 MHz, Me_4Si was used as an internal standard. The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. Chemical shifts were determined with the solvent signal as reference:

For ^{13}C-NMR: CD_3CN at 1.24 ppm, C_4D_8O at 25.30 ppm

For ^{1}H-NMR: CD_3CN at 1.94 ppm, C_4D_8O at 1.73 ppm

^{7}Li-NMR and ^{23}Na-NMR measurements were performed on a Bruker Avance 600 MHz using 1M LiCl or 0.1M NaCl in D_2O solutions in sealed-capillaries as external standard.

D - II.3 - Single-crystal X-ray diffractometry (SCXRD)

Single-crystals were mounted on a glass fiber and all geometric and intensity data were taken from this crystal. Data collection using Mo-K_α radiation (λ = 0.71073 Å) was performed, at the University of Basle on a STOE IPDS-II diffractometer or at the University of Karlsruhe on a STOE STADI 4 diffractometer equipped with an Oxford Cryosystem open flow cryostat [406].

Absorption corrections were partially integrated in the data reduction procedure [407].

The structures were solved by direct methods (SHELXS) and refined using full-matrix least-squares on F^2 (SHELXL-97 [408] or SHELXL-99 [409]). All heavy atoms could be refined anisotropically. Hydrogen atoms were introduced as fixed contributors when a residual electronic density was observed near their expected positions.

Crystallographic data for the structures **1**, **5**, **15-26**, **29** and **30** have been deposited with the Cambridge Crystallographic Data Center with the CCDC numbers 206569, 206570, 616797, 616798, 296413, 616799, 616800, 616802, 616801, 616803, 616804, 616805, 296414 , 616806, 616807 and 609599 respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

D - II.4 - Elemental analysis

Elemental analyses were performed by Dr. W. Kirsch at the Microanalytical laboratory of the University of Basle or at the University of Karlsruhe.

D - II.5 - Mass spectrometry (MS)

All the alkaline earth metal cluster compounds with general formula $[MM_6'(OPh)_8(thf)_6]$ (M = Ca, Sr, Ba; M' = Li, Na) have been submitted to a Mass Spectroscopy analysis.
Fast Atom Bombardment (FAB) and Electron Impact (EI) were recorded on a Finnigan MAT 95Q and respectively a Finnigan MAT 8400. For FAB measurements, m-nitro-benylalkohol (NBA) or glycerin (GLY) were used as matrix.
However, these measurements were impossible to perform on these samples or gave inconsistent results.

D - II.6 - Atomic absorption spectroscopy (AAS)

The AAS was carried out on a Shimadzu AA6300 with air/C_2H_2 flame, dissolving compound in milliQ water. Solutions were tested with the corresponding lamps for presence of lithium (670.8 nm, 8 mA) and sodium (589.0 nm, 12 mA), and the results compared with standardized curves.

D - II.7 - Representation of graphics

Crystal graphics were carried out using SCHAKAL [410], POV-RAY [411] and DIAMOND [412] software.

D - III - Synthesis of starting materials

D - III.1 - Synthesis of pure ethereal complexes 1-8

D - III.1.1 - [CaI(dme)$_3$]I 1

CaI$_2$ (0.245 g, 0.83 mmol) was dried under vacuum for half an hour at 300 °C, and then dissolved in 30 mL of freshly dried and distilled DME by heating to reflux for 15 minutes. The solution was filtered while hot, and colourless single-crystals of **1** formed within one day at room temperature. Out of the mother liquor, crystals quickly lose solvent, as can be observed under the microscope, where they turn from clear colourless to opaque. The yield has therefore been estimated at 70% with reference to CaI$_2$. The low evaporation temperature of DME can explain the values found for elemental analysis, where values are generally too low.

$C_{24}H_{60}Ca_2I_4O_{12}$ (1128.48 g.mol^{-1}): calcd C 25.54, H 5.36; found C 21.47, H 4.90

IR (nujol, CsI plates, cm^{-1}): υ = 2059(w), 1915(w), 1622(m), 1465(Nujol), 1374(Nujol), 1285(s), 1247(s), 1192(s), 1123(w, sh), 937(w), 863 (Nujol), 859(vs), 721(Nujol), 569(m), 387(s)

D - III.1.2 - [CaI(dme)$_3$]I 1a

CaI$_2$ (0.298 g, 1.01 mmol) was dried under vacuum for half an hour at 300 °C, and then dissolved in 20 mL of freshly dried and distilled DME by heating to reflux for 15 minutes. At room temperature, not at all dissolves, the white-yellow mixture is treated with 3 equivalents of a 2M ^{n}BuLi solution in hexane (1.52 mL) under an inert atmosphere of nitrogen. The reaction solution turned white and was allowed to stand at room temperature for two days after which colourless crystals of **1a** grow with a small amount of white precipitate. The yield has therefore been estimated at 82% with reference to CaI$_2$.

$C_{12}H_{30}CaI_2O_6$ (564.24 g.mol^{-1}): calcd C 25.54, H 5.36; found C 24.36, H 5.02 (same behaviour as **1**)

IR (cm$^{-1)}$: υ = 2836(m), 1607(m), 1451(m), 1192(w), 1093(w), 1050(s), 976(w), 855(s), 536 (vs), 470(s), 450(vs)

D - III.1.3 - Trans-[$SrI_2(dme)_3$] 2

SrI_2 (0.345 g, 1.01 mmol) was dried under vacuum for half an hour at 300 °C, and then dissolved in 30 mL of freshly dried and distilled DME by heating to reflux for 10 minutes. The solution was filtered while hot, and colourless single-crystals of **2** formed within two days at low temperature (-25°C). The yield has therefore been estimated at 74% with reference to SrI_2.

$C_{12}H_{30}SrI_2O_6$ (611.79 $g.mol^{-1}$): calcd C 23.56, H 4.94; found C 18.51, H 3.89 (same behaviour as **1**: loss of one DME molecule)

IR (cm^{-1}): υ = 2825(w), 1610(m), 1447(m), 1235(m), 1136(m), 1192(s), 1101(m), 1052(vs), 1016(w), 854(vs), 826(m), 532(vs), 419(s)

D - III.1.4 - Trans-[$BaI_2(dme)_3$] 3

BaI_2 (0.401 g, 1.02 mmol) was dried under vacuum for half an hour at 300 °C, and then dissolved in 40 mL of freshly dried and distilled DME by heating to reflux for 15 minutes. The solution was filtered while hot, and colourless single-crystals of **3** formed within one day at low temperature (-25C). Out of the mother liquor, crystals quickly lose solvent, as can be observed under the microscope, where they turn from clear colourless to opaque. The yield has therefore been estimated at 68% with reference to BaI_2.

$C_{12}H_{30}BaI_2O_6$ (661.50 $g.mol^{-1}$): calcd. C 21.79, H 4.57; found C 18.29, H 3.88 (same behaviour as **1**)

IR (cm^{-1}): υ = 1280(m), 1250(m), 1116(w), 1066(m), 854(s), 552(m), 469(s), 412(m)

D - III.1.5 - [CaI(diglyme)$_2$]I 4

CaI_2 (0.310 g, 1.05 mmol) was dried for 30 min under vacuum at 300 °C and then dissolved in 30 mL of freshly dried and distilled diglyme, heating to reflux. The solution was filtered while hot and was then left to stand at room temperature. After one week, colourless single-crystals grow at room temperature in a yield of 29% with respect to CaI_2.

$C_{12}H_{28}CaI_2O_6$ (562.24 $g.mol^{-1}$): calcd C 25.64, H 5.02; found C 25.31, H 4.93

IR (cm^{-1}): υ = 2833(m), 1610(m), 1454(m), 1094(s), 1052(s), 1009(s), 861(m), 840(m), 535(s), 527(m), 464(s), 431(m)

D - III.1.6 - Cis-[SrI$_2$(diglyme)$_2$] 5

SrI_2 (0.174 g, 0.51 mmol) was dried for 30 min under vacuum at 300 °C and then dissolved in 30 mL of freshly dried and distilled diglyme, heating to reflux under magnetic stirring. Not at all dissolves, the solution was filtered while hot and was then left to stand at room temperature. After two days, colourless single-crystals grow in a yield of 78% with respect to SrI_2.

$C_{24}H_{56}I_4O_{12}Sr_2$ (1219.52 g.mol^{-1}): calcd C 23.64, H 4.63; found C 25.97, H 5.27

The differences between found and calculated values are due to solvent, which remains on the crystals as they can't be dried under vacuum, and decompose rapidly if left in air.

IR (nujol, CsI plates, cm^{-1}): υ = 2849 (Nujol), 2077(w), 1971(w), 1939(w), 1605, 1459(Nujol), 1380(m), 1354(Nujol), 1286(m), 1269(w), 1249(vs), 1203(vs), 1129(s, sh), 944(m), 870(s), 839(s), 723(Nujol), 559(s), 489(w), 461(m), 367(w)

D - III.1.7 - Trans-[BaI$_2$(diglyme)$_2$] 6

BaI_2 (0.418 g, 1.07 mmol) was dried for 30 min under vacuum at 300 °C and then dissolved in 40 mL of freshly dried and distilled diglyme, heating to reflux. The solution was filtered while hot and was then left to stand at room temperature. After two days, colourless single-crystals grow in a yield of 62% with respect to BaI_2.

$C_{24}H_{60}Ba_2I_4O_{12}$ (1312.96 g.mol^{-1}): calcd C 21.77, H 4.57; found C 20.83, H 4.29

IR (cm^{-1}): υ = 2840(m), 1650(m), 1915(w), 1457(w), 1285(s), 1085(s), 1064(s), 868(m), 571(s), 481(w), 456(m), 340(w)

D - III.1.8 - [SrI(triglyme)$_2$]I 7

SrI_2 (0.382 g, 1.12 mmol) was dried for 30 min under vacuum at 300 °C and then dissolved in 50 mL of freshly dried and distilled triglyme, heating to reflux until complete dissolution of SrI_2. The solution was then left to stand at room temperature. After one week, colourless single-crystals grow in a yield of 61% with respect to SrI_2.

The differences between found and calculated values are due to solvent, which remains on the crystals as they can't be dried under vacuum, and decompose rapidly if left in air.

$C_{16}H_{36}SrI_2O_8$ (697.87 g.mol^{-1}): calcd C 27.51, H 5.24; found C 29.87, H 6.02

IR (cm^{-1}): υ = 2036(m), 1910(w), 1622(m), 1268(s), 1239(s), 1152(s), 923(w), 856(vs), 485(s), 460(m), 423(m) 424(m)

D - III.1.9 - [BaI(triglyme)$_2$]I 8

BaI_2 (0.403 g, 1.03 mmol) was dried for 30 min under vacuum at 300 °C and then dissolved in 50 mL of freshly dried and distilled triglyme, heating to reflux until complete dissolution of the BaI_2. The solution was then left to stand at room temperature. After three days, colourless single-crystals grow in a yield 56% respect to BaI_2. The differences between found and calculated values are due to solvent, which remains on the crystals as they can't be dried under vacuum, and decompose rapidly if left in air.

$C_{16}H_{36}BaI_2O_8$ (747.59 g.mol^{-1}): calcd C 25.71, H 4.85; found C 31.40, H 5.76 (same behaviour as **7**)

IR (cm^{-1}): υ = 2043(w), 1889(w), 1620(m), 1240(s), 1186(s), 1119(w, sh), 923(w), 861(vs), 540(s), 487(s), 438(m), 406(s)

D - III.2 - Synthesis of mixed ethereal complexes 9-12

D - III.2.1 - Trans-[CaI$_2$(dme)$_2$(thf)] 9

CaI_2 (0.365 g, 1.24 mmol) was dried for 30mn under vacuum at 300°C and then dissolved in 40mL of freshly dried and distilled 1:1 mixture of THF-DME, heating to reflux under magnetic stirring. At room temperature a light yellow solution is obtained from which colourless single-crystals of **9** grew during the night in a yield of 90% with respect to CaI_2.

The low evaporation temperature of DME and THF can explain the values found for elemental analysis, where values are generally too low.

$C_{12}H_{28}CaI_2O_5$ (546.24 g.mol^{-1}): calcd C 26.39, H 5.17; found C 23.52, H 4.79

IR (cm^{-1}): υ = 2833(w), 1646(m), 1610(s), 1440(s), 1243(m), 1193(s), 1109(s), 1052(s), 861(s), 489(m), 455(m), 437(m), 411(s)

D - III.2.2 - Trans-[SrI$_2$(dme)$_2$(thf)] 10

SrI_2 (0.39g, 1.141 mmol) was dried for 30mn under vacuum at 300°C and then dissolved in 40mL of freshly dried and distilled 3:1 mixture of THF-DME, heating to reflux under magnetic stirring. At room temperature a light yellow solution is obtained which was cooled at -25°C to give colourless single-crystals of **10** within two days in a yield of 84% with respect to SrI_2.

$C_{12}H_{28}SrI_2O_5$ (593.78 g.mol^{-1}): calcd C 24.27, H 4.75; found C 16.92, H 4.29 (same behaviour as **9**)

IR (cm^{-1}): υ = 2846(w), 1603(m), 1454(m), 1240(m), 1119(m), 1051(s), 863(s), 836(m), 686(w), 552(s), 540(vs), 526(w), 442(s), 430(m)

D - III.2.3 - Trans-[BaI$_2$(dme)$_2$(thf)$_2$] 11

BaI_2 (0.43g, 1.098 mmol) was dried for 30mn under vacuum at 300°C and then dissolved in 40mL of freshly dried and distilled 3:1 mixture of THF-DME, heating to reflux under magnetic stirring. At room temperature a light yellow solution is obtained which was cooled at -25°C to give colourless single-crystals of **11** within two days in a yield of 83% with respect to BaI_2.

$C_{16}H_{36}BaI_2O_6$ (715.59 g.mol^{-1}): calcd C 26.86, H 5.07; found C 19.30, H 3.92 (same behviour as **9**)

IR (cm^{-1}): υ = 2833(w), 1592(s), 1451(m), 1191(w), 1112(m), 1057(s), 1024(m), 856(s), 834(m), 689(w), 534(s), 530(s), 486(m), 472(m), 452(m), 414(m)

D - III.2.4 - Trans-[CaI$_2$(diglyme)(thf)$_2$] 12

CaI_2 (0.300 g, 1.02 mmol) was dried for 30mn under vacuum at 300°C and then dissolved in 40mL of freshly dried and distilled 1:1 mixture of THF-diglyme, heating to reflux under magnetic stirring. At room temperature a light yellow solution is obtained which was cooled at -25°C to give colourless single-crystals of **12** within two days in a yield 73% with respect to CaI_2.

$C_{14}H_{30}CaI_2O_5$ (572.28 g.mol^{-1}): calcd C 29.38, H 5.28; found C 27.16, H 4.99 (loss of one THF molecule)

IR (cm^{-1}): υ = 2881(w), 2825(w), 1610(w), 1458(m), 1357(w), 1244(m), 1088(s), 1052(s), 934(m), 860(s), 835(m), 532(vs), 494(m), 447(s), 429(m), 417(m)

D - III.3 - Synthesis of alkali phenoxide clusters 13-14

D - III.3.1 - [Na(OPh)(dme)]$_4$ 13

In a schlenck, SrI_2 (0.350 g, 1.02 mmol) was dried for 30 mn under vacuum at 300°C and then dissolved in 15 mL of freshly dried and distilled THF, heating to reflux under magnetic stirring. In another schlenck, $NaOPh.3H_2O$ (10 eq, 1.744 g) was dried for 30 mn under vacuum at 300°C and then dissolved in 20 mL of freshly dried and distilled THF. At room temperature, both solutions are mixed together under nitrogen. The clear light brown solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was evaporated to dryness yielding a light brown solid which was partially dissolved in 10 mL of DME. The mixture was left at room temperature under magnetic stirring one night and then filtered.

Colourless single-crystals of **13** suitable for X-ray analysis grow in a yield of 58% with respect to NaOPh at -25°C within one week at low temperature (-25°C).

$C_{40}H_{60}Na_4O_{12}$ (824.87 g.mol^{-1}): calcd C 58.24, H 7.33; found C 57.96, H 7.30

^{13}C NMR data (d^{8}-THF): 58.90 (s), 72.23 (s), 112.21 (s), 119.42 (s), 129.78 (s), 170.83 (s)

^{1}H NMR data (d^{8}-THF): 3.27 (d), 3.43 (d), 6.201 (t), 6.44 (d), 6.88 (t)

^{23}Na NMR data (d^{10}-DME): broad signal centered at 1.31 ppm

D - III.3.2 - [Li(2,6-Me_2-C_6H_3O)(dme)]$_2$ 14

CaI_2 (0.280 g, 0.95 mmol) was dried for 30mn under vacuum at 300°C and then dissolved in 20mL of freshly dried and distilled THF, heating to reflux under magnetic stirring. To this solution was added a (2,6-Me_2-C_6H_3O)Li solution in THF (~10 eq, prepared from a equal amount of 2,6-Me_2-C_6H_3OH (1.222 g, 10 mol) and ^{n}BuLi (4 mL, 10 mol)). After one night at room temperature under magnetic stirring the solution turned purple. This purple solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was evaporated to dryness yielding purple solid which was partially dissolved in 10 mL of DME. The mixture was left at room temperature under magnetic stirring one night and then filtered and then cooled at -25°C to give colourless single-crystals of **14** within two days in a yield of 26% with respect to 2,6-Me_2-C_6H_3OH.

$C_{72}H_{114}O_{18}Li_6$ (1309.26 g.mol^{-1}): calcd C 66.05, H 8.78; found C 65.63, H 8.25

^{13}C NMR data (d^{8}-THF) : 18.24 (s), 58.89 (s), 72.74 (s), 112.86 (s), 125.21 (s), 128.30 (s)

^{1}H NMR data (d^{8}-THF) : 2.15 (s), 3.27 (d), 3.43 (d), 6.14 (t), 6.72 (d)

D - III.4 - Synthesis of heterometallic alkoxide clusters 15-16

D - III.4.1 - [ICa(O^{t}Bu)$_4${Li(thf)}$_4$(OH)].THF 15

Method A:

CaI_2 (0.294 g, 1.00 mmol) was dried for 30 mn under vacuum at 300°C and then dissolved in 20 mL of freshly dried and distilled THF, heating to reflux under magnetic stirring. At room temperature, a 1M solution of LiO^{t}Bu in THF (10 eq, 10.0 mL) was added drop wise under nitrogen. The solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was filtered. The yellow brown solution was cooled at -25°C to give colourless single-crystals of **15** with a small amount of white precipitate within one week in a yield of 45% with respect to CaI_2.

Method B:

CaI_2 (0.302 g, 1.03 mmol) was dried for 30 mn under vacuum at 300°C and then dissolved in 30 mL a 1:1 mixture of freshly dried and distilled THF/DME, heating to reflux under magnetic stirring to give the starting material [CaI_2(dme)$_2$(thf)] **9**. At room temperature, a 1M solution of LiO^{t}Bu in THF (4 eq, 4.1 mL) was added drop wise under nitrogen. The solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was filtered. The yellow brown solution was cooled at -25°C to give colourless single-crystals of **15** with a small amount of white precipitate within three days in a yield of 70% with respect to CaI_2.

$C_{36}H_{77}Li_4CaIO_{10}$ (864.72 g.mol^{-1}): calcd C 50.00, H 8.97; found C 44.71, H 8.07 (loss of three THF molecules)

IR (cm^{-1}): υ = 2885(w), 1462(w), 1357(m), 1200(s), 1036(m), 957(s), 902(m), 758(w), 655(w), 594(m)

^{7}Li NMR data (d^8-THF): 0.953

^{13}C NMR data (CD_3CN) : 26.16 (s), 31,33 (s), 68.21 (s)

^{1}H NMR data (CD_3CN) : 1.17 (s), 1.80 (m), 2.44 (s), 3.64 (m)

D - III.4.2 - [IEu(O^{t}Bu)$_4${Li(thf)}$_4$(OH)].THF 16

In a Labmaster glovebox under an inert atmosphere of nitrogen, a 1M solution of LiO^{t}Bu in THF (5 eq, 4.3 mL) was added drop wise to EuI_2 solid (0.350 g, 0.86 mmol). At room temperature, the solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was filtered. The red brown solution was cooled at -25°C to give colourless single-crystals of **16** with a small amount of green precipitate within several months (6 months) in a very low yield which couldn't be estimated. Elemental analysis and NMR-studies were unfortunately impossible to perform on this compound.

D - III.5 - Synthesis of heterometallic phenoxide clusters 17-28

D - III.5.1 - [CaLi$_6$(OPh)$_8$(thf)$_6$] 17

Method A:

CaI_2 (0.301 g, 1.02 mmol) was dried for 30 mn under vacuum at 300°C and then dissolved in 20 mL of freshly dried and distilled THF, heating to reflux under magnetic stirring. At room temperature, a 1M solution of LiOPh in THF (10 eq, 10.2 mL) was added drop wise under nitrogen. The solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was evaporated to dryness yielding a brown solid which was partially dissolved in 15 mL of a 1:10 THF / hexane mixture. The mixture was left at room temperature under magnetic stirring one night and then filtered.

Method B:

The method is similar to the method A except that CaI_2 (0.290 g, 0.99 mmol) was dried for 30mn under vacuum at 300°C before being dissolved in a 1:1 mixture of dried and distilled THF/DME in order to form the compound [CaI_2(dme)$_2$(thf)] **9**.

Method C:

CaI_2 (0.102 g, 0.35 mmol) was dried for 30 mn under vacuum at 300°C. At room temperature, a 1M solution of LiOPh in THF (3 eq, 1.05 mL) was added drop wise under argon. The mixture was then placed in a microwave at 500W during 2mn.

Colourless single-crystals of **17** suitable for X-ray analysis grow in a yield of 72% with respect to CaI_2 at room temperature within three days.

$C_{72}H_{88}CaLi_6O_{14}$ (1259.14 g.mol^{-1}): Calcd C 68.68, H 7.04, O 17.79; Found C 67.85, H 6.99, O 17.56

^{7}Li NMR data (233.23 MHz, d^8-THF): 0.79, 1.07

^{13}C NMR data (d^8-THF) : 26.36 (s, CH_2); 68.21 (s, CH_2O); 115.01 (s), 120.31 (s), 129.53 (s)

^{1}H NMR data (d^8-THF) : 1.78 (m, CH_2); 3.62 (m, CH_2O); 6.38 (s); 6.70 (d); 6.94 (s)

^{13}C NMR data (CD_3CN) : 26.15 (s, CH_2), 68.28 (s, CH_2O), 115.59 (s), 120.71 (s), 129.49 (s), 166.58(s)

D - III.5.2 - [SrLi$_6$(OPh)$_8$(thf)$_6$] 18

Method A:

SrI_2 (0.351 g, 1.03 mmol) was dried for 30 mn under vacuum at 300°C and then dissolved in 25 mL of freshly dried and distilled THF, heating to reflux under magnetic stirring. At room temperature, a 1M solution of LiOPh in THF (10 eq, 10.3 mL) was added drop wise under nitrogen. The solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was evaporated to dryness yielding a brown solid which was partially dissolved in 15 mL of a 1:10 THF / hexane mixture. The mixture was left at room temperature under magnetic stirring one night and then filtered.

Method B:

The method is similar to the method A except that SrI_2 (0.399 g, 1.17 mmol) was dried for 30mn under vacuum at 300°C before being dissolved in a 3:1 mixture of dried and distilled THF/DME in order to form the compound [SrI_2(dme)$_2$(thf)] **10**.

Method C:

SrI_2 (0.110 g, 0.32 mmol) was dried for 30 mn under vacuum at 300°C. At room temperature, a 1M solution of LiOPh in THF (3 eq, 1.08 mL) was added drop wise under argon. The mixture was then placed in a microwave at 500W during 2mn.

Colourless single-crystals of **18** suitable for X-ray analysis grow in a yield of 56% with respect to SrI_2 at -25°C within three days. The low evaporation temperature of THF can explain the values found for elemental analysis, where values are generally too low.

$C_{72}H_{88}SrLi_6O_{14}$ (1306.68 g.mol^{-1}): Calcd C 66.18, H 6.79; Found C 64.03, H 6.67

^{7}Li NMR data (d^8-THF): 0.975 and 0.825 (hydrolysis of the solution is envisaged)

^{13}C NMR data (d^8-THF) : 26.37 (s, CH_2), 68.21 (s, CH_2O), 114.79 (s), 119.41 (s), 129.62 (s),

^{1}H NMR data (d^8-THF) : 1.78 (m, CH_2), 3.62 (m, CH_2O), 6.39 (t), 6.60 (d), 6.95 (t)

D - III.5.3 - [BaLi$_6$(OPh)$_8$(thf)$_6$] 19

Method A:

BaI_2 (0.402 g, 1.03 mmol) was dried for 30 mn under vacuum at 300°C and then dissolved in 25 mL of freshly dried and distilled THF, heating to reflux under magnetic stirring. At room temperature, a 1M solution of LiOPh in THF (10 eq, 10.3 mL) was added drop wise under nitrogen. The solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was evaporated to dryness yielding a brown solid which was partially dissolved in 15 mL of a 1:10 THF / hexane mixture. The mixture was left at room temperature under magnetic stirring one night and then filtered.

Colourless single-crystals of **19** suitable for X-ray analysis grow in a yield of 68% with respect to BaI_2 at -25°C within three days.

Method B:

The method is similar to the method A except that BaI_2 (0.135 g, 0.34 mmol) was dried for 30mn under vacuum at 300°C before being dissolved in a 3:1 mixture of dried and distilled THF/DME in order to form the compound $[BaI_2(dme)_2(thf)_2]$ **11**.

$C_{72}H_{88}BaLi_6O_{14}$ (1356.45 g.mol^{-1}): Calcd C 63.75, H 6.54; Found C 60.51, H 6.07 (similar behaviour as **18**)

^{7}Li NMR data (d^8-THF): 0.821

^{13}C NMR data (d^8-THF) : 26.36 (s, CH_2), 68.21 (s, CH_2O), 114.38 (s), 119.82 (s), 129.59 (s), 167.92 (s)

^{1}H NMR data (d^8-THF) : 1.78 (m, CH_2) 3.62 (m, CH_2O), 6.36 (t), 6,59 (d), 6.95 (t)

D - III.5.4 - [EuLi$_6$(OPh)$_8$(thf)$_6$] 20

In the labmaster glovebox, a 1M solution of LiOPh in THF (10 eq, 10.1 mL) was added drop wise under nitrogen to EuI_2 (0.410 g, 1.01 mmol). The colorless solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was evaporated to dryness yielding a light green-blue solid which was partially dissolved in 15 mL of a 1:10 THF / hexane mixture. The mixture was left at room temperature under magnetic stirring one night and then filtered.

Colourless single-crystals of **20** suitable for X-ray analysis grow in a yield of 24% with respect to EuI_2 at -25°C within two weeks. Unfortunately, crystals of **20** are very sensitive to air and moisture and the crystals melt within two minutes of the mother liquor being removed, even though working under argon. Elemental analysis and NMR-studies were unfortunately impossible to perform on these samples or gave inconsistent results.

D - III.5.5 - [SmLi$_6$(OPh)$_8$(thf)$_6$] 21

Method A:

In the labmaster glovebox, a 1M solution of LiOPh in THF (10 eq, 10 mL) was added drop wise under nitrogen to a 0.1 M solution of SmI_2 in THF (10 mL, 1.0 mmol). The blue-purple solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was evaporated to dryness yielding a blue solid which was partially dissolved in 15 mL of a 1:10 THF / hexane mixture. The mixture was left at room temperature under magnetic stirring one night and then filtered.

Method B:

In a labmaster glovebox, under an inert atmosphere of nitrogen, a 1M solution of LiOPh in THF (3 eq, 1.5 mL) was added drop wise to a 0.1 M SmI_2 solution in THF (5.0 mL, 0.5 mmol). At room temperature under argon, the mixture was placed in a microwave at 500W during 2mn.

Colourless single-crystals of **21** suitable for X-ray analysis grow in a yield of 45% with respect to SmI_2 at -25°C within two weeks.

^{13}C NMR data (d^8-THF) : 26.31 (m, CH_2), 68.18 (m, CH_2O), 115.33 (m), 118.78 (m), 129.53 (m)

^{1}H NMR data (d^8-THF) : 1.63 (m, CH_2), 3.47 (m, CH_2O), 6.28 (t), 6.45 (d), 6.82 (t)

While Sm(II) is a paramagnetic species, only little shift have been observed for the spectra compared to the others $[MLi_6(OPh)_8(thf)_6]$ compounds **17**-**19**.

D - III.5.6 - [CaNa$_6$(OPh)$_8$(thf)$_6$] 22

In a schlenck, CaI_2 (0.301 g, 1.02 mmol) was dried for 30 mn under vacuum at 300°C and then dissolved in 15 mL of freshly dried and distilled THF, heating to reflux under magnetic stirring. In another schlenck, $NaOPh.3H_2O$ (10 eq, 1.742 g) was dried for 30 mn under vacuum at 300°C and then dissolved in 20 mL of freshly dried and distilled THF. At room temperature, both solutions are mixed together under nitrogen. The solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was evaporated to dryness yielding a light brown solid which was partially dissolved in 15 mL of a 1:10 THF / hexane mixture. The mixture was left at room temperature under magnetic stirring one night and then filtered.

Colourless single-crystals of **22** suitable for X-ray analysis grow in a yield of 65% with respect to CaI_2 at -25°C within three days.

$C_{72}H_{88}CaNa_6O_{14}$ (1355.44 g.mol^{-1}): Calcd C 63.80, H 6.54; Found C 57.70, H 5.46 (similar behaviour as **18**)

^{23}Na NMR data (d^8-THF): broad signal centered at 1.23 ppm

^{13}C NMR data (d^8-THF) : 26.36 (s, CH_2), 68.21 (s, CH_2O), 114.59 (s), 119.68 (s), 129.62 (s), 167.14 (s)
^{1}H NMR data (d^8-THF) : 1.78 (m, CH_2), 3.62 (m, CH_2O), 6.35 (t), 6.68 (d), 6.92 (t)

D - III.5.7 - [SrNa$_6$(OPh)$_8$(thf)$_6$] 23

In a schlenck, SrI_2 (0.362 g, 1.06 mmol) was dried for 30 mn under vacuum at 300°C and then dissolved in 15 mL of freshly dried and distilled THF, heating to reflux under magnetic stirring. In another schlenck, NaOPh.3H_2O (10 eq, 1.804 g) was dried for 30 mn under vacuum at 300°C and then dissolved in 20 mL of freshly dried and distilled THF. At room temperature, both solutions are mixed together under nitrogen. The solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was evaporated to dryness yielding a light brown solid which was partially dissolved in 15 mL of a 1:10 THF / hexane mixture. The mixture was left at room temperature under magnetic stirring one night and then filtered.
Colourless single-crystals of **23** suitable for X-ray analysis grow in a yield of 63% with respect to SrI_2 at -25°C within three days.
$C_{72}H_{88}SrNa_6O_{14}$ (1402.98 g.mol^{-1}): Calcd C 61.62, H 6.31; Found C 59.83, H 5.95 (similar behaviour as **18**)

D - III.5.8 - [BaNa$_6$(OPh)$_8$(thf)$_6$] 24

In a schlenck, BaI_2 (0.405 g, 1.03 mmol) was dried for 30 mn under vacuum at 300°C and then dissolved in 15 mL of freshly dried and distilled THF, heating to reflux under magnetic stirring. In another schlenck, NaOPh.3H_2O (10 eq, 1.762 g) was dried for 30 mn under vacuum at 300°C and then dissolved in 20 mL of freshly dried and distilled THF. At room temperature, both solutions are mixed together under nitrogen. The solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was evaporated to dryness yielding a light brown solid which was partially dissolved in 15 mL of a 1:10 THF / hexane mixture. The mixture was left at room temperature under magnetic stirring one night and then filtered.
Colourless single-crystals of **24** suitable for X-ray analysis grow in a yield of 65% with respect to BaI_2 at -25°C within three days.

$C_{72}H_{88}BaNa_6O_{14}$ (1452.70 g.mol^{-1}): Calcd C 59.51, H 6.11; Found C 56.63, H 6.02 (similar behaviour as **18**)

^{23}Na NMR data (d^8-THF): very broad signal centered at 2.58 ppm

^{13}C NMR data (d^8-THF) : 26.36 (s, CH_2), 68.21 (s, CH_2O), 112.66 (s), 119.54 (s), 129.69 (s), 169.95 (s)

^{1}H NMR data (d^8-THF) : 1.77 (m, CH_2), 3.61 (m, CH_2O), 6.22 (d), 6.49 (d), 6.86 (t)

D - III.5.9 - [{Ca(dme)}$_2$(OPh)$_6${Li(dme)}$_2$] 25

CaI_2 (0.2696 g, 0.92 mmol) was dried for 30mn under vacuum at 300°C and then dissolved in 20 mL of freshly dried and distilled THF, heating to reflux under magnetic stirring. At room temperature, a 1M solution of LiOPh in THF (6 eq, 5.5 mL) was added drop wise under nitrogen. The solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was evaporated to dryness yielding a brown solid which was partially dissolved in 10 mL of DME. The mixture was left at room temperature under magnetic stirring one night and then filtered.

During the night at room temperature, colourless single-crystals of **25** suitable for X-ray analysis grow in a yield of 64% with respect to CaI_2.

$C_{52}H_{70}Ca_2Li_2O_{14}$ (1013.12 g.mol^{-1})**:** Calcd C 61.65, H 6.96, O 22.11; Found C 59.47, H 6.87, O 21.79

^{7}Li NMR data (233.23 MHz, d^{10}-DME): 1.01

^{13}C NMR (CD_3CN): 58.80 (s, CH_3); 72.04 (s, CH_2); 115.63 (s), 120.92 (s), 129.20 (s), 166.23(s)

^{1}H NMR data (CD_3CN) : 3.29 (s, CH_3); 3.46 (s, CH_2); 6.43 (s); 6.73 (d); 6.88 (s)

^{1}H NMR data (d^8-THF) : 3.27 (d, CH_3); 3.43 (d, CH_2); 6.42 (s); 6.72 (d); 6.95 (s)

D - III.5.10 - [{Ca(dme)}$_2$(OPh)$_6${Na(dme)}$_2$] 26

In a schlenck, CaI_2 (0.301 g, 1.02 mmol) was dried for 30 mn under vacuum at 300°C and then dissolved in 15 mL of freshly dried and distilled THF, heating to reflux under magnetic stirring. In another schlenck, $NaOPh.3H_2O$ (10 eq, 1.742 g) was dried for 30 mn under vacuum at 300°C and then dissolved in 20 mL of freshly dried and distilled THF. At room temperature, both solutions are mixed together under nitrogen. The solution was left at room temperature under magnetic stirring during two days Afterwards the solution was evaporated to dryness yielding a brown solid which was partially dissolved in 10 mL of DME. The mixture was left at room temperature under magnetic stirring one night and then filtered. Colourless single-crystals of **26** suitable for X-ray analysis grow in a yield of 65% with respect to CaI_2 at -25°C within three days.

$C_{52}H_{70}Ca_2Na_2O_{14}$ (1045.22 g.mol^{-1})**:** Calcd C 59.75, H 6.75; Found C 58.62, H 6.43

^{23}Na NMR data (d^8-THF): broad signal centered at 1.14 ppm

^{13}C NMR data (d^8-THF) : 3.27 (s, CH_3), 3.43 (s, CH_2), 6.23 (t), 6.47 (d), 6.88(t)

^{1}H NMR data (d^8-THF) : 58.90 (s, CH_3), 72.72 (s, CH_2), 112.58 (s), 119.45 (s), 129.75 (s), 170.26 (s)

D - III.5.11 - (μ-dme)[SrLi$_6$(OPh)$_8$(thf)$_4$] 27 and (μ-dme)[SrLi$_6$(OPh)$_8$(thf)$_2$(dme)$_2$] 28

SrI_2 (0.387 g, 1.13 mmol) was dried for 30 mn under vacuum at 300°C and then dissolved in 15 mL of freshly dried and distilled THF, heating to reflux under magnetic stirring. Not all dissolves, at room temperature, a 1M solution of LiOPh in THF (10 eq, 10.3 mL) was added drop wise under nitrogen to the milky white solution. The solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was evaporated to dryness yielding a brown solid which was partially dissolved in 10 mL of DME. The mixture was left at room temperature under magnetic stirring one night and then filtered. Colourless single-crystals of **27** suitable for X-ray analysis grow in a yield of ca. 22% with respect to SrI_2 at -25°C within one week. Three months later, another single-crystal was picked (single-crystals of **28**), but melt rapidly due to their sensitivity to air and moisture even working under an atmosphere of argon. The yield was impossible to estimate. It was impossible to characterize spectroscopically and analytically the compounds **27** and **28**, except using X-ray diffraction.

D - III.6 - Synthesis of heterometallic phenoxide/alkoxide cluster

D - III.6.1 - [CaLi$_6$(OPh)$_6$(O^{t}Bu)$_2$(thf)$_6$] 29

CaI_2 (0.298 g, 1.01 mmol) was dried for 30 mn under vacuum at 300°C and then dissolved in 25 mL of freshly dried and distilled THF, heating to reflux under magnetic stirring. At room temperature, a 1M solution of LiOPh in THF (5 eq, 5.1 mL) and a 1M solution of LiO^{t}Bu in THF (5 eq, 5.1 mL) was added drop wise under nitrogen. The solution was left at room temperature under magnetic stirring during two days. Afterwards the solution was evaporated to dryness yielding a brown solid which was partially dissolved in 15 mL of a 1:10 THF / hexane mixture. The mixture was left at room temperature under magnetic stirring one night and then filtered.

Colourless single-crystals of **29** suitable for X-ray analysis grow in a yield of 53% with respect to CaI_2 at -25°C within three days.

$C_{68}H_{96}CaLi_6O_{14}$ (1219.17 g.mol^{-1})**:** Calcd C 66.99, H 7.94; Found C 60.95, H 6.46 (similar behaviour as **18**)

^{13}C NMR data (CD_3CN) : 26.79 (s, CH_2), 32.03 (s, CH_3), 68.95 (s, CH_2O), 116.26 (s), 121.31 (d), 130.35 (d), 167.04 (s)

D - III.7 - Synthesis of homometallic alkoxide cluster

D - III.7.1 - [Li(thf)]$_4$[Sr$_6$(O)(μ$_3$-I)(I)$_2$(O^{t}Bu)$_7$(thf)$_3$]$_2$(μ-I)(thf)$_n$ 30

SrI_2 and NaO^{t}Bu were dried under vacuum at 300°C during 20mn. The lithium primary amide PhN(H)Li, was freshly prepared from equimolar amounts of ^{n}BuLi (0.80 mL, 2.00 mmol) and aniline ($PhNH_2$) (0.185 mL, 2.03 mmol) according to the literature [372]. To this white-yellow solid was added an equimolar amount of NaO^{t}Bu (0.200 g, 2.08 mmol) in 20 mL of an hexane solution. The resulting colorless solution was then left to stand at room temperature overnight. SrI_2 (0.679 g, 1.99 mmol) was dissolved in 40 mL of THF and then added to the first solution, resulting first in a colorless solution. After heating to reflux for 1h, the mixture became dark-colored. It was then left to stand at room temperature in the dark and produced large single-crystals of **30** within two days in a 60 % yield. Unfortunately, the crystals blacken within half a minute of the mother liquor being removed, even though working under argon. Single-crystals could only be handled in inert and dried polyether oil, but elemental analysis, thermogravimetry or NMR-studies were unfortunately impossible to perform on these samples or gave inconsistent results.

The solution was tested with the corresponding lamps for presence of lithium (670.8 nm, 8 mA) and sodium (589.0 nm, 12 mA), and the results compared with standardized curves. The results show a more than tenfold higher concentration of lithium than sodium. The values found are 2.1 mg/l for lithium (slit width 0.7 nm) and 0.1 mg/l for sodium (0.2 nm).

D - III.8 - Synthesis of heterometallic trivalent rare earth phenoxide clusters 31-32

D - III.8.1 - [Eu(OPh)$_6${Li(dme)}$_3$] 31

In the labmaster glovebox, to EuI_2 (0.402 g, 0.99 mmol) a 1M solution of LiOPh in THF (10 eq, 10.0 mL) was added drop wise under nitrogen. The slight yellow solution turns yellow within 1 hour after getting out of the labmaster glovebox. The yellow solution was left at room temperature under magnetic stirring during one day. Afterwards the solution was evaporated to dryness yielding a yellow-brown solid which was partially dissolved in 15 mL of DME. The mixture was left at room temperature under magnetic stirring one night and then filtered.

Colourless single-crystals of **31** suitable for X-ray analysis grow in a yield of 23% with respect to EuI_2 at -25°C within three days.

$C_{48}H_{60}EuLi_3O_{12}$ (1001.74 $g.mol^{-1}$)**:** Calcd C 57.51, H 6.01; Found C 56.95, H 5.87

D - III.8.2 - [Sm(OPh)$_6${Li(dme)}$_3$] 32

In the labmaster glovebox, a 1M solution of LiOPh in THF (10 eq, 10.0 mL) was added drop wise under nitrogen to a 0.1 M solution of SmI_2 in THF (10 mL, 1.00 mmol). The blue-purple solution turns yellow within 2 hours after getting out of the labmaster glovebox. The yellow solution was left at room temperature under magnetic stirring during one day. Afterwards the solution was evaporated to dryness yielding a yellow-brown solid which was partially dissolved in 15 mL of DME. The mixture was left at room temperature under magnetic stirring one night and then filtered.

Colourless single-crystals of **32** suitable for X-ray analysis grow in a yield of 35% with respect to SmI_2 at -25°C within three days.

$C_{48}H_{60}SmLi_3O_{12}$ (1000.13 $g.mol^{-1}$)**:** Calcd C 57.59, H 6.02; Found C 57.07, H 5.87

E - Crystallographic data

Definition of factors Rint, R1 and wR2

$\mathrm{Rint} = \Sigma \mid F_o^2 - F_o^2(\mathrm{mean}) \mid / \Sigma [F_o^2]$,

$\mathrm{R1} = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid$,

$\mathrm{wR2} = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$

E - I - Structural data of starting materials 1-12

Crystal data and structure refinement for [CaI(dme)$_3$]I 1

$C_{12}H_{30}I_2Ca_1O_6$, M= 564.24 gmol^{-1}, monoclinic, $P2_1/n$ (Nr. 14), a = 13.594(3), b = 17.256(4), c = 18.638(4) Å, β = 91.91(3)°, V = 4369.6(15) Å^3, Z = 8, $\rho_{calcd.}$= 1.715 Mgm^3, F(000) = 2208, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 3.131 mm^{-1}, 1.61° < θ < 25.08°, 14562 reflections of which 7691 unique, 392 parameters refined, *GOOF* (on F^2) = 1.813, R1= $\Sigma|F_o–F_c|/\Sigma F_o$ = 0.1217, *wR*2 = 0.3208 for I > 2σ(I) and R1 = 0.2172, w*R*2 = 0.3908 for all data.

The intensity from single-crystals of **1** were measured on a STOE STADI 4 diffractometer equipped with monochromated graphite Mo-K_α radiation and an Oxford Cryosystems open flow cryostat [406]. No absorption correction was possible due to decomposition of the crystals during measurement. The structure was solved with direct methods and refined by full-matrix least-squares on F^2 with the SHELX-99 package [409]. All heavy atoms could be refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms but disorder was observed for the ethyl groups of the polyether ligands in **1**. CCDC-206569 (**1**) contain the supplementary crystallographic data. The cif file can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **1**.

Identification code	[CaI(dme)$_3$]I
Empirical formula	C12 H30 Ca I2 O6
Formula weight	564.24
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	P2(1)/n	
Unit cell dimensions	a = 13.594(3) Å	α= 90°
	b = 17.256(4) Å	β= 91.91(3)°
	c = 18.638(4) Å	γ = 90°
Volume	4369.6(15) Å^3	
Z	8	
Density (calculated)	1.715 Mg/m^3	
Absorption coefficient	3.131 mm^{-1}	
F(000)	2208	
Theta range for data collection	1.61 to 25.08°	
Index ranges	-16<=h<=16, -20<=k<=20, 0<=l<=22	
Reflections collected	14562	
Independent reflections	7691 [R(int) = 0.1177]	
Completeness to theta = 25.08°	99.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7691 / 0 / 392	
Goodness-of-fit on F^2	1.813	
Final R indices [I>2sigma(I)]	R1 = 0.1217, wR2 = 0.3208	
R indices (all data)	R1 = 0.2172, wR2 = 0.3908	
Largest diff. peak and hole	3.121 and -2.123 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	2431(1)	519(1)	425(1)	91(1)
I(2)	10(1)	-2798(1)	6935(1)	102(1)
I(3)	-413(1)	-862(1)	3585(1)	98(1)
I(4)	5068(1)	-1533(1)	6229(1)	102(1)
Ca(1)	1853(2)	-851(2)	3915(1)	69(1)
Ca(2)	2412(2)	-447(2)	-991(2)	79(1)
O(1)	1970(7)	-2131(5)	3369(4)	75(3)
O(2)	3518(7)	-1334(6)	3862(5)	85(3)
O(3)	2517(7)	-364(7)	5049(5)	89(3)
O(4)	1470(8)	-1655(6)	4924(5)	94(3)
O(5)	2291(8)	-380(6)	2741(5)	87(3)

O(6)	1744(10)	533(7)	3852(5)	105(4)
O(7)	1694(8)	758(7)	-1432(5)	96(3)
O(8)	665(8)	-556(8)	-1175(7)	121(5)
O(9)	3491(7)	-96(7)	-1944(4)	91(3)
O(10)	4106(8)	-614(7)	-678(6)	102(4)
O(11)	2179(10)	-1664(7)	-292(6)	111(4)
O(12)	2460(11)	-1663(10)	-1672(6)	160(6)
C(1)	1308(14)	-2484(10)	2881(9)	114(7)
C(2)	2897(12)	-2478(11)	3374(8)	96(6)
C(3)	3536(11)	-2170(11)	3911(11)	114(7)
C(4)	4424(12)	-879(10)	4071(9)	103(6)
C(5)	3208(12)	274(10)	5207(8)	96(6)
C(6)	2321(9)	-762(10)	5682(7)	76(4)
C(7)	1820(20)	-1454(11)	5552(8)	247(11)
C(8)	926(13)	-2385(10)	4843(8)	96(6)
C(9)	2877(13)	-812(12)	2247(7)	126(7)
C(10)	2566(15)	388(11)	2726(9)	120(7)
C(11)	1796(18)	838(11)	3154(9)	127(8)
C(12)	1089(19)	971(11)	4288(10)	151(9)
C(13)	2149(18)	1557(12)	-1391(13)	156(10)
C(14)	703(12)	820(11)	-1331(10)	111(6)
C(15)	167(11)	72(14)	-1488(10)	136(8)
C(16)	175(16)	-1303(13)	-1264(15)	176(11)
C(17)	3308(16)	340(13)	-2625(8)	158(9)
C(18)	4570(18)	-161(11)	-1850(10)	138(8)
C(19)	4664(13)	-780(20)	-1285(12)	244(16)
C(20)	4501(15)	-998(14)	18(8)	142(9)
C(21)	1940(20)	-1709(11)	441(10)	200(15)
C(22)	2420(20)	-2361(11)	-594(15)	205(12)
C(23)	2365(18)	-2290(15)	-1322(13)	160(10)
C(24)	2427(16)	-1645(10)	-2396(12)	185(9)

Table 3. Bond lengths [Å] and angles [°] for **1**.

I(1)-Ca(2)	3.120(3)	Ca(1)-O(3)	2.422(9)
I(3)-Ca(1)	3.121(3)	Ca(1)-O(4)	2.409(10)
Ca(1)-O(1)	2.439(10)	Ca(1)-O(5)	2.427(9)
Ca(1)-O(2)	2.418(10)	Ca(1)-O(6)	2.394(12)

Ca(2)-O(7)	2.429(12)	O(6)-C(11)	1.408(19)
Ca(2)-O(8)	2.395(12)	O(6)-C(12)	1.44(2)
Ca(2)-O(9)	2.419(10)	O(7)-C(13)	1.51(2)
Ca(2)-O(10)	2.375(11)	O(7)-C(14)	1.370(19)
Ca(2)-O(11)	2.497(11)	O(8)-C(15)	1.40(2)
Ca(2)-O(12)	2.454(15)	O(8)-C(16)	1.46(2)
Ca(1)-C(3)	3.228(17)	O(9)-C(17)	1.49(2)
Ca(1)-C(7)	3.226(15)	O(9)-C(18)	1.47(3)
Ca(2)-C(14)	3.237(17)	O(10)-C(19)	1.41(2)
Ca(2)-C(19)	3.180(18)	O(10)-C(20)	1.539(19)
Ca(2)-C(23)	3.24(3)	O(11)-C(21)	1.42(2)
O(1)-C(1)	1.398(18)	O(11)-C(22)	1.37(3)
O(1)-C(2)	1.396(18)	O(12)-C(23)	1.27(3)
O(2)-C(3)	1.44(2)	O(12)-C(24)	1.35(2)
O(2)-C(4)	1.501(19)	C(2)-C(3)	1.41(2)
O(3)-C(5)	1.471(18)	C(6)-C(7)	1.39(2)
O(3)-C(6)	1.398(16)	C(10)-C(11)	1.55(3)
O(4)-C(7)	1.296(19)	C(14)-C(15)	1.51(3)
O(4)-C(8)	1.47(2)	C(18)-C(19)	1.50(4)
O(5)-C(9)	1.444(18)	C(22)-C(23)	1.36(3)
O(5)-C(10)	1.38(2)		

O(6)-Ca(1)-O(4)	126.7(4)	O(4)-Ca(1)-I(3)	85.0(3)
O(6)-Ca(1)-O(2)	113.5(4)	O(2)-Ca(1)-I(3)	155.4(3)
O(4)-Ca(1)-O(2)	93.4(4)	O(3)-Ca(1)-I(3)	120.8(2)
O(6)-Ca(1)-O(3)	73.6(4)	O(5)-Ca(1)-I(3)	95.4(3)
O(4)-Ca(1)-O(3)	66.5(4)	O(1)-Ca(1)-I(3)	89.4(2)
O(2)-Ca(1)-O(3)	80.4(3)	O(6)-Ca(1)-C(7)	111.4(4)
O(6)-Ca(1)-O(5)	68.8(3)	O(4)-Ca(1)-C(7)	20.8(4)
O(4)-Ca(1)-O(5)	164.4(4)	O(2)-Ca(1)-C(7)	88.2(6)
O(2)-Ca(1)-O(5)	79.7(3)	O(3)-Ca(1)-C(7)	45.7(4)
O(3)-Ca(1)-O(5)	125.2(4)	O(5)-Ca(1)-C(7)	166.5(5)
O(6)-Ca(1)-O(1)	152.5(3)	O(1)-Ca(1)-C(7)	96.0(4)
O(4)-Ca(1)-O(1)	79.8(3)	I(3)-Ca(1)-C(7)	98.1(5)
O(2)-Ca(1)-O(1)	66.2(3)	O(6)-Ca(1)-C(3)	138.2(4)
O(3)-Ca(1)-O(1)	130.6(4)	O(4)-Ca(1)-C(3)	76.5(4)
O(5)-Ca(1)-O(1)	84.6(3)	O(2)-Ca(1)-C(3)	24.7(4)
O(6)-Ca(1)-I(3)	86.4(3)	O(3)-Ca(1)-C(3)	90.2(4)

O(5)-Ca(1)-C(3)	92.2(4)	I(1)-Ca(2)-C(14)	77.9(3)
O(1)-Ca(1)-C(3)	45.9(4)	C(19)-Ca(2)-C(14)	140.9(7)
I(3)-Ca(1)-C(3)	133.6(3)	O(10)-Ca(2)-C(23)	86.6(5)
C(7)-Ca(1)-C(3)	78.8(6)	O(8)-Ca(2)-C(23)	83.3(5)
O(10)-Ca(2)-O(8)	167.1(5)	O(9)-Ca(2)-C(23)	96.6(5)
O(10)-Ca(2)-O(9)	66.6(4)	O(7)-Ca(2)-C(23)	140.4(5)
O(8)-Ca(2)-O(9)	122.5(4)	O(12)-Ca(2)-C(23)	20.4(5)
O(10)-Ca(2)-O(7)	124.2(4)	O(11)-Ca(2)-C(23)	43.3(5)
O(8)-Ca(2)-O(7)	68.5(4)	I(1)-Ca(2)-C(23)	133.3(4)
O(9)-Ca(2)-O(7)	77.5(4)	C(19)-Ca(2)-C(23)	78.7(8)
O(10)-Ca(2)-O(12)	88.9(5)	C(14)-Ca(2)-C(23)	128.1(5)
O(8)-Ca(2)-O(12)	84.4(5)	C(2)-O(1)-C(1)	112.2(12)
O(9)-Ca(2)-O(12)	78.9(4)	C(2)-O(1)-Ca(1)	117.3(9)
O(7)-Ca(2)-O(12)	125.0(4)	C(1)-O(1)-Ca(1)	128.1(10)
O(10)-Ca(2)-O(11)	84.8(4)	C(3)-O(2)-C(4)	119.6(12)
O(8)-Ca(2)-O(11)	82.4(5)	C(3)-O(2)-Ca(1)	110.8(8)
O(9)-Ca(2)-O(11)	133.2(4)	C(4)-O(2)-Ca(1)	124.8(9)
O(7)-Ca(2)-O(11)	147.2(4)	C(6)-O(3)-C(5)	109.7(10)
O(12)-Ca(2)-O(11)	63.7(4)	C(6)-O(3)-Ca(1)	119.4(9)
O(10)-Ca(2)-I(1)	82.9(3)	C(5)-O(3)-Ca(1)	130.6(8)
O(8)-Ca(2)-I(1)	98.2(3)	C(7)-O(4)-C(8)	119.5(12)
O(9)-Ca(2)-I(1)	119.9(3)	C(7)-O(4)-Ca(1)	117.9(10)
O(7)-Ca(2)-I(1)	79.7(3)	C(8)-O(4)-Ca(1)	122.4(8)
O(12)-Ca(2)-I(1)	153.5(3)	C(10)-O(5)-C(9)	109.1(13)
O(11)-Ca(2)-I(1)	90.3(3)	C(10)-O(5)-Ca(1)	114.5(9)
O(10)-Ca(2)-C(19)	24.4(5)	C(9)-O(5)-Ca(1)	124.0(9)
O(8)-Ca(2)-C(19)	156.5(6)	C(11)-O(6)-C(12)	112.1(14)
O(9)-Ca(2)-C(19)	46.1(6)	C(11)-O(6)-Ca(1)	114.4(10)
O(7)-Ca(2)-C(19)	118.3(7)	C(12)-O(6)-Ca(1)	122.3(10)
O(12)-Ca(2)-C(19)	73.4(7)	C(14)-O(7)-C(13)	108.9(14)
O(11)-Ca(2)-C(19)	94.5(7)	C(14)-O(7)-Ca(2)	113.9(10)
I(1)-Ca(2)-C(19)	105.1(4)	C(13)-O(7)-Ca(2)	127.2(11)
O(10)-Ca(2)-C(14)	144.4(4)	C(15)-O(8)-C(16)	115.2(15)
O(8)-Ca(2)-C(14)	47.4(4)	C(15)-O(8)-Ca(2)	117.7(10)
O(9)-Ca(2)-C(14)	97.8(4)	C(16)-O(8)-Ca(2)	122.2(12)
O(7)-Ca(2)-C(14)	22.8(4)	C(18)-O(9)-C(17)	106.0(12)
O(12)-Ca(2)-C(14)	120.5(5)	C(18)-O(9)-Ca(2)	121.3(9)
O(11)-Ca(2)-C(14)	124.6(5)	C(17)-O(9)-Ca(2)	131.6(10)

C(19)-O(10)-C(20)	114.0(15)	C(6)-C(7)-Ca(1)	82.3(8)
C(19)-O(10)-Ca(2)	111.7(10)	O(5)-C(10)-C(11)	106.5(15)
C(20)-O(10)-Ca(2)	124.6(10)	O(6)-C(11)-C(10)	110.1(15)
C(22)-O(11)-C(21)	114.4(16)	O(7)-C(14)-C(15)	112.2(15)
C(22)-O(11)-Ca(2)	119.2(13)	O(7)-C(14)-Ca(2)	43.3(8)
C(21)-O(11)-Ca(2)	125.9(10)	C(15)-C(14)-Ca(2)	78.4(9)
C(23)-O(12)-C(24)	122.2(18)	O(8)-C(15)-C(14)	111.0(13)
C(23)-O(12)-Ca(2)	117.2(13)	O(9)-C(18)-C(19)	101.4(15)
C(24)-O(12)-Ca(2)	119.8(12)	O(10)-C(19)-C(18)	113(2)
O(1)-C(2)-C(3)	112.2(14)	O(10)-C(19)-Ca(2)	43.9(7)
C(2)-C(3)-O(2)	108.9(15)	C(18)-C(19)-Ca(2)	86.2(13)
C(2)-C(3)-Ca(1)	81.2(10)	C(23)-C(22)-O(11)	109.0(18)
O(2)-C(3)-Ca(1)	44.4(6)	O(12)-C(23)-C(22)	126(2)
C(7)-C(6)-O(3)	112.3(12)	O(12)-C(23)-Ca(2)	42.4(11)
O(4)-C(7)-C(6)	123.4(14)	C(22)-C(23)-Ca(2)	84.1(14)
O(4)-C(7)-Ca(1)	41.3(7)		

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **1**.
The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	90(1)	111(1)	71(1)	-10(1)	2(1)	7(1)
I(2)	86(1)	120(1)	102(1)	22(1)	27(1)	11(1)
I(3)	63(1)	138(1)	93(1)	-4(1)	1(1)	10(1)
I(4)	80(1)	125(1)	100(1)	17(1)	-7(1)	-2(1)
Ca(1)	62(2)	91(2)	53(1)	2(1)	4(1)	6(2)
Ca(2)	65(2)	99(2)	72(2)	2(2)	4(1)	-3(2)
O(1)	71(6)	87(6)	67(5)	-4(5)	13(4)	12(6)
O(2)	77(6)	86(7)	93(6)	-12(6)	0(5)	-14(6)
O(3)	63(6)	139(9)	65(5)	1(6)	1(4)	-16(7)
O(4)	106(8)	113(8)	61(5)	20(5)	-2(5)	-19(7)
O(5)	91(7)	101(7)	70(5)	4(5)	16(5)	-28(7)
O(6)	135(10)	110(8)	71(6)	-4(6)	7(6)	-8(8)
O(7)	70(6)	125(8)	93(6)	12(7)	-2(5)	2(7)
O(8)	68(7)	129(10)	166(10)	-18(9)	-13(7)	18(8)
O(9)	69(6)	143(9)	61(5)	0(6)	13(4)	-5(7)
O(10)	71(7)	115(9)	121(8)	-5(7)	-6(6)	16(7)

O(11)	149(11)	100(8)	85(7)	9(6)	4(7)	-18(8)
O(12)	186(14)	226(15)	69(6)	-46(8)	37(8)	-54(13)
C(1)	111(14)	120(14)	111(12)	-24(11)	0(11)	-21(13)
C(2)	88(10)	124(14)	76(9)	6(9)	26(8)	-26(11)
C(3)	38(7)	119(14)	186(17)	19(14)	37(10)	2(10)
C(4)	82(11)	113(13)	114(11)	26(11)	10(9)	-19(11)
C(5)	75(10)	120(13)	92(10)	-10(10)	0(8)	-22(11)
C(6)	47(7)	120(12)	62(7)	10(8)	10(6)	-8(9)
C(7)	490(30)	201(14)	51(8)	33(9)	-2(14)	-270(17)
C(8)	98(11)	116(13)	74(9)	-3(9)	16(8)	-2(12)
C(9)	127(13)	203(18)	50(7)	31(10)	28(8)	76(14)
C(10)	150(16)	126(15)	87(10)	-11(10)	50(10)	-37(14)
C(11)	190(20)	95(12)	93(11)	21(10)	1(13)	5(15)
C(12)	220(20)	112(13)	124(13)	-61(11)	-11(15)	67(15)
C(13)	150(20)	124(16)	190(20)	-45(16)	7(17)	-28(16)
C(14)	70(10)	114(13)	148(14)	38(12)	-38(10)	-7(11)
C(15)	48(8)	250(20)	108(11)	64(14)	-24(8)	-10(14)
C(16)	126(16)	152(17)	250(30)	-35(19)	18(18)	-89(15)
C(17)	174(18)	240(20)	63(9)	29(12)	-24(10)	-116(18)
C(18)	190(20)	124(14)	101(12)	39(11)	3(13)	-75(15)
C(19)	50(9)	520(50)	163(17)	-160(20)	17(11)	40(20)
C(20)	137(17)	220(20)	69(9)	22(13)	-8(10)	16(18)
C(21)	430(50)	93(14)	81(12)	2(11)	4(19)	-70(20)
C(22)	230(30)	82(13)	290(30)	88(16)	-130(20)	-44(16)
C(23)	129(17)	180(20)	170(20)	31(18)	-26(16)	57(18)
C(24)	241(19)	110(11)	210(20)	-66(12)	116(16)	-148(12)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1**.

	x	y	z	U(eq)
H(1A)	1543	-2424	2398	171
H(1B)	667	-2242	2912	171
H(1C)	1256	-3031	2994	171
H(2A)	3187	-2404	2904	115
H(2B)	2825	-3037	3452	115
H(3A)	4207	-2360	3846	136

H(3B)	3326	-2334	4385	136
H(4A)	4455	-806	4587	154
H(4B)	4400	-378	3835	154
H(4C)	5003	-1160	3926	154
H(5A)	2942	608	5572	144
H(5B)	3304	572	4773	144
H(5C)	3834	64	5379	144
H(6A)	2943	-872	5943	91
H(6B)	1925	-431	5988	91
H(7A)	2269	-1871	5711	296
H(7B)	1269	-1462	5876	296
H(8A)	1365	-2786	4679	143
H(8B)	387	-2317	4495	143
H(8C)	668	-2534	5302	143
H(9A)	2814	-581	1774	189
H(9B)	2650	-1345	2226	189
H(9C)	3562	-801	2411	189
H(10A)	2575	576	2230	144
H(10B)	3225	454	2948	144
H(11A)	1978	1387	3180	153
H(11B)	1149	799	2907	153
H(12A)	1256	1517	4264	227
H(12B)	1153	796	4782	227
H(12C)	416	897	4113	227
H(13A)	2156	1781	-1868	234
H(13B)	2818	1519	-1196	234
H(13C)	1766	1884	-1083	234
H(14A)	430	1228	-1644	134
H(14B)	597	972	-833	134
H(15A)	-498	102	-1302	163
H(15B)	106	-4	-2009	163
H(16A)	-214	-1409	-848	264
H(16B)	665	-1707	-1313	264
H(16C)	-252	-1291	-1691	264
H(17A)	3565	862	-2573	238
H(17B)	2606	362	-2734	238
H(17C)	3635	80	-3013	238
H(18A)	4864	328	-1684	165

H(18B)	4874	-321	-2296	165
H(19A)	4445	-1275	-1492	292
H(19B)	5358	-833	-1135	292
H(20A)	4546	-1554	-53	213
H(20B)	4058	-891	403	213
H(20C)	5149	-793	144	213
H(21A)	1757	-2236	556	300
H(21B)	1398	-1363	531	300
H(21C)	2510	-1558	738	300
H(22A)	3086	-2512	-436	246
H(22B)	1962	-2763	-441	246
H(23A)	2860	-2646	-1504	192
H(23B)	1723	-2503	-1475	192
H(24A)	3010	-1894	-2574	278
H(24B)	2403	-1111	-2557	278
H(24C)	1845	-1917	-2575	278

Crystal data and structure refinement for [CaI(dme)$_3$]I **1a**

$C_{12}H_{30}O_6CaI_2$, M= 564.24 gmol^{-1}, monoclinic, $P2_1/c$ (Nr. 14), a = 12.3066(7), b = 10.8218(6), c = 16.2620(9) Å, $\beta = 99.733(5)°$, V = 2134.6(2) Å^3, Z = 4, $\rho_{calcd.}$= 1.756 Mgm^3, $F(000) = 1104$, T = 203 K, $\lambda = 0.71073$ Å, μ(Mo-K$_\alpha$)= 3.205 mm^{-1}, $1.68° < \theta < 27.11°$, 16219 reflections of which 4608 unique and 4135 observed, 197 parameters refined, *GOOF* (on F^2) = 1.074, R1= $\Sigma|F_o–F_c|/\Sigma F_o$ = 0.0438, $wR2 = 0.1186$ for I > 2σ(I) and R1 = 0.0481, wR2 = 0.1227 for all data.

The intensities from the single-crystals of **1a** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms.

Table 1. Crystal data and structure refinement for **1a**.

Identification code	[CaI(dme)$_3$]I
Empirical formula	C12 H30 Ca I2 O6
Formula weight	564.24
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	P2(1)/c	
Unit cell dimensions	a = 12.3066(7) Å	α= 90°
	b = 10.8218(6) Å	β= 99.733(5)°
	c = 16.2620(9) Å	γ = 90°
Volume	2134.6(2) $Å^3$	
Z	4	
Density (calculated)	1.756 Mg/m^3	
Absorption coefficient	3.205 mm^{-1}	
F(000)	1104	
Theta range for data collection	1.68 to 27.11°	
Index ranges	-15<=h<=15, -13<=k<=13, -20<=l<=20	
Reflections collected	16219	
Independent reflections	4608 [R(int) = 0.1102]	
Completeness to theta = 27.11°	97.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4608 / 0 / 197	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.1186	
R indices (all data)	R1 = 0.0481, wR2 = 0.1227	
Largest diff. peak and hole	1.326 and -0.948 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1a**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	5896(1)	7914(1)	1155(1)	44(1)
I(2)	11695(1)	7961(1)	-2372(1)	47(1)
Ca	7391(1)	7460(1)	-132(1)	29(1)
O(1)	9112(1)	8085(1)	692(1)	36(1)
O(2)	8902(1)	7121(1)	-857(1)	41(1)
O(3)	8010(1)	5599(1)	711(1)	39(1)
O(4)	6612(1)	5543(1)	-775(1)	43(1)
O(5)	6033(1)	8237(1)	-1269(1)	43(1)
O(6)	7654(1)	9693(1)	-481(1)	42(1)
C(1)	9189(1)	9046(1)	1302(1)	46(1)
C(2)	10058(1)	8049(1)	295(1)	43(1)

C(3)	9945(1)	7006(1)	-307(1)	48(1)
C(4)	8857(1)	6431(1)	-1604(1)	74(1)
C(5)	8491(1)	5694(1)	1579(1)	50(1)
C(6)	7157(1)	4688(1)	581(1)	48(1)
C(7)	6911(1)	4413(1)	-327(1)	52(1)
C(8)	6171(1)	5285(1)	-1631(1)	57(1)
C(9)	4883(1)	7971(1)	-1417(1)	63(1)
C(10)	6263(1)	9353(1)	-1690(1)	48(1)
C(11)	7426(1)	9698(1)	-1373(1)	48(1)
C(12)	7144(1)	10697(1)	-123(1)	51(1)

Table 3. Bond lengths [Å] and angles [°] for **1a**.

I(1)-Ca	3.05071(17)	O(3)-C(5)	1.4391(4)
Ca-O(1)	2.4038(3)	O(3)-C(6)	1.4290(4)
Ca-O(2)	2.3915(3)	O(4)-C(7)	1.4398(4)
Ca-O(3)	2.4824(3)	O(4)-C(8)	1.4322(5)
Ca-O(4)	2.4452(3)	O(5)-C(9)	1.4231(5)
Ca-O(5)	2.4240(3)	O(5)-C(10)	1.4396(5)
Ca-O(6)	2.5154(3)	O(6)-C(12)	1.4270(5)
Ca-C(11)	3.1577(4)	O(6)-C(11)	1.4305(4)
O(1)-C(1)	1.4290(4)	C(2)-C(3)	1.4845(5)
O(1)-C(2)	1.4238(5)	C(6)-C(7)	1.4851(6)
O(2)-C(3)	1.4406(5)	C(10)-C(11)	1.4846(6)
O(2)-C(4)	1.4190(5)		

O(2)-Ca-O(1)	68.480(9)	O(5)-Ca-O(6)	65.988(8)
O(2)-Ca-O(5)	99.843(10)	O(4)-Ca-O(6)	140.768(9)
O(1)-Ca-O(5)	139.198(9)	O(3)-Ca-O(6)	149.882(8)
O(2)-Ca-O(4)	86.570(9)	O(2)-Ca-I(1)	166.363(6)
O(1)-Ca-O(4)	136.211(8)	O(1)-Ca-I(1)	98.550(8)
O(5)-Ca-O(4)	78.341(9)	O(5)-Ca-I(1)	92.812(8)
O(2)-Ca-O(3)	87.492(9)	O(4)-Ca-I(1)	101.055(7)
O(1)-Ca-O(3)	76.188(8)	O(3)-Ca-I(1)	85.180(7)
O(5)-Ca-O(3)	144.104(8)	O(6)-Ca-I(1)	96.621(7)
O(4)-Ca-O(3)	66.995(9)	O(2)-Ca-C(11)	72.971(10)
O(2)-Ca-O(6)	84.049(9)	O(1)-Ca-C(11)	92.004(10)
O(1)-Ca-O(6)	73.812(8)	O(5)-Ca-C(11)	47.830(10)

O(4)-Ca-C(11)	115.092(10)	C(7)-O(4)-Ca	117.12(2)
O(3)-Ca-C(11)	159.930(10)	C(9)-O(5)-C(10)	111.06(3)
O(6)-Ca-C(11)	26.214(9)	C(9)-O(5)-Ca	126.60(3)
I(1)-Ca-C(11)	112.949(8)	C(10)-O(5)-Ca	119.16(2)
C(2)-O(1)-C(1)	111.80(3)	C(12)-O(6)-C(11)	112.76(3)
C(2)-O(1)-Ca	116.735(19)	C(12)-O(6)-Ca	123.88(2)
C(1)-O(1)-Ca	122.69(2)	C(11)-O(6)-Ca	102.825(19)
C(4)-O(2)-C(3)	112.83(3)	O(1)-C(2)-C(3)	109.10(3)
C(4)-O(2)-Ca	125.57(3)	O(2)-C(3)-C(2)	108.55(3)
C(3)-O(2)-Ca	113.11(2)	O(3)-C(6)-C(7)	107.87(3)
C(6)-O(3)-C(5)	111.40(3)	O(4)-C(7)-C(6)	108.97(3)
C(6)-O(3)-Ca	109.215(19)	O(5)-C(10)-C(11)	107.61(3)
C(5)-O(3)-Ca	121.35(2)	O(6)-C(11)-C(10)	111.23(3)
C(8)-O(4)-C(7)	110.43(3)	O(6)-C(11)-Ca	50.962(15)
C(8)-O(4)-Ca	129.62(2)	C(10)-C(11)-Ca	84.94(2)

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **1a**.

The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	46(1)	49(1)	42(1)	0(1)	19(1)	8(1)
I(2)	52(1)	37(1)	49(1)	3(1)	3(1)	-5(1)
Ca	31(1)	28(1)	27(1)	1(1)	7(1)	2(1)
O(1)	39(1)	36(1)	33(1)	0(1)	5(1)	-3(1)
O(2)	38(1)	51(1)	37(1)	-7(1)	12(1)	5(1)
O(3)	45(1)	34(1)	38(1)	7(1)	4(1)	-2(1)
O(4)	52(1)	34(1)	40(1)	-4(1)	-1(1)	-2(1)
O(5)	37(1)	48(1)	40(1)	1(1)	-2(1)	5(1)
O(6)	49(1)	33(1)	44(1)	5(1)	5(1)	5(1)
C(1)	55(1)	45(1)	37(1)	-6(1)	3(1)	-4(1)
C(2)	39(1)	50(1)	41(1)	3(1)	9(1)	-6(1)
C(3)	37(1)	54(1)	54(1)	0(1)	13(1)	8(1)
C(4)	68(1)	101(1)	58(1)	-42(1)	23(1)	-8(1)
C(5)	60(1)	47(1)	38(1)	13(1)	-2(1)	2(1)
C(6)	53(1)	35(1)	53(1)	11(1)	6(1)	-6(1)
C(7)	63(1)	30(1)	61(1)	-1(1)	-1(1)	-4(1)
C(8)	68(1)	59(1)	41(1)	-14(1)	1(1)	-7(1)

C(9)	40(1)	79(1)	65(1)	-7(1)	-5(1)	3(1)
C(10)	62(1)	44(1)	36(1)	6(1)	-1(1)	12(1)
C(11)	64(1)	43(1)	40(1)	14(1)	14(1)	10(1)
C(12)	56(1)	39(1)	57(1)	-3(1)	6(1)	10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1a**.

	x	y	z	U(eq)
H(1A)	9793	8871	1752	70
H(1B)	8505	9091	1522	70
H(1C)	9320	9829	1045	70
H(2A)	10724	7939	714	52
H(2B)	10125	8829	2	52
H(3A)	10549	7026	-630	57
H(3B)	9978	6218	-7	57
H(4A)	9391	6759	-1923	111
H(4B)	8123	6491	-1932	111
H(4C)	9027	5572	-1468	111
H(5A)	7964	6067	1885	75
H(5B)	9148	6204	1636	75
H(5C)	8685	4877	1800	75
H(6A)	6496	5000	772	57
H(6B)	7400	3936	895	57
H(7A)	7560	4048	-508	63
H(7B)	6303	3819	-440	63
H(8A)	6680	4761	-1866	85
H(8B)	6066	6053	-1941	85
H(8C)	5469	4865	-1664	85
H(9A)	4478	8697	-1293	94
H(9B)	4736	7294	-1061	94
H(9C)	4654	7742	-1997	94
H(10A)	5767	10016	-1575	58
H(10B)	6155	9216	-2294	58
H(11A)	7918	9113	-1588	58
H(11B)	7571	10524	-1578	58
H(12A)	7323	11466	-376	76

H(12B)	7411	10725	473	76
H(12C)	6351	10582	-223	76

Crystal data and structure refinement for *trans*-[$SrI_2(dme)_3$] 2

$C_{12}H_{30}O_6SrI_2$, M= 611.78 gmol^{-1}, monoclinic, $P2_1$ (Nr. 4), a = 8.4840(17), b = 10.566(2), c = 12.345(3) Å, β = 93.69(3)°, V = 1104.3(4) Å^3, Z = 2, $\rho_{calcd.}$= 1.840 Mgm^3, $F(000)$ = 588, T = 203 K, λ = 0.71073 Å, $\mu(\text{Mo-K}_\alpha)$= 5.254 mm^{-1}, 1.65° < θ < 25.07°, 2054 reflections of which 1646 unique and observed, 197 parameters refined, *GOOF* (on F^2) = 5.254, R1= $\Sigma|F_o–F_c|/\Sigma F_o$ = 0.1445, *wR*2 = 0.3567 for I > 2σ(I) and R1 = 0.1632, w*R*2 = 0.3962 for all data.

The intensities from the single-crystals of **2** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK_α radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms, but disorder was observed for one methyl group of one DME ligand.

Table 1. Crystal data and structure refinement for **2**.

Identification code	*trans*-[$SrI_2(dme)_3$]	
Empirical formula	C12 H30 I2 O6 Sr	
Formula weight	611.78	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.4840(17) Å	α= 90°
	b = 10.566(2) Å	β= 93.69(3)°
	c = 12.345(3) Å	γ = 90°
Volume	1104.3(4) Å^3	
Z	2	
Density (calculated)	1.840 Mg/m^3	
Absorption coefficient	5.254 mm^{-1}	
F(000)	588	
Theta range for data collection	1.65 to 25.07°	
Index ranges	-10<=h<=10, 0<=k<=12, 0<=l<=14	
Reflections collected	2054	
Independent reflections	2054 [R(int) = 0.0000]	

Completeness to theta = 25.07°	98.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2054 / 1 / 197
Goodness-of-fit on F^2	1.813
Final R indices [I>2sigma(I)]	R1 = 0.1445, wR2 = 0.3567
R indices (all data)	R1 = 0.1632, wR2 = 0.3962
Largest diff. peak and hole	4.320 and -4.885 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **2**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	1446(1)	6087(1)	9463(1)	68(1)
I(2)	-3125(1)	6152(1)	4872(1)	69(1)
Sr	-1441(1)	5966(1)	7405(1)	50(1)
O(1)	891(6)	5762(5)	6179(5)	52(2)
O(2)	207(7)	8106(6)	6991(5)	55(2)
O(3)	-3248(8)	8061(7)	7694(5)	84(2)
O(4)	-2955(8)	6098(9)	9164(5)	71(2)
O(5)	-3761(8)	4387(7)	7521(8)	89(3)
O(6)	-819(7)	3585(7)	7435(6)	70(2)
C(1)	965(12)	4658(10)	5422(8)	75(3)
C(2)	1528(9)	6794(15)	5815(9)	117(5)
C(3)	1828(10)	7765(10)	6759(11)	90(4)
C(4)	378(16)	9132(14)	7756(9)	87(5)
C(5)	-3835(11)	8989(13)	7053(10)	105(4)
C(6)	-3994(13)	8352(14)	8688(8)	88(4)
C(7)	-3112(13)	7425(11)	9611(11)	86(4)
C(8)	-2950(20)	5350(30)	9944(11)	172(10)
C(9)	-5389(9)	4884(11)	7328(11)	121(4)
C(10)	-3516(13)	3230(12)	6906(9)	78(3)
C(11)	-2022(12)	2631(7)	7427(8)	54(3)
C(12)	558(13)	3004(10)	7849(10)	79(4)

Table 3. Bond lengths [Å] and angles [°] for **2**.

I(1)-Sr	3.4163(14)	O(2)-C(4)	1.439(15)
I(2)-Sr	3.3588(13)	O(3)-C(5)	1.336(14)
Sr-O(1)	2.576(6)	O(3)-C(6)	1.450(13)
Sr-O(2)	2.725(6)	O(4)-C(7)	1.517(15)
Sr-O(3)	2.729(7)	O(4)-C(8)	1.25(2)
Sr-O(4)	2.596(6)	O(5)-C(9)	1.483(11)
Sr-O(5)	2.591(7)	O(5)-C(10)	1.461(14)
Sr-O(6)	2.570(8)	O(6)-C(11)	1.434(11)
Sr-C(2)	3.406(10)	O(6)-C(12)	1.388(13)
O(1)-C(1)	1.498(12)	C(2)-C(3)	1.560(18)
O(1)-C(2)	1.309(16)	C(6)-C(7)	1.645(17)
O(2)-C(3)	1.467(11)	C(10)-C(11)	1.522(15)

O(6)-Sr-O(1)	76.2(2)	O(5)-Sr-C(2)	142.2(3)
O(6)-Sr-O(5)	61.6(2)	O(4)-Sr-C(2)	153.1(3)
O(1)-Sr-O(5)	126.4(2)	O(2)-Sr-C(2)	43.2(3)
O(6)-Sr-O(4)	98.8(3)	O(3)-Sr-C(2)	108.0(3)
O(1)-Sr-O(4)	159.35(19)	I(2)-Sr-C(2)	74.61(17)
O(5)-Sr-O(4)	64.5(3)	O(6)-Sr-I(1)	83.64(15)
O(6)-Sr-O(2)	135.05(19)	O(1)-Sr-I(1)	84.22(13)
O(1)-Sr-O(2)	62.37(18)	O(5)-Sr-I(1)	119.6(2)
O(5)-Sr-O(2)	161.0(2)	O(4)-Sr-I(1)	75.27(14)
O(4)-Sr-O(2)	113.6(2)	O(2)-Sr-I(1)	75.90(13)
O(6)-Sr-O(3)	155.3(2)	O(3)-Sr-I(1)	104.72(15)
O(1)-Sr-O(3)	127.12(19)	I(2)-Sr-I(1)	158.73(3)
O(5)-Sr-O(3)	94.6(2)	C(2)-Sr-I(1)	84.12(17)
O(4)-Sr-O(3)	62.3(2)	C(2)-O(1)-C(1)	113.6(8)
O(2)-Sr-O(3)	69.5(2)	C(2)-O(1)-Sr	118.8(6)
O(6)-Sr-I(2)	98.37(17)	C(1)-O(1)-Sr	119.7(5)
O(1)-Sr-I(2)	75.80(13)	C(4)-O(2)-C(3)	104.9(8)
O(5)-Sr-I(2)	79.0(2)	C(4)-O(2)-Sr	122.2(6)
O(4)-Sr-I(2)	124.85(14)	C(3)-O(2)-Sr	109.3(5)
O(2)-Sr-I(2)	88.24(14)	C(5)-O(3)-C(6)	100.3(9)
O(3)-Sr-I(2)	82.25(14)	C(5)-O(3)-Sr	135.2(7)
O(6)-Sr-C(2)	95.8(3)	C(6)-O(3)-Sr	124.2(7)
O(1)-Sr-C(2)	19.7(3)	C(8)-O(4)-C(7)	107.7(13)

C(8)-O(4)-Sr	129.3(11)	O(1)-C(2)-C(3)	110.0(9)
C(7)-O(4)-Sr	114.5(6)	O(1)-C(2)-Sr	41.5(4)
C(10)-O(5)-C(9)	112.1(8)	C(3)-C(2)-Sr	80.2(5)
C(10)-O(5)-Sr	112.1(6)	O(2)-C(3)-C(2)	101.4(7)
C(9)-O(5)-Sr	117.8(6)	O(3)-C(6)-C(7)	104.8(9)
C(12)-O(6)-C(11)	105.8(8)	O(4)-C(7)-C(6)	110.2(9)
C(12)-O(6)-Sr	127.3(6)	O(5)-C(10)-C(11)	105.7(8)
C(11)-O(6)-Sr	122.9(5)	O(6)-C(11)-C(10)	106.5(7)

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for **2**.
The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	57(1)	75(1)	72(1)	-6(1)	7(1)	8(1)
I(2)	62(1)	66(1)	79(1)	-1(1)	-2(1)	4(1)
Sr	37(1)	40(1)	74(1)	0(1)	17(1)	-1(1)
O(1)	45(2)	34(3)	80(4)	-9(3)	19(2)	-10(2)
O(2)	45(3)	46(3)	75(4)	-3(3)	13(3)	-16(2)
O(3)	115(4)	54(3)	92(4)	33(3)	78(3)	44(3)
O(4)	85(4)	72(4)	55(3)	26(4)	5(3)	-5(4)
O(5)	64(3)	29(3)	178(8)	-4(4)	33(4)	-2(3)
O(6)	59(3)	47(4)	107(5)	-18(4)	26(3)	-3(3)
C(1)	90(6)	52(5)	87(6)	-26(5)	43(5)	-8(5)
C(2)	41(3)	199(12)	116(7)	77(8)	45(4)	56(5)
C(3)	61(4)	38(5)	180(9)	-20(6)	71(4)	-17(4)
C(4)	97(7)	83(9)	81(8)	2(7)	8(6)	-6(8)
C(5)	47(5)	105(7)	162(10)	85(6)	-17(6)	-1(5)
C(6)	80(6)	109(8)	78(5)	-56(5)	37(4)	-24(6)
C(7)	73(5)	63(6)	125(9)	-38(6)	27(5)	9(5)
C(8)	180(15)	290(30)	48(7)	7(11)	4(9)	-98(15)
C(9)	27(3)	110(6)	231(12)	-110(6)	40(5)	-42(4)
C(10)	77(5)	77(6)	83(6)	-38(5)	20(5)	-34(5)
C(11)	92(5)	17(3)	57(5)	-7(3)	20(4)	-4(4)
C(12)	74(5)	45(5)	123(9)	-27(5)	40(5)	1(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **2**.

	x	y	z	U(eq)
H(1A)	736	4942	4681	112
H(1B)	194	4028	5604	112
H(1C)	2014	4289	5491	112
H(2A)	821	7168	5243	141
H(2B)	2529	6587	5503	141
H(3A)	2395	7376	7390	108
H(3B)	2420	8502	6527	108
H(4A)	1070	8873	8373	131
H(4B)	-649	9354	8002	131
H(4C)	829	9859	7410	131
H(5A)	-4976	9006	7074	158
H(5B)	-3554	8841	6315	158
H(5C)	-3402	9794	7307	158
H(6A)	-5129	8173	8609	106
H(6B)	-3841	9244	8884	106
H(7A)	-2062	7763	9826	103
H(7B)	-3727	7401	10256	103
H(8A)	-1918	5351	10330	258
H(8B)	-3186	4499	9676	258
H(8C)	-3743	5602	10432	258
H(9A)	-5353	5707	6982	182
H(9B)	-5874	4965	8015	182
H(9C)	-6006	4307	6860	182
H(10A)	-3384	3426	6141	94
H(10B)	-4417	2656	6949	94
H(11A)	-2192	2357	8169	65
H(11B)	-1715	1894	7007	65
H(12A)	341	2524	8493	119
H(12B)	1350	3642	8037	119
H(12C)	945	2437	7308	119

Crystal data and structure refinement for *trans*-[$BaI_2(dme)_3$] 3

$C_{12}H_{30}O_6BaI_2$, M= 661.50 gmol^{-1}, monoclinic, *C*2/*c* (Nr. 15), a = 13.085(3), b = 11.145(2), c = 15.767(3) Å, β = 95.54(3)°, V = 2288.7(8) Å^3, Z = 4, $\rho_{calcd.}$= 1.920 Mgm^3, *F*(000) = 1248, T = 203 K, λ = 0.71073 Å, μ(Mo-K_α)= 4.450 mm^{-1}, 2.80° < θ < 26.90°, 11733 reflections of which 2318 unique and 2285 observed, 100 parameters refined, *GOOF* (on F^2) = 1.253, $R1= \Sigma|F_o-F_c|/\Sigma F_o = 0.0946$, *w*R2 = 0.2576 for I > 2σ(I) and R1 = 0.0954, wR2 = 0.2605 for all data.

The intensities from the single-crystals of **3** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK_α radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms.

Table 1. Crystal data and structure refinement for **3**.

Identification code	*trans*-[$BaI_2(dme)_3$]	
Empirical formula	C12 H30 Ba I2 O6	
Formula weight	661.50	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 13.085(3) Å	α= 90°
	b = 11.145(2) Å	β= 95.54(3)°
	c = 15.767(3) Å	γ = 90°
Volume	2288.7(8) Å^3	
Z	4	
Density (calculated)	1.920 Mg/m^3	
Absorption coefficient	4.450 mm^{-1}	
F(000)	1248	
Theta range for data collection	2.80 to 26.90°	
Index ranges	-16<=h<=15, -13<=k<=14, -20<=l<=20	
Reflections collected	7988	
Independent reflections	2318 [R(int) = 0.2021]	
Completeness to theta = 26.90°	94.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2318 / 0 / 100	
Goodness-of-fit on F^2	1.253	
Final R indices [I>2sigma(I)]	R1 = 0.0946, wR2 = 0.2576	

R indices (all data)	R1 = 0.0954, wR2 = 0.2605
Largest diff. peak and hole	2.340 and -2.413 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **3**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ba	10000	1142(1)	2500	42(1)
I	12417(1)	877(1)	3614(1)	65(1)
O(1)	8658(2)	1198(3)	3822(2)	71(1)
O(2)	9647(3)	-888(3)	3479(3)	87(1)
O(3)	10107(2)	3345(2)	3371(2)	59(1)
C(1)	7929(4)	2130(7)	3771(4)	109(2)
C(2)	8218(3)	-2(6)	3914(3)	86(2)
C(3)	8995(3)	-870(5)	4120(3)	84(1)
C(4)	10426(5)	-1904(6)	3561(6)	147(3)
C(5)	10451(6)	3408(5)	4257(3)	115(2)
C(6)	10329(5)	4367(4)	2925(3)	79(2)

Table 3. Bond lengths [Å] and angles [°] for **3**.

Ba-I	3.4791(10)	O(1)-C(1)	1.407(7)
Ba-I#1	3.4791(10)	O(1)-C(2)	1.469(7)
Ba-O(1)	2.852(3)	O(2)-C(3)	1.384(6)
Ba-O(1)#1	2.852(3)	O(2)-C(4)	1.521(7)
Ba-O(2)	2.802(4)	O(3)-C(5)	1.427(6)
Ba-O(2)#1	2.802(4)	O(3)-C(6)	1.385(5)
Ba-O(3)	2.810(3)	C(2)-C(3)	1.419(7)
Ba-O(3)#1	2.810(3)	C(6)-C(6)#1	1.521(10)
O(2)#1-Ba-O(2)	72.31(16)	O(2)#1-Ba-O(1)#1	57.94(10)
O(2)#1-Ba-O(3)	166.29(9)	O(2)-Ba-O(1)#1	124.45(10)
O(2)-Ba-O(3)	116.05(10)	O(3)-Ba-O(1)#1	109.46(9)
O(2)#1-Ba-O(3)#1	116.05(10)	O(3)#1-Ba-O(1)#1	68.23(9)
O(2)-Ba-O(3)#1	166.29(9)	O(2)#1-Ba-O(1)	124.45(10)
O(3)-Ba-O(3)#1	58.25(10)	O(2)-Ba-O(1)	57.94(10)

O(3)-Ba-O(1)	68.23(9)	O(1)-Ba-I	103.10(6)
O(3)#1-Ba-O(1)	109.46(9)	I#1-Ba-I	170.251(14)
O(1)#1-Ba-O(1)	177.53(14)	C(1)-O(1)-C(2)	114.0(4)
O(2)#1-Ba-I#1	81.00(7)	C(1)-O(1)-Ba	115.8(3)
O(2)-Ba-I#1	91.10(7)	C(2)-O(1)-Ba	109.1(2)
O(3)-Ba-I#1	108.74(6)	C(3)-O(2)-C(4)	113.8(5)
O(3)#1-Ba-I#1	80.05(6)	C(3)-O(2)-Ba	122.5(3)
O(1)#1-Ba-I#1	103.10(6)	C(4)-O(2)-Ba	120.2(4)
O(1)-Ba-I#1	77.12(6)	C(6)-O(3)-C(5)	113.3(4)
O(2)#1-Ba-I	91.10(7)	C(6)-O(3)-Ba	118.3(2)
O(2)-Ba-I	81.00(7)	C(5)-O(3)-Ba	121.2(3)
O(3)-Ba-I	80.05(6)	C(3)-C(2)-O(1)	111.3(4)
O(3)#1-Ba-I	108.74(6)	O(2)-C(3)-C(2)	108.7(4)
O(1)#1-Ba-I	77.12(6)	O(3)-C(6)-C(6)#1	108.6(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y,-z+1/2

Table 4. Anisotropic displacement parameters (Å^{2}x 10^{3}) for **3**.

The anisotropic displacement factor exponent takes the form: $-2p^{2}[h^{2}a^{*2}U^{11} + ... + 2 h k a^{*} b^{*} U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ba	44(1)	40(1)	42(1)	0	6(1)	0
I	56(1)	82(1)	55(1)	-9(1)	-4(1)	0(1)
O(1)	63(1)	88(2)	63(1)	7(1)	16(1)	-5(2)
O(2)	66(2)	71(2)	122(2)	45(2)	-6(2)	-8(1)
O(3)	81(2)	45(1)	52(1)	0(1)	3(1)	3(1)
C(1)	102(3)	136(5)	96(3)	-13(3)	44(2)	43(3)
C(2)	62(2)	133(4)	62(2)	16(2)	6(2)	-39(2)
C(3)	64(2)	101(3)	81(2)	34(2)	-18(2)	-44(2)
C(4)	93(4)	102(3)	238(6)	90(3)	-23(4)	15(3)
C(5)	202(6)	78(3)	60(2)	-6(2)	-18(3)	-50(3)
C(6)	122(4)	44(2)	70(2)	-11(2)	2(2)	-13(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **3**.

	x	y	z	U(eq)
H(1A)	7568	2144	3204	163
H(1B)	8275	2891	3885	163
H(1C)	7443	1996	4188	163
H(2A)	7750	15	4363	103
H(2B)	7819	-229	3380	103
H(3A)	9381	-667	4665	100
H(3B)	8685	-1663	4175	100
H(4A)	10843	-1837	4102	221
H(4B)	10863	-1855	3099	221
H(4C)	10069	-2667	3534	221
H(5A)	11191	3313	4334	173
H(5B)	10130	2773	4559	173
H(5C)	10265	4180	4481	173
H(6A)	11058	4377	2830	95
H(6B)	10182	5084	3253	95

Crystal data and structure refinement for [CaI(diglyme)$_2$]I 4

$C_{12}H_{28}I_2CaO_6$, M= 562.22 gmol^{-1}, monoclinic, $P2_1/c$ (Nr. 14), a = 9.0690(18), b = 16.491(3), c = 13.865(3) Å, β = 90.24(3)°, V = 2073.6(7) Å^3, Z = 4, $\rho_{calcd.}$= 1.801 Mgm^3, $F(000)$ = 1096, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 3.299 mm^{-1}, 1.92° < θ < 25.99°, 2070 reflections unique and observed, 131 parameters refined, *GOOF* (on F^2) = 2.739, R1= $\Sigma|F_o–F_c|/\Sigma F_o$ = 0.2008, $wR2$ = 0.5461 for I > 2σ(I) and R1 = 0.2008, w$R2$ = 0.5461 for all data. The intensities from the single-crystals of **4** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically except the carbon atoms of the polyether ligands due to a high disorder. The positions of the hydrogen atoms could not be calculated due to the heavy disorder, but were included in the determination of the molar mass.

Table 1. Crystal data and structure refinement for **4**.

Identification code	[CaI(diglyme)$_2$]I
Empirical formula	C12 H28 Ca I2 O6

Formula weight	562.22	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.0690(18) Å	α= 90°
	b = 16.491(3) Å	β= 90.24(3)°
	c = 13.865(3) Å	γ = 90°
Volume	2073.6(7) Å^3	
Z	4	
Density (calculated)	1.801 Mg/m^3	
Absorption coefficient	3.299 mm^{-1}	
F(000)	1096	
Theta range for data collection	1.92 to 25.99°	
Index ranges	0<=h<=11, 0<=k<=20, -16<=l<=17	
Reflections collected	2070	
Independent reflections	2070 [R(int) = 0.0000]	
Completeness to theta = 25.99°	50.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2070 / 0 / 131	
Goodness-of-fit on F^2	2.739	
Final R indices [I>2sigma(I)]	R1 = 0.2008, wR2 = 0.5461	
R indices (all data)	R1 = 0.2008, wR2 = 0.5461	
Largest diff. peak and hole	3.617 and -4.628 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **4**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	6177(4)	2085(2)	450(2)	56(1)
I(2)	-752(3)	5706(2)	2340(2)	54(1)
Ca	1836(7)	4474(4)	2421(4)	30(2)
O(1)	3820(30)	3470(14)	2769(19)	50(7)
O(2)	4160(50)	5099(15)	2733(18)	75(11)
O(3)	2750(30)	5369(16)	1117(19)	57(8)
O(4)	1240(30)	3605(13)	1087(15)	38(6)

O(5)	300(30)	3394(14)	2802(15)	40(6)
O(6)	1250(30)	4373(12)	4133(14)	39(6)
C(1)	3590(40)	2640(20)	2810(30)	44(9)
C(2)	5020(50)	3790(30)	2840(30)	55(10)
C(3)	5420(70)	4670(30)	3310(40)	85(16)
C(4)	4510(50)	5680(30)	2160(30)	57(11)
C(5)	3570(50)	6040(30)	1560(30)	59(11)
C(6)	1940(40)	5630(20)	250(30)	43(9)
C(7)	2650(40)	3430(20)	380(30)	40(8)
C(8)	300(50)	2970(20)	1220(30)	49(9)
C(9)	-670(50)	3150(30)	1890(30)	56(11)
C(10)	-760(40)	3500(20)	3700(30)	42(8)
C(11)	590(40)	3750(20)	4360(20)	39(8)
C(12)	2020(60)	4630(30)	4850(40)	68(13)

Table 3. Bond lengths [Å] and angles [°] for **4**.

I(2)-Ca	3.106(7)	O(2)-C(4)	1.29(5)
Ca-O(1)	2.49(3)	O(3)-C(5)	1.47(5)
Ca-O(2)	2.39(4)	O(3)-C(6)	1.47(5)
Ca-O(3)	2.48(3)	O(4)-C(7)	1.65(4)
Ca-O(4)	2.40(2)	O(4)-C(8)	1.36(5)
Ca-O(5)	2.32(2)	O(5)-C(9)	1.59(5)
Ca-O(6)	2.44(2)	O(5)-C(10)	1.58(4)
Ca-C(2)	3.15(5)	O(6)-C(11)	1.24(4)
Ca-C(4)	3.16(4)	O(6)-C(12)	1.28(6)
Ca-C(9)	3.23(4)	C(2)-C(3)	1.63(7)
Ca-C(11)	3.16(4)	C(4)-C(5)	1.33(6)
O(1)-C(1)	1.39(5)	C(8)-C(9)	1.32(6)
O(1)-C(2)	1.21(5)	C(10)-C(11)	1.59(5)
O(2)-C(3)	1.56(7)		

O(5)-Ca-O(2)	145.1(9)	O(5)-Ca-O(3)	145.5(9)
O(5)-Ca-O(4)	65.4(8)	O(2)-Ca-O(3)	65.0(9)
O(2)-Ca-O(4)	126.4(9)	O(4)-Ca-O(3)	82.4(8)
O(5)-Ca-O(6)	66.1(8)	O(6)-Ca-O(3)	145.5(9)
O(2)-Ca-O(6)	92.7(9)	O(5)-Ca-O(1)	83.2(8)
O(4)-Ca-O(6)	131.3(8)	O(2)-Ca-O(1)	67.2(9)

O(4)-Ca-O(1)	85.0(8)	O(1)-Ca-C(9)	95.9(10)
O(6)-Ca-O(1)	85.7(9)	I(2)-Ca-C(9)	84.4(8)
O(3)-Ca-O(1)	107.1(10)	C(2)-Ca-C(9)	116.4(11)
O(5)-Ca-I(2)	93.2(6)	C(11)-Ca-C(9)	71.7(10)
O(2)-Ca-I(2)	113.1(7)	C(4)-Ca-C(9)	159.7(11)
O(4)-Ca-I(2)	101.2(6)	C(2)-O(1)-C(1)	124(3)
O(6)-Ca-I(2)	85.0(6)	C(2)-O(1)-Ca	112(2)
O(3)-Ca-I(2)	80.7(7)	C(1)-O(1)-Ca	124(2)
O(1)-Ca-I(2)	170.7(7)	C(4)-O(2)-C(3)	118(4)
O(5)-Ca-C(2)	103.6(10)	C(4)-O(2)-Ca	116(3)
O(2)-Ca-C(2)	46.4(11)	C(3)-O(2)-Ca	123(3)
O(4)-Ca-C(2)	97.7(10)	C(5)-O(3)-C(6)	112(3)
O(6)-Ca-C(2)	89.8(10)	C(5)-O(3)-Ca	108(2)
O(3)-Ca-C(2)	92.2(11)	C(6)-O(3)-Ca	127(2)
O(1)-Ca-C(2)	21.0(9)	C(8)-O(4)-C(7)	116(2)
I(2)-Ca-C(2)	158.7(8)	C(8)-O(4)-Ca	120(2)
O(5)-Ca-C(11)	45.5(8)	C(7)-O(4)-Ca	113.1(17)
O(2)-Ca-C(11)	109.1(9)	C(10)-O(5)-C(9)	109(2)
O(4)-Ca-C(11)	110.5(9)	C(10)-O(5)-Ca	117.5(18)
O(6)-Ca-C(11)	20.9(8)	C(9)-O(5)-Ca	109.9(19)
O(3)-Ca-C(11)	165.7(9)	C(11)-O(6)-C(12)	110(3)
O(1)-Ca-C(11)	81.0(9)	C(11)-O(6)-Ca	115(2)
I(2)-Ca-C(11)	90.4(7)	C(12)-O(6)-Ca	128(3)
C(2)-Ca-C(11)	92.1(10)	O(1)-C(2)-C(3)	129(4)
O(5)-Ca-C(4)	166.0(10)	O(1)-C(2)-Ca	47(2)
O(2)-Ca-C(4)	21.6(10)	C(3)-C(2)-Ca	88(3)
O(4)-Ca-C(4)	117.3(10)	O(2)-C(3)-C(2)	92(4)
O(6)-Ca-C(4)	108.9(10)	O(2)-C(4)-C(5)	124(4)
O(3)-Ca-C(4)	44.2(10)	O(2)-C(4)-Ca	43(2)
O(1)-Ca-C(4)	83.4(10)	C(5)-C(4)-Ca	82(3)
I(2)-Ca-C(4)	99.5(8)	C(4)-C(5)-O(3)	105(4)
C(2)-Ca-C(4)	62.7(11)	C(9)-C(8)-O(4)	110(4)
C(11)-Ca-C(4)	127.8(10)	C(8)-C(9)-O(5)	105(3)
O(5)-Ca-C(9)	27.5(9)	C(8)-C(9)-Ca	81(3)
O(2)-Ca-C(9)	162.4(11)	O(5)-C(9)-Ca	42.6(14)
O(4)-Ca-C(9)	42.7(10)	O(5)-C(10)-C(11)	91(3)
O(6)-Ca-C(9)	91.2(10)	O(6)-C(11)-C(10)	116(3)
O(3)-Ca-C(9)	118.1(10)	O(6)-C(11)-Ca	44.5(16)

C(10)-C(11)-Ca 83.1(19)

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for **4**.
The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	78(2)	60(2)	31(1)	-5(1)	10(1)	0(2)
I(2)	79(2)	48(1)	34(1)	3(1)	2(1)	19(1)
Ca	29(3)	40(3)	20(3)	1(2)	2(3)	0(3)
O(1)	59(16)	29(12)	61(16)	-1(11)	-5(13)	-22(12)
O(2)	160(30)	30(13)	36(13)	11(11)	28(17)	-9(18)
O(3)	71(18)	56(15)	45(14)	21(12)	-23(14)	-14(14)
O(4)	59(15)	31(11)	24(10)	-12(9)	3(11)	-2(11)
O(5)	37(13)	50(14)	33(11)	-19(10)	9(10)	-3(12)
O(6)	67(16)	32(11)	17(9)	-1(8)	-15(11)	2(12)

Crystal data and structure refinement for *cis*-[SrI$_2$(diglyme)$_2$] 5

$C_{12}H_{56}I_2SrO_6$, M= 609.76 gmol^{-1}, monoclinic, *P*2$_1$/*c* (Nr. 14), a = 19.723(4), b = 15.262(3), c = 14.066(3) Å, β = 90.50(3)°, V = 4233.9(2) Å^3, Z = 8, $\rho_{calcd.}$= 1.913 Mgm^3, *F*(000) = 2336, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 5.482 mm^{-1}, 1.69° < θ < 22.54°, 5539 reflections of which 5539 unique and 5304 observed, 388 parameters refined, *GOOF* (on F^2) = 1.010, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.1119, *wR*2 = 0.2749 for I > 2σ(I) and R1 = 0.1701, w*R*2 = 0.3213 for all data.

Crystal data for **5** were measured on a STOE STADI 4 diffractometer equipped with monochromated graphite Mo-K_α radiation and an Oxford Cryosystems open flow cryostat [406]. No absorption correction was possible due to decomposition of the crystals during measurement. The structure was solved with direct methods and refined by full-matrix least-squares on F^2 with the SHELX-99 package [409]. All heavy atoms could be refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms but disorder was observed for the ethyl groups of the polyether ligands in **5**. CCDC-206570 (**5**) contains the supplementary crystallographic data for **5**. The cif file for the structure of **5** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **5**.

Identification code	cis-[SrI$_2$(diglyme)$_2$]

Empirical formula	$C_{12} H_{28} I_2 O_6 Sr$	
Formula weight	609.76	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 19.723(4) Å	α= 90°
	b = 15.262(3) Å	β= 90.50(3)°
	c = 14.066(3) Å	γ = 90°
Volume	4233.9(15) Å^3	
Z	8	
Density (calculated)	1.913 Mg/m^3	
Absorption coefficient	5.482 mm^{-1}	
F(000)	2336	
Theta range for data collection	1.69 to 22.54°	
Index ranges	0<=h<=21, -16<=k<=0, -15<=l<=15	
Reflections collected	5539	
Independent reflections	5539 [R(int) = 0.0000]	
Completeness to theta = 22.54°	99.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5539 / 0 / 387	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.1125, wR2 = 0.2766	
R indices (all data)	R1 = 0.1706, wR2 = 0.3207	
Largest diff. peak and hole	2.957 and -3.365 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **5**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	4658(1)	8967(1)	2137(2)	49(1)
I(2)	-342(1)	8966(1)	2865(2)	49(1)
I(3)	6589(1)	8514(1)	4114(2)	57(1)
I(4)	1588(1)	8512(1)	888(2)	57(1)
Sr(5)	6087(1)	10042(2)	2575(2)	34(1)
Sr(6)	1088(1)	10043(2)	2422(2)	34(1)

O(1)	5544(12)	10711(14)	4170(17)	57(6)
O(2)	5230(10)	11349(12)	2511(16)	49(5)
O(3)	6065(11)	11074(14)	1058(15)	55(6)
O(4)	6499(11)	9021(15)	1095(13)	55(6)
O(5)	7380(10)	9908(12)	2138(12)	39(5)
O(6)	6938(10)	11247(14)	3162(15)	49(5)
O(7)	557(12)	10682(15)	796(17)	64(6)
O(8)	223(11)	11356(12)	2483(17)	51(6)
O(9)	1082(13)	11065(14)	3939(15)	59(6)
O(10)	1942(10)	11250(14)	1836(16)	54(6)
O(11)	2396(10)	9907(14)	2885(13)	47(5)
O(12)	1496(11)	9009(16)	3897(17)	64(7)
C(1)	5860(20)	10730(20)	5030(30)	79(12)
C(2)	5040(20)	11380(20)	4120(20)	62(11)
C(3)	4713(13)	11330(20)	3210(20)	45(8)
C(4)	4985(18)	11530(20)	1550(30)	65(10)
C(5)	5588(17)	11680(20)	920(30)	58(9)
C(6)	6645(19)	11200(30)	510(30)	76(12)
C(7)	6094(17)	8930(20)	270(30)	66(10)
C(8)	7178(16)	8840(20)	890(20)	62(10)
C(9)	7564(17)	9060(20)	1790(20)	55(9)
C(10)	7815(18)	10270(30)	2810(30)	85(13)
C(11)	7613(15)	11210(20)	2870(20)	55(9)
C(12)	6700(18)	12120(20)	3180(30)	71(11)
C(13)	920(20)	10700(20)	-50(20)	60(10)
C(14)	50(16)	11370(20)	840(20)	50(8)
C(15)	-293(14)	11330(20)	1810(20)	51(8)
C(16)	-20(20)	11530(20)	3450(30)	82(14)
C(17)	598(19)	11740(20)	4050(30)	65(10)
C(18)	1621(19)	11200(20)	4530(20)	64(11)
C(19)	1711(16)	12140(19)	1810(30)	72(12)
C(20)	2640(15)	11210(20)	2100(30)	54(9)
C(21)	2853(17)	10250(20)	2240(20)	59(10)
C(22)	2585(17)	9050(18)	3150(20)	50(8)
C(23)	2203(17)	8800(30)	4090(20)	62(10)
C(24)	1085(16)	8930(20)	4690(30)	68(11)

Table 3. Bond lengths [Å] and angles [°] for **5**.

I(1)-Sr(5)	3.314(3)	O(5)-C(9)	1.42(4)
I(3)-Sr(5)	3.327(3)	O(5)-C(10)	1.39(4)
I(2)-Sr(6)	3.327(3)	O(6)-C(11)	1.40(4)
I(4)-Sr(6)	3.335(3)	O(6)-C(12)	1.41(4)
Sr(5)-O(1)	2.69(2)	O(7)-C(13)	1.39(4)
Sr(5)-O(2)	2.61(2)	O(7)-C(14)	1.46(4)
Sr(5)-O(3)	2.65(2)	O(8)-C(15)	1.39(4)
Sr(5)-O(4)	2.73(2)	O(8)-C(16)	1.48(4)
Sr(5)-O(5)	2.64(2)	O(9)-C(17)	1.41(4)
Sr(5)-O(6)	2.619(19)	O(9)-C(18)	1.36(4)
Sr(6)-O(7)	2.69(2)	O(10)-C(19)	1.43(4)
Sr(6)-O(8)	2.63(2)	O(10)-C(20)	1.42(3)
Sr(6)-O(9)	2.64(2)	O(11)-C(21)	1.39(3)
Sr(6)-O(10)	2.635(19)	O(11)-C(22)	1.41(3)
Sr(6)-O(11)	2.663(19)	O(12)-C(23)	1.45(4)
Sr(6)-O(12)	2.72(3)	O(12)-C(24)	1.39(4)
O(1)-C(1)	1.36(5)	C(2)-C(3)	1.43(5)
O(1)-C(2)	1.42(4)	C(4)-C(5)	1.51(5)
O(2)-C(3)	1.42(3)	C(8)-C(9)	1.52(5)
O(2)-C(4)	1.45(4)	C(10)-C(11)	1.49(5)
O(3)-C(5)	1.34(4)	C(14)-C(15)	1.53(4)
O(3)-C(6)	1.40(4)	C(16)-C(17)	1.51(6)
O(4)-C(7)	1.42(4)	C(20)-C(21)	1.53(5)
O(4)-C(8)	1.40(4)	C(22)-C(23)	1.58(4)

O(2)-Sr(5)-O(6)	83.5(6)	O(6)-Sr(5)-O(4)	116.5(7)
O(2)-Sr(5)-O(5)	132.6(6)	O(5)-Sr(5)-O(4)	58.8(6)
O(6)-Sr(5)-O(5)	60.6(6)	O(3)-Sr(5)-O(4)	74.2(7)
O(2)-Sr(5)-O(3)	60.9(7)	O(1)-Sr(5)-O(4)	166.9(6)
O(6)-Sr(5)-O(3)	80.9(7)	O(2)-Sr(5)-I(1)	79.8(4)
O(5)-Sr(5)-O(3)	82.3(6)	O(6)-Sr(5)-I(1)	161.5(5)
O(2)-Sr(5)-O(1)	58.6(7)	O(5)-Sr(5)-I(1)	137.8(4)
O(6)-Sr(5)-O(1)	74.3(6)	O(3)-Sr(5)-I(1)	97.9(5)
O(5)-Sr(5)-O(1)	128.0(6)	O(1)-Sr(5)-I(1)	89.9(5)
O(3)-Sr(5)-O(1)	116.2(7)	O(4)-Sr(5)-I(1)	80.5(5)
O(2)-Sr(5)-O(4)	127.3(7)	O(2)-Sr(5)-I(3)	138.2(5)

O(6)-Sr(5)-I(3)	95.8(5)
O(5)-Sr(5)-I(3)	79.3(4)
O(3)-Sr(5)-I(3)	160.4(5)
O(1)-Sr(5)-I(3)	80.9(5)
O(4)-Sr(5)-I(3)	90.4(5)
I(1)-Sr(5)-I(3)	91.25(9)
O(8)-Sr(6)-O(10)	83.9(6)
O(8)-Sr(6)-O(9)	61.1(7)
O(10)-Sr(6)-O(9)	81.2(7)
O(8)-Sr(6)-O(11)	132.6(7)
O(10)-Sr(6)-O(11)	60.7(6)
O(9)-Sr(6)-O(11)	81.9(7)
O(8)-Sr(6)-O(7)	60.3(7)
O(10)-Sr(6)-O(7)	74.1(7)
O(9)-Sr(6)-O(7)	117.9(7)
O(11)-Sr(6)-O(7)	127.2(7)
O(8)-Sr(6)-O(12)	127.1(7)
O(10)-Sr(6)-O(12)	117.3(7)
O(9)-Sr(6)-O(12)	74.4(7)
O(11)-Sr(6)-O(12)	59.3(6)
O(7)-Sr(6)-O(12)	165.6(7)
O(8)-Sr(6)-I(2)	79.6(4)
O(10)-Sr(6)-I(2)	161.7(5)
O(9)-Sr(6)-I(2)	97.5(5)
O(11)-Sr(6)-I(2)	137.4(4)
O(7)-Sr(6)-I(2)	90.8(5)
O(12)-Sr(6)-I(2)	79.4(5)
O(8)-Sr(6)-I(4)	138.5(5)
O(10)-Sr(6)-I(4)	95.4(5)
O(9)-Sr(6)-I(4)	159.9(6)
O(11)-Sr(6)-I(4)	79.2(5)
O(7)-Sr(6)-I(4)	79.6(5)
O(12)-Sr(6)-I(4)	90.0(5)
I(2)-Sr(6)-I(4)	91.78(9)
C(1)-O(1)-C(2)	110(2)
C(1)-O(1)-Sr(5)	124(2)
C(2)-O(1)-Sr(5)	120.6(18)
C(3)-O(2)-C(4)	114(2)
C(3)-O(2)-Sr(5)	115.3(16)
C(4)-O(2)-Sr(5)	112.6(18)
C(5)-O(3)-C(6)	113(3)
C(5)-O(3)-Sr(5)	123(2)
C(6)-O(3)-Sr(5)	121.5(19)
C(8)-O(4)-C(7)	110(2)
C(8)-O(4)-Sr(5)	124.5(19)
C(7)-O(4)-Sr(5)	121.0(18)
C(10)-O(5)-C(9)	116(3)
C(10)-O(5)-Sr(5)	113.7(19)
C(9)-O(5)-Sr(5)	113.5(17)
C(11)-O(6)-C(12)	111(2)
C(11)-O(6)-Sr(5)	119.3(16)
C(12)-O(6)-Sr(5)	117.1(19)
C(13)-O(7)-C(14)	112(2)
C(13)-O(7)-Sr(6)	122.3(19)
C(14)-O(7)-Sr(6)	119.4(18)
C(15)-O(8)-C(16)	113(3)
C(15)-O(8)-Sr(6)	115.2(18)
C(16)-O(8)-Sr(6)	112.8(19)
C(18)-O(9)-C(17)	110(3)
C(18)-O(9)-Sr(6)	125.1(19)
C(17)-O(9)-Sr(6)	122(2)
C(20)-O(10)-C(19)	111(2)
C(20)-O(10)-Sr(6)	120.5(18)
C(19)-O(10)-Sr(6)	117.8(18)
C(21)-O(11)-C(22)	111(2)
C(21)-O(11)-Sr(6)	116.4(19)
C(22)-O(11)-Sr(6)	113.0(17)
C(24)-O(12)-C(23)	113(3)
C(24)-O(12)-Sr(6)	119.6(17)
C(23)-O(12)-Sr(6)	123.3(19)
O(1)-C(2)-C(3)	109(2)
O(2)-C(3)-C(2)	107(2)
O(2)-C(4)-C(5)	109(3)
O(3)-C(5)-C(4)	111(3)
O(4)-C(8)-C(9)	104(2)
O(5)-C(9)-C(8)	111(3)

O(5)-C(10)-C(11)	105(3)	O(9)-C(17)-C(16)	110(3)
O(6)-C(11)-C(10)	108(3)	O(10)-C(20)-C(21)	110(3)
O(7)-C(14)-C(15)	108(2)	O(11)-C(21)-C(20)	106(3)
O(8)-C(15)-C(14)	106(2)	O(11)-C(22)-C(23)	108(3)
O(8)-C(16)-C(17)	106(3)	O(12)-C(23)-C(22)	104(2)

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **5**.

The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	44(1)	48(1)	56(1)	-7(1)	8(1)	-7(1)
I(2)	43(1)	48(1)	58(1)	7(1)	6(1)	-8(1)
I(3)	53(1)	55(1)	63(1)	16(1)	19(1)	10(1)
I(4)	53(1)	57(1)	61(1)	-16(1)	-6(1)	13(1)
Sr(5)	30(1)	35(1)	36(1)	-1(1)	6(1)	0(1)
Sr(6)	34(2)	36(1)	32(1)	1(1)	6(1)	2(1)
O(1)	60(15)	55(14)	57(15)	-25(11)	12(13)	-18(11)
O(2)	42(13)	46(12)	58(13)	-2(10)	-25(12)	-3(10)
O(3)	64(15)	58(14)	41(12)	4(10)	-1(12)	6(12)
O(4)	58(14)	88(16)	19(11)	0(10)	19(11)	1(12)
O(5)	51(12)	47(11)	18(9)	-7(8)	-9(10)	-8(10)
O(6)	31(12)	64(14)	51(13)	-15(10)	-7(10)	-13(10)
O(7)	61(15)	62(15)	70(16)	21(12)	2(14)	6(12)
O(8)	46(13)	44(12)	65(14)	0(11)	15(13)	-2(10)
O(9)	81(17)	59(14)	36(12)	-10(10)	14(13)	5(13)
O(10)	41(13)	57(14)	63(14)	21(11)	-6(12)	-13(10)
O(11)	35(11)	74(14)	34(11)	8(10)	-11(10)	-11(10)
O(12)	39(13)	91(18)	61(15)	-26(13)	3(12)	-2(12)
C(1)	80(30)	60(20)	90(30)	-20(20)	30(30)	10(20)
C(2)	100(30)	47(19)	39(19)	-26(15)	40(20)	20(20)
C(3)	14(14)	59(19)	60(20)	-4(16)	19(15)	24(13)
C(4)	50(20)	50(20)	90(30)	1(19)	-30(20)	18(17)
C(5)	60(20)	50(20)	60(20)	13(17)	-30(20)	3(17)
C(6)	70(30)	90(30)	70(30)	40(20)	60(20)	10(20)
C(7)	50(20)	80(20)	70(30)	-30(20)	10(20)	10(18)
C(8)	40(20)	90(30)	50(20)	-14(18)	35(18)	11(18)
C(9)	50(20)	80(20)	33(17)	5(16)	10(17)	-7(18)

C(10)	40(20)	100(30)	120(40)	-20(30)	10(20)	-10(20)
C(11)	35(18)	80(20)	50(20)	-34(17)	-8(17)	-18(16)
C(12)	70(20)	37(19)	110(30)	-18(19)	30(20)	-12(17)
C(13)	100(30)	52(19)	24(16)	7(14)	-30(20)	10(18)
C(14)	49(19)	70(20)	31(16)	25(15)	-10(16)	1(16)
C(15)	19(15)	90(20)	45(19)	13(17)	8(15)	4(15)
C(16)	120(40)	60(20)	70(30)	-3(19)	60(30)	40(20)
C(17)	70(30)	70(20)	60(20)	6(18)	20(20)	20(20)
C(18)	90(30)	60(20)	41(19)	-23(16)	-50(20)	29(19)
C(19)	42(19)	30(17)	150(40)	0(20)	0(20)	0(14)
C(20)	25(17)	70(20)	60(20)	8(17)	-17(16)	-10(15)
C(21)	50(20)	70(20)	50(20)	-30(17)	28(18)	-28(18)
C(22)	60(20)	30(16)	55(19)	34(14)	-13(18)	18(15)
C(23)	50(20)	90(30)	50(20)	24(18)	-18(18)	22(18)
C(24)	38(19)	70(20)	90(30)	50(20)	0(20)	25(17)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **5**.

	x	y	z	U(eq)
H(1A)	6081	11297	5113	118
H(1B)	6204	10273	5053	118
H(1C)	5536	10640	5527	118
H(2A)	5258	11954	4197	75
H(2B)	4714	11301	4626	75
H(3A)	4450	10786	3157	54
H(3B)	4404	11826	3123	54
H(4A)	4691	12043	1555	78
H(4B)	4721	11025	1319	78
H(5A)	5439	11670	252	70
H(5B)	5778	12263	1050	70
H(6A)	6511	11307	-149	113
H(6B)	6931	10688	542	113
H(6C)	6893	11708	745	113
H(7A)	6242	9345	-211	99
H(7B)	5623	9040	419	99
H(7C)	6139	8338	20	99

H(8A)	7334	9195	353	74
H(8B)	7236	8217	724	74
H(9A)	7468	8623	2281	66
H(9B)	8052	9052	1669	66
H(10A)	8288	10215	2615	102
H(10B)	7762	9980	3430	102
H(11A)	7904	11517	3332	66
H(11B)	7662	11490	2251	66
H(12A)	6789	12368	3805	107
H(12B)	6217	12125	3053	107
H(12C)	6933	12459	2703	107
H(13A)	643	10457	-556	90
H(13B)	1330	10360	26	90
H(13C)	1035	11304	-200	90
H(14A)	-287	11297	330	60
H(14B)	266	11948	756	60
H(15A)	-601	11826	1888	61
H(15B)	-553	10785	1865	61
H(16A)	-259	11020	3706	98
H(16B)	-335	12032	3450	98
H(17A)	791	12297	3847	78
H(17B)	472	11785	4717	78
H(18A)	1827	11764	4383	95
H(18B)	1952	10740	4443	95
H(18C)	1469	11204	5183	95
H(19A)	1972	12486	2261	109
H(19B)	1235	12160	1975	109
H(19C)	1770	12374	1175	109
H(20A)	2717	11538	2685	65
H(20B)	2915	11472	1596	65
H(21A)	2833	9932	1640	71
H(21B)	3316	10221	2498	71
H(22A)	3077	9020	3251	60
H(22B)	2463	8638	2640	60
H(23A)	2257	8175	4239	75
H(23B)	2375	9143	4633	75
H(24A)	1208	8398	5038	102
H(24B)	614	8890	4492	102

H(24C)	1147	9431	5103	102

Crystal data and structure refinement for *trans*-[BaI$_2$(diglyme)$_2$] 6

$C_{12}H_{28}I_2Ba_{12}O_6$, M= 659.48 gmol^{-1}, triclinic, *P*-1 (Nr. 2), a = 8.5881(17), b = 9.806(2), c = 13.523(3) Å, α = 89.72(3), β = 74.97(3), γ = 89.87(3)°, V = 1099.9(4) Å^3, Z = 2, ρ_{calcd}.= 1.991 Mgm^3, *F*(000) = 620, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 4.630 mm^{-1}, 2.54° < θ < 27.03°, 3858 reflections, unique and observed, 198 parameters refined, *GOOF* (on F^2) = 1.429, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.0380, *wR*2 = 0.0878 for I > 2σ(I) and R1 = 0.0380, w*R*2 = 0.0878 for all data.

The intensities from the single-crystals of **6** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms.

Table 1. Crystal data and structure refinement for **6**.

Identification code	*trans*-[BaI$_2$(diglyme)$_2$]	
Empirical formula	C12 H28 Ba I2 O6	
Formula weight	659.48	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.5881(17) Å	α= 89.72(3)°
	b = 9.806(2) Å	β= 74.97(3)°
	c = 13.523(3) Å	γ = 89.87(3)°
Volume	1099.9(4) Å^3	
Z	2	
Density (calculated)	1.991 Mg/m^3	
Absorption coefficient	4.630 mm^{-1}	
F(000)	620	
Theta range for data collection	2.54 to 27.03°	
Index ranges	0<=h<=10, -12<=k<=12, -15<=l<=16	
Reflections collected	3858	
Independent reflections	3858 [R(int) = 0.0000]	
Completeness to theta = 27.03°	80.3 %	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	3858 / 0 / 198
Goodness-of-fit on F^2	1.430
Final R indices [I>2sigma(I)]	R1 = 0.0380, wR2 = 0.0878
R indices (all data)	R1 = 0.0380, wR2 = 0.0878
Largest diff. peak and hole	0.876 and -0.644 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **6**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ba(1)	5000	0	5000	30(1)
Ba(2)	0	-5000	0	33(1)
I(1)	7142(1)	2719(1)	5507(1)	58(1)
I(2)	2283(1)	-7758(1)	296(1)	57(1)
O(1)	7251(2)	-1968(2)	5231(2)	65(1)
O(2)	5291(2)	-903(2)	6935(1)	56(1)
O(3)	2499(2)	235(2)	6785(1)	56(1)
O(4)	12720(2)	-4167(2)	8451(1)	55(1)
O(5)	10178(2)	-5283(2)	7888(1)	43(1)
O(6)	8082(2)	-6853(2)	9247(1)	60(1)
C(1)	7734(4)	-3076(3)	4493(3)	80(1)
C(2)	7548(3)	-2272(3)	6171(2)	70(1)
C(3)	6973(3)	-1110(3)	6874(2)	73(1)
C(4)	4492(3)	26(3)	7695(2)	68(1)
C(5)	2751(4)	-81(3)	7762(2)	69(1)
C(6)	876(3)	41(3)	6744(3)	75(1)
C(7)	14306(3)	-4300(4)	8584(3)	83(1)
C(8)	12725(3)	-4218(3)	7398(2)	60(1)
C(9)	11022(3)	-4151(3)	7320(2)	54(1)
C(10)	8580(3)	-5450(2)	7771(2)	45(1)
C(11)	7981(3)	-6798(2)	8217(2)	51(1)
C(12)	7654(3)	-8178(3)	9702(2)	73(1)

Table 3. Bond lengths [Å] and angles [°] for **6**.

Ba(1)-I(1)	3.4143(10)	Ba(1)-I(1)#1	3.4143(10)

Ba(1)-O(1)	2.8021(19)	O(1)-C(1)	1.463(4)
Ba(1)-O(1)#1	2.8021(19)	O(1)-C(2)	1.391(4)
Ba(1)-O(2)	2.8306(19)	O(2)-C(3)	1.439(3)
Ba(1)-O(2)#1	2.8306(19)	O(2)-C(4)	1.414(3)
Ba(1)-O(3)	2.7939(18)	O(3)-C(5)	1.427(4)
Ba(1)-O(3)#1	2.7939(18)	O(3)-C(6)	1.422(3)
Ba(2)-I(2)	3.4194(10)	O(4)-C(7)	1.425(3)
Ba(2)-I(2)#4	3.4194(10)	O(4)-C(8)	1.423(3)
Ba(2)-O(4)#2	2.8226(18)	O(5)-C(9)	1.432(3)
Ba(2)-O(4)#3	2.8226(18)	O(5)-C(10)	1.431(3)
O(4)-Ba(2)#5	2.8226(18)	O(6)-C(11)	1.418(3)
Ba(2)-O(5)#2	2.8353(17)	O(6)-C(12)	1.442(3)
Ba(2)-O(5)#3	2.8353(17)	C(2)-C(3)	1.487(4)
O(5)-Ba(2)#5	2.8353(17)	C(4)-C(5)	1.478(4)
Ba(2)-O(6)#2	2.820(2)	C(8)-C(9)	1.494(4)
Ba(2)-O(6)#3	2.820(2)	C(10)-C(11)	1.486(3)
O(6)-Ba(2)#5	2.820(2)		

O(3)#1-Ba(1)-O(3)	180.0	O(2)#1-Ba(1)-I(1)#1	82.76(4)
O(3)#1-Ba(1)-O(1)	68.89(6)	O(3)#1-Ba(1)-I(1)	84.64(5)
O(3)-Ba(1)-O(1)	111.11(6)	O(3)-Ba(1)-I(1)	95.36(5)
O(3)#1-Ba(1)-O(1)#1	111.11(6)	O(1)-Ba(1)-I(1)	95.29(4)
O(3)-Ba(1)-O(1)#1	68.89(6)	O(1)#1-Ba(1)-I(1)	84.71(4)
O(1)-Ba(1)-O(1)#1	180.00(9)	O(2)-Ba(1)-I(1)	82.76(4)
O(3)#1-Ba(1)-O(2)	122.68(5)	O(2)#1-Ba(1)-I(1)	97.24(4)
O(3)-Ba(1)-O(2)	57.32(5)	I(1)#1-Ba(1)-I(1)	180.000(6)
O(1)-Ba(1)-O(2)	57.06(6)	O(4)#2-Ba(2)-O(4)#3	180.0
O(1)#1-Ba(1)-O(2)	122.94(6)	O(4)#2-Ba(2)-O(6)#2	111.49(6)
O(3)#1-Ba(1)-O(2)#1	57.32(5)	O(4)#3-Ba(2)-O(6)#2	68.51(6)
O(3)-Ba(1)-O(2)#1	122.68(5)	O(4)#2-Ba(2)-O(6)#3	68.51(6)
O(1)-Ba(1)-O(2)#1	122.94(6)	O(4)#3-Ba(2)-O(6)#3	111.49(6)
O(1)#1-Ba(1)-O(2)#1	57.06(6)	O(6)#2-Ba(2)-O(6)#3	180.00(7)
O(2)-Ba(1)-O(2)#1	180.0	O(4)#2-Ba(2)-O(5)#2	57.56(5)
O(3)#1-Ba(1)-I(1)#1	95.36(5)	O(4)#3-Ba(2)-O(5)#2	122.44(5)
O(3)-Ba(1)-I(1)#1	84.64(5)	O(6)#2-Ba(2)-O(5)#2	56.89(5)
O(1)-Ba(1)-I(1)#1	84.71(4)	O(6)#3-Ba(2)-O(5)#2	123.11(5)
O(1)#1-Ba(1)-I(1)#1	95.29(4)	O(4)#2-Ba(2)-O(5)#3	122.44(5)
O(2)-Ba(1)-I(1)#1	97.24(4)	O(4)#3-Ba(2)-O(5)#3	57.56(5)

O(6)#2-Ba(2)-O(5)#3	123.11(5)	C(3)-O(2)-Ba(1)	108.51(14)
O(6)#3-Ba(2)-O(5)#3	56.89(5)	C(6)-O(3)-C(5)	113.1(2)
O(5)#2-Ba(2)-O(5)#3	180.00(6)	C(6)-O(3)-Ba(1)	119.77(17)
O(4)#2-Ba(2)-I(2)	85.68(5)	C(5)-O(3)-Ba(1)	120.99(15)
O(4)#3-Ba(2)-I(2)	94.32(5)	C(8)-O(4)-C(7)	111.6(2)
O(6)#2-Ba(2)-I(2)	86.45(4)	C(8)-O(4)-Ba(2)#5	121.20(14)
O(6)#3-Ba(2)-I(2)	93.55(4)	C(7)-O(4)-Ba(2)#5	120.95(17)
O(5)#2-Ba(2)-I(2)	98.88(4)	C(10)-O(5)-C(9)	113.43(18)
O(5)#3-Ba(2)-I(2)	81.12(4)	C(10)-O(5)-Ba(2)#5	108.66(12)
O(4)#2-Ba(2)-I(2)#4	94.32(5)	C(9)-O(5)-Ba(2)#5	110.37(14)
O(4)#3-Ba(2)-I(2)#4	85.68(5)	C(11)-O(6)-C(12)	112.1(2)
O(6)#2-Ba(2)-I(2)#4	93.55(4)	C(11)-O(6)-Ba(2)#5	121.56(13)
O(6)#3-Ba(2)-I(2)#4	86.45(4)	C(12)-O(6)-Ba(2)#5	122.38(17)
O(5)#2-Ba(2)-I(2)#4	81.12(4)	O(1)-C(2)-C(3)	108.3(2)
O(5)#3-Ba(2)-I(2)#4	98.88(4)	O(2)-C(3)-C(2)	107.8(2)
I(2)-Ba(2)-I(2)#4	180.000(6)	O(2)-C(4)-C(5)	106.9(2)
C(2)-O(1)-C(1)	112.4(2)	O(3)-C(5)-C(4)	108.8(2)
C(2)-O(1)-Ba(1)	122.76(15)	O(4)-C(8)-C(9)	108.63(19)
C(1)-O(1)-Ba(1)	121.15(19)	O(5)-C(9)-C(8)	107.4(2)
C(4)-O(2)-C(3)	115.0(2)	O(5)-C(10)-C(11)	107.48(19)
C(4)-O(2)-Ba(1)	109.27(16)	O(6)-C(11)-C(10)	108.9(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1 #2 x-1,y,z-1 #3 -x+1,-y-1,-z+1

#4 -x,-y-1,-z #5 x+1,y,z+1

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for **6**.

The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ba(1)	33(1)	32(1)	28(1)	0(1)	-11(1)	-2(1)
Ba(2)	37(1)	34(1)	29(1)	4(1)	-14(1)	-3(1)
I(1)	80(1)	52(1)	47(1)	5(1)	-25(1)	-29(1)
I(2)	78(1)	42(1)	61(1)	-11(1)	-35(1)	17(1)
O(1)	57(1)	38(1)	104(1)	15(1)	-30(1)	10(1)
O(2)	59(1)	72(1)	44(1)	6(1)	-26(1)	-11(1)
O(3)	48(1)	66(1)	46(1)	-5(1)	0(1)	-5(1)

O(4)	41(1)	80(1)	44(1)	6(1)	-11(1)	-7(1)
O(5)	47(1)	48(1)	36(1)	4(1)	-16(1)	-2(1)
O(6)	72(1)	46(1)	71(1)	16(1)	-35(1)	-26(1)
C(1)	77(2)	57(2)	99(2)	10(2)	-8(2)	13(1)
C(2)	51(1)	74(2)	89(2)	38(1)	-27(1)	0(1)
C(3)	60(1)	102(2)	74(2)	34(1)	-46(1)	-22(1)
C(4)	87(2)	84(2)	37(1)	9(1)	-21(1)	-34(1)
C(5)	81(2)	83(2)	33(1)	-12(1)	4(1)	-22(1)
C(6)	47(1)	84(2)	83(2)	5(2)	1(1)	-1(1)
C(7)	44(1)	132(3)	72(2)	9(2)	-15(1)	-9(2)
C(8)	52(1)	70(2)	51(2)	-2(1)	1(1)	-5(1)
C(9)	60(1)	59(1)	44(1)	11(1)	-15(1)	-5(1)
C(10)	56(1)	48(1)	38(1)	-5(1)	-23(1)	4(1)
C(11)	61(1)	50(1)	52(1)	-10(1)	-30(1)	-4(1)
C(12)	88(2)	68(1)	61(2)	32(1)	-19(1)	-46(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **6**.

	x	y	z	U(eq)
H(1A)	8850	-3289	4416	121
H(1B)	7579	-2797	3844	121
H(1C)	7090	-3867	4735	121
H(2A)	8693	-2414	6087	84
H(2B)	6984	-3100	6453	84
H(3A)	7118	-1312	7547	88
H(3B)	7581	-293	6614	88
H(4A)	4868	948	7509	82
H(4B)	4697	-201	8349	82
H(5A)	2377	-998	7966	83
H(5B)	2150	549	8272	83
H(6A)	771	-838	6459	112
H(6B)	587	738	6323	112
H(6C)	175	93	7423	112
H(7A)	14869	-5012	8149	124
H(7B)	14242	-4523	9286	124
H(7C)	14875	-3455	8408	124

H(8A)	13226	-5058	7096	72
H(8B)	13335	-3457	7031	72
H(9A)	10526	-3300	7603	65
H(9B)	10991	-4203	6610	65
H(10A)	8592	-5415	7053	54
H(10B)	7885	-4727	8125	54
H(11A)	6872	-6923	8192	62
H(11B)	8627	-7521	7825	62
H(12A)	6643	-8458	9591	109
H(12B)	7560	-8132	10425	109
H(12C)	8475	-8825	9395	109

Crystal data and structure refinement for [SrI(triglyme)$_2$]I 7

$C_{16}H_{36}I_2SrO_8$, M= 697.87 gmol^{-1}, monoclinic, $P2_1/n$ (Nr. 14), a = 9.9945(13), b = 17.2690(15), c = 14.9109(19) Å, β = 91.606(11)°, V = 2572.5(5) Å^3, Z = 4, ρ_{calcd}.= 1.802 Mgm^3, $F(000)$ = 1360, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 4.529 mm^{-1}, 1.80° < θ < 27.13°, 19974 reflections of which 5629 unique and 3244 observed, 248 parameters refined, *GOOF* (on F^2) = 1.037, R1= $\Sigma|F_o – F_c|/\Sigma F_o$ = 0.0617, $wR2$ = 0.1277 for I > 2σ(I) and R1 = 0.1238, w$R2$ = 0.1584 for all data.

The intensities from the single-crystals of **7** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms.

Table 1. Crystal data and structure refinement for **7**.

Identification code	[SrI(triglyme)$_2$]I	
Empirical formula	C16 H36 I2 O8 Sr	
Formula weight	697.87	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.9945(13) Å	α= 90°
	b = 17.2690(15) Å	β= 91.606(11)°
	c = 14.9109(19) Å	γ = 90°
Volume	2572.5(5) Å^3	

Z	4
Density (calculated)	1.802 Mg/m^3
Absorption coefficient	4.529 mm^{-1}
F(000)	1360
Theta range for data collection	1.80 to 27.13°
Index ranges	-12<=h<=12, -22<=k<=20, -19<=l<=17
Reflections collected	19974
Independent reflections	5629 [R(int) = 0.1350]
Completeness to theta = 27.13°	98.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5629 / 0 / 248
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0617, wR2 = 0.1277
R indices (all data)	R1 = 0.1238, wR2 = 0.1584
Largest diff. peak and hole	0.876 and -0.984 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **7**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	805(1)	344(1)	2606(1)	58(1)
Sr	-1988(1)	-846(1)	2303(1)	40(1)
I(2)	-6507(1)	-2037(1)	5185(1)	68(1)
O(1)	100(1)	-1743(1)	2587(1)	56(1)
O(2)	-1312(1)	-1113(1)	3993(1)	56(1)
O(3)	-3482(1)	-272(1)	3551(1)	60(1)
O(4)	-4598(1)	-793(1)	2042(1)	74(1)
O(5)	-2983(1)	-2252(1)	2760(1)	61(1)
O(6)	-2235(1)	-1957(1)	1072(1)	67(1)
O(7)	-1657(1)	-513(1)	558(1)	73(1)
O(8)	-2610(1)	602(1)	1691(1)	70(1)
C(1)	1309(1)	-1766(1)	2107(1)	83(1)
C(2)	235(1)	-2048(1)	3482(1)	59(1)
C(3)	20(1)	-1420(1)	4127(1)	62(1)
C(4)	-1608(1)	-464(1)	4530(1)	66(1)
C(5)	-3063(1)	-318(1)	4471(1)	76(1)

C(6)	-4911(1)	-210(1)	3437(1)	82(1)
C(7)	-5277(1)	-179(1)	2454(1)	83(1)
C(8)	-5191(1)	-1003(1)	1209(1)	106(1)
C(9)	-3977(1)	-2294(1)	3441(1)	79(1)
C(10)	-3264(1)	-2807(1)	2085(1)	80(1)
C(11)	-2227(1)	-2746(1)	1407(1)	79(1)
C(12)	-1468(1)	-1854(1)	288(1)	90(1)
C(13)	-1930(1)	-1112(1)	-95(1)	91(1)
C(14)	-2171(1)	200(1)	232(1)	95(1)
C(15)	-1968(1)	819(1)	872(1)	82(1)
C(16)	-2643(1)	1239(1)	2304(1)	87(1)

Table 3. Bond lengths [Å] and angles [°] for **7**.

I(1)-Sr	3.4854(3)	O(4)-C(7)	1.4085(5)
Sr-O(1)	2.6231(3)	O(4)-C(8)	1.4078(6)
Sr-O(2)	2.6313(4)	O(5)-C(9)	1.4435(5)
Sr-O(3)	2.6143(4)	O(5)-C(10)	1.4118(5)
Sr-O(4)	2.6285(4)	O(6)-C(11)	1.4501(5)
Sr-O(5)	2.7175(3)	O(6)-C(12)	1.4272(5)
Sr-O(6)	2.6614(3)	O(7)-C(13)	1.4414(5)
Sr-O(7)	2.6936(4)	O(7)-C(14)	1.4136(5)
Sr-O(8)	2.7283(3)	O(8)-C(15)	1.4445(5)
Sr-C(4)	3.3973(5)	O(8)-C(16)	1.4310(5)
O(1)-C(1)	1.4207(5)	C(2)-C(3)	1.4683(5)
O(1)-C(2)	1.4377(4)	C(4)-C(5)	1.4761(6)
O(2)-C(3)	1.4414(4)	C(6)-C(7)	1.5023(6)
O(2)-C(4)	1.4140(4)	C(10)-C(11)	1.4723(6)
O(3)-C(5)	1.4248(5)	C(12)-C(13)	1.4720(7)
O(3)-C(6)	1.4378(4)	C(14)-C(15)	1.4437(6)
O(3)-Sr-O(1)	125.205(10)	O(1)-Sr-O(6)	75.174(11)
O(3)-Sr-O(4)	60.512(11)	O(4)-Sr-O(6)	81.405(11)
O(1)-Sr-O(4)	145.726(8)	O(2)-Sr-O(6)	123.412(9)
O(3)-Sr-O(2)	61.365(11)	O(3)-Sr-O(7)	133.993(10)
O(1)-Sr-O(2)	63.919(10)	O(1)-Sr-O(7)	99.415(11)
O(4)-Sr-O(2)	112.022(13)	O(4)-Sr-O(7)	89.869(13)
O(3)-Sr-O(6)	136.097(9)	O(2)-Sr-O(7)	157.995(8)

O(6)-Sr-O(7)	59.986(10)	C(4)-O(2)-Sr	110.604(19)
O(3)-Sr-O(5)	86.550(10)	C(3)-O(2)-Sr	114.11(2)
O(1)-Sr-O(5)	74.189(10)	C(5)-O(3)-C(6)	112.45(3)
O(4)-Sr-O(5)	72.515(8)	C(5)-O(3)-Sr	120.40(2)
O(2)-Sr-O(5)	71.913(8)	C(6)-O(3)-Sr	121.98(2)
O(6)-Sr-O(5)	60.095(10)	C(8)-O(4)-C(7)	112.45(3)
O(7)-Sr-O(5)	119.264(8)	C(8)-O(4)-Sr	120.88(2)
O(3)-Sr-O(8)	76.173(9)	C(7)-O(4)-Sr	116.72(2)
O(1)-Sr-O(8)	140.147(8)	C(10)-O(5)-C(9)	109.91(3)
O(4)-Sr-O(8)	72.707(8)	C(10)-O(5)-Sr	119.63(2)
O(2)-Sr-O(8)	122.036(8)	C(9)-O(5)-Sr	119.05(2)
O(6)-Sr-O(8)	114.492(11)	C(12)-O(6)-C(11)	113.64(3)
O(7)-Sr-O(8)	60.930(8)	C(12)-O(6)-Sr	115.70(2)
O(5)-Sr-O(8)	145.220(8)	C(11)-O(6)-Sr	116.10(2)
O(3)-Sr-C(4)	43.982(10)	C(14)-O(7)-C(13)	109.41(3)
O(1)-Sr-C(4)	83.699(12)	C(14)-O(7)-Sr	117.71(2)
O(4)-Sr-C(4)	102.774(14)	C(13)-O(7)-Sr	118.21(2)
O(2)-Sr-C(4)	22.928(8)	C(16)-O(8)-C(15)	111.11(3)
O(6)-Sr-C(4)	145.076(8)	C(16)-O(8)-Sr	120.03(2)
O(7)-Sr-C(4)	152.775(9)	C(15)-O(8)-Sr	114.68(2)
O(5)-Sr-C(4)	87.717(10)	O(1)-C(2)-C(3)	109.04(3)
O(8)-Sr-C(4)	99.594(10)	O(2)-C(3)-C(2)	109.39(3)
O(3)-Sr-I(1)	98.939(10)	O(2)-C(4)-C(5)	108.83(3)
O(1)-Sr-I(1)	72.317(10)	O(2)-C(4)-Sr	46.468(14)
O(4)-Sr-I(1)	141.869(7)	C(5)-C(4)-Sr	83.78(2)
O(2)-Sr-I(1)	78.207(10)	O(3)-C(5)-C(4)	109.24(3)
O(6)-Sr-I(1)	124.957(9)	O(3)-C(6)-C(7)	109.35(3)
O(7)-Sr-I(1)	83.098(10)	O(4)-C(7)-C(6)	107.00(3)
O(5)-Sr-I(1)	142.330(6)	O(5)-C(10)-C(11)	108.11(3)
O(8)-Sr-I(1)	71.149(9)	O(6)-C(11)-C(10)	107.86(3)
C(4)-Sr-I(1)	72.024(10)	O(6)-C(12)-C(13)	104.84(3)
C(1)-O(1)-C(2)	113.45(3)	O(7)-C(13)-C(12)	108.19(3)
C(1)-O(1)-Sr	128.26(2)	O(7)-C(14)-C(15)	111.99(4)
C(2)-O(1)-Sr	114.775(19)	C(14)-C(15)-O(8)	108.04(3)
C(4)-O(2)-C(3)	114.86(3)		

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for **7**.
The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	56(1)	57(1)	60(1)	4(1)	1(1)	-9(1)
I(2)	73(1)	64(1)	68(1)	2(1)	-3(1)	2(1)
Sr	41(1)	38(1)	41(1)	0(1)	1(1)	2(1)
O(1)	55(1)	56(1)	56(1)	10(1)	5(1)	5(1)
O(2)	70(1)	53(1)	45(1)	-4(1)	0(1)	-3(1)
O(3)	61(1)	56(1)	65(1)	2(1)	19(1)	5(1)
O(4)	60(1)	63(1)	98(1)	-11(1)	-13(1)	9(1)
O(5)	62(1)	44(1)	76(1)	-5(1)	1(1)	-3(1)
O(6)	88(1)	59(1)	54(1)	-14(1)	1(1)	5(1)
O(7)	89(1)	75(1)	55(1)	12(1)	-1(1)	4(1)
O(8)	72(1)	47(1)	91(1)	7(1)	7(1)	1(1)
C(1)	65(1)	91(1)	95(1)	19(1)	24(1)	16(1)
C(2)	56(1)	63(1)	58(1)	14(1)	-2(1)	6(1)
C(3)	59(1)	66(1)	62(1)	19(1)	-11(1)	-3(1)
C(4)	96(1)	57(1)	46(1)	-3(1)	6(1)	-10(1)
C(5)	96(1)	61(1)	73(1)	-8(1)	33(1)	1(1)
C(6)	59(1)	82(1)	105(1)	5(1)	27(1)	8(1)
C(7)	53(1)	80(1)	118(1)	16(1)	19(1)	13(1)
C(8)	81(1)	139(1)	95(1)	-5(1)	-26(1)	2(1)
C(9)	86(1)	78(1)	74(1)	25(1)	15(1)	-9(1)
C(10)	98(1)	57(1)	84(1)	-7(1)	-12(1)	-15(1)
C(11)	117(1)	50(1)	69(1)	-17(1)	-17(1)	-5(1)
C(12)	123(1)	94(1)	54(1)	-20(1)	10(1)	3(1)
C(13)	103(1)	117(1)	54(1)	-5(1)	11(1)	3(1)
C(14)	105(1)	93(1)	86(1)	21(1)	5(1)	4(1)
C(15)	86(1)	66(1)	95(1)	41(1)	16(1)	-1(1)
C(16)	90(1)	53(1)	119(1)	5(1)	7(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **7**.

	x	y	z	U(eq)
H(1A)	2019	-1542	2468	125
H(1B)	1197	-1478	1560	125
H(1C)	1525	-2294	1971	125
H(2A)	1121	-2266	3577	71
H(2B)	-418	-2455	3566	71
H(3A)	131	-1616	4734	75
H(3B)	674	-1013	4043	75
H(4A)	-1127	-14	4322	79
H(4B)	-1331	-563	5148	79
H(5A)	-3536	-734	4763	91
H(5B)	-3268	163	4773	91
H(6A)	-5223	255	3731	98
H(6B)	-5338	-653	3710	98
H(7A)	-6236	-237	2362	100
H(7B)	-5007	312	2201	100
H(8A)	-5065	-1547	1110	158
H(8B)	-4782	-715	739	158
H(8C)	-6132	-889	1211	158
H(9A)	-4810	-2091	3208	118
H(9B)	-3686	-1995	3953	118
H(9C)	-4097	-2824	3617	118
H(10A)	-4140	-2711	1811	96
H(10B)	-3261	-3323	2342	96
H(11A)	-1356	-2870	1672	95
H(11B)	-2414	-3105	919	95
H(12A)	-1630	-2274	-134	108
H(12B)	-519	-1834	441	108
H(13A)	-1464	-1003	-643	109
H(13B)	-2882	-1135	-237	109
H(14A)	-3121	144	97	113
H(14B)	-1735	331	-321	113
H(15A)	-2354	1296	637	98
H(15B)	-1019	901	987	98

H(16A)	-1753	1435	2406	131
H(16B)	-2997	1068	2862	131
H(16C)	-3202	1642	2055	131

Crystal data and structure refinement for [BaI(triglyme)$_2$]I **8**

$C1_6H_{36}I_2BaO_8$, M= 747.59 gmol^{-1}, monoclinic, $P2_1/n$ (Nr. 14), a = 11.034(2), b = 17.914(4), c = 13.401(3) Å, β = 91.47(3)°, V = 2647.9(9) Å^3, Z = 4, ρ_{calcd}.= 1.875 Mgm^3, $F(000)$ = 1432, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 3.864 mm^{-1}, 2.17° < θ < 27.19°, 8838 reflections of which 3641 unique and 3050 observed, 249 parameters refined, *GOOF* (on F^2) = 1.177, R1= $\Sigma|F_o–F_c|/\Sigma F_o$ = 0.0437, *w*R2 = .1233 for I > 2σ(I) and R1 = 0.0549, wR2 = 0.1290 for all data.

The intensities from the single-crystals of **8** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms.

Table 1. Crystal data and structure refinement for **8**.

Identification code	[BaI(triglyme)$_2$]I	
Empirical formula	C16 H36 Ba I2 O8	
Formula weight	747.59	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.034(2) Å	a= 90°
	b = 17.914(4) Å	β= 91.47(3)°
	c = 13.401(3) Å	γ = 90°
Volume	2647.9(9) Å^3	
Z	4	
Density (calculated)	1.875 Mg/m^3	
Absorption coefficient	3.864 mm^{-1}	
F(000)	1432	
Theta range for data collection	2.17 to 27.19°	
Index ranges	-12<=h<=11, -22<=k<=21, -16<=l<=16	
Reflections collected	8838	
Independent reflections	3641 [R(int) = 0.0536]	

Completeness to theta = 27.19°	61.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3641 / 0 / 249
Goodness-of-fit on F^2	1.177
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.1233
R indices (all data)	R1 = 0.0549, wR2 = 0.1290
Largest diff. peak and hole	0.920 and -0.785 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **8**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ba	7195(1)	2072(1)	8250(1)	32(1)
I(1)	7124(1)	3280(1)	6163(1)	64(1)
I(2)	7369(1)	88(1)	13213(1)	52(1)
O(1)	5524(1)	926(1)	8452(1)	54(1)
O(2)	4708(1)	2343(1)	8326(1)	73(1)
O(3)	6251(1)	3396(1)	9033(1)	57(1)
O(4)	8779(1)	3166(1)	8995(1)	64(1)
O(5)	6953(1)	1844(1)	10353(1)	78(1)
O(6)	8893(1)	1272(1)	9424(1)	77(1)
O(7)	9364(1)	1522(1)	7426(1)	60(1)
O(8)	7128(1)	1045(1)	6638(1)	53(1)
C(1)	5935(1)	201(1)	8666(2)	85(1)
C(2)	4385(1)	1089(1)	8866(1)	67(1)
C(3)	3879(1)	1730(1)	8320(1)	77(1)
C(4)	4233(1)	3001(1)	8649(1)	71(1)
C(5)	5123(1)	3622(1)	8599(1)	67(1)
C(6)	7079(1)	3997(1)	9172(1)	71(1)
C(7)	8216(1)	3686(1)	9631(1)	70(1)
C(8)	9640(1)	3482(1)	8383(1)	95(1)
C(9)	6077(1)	2190(1)	10966(1)	101(1)
C(10)	7965(1)	1606(1)	10899(1)	96(1)
C(11)	8617(1)	1001(1)	10358(1)	84(1)
C(12)	9859(1)	874(1)	8945(1)	82(1)
C(13)	10292(1)	1357(1)	8158(1)	87(1)

C(14)	9260(1)	980(1)	6655(1)	67(1)
C(15)	8159(1)	1136(1)	6035(1)	57(1)
C(16)	6028(1)	1033(1)	6023(1)	68(1)

Table 3. Bond lengths [Å] and angles [°] for **8**.

Ba-I(1)	3.5342(5)	O(4)-C(8)	1.3908(19)
Ba-O(1)	2.7776(8)	O(5)-C(9)	1.4252(19)
Ba-O(2)	2.7909(8)	O(5)-C(10)	1.3867(19)
Ba-O(3)	2.8043(9)	O(6)-C(11)	1.3839(19)
Ba-O(4)	2.7925(9)	O(6)-C(12)	1.4465(15)
Ba-O(5)	2.8675(12)	O(7)-C(13)	1.4310(16)
Ba-O(6)	2.8087(11)	O(7)-C(14)	1.4206(16)
Ba-O(7)	2.8375(9)	O(8)-C(15)	1.4217(13)
Ba-O(8)	2.8379(9)	O(8)-C(16)	1.4488(14)
O(1)-C(1)	1.4035(16)	C(2)-C(3)	1.4646(19)
O(1)-C(2)	1.4163(13)	C(4)-C(5)	1.4860(16)
O(2)-C(3)	1.4297(15)	C(6)-C(7)	1.4905(17)
O(2)-C(4)	1.3651(15)	C(10)-C(11)	1.498(2)
O(3)-C(5)	1.4188(13)	C(12)-C(13)	1.454(2)
O(3)-C(6)	1.4218(14)	C(14)-C(15)	1.4804(15)
O(4)-C(7)	1.4180(17)		

O(1)-Ba-O(2)	57.91(2)	O(1)-Ba-O(8)	65.82(3)
O(1)-Ba-O(4)	153.44(3)	O(2)-Ba-O(8)	97.69(3)
O(2)-Ba-O(4)	118.17(3)	O(4)-Ba-O(8)	136.98(3)
O(1)-Ba-O(3)	109.52(3)	O(3)-Ba-O(8)	146.16(2)
O(2)-Ba-O(3)	57.61(2)	O(6)-Ba-O(8)	95.70(3)
O(4)-Ba-O(3)	60.56(2)	O(7)-Ba-O(8)	58.97(3)
O(1)-Ba-O(6)	90.15(3)	O(1)-Ba-O(5)	73.72(3)
O(2)-Ba-O(6)	135.25(3)	O(2)-Ba-O(5)	82.65(4)
O(4)-Ba-O(6)	75.85(3)	O(4)-Ba-O(5)	79.73(3)
O(3)-Ba-O(6)	118.09(3)	O(3)-Ba-O(5)	72.99(3)
O(1)-Ba-O(7)	110.49(3)	O(6)-Ba-O(5)	56.92(3)
O(2)-Ba-O(7)	156.11(3)	O(7)-Ba-O(5)	115.70(3)
O(4)-Ba-O(7)	81.75(3)	O(8)-Ba-O(5)	130.89(3)
O(3)-Ba-O(7)	139.86(2)	O(1)-Ba-I(1)	121.90(3)
O(6)-Ba-O(7)	58.92(3)	O(2)-Ba-I(1)	85.47(3)

O(4)-Ba-I(1)	81.64(3)	C(11)-O(6)-C(12)	114.19(10)
O(3)-Ba-I(1)	77.17(2)	C(11)-O(6)-Ba	121.82(7)
O(6)-Ba-I(1)	139.16(2)	C(12)-O(6)-Ba	119.48(8)
O(7)-Ba-I(1)	84.64(3)	C(14)-O(7)-C(13)	113.60(9)
O(8)-Ba-I(1)	78.18(2)	C(14)-O(7)-Ba	117.87(5)
O(5)-Ba-I(1)	149.78(2)	C(13)-O(7)-Ba	113.62(7)
C(1)-O(1)-C(2)	113.27(9)	C(15)-O(8)-C(16)	110.49(9)
C(1)-O(1)-Ba	119.52(6)	C(15)-O(8)-Ba	110.59(6)
C(2)-O(1)-Ba	118.99(6)	C(16)-O(8)-Ba	116.59(7)
C(4)-O(2)-C(3)	114.49(8)	O(1)-C(2)-C(3)	107.22(10)
C(4)-O(2)-Ba	123.19(6)	O(2)-C(3)-C(2)	111.32(9)
C(3)-O(2)-Ba	119.76(6)	O(2)-C(4)-C(5)	111.90(9)
C(5)-O(3)-C(6)	113.04(9)	O(3)-C(5)-C(4)	109.98(10)
C(5)-O(3)-Ba	114.74(7)	O(3)-C(6)-C(7)	107.59(10)
C(6)-O(3)-Ba	116.47(6)	O(4)-C(7)-C(6)	112.02(12)
C(8)-O(4)-C(7)	113.79(11)	O(5)-C(10)-C(11)	110.97(14)
C(8)-O(4)-Ba	120.36(9)	O(6)-C(11)-C(10)	107.67(13)
C(7)-O(4)-Ba	113.33(6)	O(6)-C(12)-C(13)	106.71(11)
C(10)-O(5)-C(9)	112.25(12)	O(7)-C(13)-C(12)	112.24(9)
C(10)-O(5)-Ba	117.94(9)	O(7)-C(14)-C(15)	109.18(10)
C(9)-O(5)-Ba	125.87(9)	O(8)-C(15)-C(14)	108.48(9)

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **8**.

The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ba	34(1)	32(1)	31(1)	-1(1)	2(1)	3(1)
I(1)	74(1)	66(1)	54(1)	20(1)	7(1)	3(1)
I(2)	48(1)	52(1)	56(1)	-6(1)	0(1)	-4(1)
O(1)	60(1)	44(1)	60(1)	7(1)	13(1)	-8(1)
O(2)	44(1)	59(1)	117(1)	-2(1)	20(1)	6(1)
O(3)	67(1)	49(1)	55(1)	-13(1)	-13(1)	17(1)
O(4)	55(1)	54(1)	82(1)	-13(1)	-4(1)	-9(1)
O(5)	74(1)	109(1)	51(1)	8(1)	5(1)	12(1)
O(6)	83(1)	76(1)	72(1)	16(1)	-11(1)	36(1)
O(7)	43(1)	74(1)	64(1)	-22(1)	6(1)	5(1)
O(8)	49(1)	66(1)	45(1)	-12(1)	8(1)	-9(1)

C(1)	95(1)	53(1)	108(1)	21(1)	19(1)	-11(1)
C(2)	54(1)	68(1)	80(1)	-9(1)	24(1)	-23(1)
C(3)	41(1)	93(1)	96(1)	-18(1)	14(1)	-7(1)
C(4)	58(1)	64(1)	89(1)	-13(1)	-4(1)	22(1)
C(5)	61(1)	60(1)	81(1)	4(1)	13(1)	30(1)
C(6)	80(1)	51(1)	82(1)	-27(1)	-16(1)	6(1)
C(7)	78(1)	62(1)	69(1)	-12(1)	-10(1)	-6(1)
C(8)	99(1)	104(1)	81(1)	10(1)	3(1)	-30(1)
C(9)	114(1)	153(2)	39(1)	-3(1)	25(1)	19(1)
C(10)	118(1)	104(1)	65(1)	4(1)	-20(1)	17(1)
C(11)	95(1)	75(1)	78(1)	25(1)	-31(1)	9(1)
C(12)	86(1)	69(1)	88(1)	-21(1)	-37(1)	41(1)
C(13)	41(1)	107(1)	112(1)	-40(1)	-24(1)	17(1)
C(14)	65(1)	74(1)	63(1)	-27(1)	11(1)	16(1)
C(15)	65(1)	70(1)	37(1)	-14(1)	15(1)	3(1)
C(16)	60(1)	81(1)	63(1)	-17(1)	-6(1)	-6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **8**.

	x	y	z	U(eq)
H(1A)	6046	143	9375	128
H(1B)	6692	118	8347	128
H(1C)	5347	-155	8422	128
H(2A)	4484	1207	9570	80
H(2B)	3849	662	8797	80
H(3A)	3692	1585	7636	92
H(3B)	3130	1883	8623	92
H(4A)	3979	2943	9332	85
H(4B)	3523	3124	8240	85
H(5A)	5232	3764	7909	80
H(5B)	4819	4052	8954	80
H(6A)	6739	4372	9606	86
H(6B)	7247	4229	8536	86
H(7A)	8775	4092	9780	84
H(7B)	8029	3443	10255	84
H(8A)	9353	3956	8143	142

H(8B)	9776	3157	7827	142
H(8C)	10386	3550	8757	142
H(9A)	5968	1893	11553	152
H(9B)	5320	2230	10601	152
H(9C)	6354	2679	11155	152
H(10A)	7717	1421	11543	115
H(10B)	8509	2024	11015	115
H(11A)	9354	864	10724	100
H(11B)	8107	562	10294	100
H(12A)	9561	407	8667	98
H(12B)	10510	765	9423	98
H(13A)	10588	1819	8451	104
H(13B)	10964	1116	7835	104
H(14A)	9207	485	6943	81
H(14B)	9971	998	6244	81
H(15A)	8187	1642	5779	69
H(15B)	8114	796	5473	69
H(16A)	5935	1502	5685	102
H(16B)	5344	949	6437	102
H(16C)	6077	639	5540	102

Crystal data and structure refinement for *trans*-[CaI$_2$(dme)$_2$(thf)] 9

$C_{12}H_{28}I_2CaO_5$, M= 546.22 gmol^{-1}, monoclinic, *C*2/*c* (Nr. 15), a = 12.948(3), b = 11.279(2), c = 15.294(3) Å, β = 114.97(3)°, V = 2024.7(7) Å^3, Z = 4, ρ_{calcd}.= 1.792 Mgm^3, *F*(000) = 1064, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 3.372 mm^{-1}, 2.50° < θ < 27.08°, 7626 reflections of which 2132 unique and 1659 observed, 92 parameters refined, *GOOF* (on F^2) = 0.989, R1= $\Sigma|F_o-F_c|/\Sigma F_o$ = 0.0410, *wR*2 = 0.1112 for I > 2σ(I) and R1 = 0.0523, w*R*2 = 0.1317 for all data.

The intensities from the single-crystals of **9** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms.

Table 1. Crystal data and structure refinement for **9**.

Identification code	*trans*-[CaI$_2$(dme)$_2$(thf)]
Empirical formula	C12 H28 Ca I2 O5

Formula weight	546.22	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 12.948(3) Å	α= 90°
	b = 11.279(2) Å	β= 114.97(3)°
	c = 15.294(3) Å	γ = 90°
Volume	2024.7(7) $Å^3$	
Z	4	
Density (calculated)	1.792 Mg/m^3	
Absorption coefficient	3.372 mm^{-1}	
F(000)	1064	
Theta range for data collection	2.50 to 27.08°	
Index ranges	-16<=h<=15, -14<=k<=14, -19<=l<=19	
Reflections collected	7626	
Independent reflections	2132 [R(int) = 0.0555]	
Completeness to theta = 27.08°	95.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2132 / 0 / 92	
Goodness-of-fit on F^2	0.989	
Final R indices [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.1112	
R indices (all data)	R1 = 0.0523, wR2 = 0.1317	
Largest diff. peak and hole	0.980 and -1.056 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **9**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I	814(1)	7518(1)	837(1)	53(1)
Ca	0	7552(1)	2500	34(1)
O(1)	0	5432(2)	2500	43(1)
O(2)	2067(2)	7059(2)	3455(2)	45(1)
O(3)	1125(2)	9267(2)	3396(2)	48(1)
C(1)	207(3)	4697(3)	3334(2)	55(1)
C(2)	364(2)	3456(2)	3027(2)	67(1)

C(3)	2651(2)	6088(2)	3280(2)	59(1)
C(4)	2746(2)	8111(3)	3622(2)	49(1)
C(5)	2279(3)	9022(3)	4050(2)	54(1)
C(6)	686(3)	10225(3)	3756(3)	73(1)

Table 3. Bond lengths [Å] and angles [°] for **9**.

I-Ca	3.1378(7)	O(1)-C(1)#1	1.449(3)
Ca-I#1	3.1378(7)	O(2)-C(3)	1.419(3)
Ca-O(1)	2.391(3)	O(2)-C(4)	1.434(4)
Ca-O(2)	2.5105(19)	O(3)-C(5)	1.431(3)
Ca-O(2)#1	2.5105(19)	O(3)-C(6)	1.435(4)
Ca-O(3)	2.461(2)	C(1)-C(2)	1.517(4)
Ca-O(3)#1	2.461(2)	C(2)-C(2)#1	1.485(5)
O(1)-C(1)	1.449(3)	C(4)-C(5)	1.477(5)

O(1)-Ca-O(3)	141.81(5)	O(3)#1-Ca-I	83.14(6)
O(1)-Ca-O(3)#1	141.81(5)	O(2)#1-Ca-I	99.57(6)
O(3)-Ca-O(3)#1	76.39(9)	O(2)-Ca-I	80.12(6)
O(1)-Ca-O(2)#1	77.19(5)	I#1-Ca-I	178.60(2)
O(3)-Ca-O(2)#1	137.15(7)	C(1)-O(1)-C(1)#1	110.2(3)
O(3)#1-Ca-O(2)#1	67.38(7)	C(1)-O(1)-Ca	124.92(15)
O(1)-Ca-O(2)	77.19(5)	C(1)#1-O(1)-Ca	124.92(15)
O(3)-Ca-O(2)	67.38(7)	C(3)-O(2)-C(4)	109.7(2)
O(3)#1-Ca-O(2)	137.15(7)	C(3)-O(2)-Ca	125.71(14)
O(2)#1-Ca-O(2)	154.38(10)	C(4)-O(2)-Ca	110.06(16)
O(1)-Ca-I#1	89.298(12)	C(5)-O(3)-C(6)	110.1(2)
O(3)-Ca-I#1	83.14(6)	C(5)-O(3)-Ca	115.82(17)
O(3)#1-Ca-I#1	97.97(6)	C(6)-O(3)-Ca	124.6(2)
O(2)#1-Ca-I#1	80.12(6)	O(1)-C(1)-C(2)	104.8(3)
O(2)-Ca-I#1	99.57(6)	C(2)#1-C(2)-C(1)	103.30(15)
O(1)-Ca-I	89.298(12)	O(2)-C(4)-C(5)	108.7(3)
O(3)-Ca-I	97.97(6)	O(3)-C(5)-C(4)	109.0(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **9**.

The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I	53(1)	67(1)	40(1)	5(1)	22(1)	-2(1)
Ca	33(1)	33(1)	37(1)	0	14(1)	0
O(1)	51(1)	34(1)	45(1)	0	21(1)	0
O(2)	34(1)	47(1)	49(1)	2(1)	13(1)	4(1)
O(3)	43(1)	43(1)	54(1)	-10(1)	16(1)	-2(1)
C(1)	66(2)	47(2)	53(2)	10(1)	27(1)	3(1)
C(2)	82(2)	43(1)	90(2)	19(1)	51(2)	13(1)
C(3)	46(1)	63(2)	65(2)	2(2)	22(1)	18(1)
C(4)	33(1)	58(2)	51(2)	1(1)	12(1)	-5(1)
C(5)	48(2)	56(2)	42(1)	-4(1)	4(1)	-9(1)
C(6)	82(2)	50(2)	90(2)	-20(2)	38(2)	3(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **9**.

	x	y	z	U(eq)
H(1A)	-434	4726	3504	66
H(1B)	887	4955	3884	66
H(2A)	1155	3307	3163	80
H(2B)	110	2862	3352	80
H(3A)	2773	6243	2713	88
H(3B)	2203	5381	3184	88
H(3C)	3372	5982	3823	88
H(4A)	2731	8398	3019	59
H(4B)	3530	7938	4058	59
H(5A)	2308	8740	4659	65
H(5B)	2731	9740	4172	65
H(6A)	751	10031	4388	110
H(6B)	-101	10353	3331	110
H(6C)	1113	10932	3788	110

Crystal data and structure refinement for *trans*-[SrI$_2$(dme)$_2$(thf)] 10

$C_{12}H_{28}I_2SrO_5$, M= 593.76 gmol^{-1}, monoclinic, *C*2/*c* (Nr. 15), a = 13.1009(14), b = 11.4027(9), c = 15.4353(17) Å, β = 114.749(8)°, V = 2094.0(4) Å^3, Z = 4, $\rho_{calcd.}$= 1.883 Mgm^3, *F*(000) = 1136, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 5.535 mm^{-1}, 2.47° < θ < 27.11°, 7942 reflections of which 2255 unique and 1748 observed, 95 parameters refined, *GOOF* (on F^2) = 1.120, R1= $\Sigma|F_o-F_c|/\Sigma F_o$ = 0.0383, *wR*2 = 0.0950 for I > 2σ(I) and R1 = 0.0514, w*R*2 = 0.1007 for all data.

The intensities from the single-crystals of **10** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms.

Table 1. Crystal data and structure refinement for **10**.

Identification code	*trans*-[SrI$_2$(dme)$_2$(thf)]	
Empirical formula	C12 H28 I2 O5 Sr	
Formula weight	593.76	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 13.1009(14) Å	α= 90°
	b = 11.4027(9) Å	β= 114.749(8)°
	c = 15.4353(17) Å	γ = 90°
Volume	2094.0(4) Å^3	
Z	4	
Density (calculated)	1.883 Mg/m^3	
Absorption coefficient	5.535 mm^{-1}	
F(000)	1136	
Theta range for data collection	2.47 to 27.11°	
Index ranges	-16<=h<=16, -14<=k<=14, -19<=l<=19	
Reflections collected	7942	
Independent reflections	2255 [R(int) = 0.0531]	
Completeness to theta = 27.11°	97.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2255 / 0 / 95	
Goodness-of-fit on F^2	1.120	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.0950	

R indices (all data)	R1 = 0.0514, wR2 = 0.1007
Largest diff. peak and hole	0.968 and -0.868 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **10**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sr	0	4952(1)	2500	34(1)
I	2545(1)	4986(1)	4176(1)	54(1)
O(1)	1151(1)	5434(1)	1495(1)	44(1)
O(2)	296(1)	3209(1)	1559(1)	49(1)
O(3)	0	7158(1)	2500	46(1)
C(1)	1903(1)	6405(1)	1688(1)	62(1)
C(2)	1668(1)	4391(1)	1364(1)	52(1)
C(3)	799(1)	3477(1)	921(1)	57(1)
C(4)	-486(1)	2251(1)	1199(1)	79(1)
C(5)	605(1)	7885(1)	3328(1)	59(1)
C(6)	153(1)	9106(1)	3022(1)	72(1)

Table 3. Bond lengths [Å] and angles [°] for **10**.

Sr-I	3.2535(4)	O(1)-C(1)	1.4281(6)
Sr-I#1	3.2535(4)	O(1)-C(2)	1.4239(6)
Sr-O(1)	2.6345(4)	O(2)-C(3)	1.4281(7)
Sr-O(1)#1	2.6345(4)	O(2)-C(4)	1.4414(6)
Sr-O(2)	2.5845(4)	O(3)-C(5)	1.4495(5)
Sr-O(2)#1	2.5845(4)	O(3)-C(5)#1	1.4495(5)
Sr-O(3)	2.5155(4)	C(2)-C(3)	1.4824(7)
Sr-C(2)	3.3856(6)	C(5)-C(6)	1.5087(7)
Sr-C(2)#1	3.3856(6)	C(6)-C(6)#1	1.4888(12)
O(3)-Sr-O(2)	140.255(8)	O(2)#1-Sr-O(1)	138.489(11)
O(3)-Sr-O(2)#1	140.255(8)	O(3)-Sr-O(1)#1	77.955(7)
O(2)-Sr-O(2)#1	79.491(17)	O(2)-Sr-O(1)#1	138.489(11)
O(3)-Sr-O(1)	77.955(7)	O(2)#1-Sr-O(1)#1	64.665(11)
O(2)-Sr-O(1)	64.665(11)	O(1)-Sr-O(1)#1	155.909(14)

O(3)-Sr-I#1	89.322(1)
O(2)-Sr-I#1	84.691(8)
O(2)#1-Sr-I#1	96.357(8)
O(1)-Sr-I#1	100.261(10)
O(1)#1-Sr-I#1	79.451(10)
O(3)-Sr-I	89.322(1)
O(2)-Sr-I	96.357(8)
O(2)#1-Sr-I	84.691(8)
O(1)-Sr-I	79.451(11)
O(1)#1-Sr-I	100.261(10)
I#1-Sr-I	178.644(2)
O(3)-Sr-C(2)	100.885(9)
O(2)-Sr-C(2)	44.166(12)
O(2)#1-Sr-C(2)	115.273(13)
O(1)-Sr-C(2)	23.369(11)
O(1)#1-Sr-C(2)	175.405(8)
I#1-Sr-C(2)	105.032(11)
I-Sr-C(2)	75.233(11)
O(3)-Sr-C(2)#1	100.885(9)
O(2)-Sr-C(2)#1	115.273(13)
O(2)#1-Sr-C(2)#1	44.166(12)
O(1)-Sr-C(2)#1	175.405(8)
O(1)#1-Sr-C(2)#1	23.369(11)
I#1-Sr-C(2)#1	75.233(11)
I-Sr-C(2)#1	105.032(11)
C(2)-Sr-C(2)#1	158.229(18)
C(2)-O(1)-C(1)	110.48(4)
C(2)-O(1)-Sr	109.42(3)
C(1)-O(1)-Sr	123.63(3)
C(3)-O(2)-C(4)	110.79(4)
C(3)-O(2)-Sr	116.34(3)
C(4)-O(2)-Sr	123.37(4)
C(5)-O(3)-C(5)#1	110.20(5)
C(5)-O(3)-Sr	124.90(2)
C(5)#1-O(3)-Sr	124.90(2)
O(1)-C(2)-C(3)	109.47(4)
O(1)-C(2)-Sr	47.21(2)
C(3)-C(2)-Sr	80.45(3)
O(2)-C(3)-C(2)	108.62(4)
O(3)-C(5)-C(6)	104.69(4)
C(6)#1-C(6)-C(5)	103.38(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **10**.

The anisotropic displacement factor exponent takes the form: $-2p^2[\, h^2a^{*2}U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sr	35(1)	29(1)	41(1)	0	20(1)	0
I	44(1)	69(1)	42(1)	5(1)	12(1)	6(1)
O(1)	42(1)	47(1)	50(1)	1(1)	26(1)	-3(1)
O(2)	57(1)	39(1)	56(1)	-10(1)	29(1)	-4(1)
O(3)	49(1)	32(1)	52(1)	0	16(1)	0
C(1)	57(1)	63(1)	77(1)	6(1)	37(1)	-16(1)
C(2)	51(1)	65(1)	51(1)	3(1)	31(1)	10(1)
C(3)	75(1)	56(1)	48(1)	-4(1)	33(1)	8(1)

C(4)	91(1)	47(1)	98(1)	-21(1)	41(1)	-18(1)
C(5)	62(1)	45(1)	54(1)	-9(1)	10(1)	-8(1)
C(6)	61(1)	40(1)	110(1)	-25(1)	30(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **10**.

	x	y	z	U(eq)
H(1A)	2565	6256	2261	93
H(1B)	1540	7102	1768	93
H(1C)	2108	6510	1165	93
H(2A)	2221	4116	1976	63
H(2B)	2049	4552	957	63
H(3A)	231	3759	320	69
H(3B)	1139	2778	798	69
H(4A)	-1049	2447	577	118
H(4B)	-839	2107	1623	118
H(4C)	-92	1559	1156	118
H(5A)	1408	7857	3502	70
H(5B)	466	7630	3868	70
H(6A)	-500	9253	3150	87
H(6B)	721	9693	3346	87

Crystal data and structure refinement for *trans*-[BaI$_2$(dme)$_2$(thf)] 11

$C_{16}H_{36}I_2BaO_6$, M= 715.59 gmol^{-1}, monoclinic, *C*2/*c* (Nr. 15), a = 15.1858(13), b = 10.2936(6), c = 17.3344(14) Å, β = 105.317(6)°, V = 2613.432) Å^3, Z = 4, $\rho_{calcd.}$= 1.819 Mgm^3, *F*(000) = 1368, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 3.905 mm^{-1}, 2.54° < θ < 27.08°, 9757 reflections of which 2790 unique and 2648 observed, 117 parameters refined, *GOOF* (on F^2) = 1.194, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.0791, *wR*2 = 0.2003 for I > 2σ(I) and R1 = 0.0838, w*R*2 = 0.2086 for all data.

The intensities from the single-crystals of **11** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms, but disorder was observed on THF ligands.

Table 1. Crystal data and structure refinement for **11**.

Identification code	*trans*-[$BaI_2(dme)_2(thf)_2$]	
Empirical formula	C16 H36 Ba I2 O6	
Formula weight	715.59	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 15.1858(13) Å	α= 90°
	b = 10.2936(6) Å	β= 105.317(6)°
	c = 17.3344(14) Å	γ = 90°
Volume	2613.4(3) $Å^3$	
Z	4	
Density (calculated)	1.819 Mg/m^3	
Absorption coefficient	3.905 mm^{-1}	
F(000)	1368	
Theta range for data collection	2.54 to 27.08°	
Index ranges	-19<=h<=19, -13<=k<=13, -22<=l<=22	
Reflections collected	9757	
Independent reflections	2790 [R(int) = 0.1853]	
Completeness to theta = 27.08°	96.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2790 / 0 / 117	
Goodness-of-fit on F^2	1.212	
Final R indices [I>2sigma(I)]	R1 = 0.0767, wR2 = 0.1941	
R indices (all data)	R1 = 0.0815, wR2 = 0.2025	
Largest diff. peak and hole	2.102 and -2.853 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **11**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ba	0	82(1)	2500	37(1)
I	1528(1)	-646(1)	1404(1)	66(1)
O(1)	912(2)	-1982(3)	3377(2)	62(1)

O(2)	1445(2)	925(3)	3720(2)	57(1)
O(3)	-83(2)	2449(3)	3334(2)	54(1)
C(1)	1007(6)	-2183(7)	4238(4)	88(2)
C(2)	716(6)	-3562(8)	4275(5)	104(2)
C(3)	987(5)	-4239(6)	3581(5)	92(2)
C(4)	1230(4)	-3158(6)	3095(4)	79(1)
C(5)	2366(4)	544(7)	3788(5)	86(2)
C(6)	1400(3)	2046(5)	4203(3)	59(1)
C(7)	422(3)	2295(6)	4152(2)	60(1)
C(8)	-955(4)	3031(6)	3230(4)	73(1)

Table 3. Bond lengths [Å] and angles [°] for **11**.

Ba-I	3.4483(4)	O(1)-C(4)	1.435(7)
Ba-I#1	3.4483(4)	O(2)-C(5)	1.427(7)
Ba-O(1)	2.763(3)	O(2)-C(6)	1.437(6)
Ba-O(1)#1	2.763(3)	O(3)-C(7)	1.432(5)
Ba-O(2)	2.755(3)	O(3)-C(8)	1.420(6)
Ba-O(2)#1	2.755(3)	C(1)-C(2)	1.494(11)
Ba-O(3)	2.852(3)	C(2)-C(3)	1.538(12)
Ba-O(3)#1	2.852(3)	C(3)-C(4)	1.500(9)
O(1)-C(1)	1.476(7)	C(6)-C(7)	1.487(7)

O(2)#1-Ba-O(2)	143.30(14)	O(2)#1-Ba-I	99.24(8)
O(2)#1-Ba-O(1)#1	68.77(10)	O(2)-Ba-I	88.63(8)
O(2)-Ba-O(1)#1	147.83(10)	O(1)#1-Ba-I	80.92(8)
O(2)#1-Ba-O(1)	147.83(10)	O(1)-Ba-I	79.84(8)
O(2)-Ba-O(1)	68.77(10)	O(3)-Ba-I	126.24(6)
O(1)#1-Ba-O(1)	79.43(14)	O(3)#1-Ba-I	77.29(6)
O(2)#1-Ba-O(3)	89.28(9)	O(2)#1-Ba-I#1	88.63(8)
O(2)-Ba-O(3)	58.33(9)	O(2)-Ba-I#1	99.24(8)
O(1)#1-Ba-O(3)	148.53(10)	O(1)#1-Ba-I#1	79.84(8)
O(1)-Ba-O(3)	117.45(9)	O(1)-Ba-I#1	80.92(8)
O(2)#1-Ba-O(3)#1	58.33(9)	O(3)-Ba-I#1	77.29(6)
O(2)-Ba-O(3)#1	89.28(9)	O(3)#1-Ba-I#1	126.24(6)
O(1)#1-Ba-O(3)#1	117.45(9)	I-Ba-I#1	154.901(16)
O(1)-Ba-O(3)#1	148.53(10)	C(4)-O(1)-C(1)	105.9(4)
O(3)-Ba-O(3)#1	62.68(13)	C(4)-O(1)-Ba	128.7(3)

C(1)-O(1)-Ba	124.4(3)	O(1)-C(1)-C(2)	103.0(6)
C(5)-O(2)-C(6)	111.6(4)	C(1)-C(2)-C(3)	104.7(6)
C(5)-O(2)-Ba	122.7(4)	C(4)-C(3)-C(2)	105.0(6)
C(6)-O(2)-Ba	123.3(3)	O(1)-C(4)-C(3)	106.2(5)
C(8)-O(3)-C(7)	114.2(4)	O(2)-C(6)-C(7)	107.7(4)
C(8)-O(3)-Ba	117.5(3)	O(3)-C(7)-C(6)	110.1(4)
C(7)-O(3)-Ba	108.9(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **11**.

The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ba	42(1)	33(1)	39(1)	0	15(1)	0
I	67(1)	68(1)	74(1)	-12(1)	39(1)	6(1)
O(1)	79(2)	41(2)	67(2)	8(1)	25(1)	12(2)
O(2)	52(1)	48(2)	65(2)	-5(1)	6(1)	-3(1)
O(3)	61(1)	54(2)	53(1)	-8(1)	23(1)	7(1)
C(1)	128(5)	72(3)	66(3)	17(3)	28(3)	21(4)
C(2)	135(5)	91(4)	104(4)	36(3)	63(4)	29(4)
C(3)	107(4)	46(3)	142(5)	19(3)	66(3)	2(3)
C(4)	89(3)	52(3)	116(3)	20(3)	62(2)	14(2)
C(5)	55(2)	75(4)	117(5)	6(4)	2(3)	-3(3)
C(6)	73(2)	53(2)	50(2)	-2(2)	11(2)	-18(2)
C(7)	81(2)	61(3)	44(2)	-8(2)	26(2)	-11(2)
C(8)	73(2)	58(3)	94(3)	-3(3)	34(2)	11(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **11**.

	x	y	z	U(eq)
H(1A)	615	-1596	4434	106
H(1B)	1634	-2058	4548	106
H(2A)	62	-3617	4207	125

H(2B)	1026	-3954	4783	125
H(3A)	1505	-4810	3781	110
H(3B)	482	-4746	3263	110
H(4A)	1885	-3123	3168	95
H(4B)	936	-3284	2531	95
H(5A)	2669	1212	3569	130
H(5B)	2370	-250	3498	130
H(5C)	2677	413	4341	130
H(6A)	1667	2792	4007	71
H(6B)	1736	1888	4754	71
H(7A)	174	1574	4388	72
H(7B)	367	3075	4450	72
H(8A)	-1314	2514	3494	109
H(8B)	-1257	3085	2670	109
H(8C)	-882	3888	3457	109

Crystal data and structure refinement for *trans*-[CaI$_2$(diglyme)(thf)$_2$] 12

$C_{14}H_{30}I_2CaO_5$, M= 572.26 gmol^{-1}, orthorhombic, *P*bca (Nr. 61), a = 11.9303(6), b = 15.6370(7), c = 23.4272(10) Å, V = 4370.4(3) Å^3, Z = 8, ρ_{calcd}.= 1.739 Mgm^3, *F*(000) = 2240, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 3.129 mm^{-1}, 1.74° < θ < 27.09°, 23260 reflections of which 4737 unique and 4571 observed, 202 parameters refined, *GOOF* (on F^2) = 1.156, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.0584, *wR*2 = 0.1656 for I > 2σ(I) and R1 = 0.0598, w*R*2 = 0.1671 for all data.

The intensities from the single-crystals of **12** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms.

Table 1. Crystal data and structure refinement for **12**.

Identification code	*trans*-[CaI$_2$(diglyme)(thf)$_2$]
Empirical formula	C14 H30 Ca I2 O5
Formula weight	572.26
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca

Unit cell dimensions	a = 11.9303(6) Å	α= 90°
	b = 15.6370(7) Å	β= 90°
	c = 23.4272(10) Å	γ = 90°
Volume	4370.4(3) Å^3	
Z	8	
Density (calculated)	1.739 Mg/m^3	
Absorption coefficient	3.129 mm^{-1}	
F(000)	2240	
Theta range for data collection	1.74 to 27.09°	
Index ranges	-13<=h<=15, -19<=k<=19, -29<=l<=29	
Reflections collected	23260	
Independent reflections	4737 [R(int) = 0.2305]	
Completeness to theta = 27.09°	98.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4737 / 0 / 202	
Goodness-of-fit on F^2	1.156	
Final R indices [I>2sigma(I)]	R1 = 0.0584, wR2 = 0.1656	
R indices (all data)	R1 = 0.0598, wR2 = 0.1671	
Largest diff. peak and hole	1.729 and -0.932 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **12**

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	7296(1)	885(1)	5802(1)	41(1)
I(2)	2960(1)	2902(1)	6400(1)	53(1)
Ca	5169(1)	1915(1)	6147(1)	33(1)
O(1)	4096(1)	550(1)	6108(1)	47(1)
O(2)	4383(1)	1571(1)	5211(1)	49(1)
O(3)	5590(1)	3026(1)	5399(1)	51(1)
O(4)	5311(1)	1436(1)	7136(1)	39(1)
O(5)	6283(1)	2987(1)	6616(1)	44(1)
C(1)	4444(1)	-193(1)	6415(1)	68(1)
C(2)	3629(1)	302(1)	5572(1)	61(1)
C(3)	3369(1)	1077(1)	5242(1)	63(1)
C(4)	4412(1)	2213(1)	4788(1)	65(1)

C(5)	5495(1)	2661(1)	4839(1)	63(1)
C(6)	5224(1)	3889(1)	5436(1)	70(1)
C(7)	6363(1)	1196(1)	7401(1)	45(1)
C(8)	6082(1)	858(1)	7971(1)	67(1)
C(9)	5079(1)	1394(1)	8134(1)	70(1)
C(10)	4469(1)	1489(1)	7573(1)	50(1)
C(11)	7402(1)	3213(1)	6449(1)	58(1)
C(12)	7856(1)	3776(1)	6905(1)	57(1)
C(13)	6808(1)	4194(1)	7142(1)	56(1)
C(14)	5964(1)	3495(1)	7105(1)	52(1)

Table 3. Bond lengths [Å] and angles [°] for **12**.

I(1)-Ca	3.11226(15)	O(4)-C(7)	1.4490(7)
I(2)-Ca	3.11077(15)	O(4)-C(10)	1.4382(7)
Ca-O(1)	2.4897(4)	O(5)-C(11)	1.4357(8)
Ca-O(2)	2.4457(5)	O(5)-C(14)	1.4448(8)
Ca-O(3)	2.5195(5)	C(2)-C(3)	1.4691(10)
Ca-O(4)	2.4395(4)	C(4)-C(5)	1.4745(11)
Ca-O(5)	2.4057(4)	C(7)-C(8)	1.4754(10)
O(1)-C(1)	1.4282(8)	C(8)-C(9)	1.5099(11)
O(1)-C(2)	1.4271(9)	C(9)-C(10)	1.5093(11)
O(2)-C(3)	1.4365(8)	C(11)-C(12)	1.4854(11)
O(2)-C(4)	1.4112(8)	C(12)-C(13)	1.5166(10)
O(3)-C(5)	1.4361(9)	C(13)-C(14)	1.4893(9)
O(3)-C(6)	1.4199(7)		

O(5)-Ca-O(4)	75.056(14)	O(4)-Ca-I(2)	91.749(9)
O(5)-Ca-O(2)	140.791(14)	O(2)-Ca-I(2)	87.442(10)
O(4)-Ca-O(2)	144.152(13)	O(1)-Ca-I(2)	89.830(10)
O(5)-Ca-O(1)	153.979(15)	O(3)-Ca-I(2)	87.650(11)
O(4)-Ca-O(1)	78.946(14)	O(5)-Ca-I(1)	91.631(10)
O(2)-Ca-O(1)	65.217(14)	O(4)-Ca-I(1)	91.781(9)
O(5)-Ca-O(3)	74.130(15)	O(2)-Ca-I(1)	88.044(10)
O(4)-Ca-O(3)	149.138(14)	O(1)-Ca-I(1)	88.077(10)
O(2)-Ca-O(3)	66.673(14)	O(3)-Ca-I(1)	90.765(11)
O(1)-Ca-O(3)	131.888(15)	I(2)-Ca-I(1)	175.480(4)
O(5)-Ca-I(2)	92.006(10)	C(2)-O(1)-C(1)	109.60(5)

C(2)-O(1)-Ca	117.80(4)	C(14)-O(5)-Ca	126.81(3)
C(1)-O(1)-Ca	121.91(4)	O(1)-C(2)-C(3)	108.68(5)
C(4)-O(2)-C(3)	116.09(5)	O(2)-C(3)-C(2)	107.00(5)
C(4)-O(2)-Ca	117.59(4)	O(2)-C(4)-C(5)	107.68(6)
C(3)-O(2)-Ca	113.26(4)	O(3)-C(5)-C(4)	109.31(6)
C(6)-O(3)-C(5)	114.16(6)	O(4)-C(7)-C(8)	106.52(5)
C(6)-O(3)-Ca	123.50(5)	C(7)-C(8)-C(9)	102.15(6)
C(5)-O(3)-Ca	110.23(4)	C(10)-C(9)-C(8)	102.47(6)
C(10)-O(4)-C(7)	108.30(4)	O(4)-C(10)-C(9)	106.16(5)
C(10)-O(4)-Ca	127.62(3)	O(5)-C(11)-C(12)	106.73(6)
C(7)-O(4)-Ca	123.14(3)	C(11)-C(12)-C(13)	102.69(5)
C(11)-O(5)-C(14)	109.07(5)	C(14)-C(13)-C(12)	102.66(5)
C(11)-O(5)-Ca	124.12(4)	O(5)-C(14)-C(13)	105.75(5)

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **12**.
The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	35(1)	41(1)	46(1)	-5(1)	2(1)	4(1)
I(2)	36(1)	63(1)	62(1)	-2(1)	2(1)	15(1)
Ca	26(1)	36(1)	36(1)	-2(1)	-3(1)	-1(1)
O(1)	42(1)	48(1)	53(1)	-7(1)	-4(1)	-12(1)
O(2)	47(1)	51(1)	50(1)	1(1)	-18(1)	-1(1)
O(3)	55(1)	46(1)	51(1)	7(1)	-8(1)	-3(1)
O(4)	28(1)	52(1)	38(1)	4(1)	-1(1)	0(1)
O(5)	45(1)	46(1)	40(1)	-13(1)	7(1)	-11(1)
C(1)	81(1)	47(1)	76(1)	2(1)	-7(1)	-15(1)
C(2)	62(1)	61(1)	61(1)	-10(1)	-15(1)	-17(1)
C(3)	52(1)	65(1)	72(1)	-11(1)	-29(1)	-7(1)
C(4)	76(1)	65(1)	55(1)	5(1)	-28(1)	4(1)
C(5)	70(1)	73(1)	45(1)	13(1)	-6(1)	0(1)
C(6)	80(1)	49(1)	81(1)	18(1)	-3(1)	-1(1)
C(7)	36(1)	54(1)	44(1)	1(1)	-11(1)	8(1)
C(8)	61(1)	82(1)	60(1)	22(1)	-12(1)	-5(1)
C(9)	57(1)	101(1)	54(1)	9(1)	9(1)	-13(1)
C(10)	36(1)	60(1)	53(1)	8(1)	6(1)	-3(1)
C(11)	51(1)	51(1)	71(1)	-16(1)	12(1)	-12(1)

C(12)	44(1)	64(1)	63(1)	-7(1)	6(1)	-18(1)
C(13)	67(1)	49(1)	52(1)	-17(1)	5(1)	-9(1)
C(14)	56(1)	52(1)	48(1)	-14(1)	17(1)	-5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **12**.

	x	y	z	U(eq)
H(1A)	3803	-541	6499	102
H(1B)	4800	-23	6764	102
H(1C)	4965	-513	6187	102
H(2A)	2952	-29	5632	73
H(2B)	4160	-49	5364	73
H(3A)	3115	926	4862	76
H(3B)	2783	1403	5430	76
H(4A)	3799	2612	4844	78
H(4B)	4339	1960	4412	78
H(5A)	6105	2261	4775	75
H(5B)	5544	3108	4553	75
H(6A)	5732	4249	5228	105
H(6B)	5207	4063	5829	105
H(6C)	4487	3938	5275	105
H(7A)	6851	1690	7434	54
H(7B)	6740	763	7175	54
H(8A)	6696	939	8237	81
H(8B)	5892	256	7954	81
H(9A)	4617	1105	8415	84
H(9B)	5307	1946	8284	84
H(10A)	3921	1036	7528	60
H(10B)	4085	2035	7556	60
H(11A)	7394	3512	6086	69
H(11B)	7861	2704	6410	69
H(12A)	8367	4198	6749	69
H(12B)	8241	3446	7195	69
H(13A)	6918	4376	7534	67
H(13B)	6587	4683	6914	67
H(14A)	5972	3151	7449	63

H(14B)	5217	3729	7054	63

E - II - Structural data of metal clusters 13-32

Crystal data and structure refinement for $[Na(Oh)(dme)]_4$ 13

$C_{40}H_{60}Na_4O_{12}$, M= 824.84 gmol^{-1}, triclinic, *P*-1 (Nr. 2), a = 11.0020(8), b = 12.7656(9), c = 17.3975(13) Å, α = 93.061(6), β = 105.033(6), γ = 104.937(6)°, V = 2261.1(3) Å^3, Z = 2, ρ_{calcd}.= 1.212 Mgm^3, *F*(000) = 880, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.120 mm^{-1}, 1.66° < θ < 27.11°, 17660 reflections of which 9038 unique and 7648 observed, 514 parameters refined, *GOOF* (on F^2) = 1.025, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.0697, *w*R2 = 0.1856 for I > 2σ(I) and R1 = 0.0790, wR2 = 0.1955 for all data.

The intensities from the single-crystals of **13** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms.

Table 1. Crystal data and structure refinement for **13**.

Identification code	$[Na(OPh)(dme)]_4$	
Empirical formula	C40 H60 Na4 O12	
Formula weight	824.84	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.0020(8) Å	α= 93.061(6)°
	b = 12.7656(9) Å	β= 105.033(6)°
	c = 17.3975(13) Å	γ = 104.937(6)°
Volume	2261.1(3) Å^3	
Z	2	
Density (calculated)	1.212 Mg/m^3	
Absorption coefficient	0.120 mm^{-1}	
F(000)	880	
Theta range for data collection	1.66 to 27.11°	
Index ranges	-14<=h<=14, -16<=k<=16, -22<=l<=20	
Reflections collected	17660	
Independent reflections	9038 [R(int) = 0.0858]	

Completeness to theta = 27.11°	90.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9038 / 0 / 514
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0697, wR2 = 0.1856
R indices (all data)	R1 = 0.0790, wR2 = 0.1955
Largest diff. peak and hole	0.777 and -0.468 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **13**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Na(1)	5027(1)	8645(1)	2521(1)	41(1)
Na(2)	4031(1)	5952(1)	2355(1)	44(1)
Na(3)	6857(1)	7367(1)	3609(1)	44(1)
Na(4)	6310(1)	7101(1)	1577(1)	44(1)
O(1)	4708(1)	7363(1)	3401(1)	48(1)
O(2)	4203(1)	7174(1)	1431(1)	46(1)
O(3)	6159(1)	5910(1)	2560(1)	48(1)
O(4)	7109(1)	8539(1)	2643(1)	44(1)
O(5)	5039(1)	10239(1)	1795(1)	46(1)
O(6)	4114(1)	9919(1)	3116(1)	51(1)
O(7)	2012(1)	4606(1)	1615(1)	59(1)
O(8)	3389(2)	4556(1)	3160(1)	70(1)
O(9)	7982(2)	6792(1)	4896(1)	78(1)
O(10)	8172(2)	8904(1)	4635(1)	93(1)
O(11)	6742(1)	5788(1)	706(1)	62(1)
O(12)	7067(1)	7939(1)	405(1)	64(1)
C(1)	3905(1)	7255(1)	3853(1)	41(1)
C(2)	4336(2)	7250(1)	4684(1)	49(1)
C(3)	3509(2)	7154(2)	5161(1)	66(1)
C(4)	2205(2)	7069(2)	4846(2)	75(1)
C(5)	1742(2)	7062(2)	4037(2)	82(1)
C(6)	2564(2)	7142(2)	3536(1)	64(1)
C(7)	3267(1)	7443(1)	920(1)	38(1)
C(8)	3124(2)	7366(1)	88(1)	46(1)

C(9)	2155(2)	7692(2)	-436(1)	56(1)
C(10)	1273(2)	8103(2)	-167(1)	58(1)
C(11)	1369(2)	8170(1)	640(1)	53(1)
C(12)	2335(2)	7845(1)	1173(1)	46(1)
C(13)	6772(1)	5156(1)	2621(1)	39(1)
C(14)	8083(2)	5378(2)	3066(1)	64(1)
C(15)	8774(2)	4608(2)	3146(2)	85(1)
C(16)	8177(2)	3566(2)	2792(2)	81(1)
C(17)	6890(2)	3298(1)	2343(1)	76(1)
C(18)	6189(2)	4076(1)	2252(1)	57(1)
C(19)	8217(1)	9187(1)	2586(1)	37(1)
C(20)	8362(1)	10294(1)	2478(1)	40(1)
C(21)	9502(2)	10950(1)	2373(1)	51(1)
C(22)	10553(2)	10548(2)	2375(1)	60(1)
C(23)	10454(2)	9476(2)	2507(1)	60(1)
C(24)	9312(2)	8806(1)	2609(1)	50(1)
C(25)	5022(2)	10137(2)	972(1)	60(1)
C(26)	4100(2)	10745(1)	1930(1)	47(1)
C(27)	4317(2)	10941(1)	2815(1)	49(1)
C(28)	4070(2)	10023(2)	3919(1)	73(1)
C(29)	999(2)	4885(2)	1050(2)	73(1)
C(30)	1516(2)	3805(2)	2071(1)	70(1)
C(31)	2654(3)	3602(2)	2688(1)	77(1)
C(32)	4391(2)	4433(2)	3796(1)	76(1)
C(33)	8151(2)	5751(2)	5052(2)	79(1)
C(34)	8931(2)	7653(2)	5428(1)	65(1)
C(35)	8582(3)	8668(2)	5380(2)	92(1)
C(36)	7761(3)	9869(2)	4539(2)	83(1)
C(37)	7954(2)	5535(2)	929(1)	71(1)
C(38)	6408(2)	6067(2)	-84(1)	66(1)
C(39)	7209(2)	7166(2)	-164(1)	59(1)
C(40)	7881(2)	8995(2)	416(1)	60(1)

Table 3. Bond lengths [Å] and angles [°] for **13**.

Na(1)-O(1)	2.3229(13)	Na(1)-O(5)	2.4504(13)
Na(1)-O(2)	2.4079(12)	Na(1)-O(6)	2.4347(13)
Na(1)-O(4)	2.2854(12)	Na(2)-O(1)	2.3176(13)

Na(2)-O(2)	2.3072(13)	O(9)-C(34)	1.398(2)
Na(2)-O(3)	2.2904(13)	O(10)-C(35)	1.334(3)
Na(2)-O(7)	2.4192(13)	O(10)-C(36)	1.422(3)
Na(2)-O(8)	2.4016(15)	O(11)-C(37)	1.414(2)
Na(3)-O(1)	2.2962(13)	O(11)-C(38)	1.417(3)
Na(3)-O(3)	2.3568(12)	O(12)-C(39)	1.426(2)
Na(3)-O(4)	2.3316(13)	O(12)-C(40)	1.409(2)
Na(3)-O(9)	2.5073(17)	C(1)-C(2)	1.400(2)
Na(3)-O(10)	2.4400(16)	C(1)-C(6)	1.400(2)
Na(4)-O(2)	2.2929(12)	C(2)-C(3)	1.370(3)
Na(4)-O(3)	2.3571(13)	C(3)-C(4)	1.369(3)
Na(4)-O(4)	2.3542(12)	C(4)-C(5)	1.365(4)
Na(4)-O(11)	2.4169(15)	C(5)-C(6)	1.400(3)
Na(4)-O(12)	2.5784(16)	C(7)-C(8)	1.410(2)
Na(1)-Na(2)	3.3005(8)	C(7)-C(12)	1.410(2)
Na(1)-Na(3)	3.2164(9)	C(8)-C(9)	1.380(2)
Na(1)-Na(4)	3.2969(9)	C(9)-C(10)	1.381(3)
Na(2)-Na(3)	3.2953(9)	C(10)-C(11)	1.376(3)
Na(2)-Na(4)	3.2164(9)	C(11)-C(12)	1.385(2)
Na(3)-Na(4)	3.4113(9)	C(13)-C(14)	1.395(2)
Na(1)-C(7)	3.0129(15)	C(13)-C(18)	1.400(2)
Na(2)-C(1)	3.0701(17)	C(14)-C(15)	1.382(3)
Na(4)-C(19)	3.0473(14)	C(15)-C(16)	1.354(3)
O(1)-C(1)	1.314(2)	C(16)-C(17)	1.371(3)
O(2)-C(7)	1.3072(18)	C(17)-C(18)	1.398(3)
O(3)-C(13)	1.3037(18)	C(19)-C(24)	1.404(2)
O(4)-C(19)	1.3149(17)	C(19)-C(20)	1.409(2)
O(5)-C(25)	1.425(2)	C(20)-C(21)	1.380(2)
O(5)-C(26)	1.412(2)	C(21)-C(22)	1.380(3)
O(6)-C(27)	1.4174(19)	C(22)-C(23)	1.381(3)
O(6)-C(28)	1.412(2)	C(23)-C(24)	1.385(2)
O(7)-C(29)	1.417(3)	C(26)-C(27)	1.493(2)
O(7)-C(30)	1.412(2)	C(30)-C(31)	1.513(3)
O(8)-C(31)	1.360(2)	C(34)-C(35)	1.443(3)
O(8)-C(32)	1.393(3)	C(38)-C(39)	1.488(3)
O(9)-C(33)	1.420(3)		

O(4)-Na(1)-O(1)	91.78(4)	O(4)-Na(1)-O(2)	89.62(4)

O(1)-Na(1)-O(2)	88.85(4)
O(4)-Na(1)-O(6)	134.05(4)
O(1)-Na(1)-O(6)	95.60(5)
O(2)-Na(1)-O(6)	135.69(4)
O(4)-Na(1)-O(5)	100.25(4)
O(1)-Na(1)-O(5)	164.16(5)
O(2)-Na(1)-O(5)	101.40(4)
O(6)-Na(1)-O(5)	68.62(4)
O(4)-Na(1)-C(7)	108.83(5)
O(1)-Na(1)-C(7)	103.48(4)
O(2)-Na(1)-C(7)	24.84(4)
O(6)-Na(1)-C(7)	113.26(4)
O(5)-Na(1)-C(7)	82.47(4)
O(4)-Na(1)-Na(3)	46.44(3)
O(1)-Na(1)-Na(3)	45.53(3)
O(2)-Na(1)-Na(3)	92.19(3)
O(6)-Na(1)-Na(3)	121.64(4)
O(5)-Na(1)-Na(3)	144.26(3)
C(7)-Na(1)-Na(3)	116.78(3)
O(4)-Na(1)-Na(4)	45.56(3)
O(1)-Na(1)-Na(4)	90.44(4)
O(2)-Na(1)-Na(4)	44.06(3)
O(6)-Na(1)-Na(4)	173.96(4)
O(5)-Na(1)-Na(4)	105.33(4)
C(7)-Na(1)-Na(4)	64.93(3)
Na(3)-Na(1)-Na(4)	63.15(2)
O(4)-Na(1)-Na(2)	88.83(3)
O(1)-Na(1)-Na(2)	44.60(3)
O(2)-Na(1)-Na(2)	44.34(3)
O(6)-Na(1)-Na(2)	126.58(4)
O(5)-Na(1)-Na(2)	144.87(3)
C(7)-Na(1)-Na(2)	62.55(3)
Na(3)-Na(1)-Na(2)	60.733(19)
Na(4)-Na(1)-Na(2)	58.356(19)
O(3)-Na(2)-O(2)	92.48(5)
O(3)-Na(2)-O(1)	89.81(4)
O(2)-Na(2)-O(1)	91.48(4)
O(3)-Na(2)-O(8)	97.74(5)
O(2)-Na(2)-O(8)	168.28(5)
O(1)-Na(2)-O(8)	94.27(5)
O(3)-Na(2)-O(7)	129.79(5)
O(2)-Na(2)-O(7)	99.90(5)
O(1)-Na(2)-O(7)	137.62(5)
O(8)-Na(2)-O(7)	69.09(5)
O(3)-Na(2)-C(1)	107.23(4)
O(2)-Na(2)-C(1)	105.60(4)
O(1)-Na(2)-C(1)	23.30(4)
O(8)-Na(2)-C(1)	76.87(5)
O(7)-Na(2)-C(1)	115.54(5)
O(3)-Na(2)-Na(4)	47.07(3)
O(2)-Na(2)-Na(4)	45.45(3)
O(1)-Na(2)-Na(4)	92.57(3)
O(8)-Na(2)-Na(4)	144.12(5)
O(7)-Na(2)-Na(4)	124.14(4)
C(1)-Na(2)-Na(4)	115.71(3)
O(3)-Na(2)-Na(3)	45.66(3)
O(2)-Na(2)-Na(3)	92.09(3)
O(1)-Na(2)-Na(3)	44.16(3)
O(8)-Na(2)-Na(3)	99.15(4)
O(7)-Na(2)-Na(3)	167.60(4)
C(1)-Na(2)-Na(3)	63.43(3)
Na(4)-Na(2)-Na(3)	63.170(19)
O(3)-Na(2)-Na(1)	89.36(3)
O(2)-Na(2)-Na(1)	46.84(3)
O(1)-Na(2)-Na(1)	44.73(3)
O(8)-Na(2)-Na(1)	138.54(5)
O(7)-Na(2)-Na(1)	133.19(4)
C(1)-Na(2)-Na(1)	62.10(3)
Na(4)-Na(2)-Na(1)	60.766(19)
Na(3)-Na(2)-Na(1)	58.372(18)
O(1)-Na(3)-O(4)	91.28(4)
O(1)-Na(3)-O(3)	88.70(4)
O(4)-Na(3)-O(3)	87.12(4)
O(1)-Na(3)-O(10)	106.69(7)
O(4)-Na(3)-O(10)	88.24(5)
O(3)-Na(3)-O(10)	164.02(7)

O(1)-Na(3)-O(9)	117.98(6)
O(4)-Na(3)-O(9)	145.31(5)
O(3)-Na(3)-O(9)	110.23(5)
O(10)-Na(3)-O(9)	66.70(5)
O(1)-Na(3)-Na(1)	46.21(3)
O(4)-Na(3)-Na(1)	45.25(3)
O(3)-Na(3)-Na(1)	90.27(3)
O(10)-Na(3)-Na(1)	97.29(5)
O(9)-Na(3)-Na(1)	155.15(5)
O(1)-Na(3)-Na(2)	44.68(3)
O(4)-Na(3)-Na(2)	88.18(3)
O(3)-Na(3)-Na(2)	44.03(3)
O(10)-Na(3)-Na(2)	151.03(6)
O(9)-Na(3)-Na(2)	125.38(4)
Na(1)-Na(3)-Na(2)	60.896(18)
O(1)-Na(3)-Na(4)	88.08(3)
O(4)-Na(3)-Na(4)	43.54(3)
O(3)-Na(3)-Na(4)	43.65(3)
O(10)-Na(3)-Na(4)	130.54(5)
O(9)-Na(3)-Na(4)	145.27(5)
Na(1)-Na(3)-Na(4)	59.576(19)
Na(2)-Na(3)-Na(4)	57.287(19)
O(2)-Na(4)-O(4)	90.79(4)
O(2)-Na(4)-O(3)	91.13(4)
O(4)-Na(4)-O(3)	86.59(4)
O(2)-Na(4)-O(11)	120.13(5)
O(4)-Na(4)-O(11)	149.08(5)
O(3)-Na(4)-O(11)	92.55(5)
O(2)-Na(4)-O(12)	108.15(5)
O(4)-Na(4)-O(12)	104.91(4)
O(3)-Na(4)-O(12)	157.09(5)
O(11)-Na(4)-O(12)	67.32(5)
O(2)-Na(4)-C(19)	109.21(4)
O(4)-Na(4)-C(19)	24.08(4)
O(3)-Na(4)-C(19)	101.35(4)
O(11)-Na(4)-C(19)	128.30(5)
O(12)-Na(4)-C(19)	84.26(4)
O(2)-Na(4)-Na(2)	45.82(3)
O(4)-Na(4)-Na(2)	89.70(3)
O(3)-Na(4)-Na(2)	45.35(3)
O(11)-Na(4)-Na(2)	111.41(4)
O(12)-Na(4)-Na(2)	151.16(4)
C(19)-Na(4)-Na(2)	113.61(4)
O(2)-Na(4)-Na(1)	46.91(3)
O(4)-Na(4)-Na(1)	43.88(3)
O(3)-Na(4)-Na(1)	88.32(4)
O(11)-Na(4)-Na(1)	167.03(4)
O(12)-Na(4)-Na(1)	113.79(4)
C(19)-Na(4)-Na(1)	63.98(3)
Na(2)-Na(4)-Na(1)	60.878(19)
O(2)-Na(4)-Na(3)	89.42(4)
O(4)-Na(4)-Na(3)	43.02(3)
O(3)-Na(4)-Na(3)	43.64(3)
O(11)-Na(4)-Na(3)	129.78(4)
O(12)-Na(4)-Na(3)	144.83(4)
C(19)-Na(4)-Na(3)	60.95(3)
Na(2)-Na(4)-Na(3)	59.543(19)
Na(1)-Na(4)-Na(3)	57.272(18)
C(1)-O(1)-Na(3)	134.59(10)
C(1)-O(1)-Na(2)	112.47(8)
Na(3)-O(1)-Na(2)	91.16(5)
C(1)-O(1)-Na(1)	127.45(10)
Na(3)-O(1)-Na(1)	88.26(4)
Na(2)-O(1)-Na(1)	90.67(4)
C(7)-O(2)-Na(4)	139.58(10)
C(7)-O(2)-Na(2)	128.68(9)
Na(4)-O(2)-Na(2)	88.73(4)
C(7)-O(2)-Na(1)	104.45(9)
Na(4)-O(2)-Na(1)	89.04(4)
Na(2)-O(2)-Na(1)	88.83(4)
C(13)-O(3)-Na(2)	136.05(9)
C(13)-O(3)-Na(3)	118.53(9)
Na(2)-O(3)-Na(3)	90.31(5)
C(13)-O(3)-Na(4)	120.44(10)
Na(2)-O(3)-Na(4)	87.58(4)
Na(3)-O(3)-Na(4)	92.71(4)

C(19)-O(4)-Na(1)	136.89(10)	C(5)-C(4)-C(3)	118.1(2)
C(19)-O(4)-Na(3)	126.69(9)	C(4)-C(5)-C(6)	121.63(19)
Na(1)-O(4)-Na(3)	88.31(4)	C(5)-C(6)-C(1)	120.83(19)
C(19)-O(4)-Na(4)	108.99(9)	O(2)-C(7)-C(8)	122.90(15)
Na(1)-O(4)-Na(4)	90.55(4)	O(2)-C(7)-C(12)	121.57(14)
Na(3)-O(4)-Na(4)	93.44(4)	C(8)-C(7)-C(12)	115.53(14)
C(26)-O(5)-C(25)	112.30(13)	O(2)-C(7)-Na(1)	50.71(7)
C(26)-O(5)-Na(1)	110.71(9)	C(8)-C(7)-Na(1)	143.20(10)
C(25)-O(5)-Na(1)	119.13(11)	C(12)-C(7)-Na(1)	82.10(9)
C(28)-O(6)-C(27)	111.76(13)	C(9)-C(8)-C(7)	121.80(17)
C(28)-O(6)-Na(1)	125.87(12)	C(8)-C(9)-C(10)	121.26(17)
C(27)-O(6)-Na(1)	113.52(10)	C(11)-C(10)-C(9)	118.49(17)
C(30)-O(7)-C(29)	112.22(16)	C(10)-C(11)-C(12)	120.91(18)
C(30)-O(7)-Na(2)	114.19(11)	C(11)-C(12)-C(7)	121.99(16)
C(29)-O(7)-Na(2)	122.35(11)	O(3)-C(13)-C(14)	121.60(13)
C(31)-O(8)-C(32)	113.77(18)	O(3)-C(13)-C(18)	123.65(14)
C(31)-O(8)-Na(2)	110.71(13)	C(14)-C(13)-C(18)	114.75(15)
C(32)-O(8)-Na(2)	115.65(13)	C(15)-C(14)-C(13)	123.67(17)
C(34)-O(9)-C(33)	113.09(17)	C(16)-C(15)-C(14)	120.2(2)
C(34)-O(9)-Na(3)	113.68(12)	C(15)-C(16)-C(17)	118.9(2)
C(33)-O(9)-Na(3)	129.15(13)	C(16)-C(17)-C(18)	121.25(17)
C(35)-O(10)-C(36)	117.9(2)	C(17)-C(18)-C(13)	121.26(16)
C(35)-O(10)-Na(3)	116.59(14)	O(4)-C(19)-C(24)	121.80(13)
C(36)-O(10)-Na(3)	113.89(14)	O(4)-C(19)-C(20)	122.04(13)
C(37)-O(11)-C(38)	113.80(17)	C(24)-C(19)-C(20)	116.14(13)
C(37)-O(11)-Na(4)	119.64(12)	O(4)-C(19)-Na(4)	46.93(7)
C(38)-O(11)-Na(4)	107.68(12)	C(24)-C(19)-Na(4)	92.80(9)
C(40)-O(12)-C(39)	111.39(15)	C(20)-C(19)-Na(4)	130.98(10)
C(40)-O(12)-Na(4)	127.84(12)	C(21)-C(20)-C(19)	121.57(15)
C(39)-O(12)-Na(4)	114.22(11)	C(20)-C(21)-C(22)	121.19(16)
O(1)-C(1)-C(6)	122.26(16)	C(21)-C(22)-C(23)	118.46(16)
O(1)-C(1)-C(2)	122.12(14)	C(22)-C(23)-C(24)	120.97(17)
C(6)-C(1)-C(2)	115.62(17)	C(23)-C(24)-C(19)	121.61(15)
O(1)-C(1)-Na(2)	44.23(7)	O(5)-C(26)-C(27)	107.83(13)
C(6)-C(1)-Na(2)	92.69(12)	O(6)-C(27)-C(26)	108.67(12)
C(2)-C(1)-Na(2)	136.00(11)	O(7)-C(30)-C(31)	108.85(17)
C(3)-C(2)-C(1)	122.52(17)	O(8)-C(31)-C(30)	109.54(19)
C(4)-C(3)-C(2)	121.3(2)	O(9)-C(34)-C(35)	112.17(19)

O(10)-C(35)-C(34)	114.7(2)	O(12)-C(39)-C(38)	107.61(17)
O(11)-C(38)-C(39)	113.07(16)		

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **13**.

The anisotropic displacement factor exponent takes the form: $-2p^2[\, h^2a^{*2}U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Na(1)	45(1)	38(1)	45(1)	13(1)	15(1)	16(1)
Na(2)	39(1)	38(1)	51(1)	16(1)	6(1)	7(1)
Na(3)	45(1)	39(1)	46(1)	10(1)	6(1)	11(1)
Na(4)	44(1)	42(1)	48(1)	9(1)	14(1)	16(1)
O(1)	53(1)	48(1)	50(1)	18(1)	22(1)	14(1)
O(2)	43(1)	49(1)	47(1)	18(1)	8(1)	18(1)
O(3)	46(1)	40(1)	57(1)	12(1)	8(1)	18(1)
O(4)	41(1)	37(1)	54(1)	12(1)	16(1)	7(1)
O(5)	47(1)	52(1)	42(1)	14(1)	13(1)	18(1)
O(6)	72(1)	41(1)	49(1)	10(1)	26(1)	20(1)
O(7)	51(1)	56(1)	55(1)	15(1)	8(1)	-5(1)
O(8)	71(1)	58(1)	71(1)	31(1)	5(1)	10(1)
O(9)	81(1)	55(1)	78(1)	3(1)	-19(1)	29(1)
O(10)	150(2)	46(1)	61(1)	1(1)	4(1)	19(1)
O(11)	67(1)	60(1)	66(1)	11(1)	26(1)	25(1)
O(12)	70(1)	54(1)	67(1)	2(1)	26(1)	11(1)
C(1)	43(1)	33(1)	47(1)	14(1)	12(1)	10(1)
C(2)	51(1)	45(1)	47(1)	12(1)	12(1)	9(1)
C(3)	92(1)	53(1)	62(1)	16(1)	37(1)	19(1)
C(4)	81(1)	64(1)	105(1)	31(1)	57(1)	28(1)
C(5)	45(1)	82(1)	129(2)	39(1)	33(1)	24(1)
C(6)	47(1)	69(1)	74(1)	28(1)	9(1)	16(1)
C(7)	37(1)	32(1)	42(1)	11(1)	7(1)	6(1)
C(8)	44(1)	47(1)	43(1)	6(1)	9(1)	11(1)
C(9)	55(1)	61(1)	38(1)	8(1)	-2(1)	8(1)
C(10)	46(1)	54(1)	58(1)	11(1)	-10(1)	13(1)
C(11)	41(1)	52(1)	62(1)	3(1)	4(1)	17(1)
C(12)	43(1)	51(1)	44(1)	9(1)	10(1)	15(1)
C(13)	49(1)	30(1)	39(1)	8(1)	11(1)	12(1)
C(14)	57(1)	53(1)	70(1)	-10(1)	-10(1)	27(1)

C(15)	85(1)	88(1)	81(2)	-2(1)	-7(1)	59(1)
C(16)	109(1)	62(1)	98(1)	23(1)	42(1)	54(1)
C(17)	95(1)	33(1)	112(1)	2(1)	61(1)	11(1)
C(18)	52(1)	43(1)	71(1)	-5(1)	24(1)	0(1)
C(19)	37(1)	34(1)	37(1)	6(1)	8(1)	9(1)
C(20)	38(1)	35(1)	48(1)	8(1)	12(1)	11(1)
C(21)	49(1)	37(1)	59(1)	6(1)	13(1)	3(1)
C(22)	41(1)	60(1)	75(1)	5(1)	22(1)	2(1)
C(23)	39(1)	67(1)	77(1)	5(1)	16(1)	22(1)
C(24)	48(1)	43(1)	61(1)	9(1)	12(1)	21(1)
C(25)	70(1)	61(1)	49(1)	16(1)	24(1)	12(1)
C(26)	47(1)	42(1)	53(1)	15(1)	8(1)	17(1)
C(27)	57(1)	40(1)	54(1)	9(1)	16(1)	19(1)
C(28)	118(1)	60(1)	56(1)	15(1)	41(1)	35(1)
C(29)	54(1)	67(1)	86(1)	17(1)	4(1)	10(1)
C(30)	62(1)	62(1)	70(1)	16(1)	21(1)	-11(1)
C(31)	103(2)	50(1)	69(1)	22(1)	22(1)	5(1)
C(32)	75(1)	87(1)	67(1)	39(1)	13(1)	24(1)
C(33)	86(1)	63(1)	85(1)	24(1)	8(1)	29(1)
C(34)	58(1)	74(1)	53(1)	5(1)	2(1)	14(1)
C(35)	97(2)	74(1)	82(2)	-17(1)	-18(2)	32(1)
C(36)	130(2)	57(1)	76(1)	10(1)	42(1)	33(1)
C(37)	77(1)	68(1)	88(1)	24(1)	38(1)	37(1)
C(38)	65(1)	63(1)	61(1)	-1(1)	13(1)	13(1)
C(39)	65(1)	63(1)	49(1)	7(1)	15(1)	20(1)
C(40)	61(1)	55(1)	62(1)	14(1)	14(1)	18(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **13**.

	x	y	z	U(eq)
H(2)	5227	7316	4923	58
H(3)	3843	7146	5715	79
H(4)	1645	7017	5178	90
H(5)	849	7001	3811	98
H(6)	2212	7119	2980	77
H(8)	3705	7085	-115	55

H(9)	2094	7633	-986	67
H(10)	622	8331	-526	69
H(11)	770	8441	832	64
H(12)	2370	7893	1720	55
H(14)	8521	6092	3326	77
H(15)	9660	4808	3447	101
H(16)	8637	3035	2853	97
H(17)	6470	2578	2092	91
H(18)	5309	3870	1937	69
H(20)	7664	10592	2477	49
H(21)	9564	11684	2298	61
H(22)	11319	10994	2289	72
H(23)	11171	9197	2527	72
H(24)	9271	8079	2696	59
H(25A)	4151	9730	646	90
H(25B)	5649	9753	903	90
H(25C)	5256	10859	808	90
H(26A)	3212	10272	1671	57
H(26B)	4200	11439	1705	57
H(27A)	5213	11399	3074	59
H(27B)	3705	11323	2931	59
H(28A)	4880	10529	4250	109
H(28B)	3962	9315	4111	109
H(28C)	3337	10298	3949	109
H(29A)	457	4242	678	110
H(29B)	1382	5444	758	110
H(29C)	464	5160	1329	110
H(30A)	1000	3126	1718	84
H(30B)	943	4057	2339	84
H(31A)	2324	3064	3020	92
H(31B)	3197	3309	2418	92
H(32A)	4024	3904	4114	115
H(32B)	4830	5131	4130	115
H(32C)	5017	4181	3589	115
H(33A)	9013	5729	5024	119
H(33B)	7485	5189	4656	119
H(33C)	8070	5623	5584	119
H(34A)	9772	7747	5308	78

H(34B)	9041	7470	5977	78
H(35A)	7888	8637	5642	111
H(35B)	9348	9264	5680	111
H(36A)	6876	9732	4586	125
H(36B)	7779	10081	4013	125
H(36C)	8349	10453	4950	125
H(37A)	7970	4993	521	106
H(37B)	8058	5245	1439	106
H(37C)	8665	6191	979	106
H(38A)	5480	6048	-243	79
H(38B)	6526	5518	-452	79
H(39A)	8133	7179	-59	70
H(39B)	6904	7344	-709	70
H(40A)	8789	8980	550	90
H(40B)	7774	9498	814	90
H(40C)	7641	9232	-108	90

Crystal data and structure refinement for [Li(2,6-Me$_2$-C$_6$H$_3$O)(dme)]$_2$ 14

$C_{24}H_{38}Li_2O_6$, M= 436.42 gmol^{-1}, monoclinic, $P2_1/c$ (Nr. 14), a = 38.784(8), b = 12.142(2), c = 17.447(4) Å, β = 102.47(3), V = 8023(3) Å^3, Z = 12, $\rho_{calcd.}$= 1.084 Mgm^3, $F(000)$ = 2832, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.075 mm^{-1}, 1.61° < θ < 27.21°, 44746 reflections of which 16589 unique and 9673 observed, 890 parameters refined, *GOOF* (on F^2) = 1.284, R1= $\Sigma|F_o – F_c|/\Sigma F_o$ = 0.0820, *w*R2 = 0.2206 for I > 2σ(I) and R1 = 0.1319, wR2 = 0.2532 for all data.

The intensities from the single-crystals of **13** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms but some disorder was observed on the methyl groups of the aryloxide ligands and on the DME ligands.

Table 1. Crystal data and structure refinement for **14**.

Identification code	[Li(2,6-Me$_2$-C6H3O)(dme)]$_2$
Empirical formula	C24 H38 Li2 O6
Formula weight	436.42
Temperature	203(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 38.784(8) Å	α= 90°.
	b = 12.142(2) Å	β= 102.47(3)°.
	c = 17.447(4) Å	γ = 90°.
Volume	8023(3) Å^3	
Z	12	
Density (calculated)	1.084 Mg/m^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	2832	
Theta range for data collection	1.61 to 27.21°	
Index ranges	-47<=h<=49, -15<=k<=15, -22<=l<=22	
Reflections collected	44746	
Independent reflections	16589 [R(int) = 0.1078]	
Completeness to theta = 27.21°	92.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16589 / 0 / 890	
Goodness-of-fit on F^2	1.284	
Final R indices [I>2sigma(I)]	R1 = 0.0820, wR2 = 0.2206	
R indices (all data)	R1 = 0.1319, wR2 = 0.2532	
Largest diff. peak and hole	0.383 and -0.291 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **14**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Li(1)	4204(1)	1128(2)	4830(2)	62(1)
Li(2)	4126(1)	3095(2)	5173(2)	58(1)
Li(3)	2338(1)	8047(3)	531(2)	63(1)
Li(4)	2683(1)	7874(2)	-530(2)	60(1)
Li(5)	861(1)	3168(2)	-154(2)	60(1)
Li(6)	818(1)	1193(2)	229(2)	65(1)
O(1)	3814(1)	2063(1)	4613(1)	61(1)
O(2)	4493(1)	2098(1)	5509(1)	61(1)
O(3)	4468(1)	620(1)	4002(1)	99(1)
O(4)	4108(1)	-522(1)	4829(1)	93(1)

O(5)	4103(1)	4298(1)	5977(1)	74(1)
O(6)	4125(1)	4470(1)	4473(1)	80(1)
O(7)	2807(1)	7674(1)	559(1)	58(1)
O(8)	2202(1)	8062(1)	-570(1)	69(1)
O(9)	2061(1)	7371(2)	1291(1)	120(1)
O(10)	2259(1)	9395(1)	1145(1)	106(1)
O(11)	2871(1)	7010(1)	-1346(1)	88(1)
O(12)	2922(1)	9144(1)	-1014(1)	85(1)
O(13)	1187(1)	2184(1)	447(1)	63(1)
O(14)	513(1)	2107(1)	-479(1)	63(1)
O(15)	867(1)	4353(1)	-986(1)	71(1)
O(16)	852(1)	4580(1)	512(1)	79(1)
O(17)	924(1)	9549(1)	235(1)	95(1)
O(18)	531(1)	10652(1)	1018(1)	100(1)
C(1)	3469(1)	2020(1)	4344(1)	56(1)
C(2)	3237(1)	2142(1)	4862(1)	65(1)
C(3)	2875(1)	2097(2)	4564(2)	92(1)
C(4)	2732(1)	1946(2)	3792(2)	106(1)
C(5)	2954(1)	1830(2)	3285(2)	97(1)
C(6)	3323(1)	1849(2)	3540(1)	75(1)
C(7)	3386(1)	2334(2)	5716(1)	85(1)
C(8)	3563(1)	1662(2)	2988(1)	106(1)
C(9)	4742(1)	2170(1)	6153(1)	55(1)
C(10)	5019(1)	2929(1)	6202(1)	68(1)
C(11)	5275(1)	3009(2)	6896(1)	86(1)
C(12)	5263(1)	2371(2)	7530(1)	97(1)
C(13)	4992(1)	1610(2)	7483(1)	83(1)
C(14)	4731(1)	1501(1)	6807(1)	61(1)
C(15)	5041(1)	3633(2)	5511(2)	98(1)
C(16)	4436(1)	686(2)	6747(1)	85(1)
C(17)	4737(1)	1247(3)	3797(2)	116(1)
C(18)	4498(1)	-474(2)	3986(2)	112(1)
C(19)	4235(1)	-1057(2)	4259(2)	110(1)
C(20)	3849(1)	-1038(3)	5156(2)	153(1)
C(21)	4257(1)	4187(2)	6786(1)	94(1)
C(22)	4155(1)	5353(2)	5670(1)	94(1)
C(23)	3982(1)	5354(2)	4829(2)	98(1)
C(24)	3978(1)	4372(2)	3653(1)	126(1)

C(25)	3097(1)	7409(1)	1070(1)	52(1)
C(26)	3340(1)	8224(2)	1422(1)	68(1)
C(27)	3648(1)	7901(2)	1950(1)	85(1)
C(28)	3717(1)	6819(2)	2143(1)	93(1)
C(29)	3480(1)	6027(2)	1815(1)	79(1)
C(30)	3170(1)	6301(2)	1283(1)	61(1)
C(31)	3260(1)	9392(2)	1224(1)	97(1)
C(32)	2913(1)	5413(2)	939(1)	87(1)
C(33)	1908(1)	7810(2)	-1071(1)	58(1)
C(34)	1689(1)	8641(2)	-1474(1)	73(1)
C(35)	1371(1)	8330(2)	-1986(1)	99(1)
C(36)	1277(1)	7238(3)	-2100(1)	107(1)
C(37)	1492(1)	6442(2)	-1731(1)	96(1)
C(38)	1807(1)	6703(2)	-1215(1)	75(1)
C(39)	1799(1)	9810(2)	-1355(2)	114(1)
C(40)	2044(1)	5803(2)	-812(2)	124(1)
C(41)	1991(1)	6252(3)	1420(2)	151(1)
C(42)	2061(1)	8036(3)	1898(2)	144(1)
C(43)	2070(1)	9167(3)	1716(2)	142(1)
C(44)	2285(1)	10496(2)	942(2)	134(1)
C(45)	2943(1)	5877(2)	-1420(2)	132(1)
C(46)	3063(1)	7686(2)	-1751(2)	115(1)
C(47)	2948(1)	8827(2)	-1737(1)	104(1)
C(48)	2839(1)	10272(2)	-966(2)	107(1)
C(49)	1505(1)	2495(1)	829(1)	54(1)
C(50)	1606(1)	2402(2)	1654(1)	65(1)
C(51)	1931(1)	2804(2)	2041(1)	83(1)
C(52)	2162(1)	3264(2)	1637(2)	93(1)
C(53)	2074(1)	3314(2)	837(1)	79(1)
C(54)	1749(1)	2919(1)	415(1)	60(1)
C(55)	1356(1)	1866(2)	2095(1)	99(1)
C(56)	1662(1)	2915(2)	-464(1)	80(1)
C(57)	270(1)	2146(1)	-1133(1)	53(1)
C(58)	-18(1)	2887(1)	-1219(1)	62(1)
C(59)	-264(1)	2932(2)	-1926(1)	76(1)
C(60)	-239(1)	2272(2)	-2543(1)	88(1)
C(61)	39(1)	1535(2)	-2463(1)	77(1)
C(62)	295(1)	1458(1)	-1769(1)	60(1)

C(63)	-52(1)	3613(2)	-545(1)	89(1)
C(64)	596(1)	667(2)	-1687(1)	82(1)
C(65)	712(1)	4230(2)	-1798(1)	87(1)
C(66)	817(1)	5417(2)	-701(1)	91(1)
C(67)	996(1)	5436(2)	138(2)	100(1)
C(68)	976(1)	4567(3)	1341(1)	131(1)
C(69)	1185(1)	8995(3)	-63(2)	146(1)
C(70)	771(1)	8978(2)	759(2)	114(1)
C(71)	496(1)	9565(2)	999(2)	119(1)
C(72)	258(1)	11272(3)	1200(2)	113(1)

Table 3. Bond lengths [Å] and angles [°] for **14**.

Li(1)-Li(2)	2.496(4)	Li(6)-O(17)#1	2.037(3)
Li(3)-Li(4)	2.515(4)	O(17)-Li(6)#2	2.037(3)
Li(5)-Li(6)	2.504(4)	Li(6)-O(18)#1	2.055(4)
Li(1)-O(1)	1.865(3)	O(18)-Li(6)#2	2.055(4)
Li(1)-O(2)	1.862(3)	Li(4)-C(47)	2.786(4)
Li(1)-O(3)	2.040(3)	O(1)-C(1)	1.3199(19)
Li(1)-O(4)	2.038(3)	O(2)-C(9)	1.3174(18)
Li(2)-O(1)	1.865(3)	O(3)-C(17)	1.398(3)
Li(2)-O(2)	1.865(3)	O(3)-C(18)	1.335(3)
Li(2)-O(5)	2.040(3)	O(4)-C(19)	1.365(3)
Li(2)-O(6)	2.068(3)	O(4)-C(20)	1.407(3)
Li(3)-O(7)	1.865(3)	O(5)-C(21)	1.416(2)
Li(3)-O(8)	1.880(3)	O(5)-C(22)	1.419(3)
Li(3)-O(9)	2.052(4)	O(6)-C(23)	1.412(3)
Li(3)-O(10)	2.016(3)	O(6)-C(24)	1.426(3)
Li(4)-O(7)	1.871(3)	O(7)-C(25)	1.3147(17)
Li(4)-O(8)	1.864(3)	O(8)-C(33)	1.3141(19)
Li(4)-O(11)	2.027(3)	O(9)-C(41)	1.412(4)
Li(4)-O(12)	2.071(3)	O(9)-C(42)	1.331(3)
Li(5)-O(13)	1.885(3)	O(10)-C(43)	1.388(4)
Li(5)-O(14)	1.863(3)	O(10)-C(44)	1.391(3)
Li(5)-O(15)	2.048(3)	O(11)-C(45)	1.415(3)
Li(5)-O(16)	2.076(3)	O(11)-C(46)	1.397(3)
Li(6)-O(13)	1.846(3)	O(12)-C(47)	1.342(3)
Li(6)-O(14)	1.878(3)	O(12)-C(48)	1.414(3)

O(13)-C(49)	1.3234(19)	C(29)-C(30)	1.391(2)
O(14)-C(57)	1.3150(18)	C(25)-C(30)	1.407(2)
O(15)-C(65)	1.421(2)	C(26)-C(31)	1.478(3)
O(15)-C(66)	1.412(2)	C(30)-C(32)	1.504(3)
O(16)-C(67)	1.406(3)	C(33)-C(34)	1.406(3)
O(16)-C(68)	1.422(3)	C(34)-C(35)	1.410(3)
O(17)-C(69)	1.405(3)	C(35)-C(36)	1.379(4)
O(17)-C(70)	1.380(3)	C(36)-C(37)	1.346(4)
O(18)-C(71)	1.327(3)	C(37)-C(38)	1.388(3)
O(18)-C(72)	1.393(3)	C(33)-C(38)	1.408(3)
C(1)-C(6)	1.410(2)	C(34)-C(39)	1.483(3)
C(1)-C(2)	1.414(3)	C(38)-C(40)	1.504(3)
C(2)-C(3)	1.386(3)	C(42)-C(43)	1.412(5)
C(2)-C(7)	1.495(3)	C(46)-C(47)	1.458(4)
C(3)-C(4)	1.354(4)	C(49)-C(50)	1.413(2)
C(4)-C(5)	1.368(4)	C(50)-C(51)	1.386(3)
C(5)-C(6)	1.404(3)	C(51)-C(52)	1.373(3)
C(6)-C(8)	1.494(3)	C(52)-C(53)	1.364(3)
C(9)-C(10)	1.403(2)	C(53)-C(54)	1.399(2)
C(10)-C(11)	1.392(3)	C(49)-C(54)	1.405(2)
C(11)-C(12)	1.360(3)	C(50)-C(55)	1.510(3)
C(12)-C(13)	1.389(3)	C(54)-C(56)	1.497(3)
C(13)-C(14)	1.384(3)	C(57)-C(58)	1.416(2)
C(9)-C(14)	1.410(2)	C(58)-C(59)	1.387(3)
C(10)-C(15)	1.496(3)	C(58)-C(63)	1.499(3)
C(14)-C(16)	1.499(3)	C(59)-C(60)	1.361(3)
C(18)-C(19)	1.405(4)	C(60)-C(61)	1.384(3)
C(22)-C(23)	1.475(3)	C(61)-C(62)	1.393(2)
C(25)-C(26)	1.412(2)	C(57)-C(62)	1.410(2)
C(26)-C(27)	1.397(3)	C(62)-C(64)	1.494(3)
C(27)-C(28)	1.369(4)	C(66)-C(67)	1.478(3)
C(28)-C(29)	1.368(3)	C(70)-C(71)	1.417(4)

O(2)-Li(1)-O(1)	95.46(14)	O(4)-Li(1)-O(3)	79.71(12)
O(2)-Li(1)-O(4)	134.98(16)	O(2)-Li(1)-Li(2)	48.01(10)
O(1)-Li(1)-O(4)	117.24(16)	O(1)-Li(1)-Li(2)	47.99(10)
O(2)-Li(1)-O(3)	108.46(15)	O(4)-Li(1)-Li(2)	155.40(17)
O(1)-Li(1)-O(3)	123.40(16)	O(3)-Li(1)-Li(2)	124.40(16)

O(1)-Li(2)-O(2)	95.36(14)
O(1)-Li(2)-O(5)	136.18(17)
O(2)-Li(2)-O(5)	113.10(14)
O(1)-Li(2)-O(6)	108.40(13)
O(2)-Li(2)-O(6)	127.85(17)
O(5)-Li(2)-O(6)	80.37(11)
O(1)-Li(2)-Li(1)	47.99(10)
O(2)-Li(2)-Li(1)	47.91(10)
O(5)-Li(2)-Li(1)	151.08(15)
O(6)-Li(2)-Li(1)	128.02(15)
O(7)-Li(3)-O(8)	94.93(15)
O(7)-Li(3)-O(10)	116.29(16)
O(8)-Li(3)-O(10)	119.58(16)
O(7)-Li(3)-O(9)	122.12(16)
O(8)-Li(3)-O(9)	126.41(16)
O(10)-Li(3)-O(9)	79.66(13)
O(7)-Li(3)-Li(4)	47.81(10)
O(8)-Li(3)-Li(4)	47.55(10)
O(10)-Li(3)-Li(4)	128.65(17)
O(9)-Li(3)-Li(4)	151.51(17)
O(8)-Li(4)-O(7)	95.24(14)
O(8)-Li(4)-O(11)	123.02(15)
O(7)-Li(4)-O(11)	126.34(16)
O(8)-Li(4)-O(12)	115.23(15)
O(7)-Li(4)-O(12)	118.04(15)
O(11)-Li(4)-O(12)	80.66(12)
O(8)-Li(4)-Li(3)	48.07(10)
O(7)-Li(4)-Li(3)	47.60(10)
O(11)-Li(4)-Li(3)	152.77(17)
O(12)-Li(4)-Li(3)	126.47(15)
O(8)-Li(4)-C(47)	116.68(14)
O(7)-Li(4)-C(47)	139.86(15)
O(11)-Li(4)-C(47)	55.72(9)
O(12)-Li(4)-C(47)	27.36(7)
Li(3)-Li(4)-C(47)	149.63(15)
O(14)-Li(5)-O(13)	94.95(14)
O(14)-Li(5)-O(15)	112.80(14)
O(13)-Li(5)-O(15)	137.00(17)
O(14)-Li(5)-O(16)	130.01(17)
O(13)-Li(5)-O(16)	107.59(13)
O(15)-Li(5)-O(16)	79.66(11)
O(14)-Li(5)-Li(6)	48.23(10)
O(13)-Li(5)-Li(6)	47.17(10)
O(15)-Li(5)-Li(6)	150.91(16)
O(16)-Li(5)-Li(6)	129.11(15)
O(13)-Li(6)-O(14)	95.77(14)
O(13)-Li(6)-O(17)#1	119.39(17)
O(14)-Li(6)-O(17)#1	132.83(16)
O(13)-Li(6)-O(18)#1	125.37(16)
O(14)-Li(6)-O(18)#1	105.93(16)
O(17)#1-Li(6)-O(18)#1	79.72(12)
O(13)-Li(6)-Li(5)	48.51(10)
O(14)-Li(6)-Li(5)	47.72(10)
O(17)#1-Li(6)-Li(5)	156.10(18)
O(18)#1-Li(6)-Li(5)	124.16(16)
C(1)-O(1)-Li(1)	139.90(14)
C(1)-O(1)-Li(2)	134.90(14)
Li(1)-O(1)-Li(2)	84.02(13)
C(9)-O(2)-Li(1)	144.54(13)
C(9)-O(2)-Li(2)	126.49(13)
Li(1)-O(2)-Li(2)	84.08(13)
C(18)-O(3)-C(17)	117.7(2)
C(18)-O(3)-Li(1)	111.94(17)
C(17)-O(3)-Li(1)	122.20(17)
C(19)-O(4)-C(20)	119.1(2)
C(19)-O(4)-Li(1)	111.99(16)
C(20)-O(4)-Li(1)	125.7(2)
C(21)-O(5)-C(22)	113.56(17)
C(21)-O(5)-Li(2)	123.06(15)
C(22)-O(5)-Li(2)	110.87(15)
C(23)-O(6)-C(24)	113.29(19)
C(23)-O(6)-Li(2)	107.76(15)
C(24)-O(6)-Li(2)	118.31(16)
C(25)-O(7)-Li(3)	139.66(13)
C(25)-O(7)-Li(4)	135.74(14)
Li(3)-O(7)-Li(4)	84.59(14)

C(33)-O(8)-Li(4)	135.61(14)	C(1)-C(2)-C(7)	119.33(16)
C(33)-O(8)-Li(3)	133.54(15)	C(4)-C(3)-C(2)	122.9(2)
Li(4)-O(8)-Li(3)	84.38(13)	C(3)-C(4)-C(5)	118.5(2)
C(42)-O(9)-C(41)	115.2(2)	C(4)-C(5)-C(6)	122.2(2)
C(42)-O(9)-Li(3)	111.1(2)	C(5)-C(6)-C(1)	118.7(2)
C(41)-O(9)-Li(3)	129.2(2)	C(5)-C(6)-C(8)	121.7(2)
C(43)-O(10)-C(44)	116.9(2)	C(1)-C(6)-C(8)	119.52(18)
C(43)-O(10)-Li(3)	112.6(2)	O(2)-C(9)-C(10)	120.54(15)
C(44)-O(10)-Li(3)	128.14(19)	O(2)-C(9)-C(14)	120.41(14)
C(46)-O(11)-C(45)	112.9(2)	C(10)-C(9)-C(14)	119.04(15)
C(46)-O(11)-Li(4)	111.22(16)	C(11)-C(10)-C(9)	119.43(18)
C(45)-O(11)-Li(4)	132.46(18)	C(11)-C(10)-C(15)	120.45(18)
C(47)-O(12)-C(48)	113.33(18)	C(9)-C(10)-C(15)	120.11(16)
C(47)-O(12)-Li(4)	107.49(15)	C(12)-C(11)-C(10)	121.7(2)
C(48)-O(12)-Li(4)	124.67(17)	C(11)-C(12)-C(13)	119.26(19)
C(49)-O(13)-Li(6)	152.44(14)	C(14)-C(13)-C(12)	121.2(2)
C(49)-O(13)-Li(5)	122.64(13)	C(13)-C(14)-C(9)	119.38(17)
Li(6)-O(13)-Li(5)	84.32(13)	C(13)-C(14)-C(16)	121.90(18)
C(57)-O(14)-Li(5)	125.20(13)	C(9)-C(14)-C(16)	118.72(15)
C(57)-O(14)-Li(6)	145.56(14)	O(3)-C(18)-C(19)	115.1(2)
Li(5)-O(14)-Li(6)	84.05(13)	O(4)-C(19)-C(18)	114.1(2)
C(66)-O(15)-C(65)	112.81(16)	O(5)-C(22)-C(23)	107.80(17)
C(66)-O(15)-Li(5)	111.76(14)	O(6)-C(23)-C(22)	107.46(18)
C(65)-O(15)-Li(5)	124.47(15)	O(7)-C(25)-C(30)	120.39(14)
C(67)-O(16)-C(68)	113.57(19)	O(7)-C(25)-C(26)	121.04(16)
C(67)-O(16)-Li(5)	107.07(15)	C(30)-C(25)-C(26)	118.56(14)
C(68)-O(16)-Li(5)	121.19(16)	C(27)-C(26)-C(25)	119.02(19)
C(70)-O(17)-C(69)	116.9(2)	C(27)-C(26)-C(31)	122.06(19)
C(70)-O(17)-Li(6)#2	112.33(17)	C(25)-C(26)-C(31)	118.92(17)
C(69)-O(17)-Li(6)#2	128.9(2)	C(28)-C(27)-C(26)	121.71(19)
C(71)-O(18)-C(72)	117.7(2)	C(29)-C(28)-C(27)	119.58(18)
C(71)-O(18)-Li(6)#2	111.61(19)	C(28)-C(29)-C(30)	121.1(2)
C(72)-O(18)-Li(6)#2	122.01(18)	C(29)-C(30)-C(25)	119.99(17)
O(1)-C(1)-C(6)	121.16(17)	C(29)-C(30)-C(32)	119.82(18)
O(1)-C(1)-C(2)	120.35(15)	C(25)-C(30)-C(32)	120.19(15)
C(6)-C(1)-C(2)	118.49(16)	O(8)-C(33)-C(34)	120.64(17)
C(3)-C(2)-C(1)	119.17(19)	O(8)-C(33)-C(38)	120.64(16)
C(3)-C(2)-C(7)	121.5(2)	C(34)-C(33)-C(38)	118.72(16)

C(33)-C(34)-C(35)	118.4(2)	C(53)-C(52)-C(51)	119.76(19)
C(33)-C(34)-C(39)	119.48(18)	C(52)-C(53)-C(54)	121.5(2)
C(35)-C(34)-C(39)	122.1(2)	C(53)-C(54)-C(49)	118.90(17)
C(36)-C(35)-C(34)	121.2(2)	C(53)-C(54)-C(56)	121.30(18)
C(37)-C(36)-C(35)	120.3(2)	C(49)-C(54)-C(56)	119.78(15)
C(36)-C(37)-C(38)	120.9(3)	O(14)-C(57)-C(62)	120.13(14)
C(37)-C(38)-C(33)	120.5(2)	O(14)-C(57)-C(58)	121.19(15)
C(37)-C(38)-C(40)	120.1(2)	C(62)-C(57)-C(58)	118.67(15)
C(33)-C(38)-C(40)	119.42(18)	C(59)-C(58)-C(57)	119.55(17)
O(9)-C(42)-C(43)	114.1(2)	C(59)-C(58)-C(63)	121.04(17)
O(10)-C(43)-C(42)	113.4(3)	C(57)-C(58)-C(63)	119.41(16)
O(11)-C(46)-C(47)	110.7(2)	C(60)-C(59)-C(58)	121.84(19)
O(12)-C(47)-C(46)	111.8(2)	C(59)-C(60)-C(61)	119.21(18)
O(12)-C(47)-Li(4)	45.15(11)	C(60)-C(61)-C(62)	121.57(19)
C(46)-C(47)-Li(4)	77.36(15)	C(61)-C(62)-C(57)	119.15(17)
O(13)-C(49)-C(54)	120.20(14)	C(61)-C(62)-C(64)	121.43(17)
O(13)-C(49)-C(50)	120.78(16)	C(57)-C(62)-C(64)	119.42(15)
C(54)-C(49)-C(50)	119.01(15)	O(15)-C(66)-C(67)	107.02(17)
C(51)-C(50)-C(49)	119.39(19)	O(16)-C(67)-C(66)	107.52(18)
C(51)-C(50)-C(55)	121.38(18)	O(17)-C(70)-C(71)	113.7(2)
C(49)-C(50)-C(55)	119.23(16)	O(18)-C(71)-C(70)	115.4(2)
C(52)-C(51)-C(50)	121.2(2)		

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 x,y+1,z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **14**.

The anisotropic displacement factor exponent takes the form: $-2p^2[\, h^2a^{*2}U^{11} + ... + 2\,h\,k\,a^*\,b^*\,U^{12}\,]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Li(1)	59(1)	58(2)	70(2)	-6(1)	16(1)	2(1)
Li(2)	53(1)	55(1)	63(1)	3(1)	3(1)	2(1)
Li(3)	54(1)	72(2)	64(1)	-7(1)	12(1)	10(1)
Li(4)	59(1)	66(2)	58(1)	-4(1)	15(1)	-5(1)
Li(5)	58(1)	59(2)	58(1)	2(1)	2(1)	-3(1)
Li(6)	65(2)	60(2)	69(2)	8(1)	11(1)	-6(1)
O(1)	46(1)	66(1)	67(1)	-10(1)	3(1)	1(1)

O(2)	51(1)	61(1)	66(1)	9(1)	-2(1)	-2(1)
O(3)	96(1)	81(1)	139(1)	-18(1)	68(1)	-5(1)
O(4)	133(1)	73(1)	86(1)	-9(1)	53(1)	-14(1)
O(5)	75(1)	69(1)	77(1)	-10(1)	15(1)	-4(1)
O(6)	86(1)	71(1)	80(1)	15(1)	9(1)	0(1)
O(7)	47(1)	69(1)	55(1)	0(1)	6(1)	8(1)
O(8)	54(1)	87(1)	60(1)	-4(1)	1(1)	2(1)
O(9)	145(1)	131(1)	101(1)	-30(1)	68(1)	-42(1)
O(10)	140(1)	90(1)	100(1)	-6(1)	50(1)	41(1)
O(11)	121(1)	66(1)	90(1)	-11(1)	51(1)	-6(1)
O(12)	114(1)	61(1)	91(1)	3(1)	47(1)	-9(1)
O(13)	50(1)	71(1)	65(1)	12(1)	3(1)	-7(1)
O(14)	53(1)	65(1)	64(1)	-8(1)	-2(1)	1(1)
O(15)	74(1)	68(1)	73(1)	8(1)	18(1)	8(1)
O(16)	89(1)	76(1)	67(1)	-13(1)	5(1)	5(1)
O(17)	132(1)	72(1)	93(1)	9(1)	51(1)	14(1)
O(18)	89(1)	83(1)	143(1)	22(1)	57(1)	-1(1)
C(1)	51(1)	42(1)	69(1)	1(1)	1(1)	2(1)
C(2)	57(1)	47(1)	92(1)	7(1)	16(1)	0(1)
C(3)	58(1)	65(1)	156(2)	15(1)	26(1)	2(1)
C(4)	53(1)	78(1)	168(2)	19(2)	-19(1)	-3(1)
C(5)	87(1)	67(1)	109(2)	8(1)	-40(1)	-4(1)
C(6)	79(1)	57(1)	75(1)	-5(1)	-13(1)	-2(1)
C(7)	94(1)	80(1)	89(1)	-6(1)	38(1)	-11(1)
C(8)	126(2)	124(2)	62(1)	-21(1)	4(1)	-4(2)
C(9)	42(1)	52(1)	66(1)	-2(1)	4(1)	7(1)
C(10)	45(1)	56(1)	97(1)	-6(1)	4(1)	7(1)
C(11)	50(1)	76(1)	121(2)	-27(1)	-5(1)	6(1)
C(12)	74(1)	114(2)	86(1)	-32(1)	-20(1)	24(1)
C(13)	74(1)	105(1)	65(1)	-2(1)	4(1)	29(1)
C(14)	54(1)	66(1)	62(1)	4(1)	11(1)	16(1)
C(15)	63(1)	76(1)	151(2)	25(1)	15(1)	-10(1)
C(16)	80(1)	90(1)	88(1)	27(1)	23(1)	3(1)
C(17)	103(2)	149(2)	110(2)	-12(2)	50(1)	-32(2)
C(18)	157(2)	87(2)	110(2)	1(1)	69(2)	31(2)
C(19)	136(2)	75(1)	131(2)	-30(1)	54(2)	-7(1)
C(20)	170(2)	156(2)	154(2)	-28(2)	81(2)	-81(2)
C(21)	90(1)	115(2)	77(1)	-24(1)	16(1)	15(1)

C(22)	104(1)	62(1)	128(2)	-19(1)	49(1)	-12(1)
C(23)	99(2)	71(1)	129(2)	25(1)	35(1)	14(1)
C(24)	164(3)	126(2)	75(1)	33(1)	-1(2)	-17(2)
C(25)	41(1)	72(1)	43(1)	-1(1)	12(1)	1(1)
C(26)	58(1)	88(1)	58(1)	1(1)	14(1)	-18(1)
C(27)	56(1)	133(2)	63(1)	6(1)	5(1)	-35(1)
C(28)	49(1)	149(2)	77(1)	34(1)	3(1)	-2(1)
C(29)	54(1)	102(1)	79(1)	22(1)	15(1)	21(1)
C(30)	51(1)	76(1)	59(1)	-1(1)	14(1)	11(1)
C(31)	101(2)	83(1)	104(2)	-5(1)	14(1)	-24(1)
C(32)	82(1)	67(1)	105(2)	-12(1)	3(1)	6(1)
C(33)	46(1)	85(1)	45(1)	2(1)	11(1)	1(1)
C(34)	60(1)	97(1)	61(1)	11(1)	13(1)	18(1)
C(35)	68(1)	152(2)	74(1)	19(1)	7(1)	34(1)
C(36)	60(1)	173(3)	82(1)	-24(2)	3(1)	-12(2)
C(37)	68(1)	129(2)	93(1)	-23(1)	22(1)	-29(1)
C(38)	65(1)	95(1)	67(1)	-1(1)	15(1)	-11(1)
C(39)	111(2)	95(2)	137(2)	25(2)	28(2)	26(2)
C(40)	134(2)	79(2)	147(2)	27(2)	5(2)	-5(2)
C(41)	156(2)	152(3)	156(2)	-4(2)	59(2)	-60(2)
C(42)	201(3)	148(3)	101(2)	-8(2)	76(2)	17(2)
C(43)	159(2)	176(3)	103(2)	-50(2)	54(2)	30(2)
C(44)	167(3)	83(2)	151(2)	-13(2)	31(2)	38(2)
C(45)	177(3)	74(2)	156(2)	-13(2)	63(2)	10(2)
C(46)	146(2)	96(2)	131(2)	-1(1)	90(1)	-5(2)
C(47)	154(2)	85(1)	86(1)	9(1)	56(1)	-16(2)
C(48)	127(2)	64(1)	141(2)	3(1)	52(2)	-11(1)
C(49)	44(1)	49(1)	66(1)	4(1)	7(1)	6(1)
C(50)	59(1)	68(1)	62(1)	6(1)	4(1)	10(1)
C(51)	73(1)	81(1)	80(1)	-6(1)	-15(1)	14(1)
C(52)	51(1)	83(1)	132(2)	-11(1)	-13(1)	-2(1)
C(53)	48(1)	69(1)	119(2)	4(1)	15(1)	1(1)
C(54)	51(1)	50(1)	79(1)	5(1)	16(1)	8(1)
C(55)	93(2)	138(2)	63(1)	31(1)	10(1)	8(2)
C(56)	85(1)	77(1)	86(1)	11(1)	38(1)	8(1)
C(57)	44(1)	54(1)	61(1)	0(1)	7(1)	-9(1)
C(58)	47(1)	53(1)	82(1)	1(1)	8(1)	-6(1)
C(59)	51(1)	76(1)	94(1)	16(1)	-1(1)	-6(1)

C(60)	65(1)	111(2)	74(1)	15(1)	-15(1)	-17(1)
C(61)	73(1)	92(1)	62(1)	-7(1)	9(1)	-19(1)
C(62)	54(1)	65(1)	61(1)	-7(1)	12(1)	-11(1)
C(63)	70(1)	73(1)	122(2)	-24(1)	15(1)	9(1)
C(64)	77(1)	89(1)	80(1)	-18(1)	18(1)	6(1)
C(65)	82(1)	114(2)	67(1)	18(1)	18(1)	-4(1)
C(66)	107(1)	66(1)	112(1)	16(1)	50(1)	9(1)
C(67)	92(1)	73(1)	139(2)	-33(1)	31(1)	-16(1)
C(68)	163(2)	142(2)	70(1)	-34(1)	-12(2)	61(2)
C(69)	151(2)	147(3)	153(2)	18(2)	64(2)	58(2)
C(70)	133(2)	79(1)	140(2)	33(1)	54(2)	6(2)
C(71)	163(2)	89(2)	123(2)	-7(1)	73(2)	-37(2)
C(72)	98(2)	137(2)	113(2)	11(2)	46(1)	21(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **14**.

	x	y	z	U(eq)
H(3)	2723	2175	4913	111
H(4)	2486	1922	3608	128
H(5)	2856	1735	2747	116
H(7A)	3196	2337	5998	127
H(7B)	3506	3038	5784	127
H(7C)	3551	1752	5919	127
H(8A)	3423	1556	2461	160
H(8B)	3705	1012	3148	160
H(8C)	3715	2296	2996	160
H(11)	5461	3515	6926	103
H(12)	5436	2445	7996	116
H(13)	4985	1161	7919	99
H(15A)	5222	4189	5669	147
H(15B)	4816	3987	5315	147
H(15C)	5101	3178	5101	147
H(16A)	4451	332	7251	128
H(16B)	4455	134	6356	128
H(16C)	4212	1064	6594	128
H(17A)	4931	1321	4250	174

H(17B)	4647	1971	3625	174
H(17C)	4820	883	3376	174
H(18A)	4729	-683	4305	135
H(18B)	4492	-703	3445	135
H(19A)	4038	-1204	3815	132
H(19B)	4332	-1769	4467	132
H(20A)	3677	-1391	4743	230
H(20B)	3732	-491	5417	230
H(20C)	3959	-1586	5535	230
H(21A)	4510	4283	6869	142
H(21B)	4205	3459	6963	142
H(21C)	4160	4741	7080	142
H(22A)	4407	5505	5736	113
H(22B)	4051	5923	5947	113
H(23A)	3726	5262	4764	118
H(23B)	4027	6053	4587	118
H(24A)	3724	4281	3569	189
H(24B)	4080	3738	3446	189
H(24C)	4031	5032	3386	189
H(27)	3812	8441	2178	102
H(28)	3926	6621	2499	112
H(29)	3526	5285	1952	94
H(31A)	3456	9848	1485	146
H(31B)	3048	9605	1397	146
H(31C)	3223	9491	660	146
H(32A)	2680	5597	1022	131
H(32B)	2988	4717	1193	131
H(32C)	2903	5352	381	131
H(35)	1221	8877	-2256	119
H(36)	1061	7048	-2436	129
H(37)	1428	5700	-1825	115
H(39A)	1817	10009	-810	171
H(39B)	1626	10276	-1687	171
H(39C)	2027	9908	-1492	171
H(40A)	1929	5096	-937	186
H(40B)	2092	5918	-249	186
H(40C)	2264	5814	-990	186
H(41A)	2184	5948	1811	226

H(41B)	1969	5846	932	226
H(41C)	1773	6192	1604	226
H(42A)	2267	7862	2315	172
H(42B)	1850	7889	2103	172
H(43A)	1827	9432	1536	171
H(43B)	2176	9573	2195	171
H(44A)	2051	10796	752	201
H(44B)	2419	10551	533	201
H(44C)	2405	10907	1399	201
H(45A)	2918	5694	-1970	198
H(45B)	2778	5442	-1200	198
H(45C)	3182	5718	-1140	198
H(46A)	3029	7436	-2295	138
H(46B)	3315	7635	-1508	138
H(47A)	3116	9306	-1922	124
H(47B)	2717	8912	-2096	124
H(48A)	3007	10713	-1172	161
H(48B)	2850	10469	-423	161
H(48C)	2603	10408	-1272	161
H(51)	1996	2760	2592	99
H(52)	2380	3544	1909	112
H(53)	2234	3621	564	95
H(55A)	1456	1900	2655	149
H(55B)	1319	1103	1934	149
H(55C)	1131	2252	1981	149
H(56A)	1539	2239	-651	119
H(56B)	1878	2963	-657	119
H(56C)	1512	3541	-654	119
H(59)	-452	3432	-1982	92
H(60)	-408	2316	-3017	105
H(61)	56	1076	-2888	92
H(63A)	-223	4191	-730	134
H(63B)	175	3940	-319	134
H(63C)	-131	3178	-149	134
H(64A)	817	1068	-1559	122
H(64B)	580	274	-2178	122
H(64C)	585	145	-1272	122
H(65A)	460	4366	-1886	131

H(65B)	753	3487	-1963	131
H(65C)	818	4753	-2098	131
H(66A)	565	5574	-762	110
H(66B)	920	5973	-992	110
H(67A)	1251	5327	195	120
H(67B)	957	6146	372	120
H(68A)	1230	4457	1466	196
H(68B)	862	3973	1564	196
H(68C)	920	5264	1558	196
H(69A)	1339	8597	359	219
H(69B)	1323	9525	-286	219
H(69C)	1074	8481	-466	219
H(70A)	954	8798	1225	136
H(70B)	676	8284	516	136
H(71A)	272	9380	641	142
H(71B)	482	9311	1524	142
H(72A)	78	11396	728	169
H(72B)	349	11975	1419	169
H(72C)	156	10877	1581	169

Crystal data and structure refinement for $[ICa(O^tBu)_4\{Li(thf)\}_4(OH)].THF$ 15

$C_{36}H_{77}ILi_4CaO_{10}$, M= 864.72 gmol^{-1}, tetragonal, *P*4/nmm (Nr. 129), a = 15.5962(14), c = 9.9953(9) Å, V = 2431.3(4) Å^3, Z = 2, $\rho_{calcd.}$= 1.181 Mgm^3, *F*(000) = 916, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.807 mm^{-1}, 2.04° < θ < 27.20°, 1525 reflections of which 1525 unique and 596 observed, 69 parameters refined, *GOOF* (on F^2) = 0.987, R1= $\Sigma|F_o{-}F_c|/\Sigma F_o$ = 0.1061, *w*R2 = 0.3143 for I > 2σ(I) and R1 = 0.1624, wR2 = 0.3476 for all data. The intensities from the single-crystals of **15** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically, except for the methyl groups of disordered ^{t}Bu-units and some disordered THF-molecules. Several batches of crystals were measured, trying to improve the crystal quality and the data, but without success so far. However, the structure of the cluster could be attributed without any doubt. The disorder observed for ^{t}Bu-groups and THF, leads to the high R1 value. The highest peak in remaining electron density of 0.72 is found near iodide ions. The positions of the hydrogen atoms could not be calculated due to the heavy disorder, but were included in the determination of the molar mass. CCDC-616797 (**15**) contains the supplementary crystallographic data for **15**. The cif file for the structure of **15** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **15**.

Identification code	$[ICa(O^tBu)_4\{Li(thf)\}_4(OH)].(THF)_n$	
Empirical formula	C36 H77 Ca I Li4 O10	
Formula weight	864.72	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4/nmm	
Unit cell dimensions	a = 15.5962(14) Å	α= 90°
	b = 15.5962(14) Å	β= 90°
	c = 9.9953(9) Å	γ = 90°
Volume	2431.3(4) $Å^3$	
Z	2	
Density (calculated)	1.181 Mg/m^3	
Absorption coefficient	0.807 mm^{-1}	
F(000)	916	
Theta range for data collection	2.04 to 27.20°	
Index ranges	0<=h<=14, 0<=k<=20, 0<=l<=12	
Reflections collected	1525	
Independent reflections	1525 [R(int) = 0.0000]	
Completeness to theta = 27.20°	99.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1525 / 0 / 69	
Goodness-of-fit on F^2	0.987	
Final R indices [I>2sigma(I)]	R1 = 0.1061, wR2 = 0.3143	
R indices (all data)	R1 = 0.1624, wR2 = 0.3476	
Largest diff. peak and hole	0.723 and -0.393 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **15**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ca	2500	2500	1448(2)	68(1)
I	2500	2500	-1626(1)	195(1)
O(1)	2500	2500	4145(7)	65(2)

O(2)	3477(2)	3477(2)	2393(4)	79(1)
O(3)	2500	4577(3)	4998(4)	104(1)
Li	2500	3733(6)	3514(10)	81(3)
C(1)	4057(3)	4057(3)	1811(7)	97(2)
C(2)	4547(9)	4547(9)	2913(17)	236(7)
C(2A)	4008(10)	4008(10)	210(20)	259(8)
C(3)	3596(9)	4808(9)	1002(13)	263(5)
C(3A)	3889(13)	4970(15)	2295(14)	334(8)
C(4)	1804(13)	4539(12)	5864(17)	326(8)
C(4A)	2093(11)	5600(12)	5037(17)	322(9)
C(5)	2095(7)	5189(8)	7107(11)	220(5)
C(5A)	2500	5946(15)	6477(19)	250(8)
C(6)	2500	7075(11)	1176(18)	224(7)
C(7)	1680(20)	7500	440(40)	384(16)

Table 3. Bond lengths [Å] and angles [°] for **15**.

Ca-I	3.072(2)	O(3)-C(4)	1.390(19)
Ca-O(1)	2.696(7)	O(3)-C(4)#4	1.390(19)
Ca-O(2)	2.352(4)	O(3)-C(4A)	1.718(18)
Ca-O(2)#1	2.352(4)	O(3)-C(4A)#4	1.718(18)
Ca-O(2)#2	2.352(4)	C(1)-C(2)	1.544(19)
Ca-O(2)#3	2.352(4)	C(1)-C(2A)	1.61(2)
Ca-Li	2.822(10)	C(1)-C(3)	1.595(15)
Ca-Li#1	2.822(10)	C(1)-C(3A)	1.53(2)
Ca-Li#2	2.822(10)	C(1)-C(3A)#5	1.53(2)
Ca-Li#3	2.822(10)	C(1)-C(3)#5	1.595(15)
Li-Li#1	2.719(13)	C(2)-C(3A)	1.37(2)
Li-Li#3	2.719(13)	C(2)-C(3A)#5	1.37(2)
O(1)-Li	2.024(10)	C(2A)-C(3)	1.612(18)
O(1)-Li#1	2.024(10)	C(2A)-C(3)#5	1.612(18)
O(1)-Li#2	2.024(10)	C(3)-C(3A)	1.39(2)
O(1)-Li#3	2.024(10)	C(4)-C(4A)	1.90(2)
O(2)-Li	1.933(6)	C(4A)-C(4A)#4	1.27(3)
O(2)-Li#1	1.933(6)	C(4)-C(5)	1.67(2)
Li-O(2)#3	1.933(6)	C(4A)-C(5A)	1.66(2)
O(3)-Li	1.983(11)	C(5A)-C(4A)#4	1.66(2)
O(2)-C(1)	1.406(8)	C(5)-C(5)#4	1.26(2)

C(5)-C(5A)	1.48(2)	C(7)-C(6)#6	1.62(3)
C(5A)-C(5)#4	1.48(2)	C(6)-C(7)#7	1.73(4)
C(6)-C(6)#6	1.33(4)	C(7)-C(6)#8	1.73(4)
C(6)-C(7)	1.62(3)	C(7)-C(7)#7	2.02(5)
C(6)-C(7)#6	1.62(3)	C(7)-C(7)#8	2.02(5)

O(2)-Ca-O(2)#1	80.72(7)	O(1)-Ca-Li#3	42.96(19)
O(2)-Ca-O(2)#2	132.65(19)	Li#1-Ca-Li#3	85.9(4)
O(2)#1-Ca-O(2)#2	80.72(7)	Li-Ca-Li#3	57.6(2)
O(2)-Ca-O(2)#3	80.72(7)	Li#2-Ca-Li#3	57.6(2)
O(2)#1-Ca-O(2)#3	132.65(19)	O(2)-Ca-I	113.67(10)
O(2)#2-Ca-O(2)#3	80.72(7)	O(2)#1-Ca-I	113.67(10)
O(2)-Ca-O(1)	66.33(10)	O(2)#2-Ca-I	113.67(10)
O(2)#1-Ca-O(1)	66.33(10)	O(2)#3-Ca-I	113.67(10)
O(2)#2-Ca-O(1)	66.33(10)	O(1)-Ca-I	180.0
O(2)#3-Ca-O(1)	66.33(10)	Li#1-Ca-I	137.04(19)
O(2)-Ca-Li#1	42.68(9)	Li-Ca-I	137.04(19)
O(2)#1-Ca-Li#1	42.68(9)	Li#2-Ca-I	137.04(19)
O(2)#2-Ca-Li#1	98.48(17)	Li#3-Ca-I	137.04(19)
O(2)#3-Ca-Li#1	98.48(17)	Li#1-O(1)-Li#2	84.4(2)
O(1)-Ca-Li#1	42.96(19)	Li#1-O(1)-Li	84.4(2)
O(2)-Ca-Li	42.68(9)	Li#2-O(1)-Li	143.7(7)
O(2)#1-Ca-Li	98.48(17)	Li#1-O(1)-Li#3	143.7(7)
O(2)#2-Ca-Li	98.48(17)	Li#2-O(1)-Li#3	84.4(2)
O(2)#3-Ca-Li	42.68(9)	Li-O(1)-Li#3	84.4(2)
O(1)-Ca-Li	42.96(19)	Li#1-O(1)-Ca	71.8(3)
Li#1-Ca-Li	57.6(2)	Li#2-O(1)-Ca	71.8(3)
O(2)-Ca-Li#2	98.48(17)	Li-O(1)-Ca	71.8(3)
O(2)#1-Ca-Li#2	42.68(9)	Li#3-O(1)-Ca	71.8(3)
O(2)#2-Ca-Li#2	42.68(9)	C(1)-O(2)-Li#1	127.9(3)
O(2)#3-Ca-Li#2	98.48(17)	C(1)-O(2)-Li	127.9(3)
O(1)-Ca-Li#2	42.96(19)	Li#1-O(2)-Li	89.4(6)
Li#1-Ca-Li#2	57.6(2)	C(1)-O(2)-Ca	131.9(3)
Li-Ca-Li#2	85.9(4)	Li#1-O(2)-Ca	81.8(3)
O(2)-Ca-Li#3	98.48(17)	Li-O(2)-Ca	81.8(3)
O(2)#1-Ca-Li#3	98.48(17)	C(4)#4-O(3)-C(4)	102.8(15)
O(2)#2-Ca-Li#3	42.68(9)	C(4)#4-O(3)-C(4A)#4	74.7(9)
O(2)#3-Ca-Li#3	42.68(9)	C(4)-O(3)-C(4A)#4	108.3(10)

C(4)#4-O(3)-C(4A)	108.3(10)
C(4)-O(3)-C(4A)	74.7(9)
C(4A)#4-O(3)-C(4A)	43.4(12)
C(4)#4-O(3)-Li	115.9(8)
C(4)-O(3)-Li	115.9(8)
C(4A)#4-O(3)-Li	129.3(7)
C(4A)-O(3)-Li	129.3(7)
O(2)-Li-O(2)#3	104.0(5)
O(2)-Li-O(3)	124.8(3)
O(2)#3-Li-O(3)	124.8(3)
O(2)-Li-O(1)	89.1(4)
O(2)#3-Li-O(1)	89.1(4)
O(3)-Li-O(1)	113.4(5)
O(2)-Li-Li#1	45.3(3)
O(2)#3-Li-Li#1	114.3(3)
O(3)-Li-Li#1	118.00(18)
O(1)-Li-Li#1	47.79(10)
O(2)-Li-Li#3	114.3(3)
O(2)#3-Li-Li#3	45.3(3)
O(3)-Li-Li#3	118.00(18)
O(1)-Li-Li#3	47.79(10)
Li#1-Li-Li#3	90.000(1)
O(2)-Li-Ca	55.6(3)
O(2)#3-Li-Ca	55.6(3)
O(3)-Li-Ca	178.6(5)
O(1)-Li-Ca	65.2(3)
Li#1-Li-Ca	61.19(11)
Li#3-Li-Ca	61.19(11)
O(2)-C(1)-C(3A)#5	111.1(8)
O(2)-C(1)-C(3A)	111.1(8)
C(3A)#5-C(1)-C(3A)	102.7(15)
O(2)-C(1)-C(2)	110.1(8)
C(3A)#5-C(1)-C(2)	52.9(7)
C(3A)-C(1)-C(2)	52.9(7)
O(2)-C(1)-C(3)#5	113.1(6)
C(3A)#5-C(1)-C(3)#5	53.0(8)
C(3A)-C(1)-C(3)#5	135.0(10)
C(2)-C(1)-C(3)#5	102.8(7)
O(2)-C(1)-C(3)	113.1(6)
C(3A)#5-C(1)-C(3)	135.0(10)
C(3A)-C(1)-C(3)	53.0(8)
C(2)-C(1)-C(3)	102.8(7)
C(3)#5-C(1)-C(3)	113.8(11)
O(2)-C(1)-C(2A)	110.5(9)
C(3A)#5-C(1)-C(2A)	110.6(8)
C(3A)-C(1)-C(2A)	110.6(8)
C(2)-C(1)-C(2A)	139.4(11)
C(3)#5-C(1)-C(2A)	60.5(6)
C(3)-C(1)-C(2A)	60.5(6)
C(3A)#5-C(2)-C(3A)	121(2)
C(3A)#5-C(2)-C(1)	62.9(12)
C(3A)-C(2)-C(1)	62.9(12)
C(1)-C(2A)-C(3)#5	59.4(8)
C(1)-C(2A)-C(3)	59.4(8)
C(3)#5-C(2A)-C(3)	112.0(16)
C(3A)-C(3)-C(1)	61.0(11)
C(3A)-C(3)-C(2A)	117.8(16)
C(1)-C(3)-C(2A)	60.1(9)
C(2)-C(3A)-C(3)	125.3(19)
C(2)-C(3A)-C(1)	64.2(13)
C(3)-C(3A)-C(1)	66.0(11)
O(3)-C(4)-C(5)	103.0(12)
O(3)-C(4)-C(4A)	60.5(9)
C(5)-C(4)-C(4A)	74.4(10)
C(4A)#4-C(4A)-C(5A)	67.5(7)
C(4A)#4-C(4A)-O(3)	68.3(6)
C(5A)-C(4A)-O(3)	100.3(12)
C(4A)#4-C(4A)-C(4)	103.7(8)
C(5A)-C(4A)-C(4)	89.8(13)
O(3)-C(4A)-C(4)	44.8(7)
C(5)#4-C(5)-C(5A)	64.7(6)
C(5)#4-C(5)-C(4)	105.8(8)
C(5A)-C(5)-C(4)	106.5(12)
C(5)#4-C(5A)-C(5)	50.6(12)
C(5)#4-C(5A)-C(4A)	105.9(16)
C(5)-C(5A)-C(4A)	87.0(12)

C(5)#4-C(5A)-C(4A)#4	87.0(12)
C(5)-C(5A)-C(4A)#4	105.9(16)
C(4A)-C(5A)-C(4A)#4	44.9(13)
C(6)#6-C(6)-C(7)#6	65.8(8)
C(6)#6-C(6)-C(7)	65.8(8)
C(7)#6-C(6)-C(7)	105(2)
C(6)#6-C(6)-C(7)#7	111.0(13)
C(7)#6-C(6)-C(7)#7	74.0(14)
C(7)-C(6)-C(7)#7	74.0(14)
C(6)#6-C(7)-C(6)	48.3(17)
C(6)#6-C(7)-C(6)#8	98(2)
C(6)-C(7)-C(6)#8	98(2)
C(6)#6-C(7)-C(7)#8	55.6(12)
C(6)-C(7)-C(7)#8	87.4(13)
C(6)#8-C(7)-C(7)#8	50.4(15)
C(6)#6-C(7)-C(7)#7	87.4(13)
C(6)-C(7)-C(7)#7	55.6(12)
C(6)#8-C(7)-C(7)#7	50.4(15)
C(7)#8-C(7)-C(7)#7	78.9(16)

Symmetry transformations used to generate equivalent atoms:

#1 y,-x+1/2,z #2 -x+1/2,-y+1/2,z #3 -y+1/2,x,z

#4 -x+1/2,y,z #5 y,x,z #6 -x+1/2,-y+3/2,z

#7 -y+1,x+1/2,-z #8 y-1/2,-x+1,-z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **15**.

The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ca	74(1)	74(1)	57(1)	0	0	0
I	259(1)	259(1)	68(1)	0	0	0
O(1)	66(2)	66(2)	63(4)	0	0	0
O(2)	80(1)	80(1)	79(2)	10(1)	10(1)	-22(2)
O(3)	127(3)	96(3)	90(2)	-31(2)	0	0
Li	83(5)	68(5)	92(6)	3(5)	0	0

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **15**.

	x	y	z	U(eq)
H	2500	2500	4760(110)	60(30)

Crystal data and structure refinement for $[IEu(O^tBu)_4\{Li(thf)\}_4(OH)].THF$ 16

$C_{36}H_{77}ILi_4EuO_{10}$, M= 976.60 gmol^{-1}, tetragonal, *P*4/nmm (Nr. 129), a = 15.4602(8), c = 12.800(1) Å, V = 2437.4(2) Å^3, Z = 2, $\rho_{calcd.}$= 1.331 Mgm^3, *F*(000) = 1002, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 1.963 mm^{-1}, 1.86° < θ < 27.15°, 18914 reflections of which 1524 unique and 1339 observed, 68 parameters refined, *GOOF* (on F^2) = 1.731, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ =0.0770, *w*R2 = 0,2022 for I > 2σ(I) and R1 = 0.0918, wR2 = 0.2141 for all data.

The intensities from the single-crystals of **16** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically, except for the methyl groups of disordered ^{t}Bu-units and some disordered THF-molecules. However, the structure of the cluster **16** could be attributed without any doubt. The disorder observed for ^{t}Bu-groups and THF, leads to the reasonable R1 value. The highest peak in remaining electron density of 1.32 is found near iodide ions. The positions of the hydrogen atoms could not be calculated due to the heavy disorder, but were included in the determination of the molar mass. CCDC-616798 (**16**) contains the supplementary crystallographic data for **16**. The cif file for the structure of **16** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **16**.

Identification code	$[IEu(O^tBu)_4\{Li(thf)\}_4(OH)].(THF)_n$	
Empirical formula	C36 H77 Eu I Li4 O10	
Formula weight	976.60	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4/nmm	
Unit cell dimensions	a = 15.4602(8) Å	α= 90°
	b = 15.4602(8) Å	β= 90°
	c = 10.1975(6) Å	γ = 90°
Volume	2437.4(2) Å^3	
Z	2	
Density (calculated)	1.331 Mg/m^3	
Absorption coefficient	1.963 mm^{-1}	
F(000)	1002	
Theta range for data collection	1.86 to 27.15°	
Index ranges	-18<=h<=19, -19<=k<=19, -13<=l<=13	

Reflections collected	18914
Independent reflections	1524 [R(int) = 0.0820]
Completeness to theta = 27.15°	99.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1524 / 0 / 68
Goodness-of-fit on F^2	1.731
Final R indices [I>2sigma(I)]	R1 = 0.0770, wR2 = 0.2022
R indices (all data)	R1 = 0.0918, wR2 = 0.2141
Largest diff. peak and hole	1.321 and -0.953 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **16**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Eu	2500	2500	1240(1)	56(1)
I	2500	2500	-1908(1)	178(1)
O(1)	2500	2500	4157(6)	51(2)
O(2)	3499(2)	1501(2)	2403(4)	67(1)
O(3)	4603(4)	2500	4920(6)	87(1)
Li	3723(6)	2500	3531(9)	62(2)
C(1)	4074(4)	926(4)	1775(8)	94(2)
C(2)	3971(9)	1029(9)	318(17)	175(7)
C(3)	4869(9)	661(9)	2633(16)	206(6)
C(3A)	3611(15)	-46(14)	1648(18)	252(8)
C(4)	4528(10)	3173(11)	5843(14)	187(5)
C(4A)	5442(16)	3016(14)	4870(20)	282(10)
C(5)	5200(9)	2862(8)	6922(14)	191(5)
C(5A)	5880(17)	2500	6180(20)	204(9)
C(6)	2500	7176(16)	1227(16)	196(9)
C(7)	1926(19)	6926(19)	0	370(20)

Table 3. Bond lengths [Å] and angles [°] for **16**.

Eu-I	3.2102(14)	Eu-O(2)#1	2.485(4)
Eu-O(1)	2.974(7)	Eu-O(2)#2	2.485(4)
Eu-O(2)	2.485(4)	Eu-O(2)#3	2.485(4)

Eu-Li	3.005(9)	C(1)-C(3)#5	1.563(16)
Eu-Li#1	3.005(9)	C(1)-C(3A)	1.67(2)
Eu-Li#2	3.005(9)	C(1)-C(3A)#5	1.67(2)
Eu-Li#3	3.005(9)	C(3)-C(3)#5	1.16(3)
Li-Li#1	2.673(13)	C(3)-C(3A)#5	1.53(2)
Li-Li#3	2.673(13)	C(3A)-C(3)#5	1.53(2)
O(1)-Li	1.995(10)	C(4)-C(5)	1.587(19)
O(1)-Li#1	1.995(10)	C(4)-C(4A)	1.75(3)
O(1)-Li#2	1.995(10)	C(4A)-C(4A)#4	1.59(4)
O(1)-Li#3	1.995(10)	C(4A)-C(5A)	1.70(3)
O(2)-Li	1.957(7)	C(5)-C(5)#4	1.12(2)
O(2)-Li#3	1.957(6)	C(5)-C(5A)	1.41(3)
Li-O(2)#1	1.957(6)	C(5A)-C(5)#4	1.41(3)
O(3)-Li	1.964(11)	C(5A)-C(4A)#4	1.70(3)
O(2)-C(1)	1.412(8)	C(6)-C(6)#6	1.00(5)
O(3)-C(4)	1.409(16)	C(6)-C(7)	1.58(3)
O(3)-C(4)#4	1.409(16)	C(6)-C(7)#7	1.58(3)
O(3)-C(4A)	1.52(2)	C(7)-C(6)#8	1.58(3)
O(3)-C(4A)#4	1.52(2)	C(7)-C(7)#8	1.78(6)
C(1)-C(2)	1.503(19)	C(7)-C(7)#7	1.78(6)
C(1)-C(3)	1.563(16)		

O(2)#1-Eu-O(2)#2	76.84(8)	O(2)#2-Eu-Li	91.14(16)
O(2)#1-Eu-O(2)	76.84(8)	O(2)-Eu-Li	40.38(9)
O(2)#2-Eu-O(2)	123.01(19)	O(2)#3-Eu-Li	91.14(16)
O(2)#1-Eu-O(2)#3	123.01(19)	O(1)-Eu-Li	38.97(18)
O(2)#2-Eu-O(2)#3	76.84(8)	Li#1-Eu-Li	52.8(2)
O(2)-Eu-O(2)#3	76.84(8)	O(2)#1-Eu-Li#2	91.14(16)
O(2)#1-Eu-O(1)	61.50(9)	O(2)#2-Eu-Li#2	40.38(9)
O(2)#2-Eu-O(1)	61.50(9)	O(2)-Eu-Li#2	91.14(16)
O(2)-Eu-O(1)	61.50(9)	O(2)#3-Eu-Li#2	40.38(9)
O(2)#3-Eu-O(1)	61.50(9)	O(1)-Eu-Li#2	38.97(18)
O(2)#1-Eu-Li#1	40.38(9)	Li#1-Eu-Li#2	52.8(2)
O(2)#2-Eu-Li#1	40.38(9)	Li-Eu-Li#2	77.9(4)
O(2)-Eu-Li#1	91.14(16)	O(2)#1-Eu-Li#3	91.14(16)
O(2)#3-Eu-Li#1	91.14(16)	O(2)#2-Eu-Li#3	91.14(16)
O(1)-Eu-Li#1	38.97(18)	O(2)-Eu-Li#3	40.38(9)
O(2)#1-Eu-Li	40.38(9)	O(2)#3-Eu-Li#3	40.38(9)

O(1)-Eu-Li#3	38.97(18)
Li#1-Eu-Li#3	77.9(4)
Li-Eu-Li#3	52.8(2)
Li#2-Eu-Li#3	52.8(2)
O(2)#1-Eu-I	118.50(9)
O(2)#2-Eu-I	118.50(9)
O(2)-Eu-I	118.50(9)
O(2)#3-Eu-I	118.50(9)
O(1)-Eu-I	180.0
Li#1-Eu-I	141.03(18)
Li-Eu-I	141.03(18)
Li#2-Eu-I	141.03(18)
Li#3-Eu-I	141.03(18)
Li#2-O(1)-Li#1	84.1(2)
Li#2-O(1)-Li	142.7(6)
Li#1-O(1)-Li	84.1(2)
Li#2-O(1)-Li#3	84.1(2)
Li#1-O(1)-Li#3	142.7(6)
Li-O(1)-Li#3	84.1(2)
Li#2-O(1)-Eu	71.4(3)
Li#1-O(1)-Eu	71.4(3)
Li-O(1)-Eu	71.4(3)
Li#3-O(1)-Eu	71.4(3)
C(1)-O(2)-Li	130.8(3)
C(1)-O(2)-Li#3	130.8(3)
Li-O(2)-Li#3	86.2(6)
C(1)-O(2)-Eu	124.5(4)
Li-O(2)-Eu	84.2(3)
Li#3-O(2)-Eu	84.2(3)
C(4)-O(3)-C(4)#4	95.3(13)
C(4)-O(3)-C(4A)	73.0(11)
C(4)#4-O(3)-C(4A)	118.8(11)
C(4)-O(3)-C(4A)#4	118.8(11)
C(4)#4-O(3)-C(4A)#4	73.0(11)
C(4A)-O(3)-C(4A)#4	63.1(17)
C(4)-O(3)-Li	115.1(7)
C(4)#4-O(3)-Li	115.1(7)
C(4A)-O(3)-Li	124.3(10)
C(4A)#4-O(3)-Li	124.3(10)
O(2)-Li-O(2)#1	104.3(5)
O(2)-Li-O(3)	123.1(3)
O(2)#1-Li-O(3)	123.1(3)
O(2)-Li-O(1)	91.2(4)
O(2)#1-Li-O(1)	91.2(4)
O(3)-Li-O(1)	115.2(5)
O(2)-Li-Li#1	115.7(3)
O(2)#1-Li-Li#1	46.9(3)
O(3)-Li-Li#1	119.36(19)
O(1)-Li-Li#1	47.93(10)
O(2)-Li-Li#3	46.9(3)
O(2)#1-Li-Li#3	115.7(3)
O(3)-Li-Li#3	119.36(19)
O(1)-Li-Li#3	47.93(10)
Li#1-Li-Li#3	90.000(1)
O(2)-Li-Eu	55.4(3)
O(2)#1-Li-Eu	55.4(3)
O(3)-Li-Eu	175.1(5)
O(1)-Li-Eu	69.7(3)
Li#1-Li-Eu	63.59(11)
Li#3-Li-Eu	63.59(11)
O(2)-C(1)-C(2)	108.3(9)
O(2)-C(1)-C(3)	114.0(8)
C(2)-C(1)-C(3)	131.7(10)
O(2)-C(1)-C(3)#5	114.0(8)
C(2)-C(1)-C(3)#5	131.7(10)
C(3)-C(1)-C(3)#5	43.5(10)
O(2)-C(1)-C(3A)	109.4(8)
C(2)-C(1)-C(3A)	88.5(8)
C(3)-C(1)-C(3A)	98.3(10)
C(3)#5-C(1)-C(3A)	56.5(9)
O(2)-C(1)-C(3A)#5	109.4(8)
C(2)-C(1)-C(3A)#5	88.5(8)
C(3)-C(1)-C(3A)#5	56.5(9)
C(3)#5-C(1)-C(3A)#5	98.3(10)
C(3A)-C(1)-C(3A)#5	140.0(17)
C(3)#5-C(3)-C(3A)#5	130.2(10)

C(3)#5-C(3)-C(1)	68.3(5)	C(5)#4-C(5A)-C(5)	46.8(13)
C(3A)#5-C(3)-C(1)	65.3(10)	C(5)#4-C(5A)-C(4A)#4	86.5(15)
C(3)#5-C(3A)-C(1)	58.2(10)	C(5)-C(5A)-C(4A)#4	108.1(19)
O(3)-C(4)-C(5)	100.6(11)	C(5)#4-C(5A)-C(4A)	108.1(19)
O(3)-C(4)-C(4A)	56.5(9)	C(5)-C(5A)-C(4A)	86.5(15)
C(5)-C(4)-C(4A)	79.8(12)	C(4A)#4-C(5A)-C(4A)	55.8(16)
O(3)-C(4A)-C(4A)#4	58.4(9)	C(6)#6-C(6)-C(7)	104.2(13)
O(3)-C(4A)-C(5A)	93.7(15)	C(6)#6-C(6)-C(7)#7	104.2(13)
C(4A)#4-C(4A)-C(5A)	62.1(8)	C(7)-C(6)-C(7)#7	68.3(17)
O(3)-C(4A)-C(4)	50.5(9)	C(6)-C(7)-C(6)#8	111(3)
C(4A)#4-C(4A)-C(4)	98.0(9)	C(6)-C(7)-C(7)#8	75.8(13)
C(5A)-C(4A)-C(4)	86.4(15)	C(6)#8-C(7)-C(7)#8	55.9(8)
C(5)#4-C(5)-C(5A)	66.6(7)	C(6)-C(7)-C(7)#7	55.9(8)
C(5)#4-C(5)-C(4)	107.6(8)	C(6)#8-C(7)-C(7)#7	75.8(13)
C(5A)-C(5)-C(4)	103.8(13)	C(7)#8-C(7)-C(7)#7	90.000(4)

Symmetry transformations used to generate equivalent atoms:

#1 -y+1/2,x,z #2 -x+1/2,-y+1/2,z #3 y,-x+1/2,z

#4 x,-y+1/2,z #5 -y+1/2,-x+1/2,z #6 -x+1/2,-y+3/2,z

#7 -y+1,x+1/2,-z #8 y-1/2,-x+1,-z

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for **16**.

The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Eu	62(1)	62(1)	45(1)	0	0	0
I	242(1)	242(1)	50(1)	0	0	0
O(1)	60(2)	60(2)	35(3)	0	0	0
O(2)	68(1)	68(1)	65(2)	-7(1)	7(1)	19(2)
O(3)	80(3)	94(3)	86(3)	0	-26(3)	0
Li	45(4)	84(6)	56(4)	0	-2(4)	0
C(1)	101(3)	101(3)	81(4)	-15(2)	15(2)	36(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **16**.

	x	y	z	U(eq)
H	2500	2500	4870(70)	3(13)

Crystal data and structure refinement for [CaLi$_6$(OPh)$_8$(thf)$_6$] 17

$C_{72}H_{88}O_{14}Li_6Ca$, M= 1259.14 gmol^{-1}, monoclinic, $P2_1/n$ (Nr. 14), a = 12.6187(9), b = 21.0709(10), c =13.3065(10) Å, β = 92.039(6)°, V = 3535.8(4) Å^3, Z = 2, $\rho_{calcd.}$= 1.183 Mgm^3, F(000) = 1340, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.149 mm^{-1}, 1.81° < θ < 27.20°, 28126 reflections of which 7438 unique and 4715 observed, 422 parameters refined, *GOOF* (on F^2) = 1.025, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.0719, *w*R2 = 0.1856 for I > 2σ(I) and R1 = 0.1119, wR2 = 0.2137 for all data.

The intensities from the single-crystals of **17** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms. CCDC-296413 (**17**) contains the supplementary crystallographic data for **17**. The cif file for the structure of **17** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **17**.

Identification code	[CaLi$_6$(OPh)$_8$(thf)$_6$]	
Empirical formula	C72 H88 Ca Li6 O14	
Formula weight	1259.14	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.6187(9) Å	α= 90°
	b = 21.0709(10) Å	β= 92.039(6)°
	c = 13.3065(10) Å	γ = 90°
Volume	3535.8(4) Å^3	
Z	2	

Density (calculated)	1.183 Mg/m^3
Absorption coefficient	0.149 mm^{-1}
F(000)	1340
Theta range for data collection	1.81 to 27.20°
Index ranges	-15<=h<=16, -24<=k<=25, -17<=l<=17
Reflections collected	28126
Independent reflections	7438 [R(int) = 0.0719]
Completeness to theta = 27.20°	94.5 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7438 / 0 / 422
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0719, wR2 = 0.1856
R indices (all data)	R1 = 0.1119, wR2 = 0.2137
Largest diff. peak and hole	0.407 and -0.347 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **17**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ca	0	5000	5000	42(1)
O(1)	610(1)	4679(1)	6645(1)	48(1)
O(2)	-700(1)	5765(1)	6091(1)	51(1)
O(3)	1477(1)	5670(1)	5363(1)	48(1)
O(4)	1173(1)	5917(1)	7485(1)	62(1)
O(5)	579(1)	7127(1)	5854(1)	79(1)
O(6)	-1023(1)	5347(1)	8471(1)	75(1)
O(7)	3280(1)	4932(1)	6962(1)	81(1)
Li(1)	637(1)	6256(1)	6215(1)	59(1)
Li(2)	-83(1)	5382(1)	7347(1)	56(1)
Li(3)	1843(1)	5265(1)	6677(1)	55(1)
C(1)	756(1)	4097(1)	7038(1)	46(1)
C(2)	206(1)	3894(1)	7868(1)	64(1)
C(3)	344(1)	3293(1)	8265(1)	82(1)
C(4)	1031(1)	2877(1)	7850(1)	78(1)
C(5)	1587(1)	3062(1)	7046(1)	76(1)
C(6)	1454(1)	3666(1)	6639(1)	63(1)

C(7)	-1651(1)	6037(1)	6207(1)	48(1)
C(8)	-2564(1)	5809(1)	5720(1)	57(1)
C(9)	-3538(1)	6089(1)	5852(1)	73(1)
C(10)	-3639(1)	6600(1)	6486(1)	77(1)
C(11)	-2747(1)	6831(1)	6975(1)	73(1)
C(12)	-1763(1)	6561(1)	6841(1)	64(1)
C(13)	2150(1)	6009(1)	4824(1)	47(1)
C(14)	2912(1)	6403(1)	5286(1)	65(1)
C(15)	3585(1)	6766(1)	4724(1)	80(1)
C(16)	3507(1)	6760(1)	3689(1)	84(1)
C(17)	2753(1)	6380(1)	3227(1)	83(1)
C(18)	2092(1)	6006(1)	3780(1)	63(1)
C(19)	1539(1)	6239(1)	8284(1)	59(1)
C(20)	1070(1)	6796(1)	8605(1)	80(1)
C(21)	1449(1)	7112(1)	9463(1)	97(1)
C(22)	2276(1)	6891(1)	10009(1)	108(1)
C(23)	2763(2)	6360(1)	9710(1)	141(1)
C(24)	2400(1)	6023(1)	8857(1)	107(1)
C(25)	1021(2)	7680(1)	6233(1)	155(1)
C(26)	1093(2)	8123(1)	5417(2)	225(1)
C(27)	674(2)	7820(1)	4524(1)	171(1)
C(28)	146(2)	7253(1)	4875(1)	138(1)
C(29)	-2105(1)	5132(1)	8408(1)	95(1)
C(30)	-2653(1)	5440(1)	9226(1)	119(1)
C(31)	-1782(1)	5648(1)	9942(1)	189(1)
C(32)	-883(1)	5688(1)	9398(1)	106(1)
C(33)	4218(1)	5137(1)	6515(1)	130(1)
C(34)	5088(1)	4831(1)	6990(2)	263(1)
C(35)	4653(2)	4437(1)	7768(2)	294(1)
C(36)	3607(1)	4454(1)	7664(1)	107(1)

Table 3. Bond lengths [Å] and angles [°] for **17**.

Ca-O(1)	2.3928(6)	Ca-O(3)#1	2.3738(6)
Ca-O(1)#1	2.3928(6)	Ca-Li(1)	3.1891(17)
Ca-O(2)	2.3608(6)	Ca-Li(1)#1	3.1891(17)
Ca-O(2)#1	2.3608(6)	Ca-Li(2)	3.2309(15)
Ca-O(3)	2.3738(6)	Ca-Li(2)#1	3.2309(15)

Ca-Li(3)	3.2139(15)	C(4)-C(5)	1.3581(17)
Ca-Li(3)#1	3.2139(15)	C(1)-C(6)	1.3836(13)
O(1)-Li(2)	1.9731(17)	C(5)-C(6)	1.3909(16)
O(1)-Li(3)	1.9851(17)	C(7)-C(8)	1.3871(12)
O(2)-Li(1)	1.9807(17)	C(8)-C(9)	1.3805(14)
O(2)-Li(2)	1.9898(16)	C(9)-C(10)	1.3760(17)
O(3)-Li(1)	2.0046(17)	C(10)-C(11)	1.3699(16)
O(3)-Li(3)	1.9853(16)	C(11)-C(12)	1.3839(15)
O(4)-Li(1)	1.9347(17)	C(7)-C(12)	1.3988(14)
O(4)-Li(2)	1.9484(17)	C(13)-C(14)	1.3971(13)
O(4)-Li(3)	1.9556(17)	C(14)-C(15)	1.3819(16)
O(5)-Li(1)	1.8968(19)	C(15)-C(16)	1.3770(17)
O(6)-Li(2)	1.9422(17)	C(16)-C(17)	1.3724(17)
O(7)-Li(3)	1.9678(16)	C(17)-C(18)	1.3794(16)
Li(1)-Li(2)	2.566(2)	C(13)-C(18)	1.3888(12)
Li(1)-Li(3)	2.644(2)	C(19)-C(20)	1.3883(16)
Li(2)-Li(3)	2.630(2)	C(20)-C(21)	1.3927(17)
Li(1)-C(13)	2.7557(18)	C(21)-C(22)	1.334(2)
O(1)-C(1)	1.3421(11)	C(22)-C(23)	1.344(2)
O(2)-C(7)	1.3449(10)	C(23)-C(24)	1.403(2)
O(3)-C(13)	1.3375(10)	C(19)-C(24)	1.3818(17)
O(4)-C(19)	1.3297(11)	C(25)-C(26)	1.437(3)
O(5)-C(25)	1.3805(19)	C(26)-C(27)	1.433(3)
O(5)-C(28)	1.419(2)	C(27)-C(28)	1.453(3)
O(6)-C(29)	1.4389(15)	C(29)-C(30)	1.462(2)
O(6)-C(32)	1.4334(15)	C(30)-C(31)	1.494(2)
O(7)-C(33)	1.4110(17)	C(31)-C(32)	1.369(2)
O(7)-C(36)	1.4251(17)	C(33)-C(34)	1.403(3)
C(1)-C(2)	1.3938(13)	C(34)-C(35)	1.450(3)
C(2)-C(3)	1.3802(16)	C(35)-C(36)	1.323(2)
C(3)-C(4)	1.3631(17)		

O(2)#1-Ca-O(2)	180.0	O(2)#1-Ca-O(1)#1	75.28(2)
O(2)#1-Ca-O(3)#1	77.12(2)	O(2)-Ca-O(1)#1	104.72(2)
O(2)-Ca-O(3)#1	102.88(2)	O(3)#1-Ca-O(1)#1	75.95(2)
O(2)#1-Ca-O(3)	102.88(2)	O(3)-Ca-O(1)#1	104.05(2)
O(2)-Ca-O(3)	77.12(2)	O(2)#1-Ca-O(1)	104.72(2)
O(3)#1-Ca-O(3)	180.00(3)	O(2)-Ca-O(1)	75.28(2)

O(3)#1-Ca-O(1)	104.05(2)	O(1)-Ca-Li(2)#1	142.53(3)
O(3)-Ca-O(1)	75.95(2)	Li(1)#1-Ca-Li(2)#1	47.11(4)
O(1)#1-Ca-O(1)	180.0	Li(1)-Ca-Li(2)#1	132.89(4)
O(2)#1-Ca-Li(1)#1	38.28(3)	Li(3)#1-Ca-Li(2)#1	48.18(4)
O(2)-Ca-Li(1)#1	141.72(3)	Li(3)-Ca-Li(2)#1	131.82(4)
O(3)#1-Ca-Li(1)#1	38.88(3)	O(2)#1-Ca-Li(2)	142.19(3)
O(3)-Ca-Li(1)#1	141.12(3)	O(2)-Ca-Li(2)	37.81(3)
O(1)#1-Ca-Li(1)#1	72.78(3)	O(3)#1-Ca-Li(2)	107.03(3)
O(1)-Ca-Li(1)#1	107.22(3)	O(3)-Ca-Li(2)	72.97(3)
O(2)#1-Ca-Li(1)	141.72(3)	O(1)#1-Ca-Li(2)	142.53(3)
O(2)-Ca-Li(1)	38.28(3)	O(1)-Ca-Li(2)	37.47(3)
O(3)#1-Ca-Li(1)	141.12(3)	Li(1)#1-Ca-Li(2)	132.89(4)
O(3)-Ca-Li(1)	38.88(3)	Li(1)-Ca-Li(2)	47.11(4)
O(1)#1-Ca-Li(1)	107.22(3)	Li(3)#1-Ca-Li(2)	131.82(4)
O(1)-Ca-Li(1)	72.78(3)	Li(3)-Ca-Li(2)	48.18(4)
Li(1)#1-Ca-Li(1)	180.00(3)	Li(2)#1-Ca-Li(2)	180.0
O(2)#1-Ca-Li(3)#1	74.46(3)	C(1)-O(1)-Li(2)	123.97(7)
O(2)-Ca-Li(3)#1	105.54(3)	C(1)-O(1)-Li(3)	117.60(7)
O(3)#1-Ca-Li(3)#1	38.01(3)	Li(2)-O(1)-Li(3)	83.29(7)
O(3)-Ca-Li(3)#1	141.99(3)	C(1)-O(1)-Ca	130.49(5)
O(1)#1-Ca-Li(3)#1	38.04(3)	Li(2)-O(1)-Ca	94.98(5)
O(1)-Ca-Li(3)#1	141.96(3)	Li(3)-O(1)-Ca	94.00(5)
Li(1)#1-Ca-Li(3)#1	48.79(4)	C(7)-O(2)-Li(1)	121.88(7)
Li(1)-Ca-Li(3)#1	131.21(4)	C(7)-O(2)-Li(2)	113.62(7)
O(2)#1-Ca-Li(3)	105.54(3)	Li(1)-O(2)-Li(2)	80.51(7)
O(2)-Ca-Li(3)	74.46(3)	C(7)-O(2)-Ca	135.81(5)
O(3)#1-Ca-Li(3)	141.99(3)	Li(1)-O(2)-Ca	94.14(5)
O(3)-Ca-Li(3)	38.01(3)	Li(2)-O(2)-Ca	95.53(5)
O(1)#1-Ca-Li(3)	141.96(3)	C(13)-O(3)-Li(3)	124.72(6)
O(1)-Ca-Li(3)	38.04(3)	C(13)-O(3)-Li(1)	109.46(7)
Li(1)#1-Ca-Li(3)	131.21(4)	Li(3)-O(3)-Li(1)	83.02(7)
Li(1)-Ca-Li(3)	48.79(4)	C(13)-O(3)-Ca	135.81(5)
Li(3)#1-Ca-Li(3)	180.0	Li(3)-O(3)-Ca	94.58(5)
O(2)#1-Ca-Li(2)#1	37.81(3)	Li(1)-O(3)-Ca	93.11(5)
O(2)-Ca-Li(2)#1	142.19(3)	C(19)-O(4)-Li(1)	127.65(8)
O(3)#1-Ca-Li(2)#1	72.97(3)	C(19)-O(4)-Li(2)	128.89(7)
O(3)-Ca-Li(2)#1	107.03(3)	Li(1)-O(4)-Li(2)	82.71(7)
O(1)#1-Ca-Li(2)#1	37.47(3)	C(19)-O(4)-Li(3)	130.82(7)

Li(1)-O(4)-Li(3)	85.65(7)
Li(2)-O(4)-Li(3)	84.72(7)
C(25)-O(5)-C(28)	108.31(12)
C(25)-O(5)-Li(1)	135.50(11)
C(28)-O(5)-Li(1)	115.08(10)
C(32)-O(6)-C(29)	107.18(9)
C(32)-O(6)-Li(2)	125.72(9)
C(29)-O(6)-Li(2)	124.87(8)
C(33)-O(7)-C(36)	105.33(10)
C(33)-O(7)-Li(3)	126.20(10)
C(36)-O(7)-Li(3)	128.46(9)
O(5)-Li(1)-O(4)	125.96(9)
O(5)-Li(1)-O(2)	117.37(9)
O(4)-Li(1)-O(2)	98.66(8)
O(5)-Li(1)-O(3)	117.95(9)
O(4)-Li(1)-O(3)	95.20(8)
O(2)-Li(1)-O(3)	95.55(7)
O(5)-Li(1)-Li(2)	146.27(9)
O(4)-Li(1)-Li(2)	48.87(5)
O(2)-Li(1)-Li(2)	49.90(5)
O(3)-Li(1)-Li(2)	95.47(8)
O(5)-Li(1)-Li(3)	147.05(9)
O(4)-Li(1)-Li(3)	47.51(5)
O(2)-Li(1)-Li(3)	95.04(7)
O(3)-Li(1)-Li(3)	48.17(5)
Li(2)-Li(1)-Li(3)	60.62(6)
O(5)-Li(1)-C(13)	91.93(7)
O(4)-Li(1)-C(13)	106.70(7)
O(2)-Li(1)-C(13)	116.96(7)
O(3)-Li(1)-C(13)	27.24(3)
Li(2)-Li(1)-C(13)	121.80(7)
Li(3)-Li(1)-C(13)	66.41(5)
O(5)-Li(1)-Ca	131.88(7)
O(4)-Li(1)-Ca	102.14(7)
O(2)-Li(1)-Ca	47.59(4)
O(3)-Li(1)-Ca	48.01(4)
Li(2)-Li(1)-Ca	67.30(5)
Li(3)-Li(1)-Ca	66.10(5)
C(13)-Li(1)-Ca	70.78(4)
O(6)-Li(2)-O(4)	117.82(8)
O(6)-Li(2)-O(1)	128.98(9)
O(4)-Li(2)-O(1)	96.08(7)
O(6)-Li(2)-O(2)	115.52(8)
O(4)-Li(2)-O(2)	97.89(7)
O(1)-Li(2)-O(2)	94.20(7)
O(6)-Li(2)-Li(1)	135.87(9)
O(4)-Li(2)-Li(1)	48.41(5)
O(1)-Li(2)-Li(1)	95.10(7)
O(2)-Li(2)-Li(1)	49.59(5)
O(6)-Li(2)-Li(3)	148.69(8)
O(4)-Li(2)-Li(3)	47.76(5)
O(1)-Li(2)-Li(3)	48.55(5)
O(2)-Li(2)-Li(3)	95.26(7)
Li(1)-Li(2)-Li(3)	61.17(6)
O(6)-Li(2)-Ca	140.92(7)
O(4)-Li(2)-Ca	100.41(6)
O(1)-Li(2)-Ca	47.54(4)
O(2)-Li(2)-Ca	46.66(4)
Li(1)-Li(2)-Ca	65.59(5)
Li(3)-Li(2)-Ca	65.58(5)
O(4)-Li(3)-O(7)	123.88(8)
O(4)-Li(3)-O(1)	95.46(7)
O(7)-Li(3)-O(1)	119.89(9)
O(4)-Li(3)-O(3)	95.16(7)
O(7)-Li(3)-O(3)	120.48(8)
O(1)-Li(3)-O(3)	95.24(7)
O(4)-Li(3)-Li(2)	47.53(5)
O(7)-Li(3)-Li(2)	145.49(8)
O(1)-Li(3)-Li(2)	48.16(5)
O(3)-Li(3)-Li(2)	93.96(7)
O(4)-Li(3)-Li(1)	46.84(5)
O(7)-Li(3)-Li(1)	147.67(9)
O(1)-Li(3)-Li(1)	92.42(7)
O(3)-Li(3)-Li(1)	48.80(5)
Li(2)-Li(3)-Li(1)	58.21(6)
O(4)-Li(3)-Ca	100.80(6)

O(7)-Li(3)-Ca	135.32(7)	C(14)-C(13)-Li(1)	94.29(7)
O(1)-Li(3)-Ca	47.96(3)	C(15)-C(14)-C(13)	121.23(9)
O(3)-Li(3)-Ca	47.41(3)	C(16)-C(15)-C(14)	120.78(10)
Li(2)-Li(3)-Ca	66.25(4)	C(17)-C(16)-C(15)	118.55(11)
Li(1)-Li(3)-Ca	65.12(5)	C(16)-C(17)-C(18)	121.13(10)
O(1)-C(1)-C(6)	122.00(8)	C(17)-C(18)-C(13)	121.32(9)
O(1)-C(1)-C(2)	121.58(8)	O(4)-C(19)-C(24)	121.10(10)
C(6)-C(1)-C(2)	116.41(9)	O(4)-C(19)-C(20)	122.49(9)
C(3)-C(2)-C(1)	121.65(10)	C(24)-C(19)-C(20)	116.39(10)
C(4)-C(3)-C(2)	120.62(11)	C(19)-C(20)-C(21)	121.27(11)
C(5)-C(4)-C(3)	119.17(11)	C(22)-C(21)-C(20)	121.25(13)
C(4)-C(5)-C(6)	120.78(11)	C(21)-C(22)-C(23)	119.11(14)
C(1)-C(6)-C(5)	121.35(9)	C(22)-C(23)-C(24)	121.47(16)
O(2)-C(7)-C(8)	121.85(8)	C(19)-C(24)-C(23)	120.48(14)
O(2)-C(7)-C(12)	121.00(8)	O(5)-C(25)-C(26)	107.94(16)
C(8)-C(7)-C(12)	117.14(8)	C(27)-C(26)-C(25)	107.78(18)
C(9)-C(8)-C(7)	121.34(9)	C(26)-C(27)-C(28)	105.04(17)
C(10)-C(9)-C(8)	120.98(10)	O(5)-C(28)-C(27)	106.45(15)
C(11)-C(10)-C(9)	118.53(10)	O(6)-C(29)-C(30)	106.82(11)
C(10)-C(11)-C(12)	121.20(11)	C(29)-C(30)-C(31)	104.37(12)
C(11)-C(12)-C(7)	120.81(9)	C(32)-C(31)-C(30)	106.61(14)
O(3)-C(13)-C(18)	121.50(8)	C(31)-C(32)-O(6)	110.17(13)
O(3)-C(13)-C(14)	121.47(8)	C(34)-C(33)-O(7)	108.97(16)
C(18)-C(13)-C(14)	116.96(8)	C(33)-C(34)-C(35)	105.91(16)
O(3)-C(13)-Li(1)	43.31(5)	C(36)-C(35)-C(34)	108.14(19)
C(18)-C(13)-Li(1)	131.30(7)	C(35)-C(36)-O(7)	110.61(16)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **17**.

The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ca	40(1)	44(1)	41(1)	-2(1)	2(1)	-4(1)
O(1)	51(1)	49(1)	46(1)	3(1)	2(1)	-2(1)
O(2)	43(1)	55(1)	56(1)	-9(1)	5(1)	3(1)

O(3)	48(1)	50(1)	47(1)	-1(1)	6(1)	-10(1)
O(4)	63(1)	72(1)	52(1)	-17(1)	-2(1)	-9(1)
O(5)	80(1)	58(1)	99(1)	-3(1)	-13(1)	-7(1)
O(6)	77(1)	89(1)	62(1)	-7(1)	24(1)	0(1)
O(7)	50(1)	110(1)	81(1)	27(1)	1(1)	1(1)
Li(1)	61(1)	55(1)	62(1)	-9(1)	6(1)	-8(1)
Li(2)	57(1)	60(1)	51(1)	-8(1)	11(1)	-4(1)
Li(3)	49(1)	64(1)	51(1)	0(1)	-1(1)	-1(1)
C(1)	46(1)	52(1)	41(1)	1(1)	-2(1)	-6(1)
C(2)	70(1)	69(1)	53(1)	9(1)	15(1)	6(1)
C(3)	90(1)	83(1)	72(1)	30(1)	17(1)	5(1)
C(4)	87(1)	65(1)	82(1)	24(1)	1(1)	7(1)
C(5)	83(1)	66(1)	79(1)	4(1)	5(1)	20(1)
C(6)	69(1)	65(1)	56(1)	6(1)	13(1)	11(1)
C(7)	45(1)	50(1)	50(1)	4(1)	8(1)	1(1)
C(8)	49(1)	64(1)	59(1)	1(1)	8(1)	-3(1)
C(9)	50(1)	86(1)	83(1)	13(1)	4(1)	1(1)
C(10)	60(1)	77(1)	95(1)	19(1)	22(1)	18(1)
C(11)	79(1)	58(1)	84(1)	-2(1)	23(1)	17(1)
C(12)	64(1)	56(1)	71(1)	-9(1)	5(1)	4(1)
C(13)	42(1)	50(1)	49(1)	1(1)	3(1)	-5(1)
C(14)	61(1)	77(1)	57(1)	2(1)	-4(1)	-22(1)
C(15)	63(1)	85(1)	92(1)	4(1)	-1(1)	-33(1)
C(16)	80(1)	86(1)	87(1)	16(1)	20(1)	-25(1)
C(17)	95(1)	98(1)	57(1)	13(1)	12(1)	-26(1)
C(18)	62(1)	76(1)	50(1)	1(1)	2(1)	-20(1)
C(19)	66(1)	64(1)	47(1)	-9(1)	5(1)	-21(1)
C(20)	83(1)	88(1)	71(1)	-29(1)	9(1)	-12(1)
C(21)	119(1)	99(1)	76(1)	-36(1)	35(1)	-37(1)
C(22)	146(1)	112(1)	67(1)	-26(1)	0(1)	-48(1)
C(23)	175(1)	135(1)	108(1)	-28(1)	-70(1)	-6(1)
C(24)	128(1)	98(1)	92(1)	-27(1)	-48(1)	5(1)
C(25)	258(2)	78(1)	127(1)	-13(1)	-23(1)	-60(1)
C(26)	383(3)	134(1)	156(2)	33(1)	-31(2)	-143(1)
C(27)	266(3)	141(2)	107(1)	24(1)	20(2)	-46(2)
C(28)	166(1)	97(1)	145(1)	4(1)	-60(1)	9(1)
C(29)	81(1)	119(1)	85(1)	-13(1)	29(1)	-28(1)
C(30)	76(1)	175(2)	110(1)	-40(1)	28(1)	0(1)

C(31)	89(1)	329(2)	151(1)	-137(1)	40(1)	-32(1)
C(32)	94(1)	162(1)	63(1)	-28(1)	22(1)	-14(1)
C(33)	63(1)	188(2)	139(1)	63(1)	11(1)	5(1)
C(34)	65(1)	324(2)	399(2)	270(1)	-2(1)	10(1)
C(35)	87(1)	399(2)	400(2)	312(1)	35(1)	52(1)
C(36)	83(1)	118(1)	120(1)	46(1)	-12(1)	6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **17**.

	x	y	z	U(eq)
H(2)	-272	4173	8166	76
H(3)	-39	3170	8825	98
H(4)	1120	2467	8119	94
H(5)	2066	2779	6760	91
H(6)	1847	3785	6082	76
H(8)	-2518	5456	5291	69
H(9)	-4141	5928	5504	87
H(10)	-4305	6786	6581	92
H(11)	-2804	7181	7409	88
H(12)	-1161	6731	7180	76
H(14)	2968	6423	5991	78
H(15)	4103	7020	5052	96
H(16)	3960	7010	3308	101
H(17)	2687	6374	2521	99
H(18)	1592	5743	3443	75
H(20)	484	6962	8236	96
H(21)	1116	7489	9661	117
H(22)	2515	7104	10595	130
H(23)	3360	6211	10081	169
H(24)	2744	5647	8673	129
H(25A)	1728	7595	6532	186
H(25B)	577	7855	6755	186
H(26A)	685	8507	5557	270
H(26B)	1834	8245	5331	270
H(27A)	1245	7708	4076	205
H(27B)	170	8099	4162	205

H(28A)	-620	7324	4898	165
H(28B)	274	6895	4426	165
H(29A)	-2135	4669	8480	113
H(29B)	-2438	5248	7757	113
H(30A)	-3129	5142	9550	143
H(30B)	-3066	5805	8977	143
H(31A)	-1949	6061	10234	227
H(31B)	-1684	5339	10488	227
H(32A)	-281	5511	9790	127
H(32B)	-728	6135	9257	127
H(33A)	4188	5034	5796	156
H(33B)	4292	5597	6587	156
H(34A)	5584	5144	7284	315
H(34B)	5464	4571	6507	315
H(35A)	4907	4000	7704	353
H(35B)	4879	4597	8433	353
H(36A)	3302	4541	8316	128
H(36B)	3345	4040	7429	128

Crystal data and structure refinement for [SrLi$_6$(OPh)$_8$(thf)$_6$] 18

$C_{72}H_{88}Li_6SrO_{14}$, M= 1306.68 gmol^{-1}, monoclinic, $P2_1/n$ (Nr. 14), a = 12.5866(6), b = 21.3721(12), c = 13.2208(6) Å, β = 92.415(4)°, V = 3553.3(3) Å^3, Z = 2, $\rho_{calcd.}$= 1.221 Mgm^3, $F(000)$ = 1376, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.819 mm^{-1}, 2.28° < θ < 27.12°, 27501 reflections of which 7217 unique and 6059 observed, 422 parameters refined, *GOOF* (on F^2) = 0.842, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.0518, wR2 = 0.1465 for I > 2σ(I) and R1 = 0.0627, wR2 = 0.1606 for all data.

The intensities from the single-crystals of **18** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms but disorder was observed on THF ligands. CCDC-616799 (**18**) contains the supplementary crystallographic data for **18**. The cif file for the structure of **18** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **18**.

Identification code	$[SrLi_6(OPh)_8(thf)_6]$	
Empirical formula	C72 H88 Li6 O14 Sr	
Formula weight	1306.68	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.5866(6) Å	α= 90°
	b = 21.3721(12) Å	β= 92.415(4)°
	c = 13.2208(6) Å	γ = 90°
Volume	3553.3(3) $Å^3$	
Z	2	
Density (calculated)	1.221 Mg/m^3	
Absorption coefficient	0.819 mm^{-1}	
F(000)	1376	
Theta range for data collection	2.28 to 27.12°	
Index ranges	-16<=h<=15, -27<=k<=27, -16<=l<=16	
Reflections collected	27501	
Independent reflections	7217 [R(int) = 0.0523]	
Completeness to theta = 27.12°	92.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7217 / 0 / 422	
Goodness-of-fit on F^2	0.842	
Final R indices [I>2sigma(I)]	R1 = 0.0518, wR2 = 0.1465	
R indices (all data)	R1 = 0.0627, wR2 = 0.1606	
Largest diff. peak and hole	0.590 and -0.422 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **18**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sr	10000	0	10000	37(1)
O(1)	11562(1)	693(1)	10454(1)	44(1)
O(2)	9342(1)	787(1)	11223(1)	45(1)

O(3)	10686(1)	-303(1)	11762(1)	45(1)
O(4)	11252(1)	917(1)	12591(1)	57(1)
O(5)	9049(1)	329(1)	13580(1)	68(1)
O(6)	10607(1)	2105(1)	10922(1)	62(1)
O(7)	13346(1)	-63(1)	12004(1)	70(1)
Li(1)	10700(1)	1250(1)	11334(1)	52(1)
Li(2)	11911(1)	278(1)	11766(1)	50(1)
Li(3)	9989(1)	385(1)	12458(1)	49(1)
C(1)	12216(1)	1033(1)	9902(1)	41(1)
C(2)	12987(1)	1422(1)	10355(1)	60(1)
C(3)	13637(1)	1787(1)	9777(1)	76(1)
C(4)	13534(1)	1777(1)	8744(1)	81(1)
C(5)	12767(1)	1401(1)	8288(1)	79(1)
C(6)	12124(1)	1028(1)	8851(1)	59(1)
C(7)	8389(1)	1057(1)	11328(1)	42(1)
C(8)	8269(1)	1575(1)	11951(1)	57(1)
C(9)	7281(1)	1845(1)	12071(1)	72(1)
C(10)	6397(1)	1617(1)	11553(1)	74(1)
C(11)	6500(1)	1108(1)	10922(1)	69(1)
C(12)	7480(1)	829(1)	10818(1)	54(1)
C(13)	10798(1)	-892(1)	12090(1)	42(1)
C(14)	10191(1)	-1132(1)	12853(1)	57(1)
C(15)	10298(1)	-1743(1)	13172(1)	77(1)
C(16)	11001(1)	-2139(1)	12746(1)	79(1)
C(17)	11609(1)	-1917(1)	12000(1)	73(1)
C(18)	11508(1)	-1305(1)	11661(1)	59(1)
C(19)	11624(1)	1232(1)	13387(1)	53(1)
C(20)	12503(1)	1029(1)	13958(1)	99(1)
C(21)	12870(1)	1356(1)	14825(1)	126(1)
C(22)	12372(1)	1889(1)	15117(1)	107(1)
C(23)	11540(1)	2098(1)	14567(1)	93(1)
C(24)	11164(1)	1784(1)	13718(1)	78(1)
C(25)	10147(1)	2208(1)	9943(1)	94(1)
C(26)	10695(1)	2762(1)	9562(1)	151(1)
C(27)	11117(1)	3080(1)	10461(1)	181(1)
C(28)	11042(1)	2664(1)	11279(1)	138(1)
C(29)	14248(1)	113(1)	11496(1)	119(1)
C(30)	15131(1)	-233(1)	11846(1)	178(1)

C(31)	14743(1)	-575(1)	12766(1)	226(1)
C(32)	13677(1)	-518(1)	12751(1)	104(1)
C(33)	7987(1)	102(1)	13499(1)	83(1)
C(34)	7378(1)	455(1)	14251(1)	102(1)
C(35)	8232(1)	643(1)	15021(1)	139(1)
C(36)	9159(1)	695(1)	14492(1)	90(1)

Table 3. Bond lengths [Å] and angles [°] for **18**.

Sr-O(1)	2.51435(19)	O(2)-C(7)	1.3440(3)
Sr-O(1)#1	2.5143(2)	O(3)-C(13)	1.3371(3)
Sr-O(2)	2.49863(19)	O(4)-C(19)	1.3180(3)
Sr-O(2)#1	2.49863(19)	O(5)-C(33)	1.4224(5)
Sr-O(3)	2.5346(2)	O(5)-C(36)	1.4393(5)
Sr-O(3)#1	2.5346(2)	O(6)-C(25)	1.4139(5)
Sr-Li(1)	3.3003(5)	O(6)-C(28)	1.3889(5)
Sr-Li(1)#1	3.3003(5)	O(7)-C(29)	1.3957(6)
Sr-Li(2)	3.3338(5)	O(7)-C(32)	1.4362(6)
Sr-Li(2)#1	3.3338(5)	C(1)-C(2)	1.3939(4)
Sr-Li(3)	3.3531(5)	C(2)-C(3)	1.3836(5)
Sr-Li(3)#1	3.3531(5)	C(3)-C(4)	1.3673(6)
O(1)-Li(2)	1.9810(5)	C(4)-C(5)	1.3747(5)
O(1)-Li(1)	2.0135(5)	C(5)-C(6)	1.3769(5)
O(2)-Li(1)	1.9751(5)	C(1)-C(6)	1.3898(4)
O(2)-Li(3)	1.9886(5)	C(7)-C(8)	1.3907(4)
O(3)-Li(2)	1.9802(5)	C(8)-C(9)	1.3860(5)
O(3)-Li(3)	1.9621(5)	C(9)-C(10)	1.3698(5)
O(4)-Li(1)	1.9126(5)	C(10)-C(11)	1.3804(5)
O(4)-Li(2)	1.9549(5)	C(11)-C(12)	1.3824(4)
O(4)-Li(3)	1.9560(5)	C(7)-C(12)	1.3911(4)
O(5)-Li(3)	1.9393(5)	C(13)-C(14)	1.3888(4)
O(6)-Li(1)	1.9082(5)	C(14)-C(15)	1.3763(5)
O(7)-Li(2)	1.9600(5)	C(15)-C(16)	1.3627(6)
Li(1)-Li(2)	2.6256(7)	C(16)-C(17)	1.3586(6)
Li(1)-Li(3)	2.5577(7)	C(17)-C(18)	1.3860(5)
Li(2)-Li(3)	2.6331(7)	C(13)-C(18)	1.3936(4)
Li(1)-C(1)	2.7827(6)	C(19)-C(20)	1.3819(6)
O(1)-C(1)	1.3370(3)	C(20)-C(21)	1.4043(7)

C(21)-C(22)	1.3627(8)
C(22)-C(23)	1.3261(7)
C(23)-C(24)	1.3756(5)
C(19)-C(24)	1.3932(5)
C(25)-C(26)	1.4687(8)
C(26)-C(27)	1.4490(9)
C(27)-C(28)	1.4056(8)
C(29)-C(30)	1.3980(8)
C(30)-C(31)	1.5167(11)
C(31)-C(32)	1.3465(8)
C(33)-C(34)	1.4847(7)
C(34)-C(35)	1.5039(7)
C(35)-C(36)	1.3898(7)

O(2)#1-Sr-O(2)	180.0
O(2)#1-Sr-O(1)	105.894(6)
O(2)-Sr-O(1)	74.106(6)
O(2)#1-Sr-O(1)#1	74.106(6)
O(2)-Sr-O(1)#1	105.894(7)
O(1)-Sr-O(1)#1	180.000(6)
O(2)#1-Sr-O(3)	108.260(6)
O(2)-Sr-O(3)	71.740(6)
O(1)-Sr-O(3)	72.470(6)
O(1)#1-Sr-O(3)	107.530(6)
O(2)#1-Sr-O(3)#1	71.740(6)
O(2)-Sr-O(3)#1	108.260(6)
O(1)-Sr-O(3)#1	107.530(6)
O(1)#1-Sr-O(3)#1	72.470(6)
O(3)-Sr-O(3)#1	180.0
O(2)#1-Sr-Li(1)	143.363(10)
O(2)-Sr-Li(1)	36.637(10)
O(1)-Sr-Li(1)	37.539(10)
O(1)#1-Sr-Li(1)	142.460(10)
O(3)-Sr-Li(1)	69.090(10)
O(3)#1-Sr-Li(1)	110.910(10)
O(2)#1-Sr-Li(1)#1	36.637(10)
O(2)-Sr-Li(1)#1	143.363(10)
O(1)-Sr-Li(1)#1	142.461(10)
O(1)#1-Sr-Li(1)#1	37.539(10)
O(3)-Sr-Li(1)#1	110.910(10)
O(3)#1-Sr-Li(1)#1	69.090(10)
Li(1)-Sr-Li(1)#1	180.000(9)
O(2)#1-Sr-Li(2)	108.905(9)
O(2)-Sr-Li(2)	71.095(10)
O(1)-Sr-Li(2)	36.296(9)
O(1)#1-Sr-Li(2)	143.704(9)
O(3)-Sr-Li(2)	36.316(9)
O(3)#1-Sr-Li(2)	143.684(9)
Li(1)-Sr-Li(2)	46.625(12)
Li(1)#1-Sr-Li(2)	133.375(12)
O(2)#1-Sr-Li(2)#1	71.095(9)
O(2)-Sr-Li(2)#1	108.905(9)
O(1)-Sr-Li(2)#1	143.704(9)
O(1)#1-Sr-Li(2)#1	36.296(9)
O(3)-Sr-Li(2)#1	143.684(9)
O(3)#1-Sr-Li(2)#1	36.316(9)
Li(1)-Sr-Li(2)#1	133.375(12)
Li(1)#1-Sr-Li(2)#1	46.625(12)
Li(2)-Sr-Li(2)#1	180.0
O(2)#1-Sr-Li(3)	143.859(9)
O(2)-Sr-Li(3)	36.141(9)
O(1)-Sr-Li(3)	70.086(9)
O(1)#1-Sr-Li(3)	109.914(9)
O(3)-Sr-Li(3)	35.617(9)
O(3)#1-Sr-Li(3)	144.383(9)
Li(1)-Sr-Li(3)	45.207(12)
Li(1)#1-Sr-Li(3)	134.793(12)
Li(2)-Sr-Li(3)	46.377(12)
Li(2)#1-Sr-Li(3)	133.623(11)
O(2)#1-Sr-Li(3)#1	36.141(9)
O(2)-Sr-Li(3)#1	143.859(9)
O(1)-Sr-Li(3)#1	109.914(9)
O(1)#1-Sr-Li(3)#1	70.086(9)
O(3)-Sr-Li(3)#1	144.383(9)

O(3)#1-Sr-Li(3)#1	35.617(9)
Li(1)-Sr-Li(3)#1	134.793(12)
Li(1)#1-Sr-Li(3)#1	45.207(12)
Li(2)-Sr-Li(3)#1	133.623(12)
Li(2)#1-Sr-Li(3)#1	46.377(11)
Li(3)-Sr-Li(3)#1	180.0
C(1)-O(1)-Li(2)	127.05(2)
C(1)-O(1)-Li(1)	110.68(2)
Li(2)-O(1)-Li(1)	82.18(2)
C(1)-O(1)-Sr	133.074(15)
Li(2)-O(1)-Sr	94.998(15)
Li(1)-O(1)-Sr	92.920(15)
C(7)-O(2)-Li(1)	123.43(2)
C(7)-O(2)-Li(3)	115.93(2)
Li(1)-O(2)-Li(3)	80.37(2)
C(7)-O(2)-Sr	132.642(15)
Li(1)-O(2)-Sr	94.345(16)
Li(3)-O(2)-Sr	96.040(15)
C(13)-O(3)-Li(3)	126.67(2)
C(13)-O(3)-Li(2)	121.23(2)
Li(3)-O(3)-Li(2)	83.81(2)
C(13)-O(3)-Sr	124.477(14)
Li(3)-O(3)-Sr	95.593(15)
Li(2)-O(3)-Sr	94.392(15)
C(19)-O(4)-Li(1)	127.41(2)
C(19)-O(4)-Li(3)	128.96(2)
Li(1)-O(4)-Li(3)	82.77(2)
C(19)-O(4)-Li(2)	131.09(2)
Li(1)-O(4)-Li(2)	85.51(2)
Li(3)-O(4)-Li(2)	84.64(2)
C(33)-O(5)-C(36)	107.78(3)
C(33)-O(5)-Li(3)	124.42(3)
C(36)-O(5)-Li(3)	124.55(3)
C(28)-O(6)-C(25)	108.46(3)
C(28)-O(6)-Li(1)	135.15(3)
C(25)-O(6)-Li(1)	115.37(3)
C(29)-O(7)-C(32)	107.18(3)
C(29)-O(7)-Li(2)	125.81(3)
C(32)-O(7)-Li(2)	126.96(3)
O(4)-Li(1)-O(6)	128.31(3)
O(4)-Li(1)-O(2)	99.15(2)
O(6)-Li(1)-O(2)	114.59(3)
O(4)-Li(1)-O(1)	95.59(2)
O(6)-Li(1)-O(1)	115.43(3)
O(2)-Li(1)-O(1)	98.45(2)
O(4)-Li(1)-Li(3)	49.345(16)
O(6)-Li(1)-Li(3)	147.01(3)
O(2)-Li(1)-Li(3)	50.045(16)
O(1)-Li(1)-Li(3)	96.84(2)
O(4)-Li(1)-Li(2)	47.925(16)
O(6)-Li(1)-Li(2)	147.96(3)
O(2)-Li(1)-Li(2)	96.45(2)
O(1)-Li(1)-Li(2)	48.374(15)
Li(3)-Li(1)-Li(2)	61.044(18)
O(4)-Li(1)-C(1)	107.17(2)
O(6)-Li(1)-C(1)	90.08(2)
O(2)-Li(1)-C(1)	118.83(2)
O(1)-Li(1)-C(1)	26.712(10)
Li(3)-Li(1)-C(1)	122.81(2)
Li(2)-Li(1)-C(1)	66.898(16)
O(4)-Li(1)-Sr	104.000(19)
O(6)-Li(1)-Sr	127.67(2)
O(2)-Li(1)-Sr	49.018(12)
O(1)-Li(1)-Sr	49.541(11)
Li(3)-Li(1)-Sr	68.489(15)
Li(2)-Li(1)-Sr	67.359(15)
C(1)-Li(1)-Sr	71.151(12)
O(4)-Li(2)-O(7)	125.41(3)
O(4)-Li(2)-O(3)	95.19(2)
O(7)-Li(2)-O(3)	118.66(3)
O(4)-Li(2)-O(1)	95.31(2)
O(7)-Li(2)-O(1)	118.42(3)
O(3)-Li(2)-O(1)	97.78(2)
O(4)-Li(2)-Li(1)	46.570(16)
O(7)-Li(2)-Li(1)	148.36(3)
O(3)-Li(2)-Li(1)	92.92(2)

O(1)-Li(2)-Li(1)	49.443(16)	C(2)-C(1)-Li(1)	95.33(2)
O(4)-Li(2)-Li(3)	47.697(15)	C(3)-C(2)-C(1)	121.09(3)
O(7)-Li(2)-Li(3)	146.13(3)	C(4)-C(3)-C(2)	120.61(3)
O(3)-Li(2)-Li(3)	47.801(15)	C(3)-C(4)-C(5)	118.86(4)
O(1)-Li(2)-Li(3)	95.31(2)	C(6)-C(5)-C(4)	121.30(3)
Li(1)-Li(2)-Li(3)	58.206(18)	C(5)-C(6)-C(1)	120.64(3)
O(4)-Li(2)-Sr	101.813(18)	O(2)-C(7)-C(12)	121.28(2)
O(7)-Li(2)-Sr	132.78(2)	O(2)-C(7)-C(8)	121.48(2)
O(3)-Li(2)-Sr	49.292(11)	C(12)-C(7)-C(8)	117.24(2)
O(1)-Li(2)-Sr	48.706(11)	C(9)-C(8)-C(7)	121.30(3)
Li(1)-Li(2)-Sr	66.016(14)	C(10)-C(9)-C(8)	120.52(3)
Li(3)-Li(2)-Sr	67.198(14)	C(9)-C(10)-C(11)	119.19(3)
O(5)-Li(3)-O(4)	119.11(2)	C(10)-C(11)-C(12)	120.40(3)
O(5)-Li(3)-O(3)	127.70(3)	C(7)-C(12)-C(11)	121.33(3)
O(4)-Li(3)-O(3)	95.74(2)	O(3)-C(13)-C(14)	121.96(2)
O(5)-Li(3)-O(2)	114.40(2)	O(3)-C(13)-C(18)	121.64(2)
O(4)-Li(3)-O(2)	97.24(2)	C(14)-C(13)-C(18)	116.37(3)
O(3)-Li(3)-O(2)	96.58(2)	C(15)-C(14)-C(13)	121.48(3)
O(5)-Li(3)-Li(1)	136.80(3)	C(16)-C(15)-C(14)	121.30(4)
O(4)-Li(3)-Li(1)	47.888(16)	C(17)-C(16)-C(15)	118.54(3)
O(3)-Li(3)-Li(1)	95.45(2)	C(16)-C(17)-C(18)	121.19(3)
O(2)-Li(3)-Li(1)	49.582(16)	C(17)-C(18)-C(13)	121.10(3)
O(5)-Li(3)-Li(2)	149.27(3)	O(4)-C(19)-C(20)	121.69(3)
O(4)-Li(3)-Li(2)	47.662(16)	O(4)-C(19)-C(24)	122.96(3)
O(3)-Li(3)-Li(2)	48.388(16)	C(20)-C(19)-C(24)	115.34(3)
O(2)-Li(3)-Li(2)	95.87(2)	C(21)-C(20)-C(19)	121.17(4)
Li(1)-Li(3)-Li(2)	60.750(19)	C(22)-C(21)-C(20)	120.54(5)
O(5)-Li(3)-Sr	138.92(2)	C(23)-C(22)-C(21)	119.17(4)
O(4)-Li(3)-Sr	101.142(18)	C(22)-C(23)-C(24)	121.35(4)
O(3)-Li(3)-Sr	48.790(11)	C(23)-C(24)-C(19)	122.39(4)
O(2)-Li(3)-Sr	47.819(11)	O(6)-C(25)-C(26)	105.03(4)
Li(1)-Li(3)-Sr	66.304(15)	C(27)-C(26)-C(25)	104.95(5)
Li(2)-Li(3)-Sr	66.425(14)	C(28)-C(27)-C(26)	107.51(5)
O(1)-C(1)-C(6)	120.96(2)	C(27)-C(28)-O(6)	108.69(5)
O(1)-C(1)-C(2)	121.51(2)	O(7)-C(29)-C(30)	110.46(5)
C(6)-C(1)-C(2)	117.49(3)	C(29)-C(30)-C(31)	104.01(5)
O(1)-C(1)-Li(1)	42.605(14)	C(32)-C(31)-C(30)	107.46(6)
C(6)-C(1)-Li(1)	130.61(2)	C(31)-C(32)-O(7)	109.31(5)

O(5)-C(33)-C(34)	106.65(3)	C(36)-C(35)-C(34)	105.80(4)
C(33)-C(34)-C(35)	102.41(4)	C(35)-C(36)-O(5)	108.93(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+2

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **18**.

The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sr	35(1)	39(1)	36(1)	-5(1)	1(1)	-4(1)
O(1)	40(1)	49(1)	42(1)	-1(1)	4(1)	-9(1)
O(2)	37(1)	50(1)	50(1)	-8(1)	5(1)	3(1)
O(3)	47(1)	44(1)	45(1)	4(1)	3(1)	0(1)
O(4)	55(1)	69(1)	46(1)	-15(1)	-2(1)	-10(1)
O(5)	64(1)	86(1)	56(1)	-7(1)	20(1)	-1(1)
O(6)	63(1)	45(1)	78(1)	-3(1)	-4(1)	-6(1)
O(7)	41(1)	96(1)	74(1)	22(1)	2(1)	5(1)
Li(1)	50(1)	52(1)	56(1)	-7(1)	2(1)	-5(1)
Li(2)	43(1)	61(1)	48(1)	2(1)	2(1)	-2(1)
Li(3)	46(1)	57(1)	45(1)	-8(1)	7(1)	-1(1)
C(1)	35(1)	43(1)	46(1)	2(1)	3(1)	-2(1)
C(2)	53(1)	66(1)	59(1)	1(1)	-5(1)	-20(1)
C(3)	60(1)	75(1)	92(1)	8(1)	-2(1)	-29(1)
C(4)	72(1)	77(1)	97(1)	24(1)	23(1)	-21(1)
C(5)	88(1)	95(1)	55(1)	18(1)	13(1)	-14(1)
C(6)	57(1)	73(1)	46(1)	4(1)	2(1)	-14(1)
C(7)	38(1)	45(1)	43(1)	3(1)	7(1)	3(1)
C(8)	57(1)	52(1)	64(1)	-9(1)	7(1)	6(1)
C(9)	77(1)	58(1)	82(1)	-2(1)	26(1)	21(1)
C(10)	52(1)	75(1)	97(1)	17(1)	18(1)	20(1)
C(11)	38(1)	82(1)	88(1)	12(1)	4(1)	1(1)
C(12)	40(1)	60(1)	61(1)	-1(1)	7(1)	-3(1)
C(13)	39(1)	48(1)	38(1)	1(1)	-3(1)	-1(1)
C(14)	62(1)	58(1)	51(1)	10(1)	11(1)	3(1)
C(15)	87(1)	69(1)	75(1)	27(1)	16(1)	1(1)
C(16)	89(1)	53(1)	93(1)	22(1)	-5(1)	4(1)

C(17)	79(1)	61(1)	78(1)	-3(1)	1(1)	22(1)
C(18)	60(1)	62(1)	55(1)	3(1)	11(1)	11(1)
C(19)	58(1)	63(1)	39(1)	-8(1)	3(1)	-26(1)
C(20)	114(1)	92(1)	86(1)	-14(1)	-40(1)	-5(1)
C(21)	148(1)	137(1)	88(1)	-11(1)	-58(1)	-17(1)
C(22)	149(1)	112(1)	60(1)	-22(1)	-1(1)	-62(1)
C(23)	112(1)	98(1)	72(1)	-37(1)	30(1)	-40(1)
C(24)	77(1)	90(1)	70(1)	-29(1)	13(1)	-15(1)
C(25)	109(1)	74(1)	98(1)	4(1)	-19(1)	11(1)
C(26)	219(1)	126(1)	110(1)	29(1)	36(1)	-23(1)
C(27)	275(1)	91(1)	174(1)	28(1)	-20(1)	-85(1)
C(28)	221(1)	68(1)	123(1)	-18(1)	-13(1)	-54(1)
C(29)	61(1)	147(1)	151(1)	56(1)	26(1)	14(1)
C(30)	81(1)	218(1)	238(1)	137(1)	39(1)	36(1)
C(31)	89(1)	292(1)	297(1)	198(1)	8(1)	38(1)
C(32)	71(1)	130(1)	110(1)	49(1)	-1(1)	17(1)
C(33)	75(1)	104(1)	71(1)	-8(1)	22(1)	-19(1)
C(34)	64(1)	140(1)	103(1)	-26(1)	20(1)	3(1)
C(35)	90(1)	223(1)	107(1)	-77(1)	24(1)	-1(1)
C(36)	83(1)	128(1)	60(1)	-24(1)	24(1)	-10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **18**.

	x	y	z	U(eq)
H(2)	13066	1437	11065	72
H(3)	14154	2045	10098	91
H(4)	13980	2022	8352	98
H(5)	12680	1400	7578	95
H(6)	11618	767	8520	70
H(8)	8869	1744	12297	69
H(9)	7216	2187	12511	86
H(10)	5730	1805	11627	89
H(11)	5899	950	10560	83
H(12)	7534	479	10394	64
H(14)	9695	-872	13158	68
H(15)	9879	-1890	13694	92

H(16)	11064	-2556	12964	95
H(17)	12106	-2183	11709	87
H(18)	11925	-1167	11132	70
H(20)	12861	665	13763	118
H(21)	13464	1207	15207	152
H(22)	12615	2105	15701	129
H(23)	11202	2468	14762	112
H(24)	10574	1948	13347	94
H(25A)	9382	2286	9974	113
H(25B)	10257	1846	9505	113
H(26A)	11269	2639	9126	181
H(26B)	10197	3032	9176	181
H(27A)	11860	3198	10376	217
H(27B)	10706	3460	10582	217
H(28A)	10590	2845	11790	165
H(28B)	11749	2589	11594	165
H(29A)	14385	560	11603	143
H(29B)	14126	43	10767	143
H(30A)	15730	43	12033	214
H(30B)	15354	-529	11330	214
H(31A)	14945	-1017	12741	271
H(31B)	15059	-391	13387	271
H(32A)	13451	-387	13419	124
H(32B)	13346	-923	12589	124
H(33A)	7969	-347	13645	100
H(33B)	7681	172	12814	100
H(34A)	6842	189	14553	122
H(34B)	7029	822	13942	122
H(35A)	8056	1043	15334	167
H(35B)	8314	325	15553	167
H(36A)	9766	544	14912	108
H(36B)	9287	1134	14323	108

Crystal data and structure refinement for $[BaLi_6(OPh)_8(thf)_6]$ 19

$C_{72}H_{88}Li_6BaO_{14}$, M= 1356.40 gmol^{-1}, triclinic, *P*-1 (Nr. 2), a = 12.644(3), b = 13.113(3), c = 13.418(3) Å, α = 62.51(3), β = 66.20(3), γ = 87.96(3)°, V = 1774.3(7) Å^3, Z = 1, ρ_{calcd}.= 1.269 Mgm^3, *F*(000) = 706, T = 203 K, λ

= 0.71073 Å, μ(Mo-K$_\alpha$)= 0.620 mm^{-1}, 1.79° < θ < 29.15°, 2615 reflections unique and observed, 421 parameters refined, *GOOF* (on F^2) = 1.202, R1= $\Sigma|F_o–F_c|/\Sigma F_o$ = 0.1083, *w*R2 = 0.2545 for I > 2σ(I) and R1 = 0.1083, wR2 = 0.2545 for all data.

The intensities from the single-crystals of **19** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The position of the hydrogen atoms could be calculated using riding model. CCDC-616800 (**19**) contains the supplementary crystallographic data for **19**. The cif file for the structure of **19** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **19**.

Identification code	[BaLi$_6$(OPh)$_8$(thf)$_6$]	
Empirical formula	C72 H88 Ba Li6 O14	
Formula weight	1356.40	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.644(3) Å	α= 62.51(3)°
	b = 13.113(3) Å	β= 66.20(3)°
	c = 13.418(3) Å	γ = 87.96(3)°
Volume	1774.3(7) Å^3	
Z	1	
Density (calculated)	1.269 Mg/m^3	
Absorption coefficient	0.620 mm^{-1}	
F(000)	706	
Theta range for data collection	1.79 to 29.15°	
Index ranges	0<=h<=17, -14<=k<=15, -16<=l<=18	
Reflections collected	2615	
Independent reflections	2615 [R(int) = 0.0000]	
Completeness to theta = 29.15°	27.3 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2615 / 0 / 421	
Goodness-of-fit on F^2	1.202	
Final R indices [I>2sigma(I)]	R1 = 0.1083, wR2 = 0.2545	
R indices (all data)	R1 = 0.1083, wR2 = 0.2545	

Largest diff. peak and hole 2.678 and -0.978 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **19**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ba	0	5000	5000	17(1)
O(1)	-545(17)	5690(20)	6730(20)	78(6)
O(2)	935(17)	7270(20)	4050(30)	80(7)
O(3)	1824(18)	5260(20)	5520(20)	90(8)
O(4)	1548(16)	7272(19)	5840(20)	85(7)
O(5)	-1050(20)	8260(20)	5940(30)	101(8)
O(6)	1280(20)	4750(30)	8250(30)	111(9)
O(7)	3726(19)	7890(30)	3050(30)	101(8)
C(1)	-1680(40)	5260(50)	7570(60)	113(17)
C(2)	-2570(30)	5390(30)	7250(40)	97(12)
C(3)	-3750(30)	4870(40)	8140(70)	129(18)
C(4)	-3950(40)	4250(50)	9290(60)	117(16)
C(5)	-3160(50)	4050(40)	9740(40)	113(15)
C(6)	-1910(30)	4600(40)	8810(60)	110(16)
C(7)	1180(30)	7970(40)	2840(60)	90(13)
C(8)	1700(30)	7690(40)	1930(50)	85(11)
C(9)	1800(30)	8500(50)	750(50)	103(14)
C(10)	1380(30)	9480(50)	380(50)	119(16)
C(11)	850(30)	9760(40)	1330(60)	118(16)
C(12)	690(30)	8990(50)	2590(50)	104(13)
C(13)	2360(40)	4370(40)	5660(40)	88(11)
C(14)	1720(30)	3220(40)	6480(30)	84(10)
C(15)	2280(40)	2290(40)	6570(40)	104(13)
C(16)	3430(50)	2420(40)	5960(50)	107(13)
C(17)	4130(30)	3470(50)	5180(40)	105(14)
C(18)	3540(40)	4420(30)	5090(30)	91(12)
C(19)	2050(30)	7830(30)	6150(30)	83(10)
C(20)	1430(30)	7980(40)	7180(40)	110(14)
C(21)	1880(30)	8480(40)	7650(40)	102(13)
C(22)	3050(40)	8790(40)	7170(40)	106(13)

C(23)	3780(30)	8590(40)	6240(40)	111(14)
C(24)	3280(30)	8120(40)	5720(40)	108(14)
C(25)	-1560(40)	8250(50)	7100(70)	170(30)
C(26)	-2790(50)	8090(50)	7550(60)	160(20)
C(27)	-2960(40)	8470(40)	6420(60)	140(20)
C(28)	-1730(50)	8810(60)	5350(60)	170(20)
C(29)	2360(50)	5050(50)	8160(60)	150(20)
C(30)	2790(30)	4100(50)	8710(60)	150(20)
C(31)	1900(50)	3120(50)	9370(50)	170(20)
C(32)	870(40)	3670(60)	9200(60)	150(20)
C(33)	3780(40)	9110(50)	2490(50)	129(16)
C(34)	4990(40)	9610(50)	1760(60)	150(20)
C(35)	5540(40)	8800(50)	1380(40)	142(19)
C(36)	4610(40)	7610(40)	2240(50)	131(16)
Li(1)	140(40)	7330(40)	5600(60)	87(19)
Li(2)	920(40)	5590(50)	6780(50)	78(17)
Li(3)	2280(50)	6940(50)	4510(60)	96(19)

Table 3. Bond lengths [Å] and angles [°] for **19**.

Ba-O(1)	2.704(19)	Ba-Li(2)	3.42(5)
Ba-O(1)#1	2.704(19)	Ba-Li(2)#1	3.42(5)
Ba-O(2)	2.72(2)	Ba-C(1)	3.41(6)
Ba-O(2)#1	2.72(2)	Ba-C(1)#1	3.41(6)
Ba-O(3)	2.73(2)	Ba-C(13)	3.41(4)
Ba-O(3)#1	2.73(2)	Ba-C(13)#1	3.41(4)
O(1)-Li(2)	1.88(5)	Li(1)-Li(2)	2.54(8)
O(1)-Li(1)	1.93(6)	Li(1)-Li(3)	2.67(8)
O(2)-Li(1)	1.95(7)	Li(2)-Li(3)	2.53(8)
O(2)-Li(3)	2.01(7)	O(1)-C(1)	1.35(5)
O(3)-Li(2)	1.86(5)	O(2)-C(7)	1.35(5)
O(3)-Li(3)	1.93(6)	O(3)-C(13)	1.31(4)
O(4)-Li(1)	1.92(4)	O(4)-C(19)	1.29(4)
O(4)-Li(2)	1.96(6)	O(5)-C(28)	1.36(6)
O(4)-Li(3)	1.89(7)	O(5)-C(25)	1.41(6)
O(5)-Li(1)	1.95(6)	O(6)-C(32)	1.32(6)
O(6)-Li(2)	2.00(7)	O(6)-C(29)	1.37(5)
O(7)-Li(3)	1.94(6)	O(7)-C(33)	1.41(5)

O(7)-C(36)	1.39(5)	C(17)-C(18)	1.41(5)
C(1)-C(2)	1.33(5)	C(13)-C(18)	1.36(5)
C(2)-C(3)	1.42(5)	C(19)-C(20)	1.39(5)
C(3)-C(4)	1.29(6)	C(20)-C(21)	1.36(5)
C(4)-C(5)	1.33(6)	C(21)-C(22)	1.35(5)
C(5)-C(6)	1.50(5)	C(22)-C(23)	1.35(5)
C(1)-C(6)	1.38(6)	C(23)-C(24)	1.44(5)
C(7)-C(8)	1.34(5)	C(19)-C(24)	1.42(5)
C(8)-C(9)	1.39(5)	C(25)-C(26)	1.41(6)
C(9)-C(10)	1.33(6)	C(26)-C(27)	1.46(7)
C(10)-C(11)	1.38(6)	C(27)-C(28)	1.53(6)
C(11)-C(12)	1.44(6)	C(29)-C(30)	1.36(6)
C(7)-C(12)	1.40(6)	C(30)-C(31)	1.40(7)
C(13)-C(14)	1.40(5)	C(31)-C(32)	1.52(7)
C(14)-C(15)	1.36(5)	C(33)-C(34)	1.41(6)
C(15)-C(16)	1.33(5)	C(34)-C(35)	1.42(6)
C(16)-C(17)	1.33(5)	C(35)-C(36)	1.59(7)

O(1)#1-Ba-O(1)	180.000(2)	O(3)#1-Ba-C(1)#1	84.8(8)
O(1)#1-Ba-O(2)#1	65.9(7)	O(1)#1-Ba-C(1)	158.2(7)
O(1)-Ba-O(2)#1	114.1(7)	O(1)-Ba-C(1)	21.8(7)
O(1)#1-Ba-O(2)	114.1(7)	O(2)#1-Ba-C(1)	97.0(10)
O(1)-Ba-O(2)	65.9(7)	O(2)-Ba-C(1)	83.0(10)
O(2)#1-Ba-O(2)	180.000(2)	O(3)-Ba-C(1)	84.8(8)
O(1)#1-Ba-O(3)	114.0(6)	O(3)#1-Ba-C(1)	95.2(8)
O(1)-Ba-O(3)	66.0(6)	C(1)#1-Ba-C(1)	180.000(3)
O(2)#1-Ba-O(3)	113.7(8)	O(1)#1-Ba-C(13)	98.6(8)
O(2)-Ba-O(3)	66.3(8)	O(1)-Ba-C(13)	81.4(8)
O(1)#1-Ba-O(3)#1	66.0(6)	O(2)#1-Ba-C(13)	94.9(8)
O(1)-Ba-O(3)#1	114.0(6)	O(2)-Ba-C(13)	85.1(8)
O(2)#1-Ba-O(3)#1	66.3(8)	O(3)-Ba-C(13)	21.0(6)
O(2)-Ba-O(3)#1	113.7(8)	O(3)#1-Ba-C(13)	159.0(6)
O(3)-Ba-O(3)#1	180.0(12)	C(1)#1-Ba-C(13)	83.6(9)
O(1)#1-Ba-C(1)#1	21.8(7)	C(1)-Ba-C(13)	96.4(9)
O(1)-Ba-C(1)#1	158.2(7)	O(1)#1-Ba-C(13)#1	81.4(8)
O(2)#1-Ba-C(1)#1	83.0(10)	O(1)-Ba-C(13)#1	98.6(8)
O(2)-Ba-C(1)#1	97.0(10)	O(2)#1-Ba-C(13)#1	85.1(8)
O(3)-Ba-C(1)#1	95.2(8)	O(2)-Ba-C(13)#1	94.9(8)

O(3)-Ba-C(13)#1	159.0(6)	C(13)-O(3)-Li(2)	125(3)
O(3)#1-Ba-C(13)#1	21.0(6)	C(13)-O(3)-Li(3)	136(3)
C(1)#1-Ba-C(13)#1	96.4(9)	Li(2)-O(3)-Li(3)	83(3)
C(1)-Ba-C(13)#1	83.6(9)	C(13)-O(3)-Ba	110.4(17)
C(13)-Ba-C(13)#1	180.000(2)	Li(2)-O(3)-Ba	94.3(16)
O(1)#1-Ba-Li(2)#1	33.2(8)	Li(3)-O(3)-Ba	98(2)
O(1)-Ba-Li(2)#1	146.8(8)	C(19)-O(4)-Li(3)	127(3)
O(2)#1-Ba-Li(2)#1	63.5(12)	C(19)-O(4)-Li(1)	135(3)
O(2)-Ba-Li(2)#1	116.5(12)	Li(3)-O(4)-Li(1)	89(3)
O(3)-Ba-Li(2)#1	147.1(9)	C(19)-O(4)-Li(2)	125(3)
O(3)#1-Ba-Li(2)#1	32.9(9)	Li(3)-O(4)-Li(2)	82(2)
C(1)#1-Ba-Li(2)#1	52.2(9)	Li(1)-O(4)-Li(2)	82(2)
C(1)-Ba-Li(2)#1	127.8(9)	C(28)-O(5)-C(25)	106(3)
C(13)-Ba-Li(2)#1	131.1(11)	C(28)-O(5)-Li(1)	132(4)
C(13)#1-Ba-Li(2)#1	48.9(11)	C(25)-O(5)-Li(1)	121(4)
O(1)#1-Ba-Li(2)	146.8(8)	C(32)-O(6)-C(29)	105(4)
O(1)-Ba-Li(2)	33.2(8)	C(32)-O(6)-Li(2)	130(3)
O(2)#1-Ba-Li(2)	116.5(12)	C(29)-O(6)-Li(2)	120(3)
O(2)-Ba-Li(2)	63.5(12)	C(36)-O(7)-C(33)	110(3)
O(3)-Ba-Li(2)	32.9(9)	C(36)-O(7)-Li(3)	131(3)
O(3)#1-Ba-Li(2)	147.1(9)	C(33)-O(7)-Li(3)	116(3)
C(1)#1-Ba-Li(2)	127.8(9)	C(2)-C(1)-O(1)	123(5)
C(1)-Ba-Li(2)	52.2(9)	C(2)-C(1)-C(6)	120(5)
C(13)-Ba-Li(2)	48.9(11)	O(1)-C(1)-C(6)	117(3)
C(13)#1-Ba-Li(2)	131.1(11)	C(2)-C(1)-Ba	89(3)
Li(2)#1-Ba-Li(2)	180.0(18)	O(1)-C(1)-Ba	48.2(18)
C(1)-O(1)-Li(2)	136(3)	C(6)-C(1)-Ba	132(3)
C(1)-O(1)-Li(1)	126(3)	C(1)-C(2)-C(3)	122(5)
Li(2)-O(1)-Li(1)	83(2)	C(4)-C(3)-C(2)	117(5)
C(1)-O(1)-Ba	110(2)	C(3)-C(4)-C(5)	127(5)
Li(2)-O(1)-Ba	94.8(15)	C(4)-C(5)-C(6)	116(4)
Li(1)-O(1)-Ba	98(2)	C(1)-C(6)-C(5)	117(5)
C(7)-O(2)-Li(1)	137(3)	C(8)-C(7)-O(2)	125(4)
C(7)-O(2)-Li(3)	118(3)	C(8)-C(7)-C(12)	119(5)
Li(1)-O(2)-Li(3)	85(2)	O(2)-C(7)-C(12)	115(5)
C(7)-O(2)-Ba	115(2)	C(7)-C(8)-C(9)	117(4)
Li(1)-O(2)-Ba	96.5(17)	C(10)-C(9)-C(8)	130(4)
Li(3)-O(2)-Ba	97(2)	C(9)-C(10)-C(11)	112(4)

C(10)-C(11)-C(12)	122(4)
C(7)-C(12)-C(11)	119(5)
O(3)-C(13)-C(18)	126(3)
O(3)-C(13)-C(14)	120(4)
C(18)-C(13)-C(14)	114(4)
O(3)-C(13)-Ba	48.6(15)
C(18)-C(13)-Ba	141(3)
C(14)-C(13)-Ba	86(2)
C(15)-C(14)-C(13)	120(4)
C(16)-C(15)-C(14)	122(3)
C(15)-C(16)-C(17)	122(4)
C(16)-C(17)-C(18)	115(4)
C(13)-C(18)-C(17)	127(3)
O(4)-C(19)-C(20)	122(3)
O(4)-C(19)-C(24)	126(3)
C(20)-C(19)-C(24)	111(3)
C(21)-C(20)-C(19)	127(3)
C(22)-C(21)-C(20)	119(4)
C(23)-C(22)-C(21)	121(4)
C(22)-C(23)-C(24)	119(3)
C(19)-C(24)-C(23)	123(3)
C(26)-C(25)-O(5)	109(4)
C(25)-C(26)-C(27)	103(5)
C(26)-C(27)-C(28)	106(4)
O(5)-C(28)-C(27)	103(5)
C(30)-C(29)-O(6)	112(4)
C(29)-C(30)-C(31)	107(5)
C(30)-C(31)-C(32)	103(5)
O(6)-C(32)-C(31)	108(5)
O(7)-C(33)-C(34)	106(4)
C(33)-C(34)-C(35)	106(4)
C(34)-C(35)-C(36)	106(4)
O(7)-C(36)-C(35)	101(4)
O(4)-Li(1)-O(1)	97(2)
O(4)-Li(1)-O(2)	93(2)
O(1)-Li(1)-O(2)	99(2)
O(4)-Li(1)-O(5)	127(3)
O(1)-Li(1)-O(5)	109(3)
O(2)-Li(1)-O(5)	126(3)
O(4)-Li(1)-Li(2)	49.7(16)
O(1)-Li(1)-Li(2)	47.5(15)
O(2)-Li(1)-Li(2)	93(2)
O(5)-Li(1)-Li(2)	139(4)
O(4)-Li(1)-Li(3)	45.1(19)
O(1)-Li(1)-Li(3)	95(2)
O(2)-Li(1)-Li(3)	48(2)
O(5)-Li(1)-Li(3)	156(3)
Li(2)-Li(1)-Li(3)	58(2)
O(4)-Li(1)-Ba	103.4(19)
O(1)-Li(1)-Ba	49.5(13)
O(2)-Li(1)-Ba	50.1(13)
O(5)-Li(1)-Ba	128.9(19)
Li(2)-Li(1)-Ba	66.4(14)
Li(3)-Li(1)-Ba	68.6(18)
O(3)-Li(2)-O(1)	105(2)
O(3)-Li(2)-O(4)	97(3)
O(1)-Li(2)-O(4)	97(3)
O(3)-Li(2)-O(6)	111(3)
O(1)-Li(2)-O(6)	129(3)
O(4)-Li(2)-O(6)	113(2)
O(3)-Li(2)-Li(3)	50(2)
O(1)-Li(2)-Li(3)	100(3)
O(4)-Li(2)-Li(3)	48(2)
O(6)-Li(2)-Li(3)	130(2)
O(3)-Li(2)-Li(1)	100(3)
O(1)-Li(2)-Li(1)	49.0(19)
O(4)-Li(2)-Li(1)	48.6(18)
O(6)-Li(2)-Li(1)	146(3)
Li(3)-Li(2)-Li(1)	64(2)
O(3)-Li(2)-Ba	52.8(13)
O(1)-Li(2)-Ba	52.0(13)
O(4)-Li(2)-Ba	106(2)
O(6)-Li(2)-Ba	140(2)
Li(3)-Li(2)-Ba	71.7(19)
Li(1)-Li(2)-Ba	70.8(18)
O(4)-Li(3)-O(3)	97(3)

O(4)-Li(3)-O(7)	123(3)	O(3)-Li(3)-Li(1)	94(2)
O(3)-Li(3)-O(7)	130(4)	O(7)-Li(3)-Li(1)	135(3)
O(4)-Li(3)-O(2)	92(3)	O(2)-Li(3)-Li(1)	46.8(19)
O(3)-Li(3)-O(2)	98(2)	Li(2)-Li(3)-Li(1)	58(2)
O(7)-Li(3)-O(2)	109(3)	O(4)-Li(3)-Ba	102.9(19)
O(4)-Li(3)-Li(2)	50.1(19)	O(3)-Li(3)-Ba	49.5(14)
O(3)-Li(3)-Li(2)	47.1(19)	O(7)-Li(3)-Ba	132(3)
O(7)-Li(3)-Li(2)	158(4)	O(2)-Li(3)-Ba	49.4(14)
O(2)-Li(3)-Li(2)	92(2)	Li(2)-Li(3)-Ba	65.9(15)
O(4)-Li(3)-Li(1)	46.1(18)	Li(1)-Li(3)-Ba	67.2(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **19**.

The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ba	12(1)	28(2)	14(1)	-13(1)	-6(1)	0(1)
O(1)	69(12)	64(19)	120(17)	-54(16)	-50(12)	28(11)
O(2)	84(14)	34(19)	120(20)	-41(17)	-40(13)	11(11)
O(3)	88(14)	30(20)	160(20)	-51(18)	-66(14)	14(12)
O(4)	87(13)	50(20)	138(19)	-59(17)	-55(13)	7(11)
O(5)	104(17)	50(20)	170(30)	-62(19)	-77(18)	33(13)
O(6)	120(20)	50(30)	170(30)	-50(20)	-90(20)	19(16)
O(7)	86(15)	60(20)	140(20)	-50(20)	-37(15)	9(13)
C(1)	130(40)	90(40)	210(50)	-110(40)	-120(40)	60(30)
C(2)	140(30)	50(30)	100(30)	-40(20)	-50(20)	-20(20)
C(3)	90(30)	60(40)	230(60)	-70(40)	-70(30)	-10(20)
C(4)	140(40)	60(40)	120(40)	-40(30)	-30(30)	0(30)
C(5)	200(50)	50(30)	80(30)	-10(20)	-80(30)	10(30)
C(6)	60(20)	90(40)	190(50)	-90(40)	-40(30)	10(20)
C(7)	70(20)	20(30)	170(50)	-20(30)	-60(30)	-4(19)
C(8)	70(20)	50(30)	140(40)	-50(30)	-60(20)	20(18)
C(9)	61(19)	110(40)	150(40)	-70(40)	-40(20)	10(20)
C(10)	52(19)	120(50)	140(40)	-30(40)	-50(20)	20(20)
C(11)	60(20)	40(30)	160(50)	-10(40)	-10(20)	-4(18)

C(12)	90(20)	60(40)	130(40)	-30(30)	-40(20)	-30(30)
C(13)	120(30)	30(30)	120(30)	-30(30)	-70(20)	-10(20)
C(14)	100(20)	50(30)	110(30)	-40(30)	-50(20)	10(20)
C(15)	120(30)	40(40)	110(30)	-10(30)	-40(30)	-40(20)
C(16)	160(40)	30(30)	150(40)	-40(30)	-100(30)	30(30)
C(17)	68(19)	70(40)	170(40)	-50(30)	-60(20)	30(20)
C(18)	140(30)	50(30)	80(20)	-20(20)	-70(20)	-20(20)
C(19)	120(30)	30(30)	90(20)	-20(20)	-50(20)	40(20)
C(20)	100(20)	80(40)	150(40)	-50(30)	-60(20)	-20(20)
C(21)	80(20)	100(40)	140(30)	-70(30)	-50(20)	40(20)
C(22)	140(30)	60(40)	140(40)	-60(30)	-70(30)	30(20)
C(23)	70(20)	90(40)	150(40)	-50(30)	-40(20)	-20(20)
C(24)	70(20)	90(40)	160(40)	-80(30)	-30(20)	2(19)
C(25)	130(40)	190(60)	340(80)	-210(70)	-150(50)	70(40)
C(26)	150(50)	130(60)	180(50)	-70(40)	-70(40)	80(40)
C(27)	150(40)	50(40)	270(70)	-80(40)	-140(50)	40(30)
C(28)	120(40)	160(60)	180(50)	-80(50)	-30(40)	40(40)
C(29)	200(50)	60(40)	240(60)	-60(40)	-160(50)	10(40)
C(30)	80(20)	70(50)	220(50)	-40(40)	-30(30)	0(20)
C(31)	220(60)	80(50)	170(50)	-20(40)	-110(50)	40(40)
C(32)	120(40)	150(70)	210(60)	-90(50)	-100(40)	50(40)
C(33)	120(30)	70(40)	190(50)	-50(30)	-80(30)	-10(20)
C(34)	140(40)	70(50)	210(60)	-10(40)	-100(40)	-30(30)
C(35)	150(40)	100(60)	100(30)	0(30)	-40(30)	30(40)
C(36)	130(30)	50(40)	170(40)	-30(30)	-50(30)	20(30)
Li(1)	90(30)	10(40)	190(60)	-30(40)	-100(40)	30(20)
Li(2)	60(20)	70(50)	110(40)	-70(40)	-10(20)	0(20)
Li(3)	80(30)	20(40)	120(50)	0(30)	-30(30)	-10(30)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **19**.

	x	y	z	U(eq)
H(2)	-2400	5850	6397	116
H(3)	-4368	4979	7894	155
H(4)	-4740	3900	9875	141
H(5)	-3368	3586	10602	135

H(6)	-1295	4496	9056	132
H(8)	1986	6991	2078	102
H(9)	2233	8317	117	123
H(10)	1447	9942	-429	143
H(11)	573	10468	1149	142
H(12)	268	9160	3230	124
H(14)	913	3088	6984	101
H(15)	1821	1529	7063	125
H(16)	3775	1750	6093	128
H(17)	4947	3570	4729	126
H(18)	4015	5173	4584	109
H(20)	610	7717	7589	132
H(21)	1375	8600	8314	123
H(22)	3367	9149	7476	127
H(23)	4600	8763	5941	133
H(24)	3787	7999	5063	129
H(25A)	-1340	7613	7703	203
H(25B)	-1257	8990	6994	203
H(26A)	-3121	8568	7947	189
H(26B)	-3155	7265	8159	189
H(27A)	-3360	9138	6275	171
H(27B)	-3424	7833	6504	171
H(28A)	-1708	8547	4777	201
H(28B)	-1457	9664	4890	201
H(29A)	2910	5509	7276	184
H(29B)	2285	5534	8551	184
H(30A)	3037	4172	9287	175
H(30B)	3478	4016	8083	175
H(31A)	1731	2684	10254	203
H(31B)	2104	2594	9013	203
H(32A)	440	3215	9014	175
H(32B)	320	3671	9959	175
H(33A)	3427	9348	3130	154
H(33B)	3363	9355	1965	154
H(34A)	5318	9730	2257	185
H(34B)	5107	10363	1033	185
H(35A)	6261	8685	1505	171
H(35B)	5750	9087	500	171

H(36A)	4335	7424	1747	157
H(36B)	4938	6960	2681	157

Crystal data and structure refinement for $[EuLi_6(OPh)_8(thf)_6]$ 20

$C_{72}H_{88}Li_6EuO_{14}$, M= 1371.02 gmol^{-1}, monoclinic, $P2_1/n$ (Nr. 14), a = 12.6257(13), b = 21.4887(18), c = 13.1836(13) Å, β = 92.611(8)°, V = 3572.9(6) Å^3, Z = 2, $\rho_{calcd.}$= 1.274 Mgm^3, $F(000)$ = 1426, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.938 mm^{-1}, 1.81° < θ < 26.97°, 19472 reflections of which 7372 unique and 3467 observed, 374 parameters refined, *GOOF* (on F^2) = 1.234, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.1634, *w*R2 = 0.2930 for I > 2σ(I) and R1 = 0.2939, wR2 = 0.3550 for all data.

The intensities from the single-crystals of **20** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The position of the hydrogen atoms could be calculated using riding model. CCDC-616802 (**20**) contains the supplementary crystallographic data for **20**. The cif file for the structure of **20** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **20**.

Identification code	$[EuLi_6(OPh)_8(thf)_6]$	
Empirical formula	C72 H88 Eu Li6 O14	
Formula weight	1371.02	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.6257(13) Å	α= 90°
	b = 21.4887(18) Å	β= 92.611(8)°
	c = 13.1826(13) Å	γ = 90°
Volume	3572.9(6) Å^3	
Z	2	
Density (calculated)	1.274 Mg/m^3	
Absorption coefficient	0.938 mm^{-1}	
F(000)	1426	
Theta range for data collection	1.81 to 26.97°	
Index ranges	-15<=h<=16, -27<=k<=24, -16<=l<=16	

Reflections collected	19472
Independent reflections	7372 [R(int) = 0.3215]
Completeness to theta = 26.97°	94.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7372 / 0 / 374
Goodness-of-fit on F^2	1.234
Final R indices [I>2sigma(I)]	R1 = 0.1634, wR2 = 0.2930
R indices (all data)	R1 = 0.2939, wR2 = 0.3550
Largest diff. peak and hole	1.010 and -1.747 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **20**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Eu(1)	0	5000	0	28(1)
O(1)	1564(8)	5692(5)	480(7)	45(3)
O(2)	-660(7)	5785(5)	1246(7)	43(3)
O(3)	694(8)	4686(4)	-8209(7)	42(3)
O(4)	1272(8)	5899(5)	-7358(7)	53(3)
O(5)	610(10)	7086(5)	957(9)	65(4)
O(6)	-905(9)	5310(5)	-6387(8)	62(3)
O(7)	3366(8)	4912(6)	-7992(7)	65(3)
Li(1)	640(20)	6237(11)	1398(18)	58(7)
Li(2)	30(20)	5364(12)	-7505(16)	46(6)
Li(3)	1900(20)	5296(12)	-8162(15)	49(7)
C(1)	2247(6)	6035(3)	-93(6)	45(4)
C(2)	2151(7)	6013(4)	-1147(6)	52(4)
C(3)	2791(9)	6388(5)	-1722(6)	64(5)
C(4)	3528(9)	6783(5)	-1243(8)	61(5)
C(5)	3624(8)	6805(5)	-189(8)	72(6)
C(6)	2983(7)	6430(4)	386(6)	53(4)
C(7)	-1631(5)	6050(3)	1345(5)	31(3)
C(8)	-2520(6)	5820(4)	810(6)	40(4)
C(9)	-3504(5)	6095(5)	922(8)	63(5)
C(10)	-3598(6)	6601(5)	1570(9)	61(5)
C(11)	-2708(8)	6830(4)	2105(8)	63(5)

C(12)	-1725(6)	6555(4)	1993(6)	50(4)
C(13)	808(7)	4082(3)	-7899(6)	41(4)
C(14)	180(7)	3850(4)	-7146(7)	55(4)
C(15)	279(10)	3233(5)	-6844(8)	83(7)
C(16)	1005(10)	2846(4)	-7294(9)	65(5)
C(17)	1633(9)	3078(4)	-8047(9)	76(6)
C(18)	1534(7)	3695(4)	-8349(7)	49(4)
C(19)	1683(8)	6223(4)	-6552(6)	47(4)
C(20)	1180(9)	6759(5)	-6233(8)	88(6)
C(21)	1583(13)	7081(5)	-5386(9)	87(6)
C(22)	2490(13)	6868(7)	-4859(8)	135(9)
C(23)	2994(11)	6332(8)	-5179(9)	136(11)
C(24)	2590(9)	6009(6)	-6025(8)	88(7)
C(25)	196(19)	7205(7)	-139(12)	73(7)
C(26)	810(20)	7744(10)	-370(20)	140(10)
C(27)	1220(30)	8052(15)	560(20)	151(13)
C(28)	1060(30)	7643(9)	1368(17)	118(11)
C(29)	-1993(13)	5120(4)	-6482(11)	52(4)
C(30)	-2637(14)	5444(10)	-5730(13)	73(6)
C(31)	-1780(19)	5625(15)	-4940(20)	132(11)
C(32)	-828(15)	5693(9)	-5493(12)	69(5)
C(33)	4243(14)	5150(6)	-8519(15)	68(6)
C(34)	5127(17)	4784(11)	-8070(20)	184(11)
C(35)	4740(20)	4386(13)	-7330(20)	229(10)
C(36)	3720(14)	4464(11)	-7278(16)	84(7)

Table 3. Bond lengths [Å] and angles [°] for **20**.

Eu(1)-O(1)	2.529(10)	Eu(1)-Li(2)#3	3.38(2)
Eu(1)-O(1)#1	2.529(10)	Li(2)-Eu(1)#4	3.38(2)
Eu(1)-O(2)	2.523(9)	Eu(1)-Li(3)#2	3.39(2)
Eu(1)-O(2)#1	2.523(9)	Eu(1)-Li(3)#3	3.39(2)
Eu(1)-O(3)#2	2.570(9)	Li(1)-Li(2)#2	2.51(4)
Eu(1)-O(3)#3	2.570(9)	Li(2)-Li(1)#4	2.51(4)
O(3)-Eu(1)#4	2.570(9)	Li(1)-Li(3)#2	2.62(4)
Eu(1)-Li(1)	3.31(2)	Li(2)-Li(3)	2.56(4)
Eu(1)-Li(1)#1	3.31(2)	Li(3)-Li(1)#4	2.62(4)
Eu(1)-Li(2)#2	3.38(2)	Li(3)-Eu(1)#4	3.39(2)

O(1)-Li(1)	2.08(2)	C(5)-C(6)	1.3900
O(1)-Li(3)#2	2.01(2)	C(1)-C(6)	1.3900
Li(3)-O(1)#4	2.01(2)	C(7)-C(8)	1.3900
O(2)-Li(1)	1.91(3)	C(8)-C(9)	1.3900
O(2)-Li(2)#2	2.04(3)	C(9)-C(10)	1.3900
Li(2)-O(2)#4	2.04(3)	C(10)-C(11)	1.3900
O(3)-Li(2)	1.94(3)	C(11)-C(12)	1.3900
O(3)-Li(3)	2.01(3)	C(7)-C(12)	1.3900
Li(1)-O(4)#2	1.93(3)	C(13)-C(14)	1.3900
O(4)-Li(2)	1.94(3)	C(14)-C(15)	1.3900
O(4)-Li(3)	1.87(3)	C(15)-C(16)	1.3900
O(4)-Li(1)#4	1.93(3)	C(16)-C(17)	1.3900
O(5)-Li(1)	1.91(3)	C(17)-C(18)	1.3900
O(6)-Li(2)	1.93(3)	C(13)-C(18)	1.3900
O(7)-Li(3)	2.03(3)	C(19)-C(20)	1.3900
O(1)-C(1)	1.384(12)	C(20)-C(21)	1.3900
O(2)-C(7)	1.362(11)	C(21)-C(22)	1.3900
O(3)-C(13)	1.368(11)	C(22)-C(23)	1.3900
O(4)-C(19)	1.354(12)	C(23)-C(24)	1.3900
O(5)-C(25)	1.54(2)	C(19)-C(24)	1.3900
O(5)-C(28)	1.42(2)	C(25)-C(26)	1.44(3)
O(6)-C(29)	1.434(19)	C(26)-C(27)	1.46(4)
O(6)-C(32)	1.436(19)	C(27)-C(28)	1.41(4)
O(7)-C(36)	1.40(2)	C(29)-C(30)	1.48(2)
O(7)-C(33)	1.429(19)	C(30)-C(31)	1.52(3)
C(1)-C(2)	1.3900	C(31)-C(32)	1.44(3)
C(2)-C(3)	1.3900	C(33)-C(34)	1.47(2)
C(3)-C(4)	1.3900	C(34)-C(35)	1.41(3)
C(4)-C(5)	1.3900	C(35)-C(36)	1.31(3)

O(2)-Eu(1)-O(2)#1	180.0(3)	O(1)#1-Eu(1)-O(3)#2	107.8(3)
O(2)-Eu(1)-O(1)#1	106.2(3)	O(1)-Eu(1)-O(3)#2	72.2(3)
O(2)#1-Eu(1)-O(1)#1	73.8(3)	O(2)-Eu(1)-O(3)#3	108.3(3)
O(2)-Eu(1)-O(1)	73.8(3)	O(2)#1-Eu(1)-O(3)#3	71.7(3)
O(2)#1-Eu(1)-O(1)	106.2(3)	O(1)#1-Eu(1)-O(3)#3	72.2(3)
O(1)#1-Eu(1)-O(1)	180.000(1)	O(1)-Eu(1)-O(3)#3	107.8(3)
O(2)-Eu(1)-O(3)#2	71.7(3)	O(3)#2-Eu(1)-O(3)#3	180.0(4)
O(2)#1-Eu(1)-O(3)#2	108.3(3)	O(2)-Eu(1)-Li(1)	35.1(5)

O(2)#1-Eu(1)-Li(1)	144.9(5)
O(1)#1-Eu(1)-Li(1)	141.2(5)
O(1)-Eu(1)-Li(1)	38.8(5)
O(3)#2-Eu(1)-Li(1)	68.6(5)
O(3)#3-Eu(1)-Li(1)	111.4(5)
O(2)-Eu(1)-Li(1)#1	144.9(5)
O(2)#1-Eu(1)-Li(1)#1	35.1(5)
O(1)#1-Eu(1)-Li(1)#1	38.8(5)
O(1)-Eu(1)-Li(1)#1	141.2(5)
O(3)#2-Eu(1)-Li(1)#1	111.4(5)
O(3)#3-Eu(1)-Li(1)#1	68.6(5)
Li(1)-Eu(1)-Li(1)#1	180.000(1)
O(2)-Eu(1)-Li(2)#2	37.0(5)
O(2)#1-Eu(1)-Li(2)#2	143.0(5)
O(1)#1-Eu(1)-Li(2)#2	110.7(5)
O(1)-Eu(1)-Li(2)#2	69.3(5)
O(3)#2-Eu(1)-Li(2)#2	34.8(5)
O(3)#3-Eu(1)-Li(2)#2	145.2(5)
Li(1)-Eu(1)-Li(2)#2	44.1(6)
Li(1)#1-Eu(1)-Li(2)#2	135.9(6)
O(2)-Eu(1)-Li(2)#3	143.0(5)
O(2)#1-Eu(1)-Li(2)#3	37.0(5)
O(1)#1-Eu(1)-Li(2)#3	69.3(5)
O(1)-Eu(1)-Li(2)#3	110.7(5)
O(3)#2-Eu(1)-Li(2)#3	145.2(5)
O(3)#3-Eu(1)-Li(2)#3	34.8(5)
Li(1)-Eu(1)-Li(2)#3	135.9(6)
Li(1)#1-Eu(1)-Li(2)#3	44.1(6)
Li(2)#2-Eu(1)-Li(2)#3	180.000(1)
O(2)-Eu(1)-Li(3)#2	69.7(5)
O(2)#1-Eu(1)-Li(3)#2	110.3(5)
O(1)#1-Eu(1)-Li(3)#2	143.9(5)
O(1)-Eu(1)-Li(3)#2	36.1(5)
O(3)#2-Eu(1)-Li(3)#2	36.2(5)
O(3)#3-Eu(1)-Li(3)#2	143.8(5)
Li(1)-Eu(1)-Li(3)#2	46.0(6)
Li(1)#1-Eu(1)-Li(3)#2	134.0(6)
Li(2)#2-Eu(1)-Li(3)#2	44.4(6)
Li(2)#3-Eu(1)-Li(3)#2	135.6(6)
O(2)-Eu(1)-Li(3)#3	110.3(5)
O(2)#1-Eu(1)-Li(3)#3	69.7(5)
O(1)#1-Eu(1)-Li(3)#3	36.1(5)
O(1)-Eu(1)-Li(3)#3	143.9(5)
O(3)#2-Eu(1)-Li(3)#3	143.8(5)
O(3)#3-Eu(1)-Li(3)#3	36.2(5)
Li(1)-Eu(1)-Li(3)#3	134.0(6)
Li(1)#1-Eu(1)-Li(3)#3	46.0(6)
Li(2)#2-Eu(1)-Li(3)#3	135.6(6)
Li(2)#3-Eu(1)-Li(3)#3	44.4(6)
Li(3)#2-Eu(1)-Li(3)#3	180.000(1)
C(1)-O(1)-Li(3)#2	126.7(10)
C(1)-O(1)-Li(1)	113.3(10)
Li(3)#2-O(1)-Li(1)	79.7(11)
C(1)-O(1)-Eu(1)	132.5(6)
Li(3)#2-O(1)-Eu(1)	96.1(8)
Li(1)-O(1)-Eu(1)	91.5(8)
C(7)-O(2)-Li(1)	123.5(10)
C(7)-O(2)-Li(2)#2	117.5(10)
Li(1)-O(2)-Li(2)#2	78.8(11)
C(7)-O(2)-Eu(1)	131.8(6)
Li(1)-O(2)-Eu(1)	95.7(7)
Li(2)#2-O(2)-Eu(1)	95.0(8)
C(13)-O(3)-Li(2)	127.8(10)
C(13)-O(3)-Li(3)	122.7(10)
Li(2)-O(3)-Li(3)	80.7(11)
C(13)-O(3)-Eu(1)#4	123.4(6)
Li(2)-O(3)-Eu(1)#4	96.1(8)
Li(3)-O(3)-Eu(1)#4	94.8(7)
C(19)-O(4)-Li(3)	130.0(11)
C(19)-O(4)-Li(1)#4	126.9(10)
Li(3)-O(4)-Li(1)#4	87.0(10)
C(19)-O(4)-Li(2)	131.3(10)
Li(3)-O(4)-Li(2)	84.1(12)
Li(1)#4-O(4)-Li(2)	80.8(11)
C(28)-O(5)-C(25)	109.2(13)
C(28)-O(5)-Li(1)	133.2(14)

C(25)-O(5)-Li(1)	116.6(11)
C(29)-O(6)-C(32)	105.3(11)
C(29)-O(6)-Li(2)	124.5(11)
C(32)-O(6)-Li(2)	124.8(12)
C(36)-O(7)-C(33)	109.9(12)
C(36)-O(7)-Li(3)	127.9(12)
C(33)-O(7)-Li(3)	121.6(12)
O(2)-Li(1)-O(5)	116.4(14)
O(2)-Li(1)-O(4)#2	102.5(14)
O(5)-Li(1)-O(4)#2	128.2(13)
O(2)-Li(1)-O(1)	98.9(10)
O(5)-Li(1)-O(1)	111.5(13)
O(4)#2-Li(1)-O(1)	93.6(11)
O(2)-Li(1)-Li(2)#2	52.8(9)
O(5)-Li(1)-Li(2)#2	152.0(14)
O(4)#2-Li(1)-Li(2)#2	49.8(9)
O(1)-Li(1)-Li(2)#2	96.3(11)
O(2)-Li(1)-Li(3)#2	98.2(12)
O(5)-Li(1)-Li(3)#2	143.8(15)
O(4)#2-Li(1)-Li(3)#2	45.5(7)
O(1)-Li(1)-Li(3)#2	49.0(7)
Li(2)#2-Li(1)-Li(3)#2	59.7(10)
O(2)-Li(1)-Eu(1)	49.3(6)
O(5)-Li(1)-Eu(1)	126.5(11)
O(4)#2-Li(1)-Eu(1)	104.5(10)
O(1)-Li(1)-Eu(1)	49.7(5)
Li(2)#2-Li(1)-Eu(1)	69.4(8)
Li(3)#2-Li(1)-Eu(1)	68.6(7)
O(6)-Li(2)-O(3)	127.7(14)
O(6)-Li(2)-O(4)	118.5(12)
O(3)-Li(2)-O(4)	97.4(13)
O(6)-Li(2)-O(2)#4	112.8(14)
O(3)-Li(2)-O(2)#4	97.2(10)
O(4)-Li(2)-O(2)#4	97.6(11)
O(6)-Li(2)-Li(1)#4	134.3(14)
O(3)-Li(2)-Li(1)#4	97.7(11)
O(4)-Li(2)-Li(1)#4	49.4(8)
O(2)#4-Li(2)-Li(1)#4	48.4(8)
O(6)-Li(2)-Li(3)	149.4(13)
O(3)-Li(2)-Li(3)	50.9(9)
O(4)-Li(2)-Li(3)	46.8(8)
O(2)#4-Li(2)-Li(3)	96.9(10)
Li(1)#4-Li(2)-Li(3)	62.2(10)
O(6)-Li(2)-Eu(1)#4	138.4(11)
O(3)-Li(2)-Eu(1)#4	49.1(6)
O(4)-Li(2)-Eu(1)#4	102.0(9)
O(2)#4-Li(2)-Eu(1)#4	48.1(5)
Li(1)#4-Li(2)-Eu(1)#4	66.6(7)
Li(3)-Li(2)-Eu(1)#4	68.1(7)
O(4)-Li(3)-O(1)#4	97.7(12)
O(4)-Li(3)-O(3)	97.3(12)
O(1)#4-Li(3)-O(3)	96.7(10)
O(4)-Li(3)-O(7)	128.9(12)
O(1)#4-Li(3)-O(7)	115.2(12)
O(3)-Li(3)-O(7)	115.2(13)
O(4)-Li(3)-Li(2)	49.2(9)
O(1)#4-Li(3)-Li(2)	96.6(11)
O(3)-Li(3)-Li(2)	48.4(8)
O(7)-Li(3)-Li(2)	146.9(13)
O(4)-Li(3)-Li(1)#4	47.4(8)
O(1)#4-Li(3)-Li(1)#4	51.3(8)
O(3)-Li(3)-Li(1)#4	92.5(11)
O(7)-Li(3)-Li(1)#4	151.6(14)
Li(2)-Li(3)-Li(1)#4	58.0(10)
O(4)-Li(3)-Eu(1)#4	103.2(10)
O(1)#4-Li(3)-Eu(1)#4	47.8(5)
O(3)-Li(3)-Eu(1)#4	49.0(5)
O(7)-Li(3)-Eu(1)#4	127.9(10)
Li(2)-Li(3)-Eu(1)#4	67.5(7)
Li(1)#4-Li(3)-Eu(1)#4	65.4(7)
O(1)-C(1)-C(2)	120.0(6)
O(1)-C(1)-C(6)	119.9(6)
C(2)-C(1)-C(6)	120.0
C(3)-C(2)-C(1)	120.0
C(4)-C(3)-C(2)	120.0
C(3)-C(4)-C(5)	120.0

C(4)-C(5)-C(6)	120.0	O(4)-C(19)-C(24)	120.0(8)
C(5)-C(6)-C(1)	120.0	C(20)-C(19)-C(24)	120.0
O(2)-C(7)-C(8)	120.9(6)	C(19)-C(20)-C(21)	120.0
O(2)-C(7)-C(12)	119.1(6)	C(22)-C(21)-C(20)	120.0
C(8)-C(7)-C(12)	120.0	C(23)-C(22)-C(21)	120.0
C(9)-C(8)-C(7)	120.0	C(22)-C(23)-C(24)	120.0
C(10)-C(9)-C(8)	120.0	C(23)-C(24)-C(19)	120.0
C(9)-C(10)-C(11)	120.0	C(26)-C(25)-O(5)	99.8(17)
C(10)-C(11)-C(12)	120.0	C(25)-C(26)-C(27)	111(2)
C(11)-C(12)-C(7)	120.0	C(28)-C(27)-C(26)	107(2)
O(3)-C(13)-C(14)	119.8(7)	C(27)-C(28)-O(5)	108(2)
O(3)-C(13)-C(18)	120.2(7)	O(6)-C(29)-C(30)	111.1(12)
C(14)-C(13)-C(18)	120.0	C(29)-C(30)-C(31)	100.7(15)
C(13)-C(14)-C(15)	120.0	C(32)-C(31)-C(30)	104.9(18)
C(16)-C(15)-C(14)	120.0	O(6)-C(32)-C(31)	109.5(17)
C(15)-C(16)-C(17)	120.0	O(7)-C(33)-C(34)	101.9(14)
C(18)-C(17)-C(16)	120.0	C(35)-C(34)-C(33)	109.0(19)
C(17)-C(18)-C(13)	120.0	C(36)-C(35)-C(34)	109(2)
O(4)-C(19)-C(20)	120.0(8)	C(35)-C(36)-O(7)	109.9(18)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z #2 x,y,z+1 #3 -x,-y+1,-z-1

#4 x,y,z-1

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **20**.

The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Eu(1)	25(1)	34(1)	23(1)	-16(1)	1(1)	-23(1)
O(1)	40(6)	67(6)	30(4)	2(4)	5(5)	-10(5)
O(2)	17(4)	63(6)	50(5)	-6(5)	10(4)	11(4)
O(3)	41(6)	45(5)	39(5)	-8(4)	-3(5)	-1(4)
O(4)	45(6)	64(6)	49(6)	-17(5)	8(5)	-6(5)
O(5)	67(8)	54(6)	74(7)	2(6)	-7(7)	-4(6)
O(6)	54(7)	84(7)	49(6)	-3(5)	27(6)	-15(6)
O(7)	51(6)	80(8)	61(5)	38(6)	-8(5)	-16(7)
Li(1)	47(14)	77(14)	51(12)	-57(10)	3(11)	27(12)

Li(2)	47(14)	69(14)	23(10)	8(10)	-5(11)	-26(12)
Li(3)	40(13)	88(16)	16(9)	-10(9)	-35(10)	6(11)
C(1)	53(9)	42(7)	40(7)	1(6)	3(7)	-1(7)
C(2)	22(7)	102(11)	31(7)	7(7)	-14(6)	-30(7)
C(3)	67(12)	76(11)	47(9)	8(8)	-14(9)	-3(9)
C(4)	81(11)	40(8)	65(9)	-2(7)	41(9)	-21(8)
C(5)	72(12)	72(11)	71(11)	0(9)	6(10)	-35(9)
C(6)	61(10)	53(8)	46(8)	8(7)	21(8)	-17(7)
C(7)	22(6)	38(6)	33(6)	12(5)	7(6)	-5(5)
C(8)	22(7)	67(9)	28(6)	3(6)	-20(6)	-9(6)
C(9)	28(8)	74(10)	91(12)	27(9)	21(8)	-4(7)
C(10)	33(8)	89(11)	65(9)	44(8)	27(8)	15(8)
C(11)	19(7)	88(12)	81(12)	-19(10)	-13(8)	2(8)
C(12)	39(8)	60(9)	52(8)	-5(7)	9(7)	-10(7)
C(13)	26(7)	59(8)	36(7)	-9(6)	-13(6)	-12(6)
C(14)	68(11)	56(9)	43(8)	-2(7)	13(8)	24(8)
C(15)	48(11)	137(19)	64(11)	3(12)	14(10)	15(12)
C(16)	80(13)	38(8)	78(11)	7(8)	17(11)	0(8)
C(17)	88(14)	61(10)	79(12)	-10(9)	8(12)	19(10)
C(18)	43(9)	73(10)	33(7)	6(7)	8(7)	8(8)
C(19)	55(9)	47(8)	41(7)	-12(6)	8(7)	-15(7)
C(20)	71(12)	119(15)	77(11)	-46(11)	41(10)	-33(11)
C(21)	112(14)	80(11)	73(10)	-34(9)	58(10)	-54(10)
C(22)	140(17)	250(20)	15(7)	-16(11)	2(10)	-131(17)
C(23)	200(30)	130(20)	71(14)	-15(13)	-56(17)	-61(19)
C(24)	64(11)	105(15)	88(12)	-20(11)	-66(10)	3(10)
C(25)	122(18)	56(8)	39(10)	-10(7)	-5(11)	26(11)
C(26)	170(20)	89(13)	170(20)	81(13)	91(18)	53(15)
C(27)	150(30)	140(20)	150(30)	-30(20)	-30(20)	-50(20)
C(28)	220(30)	45(10)	82(14)	-5(10)	-29(18)	-25(15)
C(29)	89(11)	0(7)	69(8)	-3(4)	27(8)	0(5)
C(30)	35(9)	122(15)	63(11)	8(11)	12(9)	9(10)
C(31)	84(17)	190(30)	121(19)	-48(19)	33(16)	31(18)
C(32)	63(11)	87(12)	59(9)	-34(9)	24(9)	-9(9)
C(33)	79(12)	22(9)	105(13)	16(7)	28(11)	8(6)
C(34)	53(12)	175(16)	330(30)	202(16)	17(15)	30(12)
C(35)	104(16)	270(20)	320(20)	262(16)	132(15)	97(16)
C(36)	36(10)	122(17)	94(14)	27(13)	15(10)	-6(11)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **20**.

	x	y	z	U(eq)
H(2)	1653	5746	-1470	62
H(3)	2727	6373	-2435	76
H(4)	3961	7036	-1632	73
H(5)	4122	7072	134	86
H(6)	3048	6445	1099	63
H(8)	-2457	5478	371	48
H(9)	-4106	5940	560	76
H(10)	-4264	6787	1646	74
H(11)	-2772	7172	2543	76
H(12)	-1123	6710	2355	60
H(14)	-311	4112	-6842	67
H(15)	-146	3076	-6334	99
H(16)	1072	2428	-7089	78
H(17)	2124	2816	-8351	91
H(18)	1959	3852	-8858	59
H(20)	566	6903	-6589	106
H(21)	1242	7443	-5170	104
H(22)	2763	7086	-4287	162
H(23)	3607	6187	-4822	163
H(24)	2931	5647	-6241	105
H(25A)	344	6855	-587	87
H(25B)	-566	7295	-177	87
H(26A)	373	8037	-772	168
H(26B)	1408	7619	-778	168
H(27A)	1980	8141	513	182
H(27B)	847	8445	657	182
H(28A)	576	7832	1842	141
H(28B)	1732	7554	1736	141
H(29A)	-2039	4669	-6378	62
H(29B)	-2278	5213	-7169	62
H(30A)	-3163	5166	-5448	87
H(30B)	-2995	5811	-6025	87
H(31A)	-1959	6018	-4605	158

H(31B)	-1690	5301	-4416	158
H(32A)	-738	6129	-5687	83
H(32B)	-210	5568	-5065	83
H(33A)	4345	5596	-8392	82
H(33B)	4152	5079	-9252	82
H(34A)	5452	4538	-8603	221
H(34B)	5668	5062	-7769	221
H(35A)	4894	3952	-7497	275
H(35B)	5093	4480	-6666	275
H(36A)	3553	4600	-6594	101
H(36B)	3354	4069	-7417	101

Crystal data and structure refinement for [SmLi$_6$(OPh)$_8$(thf)$_6$] 21

$C_{72}H_{88}Li_6SmO_{14}$, M= 1369.41 gmol^{-1}, monoclinic, $P2_1/n$ (Nr. 14), a = 12.5617(11), b = 21.439(2), c =13.1273(13) Å, β = 92.769(7)°, V =3531.2(6) Å^3, Z = 2, $\rho_{calcd.}$= 1.288 Mgm^3, F(000) = 1424, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.892 mm^{-1}, 2.45° < θ < 27.16°, 5946 reflections of which 5072 unique and 3959 observed, 422 parameters refined, *GOOF* (on F^2) = 1.047, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.0523, *w*R2 = 0.1333 for I > 2σ(I) and R1 = 0.0668, wR2 =0.1460 for all data.

The intensities from the single-crystals of **21** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms but disorder was observed on THF ligands. CCDC-616801 (**21**) contains the supplementary crystallographic data for **21**. The cif file for the structure of **21** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **21**.

Identification code	[SmLi$_6$(OPh)$_8$(thf)$_6$]
Empirical formula	C72 H88 Li6 O14 Sm
Formula weight	1369.41
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n

Unit cell dimensions	a = 12.5617(11) Å	α= 90°
	b = 21.439(2) Å	β= 92.769(7)°
	c = 13.1273(13) Å	γ = 90°
Volume	3531.2(6) $Å^3$	
Z	2	
Density (calculated)	1.288 Mg/m^3	
Absorption coefficient	0.892 mm^{-1}	
F(000)	1424	
Theta range for data collection	2.45 to 27.16°	
Index ranges	-16<=h<=12, -20<=k<=27, -16<=l<=7	
Reflections collected	5946	
Independent reflections	5072 [R(int) = 0.0623]	
Completeness to theta = 27.16°	64.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5072 / 0 / 422	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0523, wR2 = 0.1333	
R indices (all data)	R1 = 0.0668, wR2 = 0.1460	
Largest diff. peak and hole	0.766 and -1.320 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **21**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sm	10000	0	10000	37(1)
O(1)	9356(2)	780(1)	11268(2)	44(1)
O(3)	11570(2)	693(1)	10487(2)	44(1)
O(4)	11282(2)	901(1)	12646(2)	54(1)
Li(1)	10017(4)	371(2)	12513(5)	46(1)
Li(2)	11923(4)	269(3)	11785(5)	45(1)
Li(3)	10721(5)	1244(2)	11370(5)	48(2)
O(2)	10705(2)	-311(1)	11775(2)	46(1)
O(5)	9067(2)	306(1)	13627(2)	61(1)
O(6)	13361(3)	-68(1)	12020(3)	71(1)
O(7)	10619(2)	2090(1)	10975(3)	62(1)
C(1)	8408(3)	1050(1)	11363(3)	40(1)

C(2)	8276(3)	1566(2)	11991(4)	53(1)
C(3)	7275(4)	1836(2)	12094(4)	65(1)
C(4)	6409(3)	1610(2)	11586(5)	71(1)
C(5)	6511(3)	1097(2)	10931(4)	65(1)
C(6)	7495(3)	823(2)	10843(3)	52(1)
C(7)	10813(3)	-901(1)	12090(3)	42(1)
C(8)	11526(3)	-1307(2)	11636(3)	55(1)
C(9)	11610(4)	-1928(2)	11955(4)	69(1)
C(10)	11008(4)	-2161(2)	12678(5)	72(1)
C(11)	10291(4)	-1769(2)	13124(4)	71(1)
C(12)	10182(3)	-1160(2)	12835(3)	53(1)
C(13)	12225(2)	1036(1)	9927(3)	41(1)
C(14)	12999(3)	1427(2)	10394(4)	56(1)
C(15)	13649(4)	1792(2)	9803(5)	71(1)
C(16)	13536(4)	1790(2)	8759(5)	74(1)
C(17)	12777(4)	1405(2)	8300(4)	74(1)
C(18)	12129(3)	1031(2)	8863(3)	54(1)
C(19)	11678(3)	1219(2)	13443(3)	53(1)
C(20)	12589(5)	1028(2)	13972(5)	88(2)
C(21)	12970(6)	1365(3)	14851(6)	121(2)
C(22)	12475(6)	1878(3)	15169(4)	105(2)
C(23)	11600(5)	2080(2)	14636(4)	93(2)
C(24)	11188(4)	1752(2)	13790(4)	75(1)
C(25)	9179(4)	690(2)	14531(4)	77(1)
C(26)	8242(5)	589(3)	15099(5)	103(2)
C(27)	7380(4)	432(3)	14263(5)	89(2)
C(28)	8003(4)	74(2)	13527(5)	70(1)
C(29)	13707(4)	-537(3)	12742(6)	95(2)
C(30)	14733(6)	-645(5)	12637(10)	266(4)
C(31)	15152(5)	-242(4)	11848(8)	172(3)
C(32)	14270(5)	109(3)	11497(7)	104(2)
C(33)	10165(4)	2200(3)	9982(4)	80(2)
C(34)	10757(8)	2734(3)	9601(7)	125(3)
C(35)	11211(8)	3051(3)	10464(8)	154(4)
C(36)	11042(7)	2655(2)	11349(6)	125(3)

Table 3. Bond lengths [Å] and angles [°] for **21**.

Sm-O(1)	2.520(2)
Sm-O(1)#1	2.520(2)
Sm-O(2)	2.542(3)
Sm-O(2)#1	2.542(3)
Sm-O(3)	2.528(2)
Sm-O(3)#1	2.528(2)
Sm-Li(1)	3.393(6)
Sm-Li(1)#1	3.393(6)
Sm-Li(2)	3.333(6)
Sm-Li(2)#1	3.333(6)
Sm-Li(3)	3.319(5)
Sm-Li(3)#1	3.319(5)
O(1)-Li(1)	1.999(7)
O(1)-Li(3)	1.982(6)
Li(1)-O(2)	1.976(6)
Li(2)-O(2)	1.971(6)
O(3)-Li(2)	1.962(7)
O(3)-Li(3)	1.999(7)
O(4)-Li(1)	1.954(6)
O(4)-Li(2)	1.962(7)
O(4)-Li(3)	1.931(7)
Li(1)-O(5)	1.936(7)
Li(2)-O(6)	1.956(6)
Li(3)-O(7)	1.889(6)
Li(1)-Li(2)	2.631(8)
Li(2)-Li(3)	2.620(8)
Li(1)-Li(3)	2.582(8)
Li(3)-C(13)	2.775(8)
O(1)-C(1)	1.336(4)
O(2)-C(7)	1.336(4)
O(3)-C(13)	1.347(4)
O(4)-C(19)	1.326(4)
O(5)-C(25)	1.445(6)
O(5)-C(28)	1.427(6)
O(6)-C(29)	1.434(6)
O(6)-C(32)	1.412(7)
O(7)-C(33)	1.417(6)
O(7)-C(36)	1.401(6)
C(1)-C(2)	1.394(5)
C(2)-C(3)	1.397(6)
C(3)-C(4)	1.339(7)
C(4)-C(5)	1.405(7)
C(5)-C(6)	1.379(5)
C(1)-C(6)	1.393(5)
C(7)-C(8)	1.402(5)
C(8)-C(9)	1.397(6)
C(9)-C(10)	1.339(8)
C(10)-C(11)	1.382(7)
C(11)-C(12)	1.366(5)
C(7)-C(12)	1.403(5)
C(13)-C(14)	1.403(5)
C(14)-C(15)	1.394(6)
C(15)-C(16)	1.371(8)
C(16)-C(17)	1.378(7)
C(17)-C(18)	1.382(6)
C(13)-C(18)	1.396(6)
C(19)-C(20)	1.372(7)
C(20)-C(21)	1.424(8)
C(21)-C(22)	1.341(9)
C(22)-C(23)	1.345(9)
C(23)-C(24)	1.392(7)
C(19)-C(24)	1.386(6)
C(25)-C(26)	1.440(8)
C(26)-C(27)	1.542(9)
C(27)-C(28)	1.485(8)
C(29)-C(30)	1.323(9)
C(30)-C(31)	1.466(12)
C(31)-C(32)	1.399(9)
C(33)-C(34)	1.466(9)
C(34)-C(35)	1.417(13)
C(35)-C(36)	1.463(12)

O(1)-Sm-O(1)#1	180.0
O(1)-Sm-O(3)	73.39(7)
O(1)#1-Sm-O(3)	106.61(7)
O(1)-Sm-O(3)#1	106.61(7)
O(1)#1-Sm-O(3)#1	73.39(7)
O(3)-Sm-O(3)#1	180.00(10)
O(1)-Sm-O(2)#1	108.84(8)
O(1)#1-Sm-O(2)#1	71.16(8)
O(3)-Sm-O(2)#1	108.12(8)
O(3)#1-Sm-O(2)#1	71.88(8)
O(1)-Sm-O(2)	71.16(8)
O(1)#1-Sm-O(2)	108.84(8)
O(3)-Sm-O(2)	71.88(8)
O(3)#1-Sm-O(2)	108.12(8)
O(2)#1-Sm-O(2)	180.0
O(1)-Sm-Li(3)	36.56(12)
O(1)#1-Sm-Li(3)	143.44(12)
O(3)-Sm-Li(3)	36.94(12)
O(3)#1-Sm-Li(3)	143.06(12)
O(2)#1-Sm-Li(3)	111.11(12)
O(2)-Sm-Li(3)	68.89(12)
O(1)-Sm-Li(3)#1	143.44(12)
O(1)#1-Sm-Li(3)#1	36.56(12)
O(3)-Sm-Li(3)#1	143.06(12)
O(3)#1-Sm-Li(3)#1	36.94(12)
O(2)#1-Sm-Li(3)#1	68.89(12)
O(2)-Sm-Li(3)#1	111.11(12)
Li(3)-Sm-Li(3)#1	180.00(11)
O(1)-Sm-Li(2)#1	109.52(11)
O(1)#1-Sm-Li(2)#1	70.48(11)
O(3)-Sm-Li(2)#1	144.09(12)
O(3)#1-Sm-Li(2)#1	35.91(12)
O(2)#1-Sm-Li(2)#1	36.13(11)
O(2)-Sm-Li(2)#1	143.87(11)
Li(3)-Sm-Li(2)#1	133.61(14)
Li(3)#1-Sm-Li(2)#1	46.39(14)
O(1)-Sm-Li(2)	70.48(11)
O(1)#1-Sm-Li(2)	109.52(11)
O(3)-Sm-Li(2)	35.91(12)
O(3)#1-Sm-Li(2)	144.09(12)
O(2)#1-Sm-Li(2)	143.87(11)
O(2)-Sm-Li(2)	36.13(11)
Li(3)-Sm-Li(2)	46.39(14)
Li(3)#1-Sm-Li(2)	133.61(14)
Li(2)#1-Sm-Li(2)	180.000(1)
O(1)-Sm-Li(1)#1	144.17(11)
O(1)#1-Sm-Li(1)#1	35.83(11)
O(3)-Sm-Li(1)#1	110.62(11)
O(3)#1-Sm-Li(1)#1	69.38(11)
O(2)#1-Sm-Li(1)#1	35.35(11)
O(2)-Sm-Li(1)#1	144.65(11)
Li(3)-Sm-Li(1)#1	134.77(15)
Li(3)#1-Sm-Li(1)#1	45.23(14)
Li(2)#1-Sm-Li(1)#1	46.03(14)
Li(2)-Sm-Li(1)#1	133.97(14)
O(1)-Sm-Li(1)	35.83(11)
O(1)#1-Sm-Li(1)	144.17(11)
O(3)-Sm-Li(1)	69.38(11)
O(3)#1-Sm-Li(1)	110.62(11)
O(2)#1-Sm-Li(1)	144.65(11)
O(2)-Sm-Li(1)	35.35(11)
Li(3)-Sm-Li(1)	45.23(14)
Li(3)#1-Sm-Li(1)	134.77(14)
Li(2)#1-Sm-Li(1)	133.97(14)
Li(2)-Sm-Li(1)	46.03(14)
Li(1)#1-Sm-Li(1)	180.000(1)
C(1)-O(1)-Li(3)	123.2(2)
C(1)-O(1)-Li(1)	116.8(3)
Li(3)-O(1)-Li(1)	80.8(3)
C(1)-O(1)-Sm	131.8(2)
Li(3)-O(1)-Sm	94.2(2)
Li(1)-O(1)-Sm	96.65(18)
C(13)-O(3)-Li(2)	127.5(3)
C(13)-O(3)-Li(3)	110.6(2)

Li(2)-O(3)-Li(3)	82.8(3)
C(13)-O(3)-Sm	132.2(2)
Li(2)-O(3)-Sm	95.03(18)
Li(3)-O(3)-Sm	93.58(18)
C(19)-O(4)-Li(3)	126.5(3)
C(19)-O(4)-Li(1)	130.0(3)
Li(3)-O(4)-Li(1)	83.3(3)
C(19)-O(4)-Li(2)	131.4(3)
Li(3)-O(4)-Li(2)	84.6(3)
Li(1)-O(4)-Li(2)	84.4(3)
O(5)-Li(1)-O(4)	120.2(3)
O(5)-Li(1)-O(2)	128.1(3)
O(4)-Li(1)-O(2)	95.8(3)
O(5)-Li(1)-O(1)	113.7(3)
O(4)-Li(1)-O(1)	97.0(3)
O(2)-Li(1)-O(1)	95.6(3)
O(5)-Li(1)-Li(3)	137.1(3)
O(4)-Li(1)-Li(3)	48.0(2)
O(2)-Li(1)-Li(3)	94.7(3)
O(1)-Li(1)-Li(3)	49.29(19)
O(5)-Li(1)-Li(2)	150.9(3)
O(4)-Li(1)-Li(2)	47.92(19)
O(2)-Li(1)-Li(2)	48.13(19)
O(1)-Li(1)-Li(2)	95.1(3)
Li(3)-Li(1)-Li(2)	60.3(2)
O(5)-Li(1)-Sm	137.9(3)
O(4)-Li(1)-Sm	100.9(2)
O(2)-Li(1)-Sm	48.09(16)
O(1)-Li(1)-Sm	47.53(15)
Li(3)-Li(1)-Sm	65.9(2)
Li(2)-Li(1)-Sm	65.78(19)
O(6)-Li(2)-O(4)	124.5(3)
O(6)-Li(2)-O(3)	118.5(3)
O(4)-Li(2)-O(3)	95.6(3)
O(6)-Li(2)-O(2)	118.6(3)
O(4)-Li(2)-O(2)	95.7(3)
O(3)-Li(2)-O(2)	98.3(3)
O(6)-Li(2)-Li(3)	147.8(3)
O(4)-Li(2)-Li(3)	47.2(2)
O(3)-Li(2)-Li(3)	49.2(2)
O(2)-Li(2)-Li(3)	93.6(2)
O(6)-Li(2)-Li(1)	145.4(3)
O(4)-Li(2)-Li(1)	47.67(19)
O(3)-Li(2)-Li(1)	96.1(3)
O(2)-Li(2)-Li(1)	48.29(18)
Li(3)-Li(2)-Li(1)	58.9(2)
O(6)-Li(2)-Sm	132.8(3)
O(4)-Li(2)-Sm	102.7(2)
O(3)-Li(2)-Sm	49.06(14)
O(2)-Li(2)-Sm	49.49(15)
Li(3)-Li(2)-Sm	66.52(18)
Li(1)-Li(2)-Sm	68.18(18)
O(7)-Li(3)-O(4)	128.4(3)
O(7)-Li(3)-O(1)	114.6(3)
O(4)-Li(3)-O(1)	98.4(3)
O(7)-Li(3)-O(3)	116.1(4)
O(4)-Li(3)-O(3)	95.5(3)
O(1)-Li(3)-O(3)	98.5(3)
O(7)-Li(3)-Li(1)	146.6(4)
O(4)-Li(3)-Li(1)	48.7(2)
O(1)-Li(3)-Li(1)	49.9(2)
O(3)-Li(3)-Li(1)	96.7(2)
O(7)-Li(3)-Li(2)	148.7(3)
O(4)-Li(3)-Li(2)	48.2(2)
O(1)-Li(3)-Li(2)	95.8(2)
O(3)-Li(3)-Li(2)	48.0(2)
Li(1)-Li(3)-Li(2)	60.7(2)
O(7)-Li(3)-C(13)	90.4(3)
O(4)-Li(3)-C(13)	107.4(3)
O(1)-Li(3)-C(13)	119.2(3)
O(3)-Li(3)-C(13)	27.02(13)
Li(1)-Li(3)-C(13)	122.9(2)
Li(2)-Li(3)-C(13)	67.0(2)
O(7)-Li(3)-Sm	127.6(3)
O(4)-Li(3)-Sm	104.0(2)
O(1)-Li(3)-Sm	49.21(14)

O(3)-Li(3)-Sm	49.48(13)	C(12)-C(11)-C(10)	121.5(5)
Li(1)-Li(3)-Sm	68.90(18)	C(11)-C(12)-C(7)	121.3(4)
Li(2)-Li(3)-Sm	67.09(17)	O(3)-C(13)-C(18)	121.2(3)
C(13)-Li(3)-Sm	71.19(15)	O(3)-C(13)-C(14)	121.0(4)
C(7)-O(2)-Li(2)	121.9(3)	C(18)-C(13)-C(14)	117.8(4)
C(7)-O(2)-Li(1)	126.1(3)	O(3)-C(13)-Li(3)	42.39(18)
Li(2)-O(2)-Li(1)	83.6(2)	C(18)-C(13)-Li(3)	131.0(3)
C(7)-O(2)-Sm	123.9(2)	C(14)-C(13)-Li(3)	94.9(3)
Li(2)-O(2)-Sm	94.4(2)	C(15)-C(14)-C(13)	120.3(4)
Li(1)-O(2)-Sm	96.6(2)	C(16)-C(15)-C(14)	121.3(4)
C(28)-O(5)-C(25)	109.1(4)	C(15)-C(16)-C(17)	118.4(5)
C(28)-O(5)-Li(1)	124.4(3)	C(16)-C(17)-C(18)	121.8(5)
C(25)-O(5)-Li(1)	122.7(3)	C(17)-C(18)-C(13)	120.5(4)
C(32)-O(6)-C(29)	106.5(4)	O(4)-C(19)-C(20)	121.2(4)
C(32)-O(6)-Li(2)	125.8(4)	O(4)-C(19)-C(24)	121.9(4)
C(29)-O(6)-Li(2)	127.7(4)	C(20)-C(19)-C(24)	116.9(4)
C(36)-O(7)-C(33)	107.9(4)	C(19)-C(20)-C(21)	119.9(5)
C(36)-O(7)-Li(3)	135.5(4)	C(22)-C(21)-C(20)	121.7(6)
C(33)-O(7)-Li(3)	115.5(3)	C(21)-C(22)-C(23)	118.8(5)
O(1)-C(1)-C(6)	121.2(3)	C(22)-C(23)-C(24)	121.0(5)
O(1)-C(1)-C(2)	122.1(3)	C(19)-C(24)-C(23)	121.6(5)
C(6)-C(1)-C(2)	116.6(3)	C(26)-C(25)-O(5)	106.9(4)
C(1)-C(2)-C(3)	121.3(4)	C(25)-C(26)-C(27)	103.1(5)
C(4)-C(3)-C(2)	121.0(4)	C(28)-C(27)-C(26)	101.6(4)
C(3)-C(4)-C(5)	119.5(4)	O(5)-C(28)-C(27)	106.3(4)
C(6)-C(5)-C(4)	119.6(4)	C(30)-C(29)-O(6)	108.6(6)
C(5)-C(6)-C(1)	122.0(4)	C(29)-C(30)-C(31)	110.9(6)
O(2)-C(7)-C(8)	121.0(3)	C(32)-C(31)-C(30)	104.1(6)
O(2)-C(7)-C(12)	122.5(3)	C(31)-C(32)-O(6)	110.0(6)
C(8)-C(7)-C(12)	116.4(3)	O(7)-C(33)-C(34)	104.7(5)
C(9)-C(8)-C(7)	120.3(4)	C(35)-C(34)-C(33)	107.1(7)
C(10)-C(9)-C(8)	122.1(4)	C(34)-C(35)-C(36)	106.7(6)
C(9)-C(10)-C(11)	118.3(4)	O(7)-C(36)-C(35)	106.9(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+2

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for **21**.
The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sm	37(1)	42(1)	32(1)	-6(1)	0(1)	-4(1)
O(1)	37(1)	48(1)	46(2)	-5(1)	4(1)	5(1)
O(3)	48(1)	48(1)	38(1)	3(1)	2(1)	-8(1)
O(4)	54(1)	66(1)	41(2)	-12(1)	-2(1)	-7(1)
Li(1)	41(3)	49(3)	47(3)	-3(2)	7(3)	-3(2)
Li(2)	42(3)	53(3)	41(3)	2(2)	-1(3)	-3(2)
Li(3)	49(3)	46(2)	46(3)	-9(2)	-9(3)	-3(2)
O(2)	46(1)	46(1)	45(1)	7(1)	3(1)	-1(1)
O(5)	56(2)	83(2)	46(2)	-8(1)	18(1)	-2(1)
O(6)	43(1)	98(2)	71(2)	29(1)	1(2)	7(1)
O(7)	65(2)	49(1)	71(2)	-5(1)	-7(2)	-8(1)
C(1)	40(2)	42(1)	38(2)	2(1)	4(1)	0(1)
C(2)	52(2)	51(2)	57(2)	-4(2)	4(2)	8(1)
C(3)	70(2)	57(2)	71(3)	-3(2)	20(2)	9(2)
C(4)	49(2)	68(2)	99(4)	13(2)	23(2)	18(2)
C(5)	44(2)	73(2)	79(3)	13(2)	1(2)	1(2)
C(6)	43(2)	55(2)	56(2)	-4(2)	1(2)	-3(1)
C(7)	38(1)	54(2)	33(2)	4(1)	-3(1)	0(1)
C(8)	57(2)	65(2)	44(2)	4(2)	4(2)	12(2)
C(9)	70(2)	63(2)	75(3)	-5(2)	-3(2)	25(2)
C(10)	74(3)	55(2)	85(4)	16(2)	-8(3)	5(2)
C(11)	76(3)	63(2)	74(3)	25(2)	11(3)	-2(2)
C(12)	61(2)	58(2)	40(2)	10(1)	11(2)	8(2)
C(13)	37(1)	40(1)	46(2)	1(1)	1(1)	2(1)
C(14)	47(2)	64(2)	56(3)	1(2)	-4(2)	-13(2)
C(15)	60(2)	72(2)	81(4)	8(2)	2(2)	-26(2)
C(16)	69(3)	74(2)	80(4)	20(2)	15(3)	-18(2)
C(17)	86(3)	92(3)	44(2)	18(2)	7(2)	-10(2)
C(18)	50(2)	70(2)	40(2)	5(2)	1(2)	-10(2)
C(19)	65(2)	64(2)	31(2)	-3(1)	-1(2)	-24(2)
C(20)	109(4)	84(3)	69(3)	0(2)	-35(3)	-18(3)
C(21)	150(5)	121(4)	85(4)	-1(3)	-73(4)	-36(4)
C(22)	159(5)	110(3)	45(3)	-14(2)	-12(3)	-71(3)

C(23)	115(4)	103(3)	63(3)	-38(2)	27(3)	-51(3)
C(24)	72(3)	96(3)	59(3)	-27(2)	14(2)	-24(2)
C(25)	72(3)	104(3)	55(3)	-21(2)	11(2)	-6(2)
C(26)	88(4)	158(5)	65(4)	-40(3)	21(3)	-6(3)
C(27)	60(3)	117(4)	90(4)	-12(3)	17(3)	4(3)
C(28)	64(3)	94(3)	54(3)	-5(2)	15(2)	-15(2)
C(29)	62(3)	129(4)	93(4)	47(3)	-1(3)	10(3)
C(30)	84(4)	339(7)	378(11)	274(7)	51(6)	82(5)
C(31)	67(3)	232(6)	219(8)	155(6)	29(4)	24(4)
C(32)	58(3)	143(5)	112(5)	50(4)	22(3)	8(3)
C(33)	87(3)	72(3)	80(4)	5(2)	-8(3)	11(2)
C(34)	173(7)	102(4)	102(6)	12(4)	24(6)	-25(4)
C(35)	212(8)	84(3)	163(9)	32(4)	-14(7)	-69(4)
C(36)	211(7)	66(2)	98(5)	-14(3)	-4(5)	-52(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **21**.

	x	y	z	U(eq)
H(2)	8872	1735	12353	64
H(3)	7209	2182	12527	78
H(4)	5738	1793	11667	86
H(5)	5912	942	10556	78
H(6)	7552	472	10419	62
H(8)	11949	-1161	11115	66
H(9)	12105	-2189	11652	83
H(10)	11072	-2581	12878	86
H(11)	9869	-1926	13637	85
H(12)	9674	-909	13142	63
H(14)	13080	1443	11109	67
H(15)	14175	2045	10127	85
H(16)	13966	2045	8366	89
H(17)	12698	1396	7584	89
H(18)	11620	772	8528	64
H(20)	12961	676	13754	106
H(21)	13584	1223	15218	145
H(22)	12735	2094	15753	126

H(23)	11262	2448	14838	112
H(24)	10562	1897	13446	91
H(25A)	9820	571	14940	92
H(25B)	9237	1130	14344	92
H(26A)	8054	964	15476	124
H(26B)	8346	241	15580	124
H(27A)	6808	179	14532	106
H(27B)	7074	811	13951	106
H(28A)	7987	-373	13687	84
H(28B)	7707	135	12830	84
H(29A)	13590	-395	13437	114
H(29B)	13298	-922	12619	114
H(30A)	14836	-1083	12452	319
H(30B)	15127	-568	13288	319
H(31A)	15719	29	12134	206
H(31B)	15434	-490	11295	206
H(32A)	14139	41	10764	124
H(32B)	14413	554	11609	124
H(33A)	9404	2298	10006	96
H(33B)	10249	1834	9546	96
H(34A)	11317	2591	9163	150
H(34B)	10277	3012	9204	150
H(35A)	10866	3457	10544	184
H(35B)	11975	3119	10388	184
H(36A)	11718	2582	11735	150
H(36B)	10545	2855	11800	150

Crystal data and structure refinement for [$CaNa_6(OPh)_8(thf)_6$] 22

$C_{72}H_{88}Li_6CaO_{14}$, M= 1355.44 gmol^{-1}, monoclinic, $P2_1/n$ (Nr. 14), a = 13.398(3), b = 19.727(4), c = 13.885(3) Å, β = 96.78(3)°, V = 3644.2(13) Å^3, Z = 2, $\rho_{calcd.}$= 1.235 Mgm^3, F(000) = 1436, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.182 mm^{-1}, 1.80° < θ < 2738°, 26472 reflections of which 7596 unique and 2621 observed, 422 parameters refined, *GOOF* (on F^2) = 0.951, R1= $\Sigma|F_o–F_c|/\Sigma F_o$ = 0.0939, *w*R2 = 0.2114 for I > 2σ(I) and R1 = 0.2211, wR2 = 0.2785 for all data.

The intensities from the single-crystals of **22** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms but disorder was observed on THF ligands. CCDC-616803 (**22**) contains the supplementary crystallographic data for **22**. The cif file for the structure of **22** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **22**.

Identification code	$[CaNa_6(OPh)_8(thf)_6]$	
Empirical formula	C72 H88 Ca Na6 O14	
Formula weight	1355.44	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.398(3) Å	α= 90°
	b = 19.727(4) Å	β= 96.78(3)°
	c = 13.885(3) Å	γ = 90°
Volume	3644.2(13) $Å^3$	
Z	2	
Density (calculated)	1.235 Mg/m^3	
Absorption coefficient	0.182 mm^{-1}	
F(000)	1436	
Theta range for data collection	1.80 to 27.38°	
Index ranges	-15<=h<=17, -25<=k<=25, -16<=l<=17	
Reflections collected	26472	
Independent reflections	7596 [R(int) = 0.2910]	
Completeness to theta = 27.38°	91.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7596 / 0 / 422	
Goodness-of-fit on F^2	0.951	
Final R indices [I>2sigma(I)]	R1 = 0.0939, wR2 = 0.2114	
R indices (all data)	R1 = 0.2211, wR2 = 0.2785	
Largest diff. peak and hole	0.335 and -0.341 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **22**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ca	0	5000	5000	59(1)
Na(1)	-2254(1)	5713(1)	5481(1)	78(1)
Na(2)	-499(1)	5606(1)	7239(1)	80(1)
Na(3)	-1651(1)	4255(1)	6460(1)	80(1)
O(1)	-1728(1)	4711(1)	4914(1)	68(1)
O(2)	-579(1)	5998(1)	5686(1)	72(1)
O(3)	-10(1)	4584(1)	6597(1)	70(1)
O(4)	-2124(1)	5299(1)	7044(1)	92(1)
O(5)	-3592(1)	6296(1)	4742(1)	93(1)
O(6)	604(1)	6024(1)	8459(1)	99(1)
O(7)	-2055(1)	3223(1)	7029(1)	114(1)
C(1)	-2295(1)	4261(1)	4400(1)	67(1)
C(2)	-3186(1)	4413(1)	3845(1)	76(1)
C(3)	-3746(2)	3936(1)	3301(1)	92(1)
C(4)	-3439(2)	3268(1)	3326(2)	99(1)
C(5)	-2566(2)	3095(1)	3878(1)	93(1)
C(6)	-1998(1)	3567(1)	4410(1)	74(1)
C(7)	-521(1)	6665(1)	5524(1)	67(1)
C(8)	-854(2)	6934(1)	4622(1)	84(1)
C(9)	-790(2)	7637(1)	4463(2)	111(1)
C(10)	-408(2)	8053(1)	5184(2)	104(1)
C(11)	-103(2)	7805(1)	6061(2)	94(1)
C(12)	-163(2)	7109(1)	6245(1)	85(1)
C(13)	666(1)	4316(1)	7259(1)	68(1)
C(14)	374(2)	3917(1)	8023(1)	96(1)
C(15)	1119(2)	3649(1)	8706(2)	110(1)
C(16)	2105(2)	3767(1)	8703(2)	104(1)
C(17)	2386(2)	4156(1)	7961(2)	105(1)
C(18)	1690(1)	4420(1)	7279(1)	85(1)
C(19)	-2866(1)	5218(1)	7548(1)	71(1)
C(20)	-2874(2)	5478(1)	8494(2)	101(1)
C(21)	-3671(2)	5366(1)	8997(2)	129(1)

C(22)	-4492(2)	5014(1)	8657(2)	125(1)
C(23)	-4501(2)	4751(1)	7754(2)	117(1)
C(24)	-3724(2)	4855(1)	7206(2)	95(1)
C(25)	-3642(2)	6861(1)	4098(2)	120(1)
C(26)	-4679(2)	7115(1)	4030(3)	187(1)
C(27)	-4565(2)	6158(1)	4986(2)	103(1)
C(28)	-5239(2)	6697(1)	4554(2)	132(1)
C(29)	561(3)	5794(2)	9399(2)	181(2)
C(30)	1484(3)	5771(2)	9860(2)	222(2)
C(31)	2247(2)	5926(1)	9206(2)	169(1)
C(32)	1626(2)	6161(1)	8325(2)	108(1)
C(33)	-1587(3)	2625(1)	6747(2)	215(2)
C(34)	-1482(3)	2188(1)	7580(3)	212(2)
C(35)	-2299(2)	2383(2)	8095(3)	252(2)
C(36)	-2642(2)	3041(1)	7753(2)	158(1)

Table 3. Bond lengths [Å] and angles [°] for **22**.

Ca-O(1)	2.3738(12)	Na(3)-O(1)	2.3182(13)
Ca-O(1)#1	2.3738(12)	Na(3)-O(3)	2.2794(14)
Ca-O(2)	2.3576(11)	Na(3)-O(4)	2.3282(14)
Ca-O(2)#1	2.3576(11)	Na(3)-O(7)	2.2727(15)
Ca-O(3)	2.3656(11)	Na(1)-Na(2)	3.1898(14)
Ca-O(3)#1	2.3656(11)	Na(1)-Na(3)	3.2422(10)
Ca-Na(1)	3.4678(9)	Na(2)-Na(3)	3.2025(10)
Ca-Na(1)#1	3.4678(9)	Na(3)-C(19)	3.0200(19)
Ca-Na(2)	3.4686(10)	Na(1)-C(7)	2.9821(18)
Ca-Na(2)#1	3.4686(10)	Na(2)-C(13)	2.9837(17)
Ca-Na(3)	3.4957(11)	Na(3)-C(1)	2.8880(19)
Ca-Na(3)#1	3.4957(11)	O(1)-C(1)	1.3218(18)
Na(1)-O(1)	2.2711(12)	O(2)-C(7)	1.3396(17)
Na(1)-O(2)	2.2984(14)	O(3)-C(13)	1.3224(19)
Na(1)-O(4)	2.3061(15)	O(4)-C(19)	1.292(2)
Na(1)-O(5)	2.2698(15)	O(5)-C(27)	1.412(3)
Na(2)-O(2)	2.2818(14)	O(5)-C(25)	1.425(2)
Na(2)-O(3)	2.3284(13)	O(6)-C(29)	1.390(3)
Na(2)-O(4)	2.2441(15)	O(6)-C(32)	1.428(3)
Na(2)-O(6)	2.2683(16)	O(7)-C(36)	1.394(3)

O(7)-C(33)	1.413(3)	C(17)-C(18)	1.353(3)
C(1)-C(2)	1.375(2)	C(13)-C(18)	1.385(3)
C(2)-C(3)	1.372(3)	C(19)-C(20)	1.412(3)
C(3)-C(4)	1.380(3)	C(20)-C(21)	1.359(3)
C(4)-C(5)	1.364(3)	C(21)-C(22)	1.340(4)
C(5)-C(6)	1.364(2)	C(22)-C(23)	1.355(3)
C(1)-C(6)	1.425(2)	C(23)-C(24)	1.375(3)
C(7)-C(8)	1.385(2)	C(19)-C(24)	1.390(3)
C(8)-C(9)	1.408(2)	C(25)-C(26)	1.471(3)
C(9)-C(10)	1.348(3)	C(26)-C(28)	1.380(4)
C(10)-C(11)	1.330(3)	C(27)-C(28)	1.476(3)
C(11)-C(12)	1.400(2)	C(29)-C(30)	1.325(5)
C(7)-C(12)	1.373(2)	C(30)-C(31)	1.476(5)
C(13)-C(14)	1.413(3)	C(31)-C(32)	1.470(4)
C(14)-C(15)	1.396(3)	C(33)-C(34)	1.437(4)
C(15)-C(16)	1.342(3)	C(34)-C(35)	1.428(5)
C(16)-C(17)	1.373(3)	C(35)-C(36)	1.438(4)

O(2)-Ca-O(2)#1	180.0	O(1)#1-Ca-Na(1)	139.41(3)
O(2)-Ca-O(3)	82.66(4)	O(2)-Ca-Na(1)#1	138.79(3)
O(2)#1-Ca-O(3)	97.34(4)	O(2)#1-Ca-Na(1)#1	41.21(3)
O(2)-Ca-O(3)#1	97.34(4)	O(3)-Ca-Na(1)#1	98.13(4)
O(2)#1-Ca-O(3)#1	82.66(4)	O(3)#1-Ca-Na(1)#1	81.87(4)
O(3)-Ca-O(3)#1	180.0	O(1)-Ca-Na(1)#1	139.41(3)
O(2)-Ca-O(1)	81.68(4)	O(1)#1-Ca-Na(1)#1	40.59(3)
O(2)#1-Ca-O(1)	98.32(4)	Na(1)-Ca-Na(1)#1	180.0
O(3)-Ca-O(1)	81.41(5)	O(2)-Ca-Na(2)	40.79(3)
O(3)#1-Ca-O(1)	98.59(5)	O(2)#1-Ca-Na(2)	139.21(3)
O(2)-Ca-O(1)#1	98.32(4)	O(3)-Ca-Na(2)	41.95(3)
O(2)#1-Ca-O(1)#1	81.68(4)	O(3)#1-Ca-Na(2)	138.05(3)
O(3)-Ca-O(1)#1	98.59(5)	O(1)-Ca-Na(2)	80.66(4)
O(3)#1-Ca-O(1)#1	81.41(5)	O(1)#1-Ca-Na(2)	99.34(4)
O(1)-Ca-O(1)#1	180.0	Na(1)-Ca-Na(2)	54.76(3)
O(2)-Ca-Na(1)	41.21(3)	Na(1)#1-Ca-Na(2)	125.24(3)
O(2)#1-Ca-Na(1)	138.79(3)	O(2)-Ca-Na(2)#1	139.21(3)
O(3)-Ca-Na(1)	81.87(4)	O(2)#1-Ca-Na(2)#1	40.79(3)
O(3)#1-Ca-Na(1)	98.13(4)	O(3)-Ca-Na(2)#1	138.05(3)
O(1)-Ca-Na(1)	40.59(3)	O(3)#1-Ca-Na(2)#1	41.95(3)

O(1)-Ca-Na(2)#1	99.34(4)
O(1)#1-Ca-Na(2)#1	80.66(4)
Na(1)-Ca-Na(2)#1	125.24(3)
Na(1)#1-Ca-Na(2)#1	54.76(3)
Na(2)-Ca-Na(2)#1	180.000(9)
O(2)-Ca-Na(3)	81.71(3)
O(2)#1-Ca-Na(3)	98.29(3)
O(3)-Ca-Na(3)	40.27(3)
O(3)#1-Ca-Na(3)	139.73(3)
O(1)-Ca-Na(3)	41.23(3)
O(1)#1-Ca-Na(3)	138.77(3)
Na(1)-Ca-Na(3)	55.50(2)
Na(1)#1-Ca-Na(3)	124.50(2)
Na(2)-Ca-Na(3)	54.75(2)
Na(2)#1-Ca-Na(3)	125.25(2)
O(2)-Ca-Na(3)#1	98.29(3)
O(2)#1-Ca-Na(3)#1	81.71(3)
O(3)-Ca-Na(3)#1	139.73(3)
O(3)#1-Ca-Na(3)#1	40.27(3)
O(1)-Ca-Na(3)#1	138.77(3)
O(1)#1-Ca-Na(3)#1	41.23(3)
Na(1)-Ca-Na(3)#1	124.50(2)
Na(1)#1-Ca-Na(3)#1	55.50(2)
Na(2)-Ca-Na(3)#1	125.25(2)
Na(2)#1-Ca-Na(3)#1	54.75(2)
Na(3)-Ca-Na(3)#1	180.000(17)
O(5)-Na(1)-O(1)	122.99(5)
O(5)-Na(1)-O(2)	129.75(5)
O(1)-Na(1)-O(2)	85.23(4)
O(5)-Na(1)-O(4)	125.00(6)
O(1)-Na(1)-O(4)	91.48(5)
O(2)-Na(1)-O(4)	90.33(6)
O(5)-Na(1)-C(7)	105.16(5)
O(1)-Na(1)-C(7)	106.40(5)
O(2)-Na(1)-C(7)	25.42(4)
O(4)-Na(1)-C(7)	103.41(6)
O(5)-Na(1)-Na(2)	148.34(4)
O(1)-Na(1)-Na(2)	88.66(4)
O(2)-Na(1)-Na(2)	45.65(4)
O(4)-Na(1)-Na(2)	44.70(4)
C(7)-Na(1)-Na(2)	61.61(4)
O(5)-Na(1)-Na(3)	141.54(4)
O(1)-Na(1)-Na(3)	45.64(3)
O(2)-Na(1)-Na(3)	88.49(4)
O(4)-Na(1)-Na(3)	45.88(4)
C(7)-Na(1)-Na(3)	113.29(4)
Na(2)-Na(1)-Na(3)	59.72(2)
O(5)-Na(1)-Ca	141.00(5)
O(1)-Na(1)-Ca	42.85(3)
O(2)-Na(1)-Ca	42.51(3)
O(4)-Na(1)-Ca	93.81(5)
C(7)-Na(1)-Ca	64.24(4)
Na(2)-Na(1)-Ca	62.63(2)
Na(3)-Na(1)-Ca	62.69(2)
O(4)-Na(2)-O(6)	136.50(6)
O(4)-Na(2)-O(2)	92.35(6)
O(6)-Na(2)-O(2)	122.43(5)
O(4)-Na(2)-O(3)	91.92(5)
O(6)-Na(2)-O(3)	114.34(5)
O(2)-Na(2)-O(3)	85.15(4)
O(4)-Na(2)-C(13)	105.67(5)
O(6)-Na(2)-C(13)	90.51(5)
O(2)-Na(2)-C(13)	105.31(5)
O(3)-Na(2)-C(13)	25.17(4)
O(4)-Na(2)-Na(1)	46.29(4)
O(6)-Na(2)-Na(1)	154.68(4)
O(2)-Na(2)-Na(1)	46.07(4)
O(3)-Na(2)-Na(1)	88.86(4)
C(13)-Na(2)-Na(1)	113.67(4)
O(4)-Na(2)-Na(3)	46.62(4)
O(6)-Na(2)-Na(3)	143.17(4)
O(2)-Na(2)-Na(3)	89.76(4)
O(3)-Na(2)-Na(3)	45.34(3)
C(13)-Na(2)-Na(3)	61.60(4)
Na(1)-Na(2)-Na(3)	60.96(2)
O(4)-Na(2)-Ca	94.93(5)

O(6)-Na(2)-Ca	128.09(5)
O(2)-Na(2)-Ca	42.45(3)
O(3)-Na(2)-Ca	42.77(3)
C(13)-Na(2)-Ca	63.80(4)
Na(1)-Na(2)-Ca	62.61(2)
Na(3)-Na(2)-Ca	63.05(2)
O(7)-Na(3)-O(3)	119.54(6)
O(7)-Na(3)-O(1)	133.10(5)
O(3)-Na(3)-O(1)	84.48(5)
O(7)-Na(3)-O(4)	125.84(6)
O(3)-Na(3)-O(4)	91.04(5)
O(1)-Na(3)-O(4)	89.74(5)
O(7)-Na(3)-C(1)	107.00(5)
O(3)-Na(3)-C(1)	104.71(6)
O(1)-Na(3)-C(1)	26.65(4)
O(4)-Na(3)-C(1)	106.29(5)
O(7)-Na(3)-C(19)	103.01(6)
O(3)-Na(3)-C(19)	110.53(5)
O(1)-Na(3)-C(19)	104.57(5)
O(4)-Na(3)-C(19)	23.74(5)
C(1)-Na(3)-C(19)	112.19(5)
O(7)-Na(3)-Na(2)	138.83(5)
O(3)-Na(3)-Na(2)	46.61(3)
O(1)-Na(3)-Na(2)	87.54(4)
O(4)-Na(3)-Na(2)	44.47(4)
C(1)-Na(3)-Na(2)	114.03(4)
C(19)-Na(3)-Na(2)	64.82(4)
O(7)-Na(3)-Na(1)	151.99(5)
O(3)-Na(3)-Na(1)	88.42(4)
O(1)-Na(3)-Na(1)	44.47(3)
O(4)-Na(3)-Na(1)	45.32(4)
C(1)-Na(3)-Na(1)	63.35(4)
C(19)-Na(3)-Na(1)	61.92(4)
Na(2)-Na(3)-Na(1)	59.33(3)
O(7)-Na(3)-Ca	140.46(5)
O(3)-Na(3)-Ca	42.13(3)
O(1)-Na(3)-Ca	42.45(3)
O(4)-Na(3)-Ca	92.70(4)
C(1)-Na(3)-Ca	63.87(4)
C(19)-Na(3)-Ca	116.17(4)
Na(2)-Na(3)-Ca	62.19(2)
Na(1)-Na(3)-Ca	61.816(19)
C(1)-O(1)-Na(1)	126.21(10)
C(1)-O(1)-Na(3)	101.48(9)
Na(1)-O(1)-Na(3)	89.89(5)
C(1)-O(1)-Ca	133.08(10)
Na(1)-O(1)-Ca	96.57(4)
Na(3)-O(1)-Ca	96.32(5)
C(7)-O(2)-Na(2)	119.62(10)
C(7)-O(2)-Na(1)	107.14(10)
Na(2)-O(2)-Na(1)	88.28(6)
C(7)-O(2)-Ca	136.45(11)
Na(2)-O(2)-Ca	96.76(4)
Na(1)-O(2)-Ca	96.28(4)
C(13)-O(3)-Na(3)	121.23(10)
C(13)-O(3)-Na(2)	106.34(9)
Na(3)-O(3)-Na(2)	88.05(5)
C(13)-O(3)-Ca	135.35(11)
Na(3)-O(3)-Ca	97.61(5)
Na(2)-O(3)-Ca	95.28(4)
C(19)-O(4)-Na(2)	140.01(11)
C(19)-O(4)-Na(1)	125.12(11)
Na(2)-O(4)-Na(1)	89.01(6)
C(19)-O(4)-Na(3)	109.74(10)
Na(2)-O(4)-Na(3)	88.90(5)
Na(1)-O(4)-Na(3)	88.79(5)
C(27)-O(5)-C(25)	108.98(15)
C(27)-O(5)-Na(1)	119.70(11)
C(25)-O(5)-Na(1)	130.99(13)
C(29)-O(6)-C(32)	109.3(2)
C(29)-O(6)-Na(2)	119.14(16)
C(32)-O(6)-Na(2)	121.46(12)
C(36)-O(7)-C(33)	106.90(19)
C(36)-O(7)-Na(3)	131.28(14)
C(33)-O(7)-Na(3)	121.34(17)
O(1)-C(1)-C(2)	124.12(14)

O(1)-C(1)-C(6)	119.94(14)	C(16)-C(15)-C(14)	123.9(2)
C(2)-C(1)-C(6)	115.93(15)	C(15)-C(16)-C(17)	117.1(2)
O(1)-C(1)-Na(3)	51.87(7)	C(18)-C(17)-C(16)	120.9(2)
C(2)-C(1)-Na(3)	133.91(13)	C(17)-C(18)-C(13)	123.77(19)
C(6)-C(1)-Na(3)	86.35(10)	O(4)-C(19)-C(24)	122.56(17)
C(3)-C(2)-C(1)	122.80(16)	O(4)-C(19)-C(20)	123.37(17)
C(2)-C(3)-C(4)	119.83(18)	C(24)-C(19)-C(20)	114.06(18)
C(5)-C(4)-C(3)	119.18(18)	O(4)-C(19)-Na(3)	46.52(8)
C(6)-C(5)-C(4)	121.28(17)	C(24)-C(19)-Na(3)	88.74(12)
C(5)-C(6)-C(1)	120.92(16)	C(20)-C(19)-Na(3)	139.27(13)
O(2)-C(7)-C(12)	121.82(15)	C(21)-C(20)-C(19)	120.8(2)
O(2)-C(7)-C(8)	120.59(14)	C(22)-C(21)-C(20)	124.4(2)
C(12)-C(7)-C(8)	117.56(14)	C(21)-C(22)-C(23)	116.2(2)
O(2)-C(7)-Na(1)	47.44(8)	C(22)-C(23)-C(24)	122.0(2)
C(12)-C(7)-Na(1)	128.36(13)	C(23)-C(24)-C(19)	122.5(2)
C(8)-C(7)-Na(1)	93.20(11)	O(5)-C(25)-C(26)	106.4(2)
C(7)-C(8)-C(9)	119.96(16)	C(28)-C(26)-C(25)	109.3(2)
C(10)-C(9)-C(8)	120.59(19)	O(5)-C(27)-C(28)	107.53(18)
C(11)-C(10)-C(9)	120.22(17)	C(26)-C(28)-C(27)	107.5(2)
C(10)-C(11)-C(12)	120.68(18)	C(30)-C(29)-O(6)	108.9(3)
C(7)-C(12)-C(11)	120.96(17)	C(29)-C(30)-C(31)	111.8(3)
O(3)-C(13)-C(18)	123.32(15)	C(32)-C(31)-C(30)	102.2(2)
O(3)-C(13)-C(14)	121.20(17)	O(6)-C(32)-C(31)	106.8(2)
C(18)-C(13)-C(14)	115.44(16)	O(7)-C(33)-C(34)	106.4(3)
O(3)-C(13)-Na(2)	48.49(7)	C(35)-C(34)-C(33)	103.5(3)
C(18)-C(13)-Na(2)	112.91(10)	C(34)-C(35)-C(36)	108.2(3)
C(14)-C(13)-Na(2)	106.95(12)	O(7)-C(36)-C(35)	106.6(2)
C(15)-C(14)-C(13)	118.8(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **22**.

The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ca	63(1)	52(1)	65(1)	0(1)	18(1)	0(1)

Na(1)	70(1)	71(1)	95(1)	0(1)	17(1)	8(1)
Na(2)	87(1)	77(1)	79(1)	-6(1)	25(1)	-3(1)
Na(3)	86(1)	68(1)	90(1)	9(1)	29(1)	-7(1)
O(1)	68(1)	64(1)	74(1)	-2(1)	16(1)	-9(1)
O(2)	80(1)	51(1)	86(1)	2(1)	19(1)	2(1)
O(3)	74(1)	71(1)	68(1)	12(1)	15(1)	5(1)
O(4)	84(1)	100(1)	97(1)	-8(1)	36(1)	-4(1)
O(5)	73(1)	89(1)	118(1)	19(1)	18(1)	9(1)
O(6)	116(1)	111(1)	71(1)	-6(1)	20(1)	-22(1)
O(7)	139(1)	91(1)	124(1)	25(1)	62(1)	-8(1)
C(1)	66(1)	72(1)	64(1)	2(1)	15(1)	-9(1)
C(2)	73(1)	81(1)	77(1)	4(1)	17(1)	-13(1)
C(3)	73(1)	121(1)	80(1)	-3(1)	6(1)	-24(1)
C(4)	98(1)	110(1)	94(1)	-26(1)	33(1)	-44(1)
C(5)	101(1)	77(1)	111(1)	-20(1)	46(1)	-22(1)
C(6)	69(1)	66(1)	89(1)	2(1)	18(1)	-1(1)
C(7)	66(1)	61(1)	78(1)	-4(1)	21(1)	4(1)
C(8)	104(1)	68(1)	82(1)	-3(1)	18(1)	-1(1)
C(9)	164(2)	75(1)	99(1)	14(1)	34(2)	-5(1)
C(10)	122(2)	60(1)	133(2)	8(1)	28(1)	-13(1)
C(11)	100(2)	64(1)	118(2)	-23(1)	15(1)	-5(1)
C(12)	100(1)	60(1)	97(1)	-6(1)	20(1)	0(1)
C(13)	86(1)	49(1)	71(1)	-7(1)	16(1)	1(1)
C(14)	102(2)	97(1)	95(1)	37(1)	31(1)	2(1)
C(15)	144(2)	99(1)	87(1)	29(1)	9(1)	9(1)
C(16)	114(2)	71(1)	120(2)	5(1)	-9(1)	12(1)
C(17)	83(1)	107(1)	124(2)	12(1)	9(1)	-5(1)
C(18)	82(1)	89(1)	82(1)	14(1)	0(1)	-4(1)
C(19)	73(1)	67(1)	74(1)	5(1)	13(1)	8(1)
C(20)	94(2)	123(2)	88(1)	-7(1)	19(1)	-3(1)
C(21)	126(2)	178(2)	90(1)	-4(2)	49(1)	12(2)
C(22)	105(2)	166(2)	114(2)	34(1)	53(1)	16(2)
C(23)	77(1)	119(1)	163(2)	21(1)	46(1)	-14(1)
C(24)	93(1)	86(1)	105(1)	-14(1)	12(1)	-4(1)
C(25)	122(2)	114(1)	130(2)	39(1)	42(2)	5(1)
C(26)	93(2)	164(2)	310(3)	118(2)	49(2)	47(1)
C(27)	82(1)	109(1)	121(2)	26(1)	17(1)	15(1)
C(28)	80(1)	146(2)	174(2)	49(2)	34(2)	24(1)

C(29)	221(3)	247(3)	75(2)	39(2)	17(2)	-54(3)
C(30)	260(4)	291(4)	109(2)	75(2)	3(3)	45(3)
C(31)	125(2)	155(2)	207(3)	24(2)	-61(2)	-23(2)
C(32)	111(2)	92(1)	119(2)	-10(1)	8(2)	-17(1)
C(33)	394(5)	95(2)	179(2)	29(2)	130(3)	48(2)
C(34)	257(4)	116(2)	264(4)	44(2)	32(3)	41(2)
C(35)	144(2)	278(2)	347(3)	234(2)	89(2)	71(2)
C(36)	112(2)	207(2)	162(2)	102(2)	42(2)	9(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **22**.

	x	y	z	U(eq)
H(2)	-3418	4857	3838	91
H(3)	-4331	4064	2915	110
H(4)	-3822	2940	2972	119
H(5)	-2354	2645	3892	112
H(6)	-1410	3434	4786	89
H(8)	-1121	6651	4121	101
H(9)	-1012	7815	3856	134
H(10)	-357	8516	5069	125
H(11)	151	8097	6556	113
H(12)	44	6946	6865	102
H(14)	-302	3833	8071	115
H(15)	920	3373	9191	132
H(16)	2578	3593	9184	124
H(17)	3064	4240	7927	126
H(18)	1912	4687	6795	102
H(20)	-2329	5728	8778	121
H(21)	-3643	5547	9618	154
H(22)	-5025	4952	9020	150
H(23)	-5050	4494	7497	141
H(24)	-3775	4675	6584	114
H(25A)	-3480	6722	3464	144
H(25B)	-3171	7210	4348	144
H(26A)	-4682	7573	4285	224
H(26B)	-4971	7126	3357	224

H(27A)	-4560	6153	5685	124
H(27B)	-4793	5719	4734	124
H(28A)	-5793	6501	4133	158
H(28B)	-5512	6952	5060	158
H(29A)	149	6097	9736	217
H(29B)	260	5346	9385	217
H(30A)	1610	5322	10134	266
H(30B)	1543	6094	10389	266
H(31A)	2703	6278	9474	202
H(31B)	2631	5526	9078	202
H(32A)	1723	6642	8232	129
H(32B)	1807	5921	7761	129
H(33A)	-934	2728	6547	258
H(33B)	-1997	2410	6210	258
H(34A)	-1537	1715	7389	255
H(34B)	-842	2259	7971	255
H(35A)	-2079	2401	8786	302
H(35B)	-2840	2056	7984	302
H(36A)	-3346	3022	7493	190
H(36B)	-2563	3368	8278	190

Crystal data and structure refinement for $[SrNa_6(OPh)_8(thf)_6]$ 23

$C_{72}H_{88}Li_6SrO_{14}$, M= 1402.98 gmol^{-1}, monoclinic, $P2_1/n$ (Nr. 14), a = 13.1422(12), b = 21.5560(3), c = 13.3541(11) Å, β = 100.512(7)°, V = 3719.6(5) Å^3, Z = 2, $\rho_{calcd.}$= 1.253 Mgm^3, F(000) = 1472, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.819 mm^{-1}, 2.21° < θ < 27.18°, 12490 reflections of which 6585 unique and 4459 observed, 422 parameters refined, *GOOF* (on F^2) = 1.119, R1= $\Sigma|F_o–F_c|/\Sigma F_o$ = 0.0719, wR2 = 0.1889 for I > 2σ(I) and R1 = 0.1106, wR2 = 0.2112 for all data.

The intensities from the single-crystals of **23** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms but disorder was observed on THF ligands. CCDC-616804 (**23**) contains the supplementary crystallographic data for **23**. The cif file for the structure of **23** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **23**.

Identification code	$[SrNa_6(OPh)_8(thf)_6]$	
Empirical formula	C72 H88 Na6 O14 Sr	
Formula weight	1402.98	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.1422(12) Å	α= 90°
	b = 21.5560(15) Å	β= 100.512(7)°
	c = 13.3541(11) Å	γ = 90°
Volume	3719.6(5) Å^3	
Z	2	
Density (calculated)	1.253 Mg/m^3	
Absorption coefficient	0.819 mm^{-1}	
F(000)	1472	
Theta range for data collection	2.21 to 27.18°	
Index ranges	-10<=h<=16, -17<=k<=27, -17<=l<=17	
Reflections collected	12490	
Independent reflections	6585 [R(int) = 0.1166]	
Completeness to theta = 27.18°	79.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6585 / 0 / 422	
Goodness-of-fit on F^2	1.119	
Final R indices [I>2sigma(I)]	R1 = 0.0719, wR2 = 0.1889	
R indices (all data)	R1 = 0.1106, wR2 = 0.2112	
Largest diff. peak and hole	0.516 and -0.531 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **23**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sr	5000	0	5000	45(1)
Na(1)	5542(1)	517(1)	2610(1)	64(1)
Na(2)	7507(1)	296(1)	4389(1)	63(1)

Na(3)	6270(1)	-887(1)	3285(1)	63(1)
O(1)	6696(1)	-556(1)	4946(1)	57(1)
O(2)	4745(1)	-329(1)	3157(1)	55(1)
O(3)	5994(1)	839(1)	4300(1)	55(1)
O(4)	7053(1)	-20(1)	2730(1)	75(1)
O(5)	5110(1)	1161(1)	1263(1)	101(1)
O(6)	9001(1)	702(1)	5270(1)	82(1)
O(7)	3545(1)	1924(1)	7078(1)	81(1)
C(1)	7241(1)	-878(1)	5707(1)	50(1)
C(2)	7481(1)	-633(1)	6688(1)	64(1)
C(3)	8007(2)	-982(1)	7491(1)	82(1)
C(4)	8305(2)	-1576(1)	7352(2)	93(1)
C(5)	8081(2)	-1829(1)	6396(2)	82(1)
C(6)	7559(1)	-1487(1)	5591(1)	64(1)
C(7)	3962(1)	-637(1)	2580(1)	51(1)
C(8)	3425(1)	-394(1)	1670(1)	60(1)
C(9)	2600(2)	-713(1)	1095(1)	77(1)
C(10)	2304(2)	-1281(1)	1398(2)	84(1)
C(11)	2827(2)	-1529(1)	2292(1)	76(1)
C(12)	3651(1)	-1210(1)	2877(1)	61(1)
C(13)	5886(1)	1451(1)	4313(1)	50(1)
C(14)	6693(2)	1847(1)	4775(1)	71(1)
C(15)	6557(2)	2481(1)	4785(2)	88(1)
C(16)	5636(2)	2741(1)	4343(2)	93(1)
C(17)	4837(2)	2366(1)	3901(2)	92(1)
C(18)	4955(1)	1728(1)	3894(1)	65(1)
C(19)	7674(1)	-100(1)	2082(1)	54(1)
C(20)	7456(2)	-553(1)	1319(1)	79(1)
C(21)	8104(2)	-673(1)	647(2)	103(1)
C(22)	9025(2)	-382(1)	733(2)	109(1)
C(23)	9272(2)	86(1)	1451(2)	96(1)
C(24)	8593(2)	213(1)	2123(1)	80(1)
C(25)	5555(2)	1051(1)	391(2)	112(1)
C(26)	5350(3)	1615(2)	-234(2)	134(1)
C(27)	4638(3)	1978(1)	174(2)	159(2)
C(28)	4505(3)	1715(1)	1129(2)	144(1)
C(29)	9908(2)	954(1)	4995(2)	100(1)
C(30)	10557(2)	1190(2)	5945(2)	112(1)

C(31)	9833(2)	1260(1)	6653(2)	107(1)
C(32)	9057(2)	751(1)	6351(2)	88(1)
C(33)	4220(2)	2366(1)	6736(2)	117(1)
C(34)	3638(4)	2976(1)	6698(3)	171(2)
C(35)	2951(4)	2919(2)	7414(3)	161(2)
C(36)	2746(2)	2233(1)	7462(2)	106(1)

Table 3. Bond lengths [Å] and angles [°] for **23**.

Sr-O(1)	2.5430(11)	Na(3)-C(7)	3.0541(17)
Sr-O(1)#1	2.5430(11)	O(1)-C(1)	1.3272(17)
Sr-O(2)	2.5245(10)	O(2)-C(7)	1.3425(17)
Sr-O(2)#1	2.5245(10)	O(3)-C(13)	1.3286(18)
Sr-O(3)	2.5097(11)	O(4)-C(19)	1.306(2)
Sr-O(3)#1	2.5097(11)	O(5)-C(25)	1.415(3)
Sr-Na(1)	3.5726(7)	O(5)-C(28)	1.427(3)
Sr-Na(1)#1	3.5726(7)	O(6)-C(29)	1.417(3)
Sr-Na(2)	3.5937(8)	O(6)-C(32)	1.436(3)
Sr-Na(2)#1	3.5937(8)	O(7)-C(36)	1.416(3)
Sr-Na(3)	3.6167(7)	O(7)-C(33)	1.432(3)
Sr-Na(3)#1	3.6167(7)	C(1)-C(2)	1.393(2)
Na(1)-O(2)	2.2884(13)	C(2)-C(3)	1.386(3)
Na(1)-O(3)	2.3311(11)	C(3)-C(4)	1.363(3)
Na(1)-O(4)	2.2783(16)	C(4)-C(5)	1.370(3)
Na(1)-O(5)	2.2611(15)	C(5)-C(6)	1.379(3)
Na(2)-O(1)	2.3137(13)	C(1)-C(6)	1.395(2)
Na(2)-O(3)	2.2909(13)	C(7)-C(8)	1.392(2)
Na(2)-O(4)	2.2902(14)	C(8)-C(9)	1.392(3)
Na(2)-O(6)	2.2721(14)	C(9)-C(10)	1.367(3)
Na(3)-O(1)	2.3003(12)	C(10)-C(11)	1.372(3)
Na(3)-O(2)	2.3166(13)	C(11)-C(12)	1.394(3)
Na(3)-O(4)	2.3196(16)	C(7)-C(12)	1.383(2)
Na(3)-O(7)#1	2.3103(15)	C(13)-C(14)	1.412(2)
O(7)-Na(3)#1	2.3103(15)	C(14)-C(15)	1.379(3)
Na(1)-Na(2)	3.2094(9)	C(15)-C(16)	1.367(3)
Na(1)-Na(3)	3.2513(10)	C(16)-C(17)	1.372(3)
Na(2)-Na(3)	3.2326(9)	C(17)-C(18)	1.384(3)
Na(1)-C(13)	3.0092(15)	C(13)-C(18)	1.383(2)

C(19)-C(20)	1.402(2)	C(27)-C(28)	1.435(4)
C(20)-C(21)	1.369(4)	C(29)-C(30)	1.484(3)
C(21)-C(22)	1.349(4)	C(30)-C(31)	1.467(4)
C(22)-C(23)	1.389(3)	C(31)-C(32)	1.502(4)
C(23)-C(24)	1.402(3)	C(33)-C(34)	1.518(4)
C(19)-C(24)	1.375(3)	C(34)-C(35)	1.435(6)
C(25)-C(26)	1.471(4)	C(35)-C(36)	1.505(4)
C(26)-C(27)	1.404(5)		

O(3)#1-Sr-O(3)	180.00(5)	O(3)-Sr-Na(2)	39.27(3)
O(3)#1-Sr-O(2)	100.10(3)	O(2)-Sr-Na(2)	78.04(3)
O(3)-Sr-O(2)	79.90(3)	O(2)#1-Sr-Na(2)	101.96(3)
O(3)#1-Sr-O(2)#1	79.90(3)	O(1)-Sr-Na(2)	39.87(3)
O(3)-Sr-O(2)#1	100.10(3)	O(1)#1-Sr-Na(2)	140.13(3)
O(2)-Sr-O(2)#1	180.0	Na(1)#1-Sr-Na(2)	126.788(16)
O(3)#1-Sr-O(1)	100.95(4)	Na(1)-Sr-Na(2)	53.212(16)
O(3)-Sr-O(1)	79.05(4)	O(3)#1-Sr-Na(2)#1	39.27(3)
O(2)-Sr-O(1)	78.53(3)	O(3)-Sr-Na(2)#1	140.73(3)
O(2)#1-Sr-O(1)	101.47(3)	O(2)-Sr-Na(2)#1	101.96(3)
O(3)#1-Sr-O(1)#1	79.05(4)	O(2)#1-Sr-Na(2)#1	78.04(3)
O(3)-Sr-O(1)#1	100.95(4)	O(1)-Sr-Na(2)#1	140.13(3)
O(2)-Sr-O(1)#1	101.47(3)	O(1)#1-Sr-Na(2)#1	39.87(3)
O(2)#1-Sr-O(1)#1	78.53(3)	Na(1)#1-Sr-Na(2)#1	53.212(16)
O(1)-Sr-O(1)#1	180.0	Na(1)-Sr-Na(2)#1	126.788(16)
O(3)#1-Sr-Na(1)#1	40.54(2)	Na(2)-Sr-Na(2)#1	180.0
O(3)-Sr-Na(1)#1	139.46(2)	O(3)#1-Sr-Na(3)	100.78(3)
O(2)-Sr-Na(1)#1	140.40(3)	O(3)-Sr-Na(3)	79.22(3)
O(2)#1-Sr-Na(1)#1	39.60(3)	O(2)-Sr-Na(3)	39.52(3)
O(1)-Sr-Na(1)#1	101.36(3)	O(2)#1-Sr-Na(3)	140.48(3)
O(1)#1-Sr-Na(1)#1	78.64(3)	O(1)-Sr-Na(3)	39.19(2)
O(3)#1-Sr-Na(1)	139.46(2)	O(1)#1-Sr-Na(3)	140.81(2)
O(3)-Sr-Na(1)	40.54(2)	Na(1)#1-Sr-Na(3)	126.228(16)
O(2)-Sr-Na(1)	39.60(3)	Na(1)-Sr-Na(3)	53.772(16)
O(2)#1-Sr-Na(1)	140.40(3)	Na(2)-Sr-Na(3)	53.272(16)
O(1)-Sr-Na(1)	78.64(3)	Na(2)#1-Sr-Na(3)	126.728(16)
O(1)#1-Sr-Na(1)	101.36(3)	O(3)#1-Sr-Na(3)#1	79.22(3)
Na(1)#1-Sr-Na(1)	180.0	O(3)-Sr-Na(3)#1	100.78(3)
O(3)#1-Sr-Na(2)	140.73(3)	O(2)-Sr-Na(3)#1	140.48(3)

O(2)#1-Sr-Na(3)#1	39.52(3)
O(1)-Sr-Na(3)#1	140.81(2)
O(1)#1-Sr-Na(3)#1	39.19(2)
Na(1)#1-Sr-Na(3)#1	53.772(16)
Na(1)-Sr-Na(3)#1	126.228(16)
Na(2)-Sr-Na(3)#1	126.728(16)
Na(2)#1-Sr-Na(3)#1	53.272(16)
Na(3)-Sr-Na(3)#1	180.0
O(5)-Na(1)-O(4)	117.16(6)
O(5)-Na(1)-O(2)	132.85(6)
O(4)-Na(1)-O(2)	90.95(5)
O(5)-Na(1)-O(3)	124.76(5)
O(4)-Na(1)-O(3)	91.03(5)
O(2)-Na(1)-O(3)	88.82(4)
O(5)-Na(1)-C(13)	99.89(5)
O(4)-Na(1)-C(13)	106.15(5)
O(2)-Na(1)-C(13)	107.87(4)
O(3)-Na(1)-C(13)	24.91(4)
O(5)-Na(1)-Na(2)	136.97(5)
O(4)-Na(1)-Na(2)	45.52(3)
O(2)-Na(1)-Na(2)	89.96(3)
O(3)-Na(1)-Na(2)	45.51(3)
C(13)-Na(1)-Na(2)	63.29(3)
O(5)-Na(1)-Na(3)	144.12(5)
O(4)-Na(1)-Na(3)	45.51(4)
O(2)-Na(1)-Na(3)	45.44(3)
O(3)-Na(1)-Na(3)	89.92(3)
C(13)-Na(1)-Na(3)	114.68(3)
Na(2)-Na(1)-Na(3)	60.04(2)
O(5)-Na(1)-Sr	147.18(5)
O(4)-Na(1)-Sr	95.28(4)
O(2)-Na(1)-Sr	44.68(3)
O(3)-Na(1)-Sr	44.41(3)
C(13)-Na(1)-Sr	63.94(3)
Na(2)-Na(1)-Sr	63.731(18)
Na(3)-Na(1)-Sr	63.807(17)
O(6)-Na(2)-O(4)	131.60(6)
O(6)-Na(2)-O(3)	119.34(6)
O(4)-Na(2)-O(3)	91.76(5)
O(6)-Na(2)-O(1)	122.99(5)
O(4)-Na(2)-O(1)	91.19(5)
O(3)-Na(2)-O(1)	88.59(5)
O(6)-Na(2)-Na(1)	145.99(5)
O(4)-Na(2)-Na(1)	45.22(4)
O(3)-Na(2)-Na(1)	46.54(3)
O(1)-Na(2)-Na(1)	89.99(3)
O(6)-Na(2)-Na(3)	148.81(5)
O(4)-Na(2)-Na(3)	45.85(4)
O(3)-Na(2)-Na(3)	91.11(3)
O(1)-Na(2)-Na(3)	45.35(3)
Na(1)-Na(2)-Na(3)	60.62(2)
O(6)-Na(2)-Sr	133.81(5)
O(4)-Na(2)-Sr	94.51(4)
O(3)-Na(2)-Sr	43.90(3)
O(1)-Na(2)-Sr	44.79(3)
Na(1)-Na(2)-Sr	63.057(18)
Na(3)-Na(2)-Sr	63.728(18)
O(1)-Na(3)-O(7)#1	119.09(5)
O(1)-Na(3)-O(2)	88.01(4)
O(7)#1-Na(3)-O(2)	127.57(5)
O(1)-Na(3)-O(4)	90.78(5)
O(7)#1-Na(3)-O(4)	130.03(6)
O(2)-Na(3)-O(4)	89.22(5)
O(1)-Na(3)-C(7)	107.21(5)
O(7)#1-Na(3)-C(7)	104.04(5)
O(2)-Na(3)-C(7)	24.35(4)
O(4)-Na(3)-C(7)	103.47(5)
O(1)-Na(3)-Na(2)	45.69(3)
O(7)#1-Na(3)-Na(2)	142.73(5)
O(2)-Na(3)-Na(2)	88.89(4)
O(4)-Na(3)-Na(2)	45.10(3)
C(7)-Na(3)-Na(2)	112.97(4)
O(1)-Na(3)-Na(1)	89.19(4)
O(7)#1-Na(3)-Na(1)	151.62(4)
O(2)-Na(3)-Na(1)	44.74(3)
O(4)-Na(3)-Na(1)	44.48(4)

C(7)-Na(3)-Na(1)	61.66(4)
Na(2)-Na(3)-Na(1)	59.34(2)
O(1)-Na(3)-Sr	44.32(3)
O(7)#1-Na(3)-Sr	136.30(5)
O(2)-Na(3)-Sr	43.90(3)
O(4)-Na(3)-Sr	93.39(4)
C(7)-Na(3)-Sr	63.59(3)
Na(2)-Na(3)-Sr	63.000(18)
Na(1)-Na(3)-Sr	62.421(17)
C(1)-O(1)-Na(3)	125.35(10)
C(1)-O(1)-Na(2)	116.47(9)
Na(3)-O(1)-Na(2)	88.95(4)
C(1)-O(1)-Sr	125.28(10)
Na(3)-O(1)-Sr	96.49(4)
Na(2)-O(1)-Sr	95.34(4)
C(7)-O(2)-Na(1)	123.97(9)
C(7)-O(2)-Na(3)	110.31(9)
Na(1)-O(2)-Na(3)	89.83(5)
C(7)-O(2)-Sr	130.55(9)
Na(1)-O(2)-Sr	95.73(4)
Na(3)-O(2)-Sr	96.58(4)
C(13)-O(3)-Na(2)	126.95(10)
C(13)-O(3)-Na(1)	107.44(8)
Na(2)-O(3)-Na(1)	87.95(5)
C(13)-O(3)-Sr	130.26(10)
Na(2)-O(3)-Sr	96.83(4)
Na(1)-O(3)-Sr	95.05(4)
C(19)-O(4)-Na(1)	131.58(10)
C(19)-O(4)-Na(2)	126.61(10)
Na(1)-O(4)-Na(2)	89.26(5)
C(19)-O(4)-Na(3)	118.18(11)
Na(1)-O(4)-Na(3)	90.00(5)
Na(2)-O(4)-Na(3)	89.05(5)
C(25)-O(5)-C(28)	109.96(18)
C(25)-O(5)-Na(1)	118.06(14)
C(28)-O(5)-Na(1)	131.78(15)
C(29)-O(6)-C(32)	109.97(16)
C(29)-O(6)-Na(2)	134.50(13)
C(32)-O(6)-Na(2)	115.46(13)
C(36)-O(7)-C(33)	110.29(19)
C(36)-O(7)-Na(3)#1	130.15(14)
C(33)-O(7)-Na(3)#1	118.73(15)
O(1)-C(1)-C(2)	121.33(15)
O(1)-C(1)-C(6)	122.56(13)
C(2)-C(1)-C(6)	116.03(14)
C(3)-C(2)-C(1)	121.22(18)
C(4)-C(3)-C(2)	121.23(18)
C(3)-C(4)-C(5)	118.92(19)
C(4)-C(5)-C(6)	120.3(2)
C(5)-C(6)-C(1)	122.24(16)
O(2)-C(7)-C(12)	120.91(13)
O(2)-C(7)-C(8)	121.83(15)
C(12)-C(7)-C(8)	117.26(14)
O(2)-C(7)-Na(3)	45.35(7)
C(12)-C(7)-Na(3)	94.81(10)
C(8)-C(7)-Na(3)	130.70(12)
C(7)-C(8)-C(9)	120.97(16)
C(10)-C(9)-C(8)	120.99(17)
C(9)-C(10)-C(11)	118.77(19)
C(10)-C(11)-C(12)	120.70(19)
C(7)-C(12)-C(11)	121.29(15)
O(3)-C(13)-C(18)	120.80(14)
O(3)-C(13)-C(14)	122.15(14)
C(18)-C(13)-C(14)	117.03(15)
O(3)-C(13)-Na(1)	47.65(6)
C(18)-C(13)-Na(1)	89.01(10)
C(14)-C(13)-Na(1)	136.99(13)
C(15)-C(14)-C(13)	121.02(18)
C(16)-C(15)-C(14)	120.5(2)
C(15)-C(16)-C(17)	119.5(2)
C(16)-C(17)-C(18)	120.7(2)
C(13)-C(18)-C(17)	121.17(17)
O(4)-C(19)-C(24)	123.99(15)
O(4)-C(19)-C(20)	120.29(16)
C(24)-C(19)-C(20)	115.61(18)
C(21)-C(20)-C(19)	122.5(2)

C(22)-C(21)-C(20)	120.8(2)	O(6)-C(29)-C(30)	106.8(2)
C(21)-C(22)-C(23)	119.2(2)	C(31)-C(30)-C(29)	104.3(2)
C(22)-C(23)-C(24)	119.2(2)	C(30)-C(31)-C(32)	103.9(2)
C(19)-C(24)-C(23)	122.35(19)	O(6)-C(32)-C(31)	103.36(19)
O(5)-C(25)-C(26)	105.6(2)	O(7)-C(33)-C(34)	104.4(3)
C(27)-C(26)-C(25)	107.8(3)	C(35)-C(34)-C(33)	106.2(3)
C(26)-C(27)-C(28)	108.8(3)	C(34)-C(35)-C(36)	104.6(3)
O(5)-C(28)-C(27)	106.6(3)	O(7)-C(36)-C(35)	107.2(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **23**.

The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sr	49(1)	43(1)	44(1)	1(1)	13(1)	0(1)
Na(1)	81(1)	59(1)	53(1)	9(1)	14(1)	-1(1)
Na(2)	53(1)	65(1)	71(1)	-4(1)	12(1)	-6(1)
Na(3)	75(1)	52(1)	64(1)	-7(1)	18(1)	5(1)
O(1)	60(1)	56(1)	53(1)	7(1)	5(1)	11(1)
O(2)	54(1)	58(1)	51(1)	-5(1)	6(1)	-2(1)
O(3)	67(1)	39(1)	60(1)	2(1)	17(1)	-2(1)
O(4)	80(1)	82(1)	71(1)	-1(1)	35(1)	2(1)
O(5)	137(1)	104(1)	70(1)	33(1)	38(1)	41(1)
O(6)	60(1)	92(1)	90(1)	-13(1)	8(1)	-14(1)
O(7)	91(1)	61(1)	96(1)	-13(1)	25(1)	2(1)
C(1)	46(1)	52(1)	55(1)	5(1)	13(1)	6(1)
C(2)	62(1)	66(1)	60(1)	1(1)	2(1)	8(1)
C(3)	81(1)	104(2)	60(1)	6(1)	6(1)	11(1)
C(4)	95(1)	103(1)	81(1)	36(1)	13(1)	31(1)
C(5)	92(1)	66(1)	92(1)	20(1)	27(1)	32(1)
C(6)	70(1)	53(1)	71(1)	4(1)	18(1)	11(1)
C(7)	50(1)	57(1)	47(1)	-12(1)	11(1)	-1(1)
C(8)	71(1)	52(1)	54(1)	0(1)	4(1)	-2(1)
C(9)	72(1)	87(1)	65(1)	-11(1)	-9(1)	10(1)
C(10)	81(1)	92(1)	76(1)	-23(1)	7(1)	-21(1)

C(11)	91(1)	58(1)	83(1)	-11(1)	28(1)	-19(1)
C(12)	69(1)	58(1)	59(1)	-2(1)	19(1)	1(1)
C(13)	63(1)	45(1)	47(1)	3(1)	21(1)	-8(1)
C(14)	78(1)	54(1)	80(1)	2(1)	12(1)	-18(1)
C(15)	110(2)	58(1)	96(1)	-4(1)	22(1)	-37(1)
C(16)	114(2)	46(1)	128(2)	0(1)	44(1)	-4(1)
C(17)	87(1)	63(1)	131(2)	6(1)	28(1)	16(1)
C(18)	57(1)	58(1)	82(1)	3(1)	17(1)	2(1)
C(19)	59(1)	55(1)	51(1)	7(1)	16(1)	2(1)
C(20)	109(1)	64(1)	71(1)	-5(1)	34(1)	-19(1)
C(21)	171(2)	73(1)	82(1)	-8(1)	63(1)	2(2)
C(22)	121(2)	108(2)	118(1)	38(1)	72(1)	41(1)
C(23)	73(1)	121(2)	97(1)	34(1)	25(1)	-15(1)
C(24)	87(1)	85(1)	68(1)	12(1)	14(1)	-18(1)
C(25)	168(2)	103(2)	73(1)	20(1)	49(1)	32(2)
C(26)	160(2)	148(2)	107(1)	59(1)	59(1)	32(2)
C(27)	255(4)	109(2)	123(2)	45(1)	63(2)	76(2)
C(28)	186(2)	147(2)	113(2)	52(1)	64(2)	92(2)
C(29)	85(1)	112(2)	105(1)	-15(1)	24(1)	-21(1)
C(30)	81(1)	139(2)	114(2)	4(2)	9(1)	-42(1)
C(31)	139(2)	95(2)	83(1)	-9(1)	8(1)	-30(2)
C(32)	82(1)	93(2)	90(1)	1(1)	18(1)	-1(1)
C(33)	118(2)	70(1)	172(2)	0(2)	47(2)	-13(2)
C(34)	228(4)	71(2)	231(3)	27(2)	91(3)	35(2)
C(35)	232(4)	88(2)	180(3)	-2(2)	86(2)	47(2)
C(36)	111(2)	95(2)	116(2)	-32(1)	30(1)	12(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **23**.

	x	y	z	U(eq)
H(2)	7283	-225	6806	76
H(3)	8160	-804	8144	99
H(4)	8659	-1808	7903	112
H(5)	8284	-2238	6288	99
H(6)	7413	-1670	4942	77
H(8)	3623	-7	1440	72

H(9)	2240	-537	489	93
H(10)	1754	-1498	1001	101
H(11)	2628	-1917	2512	91
H(12)	4000	-1389	3486	73
H(14)	7332	1675	5079	86
H(15)	7103	2737	5099	105
H(16)	5551	3174	4342	112
H(17)	4201	2544	3599	111
H(18)	4394	1478	3599	78
H(20)	6841	-783	1267	95
H(21)	7905	-961	120	124
H(22)	9495	-496	312	131
H(23)	9886	315	1486	115
H(24)	8773	522	2619	96
H(25A)	5238	688	17	134
H(25B)	6302	979	586	134
H(26A)	5994	1847	-223	161
H(26B)	5065	1504	-941	161
H(27A)	3973	1987	-298	190
H(27B)	4893	2404	277	190
H(28A)	4742	2006	1686	173
H(28B)	3774	1619	1119	173
H(29A)	9730	1291	4503	120
H(29B)	10281	633	4687	120
H(30A)	11107	895	6210	135
H(30B)	10871	1590	5826	135
H(31A)	9498	1668	6578	129
H(31B)	10188	1209	7360	129
H(32A)	9294	361	6693	106
H(32B)	8383	861	6516	106
H(33A)	4354	2254	6060	141
H(33B)	4881	2390	7212	141
H(34A)	4120	3321	6886	205
H(34B)	3245	3051	6011	205
H(35A)	2307	3147	7180	193
H(35B)	3277	3077	8084	193
H(36A)	2744	2106	8166	128
H(36B)	2071	2132	7048	128

Crystal data and structure refinement for [BaNa$_6$(OPh)$_8$(thf)$_6$] 24

$C_{72}H_{88}Li_6BaO_{14}$, M= 1452.70 gmol^{-1}, monoclinic, *P*2$_1$/*n* (Nr. 14), a = 13.0582(6), b = 21.4307(12), c = 13.3046(7) Å, β = 101.749(4)°, V = 3645.2(3) Å^3, Z = 2, $\rho_{calcd.}$= 1.324 Mgm^3, *F*(000) = 1508, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.641 mm^{-1}, 1.85° < θ < 27.18°, 25544 reflections of which 7974 unique and 6526 observed, 422 parameters refined, *GOOF* (on F^2) = 1.032, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.0377, *w*R2 = 0.0875 for I > 2σ(I) and R1 = 0.0495, wR2 =0.0943 for all data.

The intensities from the single-crystals of **24** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms. CCDC-616805 (**24**) contains the supplementary crystallographic data for **24**. The cif file for the structure of **24** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **24**.

Identification code	[BaNa$_6$(OPh)$_8$(thf)$_6$]	
Empirical formula	C72 H88 Ba Na6 O14	
Formula weight	1452.70	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.0582(6) Å	α= 90°
	b = 21.4307(12) Å	β= 101.749(4)°
	c = 13.3046(7) Å	γ = 90°
Volume	3645.2(3) Å^3	
Z	2	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	0.641 mm^{-1}	
F(000)	1508	
Theta range for data collection	1.85 to 27.18°	
Index ranges	-16<=h<=16, -27<=k<=27, -15<=l<=17	
Reflections collected	25544	
Independent reflections	7974 [R(int) = 0.0457]	
Completeness to theta = 27.18°	98.3 %	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7974 / 0 / 422
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0875
R indices (all data)	R1 = 0.0495, wR2 = 0.0943
Largest diff. peak and hole	0.433 and -0.576 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **24**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ba	10000	0	0	44(1)
Na(1)	8666(1)	-906(1)	1802(1)	45(1)
Na(2)	7419(1)	289(1)	732(1)	44(1)
Na(3)	9429(1)	491(1)	2500(1)	45(1)
O(1)	10216(1)	-363(1)	1971(1)	44(1)
O(2)	8165(1)	-570(1)	147(1)	44(1)
O(3)	8915(1)	840(1)	836(1)	46(1)
O(4)	7913(1)	-36(1)	2386(1)	53(1)
O(5)	11465(1)	1964(1)	7894(1)	59(1)
O(7)	9845(1)	1170(1)	3820(1)	70(1)
O(6)	5930(1)	709(1)	-191(1)	57(1)
C(1)	11062(1)	-652(1)	2485(1)	36(1)
C(2)	11655(1)	-407(1)	3397(1)	43(1)
C(3)	12535(1)	-708(1)	3919(1)	54(1)
C(4)	12864(1)	-1262(1)	3560(1)	57(1)
C(5)	12297(1)	-1510(1)	2657(1)	51(1)
C(6)	11408(1)	-1213(1)	2128(1)	40(1)
C(7)	7702(1)	-891(1)	-678(1)	36(1)
C(8)	7483(1)	-617(1)	-1650(1)	42(1)
C(9)	7035(1)	-956(1)	-2513(1)	55(1)
C(10)	6776(1)	-1575(1)	-2436(1)	63(1)
C(11)	6969(1)	-1850(1)	-1480(1)	56(1)
C(12)	7427(1)	-1519(1)	-612(1)	43(1)
C(13)	9057(1)	1449(1)	754(1)	35(1)
C(14)	8254(1)	1848(1)	285(1)	44(1)

C(15)	8426(1)	2479(1)	204(1)	56(1)
C(16)	9393(1)	2735(1)	595(1)	69(1)
C(17)	10189(1)	2349(1)	1051(1)	66(1)
C(18)	10030(1)	1716(1)	1130(1)	45(1)
C(19)	7291(1)	-145(1)	3023(1)	39(1)
C(20)	6327(1)	158(1)	2943(1)	53(1)
C(21)	5651(1)	3(1)	3586(1)	66(1)
C(22)	5919(1)	-441(1)	4335(1)	68(1)
C(23)	6866(1)	-726(1)	4451(1)	66(1)
C(24)	7544(1)	-582(1)	3814(1)	53(1)
C(25)	12242(1)	2316(1)	7532(1)	77(1)
C(26)	11968(1)	2980(1)	7554(1)	94(1)
C(27)	11290(1)	3008(1)	8340(1)	100(1)
C(28)	10758(1)	2385(1)	8234(1)	75(1)
C(29)	4982(1)	951(1)	27(1)	62(1)
C(30)	4360(1)	1195(1)	-967(1)	68(1)
C(31)	5144(1)	1282(1)	-1631(1)	65(1)
C(32)	5915(1)	768(1)	-1268(1)	55(1)
C(33)	9367(1)	1066(1)	4677(1)	73(1)
C(34)	9489(1)	1659(1)	5273(1)	93(1)
C(35)	10252(1)	2012(1)	4897(1)	120(1)
C(36)	10383(1)	1750(1)	3941(1)	92(1)

Table 3. Bond lengths [Å] and angles [°] for **24**.

Ba-O(1)	2.6941(5)	Na(1)-O(2)	2.2812(6)
Ba-O(1)#1	2.6941(5)	Na(1)-O(4)	2.3148(7)
Ba-O(2)	2.7318(5)	Na(1)-O(5)#2	2.3151(6)
Ba-O(2)#1	2.7318(5)	O(5)-Na(1)#2	2.3151(6)
Ba-O(3)	2.6699(5)	Na(2)-O(2)	2.2925(6)
Ba-O(3)#1	2.6699(5)	Na(2)-O(3)	2.2628(6)
Ba-Na(1)	3.7750(3)	Na(2)-O(4)	2.2723(6)
Ba-Na(1)#1	3.7750(3)	Na(2)-O(6)	2.2637(6)
Ba-Na(2)	3.7453(3)	Na(3)-O(1)	2.2795(6)
Ba-Na(2)#1	3.7453(3)	Na(3)-O(3)	2.3040(6)
Ba-Na(3)	3.7059(3)	Na(3)-O(4)	2.2564(6)
Ba-Na(3)#1	3.7059(3)	Na(3)-O(7)	2.2609(7)
Na(1)-O(1)	2.3051(6)	Na(1)-Na(2)	3.2081(4)

Na(1)-Na(3)	3.2303(4)	C(10)-C(11)	1.3782(12)
Na(2)-Na(3)	3.1768(4)	C(11)-C(12)	1.3832(11)
Na(1)-C(1)	3.1234(7)	C(7)-C(12)	1.4007(10)
Na(1)-C(19)	3.1158(8)	C(13)-C(14)	1.3969(9)
Na(3)-C(13)	3.0644(7)	C(14)-C(15)	1.3805(11)
O(1)-C(1)	1.3283(8)	C(15)-C(16)	1.3771(12)
O(2)-C(7)	1.3320(8)	C(16)-C(17)	1.3692(12)
O(3)-C(13)	1.3256(8)	C(17)-C(18)	1.3799(11)
O(4)-C(19)	1.3090(10)	C(13)-C(18)	1.3907(9)
O(5)-C(25)	1.4262(13)	C(19)-C(20)	1.4010(11)
O(5)-C(28)	1.4292(13)	C(20)-C(21)	1.3891(13)
O(7)-C(36)	1.4211(13)	C(21)-C(22)	1.3711(13)
O(7)-C(33)	1.4241(12)	C(22)-C(23)	1.3597(14)
O(6)-C(29)	1.4255(11)	C(23)-C(24)	1.3800(14)
O(6)-C(32)	1.4353(10)	C(19)-C(24)	1.3966(10)
C(1)-C(2)	1.4016(9)	C(25)-C(26)	1.4686(15)
C(2)-C(3)	1.3755(11)	C(26)-C(27)	1.502(2)
C(3)-C(4)	1.3823(12)	C(27)-C(28)	1.4975(15)
C(4)-C(5)	1.3821(11)	C(29)-C(30)	1.4974(12)
C(5)-C(6)	1.3836(10)	C(30)-C(31)	1.4954(14)
C(1)-C(6)	1.4002(10)	C(31)-C(32)	1.5034(13)
C(7)-C(8)	1.3953(10)	C(33)-C(34)	1.4904(15)
C(8)-C(9)	1.3833(11)	C(34)-C(35)	1.421(2)
C(9)-C(10)	1.3779(13)	C(35)-C(36)	1.4328(17)

O(3)#1-Ba-O(3)	180.00(3)	O(1)-Ba-O(2)#1	106.235(15)
O(3)#1-Ba-O(1)#1	75.457(16)	O(2)-Ba-O(2)#1	180.000(18)
O(3)-Ba-O(1)#1	104.543(16)	O(3)#1-Ba-Na(3)#1	38.188(12)
O(3)#1-Ba-O(1)	104.543(16)	O(3)-Ba-Na(3)#1	141.812(12)
O(3)-Ba-O(1)	75.457(16)	O(1)#1-Ba-Na(3)#1	37.715(12)
O(1)#1-Ba-O(1)	180.00(3)	O(1)-Ba-Na(3)#1	142.285(12)
O(3)#1-Ba-O(2)	105.999(15)	O(2)-Ba-Na(3)#1	106.090(12)
O(3)-Ba-O(2)	74.001(16)	O(2)#1-Ba-Na(3)#1	73.910(12)
O(1)#1-Ba-O(2)	106.235(15)	O(3)#1-Ba-Na(3)	141.812(12)
O(1)-Ba-O(2)	73.765(15)	O(3)-Ba-Na(3)	38.188(12)
O(3)#1-Ba-O(2)#1	74.001(15)	O(1)#1-Ba-Na(3)	142.285(12)
O(3)-Ba-O(2)#1	105.999(15)	O(1)-Ba-Na(3)	37.715(12)
O(1)#1-Ba-O(2)#1	73.765(15)	O(2)-Ba-Na(3)	73.910(12)

O(2)#1-Ba-Na(3)	106.090(12)
Na(3)#1-Ba-Na(3)	180.000(12)
O(3)#1-Ba-Na(2)#1	36.698(12)
O(3)-Ba-Na(2)#1	143.302(12)
O(1)#1-Ba-Na(2)#1	73.511(12)
O(1)-Ba-Na(2)#1	106.489(12)
O(2)-Ba-Na(2)#1	142.501(12)
O(2)#1-Ba-Na(2)#1	37.499(12)
Na(3)#1-Ba-Na(2)#1	50.469(7)
Na(3)-Ba-Na(2)#1	129.531(7)
O(3)#1-Ba-Na(2)	143.303(12)
O(3)-Ba-Na(2)	36.698(12)
O(1)#1-Ba-Na(2)	106.489(12)
O(1)-Ba-Na(2)	73.511(12)
O(2)-Ba-Na(2)	37.499(12)
O(2)#1-Ba-Na(2)	142.501(12)
Na(3)#1-Ba-Na(2)	129.531(7)
Na(3)-Ba-Na(2)	50.469(7)
Na(2)#1-Ba-Na(2)	180.000(8)
O(3)#1-Ba-Na(1)	105.678(13)
O(3)-Ba-Na(1)	74.322(13)
O(1)#1-Ba-Na(1)	142.769(11)
O(1)-Ba-Na(1)	37.231(11)
O(2)-Ba-Na(1)	36.827(11)
O(2)#1-Ba-Na(1)	143.173(11)
Na(3)#1-Ba-Na(1)	128.845(7)
Na(3)-Ba-Na(1)	51.155(7)
Na(2)#1-Ba-Na(1)	129.500(7)
Na(2)-Ba-Na(1)	50.500(7)
O(3)#1-Ba-Na(1)#1	74.322(13)
O(3)-Ba-Na(1)#1	105.678(13)
O(1)#1-Ba-Na(1)#1	37.231(11)
O(1)-Ba-Na(1)#1	142.769(11)
O(2)-Ba-Na(1)#1	143.173(11)
O(2)#1-Ba-Na(1)#1	36.827(11)
Na(3)#1-Ba-Na(1)#1	51.155(7)
Na(3)-Ba-Na(1)#1	128.845(7)
Na(2)#1-Ba-Na(1)#1	50.500(7)
Na(2)-Ba-Na(1)#1	129.499(7)
Na(1)-Ba-Na(1)#1	180.000(10)
O(2)-Na(1)-O(1)	90.48(2)
O(2)-Na(1)-O(4)	90.69(2)
O(1)-Na(1)-O(4)	89.17(2)
O(2)-Na(1)-O(5)#2	117.41(2)
O(1)-Na(1)-O(5)#2	124.85(2)
O(4)-Na(1)-O(5)#2	132.74(3)
O(2)-Na(1)-C(19)	104.82(2)
O(1)-Na(1)-C(19)	105.84(2)
O(4)-Na(1)-C(19)	22.23(2)
O(5)#2-Na(1)-C(19)	110.51(2)
O(2)-Na(1)-C(1)	107.40(2)
O(1)-Na(1)-C(1)	22.486(17)
O(4)-Na(1)-C(1)	103.35(2)
O(5)#2-Na(1)-C(1)	103.00(2)
C(19)-Na(1)-C(1)	113.998(19)
O(2)-Na(1)-Na(2)	45.604(15)
O(1)-Na(1)-Na(2)	89.816(16)
O(4)-Na(1)-Na(2)	45.085(15)
O(5)#2-Na(1)-Na(2)	144.132(19)
C(19)-Na(1)-Na(2)	61.271(15)
C(1)-Na(1)-Na(2)	112.204(16)
O(2)-Na(1)-Na(3)	89.792(16)
O(1)-Na(1)-Na(3)	44.880(15)
O(4)-Na(1)-Na(3)	44.308(16)
O(5)#2-Na(1)-Na(3)	152.418(19)
C(19)-Na(1)-Na(3)	62.746(15)
C(1)-Na(1)-Na(3)	61.504(14)
Na(2)-Na(1)-Na(3)	59.130(9)
O(2)-Na(1)-Ba	45.874(14)
O(1)-Na(1)-Ba	45.002(14)
O(4)-Na(1)-Ba	94.664(17)
O(5)#2-Na(1)-Ba	132.41(2)
C(19)-Na(1)-Ba	116.835(15)
C(1)-Na(1)-Ba	62.007(14)
Na(2)-Na(1)-Ba	64.270(8)
Na(3)-Na(1)-Ba	63.318(8)

O(3)-Na(2)-O(6)	117.46(2)
O(3)-Na(2)-O(4)	91.69(2)
O(6)-Na(2)-O(4)	133.63(3)
O(3)-Na(2)-O(2)	91.08(2)
O(6)-Na(2)-O(2)	120.84(2)
O(4)-Na(2)-O(2)	91.48(2)
O(3)-Na(2)-Na(3)	46.459(15)
O(6)-Na(2)-Na(3)	146.75(2)
O(4)-Na(2)-Na(3)	45.250(16)
O(2)-Na(2)-Na(3)	90.934(15)
O(3)-Na(2)-Na(1)	92.051(16)
O(6)-Na(2)-Na(1)	149.33(2)
O(4)-Na(2)-Na(1)	46.169(16)
O(2)-Na(2)-Na(1)	45.316(14)
Na(3)-Na(2)-Na(1)	60.784(9)
O(3)-Na(2)-Ba	44.837(14)
O(6)-Na(2)-Ba	130.06(2)
O(4)-Na(2)-Ba	96.203(17)
O(2)-Na(2)-Ba	46.503(14)
Na(3)-Na(2)-Ba	64.123(8)
Na(1)-Na(2)-Ba	65.229(8)
O(4)-Na(3)-O(7)	116.30(3)
O(4)-Na(3)-O(1)	91.28(2)
O(7)-Na(3)-O(1)	134.79(2)
O(4)-Na(3)-O(3)	91.04(2)
O(7)-Na(3)-O(3)	120.96(2)
O(1)-Na(3)-O(3)	91.47(2)
O(4)-Na(3)-C(13)	106.42(2)
O(7)-Na(3)-C(13)	97.67(2)
O(1)-Na(3)-C(13)	108.41(2)
O(3)-Na(3)-C(13)	23.579(17)
O(4)-Na(3)-Na(2)	45.659(15)
O(7)-Na(3)-Na(2)	134.00(2)
O(1)-Na(3)-Na(2)	91.066(15)
O(3)-Na(3)-Na(2)	45.391(15)
C(13)-Na(3)-Na(2)	63.287(14)
O(4)-Na(3)-Na(1)	45.773(17)
O(7)-Na(3)-Na(1)	146.20(2)
O(1)-Na(3)-Na(1)	45.526(15)
O(3)-Na(3)-Na(1)	90.724(15)
C(13)-Na(3)-Na(1)	114.279(15)
Na(2)-Na(3)-Na(1)	60.085(9)
O(4)-Na(3)-Ba	97.574(17)
O(7)-Na(3)-Ba	145.04(2)
O(1)-Na(3)-Ba	46.304(14)
O(3)-Na(3)-Ba	45.760(14)
C(13)-Na(3)-Ba	62.600(14)
Na(2)-Na(3)-Ba	65.408(8)
Na(1)-Na(3)-Ba	65.528(8)
C(1)-O(1)-Na(3)	126.51(4)
C(1)-O(1)-Na(1)	115.93(4)
Na(3)-O(1)-Na(1)	89.59(2)
C(1)-O(1)-Ba	123.16(4)
Na(3)-O(1)-Ba	95.980(18)
Na(1)-O(1)-Ba	97.767(18)
C(7)-O(2)-Na(1)	128.76(4)
C(7)-O(2)-Na(2)	122.76(4)
Na(1)-O(2)-Na(2)	89.08(2)
C(7)-O(2)-Ba	115.43(4)
Na(1)-O(2)-Ba	97.299(18)
Na(2)-O(2)-Ba	95.997(18)
C(13)-O(3)-Na(2)	129.96(4)
C(13)-O(3)-Na(3)	112.37(4)
Na(2)-O(3)-Na(3)	88.15(2)
C(13)-O(3)-Ba	122.34(5)
Na(2)-O(3)-Ba	98.466(19)
Na(3)-O(3)-Ba	96.052(18)
C(19)-O(4)-Na(3)	134.22(4)
C(19)-O(4)-Na(2)	126.20(4)
Na(3)-O(4)-Na(2)	89.09(2)
C(19)-O(4)-Na(1)	115.79(5)
Na(3)-O(4)-Na(1)	89.92(2)
Na(2)-O(4)-Na(1)	88.75(2)
C(25)-O(5)-C(28)	108.75(7)
C(25)-O(5)-Na(1)#2	131.37(6)
C(28)-O(5)-Na(1)#2	119.26(6)

C(36)-O(7)-C(33)	109.51(8)
C(36)-O(7)-Na(3)	133.32(6)
C(33)-O(7)-Na(3)	116.46(5)
C(29)-O(6)-C(32)	109.55(6)
C(29)-O(6)-Na(2)	136.06(5)
C(32)-O(6)-Na(2)	114.36(5)
O(1)-C(1)-C(6)	121.13(6)
O(1)-C(1)-C(2)	121.77(6)
C(6)-C(1)-C(2)	117.09(6)
O(1)-C(1)-Na(1)	41.58(3)
C(6)-C(1)-Na(1)	97.18(4)
C(2)-C(1)-Na(1)	131.34(5)
C(3)-C(2)-C(1)	121.27(7)
C(2)-C(3)-C(4)	120.99(7)
C(5)-C(4)-C(3)	118.73(7)
C(4)-C(5)-C(6)	120.75(7)
C(5)-C(6)-C(1)	121.16(6)
O(2)-C(7)-C(8)	121.36(6)
O(2)-C(7)-C(12)	121.54(6)
C(8)-C(7)-C(12)	117.10(6)
C(9)-C(8)-C(7)	121.43(7)
C(10)-C(9)-C(8)	120.72(8)
C(9)-C(10)-C(11)	118.73(8)
C(10)-C(11)-C(12)	121.12(8)
C(11)-C(12)-C(7)	120.90(7)
O(3)-C(13)-C(18)	120.54(6)
O(3)-C(13)-C(14)	122.24(6)
C(18)-C(13)-C(14)	117.22(6)
O(3)-C(13)-Na(3)	44.05(3)
C(18)-C(13)-Na(3)	90.63(4)
C(14)-C(13)-Na(3)	137.48(5)
C(15)-C(14)-C(13)	120.98(7)
C(16)-C(15)-C(14)	120.82(7)
C(17)-C(16)-C(15)	118.79(8)
C(16)-C(17)-C(18)	121.04(8)
C(17)-C(18)-C(13)	121.14(7)
O(4)-C(19)-C(24)	121.69(7)
O(4)-C(19)-C(20)	122.26(6)
C(24)-C(19)-C(20)	116.04(7)
O(4)-C(19)-Na(1)	41.98(3)
C(24)-C(19)-Na(1)	88.26(5)
C(20)-C(19)-Na(1)	143.83(5)
C(21)-C(20)-C(19)	121.06(8)
C(22)-C(21)-C(20)	120.90(8)
C(23)-C(22)-C(21)	119.12(9)
C(22)-C(23)-C(24)	120.73(8)
C(23)-C(24)-C(19)	122.06(8)
O(5)-C(25)-C(26)	108.27(10)
C(25)-C(26)-C(27)	103.45(10)
C(28)-C(27)-C(26)	103.15(10)
O(5)-C(28)-C(27)	106.01(9)
O(6)-C(29)-C(30)	106.60(8)
C(31)-C(30)-C(29)	104.53(7)
C(30)-C(31)-C(32)	102.31(8)
O(6)-C(32)-C(31)	104.94(7)
O(7)-C(33)-C(34)	106.01(9)
C(35)-C(34)-C(33)	105.87(10)
C(34)-C(35)-C(36)	108.84(10)
O(7)-C(36)-C(35)	107.32(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z #2 -x+2,-y,-z+1

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **24**.

The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ba	41(1)	57(1)	37(1)	1(1)	16(1)	1(1)
Na(1)	54(1)	37(1)	44(1)	5(1)	8(1)	-3(1)
Na(2)	35(1)	48(1)	49(1)	3(1)	6(1)	3(1)
Na(3)	53(1)	43(1)	39(1)	-7(1)	8(1)	0(1)
O(1)	39(1)	48(1)	43(1)	3(1)	2(1)	6(1)
O(2)	49(1)	42(1)	39(1)	-6(1)	3(1)	-7(1)
O(3)	49(1)	33(1)	54(1)	4(1)	8(1)	-3(1)
O(4)	54(1)	65(1)	47(1)	0(1)	25(1)	-3(1)
O(5)	70(1)	42(1)	65(1)	8(1)	15(1)	0(1)
O(7)	93(1)	71(1)	53(1)	-25(1)	31(1)	-30(1)
O(6)	38(1)	74(1)	57(1)	13(1)	7(1)	9(1)
C(1)	37(1)	36(1)	35(1)	5(1)	9(1)	1(1)
C(2)	50(1)	39(1)	38(1)	0(1)	3(1)	-1(1)
C(3)	53(1)	53(1)	48(1)	5(1)	-6(1)	-4(1)
C(4)	48(1)	55(1)	63(1)	13(1)	0(1)	10(1)
C(5)	56(1)	41(1)	60(1)	5(1)	20(1)	10(1)
C(6)	45(1)	40(1)	37(1)	0(1)	12(1)	-2(1)
C(7)	32(1)	39(1)	37(1)	-4(1)	8(1)	1(1)
C(8)	41(1)	43(1)	42(1)	0(1)	9(1)	0(1)
C(9)	55(1)	71(1)	38(1)	-4(1)	7(1)	-1(1)
C(10)	65(1)	73(1)	50(1)	-24(1)	10(1)	-16(1)
C(11)	59(1)	45(1)	65(1)	-16(1)	19(1)	-14(1)
C(12)	44(1)	39(1)	47(1)	-3(1)	13(1)	-5(1)
C(13)	41(1)	33(1)	35(1)	0(1)	14(1)	2(1)
C(14)	42(1)	41(1)	49(1)	-2(1)	6(1)	4(1)
C(15)	57(1)	42(1)	70(1)	4(1)	14(1)	15(1)
C(16)	67(1)	33(1)	109(1)	4(1)	20(1)	2(1)
C(17)	47(1)	43(1)	105(1)	-2(1)	10(1)	-8(1)
C(18)	38(1)	39(1)	60(1)	3(1)	11(1)	3(1)
C(19)	41(1)	41(1)	37(1)	-5(1)	11(1)	-2(1)
C(20)	54(1)	60(1)	43(1)	-8(1)	9(1)	12(1)
C(21)	45(1)	94(1)	63(1)	-32(1)	17(1)	1(1)
C(22)	78(1)	71(1)	67(1)	-26(1)	44(1)	-29(1)

C(23)	109(1)	45(1)	53(1)	-1(1)	36(1)	-9(1)
C(24)	65(1)	48(1)	49(1)	2(1)	18(1)	11(1)
C(25)	79(1)	67(1)	87(1)	22(1)	21(1)	-6(1)
C(26)	120(1)	61(1)	102(1)	13(1)	26(1)	-19(1)
C(27)	116(1)	53(1)	135(1)	-15(1)	36(1)	-10(1)
C(28)	72(1)	51(1)	102(1)	-6(1)	20(1)	1(1)
C(29)	50(1)	74(1)	63(1)	7(1)	16(1)	12(1)
C(30)	50(1)	90(1)	61(1)	1(1)	6(1)	21(1)
C(31)	79(1)	65(1)	51(1)	8(1)	12(1)	21(1)
C(32)	48(1)	62(1)	56(1)	-2(1)	11(1)	5(1)
C(33)	91(1)	77(1)	57(1)	-16(1)	31(1)	-26(1)
C(34)	115(1)	92(1)	80(1)	-39(1)	40(1)	-19(1)
C(35)	222(1)	64(1)	82(1)	-25(1)	50(1)	-49(1)
C(36)	116(1)	89(1)	78(1)	-28(1)	37(1)	-53(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **24**.

	x	y	z	U(eq)
H(2)	11444	-27	3661	51
H(3)	12921	-531	4536	64
H(4)	13470	-1469	3926	68
H(5)	12519	-1888	2397	62
H(6)	11026	-1392	1512	48
H(8)	7646	-190	-1720	50
H(9)	6905	-759	-3167	66
H(10)	6470	-1807	-3029	75
H(11)	6783	-2275	-1416	67
H(12)	7558	-1721	38	52
H(14)	7579	1681	17	53
H(15)	7871	2741	-126	67
H(16)	9505	3171	550	83
H(17)	10860	2520	1318	79
H(18)	10596	1458	1446	54
H(20)	6133	475	2441	63
H(21)	4994	208	3506	80
H(22)	5449	-548	4766	81

H(23)	7063	-1029	4977	80
H(24)	8203	-785	3917	64
H(25A)	12270	2189	6823	92
H(25B)	12938	2242	7975	92
H(26A)	11580	3122	6874	113
H(26B)	12602	3241	7763	113
H(27A)	11717	3065	9039	120
H(27B)	10776	3352	8189	120
H(28A)	10612	2248	8901	89
H(28B)	10089	2407	7727	89
H(29A)	5134	1291	540	74
H(29B)	4590	619	302	74
H(30A)	3814	892	-1278	81
H(30B)	4020	1596	-861	81
H(31A)	5481	1697	-1523	78
H(31B)	4819	1232	-2367	78
H(32A)	5688	373	-1632	66
H(32B)	6617	879	-1386	66
H(33A)	9715	718	5103	87
H(33B)	8617	962	4443	87
H(34A)	8816	1888	5167	111
H(34B)	9725	1574	6016	111
H(35A)	10925	2002	5399	144
H(35B)	10023	2452	4797	144
H(36A)	10089	2034	3367	110
H(36B)	11135	1686	3946	110

Crystal data and structure refinement for $[\{Ca(dme)\}_2(OPh)_6\{Li(dme)\}_2]$ 25

$C_{52}H_{70}Li_2Ca_2O_{14}$, M= 1013.12 gmol^{-1}, triclinic, *P*-1 (Nr. 2), a = 10.9810(14), b = 11.1620(16), c = 14.197(2) Å, α = 103.438(11), β = 99.261(11), γ = 117.736(9)°, V = 1423.0(3) Å^3, Z = 1, $\rho_{calcd.}$= 1.182 Mgm^3, *F*(000) = 540, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.259 mm^{-1}, 1.55° < θ < 27.17°, 11354 reflections of which 5814 unique and 2164 observed, 321 parameters refined, *GOOF* (on F^2) = 0.922, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.0750, *w*R2 = 0.1659 for I > 2σ(I) and R1 = 0.1885, wR2 = 0.2241 for all data.

The intensities from the single-crystals of **25** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms. CCDC-296414 (**25**) contains the supplementary crystallographic data for **25**. The cif file for the structure of **25** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **25**.

Identification code	$[\{Ca(dme)\}_2(OPh)_6\{Li(dme)\}_2]$	
Empirical formula	C52 H70 Ca2 Li2 O14	
Formula weight	1013.12	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.9810(14) Å	α= 103.438(11)°
	b = 11.1620(16) Å	β= 99.261(11)°
	c = 14.197(2) Å	γ = 117.736(9)°
Volume	1423.0(3) Å^3	
Z	1	
Density (calculated)	1.182 Mg/m^3	
Absorption coefficient	0.259 mm^{-1}	
F(000)	540	
Theta range for data collection	1.55 to 27.17°	
Index ranges	-14<=h<=14, -14<=k<=14, -18<=l<=18	
Reflections collected	11354	
Independent reflections	5814 [R(int) = 0.1214]	
Completeness to theta = 27.17°	92.0 %	
Max. and min. transmission	0.9756 and 0.8822	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5814 / 0 / 321	
Goodness-of-fit on F^2	0.922	
Final R indices [I>2sigma(I)]	R1 = 0.0750, wR2 = 0.1659	
R indices (all data)	R1 = 0.1885, wR2 = 0.2241	
Largest diff. peak and hole	0.411 and -0.706 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **25**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ca	859(1)	6768(1)	948(1)	46(1)
Li	1591(3)	8268(3)	3181(2)	78(1)
O(1)	163(1)	7669(1)	-310(1)	56(1)
O(2)	2919(1)	8984(1)	952(1)	60(1)
O(3)	-1299(1)	4610(1)	267(1)	54(1)
O(4)	399(1)	8205(1)	2062(1)	61(1)
O(5)	2080(1)	6994(1)	2487(1)	66(1)
O(6)	706(2)	8231(2)	4323(1)	132(1)
O(7)	3205(2)	10090(2)	4197(1)	135(1)
C(1)	-1317(2)	7211(2)	-712(1)	73(1)
C(2)	1118(2)	9186(1)	-28(1)	60(1)
C(3)	2603(2)	9472(1)	159(1)	66(1)
C(4)	4371(2)	9333(2)	1235(1)	79(1)
C(5)	-2253(1)	4230(1)	778(1)	52(1)
C(6)	-1922(2)	3959(2)	1658(1)	76(1)
C(7)	-2912(2)	3566(2)	2196(2)	111(1)
C(8)	-4167(2)	3458(2)	1872(2)	127(1)
C(9)	-4541(2)	3726(2)	1006(2)	110(1)
C(10)	-3580(2)	4106(2)	446(1)	77(1)
C(11)	-279(1)	8904(1)	2165(1)	52(1)
C(12)	-1786(2)	8175(2)	1865(1)	70(1)
C(13)	-2494(2)	8899(2)	1966(1)	86(1)
C(14)	-1750(2)	10374(2)	2362(1)	87(1)
C(15)	-269(2)	11138(2)	2657(1)	72(1)
C(16)	452(2)	10409(1)	2556(1)	59(1)
C(17)	2733(2)	6409(1)	2891(1)	64(1)
C(18)	3870(2)	6388(2)	2635(1)	75(1)
C(19)	4555(2)	5793(2)	3029(2)	108(1)
C(20)	4075(2)	5142(2)	3712(2)	132(1)
C(21)	2967(3)	5146(2)	4013(2)	127(1)
C(22)	2264(2)	5780(2)	3610(1)	93(1)
C(23)	-669(4)	7248(3)	4249(2)	214(2)

C(24)	1591(5)	9424(4)	5063(2)	293(3)
C(25)	2845(3)	10443(3)	5078(2)	169(2)
C(26)	4416(3)	11085(4)	4101(3)	208(2)

Table 3. Bond lengths [Å] and angles [°] for **25**.

Ca-Ca#1	3.5882(9)	O(6)-C(23)	1.360(4)
Ca-O(1)	2.4277(11)	O(6)-C(24)	1.279(3)
Ca-O(2)	2.4528(10)	O(7)-C(25)	1.396(3)
Ca-O(3)	2.2845(9)	O(7)-C(26)	1.332(4)
Ca-O(3)#1	2.3016(11)	C(2)-C(3)	1.473(2)
O(3)-Ca#1	2.3016(11)	C(5)-C(6)	1.385(2)
Ca-O(4)	2.2729(11)	C(6)-C(7)	1.391(3)
Ca-O(5)	2.2631(11)	C(7)-C(8)	1.319(4)
Ca-Li	2.994(3)	C(8)-C(9)	1.376(4)
Li-O(4)	1.853(3)	C(9)-C(10)	1.390(3)
Li-O(5)	1.875(4)	C(5)-C(10)	1.388(2)
Li-O(6)	2.019(4)	C(11)-C(12)	1.3931(19)
Li-O(7)	1.953(2)	C(12)-C(13)	1.360(3)
Ca-C(2)	3.2299(17)	C(13)-C(14)	1.365(2)
Ca-C(5)	3.1891(13)	C(14)-C(15)	1.368(2)
Li-C(11)	2.770(4)	C(15)-C(16)	1.375(3)
Li-C(24)	2.682(5)	C(11)-C(16)	1.3944(18)
Li-C(25)	2.774(3)	C(17)-C(18)	1.364(3)
O(1)-C(1)	1.4216(18)	C(18)-C(19)	1.350(3)
O(1)-C(2)	1.4226(14)	C(19)-C(20)	1.372(3)
O(2)-C(3)	1.420(2)	C(20)-C(21)	1.354(4)
O(2)-C(4)	1.4133(19)	C(21)-C(22)	1.407(4)
O(3)-C(5)	1.3335(18)	C(17)-C(22)	1.403(3)
O(4)-C(11)	1.306(2)	C(24)-C(25)	1.308(5)
O(5)-C(17)	1.321(2)		

O(5)-Ca-O(4)	76.81(4)	O(5)-Ca-O(1)	154.58(3)
O(5)-Ca-O(3)	110.27(4)	O(4)-Ca-O(1)	86.62(4)
O(4)-Ca-O(3)	103.62(4)	O(3)-Ca-O(1)	92.15(4)
O(5)-Ca-O(3)#1	107.00(4)	O(3)#1-Ca-O(1)	89.15(4)
O(4)-Ca-O(3)#1	175.74(4)	O(5)-Ca-O(2)	91.99(4)
O(3)-Ca-O(3)#1	77.04(4)	O(4)-Ca-O(2)	87.53(4)

O(3)-Ca-O(2)	156.74(4)	O(7)-Li-O(6)	82.76(12)
O(3)#1-Ca-O(2)	90.40(4)	O(4)-Li-C(24)	119.8(2)
O(1)-Ca-O(2)	67.86(3)	O(5)-Li-C(24)	139.8(2)
O(5)-Ca-Li	38.72(8)	O(7)-Li-C(24)	55.66(12)
O(4)-Ca-Li	38.19(8)	O(6)-Li-C(24)	27.18(9)
O(3)-Ca-Li	113.87(6)	O(4)-Li-C(11)	23.67(7)
O(3)#1-Ca-Li	145.45(8)	O(5)-Li-C(11)	121.85(12)
O(1)-Ca-Li	121.50(8)	O(7)-Li-C(11)	107.09(16)
O(2)-Ca-Li	87.57(6)	O(6)-Li-C(11)	90.67(15)
O(5)-Ca-C(5)	97.54(4)	C(24)-Li-C(11)	96.45(17)
O(4)-Ca-C(5)	84.70(4)	O(4)-Li-C(25)	123.90(18)
O(3)-Ca-C(5)	20.92(4)	O(5)-Li-C(25)	134.29(17)
O(3)#1-Ca-C(5)	96.56(4)	O(7)-Li-C(25)	28.08(9)
O(1)-Ca-C(5)	100.01(4)	O(6)-Li-C(25)	54.85(9)
O(2)-Ca-C(5)	166.00(4)	C(24)-Li-C(25)	27.67(11)
Li-Ca-C(5)	93.45(6)	C(11)-Li-C(25)	101.60(14)
O(5)-Ca-C(2)	130.76(3)	O(4)-Li-Ca	49.32(7)
O(4)-Ca-C(2)	76.16(4)	O(5)-Li-Ca	49.04(7)
O(3)-Ca-C(2)	115.65(4)	O(7)-Li-Ca	134.66(15)
O(3)#1-Ca-C(2)	99.72(4)	O(6)-Li-Ca	141.80(11)
O(1)-Ca-C(2)	24.22(3)	C(24)-Li-Ca	166.58(17)
O(2)-Ca-C(2)	46.66(4)	C(11)-Li-Ca	72.98(7)
Li-Ca-C(2)	103.70(7)	C(25)-Li-Ca	160.74(13)
C(5)-Ca-C(2)	119.84(4)	C(1)-O(1)-C(2)	113.12(13)
O(5)-Ca-Ca#1	114.09(3)	C(1)-O(1)-Ca	119.67(9)
O(4)-Ca-Ca#1	142.15(3)	C(2)-O(1)-Ca	111.35(8)
O(3)-Ca-Ca#1	38.69(3)	C(4)-O(2)-C(3)	112.61(13)
O(3)#1-Ca-Ca#1	38.35(2)	C(4)-O(2)-Ca	124.17(10)
O(1)-Ca-Ca#1	90.82(3)	C(3)-O(2)-Ca	114.36(7)
O(2)-Ca-Ca#1	126.12(3)	C(5)-O(3)-Ca	121.38(7)
Li-Ca-Ca#1	141.81(6)	C(5)-O(3)-Ca#1	131.09(7)
C(5)-Ca-Ca#1	58.57(3)	Ca-O(3)-Ca#1	102.96(4)
C(2)-Ca-Ca#1	112.58(3)	C(11)-O(4)-Li	121.60(13)
O(4)-Li-O(5)	98.22(13)	C(11)-O(4)-Ca	145.89(8)
O(4)-Li-O(7)	122.18(19)	Li-O(4)-Ca	92.49(12)
O(5)-Li-O(7)	115.87(18)	C(17)-O(5)-Li	127.00(13)
O(4)-Li-O(6)	109.60(18)	C(17)-O(5)-Ca	140.10(9)
O(5)-Li-O(6)	130.57(19)	Li-O(5)-Ca	92.23(10)

C(24)-O(6)-C(23)	126.6(3)	C(12)-C(11)-C(16)	116.25(16)
C(24)-O(6)-Li	106.7(2)	O(4)-C(11)-Li	34.73(8)
C(23)-O(6)-Li	125.81(16)	C(12)-C(11)-Li	129.88(13)
C(26)-O(7)-C(25)	118.4(2)	C(16)-C(11)-Li	103.88(10)
C(26)-O(7)-Li	129.8(2)	C(13)-C(12)-C(11)	121.45(13)
C(25)-O(7)-Li	110.73(17)	C(12)-C(13)-C(14)	121.00(16)
O(1)-C(2)-C(3)	107.52(14)	C(13)-C(14)-C(15)	119.7(2)
O(1)-C(2)-Ca	44.43(7)	C(14)-C(15)-C(16)	119.49(14)
C(3)-C(2)-Ca	79.74(9)	C(15)-C(16)-C(11)	122.10(13)
O(2)-C(3)-C(2)	109.34(13)	O(5)-C(17)-C(18)	122.37(16)
O(3)-C(5)-C(6)	119.89(15)	O(5)-C(17)-C(22)	120.11(18)
O(3)-C(5)-C(10)	121.17(15)	C(18)-C(17)-C(22)	117.51(19)
C(6)-C(5)-C(10)	118.94(16)	C(19)-C(18)-C(17)	123.80(19)
O(3)-C(5)-Ca	37.70(4)	C(18)-C(19)-C(20)	118.9(2)
C(6)-C(5)-Ca	100.69(8)	C(21)-C(20)-C(19)	120.4(3)
C(10)-C(5)-Ca	127.79(11)	C(20)-C(21)-C(22)	120.7(2)
C(5)-C(6)-C(7)	120.15(19)	C(17)-C(22)-C(21)	118.7(2)
C(8)-C(7)-C(6)	120.2(2)	O(6)-C(24)-C(25)	126.2(3)
C(7)-C(8)-C(9)	121.8(2)	O(6)-C(24)-Li	46.12(16)
C(8)-C(9)-C(10)	119.3(2)	C(25)-C(24)-Li	80.1(2)
C(5)-C(10)-C(9)	119.57(19)	C(24)-C(25)-O(7)	113.2(2)
O(4)-C(11)-C(12)	121.33(12)	C(24)-C(25)-Li	72.26(18)
O(4)-C(11)-C(16)	122.41(12)	O(7)-C(25)-Li	41.18(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **25**.
The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ca	42(1)	47(1)	46(1)	15(1)	11(1)	22(1)
Li	77(1)	91(1)	55(1)	17(1)	9(1)	44(1)
O(1)	47(1)	54(1)	61(1)	23(1)	10(1)	21(1)
O(2)	47(1)	63(1)	66(1)	30(1)	15(1)	24(1)
O(3)	41(1)	51(1)	59(1)	15(1)	22(1)	17(1)
O(4)	64(1)	69(1)	54(1)	16(1)	15(1)	41(1)

O(5)	72(1)	76(1)	51(1)	22(1)	8(1)	42(1)
O(6)	180(1)	126(1)	66(1)	15(1)	45(1)	69(1)
O(7)	123(1)	125(1)	75(1)	-15(1)	-3(1)	37(1)
C(1)	54(1)	81(1)	77(1)	33(1)	7(1)	32(1)
C(2)	65(1)	57(1)	59(1)	25(1)	17(1)	30(1)
C(3)	73(1)	64(1)	66(1)	30(1)	24(1)	35(1)
C(4)	43(1)	70(1)	110(1)	30(1)	14(1)	23(1)
C(5)	41(1)	39(1)	64(1)	9(1)	22(1)	13(1)
C(6)	81(1)	68(1)	67(1)	20(1)	35(1)	27(1)
C(7)	130(1)	85(1)	109(1)	33(1)	75(1)	39(1)
C(8)	152(1)	75(1)	159(1)	38(1)	116(1)	43(1)
C(9)	67(1)	66(1)	187(2)	21(1)	68(1)	29(1)
C(10)	56(1)	68(1)	103(1)	22(1)	37(1)	29(1)
C(11)	54(1)	64(1)	45(1)	21(1)	18(1)	34(1)
C(12)	58(1)	79(1)	73(1)	23(1)	23(1)	38(1)
C(13)	69(1)	116(1)	78(1)	31(1)	25(1)	52(1)
C(14)	112(1)	118(1)	75(1)	44(1)	44(1)	83(1)
C(15)	104(1)	68(1)	55(1)	22(1)	28(1)	51(1)
C(16)	67(1)	58(1)	45(1)	13(1)	15(1)	32(1)
C(17)	61(1)	58(1)	52(1)	12(1)	-2(1)	26(1)
C(18)	73(1)	75(1)	70(1)	10(1)	1(1)	46(1)
C(19)	104(1)	97(1)	107(1)	4(1)	-12(1)	69(1)
C(20)	145(1)	104(1)	110(1)	31(1)	-30(1)	63(1)
C(21)	142(2)	107(1)	104(1)	58(1)	-2(1)	46(1)
C(22)	98(1)	97(1)	75(1)	47(1)	15(1)	39(1)
C(23)	228(3)	159(2)	213(2)	70(2)	149(2)	44(2)
C(24)	343(4)	203(4)	104(2)	-34(2)	117(2)	-4(3)
C(25)	204(2)	153(2)	74(1)	-36(1)	-27(2)	94(1)
C(26)	101(2)	189(3)	205(3)	-4(3)	3(2)	28(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **25**.

	x	y	z	U(eq)
H(1A)	-1606	7657	-194	109
H(1B)	-1910	6167	-917	109
H(1C)	-1444	7496	-1298	109

H(2A)	1025	9703	589	72
H(2B)	883	9513	-576	72
H(3A)	2694	8967	-464	79
H(3B)	3293	10511	355	79
H(4A)	4551	8860	656	118
H(4B)	4541	9006	1791	118
H(4C)	5017	10372	1451	118
H(6)	-1027	4041	1893	91
H(7)	-2686	3377	2791	133
H(8)	-4824	3191	2244	153
H(9)	-5437	3652	794	132
H(10)	-3828	4278	-152	92
H(12)	-2324	7159	1587	83
H(13)	-3512	8377	1760	103
H(14)	-2253	10861	2431	105
H(15)	252	12154	2926	87
H(16)	1469	10943	2758	70
H(18)	4195	6812	2156	90
H(19)	5347	5823	2838	130
H(20)	4517	4691	3973	158
H(21)	2665	4721	4496	153
H(22)	1494	5782	3819	112
H(23A)	-752	7313	4926	320
H(23B)	-897	6283	3881	320
H(23C)	-1340	7447	3885	320
H(24A)	1795	9156	5653	352
H(24B)	1042	9890	5209	352
H(25A)	3598	10641	5670	202
H(25B)	2825	11330	5160	202
H(26A)	5065	11791	4769	312
H(26B)	4181	11566	3679	312
H(26C)	4882	10624	3785	312

Crystal data and structure refinement for [{Ca(dme)}$_2$(OPh)$_6${Na(dme)}$_2$] 26

$C_{52}H_{70}Na_2Ca_2O_{14}$, M= 1045.22 gmol^{-1}, monoclinic, $P2_1/n$ (Nr. 14), a = 11.8532(6), b = 14.7474(6), c = 16.7570(9) Å, β = 103.158(4)°, V =2852.3(2) Å^3, Z = 2, $\rho_{calcd.}$=1.217 Mgm^3, F(000) = 1112, T = 203 K, λ =

0.71073 Å, μ(Mo-K$_\alpha$)= 0.274 mm^{-1}, 2.36° < θ < 27.16°, 21471 reflections of which 5991 unique and 5518 observed, 321 parameters refined, *GOOF* (on F^2) = 1.047, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.0389, *w*R2 = 0.1058 for I > 2σ(I) and R1 = 0.0421, wR2 = 0.1086 for all data.

The intensities from the single-crystals of **26** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms. CCDC-616806 (**26**) contains the supplementary crystallographic data for **26**. The cif file for the structure of **26** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **26**.

Identification code	[{Ca(dme)}$_2$(OPh)$_6${Na(dme)}$_2$]	
Empirical formula	C52 H70 Ca2 Na2 O14	
Formula weight	1045.22	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.8532(6) Å	a= 90°
	b = 14.7474(6) Å	b= 103.158(4)°
	c = 16.7570(9) Å	g = 90°
Volume	2852.3(2) Å^3	
Z	2	
Density (calculated)	1.217 Mg/m^3	
Absorption coefficient	0.274 mm^{-1}	
F(000)	1112	
Theta range for data collection	2.36 to 27.16°	
Index ranges	-15<=h<=14, -18<=k<=18, -21<=l<=21	
Reflections collected	21471	
Independent reflections	5991 [R(int) = 0.0723]	
Completeness to theta = 27.16°	94.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5991 / 0 / 321	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.1058	

R indices (all data)	R1 = 0.0421, wR2 = 0.1086
Largest diff. peak and hole	0.191 and -0.193 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **26**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ca	4464(1)	4231(1)	696(1)	40(1)
Na(1)	3952(1)	6555(1)	670(1)	51(1)
O(1)	5493(1)	3218(1)	1812(1)	62(1)
O(2)	3101(1)	3295(1)	1267(1)	72(1)
O(3)	4487(1)	3069(1)	-159(1)	58(1)
O(4)	4069(1)	5334(1)	1524(1)	55(1)
O(5)	3967(1)	7685(1)	1695(1)	80(1)
O(6)	2361(1)	7611(1)	230(1)	86(1)
O(7)	3820(1)	5308(1)	-363(1)	42(1)
C(1)	3875(1)	2323(1)	-352(1)	50(1)
C(2)	2747(1)	2331(1)	-822(1)	73(1)
C(3)	2130(1)	1537(1)	-1041(1)	82(1)
C(4)	2603(1)	713(1)	-796(1)	72(1)
C(5)	3685(1)	684(1)	-309(1)	76(1)
C(6)	4322(1)	1475(1)	-91(1)	65(1)
C(7)	3902(1)	5425(1)	2269(1)	44(1)
C(8)	4788(1)	5273(1)	2964(1)	61(1)
C(9)	4607(1)	5365(1)	3744(1)	70(1)
C(10)	3543(1)	5618(1)	3865(1)	66(1)
C(11)	2659(1)	5753(1)	3197(1)	68(1)
C(12)	2824(1)	5661(1)	2408(1)	57(1)
C(13)	2781(1)	5089(1)	-827(1)	41(1)
C(14)	2627(1)	4887(1)	-1656(1)	58(1)
C(15)	1541(1)	4685(1)	-2134(1)	75(1)
C(16)	595(1)	4659(1)	-1797(1)	78(1)
C(17)	727(1)	4828(1)	-985(1)	81(1)
C(18)	1808(1)	5050(1)	-496(1)	61(1)
C(19)	6563(1)	2814(1)	1758(1)	78(1)
C(20)	4746(1)	2579(1)	2071(1)	75(1)

C(21)	3628(1)	3016(1)	2077(1)	76(1)
C(22)	1906(1)	3352(1)	1102(1)	117(1)
C(23)	5047(1)	7834(1)	2249(1)	99(1)
C(24)	3420(1)	8471(1)	1352(1)	92(1)
C(25)	2270(1)	8247(1)	836(1)	105(1)
C(26)	1296(1)	7443(1)	-326(1)	139(1)

Table 3. Bond lengths [Å] and angles [°] for **26**.

Ca-Ca#1	3.68164(19)	O(6)-C(25)	1.4033(8)
Ca-O(1)	2.4854(3)	O(6)-C(26)	1.4100(9)
Ca-O(2)	2.4766(4)	O(7)-C(13)	1.3382(4)
Ca-O(3)	2.2378(3)	O(7)-Ca#1	2.3303(3)
Ca-O(4)	2.2536(3)	C(1)-C(2)	1.3883(6)
Ca-O(7)	2.3747(3)	C(2)-C(3)	1.3848(8)
Ca-O(7)#1	2.3303(3)	C(3)-C(4)	1.3623(8)
Ca-C(13)	3.1273(4)	C(4)-C(5)	1.3550(8)
Ca-Na(1)	3.4794(2)	C(5)-C(6)	1.3925(7)
Ca-Na(1)#1	3.4750(2)	C(1)-C(6)	1.3887(6)
Na(1)-Ca#1	3.4750(2)	C(7)-C(8)	1.3967(5)
Na(1)-O(3)#1	2.2784(4)	C(8)-C(9)	1.3779(7)
O(3)-Na(1)#1	2.2784(4)	C(9)-C(10)	1.3747(8)
Na(1)-O(4)	2.2849(3)	C(10)-C(11)	1.3631(7)
Na(1)-O(5)	2.3896(4)	C(11)-C(12)	1.3856(7)
Na(1)-O(6)	2.4271(4)	C(7)-C(12)	1.3938(6)
Na(1)-O(7)	2.5060(3)	C(13)-C(14)	1.3922(6)
O(1)-C(19)	1.4222(7)	C(14)-C(15)	1.3841(7)
O(1)-C(20)	1.4273(7)	C(15)-C(16)	1.3661(9)
O(2)-C(21)	1.4195(6)	C(16)-C(17)	1.3568(9)
O(2)-C(22)	1.3822(7)	C(17)-C(18)	1.3936(7)
O(3)-C(1)	1.3178(5)	C(13)-C(18)	1.3886(6)
O(4)-C(7)	1.3162(5)	C(20)-C(21)	1.4760(8)
O(5)-C(24)	1.3872(7)	C(24)-C(25)	1.4767(10)
O(5)-C(23)	1.4166(8)		

O(3)-Ca-O(4)	168.714(12)	O(3)-Ca-O(7)	94.723(11)
O(3)-Ca-O(7)#1	86.052(11)	O(4)-Ca-O(7)	84.306(10)
O(4)-Ca-O(7)#1	104.615(11)	O(7)#1-Ca-O(7)	77.026(10)

O(3)-Ca-O(2)	85.655(13)
O(4)-Ca-O(2)	85.385(13)
O(7)#1-Ca-O(2)	159.547(11)
O(7)-Ca-O(2)	122.296(11)
O(3)-Ca-O(1)	86.891(11)
O(4)-Ca-O(1)	96.097(11)
O(7)#1-Ca-O(1)	92.848(11)
O(7)-Ca-O(1)	169.586(11)
O(2)-Ca-O(1)	68.059(12)
O(3)-Ca-C(13)	83.431(11)
O(4)-Ca-C(13)	91.545(10)
O(7)#1-Ca-C(13)	96.657(10)
O(7)-Ca-C(13)	23.427(9)
O(2)-Ca-C(13)	100.920(11)
O(1)-Ca-C(13)	165.915(10)
O(3)-Ca-Na(1)#1	40.125(9)
O(4)-Ca-Na(1)#1	149.914(9)
O(7)#1-Ca-Na(1)#1	46.119(7)
O(7)-Ca-Na(1)#1	81.997(8)
O(2)-Ca-Na(1)#1	124.490(10)
O(1)-Ca-Na(1)#1	92.779(10)
C(13)-Ca-Na(1)#1	86.403(9)
O(3)-Ca-Na(1)	140.693(9)
O(4)-Ca-Na(1)	40.279(8)
O(7)#1-Ca-Na(1)	82.491(7)
O(7)-Ca-Na(1)	46.066(7)
O(2)-Ca-Na(1)	115.254(10)
O(1)-Ca-Na(1)	131.004(8)
C(13)-Ca-Na(1)	60.926(7)
Na(1)#1-Ca-Na(1)	116.071(4)
O(3)-Ca-Ca#1	90.546(10)
O(4)-Ca-Ca#1	95.492(9)
O(7)#1-Ca-Ca#1	38.943(6)
O(7)-Ca-Ca#1	38.082(7)
O(2)-Ca-Ca#1	159.666(8)
O(1)-Ca-Ca#1	131.747(9)
C(13)-Ca-Ca#1	58.771(8)
Na(1)#1-Ca-Ca#1	58.094(4)
Na(1)-Ca-Ca#1	57.978(4)
O(3)#1-Na(1)-O(4)	119.221(13)
O(3)#1-Na(1)-O(5)	103.127(15)
O(4)-Na(1)-O(5)	96.342(14)
O(3)#1-Na(1)-O(6)	111.789(15)
O(4)-Na(1)-O(6)	128.952(16)
O(5)-Na(1)-O(6)	69.488(15)
O(3)#1-Na(1)-O(7)	81.180(11)
O(4)-Na(1)-O(7)	80.730(11)
O(5)-Na(1)-O(7)	175.625(15)
O(6)-Na(1)-O(7)	109.809(13)
O(3)#1-Na(1)-Ca#1	39.270(8)
O(4)-Na(1)-Ca#1	100.612(10)
O(5)-Na(1)-Ca#1	142.137(13)
O(6)-Na(1)-Ca#1	120.850(12)
O(7)-Na(1)-Ca#1	42.087(7)
O(3)#1-Na(1)-Ca	95.145(9)
O(4)-Na(1)-Ca	39.616(8)
O(5)-Na(1)-Ca	134.816(11)
O(6)-Na(1)-Ca	139.213(11)
O(7)-Na(1)-Ca	43.033(6)
Ca#1-Na(1)-Ca	63.929(4)
C(19)-O(1)-C(20)	111.49(4)
C(19)-O(1)-Ca	119.76(3)
C(20)-O(1)-Ca	113.17(3)
C(22)-O(2)-C(21)	114.64(5)
C(22)-O(2)-Ca	128.15(4)
C(21)-O(2)-Ca	110.26(3)
C(1)-O(3)-Ca	135.35(3)
C(1)-O(3)-Na(1)#1	124.00(3)
Ca-O(3)-Na(1)#1	100.605(13)
C(7)-O(4)-Ca	139.05(2)
C(7)-O(4)-Na(1)	120.84(2)
Ca-O(4)-Na(1)	100.105(13)
C(24)-O(5)-C(23)	114.13(5)
C(24)-O(5)-Na(1)	111.02(3)
C(23)-O(5)-Na(1)	115.94(4)
C(25)-O(6)-C(26)	113.01(6)

C(25)-O(6)-Na(1)	112.99(3)	C(10)-C(9)-C(8)	120.88(4)
C(26)-O(6)-Na(1)	127.18(4)	C(11)-C(10)-C(9)	118.49(5)
C(13)-O(7)-Ca#1	132.02(2)	C(10)-C(11)-C(12)	121.41(5)
C(13)-O(7)-Ca	111.70(2)	C(11)-C(12)-C(7)	121.11(4)
Ca#1-O(7)-Ca	102.974(10)	O(7)-C(13)-C(18)	121.05(3)
C(13)-O(7)-Na(1)	118.89(2)	O(7)-C(13)-C(14)	121.72(4)
Ca#1-O(7)-Na(1)	91.794(10)	C(18)-C(13)-C(14)	117.23(4)
Ca-O(7)-Na(1)	90.901(10)	O(7)-C(13)-Ca	44.874(16)
O(3)-C(1)-C(2)	122.48(4)	C(18)-C(13)-Ca	95.22(3)
O(3)-C(1)-C(6)	121.64(4)	C(14)-C(13)-Ca	129.99(3)
C(2)-C(1)-C(6)	115.88(4)	C(15)-C(14)-C(13)	121.07(5)
C(3)-C(2)-C(1)	121.65(5)	C(16)-C(15)-C(14)	120.67(5)
C(4)-C(3)-C(2)	121.22(5)	C(17)-C(16)-C(15)	119.38(5)
C(5)-C(4)-C(3)	118.51(5)	C(16)-C(17)-C(18)	120.89(5)
C(4)-C(5)-C(6)	120.98(5)	C(13)-C(18)-C(17)	120.72(5)
C(1)-C(6)-C(5)	121.69(4)	O(1)-C(20)-C(21)	109.45(4)
O(4)-C(7)-C(12)	121.74(3)	O(2)-C(21)-C(20)	108.73(5)
O(4)-C(7)-C(8)	121.81(4)	O(5)-C(24)-C(25)	109.72(5)
C(12)-C(7)-C(8)	116.44(4)	O(6)-C(25)-C(24)	111.17(6)
C(9)-C(8)-C(7)	121.65(5)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **26**.

The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ca	44(1)	38(1)	40(1)	2(1)	12(1)	-1(1)
Na(1)	61(1)	43(1)	50(1)	-2(1)	15(1)	7(1)
O(1)	72(1)	50(1)	60(1)	15(1)	6(1)	-4(1)
O(2)	68(1)	83(1)	73(1)	9(1)	27(1)	-16(1)
O(3)	67(1)	45(1)	64(1)	-13(1)	18(1)	-11(1)
O(4)	72(1)	54(1)	41(1)	-1(1)	19(1)	11(1)
O(5)	106(1)	58(1)	71(1)	-11(1)	9(1)	2(1)
O(6)	93(1)	80(1)	80(1)	-10(1)	7(1)	35(1)
O(7)	39(1)	46(1)	41(1)	1(1)	5(1)	-1(1)

C(1)	59(1)	46(1)	46(1)	-8(1)	18(1)	-8(1)
C(2)	73(1)	61(1)	75(1)	8(1)	-4(1)	-5(1)
C(3)	72(1)	82(1)	77(1)	5(1)	-11(1)	-22(1)
C(4)	77(1)	63(1)	74(1)	-9(1)	15(1)	-27(1)
C(5)	77(1)	47(1)	105(1)	-3(1)	19(1)	-6(1)
C(6)	55(1)	52(1)	84(1)	-6(1)	8(1)	-2(1)
C(7)	56(1)	37(1)	42(1)	0(1)	15(1)	4(1)
C(8)	53(1)	83(1)	49(1)	2(1)	14(1)	9(1)
C(9)	74(1)	89(1)	45(1)	2(1)	11(1)	-1(1)
C(10)	93(1)	62(1)	52(1)	-1(1)	35(1)	3(1)
C(11)	73(1)	64(1)	78(1)	8(1)	42(1)	16(1)
C(12)	54(1)	59(1)	59(1)	7(1)	15(1)	12(1)
C(13)	40(1)	36(1)	44(1)	3(1)	6(1)	2(1)
C(14)	57(1)	69(1)	46(1)	-5(1)	10(1)	-11(1)
C(15)	82(1)	78(1)	54(1)	-8(1)	-5(1)	-15(1)
C(16)	49(1)	80(1)	93(1)	-10(1)	-9(1)	-7(1)
C(17)	43(1)	98(1)	103(1)	-19(1)	19(1)	-6(1)
C(18)	48(1)	73(1)	64(1)	-11(1)	18(1)	-3(1)
C(19)	78(1)	63(1)	85(1)	16(1)	1(1)	10(1)
C(20)	103(1)	55(1)	64(1)	15(1)	16(1)	-15(1)
C(21)	107(1)	64(1)	65(1)	5(1)	37(1)	-23(1)
C(22)	70(1)	128(1)	160(1)	54(1)	41(1)	-4(1)
C(23)	111(1)	104(1)	74(1)	-25(1)	8(1)	-4(1)
C(24)	130(1)	58(1)	90(1)	-14(1)	33(1)	15(1)
C(25)	118(1)	95(1)	102(1)	-19(1)	23(1)	47(1)
C(26)	119(1)	135(1)	133(1)	-30(1)	-31(1)	56(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **26**.

	x	y	z	U(eq)
H(2)	2393	2890	-996	87
H(3)	1371	1568	-1365	98
H(4)	2188	176	-961	86
H(5)	4011	123	-116	92
H(6)	5075	1435	242	78
H(8)	5525	5104	2897	73

H(9)	5220	5252	4198	84
H(10)	3427	5697	4398	79
H(11)	1923	5912	3272	81
H(12)	2198	5760	1959	69
H(14)	3271	4889	-1896	69
H(15)	1455	4563	-2695	90
H(16)	-141	4525	-2125	94
H(17)	81	4796	-749	97
H(18)	1880	5175	63	73
H(19A)	6928	2547	2283	117
H(19B)	7069	3274	1616	117
H(19C)	6422	2347	1340	117
H(20A)	5106	2358	2622	89
H(20B)	4619	2059	1697	89
H(21A)	3122	2589	2276	91
H(21B)	3755	3543	2443	91
H(22A)	1594	2800	1282	175
H(22B)	1605	3430	518	175
H(22C)	1681	3867	1392	175
H(23A)	5583	8105	1959	148
H(23B)	5356	7260	2485	148
H(23C)	4939	8239	2682	148
H(24A)	3892	8770	1019	110
H(24B)	3332	8890	1788	110
H(25A)	1778	7999	1180	126
H(25B)	1903	8800	574	126
H(26A)	730	7243	-27	208
H(26B)	1400	6974	-709	208
H(26C)	1025	7994	-623	208

Crystal data and structure refinement for (μ-dme)[SrLi$_6$(OPh)$_8$(thf)$_4$] 27

$C_{68}H_{82}Li_6SrO_{14}$, M= 1252.60 gmol^{-1}, monoclinic, $P2_1/n$ (No. 12), a = 11.4549(18), b = 22.739(4), c = 13.396(2) Å, β = 101.438(12)°, V = 3419.9(9) Å^3, Z = 2, $\rho_{calcd.}$= 1.216 Mgm^3, *F*(000) = 1316, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.848 mm^{-1}, 2.02° < θ < 27.29°, 19599 reflections of which 7001 unique and 2596 observed, 405 parameters refined, *GOOF* (on F^2) = 1.245, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.1381, *w*R2 = 0.2776 for I > 2σ(I) and R1 = 0.2977, wR2 = 0.3483 for all data.

The intensities from the single-crystals of **27** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms but high disorder was observed on two THF ligands.

Table 1. Crystal data and structure refinement for **27**.

Identification code	(μ-dme)[SrLi$_6$(OPh)$_8$(thf)$_4$]	
Empirical formula	C68 H82 Li6 O14 Sr	
Formula weight	1252.60	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.4549(18) Å	α= 90°
	b = 22.739(4) Å	β= 101.438(12)°
	c = 13.396(2) Å	γ = 90°
Volume	3419.9(9) Å^3	
Z	2	
Density (calculated)	1.216 Mg/m^3	
Absorption coefficient	0.848 mm^{-1}	
F(000)	1316	
Theta range for data collection	2.02 to 27.29°	
Index ranges	-14<=h<=14, -28<=k<=29, -16<=l<=15	
Reflections collected	19599	
Independent reflections	7001 [R(int) = 0.2494]	
Completeness to theta = 27.29°	90.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7001 / 0 / 405	
Goodness-of-fit on F^2	1.245	
Final R indices [I>2sigma(I)]	R1 = 0.1381, wR2 = 0.2776	
R indices (all data)	R1 = 0.2977, wR2 = 0.3483	
Largest diff. peak and hole	1.190 and -0.862 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **27**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sr(1)	5000	5000	5000	55(1)
O(1)	6734(3)	5668(2)	4864(4)	57(2)
O(2)	4231(3)	5751(2)	3598(4)	57(2)
O(3)	4239(4)	5280(2)	6615(4)	66(2)
O(4)	6325(3)	5847(2)	2638(4)	58(2)
O(5)	5953(4)	7032(2)	4035(4)	69(2)
O(7)	8788(3)	4997(3)	3852(4)	62(1)
Li(1)	5752(8)	6194(6)	3781(11)	61(4)
Li(2)	4924(10)	5339(6)	2530(11)	66(4)
Li(3)	7101(9)	5288(6)	3643(10)	56(4)
O(6)	3830(6)	5199(3)	1218(6)	114(3)
C(1)	7491(5)	6024(4)	5516(6)	60(2)
C(2)	8429(5)	6315(4)	5181(8)	70(3)
C(3)	9164(7)	6690(4)	5860(10)	106(4)
C(4)	8991(8)	6769(5)	6852(11)	127(5)
C(5)	8101(8)	6470(5)	7165(10)	116(4)
C(6)	7349(6)	6106(4)	6516(7)	72(3)
C(7)	3158(5)	6040(4)	3269(6)	60(2)
C(8)	2096(5)	5712(4)	3211(7)	69(3)
C(9)	993(6)	5999(5)	2938(8)	87(3)
C(10)	940(7)	6568(5)	2709(8)	91(4)
C(11)	1973(6)	6912(4)	2753(7)	68(3)
C(12)	3071(6)	6613(4)	3050(7)	69(3)
C(13)	3994(5)	5847(3)	6708(6)	52(2)
C(14)	3220(6)	6154(4)	5905(6)	59(2)
C(15)	2954(6)	6734(4)	5967(7)	68(3)
C(16)	3480(7)	7063(4)	6805(7)	75(3)
C(17)	4245(8)	6789(4)	7550(8)	84(3)
C(18)	4525(6)	6201(4)	7514(7)	67(3)
C(19)	6557(5)	6153(3)	1841(6)	52(2)
C(20)	7675(5)	6106(4)	1544(6)	63(2)
C(21)	7861(8)	6401(5)	668(8)	92(3)

C(22)	7011(9)	6753(5)	96(8)	95(4)
C(23)	5925(9)	6806(4)	412(8)	88(3)
C(24)	5691(7)	6508(4)	1258(7)	77(3)
C(25)	6754(6)	7423(4)	3620(7)	68(3)
C(26)	6881(10)	7976(5)	4265(9)	118(4)
C(27)	5981(12)	7954(6)	4838(11)	142(5)
C(28)	5651(8)	7335(5)	4915(8)	88(3)
C(33)	9102(7)	4609(5)	3118(7)	82(3)
C(34)	9382(4)	4855(4)	4899(5)	61(2)
C(29)	3031(14)	5656(9)	560(13)	217(9)
C(30)	2530(40)	5416(10)	-280(20)	640(40)
C(31)	1746(13)	5127(14)	430(18)	415(17)
C(32)	2829(14)	4806(10)	1106(13)	214(10)

Table 3. Bond lengths [Å] and angles [°] for **27**.

Sr(1)-O(1)	2.535(4)	O(4)-Li(1)	1.947(15)
Sr(1)-O(1)#1	2.535(4)	O(4)-Li(2)	1.959(14)
Sr(1)-O(2)	2.563(5)	O(4)-Li(3)	1.936(13)
Sr(1)-O(2)#1	2.563(5)	O(7)-Li(3)	2.009(11)
Sr(1)-O(3)	2.567(6)	Li(1)-Li(2)	2.62(2)
Sr(1)-O(3)#1	2.567(6)	Li(2)-Li(3)	2.642(15)
Sr(1)-Li(2)	3.381(15)	Li(1)-Li(3)	2.604(17)
Sr(1)-Li(2)#1	3.381(15)	O(1)-C(1)	1.369(9)
Sr(1)-Li(3)	3.356(13)	O(2)-C(7)	1.386(7)
Sr(1)-Li(3)#1	3.356(13)	O(3)-C(13)	1.331(9)
Sr(1)-C(13)	3.364(8)	O(4)-C(19)	1.344(9)
Sr(1)-C(13)#1	3.364(8)	O(5)-C(25)	1.463(9)
O(1)-Li(3)	1.967(14)	O(5)-C(28)	1.465(11)
O(1)-Li(1)	2.038(13)	O(7)-C(33)	1.420(11)
O(2)-Li(1)	1.985(12)	O(7)-C(34)	1.467(8)
O(5)-Li(1)	1.943(15)	Li(1)-C(1)	2.772(14)
O(2)-Li(2)	2.001(16)	O(6)-C(32)	1.437(19)
O(3)-Li(2)#1	1.943(14)	O(6)-C(29)	1.541(18)
Li(2)-O(3)#1	1.943(14)	C(1)-C(2)	1.408(10)
Li(2)-O(6)	1.973(15)	C(2)-C(3)	1.401(13)
O(3)-Li(3)#1	1.983(13)	C(3)-C(4)	1.393(18)
Li(3)-O(3)#1	1.983(13)	C(4)-C(5)	1.360(17)

C(5)-C(6)	1.373(13)	C(19)-C(20)	1.419(9)
C(1)-C(6)	1.393(12)	C(20)-C(21)	1.404(13)
C(7)-C(8)	1.415(10)	C(21)-C(22)	1.372(14)
C(8)-C(9)	1.405(10)	C(22)-C(23)	1.397(14)
C(9)-C(10)	1.328(14)	C(23)-C(24)	1.391(14)
C(10)-C(11)	1.410(12)	C(19)-C(24)	1.392(11)
C(11)-C(12)	1.416(10)	C(25)-C(26)	1.516(14)
C(7)-C(12)	1.334(11)	C(26)-C(27)	1.402(16)
C(13)-C(14)	1.432(10)	C(27)-C(28)	1.466(15)
C(14)-C(15)	1.360(11)	C(34)-C(34)#2	1.536(12)
C(15)-C(16)	1.384(12)	C(29)-C(30)	1.28(3)
C(16)-C(17)	1.343(12)	C(30)-C(31)	1.57(5)
C(17)-C(18)	1.378(12)	C(30)-C(32)	2.28(3)
C(13)-C(18)	1.387(11)	C(31)-C(32)	1.56(3)

O(1)#1-Sr(1)-O(1)	180.0(3)	O(3)-Sr(1)-Li(2)	145.2(2)
O(1)#1-Sr(1)-O(3)	71.69(16)	O(3)#1-Sr(1)-Li(2)	34.8(2)
O(1)-Sr(1)-O(3)	108.31(16)	O(2)#1-Sr(1)-Li(2)	143.9(3)
O(1)#1-Sr(1)-O(3)#1	108.31(16)	O(2)-Sr(1)-Li(2)	36.1(3)
O(1)-Sr(1)-O(3)#1	71.69(16)	Li(2)#1-Sr(1)-Li(2)	180.000(1)
O(3)-Sr(1)-O(3)#1	180.000(1)	O(1)#1-Sr(1)-Li(3)#1	35.7(2)
O(1)#1-Sr(1)-O(2)#1	73.06(14)	O(1)-Sr(1)-Li(3)#1	144.3(2)
O(1)-Sr(1)-O(2)#1	106.94(14)	O(3)-Sr(1)-Li(3)#1	36.1(2)
O(3)-Sr(1)-O(2)#1	70.86(16)	O(3)#1-Sr(1)-Li(3)#1	143.9(2)
O(3)#1-Sr(1)-O(2)#1	109.14(16)	O(2)#1-Sr(1)-Li(3)#1	69.7(2)
O(1)#1-Sr(1)-O(2)	106.94(14)	O(2)-Sr(1)-Li(3)#1	110.3(2)
O(1)-Sr(1)-O(2)	73.06(14)	Li(2)#1-Sr(1)-Li(3)#1	46.2(3)
O(3)-Sr(1)-O(2)	109.14(16)	Li(2)-Sr(1)-Li(3)#1	133.8(3)
O(3)#1-Sr(1)-O(2)	70.86(16)	O(1)#1-Sr(1)-Li(3)	144.3(2)
O(2)#1-Sr(1)-O(2)	180.000(1)	O(1)-Sr(1)-Li(3)	35.7(2)
O(1)#1-Sr(1)-Li(2)#1	70.2(2)	O(3)-Sr(1)-Li(3)	143.9(2)
O(1)-Sr(1)-Li(2)#1	109.8(2)	O(3)#1-Sr(1)-Li(3)	36.1(2)
O(3)-Sr(1)-Li(2)#1	34.8(2)	O(2)#1-Sr(1)-Li(3)	110.3(2)
O(3)#1-Sr(1)-Li(2)#1	145.2(2)	O(2)-Sr(1)-Li(3)	69.7(2)
O(2)#1-Sr(1)-Li(2)#1	36.1(3)	Li(2)#1-Sr(1)-Li(3)	133.8(3)
O(2)-Sr(1)-Li(2)#1	143.9(3)	Li(2)-Sr(1)-Li(3)	46.2(3)
O(1)#1-Sr(1)-Li(2)	109.8(2)	Li(3)#1-Sr(1)-Li(3)	180.000(1)
O(1)-Sr(1)-Li(2)	70.2(2)	O(1)#1-Sr(1)-C(13)	85.11(16)

O(1)-Sr(1)-C(13)	94.89(16)
O(3)-Sr(1)-C(13)	20.91(18)
O(3)#1-Sr(1)-C(13)	159.09(18)
O(2)#1-Sr(1)-C(13)	89.85(17)
O(2)-Sr(1)-C(13)	90.15(17)
Li(2)#1-Sr(1)-C(13)	53.9(3)
Li(2)-Sr(1)-C(13)	126.1(3)
Li(3)#1-Sr(1)-C(13)	50.5(2)
Li(3)-Sr(1)-C(13)	129.5(2)
O(1)#1-Sr(1)-C(13)#1	94.89(16)
O(1)-Sr(1)-C(13)#1	85.11(16)
O(3)-Sr(1)-C(13)#1	159.09(18)
O(3)#1-Sr(1)-C(13)#1	20.91(18)
O(2)#1-Sr(1)-C(13)#1	90.15(17)
O(2)-Sr(1)-C(13)#1	89.85(17)
Li(2)#1-Sr(1)-C(13)#1	126.1(3)
Li(2)-Sr(1)-C(13)#1	53.9(3)
Li(3)#1-Sr(1)-C(13)#1	129.5(2)
Li(3)-Sr(1)-C(13)#1	50.5(2)
C(13)-Sr(1)-C(13)#1	180.00(18)
C(1)-O(1)-Li(3)	125.3(5)
C(1)-O(1)-Li(1)	107.3(6)
Li(3)-O(1)-Li(1)	81.1(6)
C(1)-O(1)-Sr(1)	135.7(5)
Li(3)-O(1)-Sr(1)	95.5(4)
Li(1)-O(1)-Sr(1)	94.2(3)
C(7)-O(2)-Li(2)	116.6(6)
C(7)-O(2)-Li(1)	120.0(6)
Li(2)-O(2)-Li(1)	82.1(6)
C(7)-O(2)-Sr(1)	134.7(4)
Li(2)-O(2)-Sr(1)	94.8(4)
Li(1)-O(2)-Sr(1)	94.7(4)
C(13)-O(3)-Li(2)#1	137.4(7)
C(13)-O(3)-Li(3)#1	118.4(5)
Li(2)#1-O(3)-Li(3)#1	84.6(6)
C(13)-O(3)-Sr(1)	115.6(5)
Li(2)#1-O(3)-Sr(1)	96.1(5)
Li(3)#1-O(3)-Sr(1)	94.2(4)
C(19)-O(4)-Li(3)	139.1(5)
C(19)-O(4)-Li(1)	124.5(6)
Li(3)-O(4)-Li(1)	84.2(6)
C(19)-O(4)-Li(2)	122.3(6)
Li(3)-O(4)-Li(2)	85.4(5)
Li(1)-O(4)-Li(2)	84.1(6)
C(28)-O(5)-C(25)	106.6(6)
C(28)-O(5)-Li(1)	124.3(7)
C(25)-O(5)-Li(1)	126.2(6)
C(33)-O(7)-C(34)	113.1(6)
C(33)-O(7)-Li(3)	118.4(5)
C(34)-O(7)-Li(3)	117.1(5)
O(5)-Li(1)-O(4)	119.2(7)
O(5)-Li(1)-O(2)	126.1(6)
O(4)-Li(1)-O(2)	97.0(6)
O(5)-Li(1)-O(1)	115.0(7)
O(4)-Li(1)-O(1)	95.6(5)
O(2)-Li(1)-O(1)	97.9(6)
O(5)-Li(1)-Li(3)	137.5(5)
O(4)-Li(1)-Li(3)	47.7(4)
O(2)-Li(1)-Li(3)	96.3(6)
O(1)-Li(1)-Li(3)	48.3(4)
O(5)-Li(1)-Li(2)	148.9(7)
O(4)-Li(1)-Li(2)	48.1(4)
O(2)-Li(1)-Li(2)	49.2(4)
O(1)-Li(1)-Li(2)	95.7(6)
Li(3)-Li(1)-Li(2)	60.8(5)
O(5)-Li(1)-C(1)	87.1(5)
O(4)-Li(1)-C(1)	107.8(5)
O(2)-Li(1)-C(1)	120.0(6)
O(1)-Li(1)-C(1)	28.1(3)
Li(3)-Li(1)-C(1)	67.1(4)
Li(2)-Li(1)-C(1)	122.9(6)
O(5)-Li(1)-Sr(1)	137.7(7)
O(4)-Li(1)-Sr(1)	102.3(5)
O(2)-Li(1)-Sr(1)	49.3(3)
O(1)-Li(1)-Sr(1)	48.7(3)
Li(3)-Li(1)-Sr(1)	67.0(4)

Li(2)-Li(1)-Sr(1)	67.5(4)
C(1)-Li(1)-Sr(1)	72.0(3)
O(3)#1-Li(2)-O(4)	94.8(5)
O(3)#1-Li(2)-O(2)	97.9(7)
O(4)-Li(2)-O(2)	96.1(7)
O(3)#1-Li(2)-O(6)	124.0(8)
O(4)-Li(2)-O(6)	121.9(8)
O(2)-Li(2)-O(6)	116.1(6)
O(3)#1-Li(2)-Li(3)	48.3(4)
O(4)-Li(2)-Li(3)	46.9(4)
O(2)-Li(2)-Li(3)	94.7(6)
O(6)-Li(2)-Li(3)	149.0(8)
O(3)#1-Li(2)-Li(1)	95.0(6)
O(4)-Li(2)-Li(1)	47.7(4)
O(2)-Li(2)-Li(1)	48.7(4)
O(6)-Li(2)-Li(1)	140.9(7)
Li(3)-Li(2)-Li(1)	59.4(4)
O(3)#1-Li(2)-Sr(1)	49.0(4)
O(4)-Li(2)-Sr(1)	101.6(5)
O(2)-Li(2)-Sr(1)	49.0(3)
O(6)-Li(2)-Sr(1)	136.4(6)
Li(3)-Li(2)-Sr(1)	66.4(4)
Li(1)-Li(2)-Sr(1)	66.9(4)
O(4)-Li(3)-O(1)	98.3(6)
O(4)-Li(3)-O(3)#1	94.2(5)
O(1)-Li(3)-O(3)#1	98.3(6)
O(4)-Li(3)-O(7)	127.6(7)
O(1)-Li(3)-O(7)	112.8(6)
O(3)#1-Li(3)-O(7)	120.1(7)
O(4)-Li(3)-Li(1)	48.1(4)
O(1)-Li(3)-Li(1)	50.6(4)
O(3)#1-Li(3)-Li(1)	94.4(5)
O(7)-Li(3)-Li(1)	144.9(7)
O(4)-Li(3)-Li(2)	47.6(4)
O(1)-Li(3)-Li(2)	96.7(5)
O(3)#1-Li(3)-Li(2)	47.1(4)
O(7)-Li(3)-Li(2)	150.2(7)
Li(1)-Li(3)-Li(2)	59.8(5)
O(4)-Li(3)-Sr(1)	103.0(4)
O(1)-Li(3)-Sr(1)	48.8(3)
O(3)#1-Li(3)-Sr(1)	49.7(3)
O(7)-Li(3)-Sr(1)	129.3(6)
Li(1)-Li(3)-Sr(1)	67.4(4)
Li(2)-Li(3)-Sr(1)	67.4(4)
C(29)-O(6)-C(32)	89.3(11)
C(29)-O(6)-Li(2)	127.0(9)
C(32)-O(6)-Li(2)	123.1(9)
O(1)-C(1)-C(6)	120.8(7)
O(1)-C(1)-C(2)	120.1(8)
C(6)-C(1)-C(2)	119.1(7)
O(1)-C(1)-Li(1)	44.6(4)
C(6)-C(1)-Li(1)	125.9(5)
C(2)-C(1)-Li(1)	97.7(6)
C(3)-C(2)-C(1)	118.5(9)
C(4)-C(3)-C(2)	121.1(10)
C(5)-C(4)-C(3)	119.1(10)
C(4)-C(5)-C(6)	121.4(12)
C(1)-C(6)-C(5)	120.7(9)
C(12)-C(7)-O(2)	123.7(6)
C(12)-C(7)-C(8)	118.5(6)
O(2)-C(7)-C(8)	117.7(7)
C(9)-C(8)-C(7)	119.2(8)
C(10)-C(9)-C(8)	120.7(8)
C(9)-C(10)-C(11)	122.0(8)
C(12)-C(11)-C(10)	115.9(8)
C(7)-C(12)-C(11)	123.6(7)
O(3)-C(13)-C(18)	124.6(6)
O(3)-C(13)-C(14)	120.9(7)
C(18)-C(13)-C(14)	114.3(7)
O(3)-C(13)-Sr(1)	43.5(4)
C(18)-C(13)-Sr(1)	134.8(4)
C(14)-C(13)-Sr(1)	90.7(5)
C(15)-C(14)-C(13)	122.7(8)
C(16)-C(15)-C(14)	120.4(8)
C(15)-C(16)-C(17)	117.9(9)
C(16)-C(17)-C(18)	123.0(9)

C(17)-C(18)-C(13)	121.5(8)	C(26)-C(27)-C(28)	107.5(10)
O(4)-C(19)-C(24)	120.9(6)	O(5)-C(28)-C(27)	106.8(9)
O(4)-C(19)-C(20)	121.1(6)	O(7)-C(34)-C(34)#2	108.1(7)
C(24)-C(19)-C(20)	117.9(8)	C(30)-C(29)-O(6)	109(2)
C(21)-C(20)-C(19)	119.6(7)	C(31)-C(30)-C(29)	82(2)
C(20)-C(21)-C(22)	122.5(9)	C(31)-C(30)-C(32)	43.1(10)
C(23)-C(22)-C(21)	117.2(10)	C(29)-C(30)-C(32)	65.1(15)
C(22)-C(23)-C(24)	122.2(9)	C(30)-C(31)-C(32)	93.5(18)
C(19)-C(24)-C(23)	120.5(8)	C(31)-C(32)-O(6)	107.2(18)
O(5)-C(25)-C(26)	106.5(7)	C(31)-C(32)-C(30)	43.4(16)
C(27)-C(26)-C(25)	106.5(9)	O(6)-C(32)-C(30)	72.3(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+2,-y+1,-z+1

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3)for **27**.

The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sr(1)	31(1)	65(1)	66(1)	12(1)	2(1)	-6(1)
O(1)	30(2)	72(3)	64(3)	-8(3)	-1(2)	-6(2)
O(2)	29(2)	63(3)	78(3)	8(3)	12(2)	4(2)
O(3)	43(2)	59(3)	89(4)	-10(3)	-2(2)	7(2)
O(4)	34(2)	76(4)	64(3)	7(3)	12(2)	-3(2)
O(5)	47(2)	72(4)	89(4)	-6(3)	19(2)	-8(2)
O(7)	41(2)	76(3)	66(3)	-12(4)	4(2)	7(3)
Li(1)	25(4)	64(8)	92(10)	19(7)	7(5)	8(5)
Li(2)	47(6)	68(9)	77(9)	22(7)	-2(6)	18(6)
Li(3)	42(5)	53(7)	67(8)	-14(6)	-3(5)	13(5)
O(6)	114(5)	106(6)	96(5)	2(4)	-39(4)	-23(4)
C(1)	28(3)	79(6)	72(5)	-4(5)	2(3)	3(3)
C(2)	34(3)	69(6)	108(7)	10(5)	14(4)	-2(3)
C(3)	41(4)	80(7)	176(11)	-19(7)	-25(5)	-13(4)
C(4)	78(5)	88(8)	177(11)	-44(8)	-67(6)	11(5)
C(5)	79(6)	120(9)	127(9)	-55(7)	-33(6)	29(6)
C(6)	57(4)	94(7)	64(5)	-29(5)	9(4)	1(4)
C(7)	27(3)	90(6)	62(5)	16(4)	8(3)	4(3)

C(8)	30(3)	78(6)	92(6)	16(5)	-8(3)	-9(3)
C(9)	29(3)	107(7)	121(8)	45(6)	5(4)	2(4)
C(10)	39(4)	127(9)	103(8)	12(7)	6(4)	14(5)
C(11)	52(4)	47(5)	97(7)	-1(5)	-2(4)	6(3)
C(12)	51(4)	60(5)	86(6)	19(5)	-7(4)	1(3)
C(13)	25(3)	62(5)	67(5)	-7(4)	8(3)	-6(3)
C(14)	50(4)	58(5)	66(5)	5(4)	2(3)	1(3)
C(15)	49(4)	73(6)	78(6)	13(5)	4(4)	7(4)
C(16)	70(4)	66(6)	94(7)	5(5)	29(4)	1(4)
C(17)	89(5)	81(7)	77(7)	-18(6)	0(5)	18(5)
C(18)	50(4)	59(5)	84(6)	-5(5)	-8(4)	12(3)
C(19)	36(3)	61(5)	55(5)	-11(4)	-2(3)	-9(3)
C(20)	37(3)	89(6)	64(5)	6(5)	11(3)	-6(3)
C(21)	86(5)	106(8)	86(7)	6(6)	25(5)	-28(5)
C(22)	122(7)	87(8)	75(7)	1(6)	22(5)	-35(6)
C(23)	127(7)	67(7)	61(6)	2(5)	-3(5)	11(5)
C(24)	69(4)	90(7)	69(6)	9(5)	8(4)	27(4)
C(25)	55(4)	73(6)	78(6)	17(5)	18(4)	2(4)
C(26)	146(8)	91(8)	122(10)	-27(7)	40(7)	-53(6)
C(27)	195(11)	114(11)	141(10)	-51(9)	89(8)	-42(8)
C(28)	83(5)	89(7)	102(7)	-26(6)	45(5)	-7(5)
C(33)	55(4)	114(8)	74(6)	3(6)	9(4)	9(5)
C(34)	23(2)	99(7)	60(4)	3(4)	8(3)	2(3)
C(29)	178(13)	280(20)	150(14)	-71(15)	-67(10)	82(13)
C(30)	1580(100)	48(13)	150(20)	-14(13)	-160(40)	-110(30)
C(31)	129(8)	640(50)	380(20)	-270(30)	-179(10)	147(17)
C(32)	158(13)	320(30)	145(15)	17(18)	-17(11)	-62(15)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **27**.

	x	y	z	U(eq)
H(2)	8558	6259	4516	84
H(3)	9786	6892	5644	127
H(4)	9483	7026	7299	152
H(5)	7998	6513	7840	139
H(6)	6732	5910	6749	86

H(8)	2129	5307	3353	83
H(9)	286	5786	2917	104
H(10)	190	6747	2512	109
H(11)	1935	7315	2595	81
H(12)	3778	6830	3096	82
H(14)	2883	5946	5312	71
H(15)	2408	6912	5437	81
H(16)	3308	7465	6851	90
H(17)	4607	7009	8123	101
H(18)	5088	6036	8047	81
H(20)	8288	5879	1931	76
H(21)	8597	6355	466	110
H(22)	7154	6951	-484	114
H(23)	5333	7050	41	106
H(24)	4941	6546	1437	92
H(25A)	6420	7517	2907	82
H(25B)	7532	7235	3657	82
H(26A)	7667	7989	4716	141
H(26B)	6789	8326	3831	141
H(27A)	5289	8183	4501	171
H(27B)	6270	8119	5518	171
H(28A)	6093	7164	5550	105
H(28B)	4797	7300	4907	105
H(33A)	9962	4589	3208	122
H(33B)	8769	4753	2439	122
H(33C)	8789	4220	3204	122
H(34A)	9461	4428	4984	73
H(34B)	8912	5004	5381	73
H(29A)	2425	5800	923	260
H(29B)	3513	5991	422	260
H(30A)	2105	5687	-791	764
H(30B)	3033	5141	-565	764
H(31A)	1146	4855	65	498
H(31B)	1373	5417	809	498
H(32A)	3003	4440	780	257
H(32B)	2652	4712	1774	257

Crystal data and structure refinement for (µ-dme)[SrLi$_6$(OPh)$_8$(thf)$_2$(dme)$_2$] 28

$C_{68}H_{86}Li_6SrO_{16}$, M= 1288.63 gmol^{-1}, monoclinic, *P*2$_1$/*n* (Nr. 14), a = 12.8075(11), b = 19.2227(18), c = 14.3397(15) Å, β = 94.950(8)°, V = 3517.2(6) Å^3, Z = 2, $\rho_{calcd.}$= 1.217 Mgm^3, *F*(000) = 1356, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.828 mm^{-1}, 1.78° < θ < 26.93°, 24964 reflections of which 7061 unique and 4632 observed, 415 parameters refined, *GOOF* (on F^2) = 1.116, R1= $\Sigma|F_o–F_c|/\Sigma F_o$ = 0.1233, *w*R2 = 0.3088 for I > 2σ(I) and R1 = 0.1684, wR2 = 0.3440 for all data.

The intensities from the single-crystals of **28** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms.

Table 1. Crystal data and structure refinement for **28**.

Identification code	(µ-dme)[SrLi$_6$(OPh)$_8$(thf)$_2$(dme)$_2$]	
Empirical formula	C68 H86 Li6 O16 Sr	
Formula weight	1288.63	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.8075(11) Å	α= 90°
	b = 19.2227(18) Å	β= 94.950(8)°
	c = 14.3397(15) Å	γ = 90°
Volume	3517.2(6) Å^3	
Z	2	
Density (calculated)	1.217 Mg/m^3	
Absorption coefficient	0.828 mm^{-1}	
F(000)	1356	
Theta range for data collection	1.78 to 26.93°	
Index ranges	-14<=h<=14, -24<=k<=24, -18<=l<=18	
Reflections collected	24964	
Independent reflections	7061 [R(int) = 0.1819]	
Completeness to theta = 26.93°	92.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7061 / 0 / 415	
Goodness-of-fit on F^2	1.116	
Final R indices [I>2sigma(I)]	R1 = 0.1233, wR2 = 0.3088	

R indices (all data)	R1 = 0.1684, wR2 = 0.3440
Largest diff. peak and hole	2.087 and -1.948 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **28**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sr	5000	0	5000	42(1)
O(1)	3123(1)	-30(1)	4279(1)	48(1)
O(2)	3754(1)	392(1)	6198(1)	47(1)
O(3)	4507(1)	1230(1)	4583(1)	45(1)
O(4)	2309(1)	1228(1)	5012(1)	49(1)
Li(1)	2448(3)	249(2)	5373(2)	51(1)
Li(2)	3112(4)	986(2)	3975(3)	54(1)
Li(3)	3654(4)	1356(2)	5695(2)	52(1)
O(6)	2568(1)	1196(1)	2717(1)	56(1)
O(5)	1162(2)	-232(1)	5749(1)	69(1)
O(7)	4076(2)	2172(1)	6426(1)	66(1)
O(8)	4039(2)	3744(1)	6220(2)	91(1)
C(1)	2952(2)	-473(1)	3571(1)	41(1)
C(2)	2209(2)	-1001(1)	3571(2)	56(1)
C(3)	2013(2)	-1442(1)	2806(2)	67(1)
C(4)	2598(3)	-1390(2)	2051(2)	76(1)
C(5)	3341(2)	-887(2)	2043(2)	67(1)
C(6)	3505(2)	-435(1)	2783(2)	50(1)
C(7)	3813(2)	241(1)	7116(1)	44(1)
C(8)	4056(2)	-413(1)	7457(2)	55(1)
C(9)	4125(2)	-562(2)	8411(2)	79(1)
C(10)	3936(3)	-43(2)	9044(2)	99(1)
C(11)	3677(3)	599(2)	8714(2)	96(1)
C(12)	3599(2)	744(2)	7773(2)	67(1)
C(13)	5077(2)	1767(1)	4343(1)	43(1)
C(14)	4634(2)	2394(1)	4022(2)	59(1)
C(15)	5215(3)	2952(2)	3803(2)	78(1)
C(16)	6290(3)	2910(2)	3877(2)	79(1)
C(17)	6762(3)	2316(2)	4197(2)	81(1)

C(18)	6181(2)	1745(2)	4423(2)	61(1)
C(19)	1563(2)	1696(1)	5102(1)	44(1)
C(20)	1086(2)	1765(2)	5934(2)	65(1)
C(21)	358(3)	2271(2)	6039(2)	80(1)
C(22)	19(2)	2702(2)	5302(2)	78(1)
C(23)	457(2)	2634(2)	4471(2)	75(1)
C(24)	1227(2)	2148(1)	4373(2)	56(1)
C(25)	1290(3)	-667(2)	6542(3)	149(1)
C(26)	68(2)	-139(2)	5468(2)	83(1)
C(27)	3098(3)	1507(2)	1988(2)	85(1)
C(28)	2732(3)	1165(3)	1128(2)	135(2)
C(29)	1773(3)	822(2)	1260(2)	95(1)
C(30)	1626(2)	891(2)	2301(2)	65(1)
C(31)	5163(2)	2310(2)	6583(2)	75(1)
C(32)	3439(3)	2675(2)	6785(3)	90(1)
C(33)	3191(3)	3285(2)	6176(3)	97(1)
C(34)	3842(4)	4339(2)	5635(4)	167(2)

Table 3. Bond lengths [Å] and angles [°] for **28**.

Sr-O(1)	2.5338(16)	O(2)-Li(3)	1.988(4)
Sr-O(1)#1	2.5338(16)	O(3)-Li(2)	1.976(5)
Sr-O(2)	2.5565(15)	O(3)-Li(3)	2.024(4)
Sr-O(2)#1	2.5565(15)	O(4)-Li(1)	1.955(4)
Sr-O(3)	2.5066(14)	O(4)-Li(2)	1.937(4)
Sr-O(3)#1	2.5067(14)	O(4)-Li(3)	1.922(5)
Sr-C(1)	3.313(2)	Li(1)-O(5)	2.002(5)
Sr-C(1)#1	3.313(2)	Li(2)-O(6)	1.920(4)
Sr-Li(2)	3.314(4)	Li(3)-O(7)	1.938(4)
Sr-Li(2)#1	3.314(4)	O(1)-C(1)	1.328(2)
Sr-Li(3)	3.325(4)	O(2)-C(7)	1.344(2)
Sr-Li(3)#1	3.325(4)	O(3)-C(13)	1.327(3)
Li(1)-Li(2)	2.654(6)	O(4)-C(19)	1.328(3)
Li(1)-Li(3)	2.646(6)	O(5)-C(25)	1.410(4)
Li(2)-Li(3)	2.603(5)	O(5)-C(26)	1.436(4)
O(1)-Li(1)	1.931(4)	O(6)-C(27)	1.424(3)
O(1)-Li(2)	2.001(4)	O(6)-C(30)	1.425(3)
O(2)-Li(1)	1.983(4)	O(7)-C(31)	1.416(4)

O(7)-C(32)	1.392(4)	C(14)-C(15)	1.358(4)
O(8)-C(33)	1.396(4)	C(15)-C(16)	1.375(5)
O(8)-C(34)	1.426(5)	C(16)-C(17)	1.354(5)
C(1)-C(2)	1.392(3)	C(17)-C(18)	1.380(4)
C(2)-C(3)	1.391(4)	C(13)-C(18)	1.409(4)
C(3)-C(4)	1.372(4)	C(19)-C(20)	1.392(3)
C(4)-C(5)	1.358(4)	C(20)-C(21)	1.366(4)
C(5)-C(6)	1.374(3)	C(21)-C(22)	1.383(4)
C(1)-C(6)	1.386(3)	C(22)-C(23)	1.366(4)
C(7)-C(8)	1.375(3)	C(23)-C(24)	1.376(4)
C(8)-C(9)	1.394(3)	C(19)-C(24)	1.398(3)
C(9)-C(10)	1.385(5)	C(26)-C(26)#2	1.441(6)
C(10)-C(11)	1.351(5)	C(27)-C(28)	1.440(5)
C(11)-C(12)	1.374(3)	C(28)-C(29)	1.421(6)
C(7)-C(12)	1.394(3)	C(29)-C(30)	1.526(4)
C(13)-C(14)	1.393(3)	C(32)-C(33)	1.481(5)

O(3)-Sr-O(3)#1	180.0	O(3)-Sr-C(1)#1	93.33(5)
O(3)-Sr-O(1)	73.38(5)	O(3)#1-Sr-C(1)#1	86.67(5)
O(3)#1-Sr-O(1)	106.62(5)	O(1)-Sr-C(1)#1	158.61(5)
O(3)-Sr-O(1)#1	106.62(5)	O(1)#1-Sr-C(1)#1	21.39(5)
O(3)#1-Sr-O(1)#1	73.38(5)	O(2)-Sr-C(1)#1	90.60(5)
O(1)-Sr-O(1)#1	180.00(6)	O(2)#1-Sr-C(1)#1	89.40(5)
O(3)-Sr-O(2)	73.94(5)	C(1)-Sr-C(1)#1	180.0
O(3)#1-Sr-O(2)	106.06(5)	O(3)-Sr-Li(2)	36.46(8)
O(1)-Sr-O(2)	69.87(5)	O(3)#1-Sr-Li(2)	143.54(8)
O(1)#1-Sr-O(2)	110.13(5)	O(1)-Sr-Li(2)	37.08(8)
O(3)-Sr-O(2)#1	106.06(5)	O(1)#1-Sr-Li(2)	142.92(8)
O(3)#1-Sr-O(2)#1	73.94(5)	O(2)-Sr-Li(2)	69.87(7)
O(1)-Sr-O(2)#1	110.13(5)	O(2)#1-Sr-Li(2)	110.13(7)
O(1)#1-Sr-O(2)#1	69.87(5)	C(1)-Sr-Li(2)	51.27(8)
O(2)-Sr-O(2)#1	180.0	C(1)#1-Sr-Li(2)	128.73(8)
O(3)-Sr-C(1)	86.67(5)	O(3)-Sr-Li(2)#1	143.54(8)
O(3)#1-Sr-C(1)	93.33(5)	O(3)#1-Sr-Li(2)#1	36.46(8)
O(1)-Sr-C(1)	21.39(5)	O(1)-Sr-Li(2)#1	142.92(8)
O(1)#1-Sr-C(1)	158.61(5)	O(1)#1-Sr-Li(2)#1	37.08(8)
O(2)-Sr-C(1)	89.40(5)	O(2)-Sr-Li(2)#1	110.13(7)
O(2)#1-Sr-C(1)	90.60(5)	O(2)#1-Sr-Li(2)#1	69.87(7)

C(1)-Sr-Li(2)#1	128.73(8)
C(1)#1-Sr-Li(2)#1	51.27(8)
Li(2)-Sr-Li(2)#1	180.0
O(3)-Sr-Li(3)	37.39(7)
O(3)#1-Sr-Li(3)	142.61(7)
O(1)-Sr-Li(3)	69.03(8)
O(1)#1-Sr-Li(3)	110.97(8)
O(2)-Sr-Li(3)	36.66(7)
O(2)#1-Sr-Li(3)	143.34(7)
C(1)-Sr-Li(3)	89.84(8)
C(1)#1-Sr-Li(3)	90.16(8)
Li(2)-Sr-Li(3)	46.17(9)
Li(2)#1-Sr-Li(3)	133.83(9)
O(3)-Sr-Li(3)#1	142.61(7)
O(3)#1-Sr-Li(3)#1	37.39(7)
O(1)-Sr-Li(3)#1	110.97(8)
O(1)#1-Sr-Li(3)#1	69.03(8)
O(2)-Sr-Li(3)#1	143.34(7)
O(2)#1-Sr-Li(3)#1	36.66(7)
C(1)-Sr-Li(3)#1	90.16(8)
C(1)#1-Sr-Li(3)#1	89.84(8)
Li(2)-Sr-Li(3)#1	133.83(9)
Li(2)#1-Sr-Li(3)#1	46.17(9)
Li(3)-Sr-Li(3)#1	180.0
C(1)-O(1)-Li(1)	137.94(19)
C(1)-O(1)-Li(2)	117.47(16)
Li(1)-O(1)-Li(2)	84.86(18)
C(1)-O(1)-Sr	114.52(13)
Li(1)-O(1)-Sr	97.92(13)
Li(2)-O(1)-Sr	93.16(14)
C(7)-O(2)-Li(1)	121.88(18)
C(7)-O(2)-Li(3)	123.55(17)
Li(1)-O(2)-Li(3)	83.56(18)
C(7)-O(2)-Sr	127.50(13)
Li(1)-O(2)-Sr	95.85(13)
Li(3)-O(2)-Sr	93.19(13)
C(13)-O(3)-Li(2)	124.54(17)
C(13)-O(3)-Li(3)	117.28(16)
Li(2)-O(3)-Li(3)	81.21(17)
C(13)-O(3)-Sr	131.53(14)
Li(2)-O(3)-Sr	94.62(13)
Li(3)-O(3)-Sr	93.82(12)
C(19)-O(4)-Li(3)	118.98(17)
C(19)-O(4)-Li(2)	132.22(17)
Li(3)-O(4)-Li(2)	84.85(18)
C(19)-O(4)-Li(1)	132.59(19)
Li(3)-O(4)-Li(1)	86.09(17)
Li(2)-O(4)-Li(1)	85.99(18)
O(1)-Li(1)-O(4)	95.15(18)
O(1)-Li(1)-O(2)	96.3(2)
O(4)-Li(1)-O(2)	94.43(18)
O(1)-Li(1)-O(5)	121.8(2)
O(4)-Li(1)-O(5)	117.2(2)
O(2)-Li(1)-O(5)	125.0(2)
O(1)-Li(1)-Li(3)	94.01(19)
O(4)-Li(1)-Li(3)	46.43(13)
O(2)-Li(1)-Li(3)	48.31(13)
O(5)-Li(1)-Li(3)	143.6(2)
O(1)-Li(1)-Li(2)	48.69(13)
O(4)-Li(1)-Li(2)	46.73(13)
O(2)-Li(1)-Li(2)	93.89(19)
O(5)-Li(1)-Li(2)	140.8(2)
Li(3)-Li(1)-Li(2)	58.84(14)
O(1)-Li(1)-Sr	47.74(11)
O(4)-Li(1)-Sr	99.27(16)
O(2)-Li(1)-Sr	48.59(10)
O(5)-Li(1)-Sr	143.46(19)
Li(3)-Li(1)-Sr	65.49(13)
Li(2)-Li(1)-Sr	65.17(13)
O(6)-Li(2)-O(4)	119.8(2)
O(6)-Li(2)-O(3)	127.3(2)
O(4)-Li(2)-O(3)	97.09(17)
O(6)-Li(2)-O(1)	113.9(2)
O(4)-Li(2)-O(1)	93.48(18)
O(3)-Li(2)-O(1)	98.43(19)
O(6)-Li(2)-Li(3)	151.4(2)

O(4)-Li(2)-Li(3)	47.32(14)	C(25)-O(5)-C(26)	110.0(3)
O(3)-Li(2)-Li(3)	50.20(14)	C(25)-O(5)-Li(1)	116.8(2)
O(1)-Li(2)-Li(3)	93.64(16)	C(26)-O(5)-Li(1)	132.3(2)
O(6)-Li(2)-Li(1)	135.1(2)	C(32)-O(7)-C(31)	114.3(2)
O(4)-Li(2)-Li(1)	47.28(13)	C(32)-O(7)-Li(3)	128.1(2)
O(3)-Li(2)-Li(1)	97.46(17)	C(31)-O(7)-Li(3)	117.5(2)
O(1)-Li(2)-Li(1)	46.45(13)	C(33)-O(8)-C(34)	112.5(3)
Li(3)-Li(2)-Li(1)	60.42(14)	O(1)-C(1)-C(6)	121.7(2)
O(6)-Li(2)-Sr	136.81(19)	O(1)-C(1)-C(2)	122.4(2)
O(4)-Li(2)-Sr	102.22(14)	C(6)-C(1)-C(2)	115.85(19)
O(3)-Li(2)-Sr	48.92(10)	O(1)-C(1)-Sr	44.09(10)
O(1)-Li(2)-Sr	49.76(10)	C(6)-C(1)-Sr	93.24(14)
Li(3)-Li(2)-Sr	67.13(12)	C(2)-C(1)-Sr	134.85(14)
Li(1)-Li(2)-Sr	68.21(12)	C(3)-C(2)-C(1)	121.4(2)
O(4)-Li(3)-O(7)	125.1(2)	C(4)-C(3)-C(2)	120.2(3)
O(4)-Li(3)-O(2)	95.29(18)	C(5)-C(4)-C(3)	119.3(3)
O(7)-Li(3)-O(2)	123.54(19)	C(4)-C(5)-C(6)	120.3(3)
O(4)-Li(3)-O(3)	96.00(16)	C(5)-C(6)-C(1)	122.8(2)
O(7)-Li(3)-O(3)	112.2(2)	O(2)-C(7)-C(8)	122.5(2)
O(2)-Li(3)-O(3)	98.75(18)	O(2)-C(7)-C(12)	121.0(2)
O(4)-Li(3)-Li(2)	47.83(13)	C(8)-C(7)-C(12)	116.5(2)
O(7)-Li(3)-Li(2)	140.6(2)	C(7)-C(8)-C(9)	122.0(2)
O(2)-Li(3)-Li(2)	95.32(17)	C(10)-C(9)-C(8)	119.7(3)
O(3)-Li(3)-Li(2)	48.60(13)	C(11)-C(10)-C(9)	118.7(3)
O(4)-Li(3)-Li(1)	47.48(13)	C(10)-C(11)-C(12)	121.6(3)
O(7)-Li(3)-Li(1)	151.3(2)	C(11)-C(12)-C(7)	121.4(3)
O(2)-Li(3)-Li(1)	48.13(13)	O(3)-C(13)-C(14)	122.7(2)
O(3)-Li(3)-Li(1)	96.51(16)	O(3)-C(13)-C(18)	121.7(2)
Li(2)-Li(3)-Li(1)	60.74(15)	C(14)-C(13)-C(18)	115.6(2)
O(4)-Li(3)-Sr	102.24(14)	C(15)-C(14)-C(13)	122.9(3)
O(7)-Li(3)-Sr	132.0(2)	C(14)-C(15)-C(16)	120.1(3)
O(2)-Li(3)-Sr	50.15(10)	C(17)-C(16)-C(15)	119.4(3)
O(3)-Li(3)-Sr	48.79(9)	C(16)-C(17)-C(18)	121.1(3)
Li(2)-Li(3)-Sr	66.71(12)	C(17)-C(18)-C(13)	120.9(3)
Li(1)-Li(3)-Sr	68.12(12)	O(4)-C(19)-C(20)	121.3(2)
C(27)-O(6)-C(30)	107.75(19)	O(4)-C(19)-C(24)	121.7(2)
C(27)-O(6)-Li(2)	128.3(2)	C(20)-C(19)-C(24)	117.0(2)
C(30)-O(6)-Li(2)	122.2(2)	C(21)-C(20)-C(19)	121.1(2)

C(20)-C(21)-C(22)	121.0(3)	C(29)-C(28)-C(27)	108.5(3)
C(23)-C(22)-C(21)	119.0(3)	C(28)-C(29)-C(30)	105.7(3)
C(22)-C(23)-C(24)	120.4(3)	O(6)-C(30)-C(29)	105.9(2)
C(23)-C(24)-C(19)	121.5(2)	O(7)-C(32)-C(33)	115.7(3)
O(5)-C(26)-C(26)#2	110.1(3)	O(8)-C(33)-C(32)	110.4(3)
O(6)-C(27)-C(28)	107.3(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1 #2 -x,-y,-z+1

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **28**.

The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sr	46(1)	48(1)	32(1)	1(1)	4(1)	7(1)
O(1)	61(1)	49(1)	34(1)	-7(1)	-4(1)	-2(1)
O(2)	60(1)	58(1)	22(1)	2(1)	1(1)	2(1)
O(3)	52(1)	50(1)	35(1)	5(1)	5(1)	2(1)
O(4)	50(1)	58(1)	37(1)	7(1)	1(1)	11(1)
Li(1)	56(2)	62(2)	36(2)	5(2)	5(2)	-4(2)
Li(2)	65(2)	61(2)	36(2)	-4(2)	10(2)	-1(2)
Li(3)	80(3)	46(2)	32(2)	1(1)	7(2)	-3(2)
O(6)	49(1)	88(1)	29(1)	3(1)	0(1)	-5(1)
O(5)	48(1)	95(1)	63(1)	24(1)	-2(1)	-4(1)
O(7)	79(1)	68(1)	53(1)	-15(1)	14(1)	-14(1)
O(8)	64(1)	96(1)	111(2)	15(1)	-4(1)	4(1)
C(1)	48(1)	45(1)	30(1)	-3(1)	-3(1)	3(1)
C(2)	65(2)	60(1)	42(1)	-4(1)	-3(1)	-7(1)
C(3)	56(2)	64(1)	79(2)	-16(1)	-17(1)	-16(1)
C(4)	80(2)	92(2)	52(1)	-33(1)	-6(1)	-7(2)
C(5)	73(2)	88(2)	41(1)	-14(1)	4(1)	7(1)
C(6)	51(1)	54(1)	44(1)	-5(1)	-2(1)	-3(1)
C(7)	40(1)	68(1)	24(1)	3(1)	-2(1)	0(1)
C(8)	43(1)	75(1)	48(1)	11(1)	4(1)	6(1)
C(9)	59(2)	123(2)	56(1)	44(1)	4(1)	4(2)
C(10)	75(2)	184(3)	37(1)	39(2)	-4(1)	-31(2)
C(11)	115(2)	149(3)	26(1)	-15(2)	16(1)	-36(2)

C(12)	88(2)	82(2)	33(1)	-5(1)	19(1)	0(1)
C(13)	55(1)	51(1)	24(1)	-1(1)	5(1)	-1(1)
C(14)	75(2)	49(1)	51(1)	4(1)	-5(1)	-1(1)
C(15)	97(2)	65(2)	66(2)	15(1)	-18(2)	-14(2)
C(16)	92(2)	89(2)	55(1)	12(1)	-1(1)	-33(2)
C(17)	67(2)	105(2)	71(2)	-4(2)	9(1)	-22(2)
C(18)	48(2)	75(2)	61(1)	3(1)	-1(1)	-1(1)
C(19)	44(1)	54(1)	34(1)	1(1)	0(1)	-1(1)
C(20)	76(2)	80(2)	41(1)	10(1)	21(1)	6(1)
C(21)	74(2)	104(2)	64(2)	-6(2)	21(1)	5(2)
C(22)	59(2)	97(2)	79(2)	-12(2)	8(1)	33(1)
C(23)	78(2)	74(2)	72(2)	4(1)	1(1)	25(1)
C(24)	63(2)	69(1)	37(1)	2(1)	4(1)	8(1)
C(25)	88(3)	213(3)	140(2)	133(2)	-27(2)	-32(2)
C(26)	57(2)	125(3)	66(2)	21(2)	4(1)	-5(2)
C(27)	100(2)	105(2)	51(1)	8(1)	18(1)	-29(2)
C(28)	105(3)	269(5)	33(1)	-3(2)	8(1)	-71(3)
C(29)	92(2)	137(3)	52(1)	-25(2)	-17(2)	-10(2)
C(30)	50(2)	90(2)	54(1)	15(1)	-2(1)	5(1)
C(31)	74(2)	82(2)	67(2)	-18(1)	-14(1)	-5(2)
C(32)	99(2)	67(2)	109(2)	-22(2)	42(2)	-8(2)
C(33)	51(2)	108(2)	129(3)	-39(2)	-15(2)	15(2)
C(34)	140(4)	131(3)	231(5)	89(3)	28(4)	53(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **28**.

	x	y	z	U(eq)
H(2)	1831	-1062	4099	67
H(3)	1477	-1777	2807	81
H(4)	2485	-1699	1545	91
H(5)	3745	-848	1529	81
H(6)	4013	-84	2754	60
H(8)	4179	-771	7033	66
H(9)	4298	-1014	8624	95
H(10)	3987	-134	9690	119
H(11)	3546	954	9139	115

H(12)	3398	1192	7567	80
H(14)	3899	2432	3955	71
H(15)	4881	3368	3602	93
H(16)	6695	3290	3705	94
H(17)	7497	2291	4267	97
H(18)	6526	1335	4634	74
H(20)	1269	1458	6432	78
H(21)	82	2328	6621	96
H(22)	-504	3037	5372	94
H(23)	230	2922	3963	90
H(24)	1535	2118	3802	67
H(25A)	873	-490	7023	224
H(25B)	2023	-676	6778	224
H(25C)	1062	-1135	6370	224
H(26A)	-241	179	5902	99
H(26B)	-294	-588	5489	99
H(27A)	3857	1447	2112	101
H(27B)	2943	2005	1948	101
H(28A)	2625	1507	622	162
H(28B)	3254	826	955	162
H(29A)	1807	331	1081	114
H(29B)	1190	1043	881	114
H(30A)	1023	1189	2395	78
H(30B)	1512	434	2576	78
H(31A)	5356	2671	6158	113
H(31B)	5554	1889	6475	113
H(31C)	5324	2463	7224	113
H(32A)	3783	2840	7381	108
H(32B)	2779	2454	6920	108
H(33A)	3030	3130	5529	117
H(33B)	2573	3524	6377	117
H(34A)	3637	4188	5000	250
H(34B)	4472	4619	5643	250
H(34C)	3282	4612	5865	250

Crystal data and structure refinement for $[CaLi_6(OPh)_6(O^tBu)_2(thf)_6]$ 29

$C_{68}H_{96}Li_6CaO_{14}$, M= 1219.17 gmol^{-1}, triclinic, *P*-1 (Nr. 2), a = 12.489(3), b = 13.199(3), c = 13.824(3) Å, α = 101.50(3), β = 110.16(3), γ = 114.79(3)°, V = 1776.9(7) Å^3, Z = 1, $\rho_{calcd.}$= 1.139 Mgm^3, *F*(000) = 654, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 0.146 mm^{-1}, 1.72° < θ < 27.21°, 14290 reflections of which 7296 unique and 2478 observed, 407 parameters refined, *GOOF* (on F^2) = 0.956, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.1031, *w*R2 = 0.2143 for I > 2σ(I) and R1 = 0.2481, wR2 = 0.2843 for all data.

The intensities from the single-crystals of **29** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding model for all carbon atoms. CCDC-616807 (**29**) contains the supplementary crystallographic data for **29**. The cif file for the structure of **29** can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and structure refinement for **29**.

Identification code	$[CaLi_6(OPh)_6(O^tBu)_2(thf)_6]$	
Empirical formula	C68 H96 Ca Li6 O14	
Formula weight	1219.17	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.489(3) Å	α= 101.50(3)°
	b = 13.199(3) Å	β= 110.16(3)°
	c = 13.824(3) Å	γ = 114.79(3)°
Volume	1776.9(7) Å^3	
Z	1	
Density (calculated)	1.139 Mg/m^3	
Absorption coefficient	0.146 mm^{-1}	
F(000)	654	
Theta range for data collection	1.72 to 27.21°	
Index ranges	-15<=h<=15, -16<=k<=16, -17<=l<=17	
Reflections collected	14290	
Independent reflections	7296 [R(int) = 0.1916]	
Completeness to theta = 27.21°	92.3 %	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7296 / 0 / 407
Goodness-of-fit on F^2	0.956
Final R indices [I>2sigma(I)]	R1 = 0.1031, wR2 = 0.2143
R indices (all data)	R1 = 0.2481, wR2 = 0.2843
Largest diff. peak and hole	0.438 and -0.350 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **29**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ca	10000	5000	5000	34(1)
O(1)	8308(1)	5387(1)	4070(1)	42(1)
O(2)	9909(1)	4767(1)	3206(1)	41(1)
O(3)	8079(1)	3028(1)	3727(1)	39(1)
O(4)	6927(1)	3511(1)	1769(1)	47(1)
O(5)	8903(1)	6456(1)	2103(1)	71(1)
O(6)	5208(1)	2947(1)	3270(1)	62(1)
O(7)	8476(1)	1911(1)	1424(1)	65(1)
C(1)	8210(1)	6369(1)	4251(1)	43(1)
C(2)	9254(1)	7489(1)	5048(2)	57(1)
C(3)	9176(2)	8543(1)	5197(2)	77(1)
C(4)	7993(2)	8451(2)	4546(2)	75(1)
C(5)	6933(2)	7351(2)	3736(2)	69(1)
C(6)	7015(2)	6288(1)	3586(2)	58(1)
C(7)	10777(2)	4914(1)	2815(1)	45(1)
C(8)	10509(2)	4904(2)	1772(2)	71(1)
C(9)	11403(2)	5085(2)	1352(2)	99(1)
C(10)	12636(2)	5261(2)	2037(2)	88(1)
C(11)	12920(2)	5237(2)	3052(2)	83(1)
C(12)	12012(2)	5058(2)	3457(2)	61(1)
C(13)	7384(1)	1977(1)	3799(1)	39(1)
C(14)	7228(2)	1940(1)	4740(1)	50(1)
C(15)	6490(2)	849(2)	4796(2)	61(1)
C(16)	5835(2)	-248(2)	3876(2)	64(1)
C(17)	5957(2)	-246(1)	2957(2)	65(1)

C(18)	6724(2)	859(2)	2890(2)	57(1)
C(19)	5814(2)	2985(1)	702(1)	53(1)
C(20)	5046(2)	1588(2)	293(2)	69(1)
C(21)	4864(2)	3403(2)	737(2)	93(1)
C(22)	6258(2)	3326(2)	-149(2)	82(1)
C(23)	10226(3)	7448(2)	2622(3)	162(2)
C(24)	10196(3)	8473(3)	2533(4)	179(2)
C(25)	8829(3)	8115(2)	1854(3)	161(2)
C(26)	8035(2)	6784(2)	1434(2)	90(1)
C(27)	3631(2)	2850(3)	3838(3)	144(1)
C(28)	3470(3)	1629(3)	3487(3)	173(2)
C(29)	4231(2)	1688(2)	2917(2)	101(1)
C(30)	9401(2)	1578(2)	1995(2)	111(1)
C(31)	9832(3)	1238(3)	1173(3)	171(2)
C(32)	9026(3)	1090(4)	168(3)	235(2)
C(33)	8236(2)	1605(2)	292(2)	102(1)
C(34)	4726(2)	3597(2)	3741(2)	116(1)
Li(1)	8458(3)	5122(2)	2600(2)	46(1)
Li(2)	6871(2)	3647(2)	3143(2)	43(1)
Li(3)	8217(3)	3062(3)	2363(2)	52(1)

Table 3. Bond lengths [Å] and angles [°] for **29**.

Ca-O(1)	2.3823(14)	O(2)-Li(3)	2.039(3)
Ca-O(1)#1	2.3823(14)	O(3)-Li(2)	2.013(3)
Ca-O(2)	2.3941(13)	O(3)-Li(3)	1.959(4)
Ca-O(2)#1	2.3941(13)	O(4)-Li(1)	1.897(3)
Ca-O(3)	2.378(2)	O(4)-Li(2)	1.901(3)
Ca-O(3)#1	2.378(2)	O(4)-Li(3)	1.926(4)
Ca-Li(1)	3.288(3)	O(5)-Li(1)	1.952(3)
Ca-Li(1)#1	3.288(3)	O(6)-Li(2)	1.977(3)
Ca-Li(2)	3.233(3)	O(7)-Li(3)	2.002(4)
Ca-Li(2)#1	3.233(3)	O(1)-C(1)	1.336(2)
Ca-Li(3)	3.271(3)	O(2)-C(7)	1.332(2)
Ca-Li(3)#1	3.271(3)	O(3)-C(13)	1.3387(19)
O(1)-Li(1)	2.078(4)	O(4)-C(19)	1.399(2)
O(1)-Li(2)	1.981(3)	O(5)-C(23)	1.398(3)
O(2)-Li(1)	2.006(4)	O(5)-C(26)	1.442(3)

O(6)-C(29)	1.433(3)	C(15)-C(16)	1.392(3)
O(6)-C(34)	1.415(3)	C(16)-C(17)	1.330(3)
O(7)-C(30)	1.445(3)	C(17)-C(18)	1.414(3)
O(7)-C(33)	1.423(3)	C(13)-C(18)	1.401(2)
C(1)-Li(1)	2.726(4)	C(19)-C(20)	1.538(3)
C(1)-C(2)	1.358(2)	C(19)-C(21)	1.515(4)
C(2)-C(3)	1.414(3)	C(19)-C(22)	1.532(3)
C(3)-C(4)	1.378(3)	C(23)-C(24)	1.398(5)
C(4)-C(5)	1.354(2)	C(24)-C(25)	1.435(5)
C(5)-C(6)	1.429(3)	C(25)-C(26)	1.463(3)
C(1)-C(6)	1.401(2)	C(27)-C(28)	1.491(5)
C(7)-C(8)	1.359(3)	C(28)-C(29)	1.419(5)
C(8)-C(9)	1.386(4)	C(30)-C(31)	1.485(5)
C(9)-C(10)	1.389(3)	C(31)-C(32)	1.321(5)
C(10)-C(11)	1.334(4)	C(32)-C(33)	1.449(6)
C(11)-C(12)	1.386(3)	C(27)-C(34)	1.381(4)
C(7)-C(12)	1.395(3)	Li(1)-Li(2)	2.580(4)
C(13)-C(14)	1.387(3)	Li(1)-Li(3)	2.546(5)
C(13)-Li(2)	2.769(4)	Li(2)-Li(3)	2.567(5)
C(14)-C(15)	1.382(3)		

O(3)#1-Ca-O(3)	180.0	O(1)-Ca-Li(2)	37.60(6)
O(3)#1-Ca-O(1)	104.07(5)	O(1)#1-Ca-Li(2)	142.40(6)
O(3)-Ca-O(1)	75.93(5)	O(2)-Ca-Li(2)	72.79(7)
O(3)#1-Ca-O(1)#1	75.93(5)	O(2)#1-Ca-Li(2)	107.21(7)
O(3)-Ca-O(1)#1	104.07(5)	O(3)#1-Ca-Li(2)#1	38.36(7)
O(1)-Ca-O(1)#1	180.000(1)	O(3)-Ca-Li(2)#1	141.64(7)
O(3)#1-Ca-O(2)	105.17(5)	O(1)-Ca-Li(2)#1	142.40(6)
O(3)-Ca-O(2)	74.83(5)	O(1)#1-Ca-Li(2)#1	37.60(6)
O(1)-Ca-O(2)	76.38(5)	O(2)-Ca-Li(2)#1	107.21(7)
O(1)#1-Ca-O(2)	103.62(5)	O(2)#1-Ca-Li(2)#1	72.79(7)
O(3)#1-Ca-O(2)#1	74.83(5)	Li(2)-Ca-Li(2)#1	180.00(7)
O(3)-Ca-O(2)#1	105.17(5)	O(3)#1-Ca-Li(3)	143.56(7)
O(1)-Ca-O(2)#1	103.62(5)	O(3)-Ca-Li(3)	36.44(7)
O(1)#1-Ca-O(2)#1	76.38(5)	O(1)-Ca-Li(3)	72.29(8)
O(2)-Ca-O(2)#1	180.000(1)	O(1)#1-Ca-Li(3)	107.71(8)
O(3)#1-Ca-Li(2)	141.64(7)	O(2)-Ca-Li(3)	38.39(6)
O(3)-Ca-Li(2)	38.36(7)	O(2)#1-Ca-Li(3)	141.61(7)

Li(2)-Ca-Li(3)	46.49(9)	C(7)-O(2)-Li(1)	122.30(15)
Li(2)#1-Ca-Li(3)	133.51(9)	C(7)-O(2)-Li(3)	112.94(14)
O(3)#1-Ca-Li(3)#1	36.44(7)	Li(1)-O(2)-Li(3)	78.01(13)
O(3)-Ca-Li(3)#1	143.56(7)	C(7)-O(2)-Ca	135.49(9)
O(1)-Ca-Li(3)#1	107.71(8)	Li(1)-O(2)-Ca	96.29(11)
O(1)#1-Ca-Li(3)#1	72.29(8)	Li(3)-O(2)-Ca	94.78(12)
O(2)-Ca-Li(3)#1	141.61(7)	C(13)-O(3)-Li(3)	121.64(13)
O(2)#1-Ca-Li(3)#1	38.39(6)	C(13)-O(3)-Li(2)	109.81(12)
Li(2)-Ca-Li(3)#1	133.51(9)	Li(3)-O(3)-Li(2)	80.52(15)
Li(2)#1-Ca-Li(3)#1	46.49(9)	C(13)-O(3)-Ca	136.15(9)
Li(3)-Ca-Li(3)#1	180.000(1)	Li(3)-O(3)-Ca	97.44(9)
O(3)#1-Ca-Li(1)	108.83(6)	Li(2)-O(3)-Ca	94.48(8)
O(3)-Ca-Li(1)	71.17(6)	C(19)-O(4)-Li(1)	130.58(15)
O(1)-Ca-Li(1)	39.04(7)	C(19)-O(4)-Li(2)	125.82(14)
O(1)#1-Ca-Li(1)	140.96(7)	Li(1)-O(4)-Li(2)	85.58(13)
O(2)-Ca-Li(1)	37.34(7)	C(19)-O(4)-Li(3)	130.84(15)
O(2)#1-Ca-Li(1)	142.66(7)	Li(1)-O(4)-Li(3)	83.53(14)
Li(2)-Ca-Li(1)	46.59(8)	Li(2)-O(4)-Li(3)	84.28(15)
Li(2)#1-Ca-Li(1)	133.41(8)	C(23)-O(5)-C(26)	107.9(2)
Li(3)-Ca-Li(1)	45.68(8)	C(23)-O(5)-Li(1)	120.6(2)
Li(3)#1-Ca-Li(1)	134.32(8)	C(26)-O(5)-Li(1)	129.71(15)
O(3)#1-Ca-Li(1)#1	71.17(6)	C(34)-O(6)-C(29)	104.84(18)
O(3)-Ca-Li(1)#1	108.83(6)	C(34)-O(6)-Li(2)	126.87(15)
O(1)-Ca-Li(1)#1	140.96(7)	C(29)-O(6)-Li(2)	128.29(18)
O(1)#1-Ca-Li(1)#1	39.04(7)	C(33)-O(7)-C(30)	107.9(2)
O(2)-Ca-Li(1)#1	142.66(7)	C(33)-O(7)-Li(3)	131.1(2)
O(2)#1-Ca-Li(1)#1	37.34(7)	C(30)-O(7)-Li(3)	118.17(16)
Li(2)-Ca-Li(1)#1	133.41(8)	O(1)-C(1)-C(2)	122.51(15)
Li(2)#1-Ca-Li(1)#1	46.59(8)	O(1)-C(1)-C(6)	120.56(12)
Li(3)-Ca-Li(1)#1	134.32(8)	C(2)-C(1)-C(6)	116.90(17)
Li(3)#1-Ca-Li(1)#1	45.68(8)	O(1)-C(1)-Li(1)	47.75(11)
Li(1)-Ca-Li(1)#1	180.000(1)	C(2)-C(1)-Li(1)	120.81(15)
C(1)-O(1)-Li(2)	129.31(13)	C(6)-C(1)-Li(1)	99.48(14)
C(1)-O(1)-Li(1)	103.84(14)	C(1)-C(2)-C(3)	122.55(17)
Li(2)-O(1)-Li(1)	78.88(12)	C(4)-C(3)-C(2)	120.10(14)
C(1)-O(1)-Ca	133.98(8)	C(5)-C(4)-C(3)	119.0(2)
Li(2)-O(1)-Ca	95.20(11)	C(4)-C(5)-C(6)	120.77(19)
Li(1)-O(1)-Ca	94.73(11)	C(1)-C(6)-C(5)	120.63(13)

O(2)-C(7)-C(8)	122.68(17)	O(4)-Li(1)-O(2)	100.21(15)
O(2)-C(7)-C(12)	121.08(17)	O(5)-Li(1)-O(2)	115.89(16)
C(8)-C(7)-C(12)	116.2(2)	O(4)-Li(1)-O(1)	95.84(15)
C(7)-C(8)-C(9)	124.0(2)	O(5)-Li(1)-O(1)	118.38(16)
C(8)-C(9)-C(10)	117.5(2)	O(2)-Li(1)-O(1)	92.59(13)
C(11)-C(10)-C(9)	120.3(3)	O(4)-Li(1)-Li(3)	48.72(10)
C(10)-C(11)-C(12)	121.3(2)	O(5)-Li(1)-Li(3)	146.4(2)
C(11)-C(12)-C(7)	120.6(2)	O(2)-Li(1)-Li(3)	51.56(10)
O(3)-C(13)-C(14)	122.27(14)	O(1)-Li(1)-Li(3)	94.52(15)
O(3)-C(13)-C(18)	120.56(17)	O(4)-Li(1)-Li(2)	47.27(10)
C(14)-C(13)-C(18)	117.09(16)	O(5)-Li(1)-Li(2)	148.1(2)
O(3)-C(13)-Li(2)	43.14(9)	O(2)-Li(1)-Li(2)	95.12(14)
C(14)-C(13)-Li(2)	110.55(15)	O(1)-Li(1)-Li(2)	48.89(10)
C(18)-C(13)-Li(2)	112.20(14)	Li(3)-Li(1)-Li(2)	60.11(13)
C(15)-C(14)-C(13)	121.61(16)	O(4)-Li(1)-C(1)	109.91(16)
C(14)-C(15)-C(16)	120.1(2)	O(5)-Li(1)-C(1)	90.90(13)
C(17)-C(16)-C(15)	119.86(19)	O(2)-Li(1)-C(1)	112.94(12)
C(16)-C(17)-C(18)	120.99(17)	O(1)-Li(1)-C(1)	28.41(7)
C(13)-C(18)-C(17)	120.3(2)	Li(3)-Li(1)-C(1)	122.53(15)
O(4)-C(19)-C(21)	110.96(17)	Li(2)-Li(1)-C(1)	69.06(12)
O(4)-C(19)-C(22)	110.90(15)	O(4)-Li(1)-Ca	101.53(13)
C(21)-C(19)-C(22)	108.4(2)	O(5)-Li(1)-Ca	131.41(9)
O(4)-C(19)-C(20)	109.42(17)	O(2)-Li(1)-Ca	46.37(7)
C(21)-C(19)-C(20)	108.42(17)	O(1)-Li(1)-Ca	46.23(7)
C(22)-C(19)-C(20)	108.63(18)	Li(3)-Li(1)-Ca	66.81(10)
C(24)-C(23)-O(5)	108.6(3)	Li(2)-Li(1)-Ca	65.59(10)
C(23)-C(24)-C(25)	109.1(2)	C(1)-Li(1)-Ca	69.21(8)
C(24)-C(25)-C(26)	105.7(3)	O(4)-Li(2)-O(6)	124.90(13)
O(5)-C(26)-C(25)	105.79(19)	O(4)-Li(2)-O(1)	99.04(15)
C(34)-C(27)-C(28)	104.6(3)	O(6)-Li(2)-O(1)	120.13(17)
C(29)-C(28)-C(27)	105.7(3)	O(4)-Li(2)-O(3)	96.88(16)
C(28)-C(29)-O(6)	107.9(2)	O(6)-Li(2)-O(3)	115.32(16)
O(7)-C(30)-C(31)	103.9(2)	O(1)-Li(2)-O(3)	94.33(11)
C(32)-C(31)-C(30)	110.1(3)	O(4)-Li(2)-Li(3)	48.27(12)
C(31)-C(32)-C(33)	108.6(3)	O(6)-Li(2)-Li(3)	142.68(14)
O(7)-C(33)-C(32)	107.5(2)	O(1)-Li(2)-Li(3)	96.33(13)
C(27)-C(34)-O(6)	112.5(3)	O(3)-Li(2)-Li(3)	48.83(11)
O(4)-Li(1)-O(5)	127.05(15)	O(4)-Li(2)-Li(1)	47.15(10)

O(6)-Li(2)-Li(1)	150.71(18)	O(3)-Li(3)-O(7)	125.3(2)
O(1)-Li(2)-Li(1)	52.23(10)	O(4)-Li(3)-O(2)	98.13(16)
O(3)-Li(2)-Li(1)	93.94(14)	O(3)-Li(3)-O(2)	92.95(12)
Li(3)-Li(2)-Li(1)	59.30(13)	O(7)-Li(3)-O(2)	110.92(17)
O(4)-Li(2)-C(13)	107.44(15)	O(4)-Li(3)-Li(1)	47.76(11)
O(6)-Li(2)-C(13)	89.51(13)	O(3)-Li(3)-Li(1)	96.32(16)
O(1)-Li(2)-C(13)	116.03(12)	O(7)-Li(3)-Li(1)	137.09(19)
O(3)-Li(2)-C(13)	27.05(6)	O(2)-Li(3)-Li(1)	50.43(10)
Li(3)-Li(2)-C(13)	65.59(12)	O(4)-Li(3)-Li(2)	47.45(12)
Li(1)-Li(2)-C(13)	119.61(15)	O(3)-Li(3)-Li(2)	50.65(12)
O(4)-Li(2)-Ca	103.35(12)	O(7)-Li(3)-Li(2)	154.38(13)
O(6)-Li(2)-Ca	131.53(14)	O(2)-Li(3)-Li(2)	94.70(14)
O(1)-Li(2)-Ca	47.21(7)	Li(1)-Li(3)-Li(2)	60.59(14)
O(3)-Li(2)-Ca	47.16(5)	O(4)-Li(3)-Ca	101.42(14)
Li(3)-Li(2)-Ca	67.54(8)	O(3)-Li(3)-Ca	46.12(6)
Li(1)-Li(2)-Ca	67.82(8)	O(7)-Li(3)-Ca	133.03(14)
C(13)-Li(2)-Ca	70.14(8)	O(2)-Li(3)-Ca	46.83(8)
O(4)-Li(3)-O(3)	97.87(18)	Li(1)-Li(3)-Ca	67.51(9)
O(4)-Li(3)-O(7)	124.55(15)	Li(2)-Li(3)-Ca	65.98(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **29**.

The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ca	34(1)	30(1)	34(1)	12(1)	12(1)	19(1)
O(1)	44(1)	31(1)	49(1)	15(1)	12(1)	26(1)
O(2)	41(1)	40(1)	41(1)	19(1)	19(1)	20(1)
O(3)	41(1)	31(1)	42(1)	14(1)	16(1)	21(1)
O(4)	48(1)	43(1)	35(1)	12(1)	7(1)	23(1)
O(5)	61(1)	54(1)	82(1)	38(1)	16(1)	27(1)
O(6)	48(1)	60(1)	84(1)	29(1)	35(1)	33(1)
O(7)	81(1)	60(1)	54(1)	12(1)	30(1)	43(1)
C(1)	47(1)	37(1)	48(1)	16(1)	19(1)	29(1)
C(2)	47(1)	47(1)	68(1)	13(1)	15(1)	34(1)

C(3)	70(1)	37(1)	97(2)	11(1)	14(1)	34(1)
C(4)	77(1)	64(1)	99(1)	36(1)	36(1)	54(1)
C(5)	58(1)	59(1)	93(1)	34(1)	22(1)	43(1)
C(6)	49(1)	47(1)	69(1)	17(1)	16(1)	32(1)
C(7)	49(1)	39(1)	39(1)	16(1)	18(1)	20(1)
C(8)	57(1)	106(1)	63(1)	42(1)	34(1)	45(1)
C(9)	85(1)	157(2)	70(1)	56(1)	49(1)	61(1)
C(10)	76(1)	128(1)	87(1)	52(1)	55(1)	59(1)
C(11)	82(1)	120(1)	87(1)	52(1)	54(1)	70(1)
C(12)	58(1)	82(1)	59(1)	34(1)	30(1)	46(1)
C(13)	34(1)	35(1)	45(1)	16(1)	15(1)	20(1)
C(14)	57(1)	41(1)	50(1)	20(1)	23(1)	25(1)
C(15)	65(1)	60(1)	65(1)	34(1)	37(1)	30(1)
C(16)	66(1)	48(1)	86(1)	34(1)	40(1)	31(1)
C(17)	85(1)	34(1)	79(1)	20(1)	46(1)	31(1)
C(18)	70(1)	43(1)	53(1)	19(1)	31(1)	25(1)
C(19)	51(1)	41(1)	38(1)	10(1)	6(1)	17(1)
C(20)	60(1)	48(1)	58(1)	14(1)	11(1)	14(1)
C(21)	75(1)	82(1)	74(2)	13(1)	-3(1)	44(1)
C(22)	89(1)	64(1)	45(1)	21(1)	11(1)	20(1)
C(23)	70(2)	76(1)	228(3)	77(2)	-4(2)	5(1)
C(24)	107(2)	70(2)	220(4)	56(2)	-9(3)	6(2)
C(25)	115(2)	66(1)	183(3)	57(1)	-21(2)	25(1)
C(26)	81(1)	61(1)	103(1)	48(1)	14(1)	36(1)
C(27)	133(1)	104(2)	222(2)	50(2)	140(1)	49(1)
C(28)	167(1)	108(2)	316(2)	103(2)	186(1)	67(1)
C(29)	72(1)	65(1)	161(2)	39(1)	57(1)	34(1)
C(30)	165(1)	136(1)	90(1)	52(1)	62(1)	123(1)
C(31)	205(1)	219(2)	185(3)	77(2)	116(1)	174(1)
C(32)	193(1)	414(3)	99(2)	-2(2)	55(1)	220(1)
C(33)	126(1)	122(2)	66(1)	25(1)	57(1)	70(1)
C(34)	86(1)	102(2)	167(2)	26(1)	91(1)	43(1)
Li(1)	48(1)	45(1)	39(1)	26(1)	9(1)	25(1)
Li(2)	39(1)	45(1)	41(1)	16(1)	15(1)	22(1)
Li(3)	51(1)	58(1)	41(1)	18(1)	17(1)	29(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **29**.

	x	y	z	U(eq)
H(2)	10060	7567	5520	68
H(3)	9933	9307	5741	93
H(4)	7922	9142	4663	90
H(5)	6134	7286	3266	82
H(6)	6261	5526	3036	69
H(8)	9664	4767	1307	85
H(9)	11184	5087	630	119
H(10)	13273	5399	1785	106
H(11)	13752	5343	3501	99
H(12)	12230	5034	4171	73
H(14)	7634	2676	5355	60
H(15)	6431	847	5455	73
H(16)	5308	-989	3903	77
H(17)	5526	-990	2344	78
H(18)	6791	844	2231	68
H(20A)	5636	1303	253	103
H(20B)	4276	1222	-447	103
H(20C)	4740	1358	816	103
H(21A)	4598	3219	1292	139
H(21B)	4072	2983	2	139
H(21C)	5313	4275	938	139
H(22A)	6708	4203	80	123
H(22B)	5475	2925	-888	123
H(22C)	6871	3068	-179	123
H(23A)	10692	7599	3416	194
H(23B)	10712	7275	2255	194
H(24A)	10740	8836	2188	215
H(24B)	10573	9085	3284	215
H(25A)	8742	8370	1226	193
H(25B)	8527	8482	2305	193
H(26A)	7227	6515	1523	107
H(26B)	7759	6408	635	107
H(27A)	2824	2817	3344	172

H(27B)	3800	3144	4616	172
H(28A)	3809	1456	4147	207
H(28B)	2520	989	2986	207
H(29A)	3640	1314	2101	122
H(29B)	4683	1245	3102	122
H(30A)	8954	888	2174	133
H(30B)	10171	2267	2693	133
H(31A)	10758	1879	1422	205
H(31B)	9811	479	1132	205
H(32A)	8431	220	-329	282
H(32B)	9558	1500	-168	282
H(33A)	8503	2334	128	122
H(33B)	7278	1011	-231	122
H(34A)	5451	4228	4488	140
H(34B)	4471	4004	3267	140

Crystal data and structure refinement for $[Li(thf)_4][Sr_6(O)(I)_3(O^tBu)_7(thf)_3]_2(\mu\text{-}I).(THF)_n$ 30

$C_{96}H_{214}I_7LiSr_{12}O_{27}$, M= 3747.35 gmol^{-1}, monoclinic, *C*2/*m* (Nr. 12), a = 41.172(4), b = 16.561(3), c = 12.800(1) Å, β = 105.556(7)°, V = 8407.4(2) Å^3, Z = 1, $\rho_{calcd.}$= 0.74 Mgm^3, *F*(000) = 1836, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 2.553 mm^{-1}, 1.97° < θ < 27.06°, 11733 reflections of which 7651 unique and 3397 observed, 319 parameters refined, *GOOF* (on F^2) = 1.261, R1= $\Sigma|F_o–F_c|/\Sigma F_o$ = 0.1248, *w*R2 = 0.2620 for I > 2σ(I) and R1 = 0.2364, wR2 = 0.3115 for all data.

The intensities from the single-crystals of **30** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically, except for the methyl groups of disordered ^{t}Bu-units and some disordered THF-molecules. Several batches of crystals were measured, trying to improve the crystal quality and the data, but without success so far. However, the structure of the anionic aggregate could be attributed without any doubt. The alkali metal ion with its coordinated THF ligands could not be attributed in the structure, which, together with the disorder observed for ^{t}Bu-groups and THF, leads to the high R1 value. The highest peak in remaining electron density of 1.43 is found near iodide ions. The positions of the hydrogen atoms could not be calculated due to the heavy disorder, but were included in the determination of the molar mass. CCDC-609599 (**30**). See http://dx.doi.org/10.1039/b506389b for crystallographic data in CIF or other electronic format.

Table 1. Crystal data and structure refinement for **30**.

Identification code	$[Li(thf)_4][Sr_6(O)(I)_3(O^tBu)_7(thf)_3]_2(\mu\text{-}I).(THF)_n$	
Empirical formula	C96 H214 I7 Li O27 Sr12	
Formula weight	3747.35	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/m	
Unit cell dimensions	a = 41.172(4) Å	a= 90°.
	b = 16.561(3) Å	b= 105.556(7)°.
	c = 12.7990(12) Å	g = 90°.
Volume	8407.4(17) $Å^3$	
Z	1	
Density (calculated)	0.740 Mg/m^3	
Absorption coefficient	2.553 mm^{-1}	
F(000)	1836	
Theta range for data collection	1.97 to 27.06°	
Index ranges	-52<=h<=50, -11<=k<=20, -12<=l<=16	
Reflections collected	11733	
Independent reflections	7651 [R(int) = 0.1333]	
Completeness to theta = 27.06°	79.9 %	
Absorption correction	Numerical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7651 / 0 / 318	
Goodness-of-fit on F^2	1.267	
Final R indices [I>2sigma(I)]	R1 = 0.1253, wR2 = 0.2632	
R indices (all data)	R1 = 0.2367, wR2 = 0.3128	
Largest diff. peak and hole	1.431 and -0.797 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **30**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sr(1)	803(1)	0	1300(1)	47(1)
Sr(2)	1473(1)	1116(1)	806(1)	52(1)

Sr(3)	1358(1)	1088(1)	3461(1)	48(1)
Sr(4)	2056(1)	0	3061(1)	48(1)
I(1)	0	0	0	103(1)
I(2)	1297(1)	2518(1)	5204(1)	138(1)
I(3)	2144(1)	0	518(1)	84(1)
O(1)	1439(1)	0	2078(4)	38(1)
O(2)	1101(1)	0	-203(4)	56(2)
O(3)	998(1)	1488(3)	1570(3)	57(1)
O(4)	909(1)	0	3326(4)	57(2)
O(5)	1855(1)	1436(3)	2660(3)	61(1)
O(6)	1760(1)	0	4518(4)	44(2)
O(7)	1584(1)	2145(5)	-668(4)	129(3)
O(8)	2730(1)	0	3840(7)	94(3)
C(1)	973(2)	0	-1343(7)	79(4)
C(4)	801(2)	2173(4)	1305(6)	77(3)
C(8)	654(2)	0	3921(7)	86(4)
C(11)	2068(1)	2156(5)	2844(6)	83(2)
C(15)	1923(2)	0	5625(7)	61(3)
C(2)	650(3)	0	-1731(12)	287(19)
C(3)	1085(5)	754(17)	-1776(14)	337(14)
C(5)	1027(3)	3015(10)	1558(13)	184(7)
C(6)	612(3)	2164(8)	-49(16)	222(8)
C(7)	506(2)	2163(8)	1840(9)	171(5)
C(9)	776(3)	0	4934(10)	550(40)
C(10)	373(2)	614(11)	3279(9)	252(9)
C(12)	2065(2)	2475(5)	1726(8)	134(3)
C(13)	2429(2)	1826(6)	3407(9)	115(4)
C(14)	1961(2)	2777(7)	3538(10)	131(5)
C(16)	1672(2)	0	6277(6)	83(4)
C(17)	2137(2)	783(5)	5905(7)	87(3)
C(18)	1821(3)	1947(11)	-1301(9)	205(6)
C(19)	1911(3)	2781(12)	-1596(11)	222(8)
C(20)	1629(3)	3260(8)	-1667(10)	173(5)
C(21)	1401(4)	2925(9)	-1073(13)	214(7)
C(22)	2942(2)	0	4942(10)	109(6)
C(23)	3283(2)	0	4957(11)	98(4)
C(24)	3293(2)	0	3877(9)	104(5)
C(25)	2952(3)	0	3137(15)	220(13)

O(9)	1940(4)	5000	1966(17)	268(8)
C(26)	1527(5)	5000	1430(20)	229(11)
C(27)	1557(5)	5000	140(20)	226(10)
C(28)	1903(7)	5000	290(30)	296(15)
C(29)	2134(5)	5000	1240(20)	236(11)

Table 3. Bond lengths [Å] and angles [°] for **30**.

Sr(1)-I(1)	3.2781(6)	O(1)-Sr(3)#1	2.610(4)
I(1)-Sr(1)#2	3.2781(6)	Sr(3)-O(3)	2.562(4)
Sr(2)-I(3)	3.4249(8)	Sr(3)-O(4)	2.554(3)
I(3)-Sr(2)#1	3.4249(8)	O(4)-Sr(3)#1	2.554(3)
Sr(3)-I(2)	3.3080(10)	Sr(3)-O(5)	2.587(4)
Sr(4)-I(3)	3.3712(11)	Sr(3)-O(6)	2.574(3)
Sr(1)-Sr(2)	3.5162(8)	O(6)-Sr(3)#1	2.574(3)
Sr(1)-Sr(2)#1	3.5162(8)	Sr(4)-O(1)	2.514(3)
Sr(1)-Sr(3)	3.5678(8)	Sr(4)-O(5)	2.525(4)
Sr(1)-Sr(3)#1	3.5678(8)	Sr(4)-O(5)#1	2.525(4)
Sr(2)-Sr(2)#1	3.6958(13)	Sr(4)-O(6)	2.485(5)
Sr(2)-Sr(3)	3.5558(8)	Sr(4)-O(8)	2.688(5)
Sr(2)-Sr(4)	3.7123(8)	Sr(2)-C(3)	3.317(17)
Sr(3)-Sr(3)#1	3.6052(13)	Sr(2)-C(12)	3.295(8)
Sr(3)-Sr(4)	3.5438(8)	Sr(4)-C(13)	3.368(9)
Sr(4)-Sr(2)#1	3.7123(8)	Sr(4)-C(13)#1	3.368(9)
Sr(4)-Sr(3)#1	3.5438(8)	O(2)-C(1)	1.412(9)
Sr(1)-O(1)	2.539(3)	O(3)-C(4)	1.382(8)
Sr(1)-O(2)	2.545(5)	O(4)-C(8)	1.454(10)
Sr(1)-O(3)	2.587(4)	O(5)-C(11)	1.462(8)
Sr(1)-O(3)#1	2.587(4)	O(6)-C(15)	1.396(9)
Sr(1)-O(4)	2.512(5)	O(7)-C(18)	1.464(14)
Sr(2)-O(1)	2.492(3)	O(7)-C(21)	1.515(16)
O(1)-Sr(2)#1	2.492(3)	O(8)-C(22)	1.446(13)
Sr(2)-O(2)	2.523(3)	O(8)-C(25)	1.442(19)
O(2)-Sr(2)#1	2.523(3)	O(9)-C(26)	1.66(3)
Sr(2)-O(3)	2.486(4)	O(9)-C(29)	1.38(4)
Sr(2)-O(5)	2.526(4)	C(1)-C(2)	1.289(13)
Sr(2)-O(7)	2.671(7)	C(1)-C(3)	1.49(3)
Sr(3)-O(1)	2.610(4)	C(1)-C(3)#1	1.49(3)

C(4)-C(5)	1.660(16)	C(15)-C(17)#1	1.554(8)
C(4)-C(6)	1.700(19)	C(10)-C(10)#1	2.03(4)
C(4)-C(7)	1.549(13)	C(18)-C(19)	1.50(3)
C(8)-C(9)	1.259(15)	C(19)-C(20)	1.39(2)
C(8)-C(10)	1.593(14)	C(20)-C(21)	1.47(2)
C(8)-C(10)#1	1.593(14)	C(22)-C(23)	1.401(14)
C(11)-C(12)	1.522(12)	C(23)-C(24)	1.394(18)
C(11)-C(13)	1.567(9)	C(24)-C(25)	1.470(14)
C(11)-C(14)	1.502(14)	C(26)-C(27)	1.69(4)
C(15)-C(16)	1.494(12)	C(27)-C(28)	1.38(4)
C(15)-C(17)	1.554(8)	C(28)-C(29)	1.32(4)

O(4)-Sr(1)-O(1)	73.72(14)	I(1)-Sr(1)-Sr(2)#1	129.948(19)
O(4)-Sr(1)-O(2)	142.66(13)	Sr(2)-Sr(1)-Sr(2)#1	63.41(2)
O(1)-Sr(1)-O(2)	68.93(15)	O(4)-Sr(1)-Sr(3)	45.70(7)
O(4)-Sr(1)-O(3)	84.28(10)	O(1)-Sr(1)-Sr(3)	46.97(8)
O(1)-Sr(1)-O(3)	72.34(7)	O(2)-Sr(1)-Sr(3)	104.34(8)
O(2)-Sr(1)-O(3)	84.56(10)	O(3)-Sr(1)-Sr(3)	45.86(8)
O(4)-Sr(1)-O(3)#1	84.28(10)	O(3)#1-Sr(1)-Sr(3)	105.44(8)
O(1)-Sr(1)-O(3)#1	72.34(7)	I(1)-Sr(1)-Sr(3)	137.909(18)
O(2)-Sr(1)-O(3)#1	84.56(10)	Sr(2)-Sr(1)-Sr(3)	60.254(15)
O(3)-Sr(1)-O(3)#1	144.63(14)	Sr(2)#1-Sr(1)-Sr(3)	92.000(18)
O(4)-Sr(1)-I(1)	113.33(9)	O(4)-Sr(1)-Sr(3)#1	45.70(7)
O(1)-Sr(1)-I(1)	172.94(12)	O(1)-Sr(1)-Sr(3)#1	46.97(8)
O(2)-Sr(1)-I(1)	104.01(10)	O(2)-Sr(1)-Sr(3)#1	104.34(8)
O(3)-Sr(1)-I(1)	107.64(7)	O(3)-Sr(1)-Sr(3)#1	105.44(8)
O(3)#1-Sr(1)-I(1)	107.64(7)	O(3)#1-Sr(1)-Sr(3)#1	45.86(8)
O(4)-Sr(1)-Sr(2)	104.96(8)	I(1)-Sr(1)-Sr(3)#1	137.909(18)
O(1)-Sr(1)-Sr(2)	45.11(8)	Sr(2)-Sr(1)-Sr(3)#1	92.000(18)
O(2)-Sr(1)-Sr(2)	45.81(6)	Sr(2)#1-Sr(1)-Sr(3)#1	60.254(15)
O(3)-Sr(1)-Sr(2)	44.96(9)	Sr(3)-Sr(1)-Sr(3)#1	60.70(2)
O(3)#1-Sr(1)-Sr(2)	107.08(8)	O(3)-Sr(2)-O(1)	74.85(13)
I(1)-Sr(1)-Sr(2)	129.95(2)	O(3)-Sr(2)-O(2)	87.13(14)
O(4)-Sr(1)-Sr(2)#1	104.96(8)	O(1)-Sr(2)-O(2)	70.02(12)
O(1)-Sr(1)-Sr(2)#1	45.11(8)	O(3)-Sr(2)-O(5)	86.26(12)
O(2)-Sr(1)-Sr(2)#1	45.81(6)	O(1)-Sr(2)-O(5)	70.85(13)
O(3)-Sr(1)-Sr(2)#1	107.08(8)	O(2)-Sr(2)-O(5)	140.69(14)
O(3)#1-Sr(1)-Sr(2)#1	44.96(9)	O(3)-Sr(2)-O(7)	114.89(17)

O(1)-Sr(2)-O(7)	170.08(17)	O(3)-Sr(2)-Sr(2)#1	104.37(10)
O(2)-Sr(2)-O(7)	107.49(17)	O(1)-Sr(2)-Sr(2)#1	42.13(8)
O(5)-Sr(2)-O(7)	110.43(16)	O(2)-Sr(2)-Sr(2)#1	42.91(7)
O(3)-Sr(2)-C(12)	105.9(2)	O(5)-Sr(2)-Sr(2)#1	102.12(10)
O(1)-Sr(2)-C(12)	116.08(17)	O(7)-Sr(2)-Sr(2)#1	129.63(16)
O(2)-Sr(2)-C(12)	166.5(2)	C(12)-Sr(2)-Sr(2)#1	133.11(15)
O(5)-Sr(2)-C(12)	46.13(19)	C(3)-Sr(2)-Sr(2)#1	79.6(5)
O(7)-Sr(2)-C(12)	64.3(2)	I(3)-Sr(2)-Sr(2)#1	57.347(12)
O(3)-Sr(2)-C(3)	102.5(4)	Sr(1)-Sr(2)-Sr(2)#1	58.295(12)
O(1)-Sr(2)-C(3)	114.8(5)	Sr(3)-Sr(2)-Sr(2)#1	89.270(14)
O(2)-Sr(2)-C(3)	45.0(5)	O(3)-Sr(2)-Sr(4)	103.29(9)
O(5)-Sr(2)-C(3)	170.4(4)	O(1)-Sr(2)-Sr(4)	42.35(8)
O(7)-Sr(2)-C(3)	62.6(5)	O(2)-Sr(2)-Sr(4)	102.13(7)
C(12)-Sr(2)-C(3)	126.3(5)	O(5)-Sr(2)-Sr(4)	42.69(10)
O(3)-Sr(2)-I(3)	156.66(10)	O(7)-Sr(2)-Sr(4)	132.04(11)
O(1)-Sr(2)-I(3)	81.90(9)	C(12)-Sr(2)-Sr(4)	78.51(14)
O(2)-Sr(2)-I(3)	86.90(10)	C(3)-Sr(2)-Sr(4)	136.3(5)
O(5)-Sr(2)-I(3)	84.16(9)	I(3)-Sr(2)-Sr(4)	56.198(18)
O(7)-Sr(2)-I(3)	88.42(14)	Sr(1)-Sr(2)-Sr(4)	88.458(19)
C(12)-Sr(2)-I(3)	82.33(16)	Sr(3)-Sr(2)-Sr(4)	58.316(17)
C(3)-Sr(2)-I(3)	89.0(4)	Sr(2)#1-Sr(2)-Sr(4)	60.147(11)
O(3)-Sr(2)-Sr(1)	47.32(9)	O(4)-Sr(3)-O(3)	83.96(13)
O(1)-Sr(2)-Sr(1)	46.21(8)	O(4)-Sr(3)-O(6)	83.87(10)
O(2)-Sr(2)-Sr(1)	46.33(12)	O(3)-Sr(3)-O(6)	143.59(14)
O(5)-Sr(2)-Sr(1)	105.16(10)	O(4)-Sr(3)-O(5)	139.90(14)
O(7)-Sr(2)-Sr(1)	138.87(10)	O(3)-Sr(3)-O(5)	83.43(12)
C(12)-Sr(2)-Sr(1)	146.70(18)	O(6)-Sr(3)-O(5)	84.14(14)
C(3)-Sr(2)-Sr(1)	83.8(4)	O(4)-Sr(3)-O(1)	71.85(13)
I(3)-Sr(2)-Sr(1)	115.49(2)	O(3)-Sr(3)-O(1)	71.58(12)
O(3)-Sr(2)-Sr(3)	46.10(9)	O(6)-Sr(3)-O(1)	72.02(12)
O(1)-Sr(2)-Sr(3)	47.20(9)	O(5)-Sr(3)-O(1)	68.05(12)
O(2)-Sr(2)-Sr(3)	105.17(12)	O(4)-Sr(3)-I(2)	111.53(11)
O(5)-Sr(2)-Sr(3)	46.65(9)	O(3)-Sr(3)-I(2)	108.87(10)
O(7)-Sr(2)-Sr(3)	140.84(16)	O(6)-Sr(3)-I(2)	107.53(10)
C(12)-Sr(2)-Sr(3)	86.73(18)	O(5)-Sr(3)-I(2)	108.58(10)
C(3)-Sr(2)-Sr(3)	142.9(4)	O(1)-Sr(3)-I(2)	176.59(8)
I(3)-Sr(2)-Sr(3)	114.49(2)	O(4)-Sr(3)-Sr(4)	103.36(8)
Sr(1)-Sr(2)-Sr(3)	60.593(17)	O(3)-Sr(3)-Sr(4)	106.25(9)

O(6)-Sr(3)-Sr(4)	44.51(12)
O(5)-Sr(3)-Sr(4)	45.40(9)
O(1)-Sr(3)-Sr(4)	45.12(7)
I(2)-Sr(3)-Sr(4)	132.23(2)
O(4)-Sr(3)-Sr(2)	102.96(12)
O(3)-Sr(3)-Sr(2)	44.37(9)
O(6)-Sr(3)-Sr(2)	106.20(12)
O(5)-Sr(3)-Sr(2)	45.23(9)
O(1)-Sr(3)-Sr(2)	44.46(8)
I(2)-Sr(3)-Sr(2)	133.55(3)
Sr(4)-Sr(3)-Sr(2)	63.052(18)
O(4)-Sr(3)-Sr(1)	44.76(12)
O(3)-Sr(3)-Sr(1)	46.43(9)
O(6)-Sr(3)-Sr(1)	103.99(7)
O(5)-Sr(3)-Sr(1)	102.41(9)
O(1)-Sr(3)-Sr(1)	45.32(7)
I(2)-Sr(3)-Sr(1)	137.42(2)
Sr(4)-Sr(3)-Sr(1)	90.35(2)
Sr(2)-Sr(3)-Sr(1)	59.154(17)
O(4)-Sr(3)-Sr(3)#1	45.10(6)
O(3)-Sr(3)-Sr(3)#1	104.98(9)
O(6)-Sr(3)-Sr(3)#1	45.54(6)
O(5)-Sr(3)-Sr(3)#1	102.85(10)
O(1)-Sr(3)-Sr(3)#1	46.32(8)
I(2)-Sr(3)-Sr(3)#1	135.705(18)
Sr(4)-Sr(3)-Sr(3)#1	59.425(11)
Sr(2)-Sr(3)-Sr(3)#1	90.730(14)
Sr(1)-Sr(3)-Sr(3)#1	59.652(11)
O(6)-Sr(4)-O(1)	75.14(14)
O(6)-Sr(4)-O(5)#1	87.29(11)
O(1)-Sr(4)-O(5)#1	70.50(7)
O(6)-Sr(4)-O(5)	87.29(11)
O(1)-Sr(4)-O(5)	70.50(7)
O(5)#1-Sr(4)-O(5)	140.71(15)
O(6)-Sr(4)-O(8)	112.8(2)
O(1)-Sr(4)-O(8)	172.1(2)
O(5)#1-Sr(4)-O(8)	108.98(7)
O(5)-Sr(4)-O(8)	108.98(8)
O(6)-Sr(4)-I(3)	157.85(9)
O(1)-Sr(4)-I(3)	82.71(11)
O(5)#1-Sr(4)-I(3)	85.31(10)
O(5)-Sr(4)-I(3)	85.31(10)
O(8)-Sr(4)-I(3)	89.38(18)
O(6)-Sr(4)-C(13)	101.5(2)
O(1)-Sr(4)-C(13)	115.50(13)
O(5)#1-Sr(4)-C(13)	170.27(19)
O(5)-Sr(4)-C(13)	45.13(14)
O(8)-Sr(4)-C(13)	63.95(13)
I(3)-Sr(4)-C(13)	87.9(2)
O(6)-Sr(4)-C(13)#1	101.5(2)
O(1)-Sr(4)-C(13)#1	115.50(13)
O(5)#1-Sr(4)-C(13)#1	45.13(14)
O(5)-Sr(4)-C(13)#1	170.27(19)
O(8)-Sr(4)-C(13)#1	63.95(13)
I(3)-Sr(4)-C(13)#1	87.9(2)
C(13)-Sr(4)-C(13)#1	127.8(3)
O(6)-Sr(4)-Sr(3)#1	46.56(6)
O(1)-Sr(4)-Sr(3)#1	47.38(8)
O(5)#1-Sr(4)-Sr(3)#1	46.84(9)
O(5)-Sr(4)-Sr(3)#1	105.91(8)
O(8)-Sr(4)-Sr(3)#1	138.06(12)
I(3)-Sr(4)-Sr(3)#1	116.200(19)
C(13)-Sr(4)-Sr(3)#1	142.88(17)
C(13)#1-Sr(4)-Sr(3)#1	83.34(15)
O(6)-Sr(4)-Sr(3)	46.56(6)
O(1)-Sr(4)-Sr(3)	47.38(8)
O(5)#1-Sr(4)-Sr(3)	105.91(8)
O(5)-Sr(4)-Sr(3)	46.84(9)
O(8)-Sr(4)-Sr(3)	138.06(12)
I(3)-Sr(4)-Sr(3)	116.200(19)
C(13)-Sr(4)-Sr(3)	83.34(15)
C(13)#1-Sr(4)-Sr(3)	142.88(17)
Sr(3)#1-Sr(4)-Sr(3)	61.15(2)
O(6)-Sr(4)-Sr(2)#1	103.85(8)
O(1)-Sr(4)-Sr(2)#1	41.90(8)
O(5)#1-Sr(4)-Sr(2)#1	42.70(9)

O(5)-Sr(4)-Sr(2)#1	101.69(8)
O(8)-Sr(4)-Sr(2)#1	132.53(14)
I(3)-Sr(4)-Sr(2)#1	57.588(16)
C(13)-Sr(4)-Sr(2)#1	136.57(17)
C(13)#1-Sr(4)-Sr(2)#1	80.35(15)
Sr(3)#1-Sr(4)-Sr(2)#1	58.632(15)
Sr(3)-Sr(4)-Sr(2)#1	89.190(18)
O(6)-Sr(4)-Sr(2)	103.85(8)
O(1)-Sr(4)-Sr(2)	41.90(8)
O(5)#1-Sr(4)-Sr(2)	101.69(8)
O(5)-Sr(4)-Sr(2)	42.70(9)
O(8)-Sr(4)-Sr(2)	132.53(14)
I(3)-Sr(4)-Sr(2)	57.588(16)
C(13)-Sr(4)-Sr(2)	80.35(15)
C(13)#1-Sr(4)-Sr(2)	136.57(17)
Sr(3)#1-Sr(4)-Sr(2)	89.190(18)
Sr(3)-Sr(4)-Sr(2)	58.632(15)
Sr(2)#1-Sr(4)-Sr(2)	59.71(2)
Sr(1)-I(1)-Sr(1)#2	180.00(3)
Sr(4)-I(3)-Sr(2)#1	66.214(17)
Sr(4)-I(3)-Sr(2)	66.214(17)
Sr(2)#1-I(3)-Sr(2)	65.31(2)
Sr(2)#1-O(1)-Sr(2)	95.75(17)
Sr(2)#1-O(1)-Sr(4)	95.75(11)
Sr(2)-O(1)-Sr(4)	95.75(11)
Sr(2)#1-O(1)-Sr(1)	88.69(10)
Sr(2)-O(1)-Sr(1)	88.69(10)
Sr(4)-O(1)-Sr(1)	173.4(2)
Sr(2)#1-O(1)-Sr(3)#1	88.34(2)
Sr(2)-O(1)-Sr(3)#1	174.49(16)
Sr(4)-O(1)-Sr(3)#1	87.50(11)
Sr(1)-O(1)-Sr(3)#1	87.71(11)
Sr(2)#1-O(1)-Sr(3)	174.49(16)
Sr(2)-O(1)-Sr(3)	88.34(2)
Sr(4)-O(1)-Sr(3)	87.50(11)
Sr(1)-O(1)-Sr(3)	87.71(11)
Sr(3)#1-O(1)-Sr(3)	87.35(15)
C(1)-O(2)-Sr(2)	122.5(3)
C(1)-O(2)-Sr(2)#1	122.5(3)
Sr(2)-O(2)-Sr(2)#1	94.17(14)
C(1)-O(2)-Sr(1)	131.1(5)
Sr(2)-O(2)-Sr(1)	87.86(14)
Sr(2)#1-O(2)-Sr(1)	87.86(14)
C(4)-O(3)-Sr(2)	125.4(4)
C(4)-O(3)-Sr(3)	126.6(4)
Sr(2)-O(3)-Sr(3)	89.53(10)
C(4)-O(3)-Sr(1)	127.4(3)
Sr(2)-O(3)-Sr(1)	87.72(13)
Sr(3)-O(3)-Sr(1)	87.71(13)
C(8)-O(4)-Sr(1)	126.2(4)
C(8)-O(4)-Sr(3)	125.2(2)
Sr(1)-O(4)-Sr(3)	89.54(15)
C(8)-O(4)-Sr(3)#1	125.2(2)
Sr(1)-O(4)-Sr(3)#1	89.54(15)
Sr(3)-O(4)-Sr(3)#1	89.80(13)
C(11)-O(5)-Sr(4)	125.8(3)
C(11)-O(5)-Sr(2)	121.1(4)
Sr(4)-O(5)-Sr(2)	94.62(14)
C(11)-O(5)-Sr(3)	128.6(4)
Sr(4)-O(5)-Sr(3)	87.76(14)
Sr(2)-O(5)-Sr(3)	88.12(10)
C(15)-O(6)-Sr(4)	124.2(4)
C(15)-O(6)-Sr(3)#1	126.9(2)
Sr(4)-O(6)-Sr(3)#1	88.93(14)
C(15)-O(6)-Sr(3)	126.9(2)
Sr(4)-O(6)-Sr(3)	88.93(14)
Sr(3)#1-O(6)-Sr(3)	88.92(12)
C(18)-O(7)-C(21)	110.2(10)
C(18)-O(7)-Sr(2)	121.0(8)
C(21)-O(7)-Sr(2)	128.4(7)
C(22)-O(8)-C(25)	107.0(8)
C(22)-O(8)-Sr(4)	130.9(6)
C(25)-O(8)-Sr(4)	122.1(7)
C(2)-C(1)-O(2)	117.4(10)
C(2)-C(1)-C(3)#1	104.3(9)
O(2)-C(1)-C(3)#1	108.4(8)

C(2)-C(1)-C(3)	104.3(9)	O(6)-C(15)-C(17)	108.8(5)
O(2)-C(1)-C(3)	108.4(8)	C(16)-C(15)-C(17)	107.8(5)
C(3)#1-C(1)-C(3)	114(2)	O(6)-C(15)-C(17)#1	108.8(5)
O(3)-C(4)-C(7)	111.2(7)	C(16)-C(15)-C(17)#1	107.8(5)
O(3)-C(4)-C(5)	112.3(6)	C(17)-C(15)-C(17)#1	113.1(6)
C(7)-C(4)-C(5)	112.9(9)	C(1)-C(3)-Sr(2)	84.0(8)
O(3)-C(4)-C(6)	108.8(7)	C(8)-C(10)-C(10)#1	50.3(6)
C(7)-C(4)-C(6)	104.5(7)	C(11)-C(12)-Sr(2)	85.2(4)
C(5)-C(4)-C(6)	106.6(8)	C(11)-C(13)-Sr(4)	84.7(4)
C(9)-C(8)-O(4)	113.1(7)	O(7)-C(18)-C(19)	100.3(12)
C(9)-C(8)-C(10)#1	124.5(7)	C(20)-C(19)-C(18)	106.6(12)
O(4)-C(8)-C(10)#1	104.9(6)	C(19)-C(20)-C(21)	112.9(13)
C(9)-C(8)-C(10)	124.5(7)	C(20)-C(21)-O(7)	99.8(11)
O(4)-C(8)-C(10)	104.9(6)	C(23)-C(22)-O(8)	110.7(11)
C(10)#1-C(8)-C(10)	79.3(11)	C(24)-C(23)-C(22)	106.4(9)
O(5)-C(11)-C(14)	113.2(6)	C(23)-C(24)-C(25)	111.2(10)
O(5)-C(11)-C(12)	106.3(6)	O(8)-C(25)-C(24)	104.7(12)
C(14)-C(11)-C(12)	112.8(7)	C(29)-O(9)-C(26)	116.0(19)
O(5)-C(11)-C(13)	104.2(6)	O(9)-C(26)-C(27)	93.7(17)
C(14)-C(11)-C(13)	111.1(7)	C(28)-C(27)-C(26)	102(2)
C(12)-C(11)-C(13)	108.7(7)	C(27)-C(28)-C(29)	126(3)
O(6)-C(15)-C(16)	110.5(5)	O(9)-C(29)-C(28)	102(2)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y,z #2 -x,-y,-z

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for **30**.

The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sr(1)	36(1)	60(1)	42(1)	0	7(1)	0
Sr(2)	52(1)	54(1)	50(1)	7(1)	15(1)	-2(1)
Sr(3)	48(1)	49(1)	45(1)	-4(1)	12(1)	3(1)
Sr(4)	37(1)	57(1)	47(1)	0	6(1)	0
I(1)	35(1)	197(1)	67(1)	0	-2(1)	0
I(2)	208(1)	101(1)	115(1)	-38(1)	58(1)	31(1)
I(3)	61(1)	121(1)	79(1)	0	35(1)	0

O(1)	36(2)	33(2)	47(2)	0	15(2)	0
O(2)	62(2)	81(4)	19(2)	0	3(2)	0
O(3)	57(2)	49(2)	59(2)	2(2)	4(2)	21(2)
O(4)	45(2)	77(4)	56(3)	0	26(2)	0
O(5)	56(2)	55(2)	65(3)	2(2)	6(2)	-15(2)
O(6)	46(2)	40(3)	47(3)	0	11(2)	0
O(7)	136(3)	172(6)	87(3)	40(4)	47(2)	-19(4)
O(8)	55(3)	107(6)	111(6)	0	9(3)	0
C(1)	92(5)	112(9)	36(4)	0	24(3)	0
C(4)	100(4)	50(4)	66(5)	5(4)	-6(3)	23(3)
C(8)	62(3)	143(10)	71(4)	0	49(3)	0
C(11)	76(3)	86(5)	93(5)	-17(4)	32(3)	-43(3)
C(15)	58(4)	75(6)	48(5)	0	11(3)	0
C(2)	65(6)	720(60)	76(8)	0	26(5)	0
C(3)	430(20)	460(30)	91(11)	97(14)	13(13)	-70(20)
C(5)	191(9)	111(11)	191(15)	-1(10)	-51(9)	35(8)
C(6)	237(9)	78(7)	280(20)	26(9)	-52(11)	84(6)
C(7)	139(4)	172(9)	238(9)	14(7)	113(4)	76(5)
C(9)	89(4)	1500(120)	109(6)	0	92(3)	0
C(10)	162(6)	490(30)	118(7)	63(11)	65(5)	157(8)
C(12)	212(6)	77(4)	105(6)	24(4)	29(5)	-88(4)
C(13)	90(4)	71(5)	145(9)	13(6)	-33(5)	-29(4)
C(14)	102(5)	104(8)	189(10)	-31(7)	40(5)	-8(5)
C(16)	76(4)	146(10)	41(3)	0	41(2)	0
C(17)	81(3)	76(4)	95(6)	-26(4)	11(3)	-43(3)
C(18)	213(7)	297(16)	132(6)	74(8)	95(5)	-29(9)
C(19)	201(8)	308(19)	181(9)	84(10)	91(6)	-25(10)
C(20)	262(10)	137(9)	120(8)	54(6)	49(7)	-47(8)
C(21)	286(12)	145(9)	212(12)	86(7)	68(9)	-44(9)
C(22)	84(6)	164(14)	74(7)	0	11(5)	0
C(23)	65(4)	83(8)	154(9)	0	43(5)	0
C(24)	71(4)	155(12)	96(7)	0	43(4)	0
C(25)	58(5)	450(40)	156(13)	0	36(6)	0

Crystal data and structure refinement for [Eu(OPh)$_6${Li(dme)}$_3$] 31

$C_{48}H_{60}Li_3EuO_{12}$, M= 1001.74 gmol^{-1}, trigonal, *R*-3 (Nr. 148), a = 20.4556(11), c = 20.5558(14) Å, V = 7448.9(8) Å^3, Z = 6, $\rho_{calcd.}$= 1.340 Mgm^3, *F*(000) = 3096, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 1.320 mm^{-1}, 2.50° < θ < 26.99°, 19017 reflections of which 3543 unique and 3437 observed, 196 parameters refined, *GOOF* (on F^2) = 1.131, $R1= \Sigma|F_o–F_c|/\Sigma F_o = 0.0456$, *w*R2 = 0.1186 for I > 2σ(I) and R1 = 0.0463, wR2 = 0.1198 for all data.

The intensities from the single-crystals of **31** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK$_\alpha$ radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms.

Table 1. Crystal data and structure refinement for **31**.

Identification code	[Eu(OPh)$_6${Li(dme)}$_3$]	
Empirical formula	C48 H60 Eu Li3 O12	
Formula weight	1001.74	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R-3	
Unit cell dimensions	a = 20.4556(11) Å	α= 90°
	b = 20.4556(11) Å	β= 90°
	c = 20.5558(14) Å	γ = 120°
Volume	7448.9(8) Å^3	
Z	6	
Density (calculated)	1.340 Mg/m^3	
Absorption coefficient	1.320 mm^{-1}	
F(000)	3096	
Theta range for data collection	2.50 to 26.99°	
Index ranges	-25<=h<=25, -25<=k<=25, -26<=l<=26	
Reflections collected	19017	
Independent reflections	3543 [R(int) = 0.2260]	
Completeness to theta = 26.99°	98.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3543 / 0 / 196	
Goodness-of-fit on F^2	1.131	
Final R indices [I>2sigma(I)]	R1 = 0.0456, wR2 = 0.1186	
R indices (all data)	R1 = 0.0463, wR2 = 0.1198	

Largest diff. peak and hole	3.526 and -1.929 e.Å^{-3}

Table 2. Atomic coordinates (x 10^{4}) and equivalent isotropic displacement parameters (Å^{2}x 10^{3}) for **31**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Eu	3333	6667	4309(1)	22(1)
O(1)	2517(1)	6968(1)	4811(1)	35(1)
O(2)	2234(1)	6063(1)	3736(1)	34(1)
O(3)	1053(1)	6616(1)	3595(1)	35(1)
O(4)	728(1)	5928(1)	4741(1)	41(1)
Li	1701(2)	6422(2)	4221(2)	34(1)
C(1)	2527(1)	7484(1)	5219(1)	28(1)
C(2)	2942(1)	7662(1)	5802(1)	38(1)
C(3)	2924(2)	8175(2)	6231(1)	48(1)
C(4)	2507(2)	8516(2)	6106(1)	51(1)
C(5)	2118(2)	8373(1)	5522(1)	49(1)
C(6)	2131(1)	7855(1)	5089(1)	40(1)
C(7)	1979(1)	5497(1)	3303(1)	28(1)
C(8)	1559(1)	4742(1)	3482(1)	42(1)
C(9)	1308(2)	4175(2)	3021(2)	56(1)
C(10)	1464(2)	4349(2)	2374(1)	51(1)
C(11)	1867(1)	5089(2)	2186(1)	45(1)
C(12)	2129(1)	5656(1)	2637(1)	34(1)
C(13)	1212(2)	6697(2)	2911(1)	49(1)
C(14)	286(1)	6076(2)	3726(1)	44(1)
C(15)	184(1)	6078(2)	4454(1)	45(1)
C(16)	710(2)	5951(2)	5436(1)	54(1)

Table 3. Bond lengths [Å] and angles [°] for **31**.

Eu-O(1)	2.2941(17)	Eu-O(2)#2	2.2797(15)
Eu-O(1)#1	2.2941(18)	Eu-Li	3.124(4)
Eu-O(1)#2	2.2941(17)	Eu-Li#1	3.124(4)
Eu-O(2)	2.2797(15)	Eu-Li#2	3.124(4)
Eu-O(2)#1	2.2797(15)	O(1)-Li	1.909(4)

O(2)-Li	1.875(4)	C(2)-C(3)	1.387(4)
O(3)-Li	2.024(4)	C(3)-C(4)	1.369(5)
O(4)-Li	2.029(4)	C(4)-C(5)	1.388(4)
O(1)-C(1)	1.339(3)	C(5)-C(6)	1.394(4)
O(2)-C(7)	1.342(2)	C(7)-C(8)	1.389(3)
O(3)-C(14)	1.423(3)	C(7)-C(12)	1.406(3)
O(3)-C(13)	1.435(3)	C(8)-C(9)	1.382(4)
O(4)-C(15)	1.421(4)	C(9)-C(10)	1.374(4)
O(4)-C(16)	1.432(3)	C(10)-C(11)	1.368(4)
C(1)-C(6)	1.385(4)	C(11)-C(12)	1.367(3)
C(1)-C(2)	1.407(3)	C(14)-C(15)	1.510(3)

O(2)-Eu-O(2)#1	95.67(5)	O(1)#2-Eu-Li#1	137.65(8)
O(2)-Eu-O(2)#2	95.67(5)	Li-Eu-Li#1	119.664(13)
O(2)#1-Eu-O(2)#2	95.67(5)	O(2)-Eu-Li#2	92.35(9)
O(2)-Eu-O(1)	74.01(6)	O(2)#1-Eu-Li#2	132.20(8)
O(2)#1-Eu-O(1)	89.56(6)	O(2)#2-Eu-Li#2	36.58(8)
O(2)#2-Eu-O(1)	168.89(6)	O(1)-Eu-Li#2	137.65(8)
O(2)-Eu-O(1)#1	168.89(6)	O(1)#1-Eu-Li#2	97.66(8)
O(2)#1-Eu-O(1)#1	74.01(6)	O(1)#2-Eu-Li#2	37.45(7)
O(2)#2-Eu-O(1)#1	89.56(6)	Li-Eu-Li#2	119.664(13)
O(1)-Eu-O(1)#1	101.32(5)	Li#1-Eu-Li#2	119.664(13)
O(2)-Eu-O(1)#2	89.56(6)	C(1)-O(1)-Li	121.6(2)
O(2)#1-Eu-O(1)#2	168.89(6)	C(1)-O(1)-Eu	140.06(13)
O(2)#2-Eu-O(1)#2	74.01(6)	Li-O(1)-Eu	95.58(13)
O(1)-Eu-O(1)#2	101.32(5)	C(7)-O(2)-Li	129.76(17)
O(1)#1-Eu-O(1)#2	101.32(5)	C(7)-O(2)-Eu	131.44(15)
O(2)-Eu-Li	36.58(8)	Li-O(2)-Eu	97.01(11)
O(2)#1-Eu-Li	92.35(9)	C(14)-O(3)-C(13)	111.92(17)
O(2)#2-Eu-Li	132.20(8)	C(14)-O(3)-Li	107.70(17)
O(1)-Eu-Li	37.45(7)	C(13)-O(3)-Li	120.9(2)
O(1)#1-Eu-Li	137.66(8)	C(15)-O(4)-C(16)	111.9(2)
O(1)#2-Eu-Li	97.66(8)	C(15)-O(4)-Li	110.63(17)
O(2)-Eu-Li#1	132.20(8)	C(16)-O(4)-Li	123.0(2)
O(2)#1-Eu-Li#1	36.58(8)	O(2)-Li-O(1)	93.35(18)
O(2)#2-Eu-Li#1	92.35(9)	O(2)-Li-O(3)	107.72(17)
O(1)-Eu-Li#1	97.66(8)	O(1)-Li-O(3)	139.1(2)
O(1)#1-Eu-Li#1	37.45(7)	O(2)-Li-O(4)	134.6(2)

O(1)-Li-O(4)	108.02(17)	C(4)-C(5)-C(6)	119.1(3)
O(3)-Li-O(4)	81.75(15)	C(1)-C(6)-C(5)	122.1(2)
O(2)-Li-Eu	46.42(9)	O(2)-C(7)-C(8)	122.85(18)
O(1)-Li-Eu	46.97(10)	O(2)-C(7)-C(12)	119.97(18)
O(3)-Li-Eu	139.28(16)	C(8)-C(7)-C(12)	117.18(19)
O(4)-Li-Eu	138.88(18)	C(9)-C(8)-C(7)	121.1(2)
O(1)-C(1)-C(6)	121.93(18)	C(10)-C(9)-C(8)	120.3(3)
O(1)-C(1)-C(2)	120.4(2)	C(11)-C(10)-C(9)	119.6(2)
C(6)-C(1)-C(2)	117.7(2)	C(12)-C(11)-C(10)	120.7(2)
C(3)-C(2)-C(1)	119.8(3)	C(11)-C(12)-C(7)	121.1(2)
C(4)-C(3)-C(2)	121.7(2)	O(3)-C(14)-C(15)	106.57(18)
C(3)-C(4)-C(5)	119.5(2)	O(4)-C(15)-C(14)	106.7(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+y,-x+1,z #2 -y+1,x-y+1,z

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for **31**.

The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Eu	20(1)	20(1)	28(1)	0	0	10(1)
O(1)	34(1)	40(1)	36(1)	-13(1)	-2(1)	22(1)
O(2)	32(1)	37(1)	38(1)	-16(1)	-10(1)	20(1)
O(3)	29(1)	38(1)	40(1)	2(1)	0(1)	18(1)
O(4)	35(1)	42(1)	39(1)	2(1)	-3(1)	15(1)
Li	21(1)	41(2)	45(1)	-14(1)	-7(1)	18(1)
C(1)	23(1)	21(1)	35(1)	-6(1)	2(1)	7(1)
C(2)	36(1)	38(1)	39(1)	-6(1)	-3(1)	17(1)
C(3)	47(1)	42(1)	41(1)	-17(1)	2(1)	12(1)
C(4)	42(1)	34(1)	61(1)	-21(1)	16(1)	7(1)
C(5)	37(1)	32(1)	79(1)	-11(1)	7(1)	17(1)
C(6)	32(1)	36(1)	51(1)	-8(1)	0(1)	18(1)
C(7)	25(1)	24(1)	36(1)	-8(1)	-6(1)	14(1)
C(8)	36(1)	36(1)	47(1)	3(1)	1(1)	12(1)
C(9)	41(1)	23(1)	87(2)	-11(1)	-11(2)	4(1)
C(10)	43(1)	44(1)	64(1)	-30(1)	-15(1)	20(1)
C(11)	45(1)	58(1)	38(1)	-17(1)	-7(1)	30(1)

C(12)	33(1)	31(1)	39(1)	0(1)	-1(1)	18(1)
C(13)	55(1)	53(1)	43(1)	3(1)	7(1)	30(1)
C(14)	26(1)	45(1)	51(1)	4(1)	-6(1)	12(1)
C(15)	38(1)	41(1)	55(1)	11(1)	10(1)	19(1)
C(16)	58(2)	49(2)	41(1)	4(1)	0(1)	15(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **31**.

	x	y	z	U(eq)
H(2)	3231	7433	5899	46
H(3)	3205	8292	6619	58
H(4)	2485	8845	6413	61
H(5)	1849	8621	5420	59
H(6)	1863	7756	4695	47
H(8)	1444	4615	3923	50
H(9)	1029	3667	3152	67
H(10)	1294	3962	2061	61
H(11)	1966	5209	1742	54
H(12)	2413	6161	2499	40
H(13A)	1122	6219	2734	73
H(13B)	1735	7079	2841	73
H(13C)	885	6847	2695	73
H(14A)	171	5574	3578	52
H(14B)	-51	6213	3502	52
H(15A)	265	6569	4597	54
H(15B)	-327	5688	4578	54
H(16A)	758	6427	5574	81
H(16B)	1125	5905	5613	81
H(16C)	236	5537	5593	81

Crystal data and structure refinement for [Sm(OPh)$_6${Li(dme)}$_3$] 32

$C_{48}H_{60}Li_3SmO_{12}$, M= 1000.13 gmol^{-1}, trigonal, *R*-3 (Nr. 148), a =20.456(3), c = 20.519(4) Å, V = 7436(2) Å^3, Z = 6, $\rho_{calcd.}$= 1.340 Mgm^3, *F*(000) = 3090, T = 203 K, λ = 0.71073 Å, μ(Mo-K$_\alpha$)= 1.242 mm^{-1}, 1.99° < θ < 27.04°, 4873 reflections of which 3205 unique and 2468 observed, 195 parameters refined, *GOOF* (on F^2) = 1.051, R1= $\Sigma|F_o - F_c|/\Sigma F_o$ = 0.0663, *w*R2 = 0.1586 for I > 2σ(I) and R1 = 0.0880, wR2 = 0.1720 for all data.

The intensities from the single-crystals of **32** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK_α radiation, at 203 K. The structure was solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package [408]. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms.

Table 1. Crystal data and structure refinement for **32**.

Identification code	$[\mathrm{Sm(III)(OPh)_6\{Li(dme)\}_3}]$	
Empirical formula	C48 H60 Li3 O12 Sm	
Formula weight	1000.13	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R-3	
Unit cell dimensions	a = 20.456(3) Å	α= 90°
	b = 20.456(3) Å	β= 90°
	c = 20.519(4) Å	γ = 120°
Volume	7436(2) $Å^3$	
Z	6	
Density (calculated)	1.340 Mg/m^3	
Absorption coefficient	1.242 mm^{-1}	
F(000)	3090	
Theta range for data collection	1.99 to 27.04°	
Index ranges	-23<=h<=26, -19<=k<=26, -18<=l<=26	
Reflections collected	4873	
Independent reflections	3205 [R(int) = 0.1007]	
Completeness to theta = 27.04°	88.3 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3205 / 0 / 195	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0663, wR2 = 0.1586	
R indices (all data)	R1 = 0.0880, wR2 = 0.1720	
Largest diff. peak and hole	1.285 and -1.144 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **32**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sm	3333	6667	4315(1)	36(1)
O(1)	3028(3)	7497(3)	4811(3)	47(1)
O(2)	3949(3)	7778(2)	3745(3)	45(1)
O(3)	3381(3)	8947(3)	3595(3)	49(1)
O(4)	4072(3)	9282(3)	4738(3)	51(1)
Li	3585(7)	8311(6)	4221(6)	47(3)
C(1)	2514(4)	7477(4)	5230(4)	44(2)
C(2)	2143(4)	7880(4)	5084(4)	52(2)
C(3)	1625(4)	7879(4)	5527(5)	58(2)
C(4)	1475(5)	7502(5)	6102(5)	66(2)
C(5)	1818(5)	7086(4)	6238(4)	60(2)
C(6)	2337(4)	7073(4)	5797(4)	52(2)
C(7)	4504(4)	8021(3)	3302(4)	41(1)
C(8)	5258(4)	8440(4)	3485(4)	54(2)
C(9)	5827(4)	8689(5)	3015(5)	63(2)
C(10)	5647(5)	8540(5)	2367(5)	64(2)
C(11)	4915(4)	8131(4)	2188(4)	53(2)
C(12)	4342(4)	7869(4)	2647(4)	48(2)
C(13)	3294(5)	8786(5)	2914(4)	59(2)
C(14)	3925(4)	9714(4)	3736(4)	55(2)
C(15)	3931(5)	9817(4)	4446(4)	56(2)
C(16)	4050(5)	9299(6)	5433(5)	66(2)

Table 3. Bond lengths [Å] and angles [°] for **32**.

Sm-O(1)	2.318(4)	Sm-Li#1	3.145(11)
Sm-O(1)#1	2.318(4)	Sm-Li#2	3.145(11)
Sm-O(1)#2	2.318(4)	O(1)-Li	1.907(13)
Sm-O(2)	2.294(4)	O(2)-Li	1.874(12)
Sm-O(2)#1	2.294(4)	O(3)-Li	2.015(13)
Sm-O(2)#2	2.294(4)	O(4)-Li	2.020(13)
Sm-Li	3.145(11)	O(1)-C(1)	1.343(8)

O(2)-C(7)	1.340(8)	C(5)-C(6)	1.405(11)
O(3)-C(13)	1.427(10)	C(1)-C(6)	1.367(11)
O(3)-C(14)	1.427(9)	C(7)-C(8)	1.390(10)
O(4)-C(15)	1.398(9)	C(8)-C(9)	1.397(12)
O(4)-C(16)	1.428(10)	C(9)-C(10)	1.372(14)
Li-C(14)	2.777(13)	C(10)-C(11)	1.351(13)
C(1)-C(2)	1.404(10)	C(11)-C(12)	1.386(11)
C(2)-C(3)	1.395(11)	C(7)-C(12)	1.383(11)
C(3)-C(4)	1.358(14)	C(14)-C(15)	1.470(12)
C(4)-C(5)	1.375(14)		

O(2)#1-Sm-O(2)	96.32(18)	Li-Sm-Li#1	119.63(5)
O(2)#1-Sm-O(2)#2	96.32(18)	O(2)#1-Sm-Li#2	132.5(3)
O(2)-Sm-O(2)#2	96.32(18)	O(2)-Sm-Li#2	92.1(3)
O(2)#1-Sm-O(1)	88.67(18)	O(2)#2-Sm-Li#2	36.2(2)
O(2)-Sm-O(1)	73.29(16)	O(1)-Sm-Li#2	138.2(3)
O(2)#2-Sm-O(1)	168.97(16)	O(1)#1-Sm-Li#2	97.7(3)
O(2)#1-Sm-O(1)#1	73.29(16)	O(1)#2-Sm-Li#2	37.1(3)
O(2)-Sm-O(1)#1	168.97(16)	Li-Sm-Li#2	119.63(5)
O(2)#2-Sm-O(1)#1	88.67(18)	Li#1-Sm-Li#2	119.63(5)
O(1)-Sm-O(1)#1	102.21(16)	C(1)-O(1)-Li	123.4(5)
O(2)#1-Sm-O(1)#2	168.97(16)	C(1)-O(1)-Sm	138.7(4)
O(2)-Sm-O(1)#2	88.67(18)	Li-O(1)-Sm	95.7(4)
O(2)#2-Sm-O(1)#2	73.29(16)	C(7)-O(2)-Li	130.4(5)
O(1)-Sm-O(1)#2	102.21(16)	C(7)-O(2)-Sm	131.0(4)
O(1)#1-Sm-O(1)#2	102.21(16)	Li-O(2)-Sm	97.5(4)
O(2)#1-Sm-Li	92.1(3)	C(13)-O(3)-C(14)	113.1(6)
O(2)-Sm-Li	36.2(2)	C(13)-O(3)-Li	121.1(5)
O(2)#2-Sm-Li	132.5(3)	C(14)-O(3)-Li	106.3(6)
O(1)-Sm-Li	37.1(3)	C(15)-O(4)-C(16)	112.9(6)
O(1)#1-Sm-Li	138.2(3)	C(15)-O(4)-Li	110.6(6)
O(1)#2-Sm-Li	97.7(3)	C(16)-O(4)-Li	122.8(6)
O(2)#1-Sm-Li#1	36.2(2)	O(2)-Li-O(1)	93.4(5)
O(2)-Sm-Li#1	132.5(3)	O(2)-Li-O(3)	108.3(6)
O(2)#2-Sm-Li#1	92.1(3)	O(1)-Li-O(3)	137.9(7)
O(1)-Sm-Li#1	97.7(3)	O(2)-Li-O(4)	134.5(7)
O(1)#1-Sm-Li#1	37.1(3)	O(1)-Li-O(4)	108.1(6)
O(1)#2-Sm-Li#1	138.2(3)	O(3)-Li-O(4)	81.9(4)

O(2)-Li-C(14)	116.6(6)	C(4)-C(5)-C(6)	120.4(8)
O(1)-Li-C(14)	149.5(6)	C(1)-C(6)-C(5)	120.8(7)
O(3)-Li-C(14)	29.5(3)	O(2)-C(7)-C(12)	120.9(6)
O(4)-Li-C(14)	55.0(3)	O(2)-C(7)-C(8)	121.2(7)
O(2)-Li-Sm	46.3(3)	C(12)-C(7)-C(8)	117.9(6)
O(1)-Li-Sm	47.2(3)	C(7)-C(8)-C(9)	120.3(8)
O(3)-Li-Sm	138.9(6)	C(10)-C(9)-C(8)	120.3(7)
O(4)-Li-Sm	139.1(6)	C(11)-C(10)-C(9)	119.5(7)
C(14)-Li-Sm	161.8(5)	C(10)-C(11)-C(12)	121.1(8)
O(1)-C(1)-C(6)	122.1(7)	C(7)-C(12)-C(11)	120.8(7)
O(1)-C(1)-C(2)	119.3(7)	O(3)-C(14)-C(15)	107.7(6)
C(6)-C(1)-C(2)	118.5(7)	O(3)-C(14)-Li	44.1(4)
C(3)-C(2)-C(1)	119.6(8)	C(15)-C(14)-Li	76.9(5)
C(4)-C(3)-C(2)	121.6(8)	O(4)-C(15)-C(14)	107.7(6)
C(3)-C(4)-C(5)	119.1(7)		

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,x-y+1,z   #2 -x+y,-x+1,z

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **32**.
The anisotropic displacement factor exponent takes the form: -2p^2[h^{2}a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sm	36(1)	36(1)	37(1)	0	0	18(1)
O(1)	53(3)	49(2)	47(3)	6(2)	19(2)	31(2)
O(2)	46(2)	43(2)	50(3)	10(2)	12(2)	25(2)
O(3)	54(3)	45(2)	49(3)	-3(2)	-1(2)	26(2)
O(4)	57(3)	51(3)	42(3)	1(2)	-2(2)	26(2)
Li	63(7)	45(6)	41(7)	2(5)	6(5)	34(5)
C(1)	41(3)	43(3)	42(4)	-8(3)	0(3)	17(3)
C(2)	53(4)	48(4)	58(5)	0(3)	11(3)	27(3)
C(3)	51(4)	52(4)	70(6)	-9(4)	8(4)	27(3)
C(4)	52(4)	59(4)	73(6)	-18(4)	21(4)	18(3)
C(5)	63(5)	55(4)	48(5)	1(3)	19(4)	20(4)
C(6)	54(4)	47(4)	54(5)	4(3)	8(3)	26(3)
C(7)	41(3)	38(3)	46(4)	3(3)	8(3)	20(3)
C(8)	49(4)	49(4)	53(5)	-1(3)	-3(3)	18(3)

C(9)	38(4)	58(4)	75(7)	5(4)	3(3)	12(3)
C(10)	64(5)	58(4)	65(6)	15(4)	28(4)	28(4)
C(11)	63(4)	51(4)	43(5)	6(3)	12(3)	26(3)
C(12)	48(3)	46(3)	48(5)	0(3)	0(3)	23(3)
C(13)	66(5)	66(5)	48(5)	-7(4)	2(4)	35(4)
C(14)	53(4)	43(3)	60(5)	5(3)	-4(3)	18(3)
C(15)	59(4)	46(4)	57(5)	-8(3)	-8(3)	22(3)
C(16)	63(5)	82(6)	47(5)	-5(4)	-3(4)	31(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **32**.

	x	y	z	U(eq)
H(2)	2242	8146	4695	62
H(3)	1378	8143	5427	69
H(4)	1144	7524	6400	79
H(5)	1707	6813	6624	72
H(6)	2561	6785	5892	62
H(8)	5384	8555	3922	64
H(9)	6331	8958	3142	75
H(10)	6026	8719	2054	76
H(11)	4794	8024	1749	64
H(12)	3842	7587	2512	57
H(13A)	3059	9040	2713	88
H(13B)	2983	8251	2850	88
H(13C)	3780	8957	2721	88
H(14A)	3791	10051	3516	66
H(14B)	4421	9827	3587	66
H(15A)	4322	10323	4564	67
H(15B)	3448	9746	4590	67
H(16A)	4435	9784	5586	99
H(16B)	4137	8913	5607	99
H(16C)	3564	9210	5572	99

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G - Abbreviations

T_c	Critical transition temperature
CVD	Chemical Vapor Deposition
MOCVD	Metal Organic Chemical Vapor Deposition
NLO	Non Linear Optic
CN	Coordination Number
tmhd	2,2,6,6-tetramethyl-3,5-heptanedionate
thf	Tetrahydrofuran
Me_2SO	Dimethylsulfoxide
TMEDA	Tetrametylethylenediamine
n-glyme	$CH_3(OCH_2CH_2)_nOCH_3$
DME	Ethyleneglycoldimethylether
Py	Pyridine
CH_3CN	Acetrontrile
Bipy	2,2’-Bipyridine
Me	Methyl
Et	Ethyl
OMe	Methoxy
^{i}Pr	*iso*-propyl
^{t}Bu	*tert*-butyl
OPh	Phenolate
Cp	Cyclopentadiene (C_5H_5)
Cp*	Pentamethylcyclopentadiene (C_5Me_5)
EO3	Triethylene glycol
EO5	Pentaethylene glycol
NCS	Isothiocyanate
H-Clox	$HOCPh_2CH_2C_6H_4Cl_4$
H_2-Salen	N,N'-ethylenebis(salicylideneimine)
H_2-Salphen	N,N'-o-phenylenebis(salicylideneimine)
$ON_2C_5H_{12}$	1,1,3,3-Tetramethylurea

H - Curriculum Vitae

PERSONAL INFORMATIONS

Fisrt name: William Last name: Maudez
Nationality: French
Date of Birth: 16/08/1978 Place of Birth: Paimpol, France
Marital status: Single

PERSONAL ADRESS

58 rue de Mulhouse
F-68300 Saint Louis, France
Email: w_maudez@yahoo.fr
Home Phone: +33(0)684056697

EDUCATION

2002-2006:	PhD Diploma, Department of Chemistry, Inorganic Chemistry, University of Basel, Switzerland.
2001-2002:	Master’s Degree in Solid State and Molecular Inorganic Chemistry at the “Institut National des Sciences Appliquées de Rennes” (INSA Rennes) and the University of Rennes1, France.
2000-2001:	Bachelor’s Degree in Chemistry at the “Université des Sciences et techniques”, University of Brest, France.
1997-1999:	Associate’s Degree in Chemistry at the “Institut Universitaire de Technologie de Chimie”, University of Rennes, France.
1996:	High School Diploma in Sciences at the “Lycée de Kerraoul”, Paimpol, France.

EMPLOYMENT

10/2002-10/2006:	**PhD diploma**, “*On the synthesis of new alkoxide and aryloxide clusters with alkali, alkaline earth and lanthanide metal ions*” Supervisor: Prof. K. M. Fromm, Department of Chemistry, University of Basel, Switzerland.
02/2002-06/2002:	**Master’s degree in Solid State and Molecular Inorganic Chemistry**, “*Synthesis and study of molecular materials based on lanthanides: Potentials optical amplifiers*” Supervisor: Prof. O. Guillou and Dr. C. Daiguebonne, Research Group in Chemistry and Metallurgy, Laboratory “*Chimie Inorganique des Lanthanides*”, National Institute of Applied Sciences (INSA), Rennes, France.
01/2001-03/2001:	**Bachelor’s Degree in Chemistry**, “*Synthesis of lipids based on phosphonium and arsonium cations for the DNA vectorization*” Supervisor: J.-C. Clément, Research Engineer, Laboratory of Organic Chemistry and transition metals, UMR CNRS 6521, Department of Sciences and Techniques, University of Brest, France.
04/1999-06/1999:	**Associate’s Degree in Chemistry,** “*Thermal and crystallographic studies of the trimesic acid-erbium system*” Supervisor: Prof. O. Guillou and Dr. C. Daiguebonne, Research Group in Chemistry and Metallurgy, Laboratory “*Chimie Inorganique des Lanthanides*”, National Institute of Applied Sciences (INSA), Rennes, France.

PUBLICATIONS

1) "*Interplane Distances Modulation in Lanthanide-Based Coordination Polymers.*" A. Deluzet, W. Maudez, C. Daiguebonne, O. Guillou, *Crystal Growth & Design*; **2003**, *3*(4), 475-479.

2) "*Polar Molecular Precursors for Alkali and Alkaline Earth Metal Clusters and Low-Dimensional Polymer Structures: the Solid-State Structures of* $[CaI(dme)_3]I$*, and cis-*$[SrI_2(diglyme)_2]$ *(dme =* $CH_3OC_2H_4OCH_3$*; diglyme =* $CH_3(OC_2H_4)_2OCH_3$*)*", K. M. Fromm, W. Maudez, *European Journal of Inorganic Chemistry*, **2003**, *18*, 3440-3444.

3) "*Recent advances in the chemistry of "clusters" and coordination polymers of alkali, alkaline earth metal and group 11 compounds*". K. M. Fromm, E. D. Gueneau, A. Y. Robin, W. Maudez, J. Sague, R. Bergougnant, *Zeitschrift fuer Anorganische und Allgemeine Chemie*, **2005**, *631*(10), 1725-1740.

4) "*Substitution reactions on alkaline earth metal iodides: A large anionic* Sr_{12}*-aggregate* $[\{Sr_6(O)(\mu_3\text{-}I)(I)_2(O^tBu)_7(thf)_3\}_2(\mu\text{-}I)]^-$", W. Maudez, T. Vig-Slenters, L. Mirolo, A. Fleury, K. M. Fromm, *Main Group Chemistry*, **2006**, *5*(1), 41-49.

5) "*Substitution reactions on* CaI_2*: Synthesis of mixed metal lithium-calcium-phenolates, and cluster transformation as a function of solvent*", W. Maudez, D. Häussinger, K. M. Fromm, *Zeitschrift fuer Anorganische und Allgemeine Chemie*, **2006**, 2295-2298.

CONFERENCES

- Fall Meeting of the Swiss Chemical Society (October 2002, Basel, Switzerland).
- Third International Conference on the Chemistry of the Alkali and Alkaline Earth Metals (ALKCHEM-3), (October 2003, Würzburg, Germany).
- XXXVIth International Conference on Coordination Chemistry (ICCC36), (July 2004, Mérida, Mexico).
- Fall Meeting of the Swiss Chemical Society, (October 2004, Zurich, Switzerland).
- Summer School on Advanced Materials (September 2005, Villars-sur-Ollon, Switzerland).
- Dalton Discussion 9: Functional Molecular Assembly, (April 2006, Manchester, United Kingdom).
- First European Chemistry Congress, (August 2006, Budapest, Hungary).
- Summer School on Advanced Materials (September 2006, Villars-sur-Ollon, Switzerland).

POSTER PRESENTATIONS

1) *"New polar molecular alkaline earth metal iodide adducts as potential precursors for NLO applications"* (ALKCHEM-3, October 2003, Würzburg, Germany).
2) *"Molecular alkaline earth metal iodide adducts as precursors for clusters and oxide materials"* (ICCC36, July 2004, Mérida, Mexico).
3) *"Molecular alkaline earth metal iodide adducts as precursors for clusters and oxide materials"* (Fall Meeting of the Swiss Chemical Society, October 2004, Zurich, Switzerland).
4) *"Aryloxo alkali and alkaline earth metal clusters: A new approach to oxide materials?"* (Dalton Discussion 9: Functional Molecular Assembly, April 2006, Manchester, United Kingdom).
5) *"Clusters of alkali and alkaline earth metal compounds"* (First European Chemistry Congress, August 2006, Budapest, Hungary).

ORAL PRESENTATIONS

2003-2006	Seminars in the Department of Inorganic Chemistry, University of Basel, Switzerland.

TEACHING

03/2005-07/2005	**Analytical Chemistry Tutorial I for Biology Students**, University of Basel, Switzerland.
10/2005-07/2006	**Analytical Chemistry Tutorial I for Pharmacy Students**, University of Basel, Switzerland.
10/2006-12/2006	**Analytical Chemistry Tutorial I for Pharmacy Students**, University of Basel, Switzerland.

LAB / TECHNICAL SKILLS

- Languages: French (mother tongue), English (fluent, spoken and written).
- Advanced techniques in synthetic organic and inorganic chemistry (using schlenk and glovebox techniques).
- Single-crystal X-ray measurements and structure resolution.
- Thermogravimetric techniques.
- Spectroscopic (Mass, AAS, UV, IR, NMR, X-ray diffraction) techniques.
- Making reports.

Excellent inter-personal skills. Self-motivated, organized and independent in work habits.

REFERENCES

Prof. Dr. Katharina M. Fromm
University of Fribourg
Department of Chemistry
Chemin du musée 9
CH-1700 Fribourg
(Switzerland)
katharina.fromm@unifr.ch

Prof. Dr. Edwin C. Constable
University of Basel
Department of Chemistry
Spitalstrasse 51
CH-4056 Basel
(Switzerland)
edwin.constable@unibas.ch