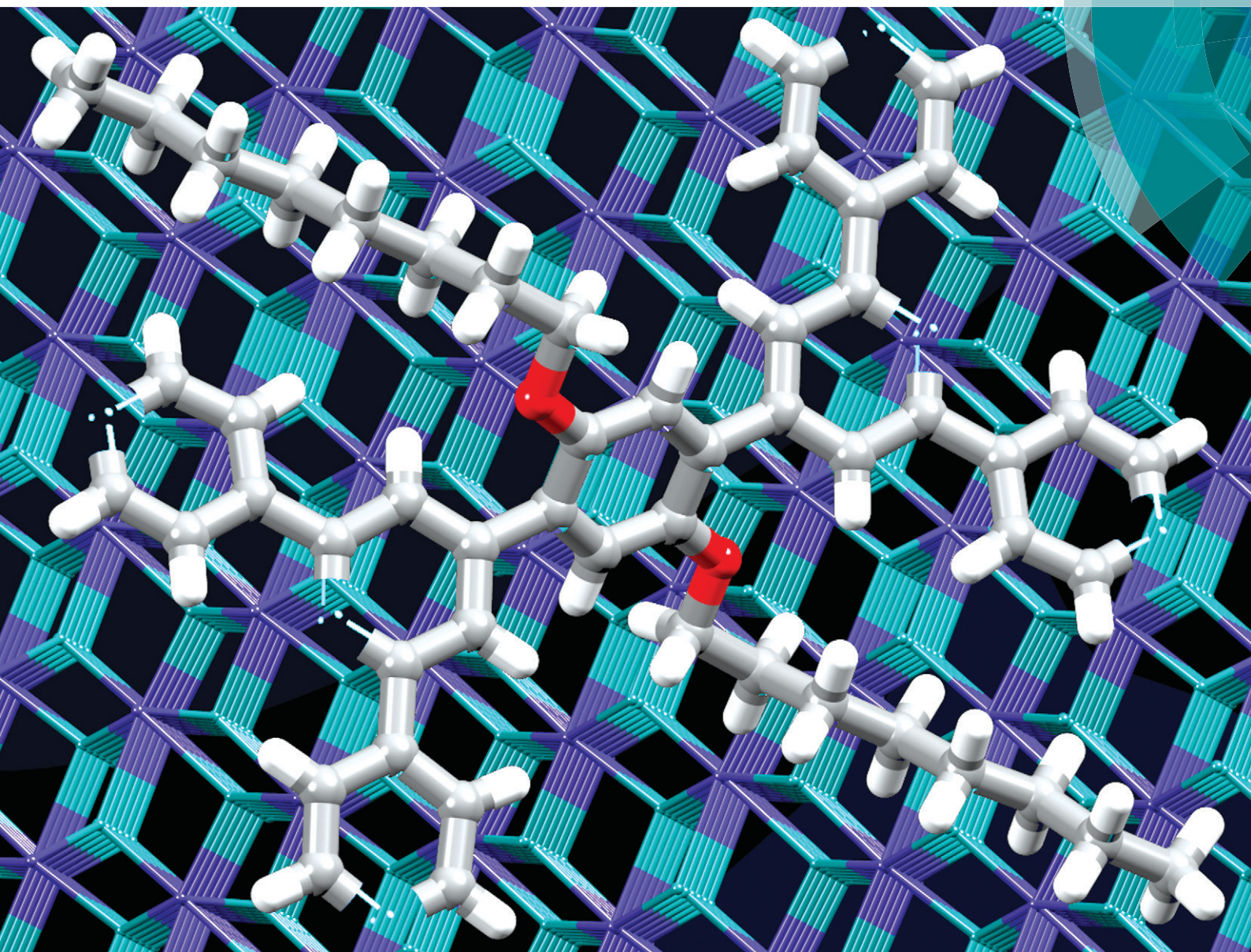


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A 3-dimensional $\{4^2 \cdot 8^4\}$ lvt net built from a ditopic bis(3,2':6',3"-terpyridine) tecton bearing long alkyl tails†

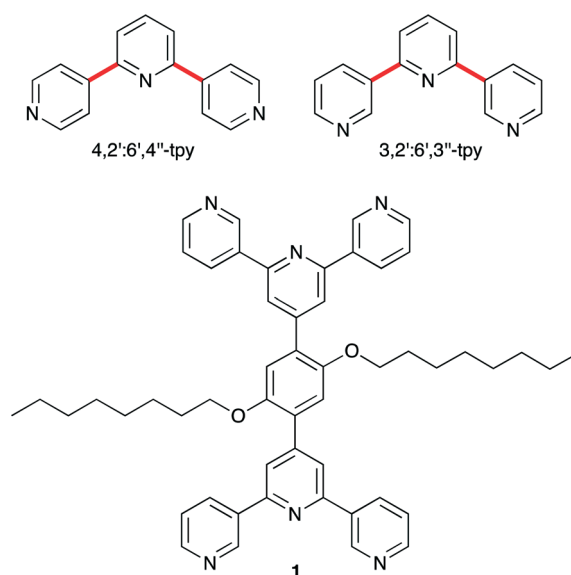
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Divergent bis(terpyridine) tectons are versatile ligands for the assembly of coordination networks; we demonstrate the assembly of a 3-dimensional $\{4^2 \cdot 8^4\}$ lvt net (still relatively sparse among 4-connected nets in metal-organic frameworks) from the reaction of 1,4-bis(*n*-octoxy)-2,5-bis(3,2':6',3"-terpyridin-4'-yl)benzene and Co(NCS)₂.

Oligopyridines¹ remain as one of the most widespread building blocks in the toolbox of a coordination chemist. The bis(chelate) 2,2':6',2"-terpyridine (2,2':6',2"-tpy) is especially popular and multitopic ligands containing peripheral 2,2':6',2"-tpy domains² have been used in a wide variety of architectures. 4,2':6',4"-Terpyridine (4,2':6',4"-tpy, Scheme 1) and 3,2':6',3"-terpyridine (3,2':6',3"-tpy, Scheme 1) are less familiar isomers of terpyridine, but in the last decade, the use of 4,2':6',4"-tpy as a building block of coordination polymers has grown significantly.³ In metal complexes of 4,2':6',4"-tpy, the central pyridine ring is non-coordinated and the remaining *N,N'*-donor set presents a divergent domain, with vectorial properties that are unaffected by inter-ring bond rotation (red bonds in Scheme 1). In contrast, rotation about the interannular bonds in 3,2':6',3"-tpy alters its divergent coordination mode.⁴

The beauty of terpyridine metal-binding domains is the ease with which substituents can be introduced into the 4'-position, for example by using Kröhnke's⁵ or Wang and Hanan's⁶ strategies. With coordinatively innocent 4'-substituents, reactions between 4,2':6',4"-terpyridines and metal ions yield metallomacrocycles, 1-dimensional chains or 2-dimensional nets.³ Extension to 3-dimensions is achieved by introducing non-innocent domains such as diphenylphosphino,⁷ carboxylato,⁸

or pyridyl⁹ functionalities, or by using co-ligands.¹⁰ An alternative approach to increase dimensionality is through the coordination capacity of multitopic 4,2':6',4"-tpy ligands, although such compounds have received scant attention.^{11–14} We have demonstrated that 1,4-bis(*n*-octoxy)-2,5-bis(4,2':6',4"-terpyridin-4'-yl)benzene reacts with ZnCl₂ to give a network consisting of (4,4)-sheets engaging in 2D → 2D parallel interpenetration,¹⁴ and a report on a triply interpenetrating network formed between cobalt(II) and 1,3-di((4,2':6',4"-terpyridin-4'-yl)benzene has appeared.¹² We now describe the synthesis of the bis(3,2':6',3"-tpy) ligand **1** (Scheme 1) and its reaction with Co(NCS)₂ to give a 3-dimensional $\{4^2 \cdot 8^4\}$ lvt net.¹⁵ The inclusion of the long alkoxy chains in **1** enhances the solubility of the ligand with respect to analogues with simple phenylene spacers,¹⁴ and also has a stabilizing influence on an infinite architecture.



Scheme 1 Structures of divergent isomers of terpyridine and the ditopic ligand **1**. See text for significance of the bonds marked in red.

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† Electronic supplementary information (ESI) available: Synthetic and crystallographic details; Fig. S1–S2 solution ¹H NMR and absorption spectra of **1**. CCDC 1035825. See DOI: 10.1039/c4ce02347a



Ligand **1** was synthesized† using the one-pot method of Wang and Hanan⁶ starting from 2,5-bis(octoxy)benzene-1,4-dicarbaldehyde and 4.7 equivalents of 3-acetylpyridine in EtOH in the presence of NH₃. Compound **1** was isolated in 41% yield. The electrospray mass spectrum exhibited a base peak at *m/z* 797.8 arising from [M+H]⁺, and ¹H (Fig. S1†) and ¹³C NMR spectra (assigned using COSY, DEPT, HMQC and HMBC techniques) were consistent with the symmetrical structure shown in Scheme 1. The absorption spectrum of **1** has broad and intense, high energy bands arising from π* ← n and π* ← π transitions which extend into the visible region (Fig. S2†).

Layering of MeOH and CHCl₃ solutions of Co(NCS)₂ and **1**, respectively, resulted in the formation of pink crystals of [Co(NCS)₂(**1**)·4CHCl₃]_n within 2–4 weeks in 14% yield. The crystal selected for single crystal X-ray diffraction was solved and refined in the non-centrosymmetric space group *Pna*2₁. The Flack parameter of 0.480(10) suggested that it was a twin by inversion¹⁶ as every attempt to either solve or refine the structure in *Pnma* failed and ADDSYM¹⁷ could not identify an alternative space group. The asymmetric unit contains one molecule of **1** and a Co(NCS)₂ unit; the octoxy chain containing atom C19 was refined isotropically and three of the C–C distances were restrained to chemically reasonable values. The cobalt ion is octahedrally coordinated, and **1** binds through the outer *N*-donors to four cobalt centres (Fig. 1), leaving the central nitrogen atoms N2 and N6 uncoordinated. Atom Co1 coordinates to two [NCS][−] ligands in a *trans*-arrangement and to four different **1** ligands in the equatorial plane. The two independent octoxy chains are in non-extended conformation, and each is folded over a 3,2':6',3"-tpy unit with close C–H⋯π contacts (H⋯centroid = 3.19 and 3.23 Å for the pyridine rings containing N1 and N4).

Pairs of cobalt atoms are either bridged by a single 4,2':6',4"-tpy (e.g. Co1 and Co1^v in Fig. 1) or by two *N*-donors

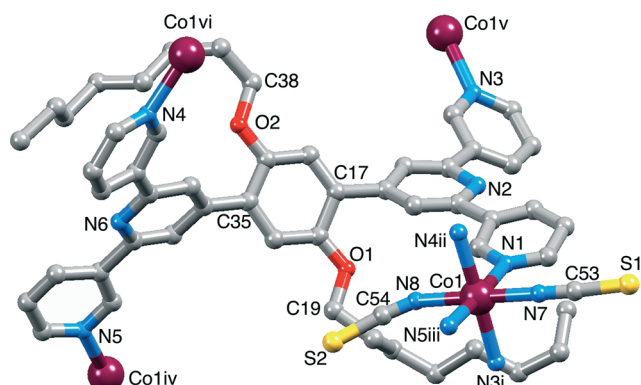


Fig. 1 The repeat unit (with symmetry generated Co atoms) in [Co(NCS)₂(**1**)·4CHCl₃]_n (H atoms and solvent molecules are omitted). Symmetry codes: i = 1/2 + x, 1/2 − y, z; ii = −x, 1 − y, −1/2 + z; iii = 1/2 − x, 1/2 + y, 1/2 − z; iv = 1/2 − x, −1/2 + y, 1/2 + z; v = −1/2 + x, 1/2 − y, z; vi = −x, 1 − y, 1/2 + z. Selected bond parameters: Co1–N1 = 2.185(8), Co1–N3i = 2.212(7), Co1–N4ii = 2.204(8), Co1–N5iii = 2.181(8), Co1–N7 = 2.096(8), Co1–N8 = 2.079(8) Å; Co1–N7–C53 = 161.0(8), Co1–N8–C54 = 151.2(8), N1–Co1–N5iii = 176.2(3), N3i–Co1–N4ii = 178.6(3)°.

from each of the two 4,2':6',4"-tpy domains of **1** (e.g. Co1 and Co1^{iv} in Fig. 1). The latter coordination mode extends to the formation of [2 + 2] metallomacrocycles (Fig. 2a) which are interlinked through the cobalt centres, as shown in Fig. 2b. The structure propagates into a 2-nodal {4²·8⁴} lvt net.¹⁴ The two 4-connected nodes are Co1 and the centroid of the arene spacer in **1**, which are planar and approximately tetrahedral, respectively. Although the local {Co(N_{tpy})₄} domain in [Co(NCS)₂(**1**)·4CHCl₃]_n is square planar (N_{tpy}–Co–N_{tpy} angles = 90.9(3), 89.1(3), 92.9(3) and 87.1(3)°), the cobalt node is distorted in the topological description of the net (centroid–Co–centroid angles = 96.6, 64.6, 132.2 and 67.4°) while remaining planar. Topological representations of the framework in [Co(NCS)₂(**1**)·4CHCl₃]_n are shown in Fig. 3. The view down the *a*-axis in Fig. 3a is directly comparable with the structure in Fig. 2b.

The voids in the net are occupied by the octoxy chains and CHCl₃ molecules. Fig. 4 illustrates that the chains lie in the *ac*-plane, a consequence of the close CH⋯π contacts between the terminal CH₂CH₃ units of each chain and pyridine rings (see above).

In conclusion, we have shown that, by adopting a conformation in which the two 3,2':6',3"-tpy metal-binding domains

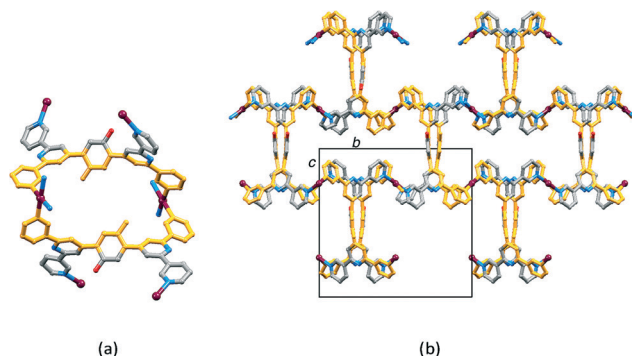


Fig. 2 (a) A [2 + 2] metallomacrocyclic structure formed from two Co1 atoms and two half-ligands (in orange). (b) Interconnection of metallomacrocycles with the unit cell viewed down the *a*-axis.

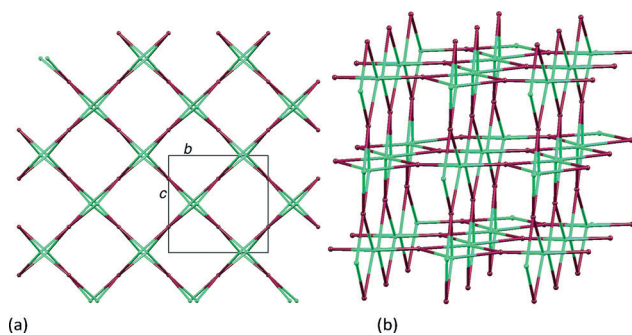


Fig. 3 TOPOS¹⁸ representations of the {4²·8⁴} lvt net in [Co(NCS)₂(**1**)·4CHCl₃]_n: (a) view down the *a*-axis for comparison with Fig. 2b, and (b) showing the 4- and 8-membered metallomacrocycles. Metal nodes, purple; ligand-centroid nodes, green.



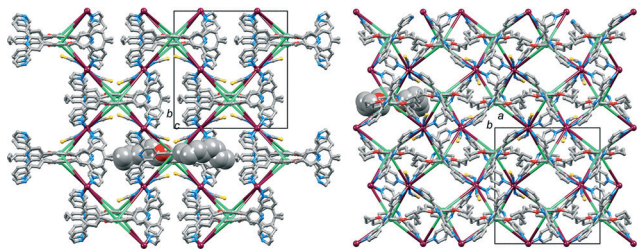


Fig. 4 Superimposition of the topological representation of the lvt net in $[\text{Co}(\text{NCS})_2(1)\cdot 4\text{CHCl}_3]_n$ and the structure (H atoms and CHCl_3 molecules are omitted); the octoxy chains of one ligand are shown in the space-filling representation: views down the (a) a -axis and (b) c -axis.

are orthogonal, ligand **1** can combine with a planar 4-connecting metal node to produce a $\{4^2\cdot 8^4\}$ lvt net. Among metal-organic frameworks, the lvt topology is scarce in comparison with other 4-connected nets.¹⁹ The conformational flexibility of ditopic bis(4,2':6',4''-tpy) and bis(3,2':6',3''-tpy) ligands allows the two tpy units to lie on a path between coplanar¹³ and orthogonal (as in the current work), making these isomeric ligands attractive tectons. We are currently developing the coordination chemistry of multitopic 4,2':6',4''-tpy and 3,2':6',3''-tpy ligands to investigate which building blocks favour the assembly of 2- versus 3-dimensional networks.

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Notes and references

- R. P. Thummel, *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier, Oxford, 2003, vol. 1, p. 41.
- See for example: E. C. Constable, *Chem. Soc. Rev.*, 2007, 36, 246; E. C. Constable, *Coord. Chem. Rev.*, 2008, 252, 842; E. C. Constable, A. M. W. Cargill Thompson, P. Harveson, L. Macko and M. Zehnder, *Chem. – Eur. J.*, 1995, 1, 360; A. Wild, A. Winter, F. Schluetter and U. S. Schubert, *Chem. Soc. Rev.*, 2011, 40, 1459; Y. Yan and J. Huang, *Coord. Chem. Rev.*, 2010, 254, 1072; E. C. Constable, *Chimia*, 2013, 67, 388, and references therein and references therein.
- C. E. Housecroft, *Dalton Trans.*, 2014, 43, 6594.
- E. C. Constable, C. E. Housecroft, M. Neuburger, S. Vujovic, J. A. Zampese and G. Zhang, *CrystEngComm*, 2012, 14, 3554.
- F. Kröhnke, *Synthesis*, 1976, 1.
- J. Wang and G. S. Hanan, *Synlett*, 2005, 1251.
- X. Tan, X. Chen, J. Zhang and C.-Y. Song, *Dalton Trans.*, 2012, 41, 3616.
- See for example: L. Wen, X. Ke, L. Qiu, Y. Zou, L. Zhou, J. Zhao and D. Li, *Cryst. Growth Des.*, 2012, 12, 4083; C. Niu, A. Ning, C. Feng, X. Wan and C. Kou, *J. Inorg. Organomet. Polym.*, 2012, 22, 519; P. Yang, M.-S. Wang, J.-J. Shen, M.-X. Li, Z.-X. Wang, M. Shao and X. He, *Dalton Trans.*, 2014, 43, 1460; Y.-L. Gai, F.-L. Jiang, L. Chen, Y. Bu, M.-Y. Wu, K. Zhou, J. Pan and M.-C. Hong, *Dalton Trans.*, 2013, 42, 9954; Y. Li, Z. Ju, B. Wu and D. Yuan, *Cryst. Growth Des.*, 2013, 13, 4125; F. Yuan, J. Xie, H.-M. Hu, C.-M. Yuan, B. Xu, M.-L. Yang, F.-X. Dong and G.-L. Xue, *CrystEngComm*, 2013, 15, 1460; F. Yuan, Q. Zhu, H.-M. Hu, J. Xie, B. Xu, C.-M. Yuan, M.-L. Yang, F.-X. Dong and G.-L. Xue, *Inorg. Chim. Acta*, 2013, 397, 117; H.-N. Zhang, F. Yuan, H.-M. Hu, S.-S. Shen and G.-L. Xue, *Inorg. Chem. Commun.*, 2013, 34, 51; W. Yang, A. J. Davies, X. Lin, M. Suyetin, R. Matsuda, A. J. Blake, C. Wilson, W. Lewis, J. E. Parker, C. C. Tang, M. W. George, P. Hubberstey, S. Kitagawa, H. Sakamoto, E. Bichoutskaia, N. R. Champness, S. Yang and M. Schröder, *Chem. Sci.*, 2012, 3, 2992; Y.-Q. Chen, S.-J. Liu, Y.-W. Li, G.-R. Li, K.-H. He, Y.-K. Qu, T.-L. Hu and X.-H. Bu, *Cryst. Growth Des.*, 2012, 12, 5426; F. Yuan, J. Xie, H.-M. Hu, C.-M. Yuan, B. Xu, M.-L. Yang, F.-X. Dong and G.-L. Xue, *CrystEngComm*, 2013, 15, 1460.
- J. Heine, J. Schmedt auf der Günne and S. Dehnen, *J. Am. Chem. Soc.*, 2011, 133, 10018; E. C. Constable, G. Zhang, C. E. Housecroft and J. A. Zampese, *CrystEngComm*, 2011, 13, 6864; V. N. Dorofeeva, S. V. Kolotilov, M. A. Kiskin, R. A. Polunin, Z. V. Dobrokhotova, O. Cadour, S. Golhen, L. Ouahab, I. L. Eremenko and V. M. Novotortsev, *Chem. – Eur. J.*, 2012, 18, 5006; Y.-Q. Chen, G.-R. Li, Y.-K. Qu, Y.-H. Zhang, K.-H. He, Q. Gao and X.-H. Bu, *Cryst. Growth Des.*, 2013, 13, 901; C. Liu, Y.-B. Ding, X.-H. Shi, D. Zhang, M.-H. Hu, Y.-G. Yin and D. Li, *Cryst. Growth Des.*, 2009, 9, 1275; J. Song, B.-C. Wang, H.-M. Hu, L. Gou, Q.-R. Wu, X.-L. Yang, Y.-Q. Shangguan, F.-X. Dong and G.-L. Xue, *Inorg. Chim. Acta*, 2011, 366, 134; K.-R. Ma, F. Ma, Y.-L. Zhu, L.-J. Yu, X.-M. Zhao, Y. Yang and W.-H. Duan, *Dalton Trans.*, 2011, 40, 9774; Y.-Q. Chen, G.-R. Li, Z. Chang, Y.-K. Qu, Y.-H. Zhang and X.-H. Bu, *Chem. Sci.*, 2013, 4, 3678.
- See for example: N. Li, Q.-E. Zhu, H.-M. Hu, H.-L. Guo, J. Xie, F. Wang, F.-X. Dong, M.-L. Yang and G.-L. Xue, *Polyhedron*, 2013, 49, 207; B.-C. Wang, X.-L. Chen, H.-M. Hu, H.-L. Yao and G.-L. Xue, *Inorg. Chem. Commun.*, 2009, 12, 856; N. Li, H.-L. Guo, H.-M. Hu, J. Song, B. Xu, M.-L. Yang, F.-X. Dong and G.-L. Xue, *J. Solid State Chem.*, 2013, 198, 416; B.-C. Wang, Q.-R. Wu, H.-M. Hu, X.-L. Chen, Z.-H. Yang, Y.-Q. Shangguan, M.-L. Yang and G.-L. Xue, *CrystEngComm*, 2010, 12, 485.
- G. W. V. Cave and C. L. Raston, *J. Chem. Soc., Perkin Trans. 1*, 2001, 3258.
- J. Yoshida, S.-I. Nishikiori and H. Yuge, *J. Coord. Chem.*, 2013, 66, 2191.
- S. A. S. Ghozlan and A. Z. A. Hassanien, *Tetrahedron*, 2002, 58, 9423.
- E. C. Constable, C. E. Housecroft, S. Vujovic and J. A. Zampese, *CrystEngComm*, 2014, 16, 3494.



- 15 S. R. Batten, S. M. Neville and D. R. Turner, *Coordination Polymers: Design, Analysis and Application*, RSC Publishing, Cambridge, 2009.
- 16 H. D. Flack, *Helv. Chim. Acta*, 2003, **86**, 905.
- 17 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
- 18 V. A. Blatov and A. P. Shevchenko, *TOPOS Professional v. 4.0*, Samara State University, Russia.
- 19 D.-S. Li, Y.-P. Wu, J. Zhao, J. Zhang and J. Y. Lu, *Coord. Chem. Rev.*, 2014, **261**, 1.

