

A double-stranded 1D-coordination polymer assembled using the tetravalent ligand 1,1'-bis(4,2':6',4''-terpyridin-4'-yl)ferrocene

Y. Maximilian Klein, Alessandro Prescimone, Edwin C. Constable, Catherine E. Housecroft*

Department of Chemistry, University of Basel, Spitalstrasse 51, CH 4056 Basel, Switzerland

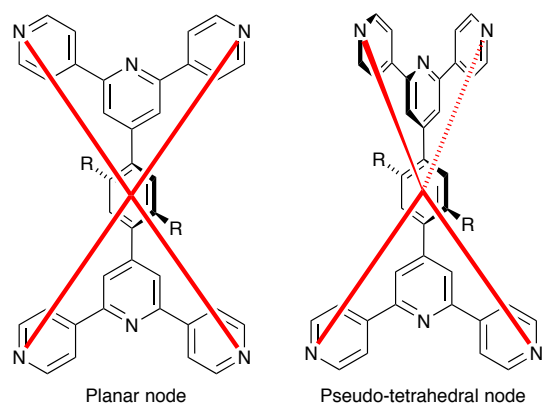
Email: catherine.housecroft@unibas.ch (C.E. Housecroft)

Abstract: 1,1'-Bis(4,2':6',4''-terpyridin-4'-yl)ferrocene (**1**) reacts with ZnCl₂ to yield a double-stranded 1D-coordination polymer [{Zn₂(**1**)Cl₄}·3CHCl₃]_n. The 1,1'-functionalized ferrocene core adopts a cisoid-conformation, giving rise to a folded conformation for **1** and a double-stranded 1D-polymer chain. This contrasts with previously reported multi-stranded chains supported by 4,2':6',4''-terpyridine ligands in which the multiple-nature of the chain arises from multinuclear metal nodes.

Keywords: X-ray; 1D-coordination polymer; zinc; ferrocene; double-stranded chain

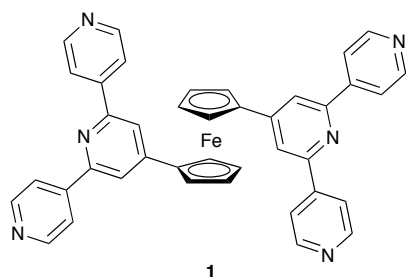
The use of polytopic ligands is a powerful strategy for directing the assembly of metallomacrocycles and coordination polymers and networks [1]. We have shown that 3,2':6',3''- or 4,2':6',4''-terpyridines (tpy) are versatile divergent polytopic ligands in which each terminal pyridyl ring can coordinate a different metal centre. The combination of multiple tpy domains generates new tectons [2] for the assembly of 2D-networks, interpenetrating 2D → 2D parallel interpenetrated networks, and 3D-frameworks [3,4,5]. In these examples to date, the 3,2':6',3''- or 4,2':6',4''-tpy domains are connected by a phenylene spacer; rotation about the C_{phenyl}-C_{tpy} bonds leads to these polytopic ligands being able to act as planar or C₂ 4-connecting nodes (Scheme 1). Additional rotational freedom can be introduced by using organometallic sandwich units as connectors, the archetype of which is ferrocene [6,7]. Despite the variety of known 1,1'-ferrocenyl-centred polytopic ligands [6,7], few exhibit pyridine or polypyridine metal-binding domains. Braga *et al.* have investigated the coordination behaviour of 1,1'-bis(pyridin-4-yl)ferrocene, demonstrating that a cisoid-conformation is favoured leading to discrete molecular rather than polymeric assemblies [8,9]. 1,1'-Bis(pyridin-2-yl)ferrocene and its permethylated analogue act as *N,N'*-chelates to Cu⁺ and Pd²⁺ [10,11,12], or can bind two metal centres in discrete complexes [12]. Here we report the first example of a polytopic bis(4,2':6',4''-terpyridine) ligand containing a 1,1'-ferrocenyl spacer and its reaction with ZnCl₂ to give

an unusual double-chain 1D-coordination polymer.



Scheme 1. Limiting topographies of 4-connecting nodes featuring polytopic 4,2':6',4''-tpy ligands with phenyl spacers (see references [3–5] for R).

Compound **1** (Scheme 2) was prepared according to the method reported by Wang and Hanan [13] and is poorly soluble in most organic solvents, although enough material dissolved in CDCl_3 to permit a ^1H NMR spectrum to be recorded [14]. The ferrocenyl unit is characterized by two multiplets (δ 4.85 and 4.59 ppm) of equal intensity, consistent with functionalization on each cyclopentadienyl ring. Signals for the tpy domain [14] were also consistent with the structure shown in Scheme 2. In the MALDI mass spectrum, the highest mass peak envelope at m/z 649.52 was assigned to $[\text{M}+\text{H}]^+$.



Scheme 2. Structure of ligand **1**.

Red crystals of $[\{\text{Zn}_2(\mathbf{1})\text{Cl}_4\} \cdot 3\text{CHCl}_3]_n$ were obtained from reaction of ZnCl_2 with **1** under room temperature crystallization conditions [15]. The very poor solubility of **1** resulted in a suspension in CHCl_3 rather than a solution of the free ligand being used, and insufficient bulk material of the product for powder diffraction or elemental analysis was obtained. Single-crystal structure determination [16] revealed the formation of the coordination polymer $[\{\text{Zn}_2(\mathbf{1})\text{Cl}_4\} \cdot 3\text{CHCl}_3]_n$. The complex crystallizes in the monoclinic space group

$P2_1/n$, and Fig. 1 shows the asymmetric unit which contains two independent Zn atoms (each tetrahedrally coordinated) and two halves of two ligands **1**. As expected [17], the 4,2':6',4"-tpy unit binds the Zn centres only through the outer pyridine rings. The second half of each ligand is generated by a 2-fold screw axis, with **1** adopting a cisoid-conformation. Bond lengths (caption to Fig. 1) and angles in the coordination spheres of Zn1 and Zn2 and in the ferrocene unit are typical.

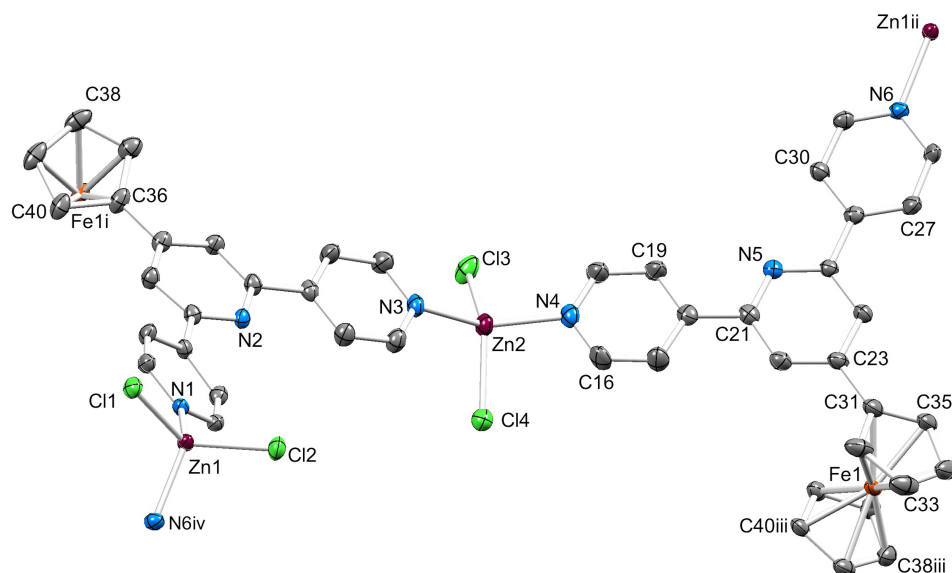


Fig. 1. The asymmetric unit in $[\{Zn_2(\mathbf{1})Cl_4\} \cdot 3CHCl_3]_n$ with symmetry-generated atoms; H atoms and solvent molecules are omitted for clarity. Symmetry codes: i = $3/2-x, -1/2+y, 3/2-z$; ii = $x, 1+y, z$; iii = $3/2-x, 1/2+y, 3/2-z$; iv = $x, -1+y, z$. Selected bond distances: Zn1–N6iv = 2.042(4), Zn1–N1 = 2.035(4), Zn1–Cl1 = 2.2453(13), Zn1–Cl2 = 2.2435(13), Zn2–N3 = 2.076(4), Zn2–N4 = 2.079(4), Zn2–Cl3 = 2.2499(15), Zn2–Cl4 = 2.2708(14) Å.

The cisoid-conformation of **1** results in a double-stranded chain, with tpy units in the same ligand lying over the top of each other (Fig. 2). However, each tpy domain is significantly bowed, and only the central pyridine rings of the two tpy units are able to engage in face-to-face π -stacking (centroid...centroid separation = 3.60 Å and centroid...ring-plane distance = 3.35 Å). Double-stranded chains have previously been observed for $[Cd_2(OAc)_4(4'-(biphenyl-4-yl)-4,2':6',4''-tpy)_2]_n$ [18], but in this case, the origin of the double-strands is the presence of dinuclear $\{Cd_2(OAc)_4\}$ nodes, each node binding four separate 4,2':6',4"-tpy ligands. Similarly, in $[Mn_3(OAc)_6(4'-(4-BrC_6H_4)-4,2':6',4''-tpy)_3]_n$, trinuclear $\{Mn_3(OAc)_6\}$ nodes gives rise to a triple-stranded chain [19], and in $[\{Zn_5(OAc)_{10}(4'-(pentafluorobiphenyl-4-yl)-4,2':6',4''-tpy)\} \cdot 11H_2O]_n$, $\{Zn_5(OAc)_{10}\}$ nodes lead to an unusual quadruple-stranded chain [20]. The assembly of $[\{Zn_2(\mathbf{1})Cl_4\} \cdot 3CHCl_3]_n$ is, to the best of our knowledge, the first example of a 1D-coordination polymer with

4,2':6',4"-tpy ligand linkers in which a bis(4,2':6',4"-tpy) presents a folded conformation to generate a double-stranded chain. The closest Zn...Zn separation across the chain is 4.678(1) Å. Atoms Cl3 and Cl4 of one ZnCl₂ unit face atom Zn1 across the chain (Fig. 2) but the Zn1...Cl3 and Zn1...Cl4 distances of 4.291(2) and 4.155(2) Å are too long to be considered meaningful interactions.

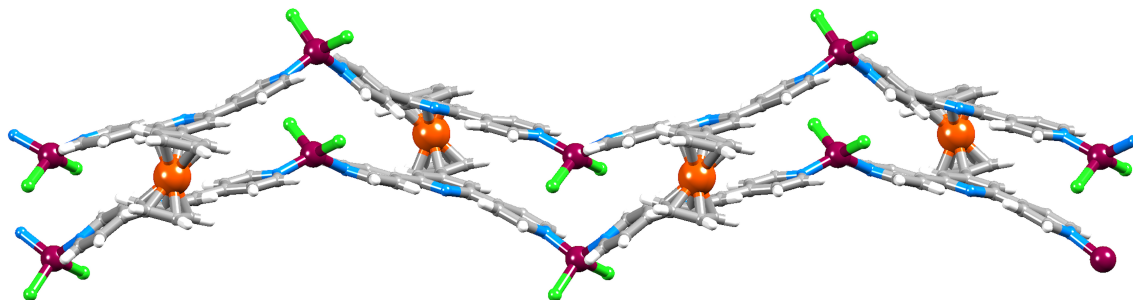


Fig. 2. Part of one chain in $[\{\text{Zn}_2(\mathbf{1})\text{Cl}_4\} \cdot 3\text{CHCl}_3]_n$.

The double-stranded chains propagate along the *b*-axis, with their zig-zag form (Fig. 3) arising from the V-shape of the 4,2':6',4"-tpy domains. Adjacent chains nest together forming sheets, but, in contrast to related structures [^{17, 18, 19, 20, 21,}], there are no close contacts between neighbouring chains (coloured blue in Fig. 3a). This results in void space which is occupied by CHCl₃ molecules.

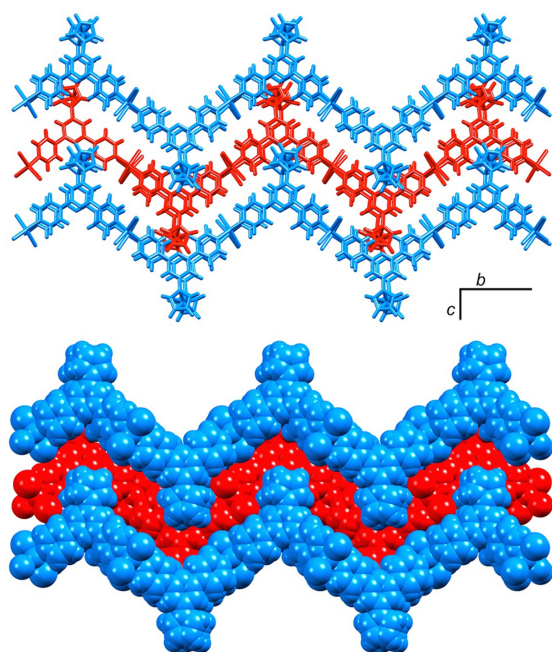


Fig. 3. Stick and space-filling representations of double-stranded chains in $[\{\text{Zn}_2(\mathbf{1})\text{Cl}_4\} \cdot 3\text{CHCl}_3]_n$ to illustrate packing. The structure is viewed down the *a*-axis, and chains coloured blue pack into sheets in the *bc*-plane. Solvent molecules are omitted.

In conclusion, the ferrocenyl-centred polytopic ligand **1** exhibits a folded conformation in the 1D-coordination polymer $[\{Zn_2(\mathbf{1})Cl_4\} \cdot 3CHCl_3]_n$ leading to a double-stranded zigzag chain. This contrasts with previously reported multiply-stranded chains containing 4,2':6',4"-terpyridine ligands in which the nature of the chain arises from di-, tri- or pentanuclear metal nodes.

Acknowledgements

We thank the Swiss National Science Foundation (Grant number 200020_144500) and the University of Basel for support.

Appendix A. Supplementary data

CCDC 1476545 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk)

References

- 1 E. C. Constable and C.E. Housecroft in *Comprehensive Inorganic Chemistry II*, eds. J. Reedijk and K. R. Poeppelmeier, Elsevier, Oxford, 2013, vol. 8, Chapter 8.01, p. 1.
- 2 M. W. Hosseini, *Acc. Chem. Res.* 38 (2005) 313.
- 3 E. C. Constable, C. E. Housecroft, S. Vujovic, J. A. Zampese, *CrystEngComm* 16 (2014) 3494.
- 4 S. Vujovic, E. C. Constable, C. E. Housecroft, C. D. Morris, M. Neuburger, A. Prescimone, *Polyhedron* 92 (2015) 77.
- 5 Y. M. Klein, E. C. Constable, C. E. Housecroft, A. Prescimone, *CrystEngComm* 17 (2015) 2070.
- 6 R. Horikoshi, *Coord. Chem. Rev.* 257 (2013) 621.
- 7 R. Horikoshi, T. Mochida, *Eur. J. Inorg. Chem.* (2010) 5355.
- 8 D. Braga, M. Polito, D. D'Addario, E. Tagliavini, D.M. Proserpio, F. Grepioni, J.W. Steed, *Organometallics* 22 (2003) 4532.
- 9 D. Braga, M. Polito, M. Braccacini, D. D'Addario, E. Tagliavini, D.M. Proserpio, F. Grepioni, *Chem. Commun.* (2002) 1080.
- 10 U. Siemeling, U. Vorfeld, B. Neumann, H.-G. Stammler, *Chem. Comm.* (1997) 1723.
- 11 B. Neumann, U. Siemeling, H.-G. Stammler, U. Vorfeld, J.G.P. Delis, P.W.N.M. van Leeuwen, K. Vrieze, J. Fraanje, K. Goubitz, F. Fabrizi de Bianni, P. Zanello, *J. Chem. Soc., Dalton Trans.* (1997) 4705.

-
- 12 J.G.P. Delis, P.W.N.M. van Leeuwen, K. Vrieze, N. Veldman, A.L. Spek, J. Fraanje, K. Goubitz, *J. organomet. Chem.* 514 (1996) 125.
 - 13 J. Wang, G.S. Hanan, *Synlett* (2005) 1251.
 - 14 1,1'-Ferrocenedicarboxaldehyde (0.20 g, 0.83 mmol) was dissolved in EtOH (70 mL). 4-Acetylpyridine (0.45 g, 3.63 mmol) and KOH (0.23 g, 4.13 mmol) were added to the solution. Aqueous NH₃ (32%, 6.36 mL) was slowly added to the reaction mixture which was then stirred at room temperature overnight. The solid that formed was collected by filtration, washed with EtOH (3 × 20 mL) and H₂O (3 × 20 mL) and dried in vacuo. Compound **1** was isolated as a red powder (0.24 g, 0.37 mmol, 44.8%). Decomp > 300°C. ¹H NMR (500 MHz, CDCl₃, 298 K) δ / ppm 8.60 (m, 4H, H^{A2}), 7.67 (m, 4H, H^{A3}), 7.41 (m, 2H, H^{B3}), 4.85 (m, 2H, H^{Cp}), 4.59 (m, 2H, H^{Cp}). IR (ν / cm⁻¹) 3032 (w), 1612 (m), 1596 (s), 1559 (m), 1541 (m), 1431 (m), 1411 (m), 1398 (m), 1261 (w), 1226 (w), 1067 (w), 1036 (w), 994 (m), 892 (w), 827 (s), 764 (w), 741 (w), 679 (w), 649 (m), 629 (s), 597 (w), 570 (m), 508 (m), 475 (m). MALDI-MS (α-cyano-4-hydroxycinnamic acid matrix) *m/z* 649.52 [M+H]⁺ (calc. 649.18). Found C 70.44, H 4.65, N 12.38; calculated for C₄₀H₂₈FeN₆·2H₂O C 70.18, H 4.71, N 12.28.
 - 15 A solution of ZnCl₂ (1.36 mg, 0.01 mmol) in MeOH (8 mL) was layered over a suspension of **1** (6.49 mg, 0.01 mmol) in CHCl₃ (5 mL). Red crystals of [Zn₂(**1**)Cl₄]·3CHCl₃ (0.2 mg, 0.156 μmol, 1.6% based on **1**) were obtained after 2-4 weeks. Insufficient amount of crystalline material was obtained for bulk analysis.
 - 16 Crystal data for [Zn₂(**1**)Cl₄]·3CHCl₃: C₄₃H₃₁Cl₁₃FeN₆Zn₂, *M* = 1279.25, red block, monoclinic, space group *P*2₁/*n*, *a* = 13.5721(11), *b* = 23.659(2), *c* = 15.0438(12) Å, β = 94.479(3)°, *U* = 4815.8(7) Å³, *Z* = 4, *D_c* = 1.764 Mg m⁻³, μ(Cu-Kα) = 10.517 mm⁻¹, *T* = 123 K. Total 49487 reflections, 8941 unique, *R*_{int} = 0.027. Refinement of 8630 reflections (586 parameters) with *I* > 2σ (*I*) converged at final *R*₁ = 0.0749 (*R*₁ all data = 0.0765), *wR*₂ = 0.1882 (*wR*₂ all data = 0.1890), *gof* = 0.9829.
 - 17 C. E. Housecroft, *Dalton Trans.* 43 (2014) 6594.
 - 18 E. C. Constable, C. E. Housecroft, M. Neuburger, J. Schönle, S. Vujovic, J. A. Zampese, *Polyhedron* 62 (2013) 120.
 - 19 E. C. Constable, G. Zhang, E. Coronado, C. E. Housecroft, M. Neuburger, *CrystEngComm* 12 (2010) 2139.
 - 20 E. C. Constable, C. E. Housecroft, S. Vujovic, J. A. Zampese, A. Crochet, S. R. Batten, *CrystEngComm* 15 (2013) 10068.
 - 21 L. Li, Y.Z. Zhang, C. Yang, E. Liu, J.A. Golen and G. Zhang, *Polyhedron* 105 (2016) 115.