

Assembling coordination ladders with 4'-(4-methoxyphenyl)-4,2':6',4''-terpyridine as rails and rungs

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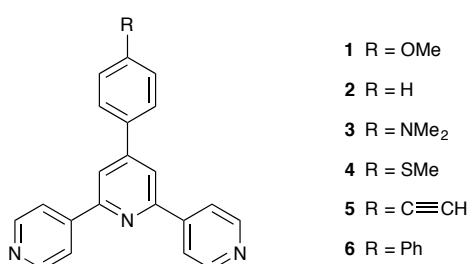
Abstract: The divergent ligand 4'-(4-methoxyphenyl)-4,2':6',4''-terpyridine (**1**) reacts with $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ under room temperature crystallization conditions ($\text{MeOH}/\text{CHCl}_3$) to give the coordination polymer $[\{\text{Cd}_2(\mathbf{1})_3(\text{NO}_3)_4\} \cdot \text{CHCl}_3 \cdot \text{MeOH}]_n$. The polymer adopts a ladder structure with **1** bridging pairs of cadmium(II) centres along both the edges (rails) and rungs of the ladder.

Keywords: X-ray; coordination polymer; cadmium; ladder structure

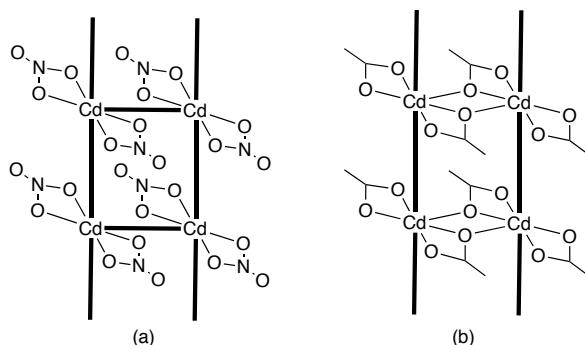
The coordination chemistry of ligands containing the divergent 4,2':6',4''-terpyridine (4,2':6',4''-tpy) metal-binding domain is attracting increased attention [1], and a search of the Cambridge Structural Database (CSD v. 5.35 with updates to and including May 2014 [2,3]) confirms a significant growth in structural data (11 to 77 entries) over the past five years. 4,2':6',4''-Terpyridines typically coordinate through the two outer nitrogen atoms, although the coordination capacity can be increased by the incorporation of non-innocent substituents such as pyridyl or carboxylate groups [4,5,6,7,8,9]. Reactions of 4,2':6',4''-tpy ligands with zinc(II) acetate, copper(II) acetate or zinc(II) halides lead to the formation of one-dimensional coordination polymers [1], although with ZnCl_2 or ZnBr_2 nodes, the assembly of metallohexacycles or metallosquares competes with polymer formation [10,11]. Metal ions that favour higher coordination numbers (e.g. Ni^{2+} , Co^{2+} , Cd^{2+}) give access to two-dimensional networks [12,13,14,15]. Reactions of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ are of particular note, since the assembly process appears to depend on the 4'-substituent in the 4,2':6',4''-tpy ligand. Two-dimensional sheet (metal–ligand ratio = 1 : 2), one-dimensional chain (metal–ligand ratio = 1 : 1) or one-dimensional ladder (metal–ligand ratio = 2 : 3) architectures have been observed when $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ reacts with **2**, **3** or **4**, respectively (Scheme 1) and the ladder motif (Scheme 2a) is also observed with **5** [14,16]. In contrast, the

reaction of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ with **6** (Scheme 1) leads to a one-dimensional polymer consisting of a double chain (metal–ligand ratio = 1 : 1) with $\{\text{Cd}_2(\mu, \kappa^3\text{-}O, O':O'-\text{OAc})_2(\kappa^2\text{-}O, O'-\text{OAc})_2\}$ motifs interconnecting the chains (Scheme 2b) [17]. The latter structure may also be described as a ladder, but is structurally distinct from that formed with cadmium nitrate. It also fits into a family of 4,2':6',4''-tpy-containing multiply-stranded coordination polymers containing $\{\text{M}_n(\text{OAc})_{2n}\}$ nodes ($n = 1, 2, 3$ or 5) [1].

Ladder assemblies with 4,2':6',4''-tpy ligands as both rungs and rails are still sparse, and we report here a further example of access to this favourable motif.



Scheme 1. Ligand structures.



Scheme 2. Schematic representations of (a) 2 : 3 (Cd to L) and (b) 1 : 1 (Cd to L) ladders formed between $\text{Cd}(\text{NO}_3)_2$ or $\text{Cd}(\text{OAc})_2$ and different 4,2':6',4''-tpy ligands (represented by the bold line).

Compound **1** (Scheme 1) was prepared using the general method described by Wang and Hanan [18]. Layering of a MeOH solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ over a CHCl_3 solution of ligand **1** resulted in the formation of colourless crystals after 10 days [19]. Bulk-sample analysis indicated a cadmium to ligand ratio of 2 : 3 and X-ray diffraction analysis of a single crystal selected from the bulk sample revealed the formation of the coordination polymer $[\{\text{Cd}_2(\mathbf{1})_3(\text{NO}_3)_4\}]_n$. The program SQUEEZE [20] was used to treat the solvent region as the electron density was too diffuse: the SQUEEZE output was modelled as a mixture of

CHCl₃ and MeOH solvent molecules giving an overall formula of $[\{\text{Cd}_2(\mathbf{1})_3(\text{NO}_3)_4\} \cdot \text{CHCl}_3 \cdot \text{MeOH}]_n$ [21]. The complex crystallizes in the monoclinic *C2/c* space group and the asymmetric unit contains one Cd atom (Cd1) and one whole (containing N10 and N20) and one half ligand **1** (containing N36). The latter lies on a 2-fold axis, with the consequence that the methoxy substituent is necessarily disordered and each methyl group is half-occupancy. Each ligand **1** bridges two Cd atoms and propagation of the structure gives a ladder (Fig. 1a) consistent with the Cd to **1** ratio of 2 : 3 (Scheme 2a). The ligand containing the disordered OMe substituent forms each rung. The Cd–N bond distances are unexceptional (Cd1–N36 = 2.324(5), Cd1–N10 = 2.322(5) and Cd1ⁱ–N20 = 2.306(5) Å, symmetry code $i = \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$). The coordination sphere of Cd1 is completed by two bidentate nitrate ligands: Cd1–O2 = 2.381(5), Cd1–O4 = 2.451(6) Å, O2–Cd1–O4 = 53.28(19)°, and Cd1–O6 = 2.514(5), Cd1–O8 = 2.389(5) Å, O6–Cd1–O8 = 52.52(18)°.

The view of part of one polymer chain in Figure 1b illustrates that all the 4'-methoxyphenyl substituents (both 'rung' and 'side' supports) project from either side of the chain. The ladders slice obliquely through the unit cell and pack parallel to one another. The primary stacking interaction involves the interdigitation and π -stacking of 4'-methoxyphenylpyridine units of adjacent chains (Figure 2a) with the ligand that forms the rung of the ladder sandwiched between a pair of ligands that form the sides of the ladder. The twist angles between phenyl and pyridine rings in each independent ligand are 26.3 and 29.3°, respectively, consistent with efficient π -stacking between them. For each of the connected Ph...py...Ph and py...Ph...py stacks (Figure 2a), angles between stacked-ring planes are 2.7 and 4.3°, respectively. In the Ph...py...Ph stack, Ph_{plane}...py_{centroid} and Ph_{centroid}...py_{centroid} distances are 3.47 and 3.52 Å; corresponding separations in the py...Ph...py stack are 3.26 and 3.47 Å. Triple-decker sandwiches (Figure 2a) mediate the assembly of chains into sheets (Figure 2b).

Independent crystallization tubes were investigated and crystals obtained from the bulk samples gave satisfactory elemental analysis for $[\{\text{Cd}_2(\mathbf{1})_3(\text{NO}_3)_4\}]_n$. The space group and unit cell parameters (monoclinic, *C2/c*, $a = 27.328(2)$, $b = 13.2669(9)$, $c = 21.2176(16)$ Å, $\beta = 116.894(3)^\circ$) on a crystal selected from the second experiment were consistent with the first [21].

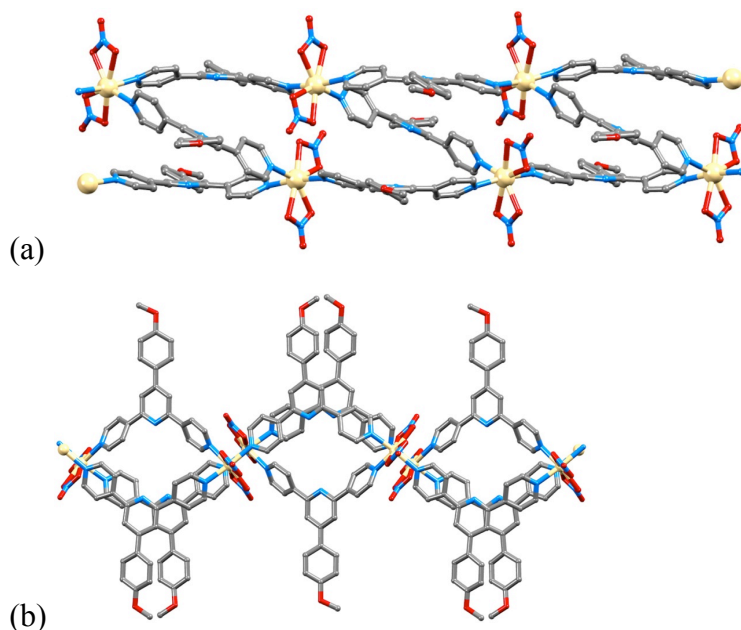


Fig. 1 (a) Part of the ladder polymer chain in $[\{Cd_2(\mathbf{1})_3(NO_3)_4\} \cdot CHCl_3 \cdot MeOH]_n$. Only one position of the disordered OMe group in each ligand connecting the upper and lower chains is shown. H atoms are omitted for clarity. (b) View of the chain to emphasize the projection of all 4'-methoxyphenyl units.

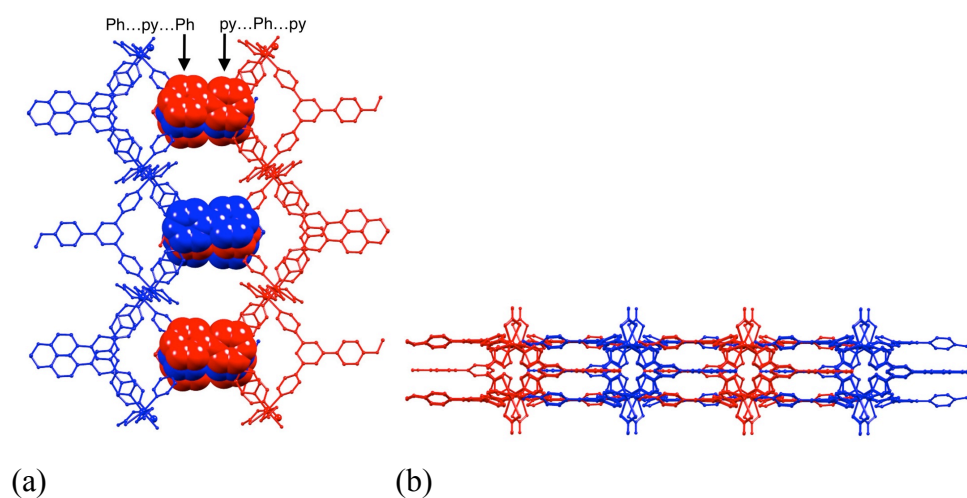


Fig. 2 (a) Interdigitation and π -stacking of 4'-methoxyphenylpyridine units of adjacent chains (red and blue) in $[\{Cd_2(\mathbf{1})_3(NO_3)_4\} \cdot CHCl_3 \cdot MeOH]_n$; the Ph...py...Ph and py...Ph...py stacks (see text) are defined. (b) Part of a two-dimensional sheet assembled from interdigitated chains.

In conclusion, a one-dimensional ladder structure with a $\{Cd_2(4'-(4-MeOC_6H_4)-4,2':6',4''-tpy)_3\}$ framework results with nitrate as co-ligand. We are currently investigating the crystallization conditions under which the different ladder structures (Scheme 2) containing **1** or analogous ligands with extended alkyl chains are produced.

Acknowledgements

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Appendix A. Supplementary data

CCDC 1018703 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)

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- 19 $[\{\text{Cd}_2(\mathbf{1})_3(\text{NO}_3)_4\} \cdot \text{CHCl}_3 \cdot \text{MeOH}]_n$. A MeOH (5 cm³) solution of Cd(NO₃)₂·4H₂O (27.8 mg, 0.09 mmol) was layered over an CHCl₃ solution (5 cm³) of **1** (10.2 mg, 0.03 mmol) in a test tube. The tube was sealed and left to stand at room temperature for 2 weeks during which time colourless plates grew. These were collected by filtration, washed with CHCl₃ and MeOH, dried in air and in vacuo. Yield: 15.8 mg (96%, calc. based on **1**). IR (solid, cm⁻¹): 3538 w, 3062 w, 2832 w, 1610 s, 1598 s, 1560 m, 1537 m, 1518 m, 1504 m, 1434 s, 1400 s, 1321 m, 1294 s, 1261 s, 1242 s, 1217 s, 1187 s, 1179 s, 1125 m, 1062 m, 1049 m, 1030 s, 1019 s, 991 m, 893 w, 854 m, 828 s, 819 s, 776 m, 749 s, 734 s, 677 s, 666 m, 646 s, 638 s, 619 m, 590 m, 571 s, 526 s, 506 m, 491 m, 464 m. Found C 48.75, H 3.55, N 11.59; required for C₆₈H₅₆Cd₂Cl₃N₁₃O₁₆·H₂O C 49.19, H 3.52, N 10.97%.
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- 21 $[\{\text{Cd}_2(\mathbf{1})_3(\text{NO}_3)_4\} \cdot \text{CHCl}_3 \cdot \text{MeOH}]_n$. After SQUEEZE and with modelled solvent: C₆₈H₅₆Cd₂Cl₃N₁₃O₁₆, *M* = 1642.44, colourless block, monoclinic, space group *C2/c*, *a* = 27.520(4), *b* = 13.138(2), *c* = 20.983(3) Å, *β* = 117.788(8)°, *U* = 6711.5(11) Å³, *Z* = 2, *D_c* = 1.63 Mg m⁻³, *μ*(Cu-Kα) = 6.853 mm⁻¹, *T* = 123 K. Total 24423 reflections, 5816 unique, *R*_{int} = 0.067. Refinement of 5789 reflections (416 parameters) with *I* > 2σ (*I*) converged at final *R*1 = 0.0658 (*R*1 all data = 0.0838), *wR*2 = 0.1726 (*wR*2 all data = 0.1909), *gof* = 0.9894.

