Letter

Parallel interpenetration in novel herringbone sheets formed by Co(II) and Cd(II) complexes with *trans*-4,4′-azobis(pyridine)

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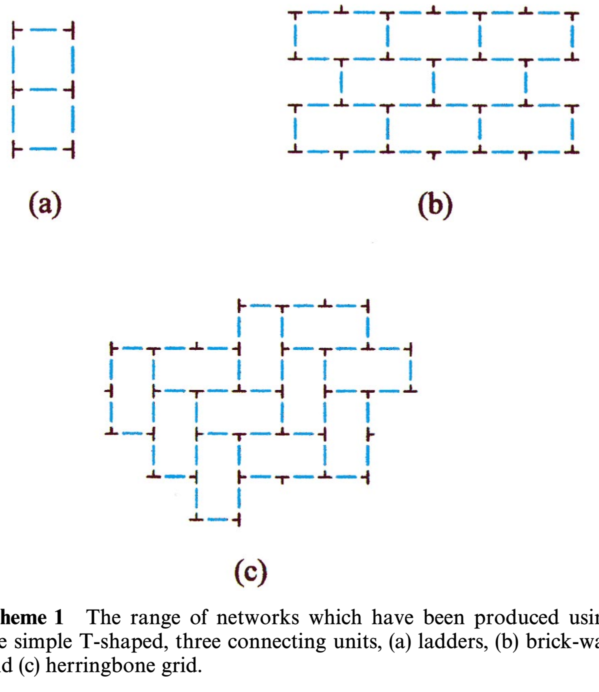
The complexes $\{[M_2(\mu\text{-}4,4'\text{-apy})_3(NO_3)_4]\cdot CH_2Cl_2\}_\infty$ (1, M = Co; 2 M = Cd; 4,4′-apy = *trans*-4,4′-azobis(pyridine)) form interpenetrated 2-D grids with a (6,3) topology. These sheets exhibit a new herringbone motif in which Co(II) or Cd(II) centres are bridged by co-ordinated 4,4′-apy ligands.

The field of crystal engineering using bridging bidentate ligands with late transition metals to form co-ordination polymers has received growing attention.[1,2] Much of this work has used the 4,4′-bipyridine (4,4′-bipy) ligand and its analogues.[1,2] The co-ordination polymers produced have been shown to form a wide range of interesting network topologies. These range from chains[3–5] to ladders,[6–12] to grids[13–15] and adamantoid networks.[16–18] The $M(NO_3)_2$ [M = Cd(II),[6,7,12] Co(II),[8–10] Zn(II)[12]] unit has been used as a T-shaped building-block in co-ordination polymer construction. Most commonly, these connecting units afford molecular ladder structures (Scheme 1a) but there have also been reports of brick-wall structures (Scheme 1b) in which alternate rungs of a ladder are oriented in opposing directions forming a 2-D sheet. We now report a novel network type, $\{[M_2(\mu\text{-}4,4'\text{-apy})_3(NO_3)_4]\cdot CH_2Cl_2\}_\infty$ [1 M = Co; 2 M = Cd; 4,4′-apy = *trans*-4,4′-azobis(pyridine)], which is related to both the molecular ladders and the brick-wall arrangement but displays a herringbone grid motif (Scheme 1c) where the metal centres are bridged by co-ordinated 4,4′-apy ligands.



Scheme 1 The range of networks which have been produced using the simple T-shaped, three connecting units, (a) ladders, (b) brick-wall and (c) herringbone grid.

A solution of $M(NO_3)_2\cdot 6H_2O$ (**1** M = Co; **2** M = Cd) in EtOH (10 cm^3) was layered on to a solution of 4,4′-apy[19] in CH_2Cl_2 (10 cm^3).† Crystals were formed at the interface of the solutions (**1**) or by diffusion of Et_2O into the mother liquor once diffusion was complete (**2**).‡ Despite using a 2 : 1 ligand : metal ratio, the isolated complexes **1** and **2** both exhibit a 3 : 2 ratio of ligand : metal. Complexes **1** and **2** are isostructural and are based on a distorted pentagonal bipyramidal metal centre (Fig. 1). The co-ordination sphere comprises two bidentate nitrates and three pyridyl N-donors from 4,4′-apy ligands. Therefore, as expected, each metal centre forms a T-shaped connecting unit for the bidentate bridging 4,4′-apy ligands. These T-shaped units are arranged to produce the 2-D herringbone grid motif (Fig. 2) with large rectangular voids. Both networks in **1** and **2** and the brick-wall structure of $[Cd_2(\mu\text{-}L)_3(NO_3)_4]_\infty$[3,6] [L = 1,4-bis(pyridin-4-yl)methyl-2,3,5,6-tetrafluorobenzene] exhibit a (6,3) network topology, but in the examples reported here the different orientation of the simple T-shaped connecting units results in a herringbone motif.

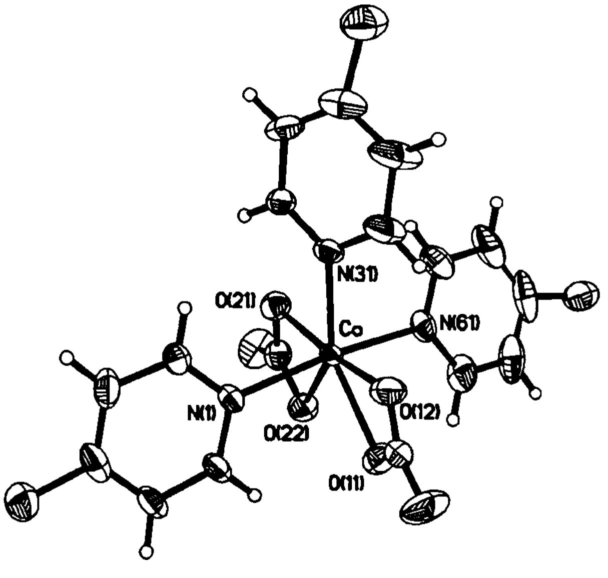


Fig. 1 The pentagonal bipyramidal arrangement at the metal centre in $\{[Co_2(\mu\text{-}4,4'\text{-apy})_3(NO_3)_4]\}_\infty$ **1** (50% displacement ellipsods). The same arrangement is observed in complex **2**. Selected bond lengths (Å) [**1** Co–O(11) 2.176(5), Co–O(12) 2.318(5), Co–O(21) 2.191(5), Co–O(22) 2.387(5), Co–N(1) 2.159(5), Co–N(31) 2.182(6), Co–N(61) 2.159(5); **2** Cd–O(11) 2.370(4), Cd–O(12) 2.535(5), Cd–O(21) 2.583(5), Cd–O(22) 2.489(5); Cd–N(1) 2.260(5), Cd–N(31) 2.240(4), Cd–N(61) 2.305(5)].

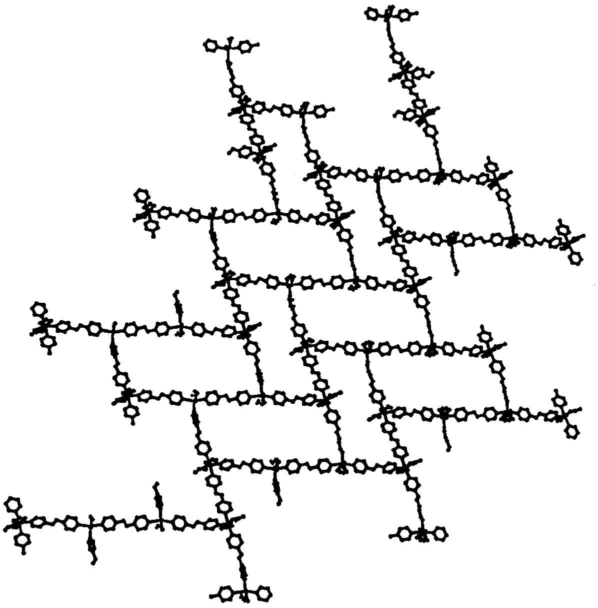


Fig. 2 The herringbone grid formed by $\{[M_2(\mu\text{-}4,4'\text{-apy})_3(NO_3)_4]\}_\infty$ (**1** M = Co; **2** M = Cd).

In **1** and **2**, each herringbone sheet undulates, and as a result, two further sheets interpenetrate parallel to the original (Fig. 3 and 4). Interpenetration of independent co-ordination polymer networks is an increasingly encountered phenomenon.[1] 2-D networks can exhibit both perpendicular and parallel interpenetration. Whereas perpendicular interpenetration results in the formation of 3-D polycatenated architectures, parallel interpenetration yields 2-D polycatenated sheets.[1] Thus, the nature of the observed interpenetration in any given system results in a totally different long-range network structure. Parallel interpenetration requires undulation of individual sheets and has been observed for both (4,4) and (6,3) co-ordination networks. Of the (6,3) co-ordination networks that exhibit parallel interpenetration only one example is triply-interpenetrated[6] with all other known examples being doubly-interpenetrated.[1,20,21] There is also one example of a hydrogen-bonded honeycomb network that has triply-interpenetrated parallel sheets.[22] Interestingly, the only previously reported example of a co-ordination polymer that exhibits triply-interpenetrated parallel sheets is the brick-wall network **3**,[6] which, like the structures reported here, is constructed from $M(NO_3)_2$ T-shaped connecting units and bridging bipyridyl donors. The high degree of interpenetration in **1**, **2** and the brick-wall structure **3**[6] arises (probably) from the relative length of the linking ligand; smaller linkers lead to doubly-interpenetrated (6,3) networks, many of which are based on tricyanomethanide ligands.[20] It can be postulated that the sheets in **1**, **2** and **3** distort from planarity to allow parallel interpenetration in order to inhibit unfavourable interactions between the co-ordinated nitrate anions and adjacent 4,4′-apy ligands.

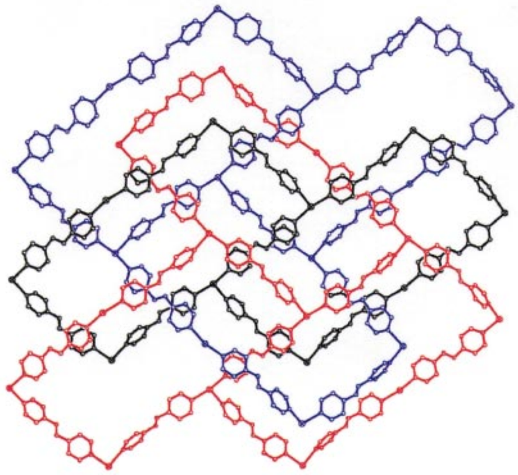


Fig. 4 The interpenetrating sheets formed by **1** and **2** viewed from the top.

The only other example of a brick-wall (6,3) network using bridging bipyridyl ligands is $\{[Ni(4,4'\text{-apy})_2(NO_3)_2]_2\text{-}[Ni_2(4,4'\text{-apy})_3(NO_3)_4]\cdot 4CH_2Cl_2\}_\infty$ **4**[14] which exhibits perpendicular interpenetration of brick-wall (6,3) $[Ni_2(4,4'\text{-apy})_3(NO_3)_4]_\infty$ grids through square (4,4) $[Ni(4,4'\text{-apy})_2(NO_3)_2]_\infty$ grids, representing a further variety of structure formed from both $M(NO_3)_2$ connecting units. Despite compounds **1–4** all exhibiting the (6,3) topology, the motifs displayed are different, a herringbone grid in **1** and **2** and a brick-wall in **3**[6] and **4**.[14]

Although each $\{[M_2(\mu\text{-}4,4'\text{-apy})_3(NO_3)_4]\}_\infty$ framework forms large rectangular cavities (Fig. 2) (M = Co, 21.3 × 8.6 Å; M = Cd, 21.4 × 8.9 Å), the three-fold interpenetration fills any spaces within each sheet. However, there are cavities between adjacent sheets (14.2% by volume in **1**, and 15.1% in **2**)[23] which are filled by guest solvent molecules.

The new herringbone motif observed in compounds **1** and **2** illustrates the range of potential network structures that seemingly simple combinations of building-blocks can afford. This new structural form also indicates and reflects the sensitivity of co-ordination frameworks to subtle changes in building-block design which result in gross changes in extended network structure. We are currently pursuing further understanding of the factors that influence network structure and topology.

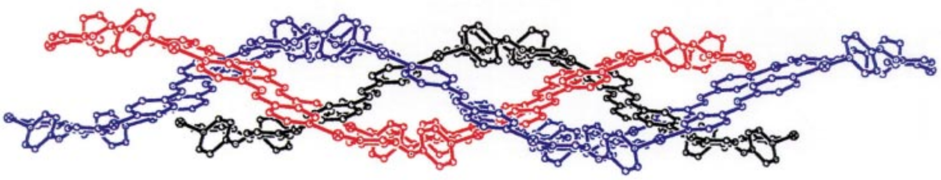


Fig. 3 The interpenetrating undulating sheets formed by **1** and **2** viewed from the side.

Notes and references

† A solution of $M(NO_3)_2\cdot 6H_2O$ (for **1**, M = Co, 0.039 g, 1.36×10^{-4} mol; for **2**, M = Cd, 0.042 g, 1.36×10^{-4} mol) in EtOH (10 cm^3) was layered on to a solution of 4,4′-apy (0.05 g, 2.71×10^{-4} mol) in CH_2Cl_2 (10 cm^3). Red crystals formed at the interface of the solutions (**1**) or upon diffusion of Et_2O into the mother-liquor once diffusion was complete (**2**). Complex **1**: yield = 20% (Found: C, 35.94; H, 2.72; N, 22.11. Calc. for $C_{31}H_{30}Co_2Cl_2N_{16}O_{14}$: C, 32.47; H, 2.62; N, 19.55%). IR (KBr)/cm^{-1}: 3185s, 1603m, 1472m, 1417m, 1384s, 1305w, 1226w, 1050w, 845m, 570m, 546w. Mp 275 °C (decomp.). Complex **2**: yield = 21% (Found: C, 32.81; H, 2.36; N, 20.33. Calc. for $C_{31}H_{24}Cl_2Cd_2N_{16}O_{12}$: C, 33.53; H, 2.36; N, 20.18%). IR (KBr)/cm^{-1}: 3454w, 1600s, 1452s, 1418s, 1384s, 1292s, 1227m, 1056m, 1013m, 843m, 568m. Mp 280 °C (decomp.).

‡ Diffraction data for **1** and **2** were collected on a Stoë Stadi-4 diffractometer equipped with an Oxford Cryosystems open-flow cryostat

using ω–θ scans and graphite monochromated Mo-Kα radiation.[24] The structures were solved by direct methods (SHELXS-97)[25] and refined on F^2 (SHELXL-97).[26] All non-hydrogen atoms were refined aniosotropically except for dichloromethane C in **1** and water O atoms in **2**. All hydrogens were placed geometrically and allowed to ride with their parent atoms. No hydrogens were found for the water molecules in **2**. Compound **1**: $C_{15.5}H_{13}ClCoN_8O_6$, $M = 501.72$, monoclinic, $C2/c$, $a = 20.802(9)$, $b = 11.124(4)$, $c = 20.806(9)$ Å, $\beta = 119.27(4)°$, $U = 4200(3)$ Å^3, $Z = 8$, $F(000) = 2032$, $D_c = 1.587$ g cm^{-3}, $\mu = 0.995$ mm^{-1}, red plate ($0.47 \times 0.38 \times 0.18$ mm^3), $T = 150(2)$ K, ψ-scan absorption corrections were applied to the data ($T_{min} = 0.684$, $T_{max} = 0.810$), 3609 unique reflections ($2\theta_{max} = 50°$), of which 2681 had $F_o \geqslant 4\sigma(F_o)$. Final R_1 $[F_o \geqslant 4\sigma(F_o)] = 0.0740$ and wR_2 (all data) $= 0.1942$ for 293 refined parameters with 99 restraints, $S = 1.121$, $(\Delta/\sigma)_{max} = 0.001$, $\Delta\rho_{max} = 1.17$ e Å^{-3}, $\Delta\rho_{min} = -1.02$ e Å^{-3}. Compound **2**: $C_{15.5}H_{15}CdClN_8O_7$, $M = 573.21$, monoclinic, $C2/c$, $a = 21.197(5)$, $b = 11.166(12)$, $c = 21.389(4)$ Å, $\beta = 122.24(2)°$, $U = 4282(5)$ Å^3, $Z = 8$, $F(000) = 2280$, $D_c = 1.778$ g cm^{-3}, $\mu = 1.201$ mm^{-1}, irregular red tablet ($0.60 \times 0.35 \times 0.27$ mm^3). $T = 150(2)$ K, ψ-scan absorption corrections were applied to the data ($T_{min} = 0.683$, $T_{max} = 0.765$), 3771 unique reflections ($2\theta_{max} = 52°$), of which 3210 had $F_o \geqslant 4\sigma(F_o)$. Final R_1 $[F_o \geqslant 4\sigma(F_o)] = 0.0450$ and wR_2 (all data) $= 0.118$ for 306 refined parameters with 100 restraints, $S = 1.164$, $(\Delta/\sigma)_{max} = 0.001$, $\Delta\rho_{max} = 1.09$ e Å^{-3}, $\Delta\rho_{min} = -0.82$ e Å^{-3}. CCDC reference number 440/107. See http://www.rsc.org/suppdata/rj/1999/573/ for crystallographic files in .cif format.

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