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Coordination Networks with 1,3-Bis(4-pyridyl)propane. A Flexible Ligand Exhibiting Supramolecular Isomerism

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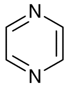
An open framework rectangular grid is formed by the self-assembly of 1,3-bis(4-pyridyl)propane with copper nitrate and copper perchlorate.

Crystal engineering of new solid state coordination architectures with bidentate ligands and various transition metal ions offers an exciting approach to the discovery of novel multi-dimensional arrays which may possess functional properties. A variety of coordination polymers have been prepared from pyrazine **1** and 4,4-dipyridyl **2**. Structural motifs for coordination polymers include adamantoid,[1] honeycomb,[2] grid,[3] ladder,[4] brick wall[4] and octahedral[5] network features. Tetrahedral, trigonal and octahedral metal coordination environments are propagated in one, two or three dimensions by the rigid ligands which allows some structural predictions to be made.



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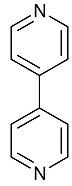

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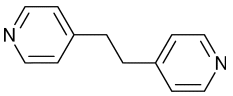

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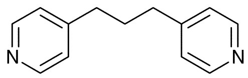

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Pore volume in the lattice, a prerequisite for desirable functional properties, is frequently minimised during crystallisation by the formation of interpenetrating lattice or the formation of infinite polycatenanes and polyrotaxanes. Coordination networks from flexible bidentate ligands[6] are rarer and have less predictable structures owing to the possible occurrence of supramolecular isomerism which involves the adoption of different ligand conformations in the lattice.[6a,7] Notably 1,2-bis(4-pyridyl)ethane **3** can adopt either a *gauche* or *anti* geometry and indeed in $[Co(NO_3)_2\{1,2\text{-bis(4-pyridyl)ethane}\}_{1.5}]_n$ occurs in either all *anti*, 2 *gauche*:1 *anti* or 2 *anti*:1 *gauche* conformations depending upon the solvent of crystallisation and guest clathration.[7] Supramolecular isomerism is related to polymorphism in molecular crystals although the former is more likely to have a greater influence on crystal structure owing to the coordinative network structure. Here we report coordination polymers prepared from the flexible ligand 1,3-bis(4-pyridyl)propane **4** which can exist in *anti–anti*, *gauche–anti*, *gauche–gauche* and *gauche–gauche′* conformations.[8]

Blue crystals of **5a** were obtained by layering a solution of 1,3-bis(4-pyridyl)propane **4** in EtOH onto a solution of $Cu(NO_3)\cdot 6H_2O$ in H_2O. An X-ray structure determination showed the structure to consist of an infinite 2D rectangular grid of composition $\{[Cu(NO_3)_2\{1,3\text{-bis(4-pyridyl)-propane}\}_2]\cdot 0.25H_2O\}_n$ (Fig. 1).[9] The copper atoms are square planar with the nitrate anions occupying pseudo-octahedral positions. The Cu–O bond lengths are in the range 2.45–2.49 Å. Two distinct conformations of the ligand are present in equal numbers. One ligand adopts an *anti–anti* conformation with dihedral angles of −178.6(5)° (C4–C7–C8–C9) and −172.8(4)° (C7–C8–C9–C10). The other unique ligand adopts a *gauche–gauche* conformation with dihedral angles of −63.7(6)° (C24–C27–C28–C29) and −62.9(6)° (C27–C28–C29–C30). Identical ligand conformations are *cis* with respect to the copper atom as opposed to *trans*. The distances between the pyridine nitrogen atoms are about 9.7 Å (N1–N13) and 7.8 Å (N21–N33) for the *anti–anti* and *gauche–gauche* ligand conformations respectively. As a consequence of this difference in spacer length each molecular box is rectangular, as opposed to square shaped, and has approximate dimensions of 9.65 × 11.80 Å. Each 2D grid is stacked on top of the adjacent layer forming channels along the *c* axis which are occupied by the disordered water molecules (Fig. 2). The water molecules form hydrogen bonds each of *ca.* 3 Å in length to the nitrate anions. The use of $Cu(ClO_4)_2\cdot 6H_2O$ in place of $Cu(NO_3)_2\cdot 6H_2O$ gives a similar structure **5b** of composition $[Cu(ClO_4)_2\{1,3\text{-bis(4-pyridyl)propane}\}_2]_n$ which contains no solvent molecules. The perchlorate anions occupy pseudo-octahedral positions with average Cu–O bond distances of 2.48 and 2.55 Å. The two ligand conformations are similar but not identical to those in structure **5a** with dihedral angles of −178.6(4)° (C4–C7–C8–C9) and −178.9(4)° (C7–C8–C9–C10) (*anti–anti*) and −69.5(6)° (C24–C27–C28–C29) and −76.5(6)° (C27–C28–C29–C30)

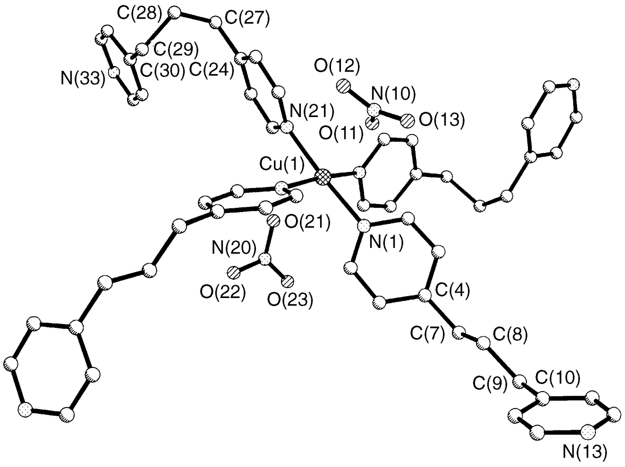

Fig. 1 Ball and stick representation of $[Cu(NO_3)_2\{1,3\text{-bis-(4-pyridyl)propane}\}_2]\cdot 0.25H_2O$ **5a** showing the square planar Cu coordination geometry with the nitrate anions occupying pseudo-octahedral positions. Hydrogen atoms are omitted for clarity. Selected dihedral angles (°): C4–C7–C8–C9 −178.6(5), C7–C8–C9–C10 −172.8(4), C24–C27–C28–C29 −63.7(6), C27–C28–C29–C30 −62.9(6)

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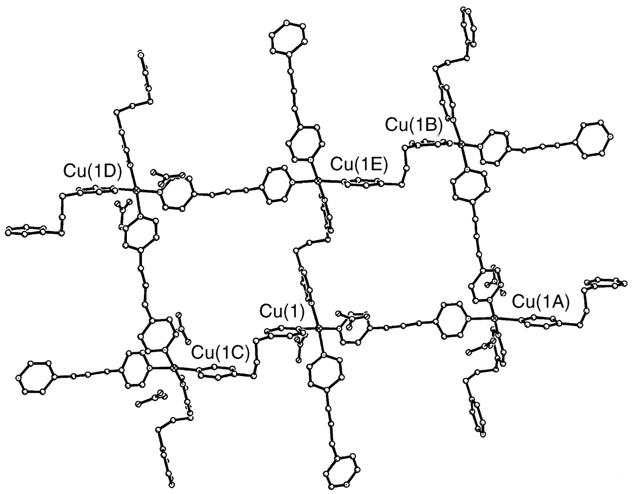

Fig. 2 Ball and stick representation of $[Cu(NO_3)_2\{1,3\text{-bis-}(4\text{-pyridyl})\text{propane}\}_2]\cdot 0.25H_2O$ **5a** showing the 2D grid framework

(*gauche–gauche*). The distances between the pyridine nitrogen atoms are about 9.6 Å (N1–N13) and 8.6 Å (N21–N33) for the *anti–anti* and *gauche–gauche* ligand conformations respectively. The molecular boxes have similar dimensions to those of **5a**.

Ion exchange properties, a characteristic feature of some open framework coordination networks,[9] was investigated by standing a sample of **5a** in an aqueous solution of 1 M $NaClO_4$ for 5 days followed by washing with H_2O. No evidence for anion exchange was detected by IR spectroscopy. However evidence for partial anion exchange was observed by standing a sample of **5b** in an aqueous solution of 1 M $NaNO_3$ for 5 days. The IR spectrum showed a weakening of the perchlorate peaks at 1105–1120 cm^{-1} and the appearance of nitrate ion peaks at 1308, 1384 and 1405 cm^{-1}. The exchange of perchlorate anions for nitrate anions and not *vice versa* suggests that the latter are more tightly bound to the copper cations. This is evidenced by the Cu–O bonds for **5a** of 2.45–2.49 Å while those for **5b** of 2.48 and 2.55 Å are longer. Only partial anion exchange may occur because the anions in the lattice are coordinated to the copper cations and are poorly solvated which will restrict their ability to dissociate from the copper cations. Solvated anions in solution would require extensive desolvation upon absorption which would be unfavourable. The pore size appears to prevent the clathration of sufficient solvating water molecules and excludes the selective formation of a partially dehydrated lattice in which the anions might have greater mobility.[9] Standing either **5a** or **5b** in 1 M $NaPF_6$ or 1 M $NaBF_4$ caused slow dissolution of the material. This may be due to the acidity of the solution which dropped to pH 1–2 presumably owing to partial hydrolysis of the anions.

This paper illustrates the scope that flexible ligands have to give coordination architectures with an open framework structure. The adoption of different ligand conformations increases the potential diversity and elegance of networked materials that might crystallise and suggests that new flexible ligands, a multitude of which can be envisioned, may give new coordination networks.

Crystal Data for **5a**.—$0.03 \times 0.15 \times 0.15$ mm, blue plates, monoclinic, space group $P2_1/n$, $a = 10.56730(10)$, $b = 17.2019(5)$, $c = 15.5148(4)$ Å, $\beta = 102.190(2)°$, $Z = 4$, $V = 2756.66(11)$ Å^3, $D_c = 1.417$ Mg m^{-3}, For **5a** and **5b** Mo-Kα radiation ($\lambda = 0.71069$ Å), SMART system and hemisphere data collection. The structure was solved by direct methods and refined against F^2 using SHELXTL (Version 5.01 Bruker AXS, Madison, Wisconsin) Final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0578$, $wR_2 = 0.1135$, for all data $R_1 = 0.1980$ and $wR = 0.1768$.

Crystal Data for **5b**.—$0.02 \times 0.2 \times 0.2$ mm, blue plates, orthorhombic, space group $Pcab$, $a = 15.9520(2)$, $b = 18.74180(10)$, $c = 19.5094(3)$ Å, $Z = 8$, $V = 5832.71(12)$ Å^3, $D_c = 1.501$ Mg m^{-3}. Final R indices $[I > 2\sigma(I)]$ $R_1 = 0.0439$, $wR_2 = 0.1058$, for all data $R_1 = 0.0794$ and $wR_2 = 0.1404$. The estimated standard deviations for the geometrical parameters involving non-hydrogen atoms lie within the following ranges: For **5a** bond lengths 0.004–0.007 Å; bond angles 0.14–0.6°; For **5b** bond lengths 0.003–0.02 Å; bond angles 0.2–1.2°.

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Techniques used: IR and X-ray crystallography

References: 9

Appendix: Tables: 10 (crystal data and structure refinement, atomic coordinates and U_{eq} values, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters).

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