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Topological isomerism in coordination polymers†

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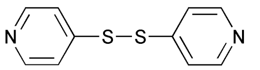
Three coordination polymers formed between CuI and bpds [bpds = bis(4-pyridyl)disulfide] have been prepared and fully characterised illustrating rare examples of solvent dependent topological isomerism in [(CuI)$_2$(bpds)]$_\infty$; tetrahedral Cu$_4$I$_4$ cubane junctions are linked to give either necklace or tubular polymers.

The study of inorganic coordination frameworks has received increasing attention over recent years with a growing range of structural motifs being discovered.[1–4] Many of these studies have heightened awareness of the influence not only of metal ion and ligand[2] but also of anion[3] and solvent.[4,5] Many of the architectures reported to date are based upon rigid linear linker ligands,[1–4] with only recent efforts focusing on the use of ligands showing conformational flexibility.[5–7] The term 'supramolecular isomerism' has been used by Zaworotko and coworkers[5] to describe the two forms of the coordination polymer [Co(NO$_3$)$_2$(L)$_{1.5}$]$_\infty$ obtained from the reaction of Co(NO$_3$)$_2$ with 1,2-bis(4-pyridyl)ethane (L). The two isomers differ due to the conformational flexibility of L which is *gauche* in one isomer and *anti* in the other.[5] More recently, the various different isomers of T-shaped metal–ligand building blocks have been recognised.[8] We prefer the term topological isomerism as we believe that this describes the differences in the topology and connectivity of the coordination polymer. We report herein an unusual example of topological isomerism in which both isomers (**2** and **3**) have the same stoichiometry, the same metal-fragment and ligand-linker combinations, the same ligand conformations, and the same metal ion stereochemistry. Compounds **2** and **3** differ purely in their metal to ligand coordinative connectivity to give isomers of different topology.

We were interested in developing neutral metal–organic networks and chose to investigate metal–halide aggregation with heterocyclic ligands.[9] The coordination polymers [CuI(bpds)]$_\infty$ and [(CuI)$_2$(bpds)]$_\infty$ [bpds = bis(4-pyridyl)disulfide] can be prepared systematically as yellow powders. Bulk quantities of the compounds are obtained by the stoichiometric reaction of CuI with the ligand in MeCN or EtCN. Crystals of the compounds were grown by slow diffusion between CuI solutions in EtCN (or MeCN) and bpds in CH$_2$Cl$_2$. Regardless of the metal : ligand ratios used, crystals of both compounds were found in the same reaction solution. Over the period of a week, yellow needles of [CuI(bpds)]$_\infty$ **1** grew in the ligand-rich region of the solution while pale-yellow blocks of [(CuI)$_2$(bpds)]$_\infty$, **2** or **3**, grew in the metal-rich region.‡


bpds

Although the structure of [CuI(bpds)]$_\infty$ **1** consists of Cu$_2$I$_2$ cores connected by bpds to form a planar ribbon of known topology[10] (whether grown from MeCN–CH$_2$Cl$_2$ **1a** or EtCN–CH$_2$Cl$_2$ **1b**), the single crystal X-ray structure determinations of the 2 : 1 complex [(CuI)$_2$(bpds)]$_\infty$ revealed two different structural motifs depending upon the solvent used in crystallisation. In both cases the [(CuI)$_2$(bpds)]$_\infty$ consists of Cu$_4$I$_4$ cubane tetramers which are linked by two bpds ligands to form a square-shaped cavity (Fig. 1). Crystals of **2** grown from EtCN–CH$_2$Cl$_2$ reveals tetrahedral Cu$_4$I$_4$ cubane junctions§ linked by bpds ligands [C–S–S–C 77.4(2)°] to give a necklace structure (Fig. 1). However, in this case the tetrahedral geometry of the Cu$_4$I$_4$ cubane results in alternating square-shaped units being orientated perpendicular to each other in adjacent links of the necklace. The square-shaped cavities are packed to give channels which run parallel to the *b*-axis (potential solvent accessible volume 21.5%)[11] that accommodate EtCN molecules.

Using MeCN–CH$_2$Cl$_2$ as the crystallisation solvent results in a different structural isomer of [(CuI)$_2$(bpds)]$_\infty$ **3**. As in **2**, Cu$_4$I$_4$ cubane tetramers are linked by two bpds ligands to form a square-shaped cavity. However, the tetrahedral junctions§ of these cubane units now allow these squares to interlink *via* two further bpds ligands forming a tubular polymer[6] (Fig. 2). The conformation adopted by the bpds ligands is similar to that observed for the 1 : 1 compound [within the square C–S–S–C 78.4(3)°, interlinkers C–S–S–C 88.3(3)°]. In **3** the spaces between the bands of the square-shaped cavities are interdigitated by the bands of two adjacent tubes translated by half the repeat unit (Fig. 3). Despite the interdigitation this packing arrangement allows the formation of two criss-crossed channels parallel to the *a* and *b* axes, giving a potential solvent accessible volume of 14.4%.[11] Both of these channels run diagonally through the square-shaped cavities of adjacent tubes and are occupied by MeCN solvent molecules (Fig. 4).

Powder X-ray diffraction studies of **2** and **3** were used to study whether each solvent mixture results exclusively in a single isomer. Compound **2** was found to undergo irreversible and rapid desolvation during the period of the diffraction

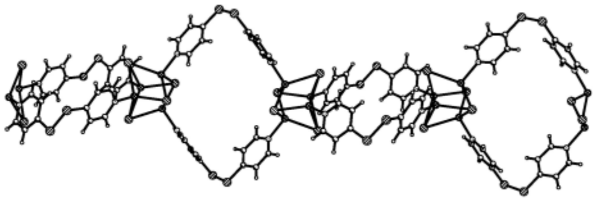


Fig. 1 The necklace isomer **2** of [(CuI)$_2$(bpds)]$_\infty$ showing alternating square-shaped units perpendicular to each other.

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† Electronic supplementary information (ESI) available: full experimental details. See http://www.rsc.org/suppdata/cc/b1/b103612m/

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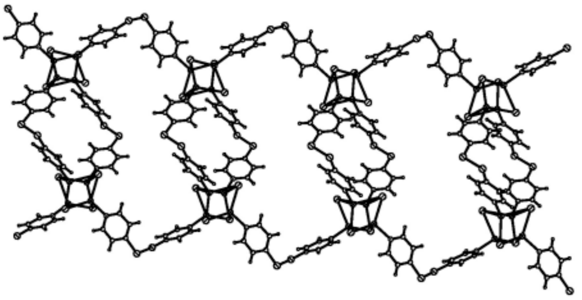

Fig. 2 The tubular isomer **3** of $[(\mathrm{CuI})_2(\mathrm{bpds})]_\infty$ illustrating the alternative linking of $(\mathrm{Cu_4I_4})$ cubane units compared to its topological isomer **2**.

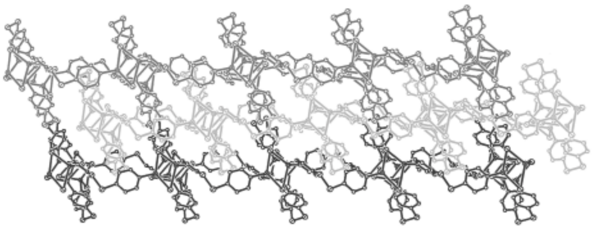

Fig. 3 Interdigitation of adjacent $[(\mathrm{CuI})_2(\mathrm{bpds})]_\infty$ tubes in **3** resulting in the formation of solvent-filled channels.

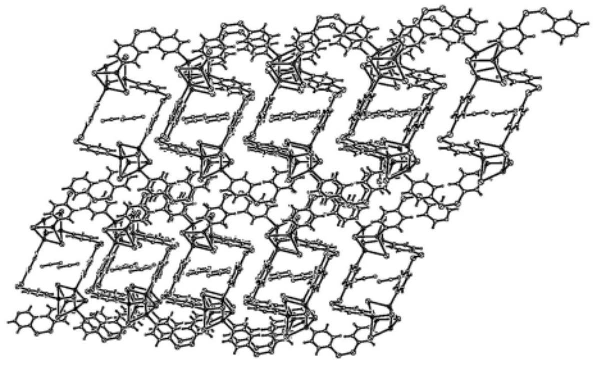

Fig. 4 The solvent-filled channels formed in **3** viewed down the *b*-axis illustrating the positioning of the MeCN solvent molecules.

experiment giving a new diffraction pattern that was not consistent with the single crystal X-ray structure. In contrast, bulk samples of **3** were found to give diffraction patterns in good agreement with that expected from the single crystal studies. No evidence for the presence of the desolvated form of **2** was found in the diffraction pattern of **3** and *vice versa*. Thus, we conclude that the formation of each isomer is exclusively dependent on solvent of crystallisation, and that due to interdigitation **3** is a more robust framework for potential reversible solvent inclusion. Indeed upon heating single crystals of **3** to 100 °C for 10 h *in vacuo* up to 58% of the guest MeCN molecules can be removed as evidenced by single crystal X-ray diffraction experiments. Further details of the desolvation processes of compound **3** will form part of a future study.

As both isomers of $[(\mathrm{CuI})_2(\mathrm{bpds})]_\infty$ form under similar reaction conditions, but with a change in the nitrile solvent, it is reasonable to conclude that there are only minor energy differences in the formation of the two polymers. The two isomers of $[(\mathrm{CuI})_2(\mathrm{bpds})]_\infty$ **2** and **3** are very rare examples of metal–organic architectures which exhibit topological isomerism, and illustrate the profound effect of solvent-template effects in their formation.[5,8] We prefer the description 'topological isomerism' rather than 'polymorphism'[12] in this case to reflect the different coordinative connectivities between **2** and **3** rather than the different crystal packing.

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Notes and references

‡ *Crystal data*: $\{[\mathrm{CuI(bpds)}](\mathrm{MeCN})\}_\infty$ **1a**: $\mathrm{C_{12}H_{11}CuIN_3S_2}$, M = 451.8, triclinic, space group $P\bar{1}$ (no. 2), yellow needles, a = 8.745(2), b = 8.955(4), c = 10.636(3) Å, α = 94.48(4), β = 96.63(3), γ = 106.11(4)°, U = 789.5(5) Å^3, Z = 2, D_c = 1.900 g cm^{-3}, $\mu(\text{Mo-}K\alpha)$ = 3.591 mm^{-1}, T = 150(2) K. 2775 unique reflections [R_int = 0.00] [2415 with $I \geqslant 2\sigma(I)$]. Final R = 0.0400, wR_2(all data) = 0.0982.

$\{[\mathrm{CuI(bpds)}](\mathrm{CH_2Cl_2})\}_\infty$ **1b**: $\mathrm{C_{11}H_{10}Cl_2CuIN_2S_2}$, M = 495.67, triclinic, space group $P\bar{1}$ (no. 2), yellow needles, a = 8.425(2), b = 10.318(2), c = 10.670(2) Å, α = 113.92(3), β = 97.23(3), γ = 92.21(3)°, U = 837.0(3) Å^3, Z = 2, D_c = 1.967 g cm^{-3}, $\mu(\text{Mo-}K\alpha)$ = 3.704 mm^{-1}, T = 193(2) K. 3415 unique reflections [R_int = 0.039] [3255 with $I > 2\sigma(I)$]. Final R = 0.0541, wR_2(all data) = 0.1496.

$\{[(\mathrm{CuI})_2(\mathrm{bpds})]\cdot 0.5\mathrm{EtCN}\}_\infty$ **2**: $\mathrm{C_{11.5}H_{10.5}Cu_2I_2N_{2.5}S_2}$, M = 628.72, orthorhombic, space group $Pccn$ (no. 56), yellow block, a = 19.493(4), b = 10.760(2), c = 17.334(4) Å, U = 3635.7(13) Å^3, Z = 8, D_c = 2.297 g cm^{-3}, $\mu(\text{Mo-}K\alpha)$ = 5.957 mm^{-1}, T = 193(2) K. 3999 unique reflections [R_int = 0.036] [3475 with $I > 2\sigma(I)$]. Final R = 0.0336, wR_2(all data) = 0.0949.

$\{[(\mathrm{CuI})_2(\mathrm{bpds})]\cdot 0.5\mathrm{MeCN}\}_\infty$ **3**: $\mathrm{C_{22}H_{19}Cu_4I_4N_5S_4}$, M = 1243.43, triclinic, space group $P\bar{1}$ (no. 2), yellow column, a = 8.878(1), b = 10.212(1), c = 19.307(2) Å, α = 90.249(2), β = 103.023(2), γ = 92.796(2) °, U = 1703.2(3) Å^3, Z = 2, D_c = 2.419 g cm^{-3}, $\mu(\text{Mo-}K\alpha)$ = 6.356 mm^1, T = 150(2) K. 7690 unique reflections [R_int = 0.024] [6494 with $I \geqslant 2\sigma(I)$]. Final R = 0.0255, wR_2(all data) = 0.0643.

CCDC reference numbers 116866 and 164101–164103. See http://www.rsc.org/suppdata/cc/b1/b103612m/ for crystallographic data in CIF or other electronic format.

§ Considering the centre of the $\mathrm{Cu_4}$ tetrahedron to be the 'centre' of the cubane, junction angles between the nitrogen donors range between 108.0 and 110.7° for **2** and 103.8 and 119.7° for **3**.

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