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Structural isomerism in CuSCN coordination polymers

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CuSCN reacts with the angular ligand 2,4-bis(4-pyridyl)-1,3,5-triazine (dpt) to afford rare examples of coordination polymer structural isomers including a non-centrosymmetric three-dimensional framework with Cd(SO$_4$) topology constructed from tetrahedral metal cations.

The construction of coordination frameworks using transition metal cations and ligands that enforce metal bridging is an extremely topical area of inorganic and materials chemistry. Notable advances have been made in understanding the factors that influence network topology using the building-block methodology originally advanced by Robson *et al.*[1] The simple concept of using transition metal geometries to develop extended arrays is highly adaptable, but framework structures can be readily influenced by weaker supramolecular forces and by the coordinating ability of the anion.[2] Within the general field of coordination frameworks, it is possible for different forms of isomerism to be observed for the overall polymer structure. These include topological isomerism[3] and supramolecular isomerism[4] which are commonly combined with a variation in guest molecules within the crystal lattice. Polymorphism, which can be considered a specific subset of supramolecular isomerism,[4] is particularly rare for coordination polymers.[5] Another form of isomerism that can potentially be observed in coordination frameworks is structural isomerism in which the coordination sphere of the metal cation differs between the two isomers. To our knowledge, such isomerism has only been observed previously in [M(dca)$_2$(pyrazine)]$_\infty$ (dca = dicyanamide)[6] and [Ag(4-cyanopyrdine)$_2$]BF$_4$]$_\infty$[7] frameworks which adopt both 2D and 3D forms. For some time we,[8] amongst others,[9] have been interested in coordination polymers formed by Cu(I) halides or Cu(I) thiocyanate and have been studying the influence of ligand geometry on the CuX (X = halide, SCN$^-$) moiety which is formed. The inherent plasticity of Cu(I) halides and pseudohalides makes these species attractive targets for isolating coordination frameworks which exhibit isomerism, although it should be noted that prior to this study no examples of structural, or indeed, supramolecular isomerism had been identified for such species.

The reaction of CuSCN with dpt in a degassed aqueous NH$_3$/MeOH solvent mixture affords a brown precipitate over the period of an hour in *ca.* 50% yield.† Elemental analysis of this product is consistent with the formulation [Cu(SCN)(dpt)]$_\infty$. Attempts were made to grow single crystals of the product by slow diffusion of dpt in MeOH layered over CuSCN in degassed NH$_3$(aq). This produced crystals with two distinct colours and morphologies; red blocks, **1**, which formed after approximately a day of diffusion and orange laths, **2**, which appeared more slowly, after *ca.* three days. Interestingly, analysis by powder X-ray diffraction of samples produced by the rapid precipitation of [Cu(SCN)(dpt)]$_\infty$ were consistent with the formation of a pure phase of **1**. Powder X-ray diffraction analysis of the product from the longer diffusion experiment confirmed the presence of the two distinct phases, **1** and **2**. Once formed both **1** and **2** appear stable with respect to interconversion in contrast to the [Cu(dca)$_2$(pyrazine)]$_\infty$ frameworks which interconvert *via* a solvent-mediated process.[6]

The single crystal structural determination‡ for compound **1** reveals that it adopts a three-dimensional structure in which each Cu(I) cation exhibits a N$_3$S coordination sphere using two dpt ligands and two SCN$^-$ anions. The (CuSCN)$_\infty$ motif thus formed is a single-stranded chain. These chains are linked *via* bridging bidentate dpt ligands (Fig. 1) and, therefore, both SCN$^-$ anions and dpt ligands generate polymer propagation. The (CuSCN)$_\infty$ chains on opposing ends of any given dpt ligand are orthogonally disposed leading to the 3D framework structure which has a 6^5.8 topology [the Cd(SO$_4$)-type structure] (Fig. 2). Such frameworks have been previously observed for coordination polymers with bridging bipyridyl ligands, but this structural type is more commonly associated with square-planar metal centres.[10] In the case reported here, the near-tetrahedral Cu(I) centre would normally be expected to form a diamondoid (6^6) structure with linear bridges,[11] but the angle subtended at the SCN$^-$ S-donors and the 120° angle formed by

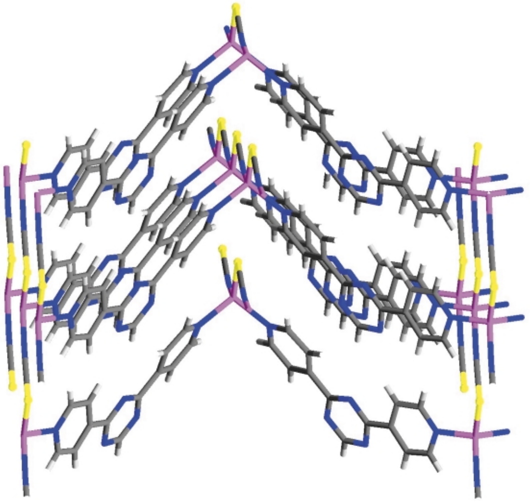

Fig. 1 View of the structure of **1** illustrating the non-centrosymmetric arrangement of the framework (copper, purple; sulfur, yellow; nitrogen, blue).

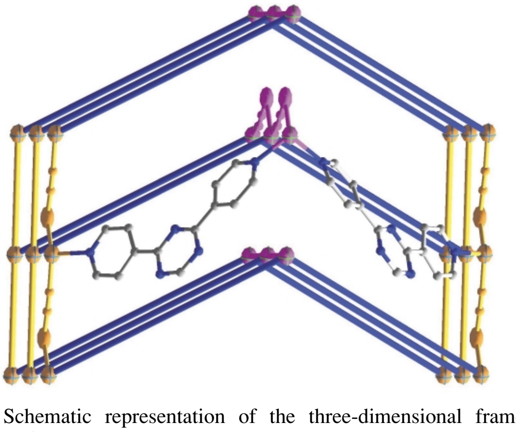

Fig. 2 Schematic representation of the three-dimensional framework formed by **1**, illustrating the Cd(SO$_4$) topology.

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the dpt ligand induce the more unusual $6^5.8$ topology framework. The structure observed is non-centrosymmetric, crystallising in the orthorhombic space group *Ama*2.

Compound **2** was similarly studied by single crystal X-ray diffraction‡ and in this case an entirely different structural arrangement was observed despite the same product stoichiometry. The structure determination of **2** revealed a one-dimensional ribbon polymer constructed from dpt-decorated $(\mathrm{CuSCN})_\infty$ stair polymers (Fig. 3). Each Cu(I) centre sits within a N_2S_2 coordination sphere formed by three SCN^- anions (two S-donors and one N-donor) and a single dpt ligand. In contrast to **1** each dpt ligand is only mono-coordinated, affording no dpt-based polymer propagation. The ribbons are stacked in a parallel fashion such that the $(\mathrm{CuSCN})_\infty$ stair polymer from one ribbon is placed in the pocket below the triazine moiety of a dpt ligand on the next ribbon. Although examples of mono-coordination by a potentially bridging bipyridyl ligand have not been encountered in CuSCN–bipyridyl products,[8,9] such compounds have been encountered from the reaction of dpt with $\mathrm{Cd(NO_3)_2}$.[12]

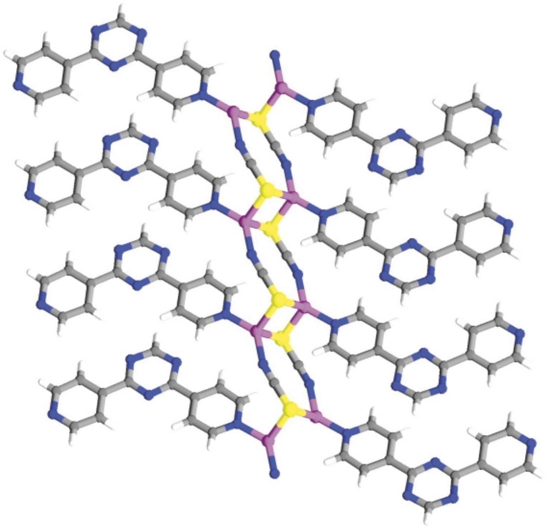

Fig. 3 View of the dpt-decorated one-dimensional ribbons formed by **2** (copper, purple; sulfur, yellow; nitrogen, blue).

The two compounds, **1** and **2**, presented in this study represent structural isomers, an extremely rare observation amongst coordination frameworks. The term structural isomerism is, we believe, a more appropriate term to describe the structures of **1** and **2** than supramolecular isomerism. Supramolecular isomerism as defined by Zaworotko is 'the existence of more than one type of network superstructure for the *same molecular building-blocks*.'[4] Also clearly delineated by Zaworotko are structural supramolecular isomers in which the metal-moiety and the exofunctional organic ligands remain the same but combine to give a different superstructure.[4] The example reported here broadly fits with this definition except that the $(\mathrm{CuSCN})_\infty$ moieties are clearly different between the two structures. Thus, the SCN^- and dpt ligands act differently in **1** and **2**, in a localised topological sense, *i.e.* the dpt is bidentate in **1** and monodentate in **2** and SCN^- acts as a two-connecting unit in **1** but a three-connecting unit in **2**. This contrasts with the previous examples of structural isomerism[6,7] or structures which have previously been described as supramolecular isomers[13] in coordination polymers, where the local connectivity of both the metals and ligands are the same in each isomer.

In conclusion we have demonstrated the formation of structural isomers of a Cu(I)-based coordination polymer, including a rare example of a $6^5.8$ topology framework constructed using tetrahedral Cu(I) metal centres.

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Notes and references

† *Synthesis*: CuSCN (79.4 mg, 0.637 mmol) was dissolved in degassed dilute aqueous NH_3 (30 cm^3) and a solution of dpt (74.9 mg, 0.318 mmol) in MeOH (20 cm^3) was added. A brown solid precipitated over a period of 1 h. Yield 54%. Crystals of suitable quality for single crystal X-ray diffraction experiments were grown by layering a solution of dpt (27.9 mg, 0.119 mmol) in MeOH (5 cm^3) over a solution of CuSCN (28.8 mg, 0.237 mmol) in NH_3(aq) (5 cm^3). Crystals grew over the period of a week.

‡ *Crystal data*: $[\mathrm{Cu(SCN)(dpt)}]_\infty$ **1**: $C_{14}H_9CuN_6S$, M = 356.87, orthorhombic, space group *Ama*2 (no. 40), red blocks, a = 20.649(2), b = 8.9701(9), c = 7.4121(7) Å, U = 1372.9(4) Å^3, Z = 4, D_c = 1.727 g cm^{-3}, μ(Mo-Kα) = 1.747 mm^{-1}, T = 150(2) K. 1746 unique reflections [R_{int} = 0.029] [1489 with $I > 2\sigma(I)$]. Final R = 0.0281, wR_2(all data) = 0.0672. Flack parameter = −0.030(14).

$[\mathrm{Cu(SCN)(dpt)}]_\infty$ **2**: $C_{14}H_9CuN_6S$, M = 356.87, triclinic, space group $P\bar{1}$ (no.2), orange laths, a = 5.6960(4), b = 8.4957(6), c = 14.178(1) Å, α = 83.643(1), β = 82.941(1), γ = 84.974(1), U = 674.80(8) Å^3, Z = 2, D_c = 1.756 g cm^{-3}, μ(Mo-Kα) = 1.777 mm^{-1}, T = 150(2) K. 3080 unique reflections [R_{int} = 0.022] [2686 with $I > 2\sigma(I)$]. Final R = 0.0296, wR_2(all data) = 0.0955.

CCDC reference numbers 184538 and 184539. See http://www.rsc.org/suppdata/cc/b2/b203661d/ for crystallographic data in CIF or other electronic format.

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