Mutual structure-directing effects of a non-interpenetrated square grid coordination polymer and its complementary complex anion net†

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The cationic grid, {[Cu(1,2-bis(4-pyridylethane)$_2$)(H$_2$O)$_2$]$^{2+}$]$_n$, and the complex anion, Cu(4-pySO$_3$)$_4$(H$_2$O)$_2$]$^{2-}$, neither of which have been previously observed, form a perfectly complementary supramolecular pair with respect to charge and H-bonding, to mutually stabilize each others formation.

A fundamental point of interest for a coordination solid is the formation of an open structure and the associated ability to include other molecular species within that structure.[1] Depending on the topology of a network, self-interpenetration can occur to destroy any possible void space which may be found in a framework.[2] A likely structure envisionable with a divalent 6-coordinate center and a linear spacer would be a square grid where the square is defined by the equatorial sites on the metal with counter ions occupying the axial sites.[3] To date, a number of assemblies between Cu^{2+} and 1,2-bis(4-pyridylethane) (L1) have been reported and these assemblies are considerably more complex. With nitrate counter ions, a 2-fold interpenetrated NbO three-dimensional lattice has been reported which retained sufficient void space for guest inclusion.[4] With sulfate ions, two structural motifs have been reported. The first was a complicated structure with a $(6^4,8^2)(6,8^5)$ net topology composed of four-connected nodes linking 2-connected centers.[5] The second was a simpler 1-D chain cross-linked by SO$_4^{2-}$ ions.[6] Surprisingly, the simple square grid structure had not been observed with Cu^{2+} and L1. With *trans*-1,2-bis(4-pyridylethene) and CuSO$_4$, the square grid structure is observed with threads of linear Cu(*trans*-1,2-bis(4-pyridylethene) chains running through.[7]

This work presents {[Cu(1,2-bis(4-pyridylethane)$_2$)(H$_2$O)$_2$][Cu(4-pySO$_3$)$_4$(H$_2$O)$_2$]}, **1**. This complex is interesting for several reasons: (i) the cationic portion of the structure forms a non-interpenetrated square grid solid not observed with Cu^{2+} and simple anions; (ii) the formation of the grid is enabled by charge compensation *via* a complex anion, rare for a coordination solid; (iii) the complex counter anion itself is not isolable but is stabilized by incorporation as part of the ion pair with the grid. This is an unusual example of a mutual host–guest stabilization effect in a coordination framework as neither component exists in the absence of the other.

Cu(NO$_3$)$_2$ was complexed with two equivalents of 4-pyridinesulfonic acid (HL2) in water. Diffusion of THF into this solution gave 82% yield of blue crystalline solid, confirmed as *trans*-[Cu(L2)$_2$(H$_2$O)$_4$] by X-ray crystallography.[8] Complexation of *trans*-[Cu(L2)$_2$(H$_2$O)$_4$] with L1 in water followed by diffusion of THF gave a 45% yield of crystals of {[Cu(L1)$_2$(H$_2$O)$_2$]-[Cu(L2)$_4$(H$_2$O)$_2$]}, **1**.‡ The preparation of **1** is particular in some respects. Combining Cu(NO$_3$)$_2$, L1 and HL2 in a one-pot aqueous preparation does not give **1**. Further, even allowing Cu(NO$_3$)$_2$ and HL2 to stir in water for 4 hours, to potentially form [Cu(L2)$_2$(H$_2$O)$_4$] *in situ*, followed by addition of L1 does not give **1**. That said, if [Cu(L2)$_2$(H$_2$O)$_4$] is isolated as an intermediate solid, **1** can be precipitated rapidly from aqueous solution *via* THF addition as a microcrystalline powder. Use of NaL2 in analogous preparations also does not yield **1**.

The structure of complex **1** is shown in Fig. 1. The cationic component, {[Cu(L1)$_2$(H$_2$O)$_2$]$^{2+}$]$_n$, forms a simple two-dimensional (4,4) grid. The vertices are square pyramidal Cu^{2+} ions with equatorial planes filled by N atoms from four different molecules of L1 (Cu2–N = 2.016(1), 2.019(2) Å). The axial site is filled by a molecule of water (Cu2–O15 = 2.233(1) Å). A molecule of water forms a longer contact with the second axial site (Cu2–O16 = 3.211(1) Å). The geometry of the metal center is slightly distorted from the ideal (∠ N–Cu2–N = 86.9(1) and 92.2(1)°). The grid lies in the *ac* crystallographic plane and contains openings of a minimum size 8.6 × 8.7 Å as defined by the shortest transannular distance factoring van der Waals radii. Adjacent grids are offset by one half an axis length along *a*.

The anionic component of **1** is the complex anion, *trans*-[Cu(L2)$_4$(H$_2$O)$_2$]$^{2-}$. The use of a complex anion for a coordination network is very unusual. In this case, the size of the anion prevents the formation of an interpenetrated grid. The complex has a

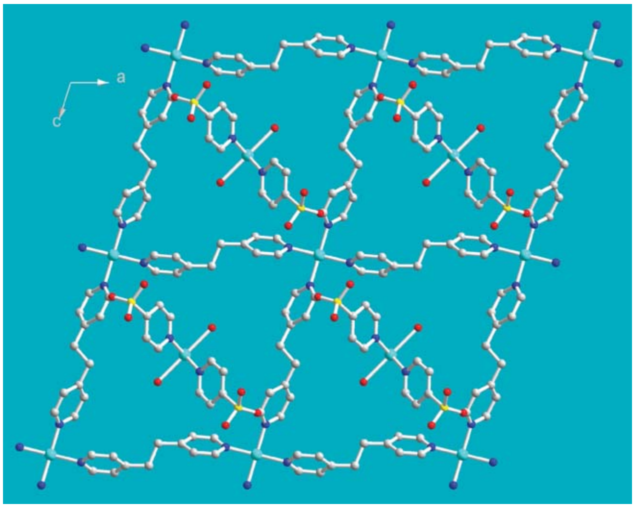

Fig. 1 Single crystal X-ray structure of the grid, {[Cu(bpe)$_2$(H$_2$O)$_2$]$^{2+}$]$_n$}. Each square is occupied by the anion, [Cu(4-pySO$_3$)$_4$(H$_2$O)$_2$]$^{2-}$.

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† Electronic supplementary information (ESI) available: preparation, spectral characterization and PXRD data for **1**. See http://www.rsc.org/suppdata/cc/b4/b417095d/

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Jahn–Teller distorted Cu^{2+} center with four equatorially ligated molecules of L2 (Cu1–N = 2.024(8), 2.037(7) Å) and two axially ligated molecules of water (Cu1–O = 2.43(1) Å). The complex anion orients along the diagonal of each square between the *a* and *c* axes. The grid compresses significantly along this direction to maximize the electrostatic interaction with the complex anion. The two diagonals of each square, as defined by the transannular Cu2–Cu2 distances are 15.52 and 21.15 Å. Somewhat surprisingly, the *trans*-$[Cu(L2)_4(H_2O)_2]^{2-}$ centers are not situated directly in the *ac* plane (Fig. 2). Rather they are displaced to one side by 0.4 Å, the explanation of which is forthcoming. The four L2 appendages of the complex anion do not extend outside of each square. Two of the pyridine rings from L1 form weak edge-to-face interactions with the pyridine groups of the surrounding L2 molecules (C33–C34···C3–C4 = 3.66 Å, C12–C13···C23–C24 = 3.83 Å). This is a relative paucity of aryl–aryl interactions for a system rich in aromatic rings. This is due to the fact that the structure is strongly determined by H-bonding between the grid and complex anions and between anionic complexes themselves.

As mentioned, the Cu centers in the grid each have only one coordinated water molecule all located to the same side in all the layers. As shown in Fig. 2, the two sulfonate groups of the $[Cu(L2)_4(H_2O)_2]^{2-}$ complexes which lay on that side of the grid form strong H-bonds through a single sulfonate oxygen atom (O1···O15 = 2.764(4) Å). In order to efficiently form these interactions, the anionic complexes cannot be situated in the plane of the grid, hence the 0.4 Å displacement mentioned earlier. To the opposite face of the Cu centers in the grid is the additional molecule of water which forms the long contact. This water molecule is also H-bonded to an oxygen atom of the SO_3 groups of the molecules of the complex anion directed out of the grid in this direction (O9···O16 = 2.949(4) Å).

Sulfonate–water H-bonding interactions permeate the solid to define the supramolecular structure.[9] In addition to the H-bonds discussed above, one of the remaining oxygen atoms of each SO_3 group forms a short H-bond contact with a coordinated water molecule of each $[Cu(L2)_4(H_2O)_2]^{2-}$ unit in an adjacent layer (O2···O13 = 2.810(6) Å, O7···O13 = 2.678(7) Å). Conversely, each aquo ligand in the complex anion is H-bonded to four different SO_3 groups each from a different anionic complex. The total H-bonding network is shown in Fig. 3.

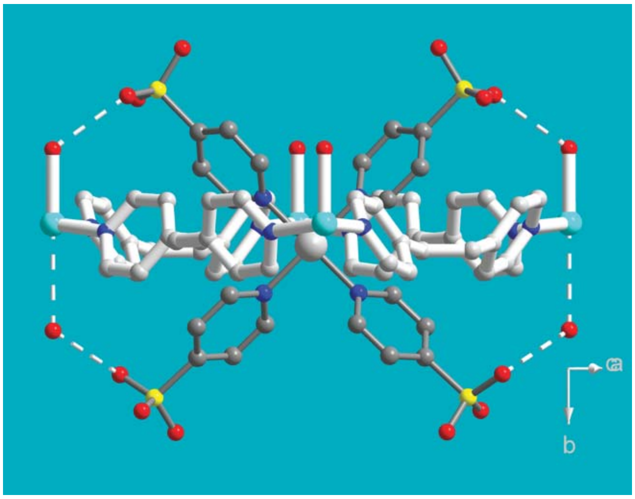

Fig. 2 View in the plane of the grid (thick bonds) showing the H-bonds between the axially interacting water molecules on the grid Cu centers and the SO_3 groups of the anion (dark grey). Note the displacement from the grid plane of the complex anion Cu ion shown as a metallic sphere.

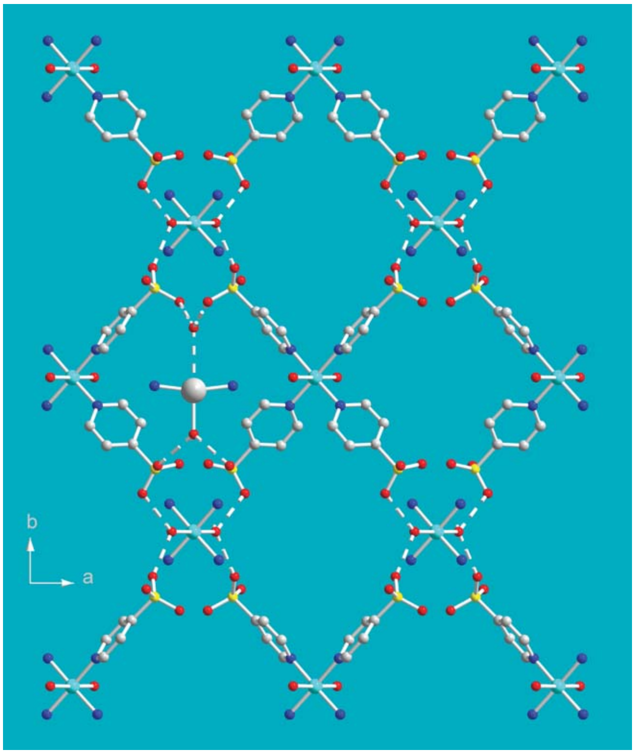

Fig. 3 The H-bond net formed between aquo ligands and sulfonate groups of the anionic $[Cu(L2)_4(H_2O)_2]^{2-}$ units. The cationic grid would lie perpendicular to the page. A single Cu center from the cationic grid (shown as a metallic sphere) and its H-bonding interactions are included.

TGA data showed that **1** loses all water molecules steadily from 113–206 °C and becomes amorphous. However, **1** can be rehydrated without dissolution to reform the nascent solid as confirmed by PXRD. As the CuL1 component itself had not been reported as a square grid, attempts were made to exchange the complex anion for SO_4^{2-}, to yield the non-interpenetrated square grid. These resulted in amorphous solids.

Complex **1** has a number of exceptional features. Foremost is the fact that neither the cationic (the CuL1 grid) nor the anionic component (the CuL2 complex) of this solid have been isolated with other charge compensating partners. The mutual stabilization of this species is due to the perfect spatial and charge complementarity of the cationic square grid and the complex anion (along with its supramolecular H-bonded net). This is a rare example of a supramolecular stabilizing effect where neither partner is isolable in the absence of the other.

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Notes and references

‡ Crystal data for **1**, $\{[Cu(L1)_2(H_2O)_2][Cu(L2)_4(H_2O)_2]\}$: $C_{44}H_{42}Cu_2N_8O_{16}S_4$, *M* = 1194.18, monoclinic, space group

*C*2 (no. 5), a = 13.0227(3), b = 15.7828(5), c = 13.2204(5) Å, $\alpha = \gamma = 90°$, β = 107.465(1)°, V = 2591.99(14) Å^3, Z = 2, D_c = 1.530 Mg m^3, μ(Mo–Kα) = 1.057 mm^{-1}, crystal size 0.25 × 0.25 × 0.20 mm^3. Data were collected on a Nonius Kappa CCD diffractometer using Mo–Kα radiation. A total of 5799 reflections ($1.44° < \theta < 25.35°$) were processed of which 4404 were unique and considered significant with $I_{net} > 2\sigma(I_{net})$. Structure solution, refinement and molecular graphics were carried out with the SHELXS-97 software package, release 5.1.[10] Final residuals for $I_{net} > 2\sigma(I_{net})$ were R = 0.0486 and R_w = 0.1208 (GoF = 0.771) for 338 parameters. Flack parameter = 0.000(5). CCDC 255668. See http://www.rsc.org/suppdata/cc/b4/b417095d/ for crystallographic data in .cif or other electronic format.

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