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Templation of a square grid copper(II) 4,4'-bipyridine network by a 3D PtS-related Cu(I)-Cu(II) 4,4'-bipyridine crystal

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Two cationic networks, $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{bipy})_4(\text{H}_2\text{O})_2]^{3+}$ and $[\text{Cu}^{\text{II}}(4,4'\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$ have been formed from a solution in which Cu(I) undergoes aerial oxidation. Whilst the topologies of the two networks are different the arrangement of Cu centres is almost identical, a structural feature which presumably allows for $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{bipy})_4(\text{H}_2\text{O})_2]^{3+}$ to serve as a crystalline template for $[\text{Cu}^{\text{II}}(4,4'\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$.

The design and synthesis of coordination polymers in the early 1990's focussed on the use of relatively simple bridging anions such as cyanide and neutral bridging ligands such as 4,4'-bipyridine (4,4'bipy).¹⁻¹¹ This early work was important in establishing crystal engineering principles that provided a foundation for the creation of the wide ranging assortment of coordination networks that have been generated in the last 25 years. Early workers in the field, such as the groups of Zaworotko^{4,9,10,12}, Kitagawa^{13,14}, Yaghi^{6,8,15} and Robson^{1,2} used 4,4'bipy in combination with metal ions to create a range of 2D and 3D networks with topologies that are now commonly seen in a variety of coordination networks. Furthermore, the description of coordination polymers as metal-organic frameworks was first used in a paper that described a Cu-4,4'bipy network.⁸ In the investigation of metal-4,4'bipy networks the preference of metal centres for specific coordination geometries permitted an element of design to be introduced in the generation of new materials. The use of relatively long bridging ligands such as 4,4'bipy led to important early examples of the phenomenon of multiple interpenetration in coordination networks.^{2,5,6,8,9,12,17,18} Two significant networks reported in these early days were the diamond network,^{4,5} in which a tetrahedral metal centre was linked to four crystallographically related centres, and a square grid network (a 4,4 net) in which a square planar or octahedral metal centre (with terminal *trans* ligands) binds to four

bridging 4,4'bipy ligands.^{2,4,5,12,16} In this current work we report a pair of crystalline networks that share an almost identical arrangement of Cu centres, a feature that appears to allow one crystal to serve as a template for the growth of a topologically distinct second crystal.

We have recently been interested in exploring Cu(I) complexes derived from aqueous solutions that contain the reducing sulphite anion (SO_3^{2-}).^{17,18} We have found that the tetrahedral $\text{Cu}^{\text{I}}(\text{SO}_3)_4^{7-}$ anion is readily formed by the addition of Cu(II) to a sulphite solution and this solution can be used in the generation of a range of discrete and polymeric species in which the $\text{Cu}^{\text{I}}(\text{SO}_3)_4^{7-}$ anion binds to multiple metal centres. For example, when 2,2'-bipyridine (2,2'bipy) is added to a solution of $\text{Cu}^{\text{I}}(\text{SO}_3)_4^{7-}$, a mixed Cu(I) – Cu(II) pentanuclear complex cation of composition $[\text{Cu}^{\text{I}}(\text{SO}_3)_4(\text{Cu}^{\text{II}}(2,2'\text{bipy})(\text{H}_2\text{O})_4)]^+$ is formed.¹⁸ The Cu(II) ions arise from slow aerial oxidation of Cu(I). The results presented arose out of the extension of such studies to the replacement of 2,2'bipy by 4,4'bipy.

When an ethanolic solution of 4,4'bipy is added to an aqueous solution of $\text{Cu}(\text{SO}_3)_4^{7-}$ (generated by the addition of sodium sulphite and sodium hydrogen sulphite to cupric nitrate in water) a mixture of crystalline products is obtained.† The major product is rod-like crystals with a square cross-section. Quite remarkably, the middle section of these crystalline blocks is orange while the ends of the crystals are blue as indicated in Figure 1. Another photograph is included in the ESI. By cutting the crystal along a direction normal to the long axis of the crystal it is possible to separate the blue and orange components. The orange components of these crystals are tetragonal, $P4/ncc$, $a = 11.4766(3)$ and $c = 30.5554(11)$ Å whilst the blue components (also tetragonal, $P4/ncc$) have a unit cell of approximately half the volume $a = 11.5095(5)$ and $c = 15.4286(7)$ Å. Whilst it was possible to obtain datasets on the orange and blue fragments of the composite crystals, extensive twinning in the crystal fragments led to less than satisfactory structure determinations. Nevertheless, the connectivity of the networks in both the blue and orange crystals was clearly apparent in these crude structure determinations. It was possible to isolate single orange crystals from the same reaction mixture that yielded the composite

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† Electronic Supplementary Information (ESI) available: Supplementary figures showing channel contents, experimental and calculated powder diffraction patterns and crystals photograph. CCDC 1429131 and 1429132. See DOI: 10.1039/x0xx00000x

crystals and the corresponding structure determination indicated that the crystal structure was the same as the orange component of the composite crystals. The structure of the orange crystals, described below, is based upon a structure determination on an isolated single crystal.

The orange crystals have the composition $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{-bipy})_4(\text{H}_2\text{O})_2](\text{S}_2\text{O}_6)(\text{NO}_3)\cdot\text{H}_2\text{O}$ and consist of four interpenetrating, cationic 3D networks in which Cu(II) centres are bound to four Cu(I) centres via bridging 4,4'-bipy ligands; the Cu(I) centres are in turn bound to four Cu(II) centres. Each of the Cu(II) centres has a Jahn-Teller distorted octahedral coordination environment in which two water molecules occupy *trans* sites. Within the network the Cu(II) ions serve as planar 4-connecting centres whereas the Cu(I) ions may be considered as tetrahedral centres (see Fig. 2a). The resulting network has the same topology as platinum sulphide in which square planar Pt(II) cations are linked by tetrahedral sulphide anions within a 3D network. Inspection of the network along a direction normal to the unique axis reveals channels with hexagonal and square cross-sections. When viewed along the direction of the unique tetragonal axis only square channels are apparent (Fig. 2b). Although PtS is a relatively dense structure, the large separation between the two distinct types of Cu centres (11.145 Å) leads to intra-framework voids that are large enough to accommodate three further equivalent networks. The interpenetration of the four cationic networks leads to the formation of square channels parallel to the *c* axis with a cross sectional area one quarter the size of that found in a single network. The channels are occupied by orientationally disordered nitrate and dithionate anions and water molecules. The dithionate dianions, $\text{S}_2\text{O}_6^{2-}$, are formed by oxidation of the sulphite ions whilst the nitrate ions were introduced into the reaction mixture as $\text{Cu}(\text{NO}_3)_2$. Dithionate is known to form from the oxidation of sulphite in the presence of Cu ions.¹⁹

As indicated above, blue crystal fragments from the composite crystals exhibited severe twinning. Nevertheless it was possible to determine the composition of the crystals from a crude structure determination. Based upon the formulation indicated by the crystallographic analysis, the deliberate, direct synthesis of $[\text{Cu}^{\text{II}}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2]\text{S}_2\text{O}_6$ was undertaken and a homogenous blue product with the desired composition was obtained.† A full single crystal structural analysis was performed on a crystal obtained by this procedure. Powder diffraction indicated that the bulk product was identical to the blue crystal that grew on the orange $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{-bipy})_4(\text{H}_2\text{O})_2](\text{S}_2\text{O}_6)(\text{NO}_3)\cdot\text{H}_2\text{O}$ crystals. The blue crystals are of composition $[\text{Cu}^{\text{II}}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2]\text{S}_2\text{O}_6$ and consist of cationic square grid sheets. The structure of a single $[\text{Cu}^{\text{II}}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2]^{2+}$ network is presented in Fig. 3a. The four nitrogen atoms form a square planar arrangement around each of the Cu(II) centres. As with the Cu(II) centres in the aforementioned PtS-related structure a tetragonally distorted octahedral environment is completed by a pair of *trans* water molecules. Each $[\text{Cu}^{\text{II}}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2]^{2+}$ sheet is part of an infinite set of parallel sheets that are interpenetrated by a second set of symmetry-related sheets stacking in a direction

normal to that of the first. Thus every $[\text{Cu}^{\text{II}}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2]^{2+}$ sheet is interpenetrated by an infinite number of $[\text{Cu}^{\text{II}}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2]^{2+}$ sheets. This “infinite interpenetration”²⁰ leads to the generation of square channels that extend in a direction parallel to the *c* axis. A schematic representation of the interpenetration is presented in Fig. 3b. A similar type of interpenetration is apparent in other metal(II)-4,4'-bipy networks.² The square channels are occupied only by dithionate anions that exhibit a similar orientational disorder to that observed in the orange crystals.

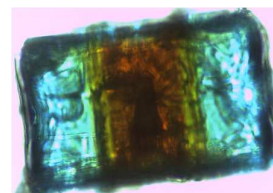


Fig. 1 A microscopic image of composite tetragonal crystals. Orange crystal: $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{-bipy})_4(\text{H}_2\text{O})_2](\text{S}_2\text{O}_6)(\text{NO}_3)\cdot\text{H}_2\text{O}$; blue crystal: $[\text{Cu}^{\text{II}}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2]\text{S}_2\text{O}_6$.

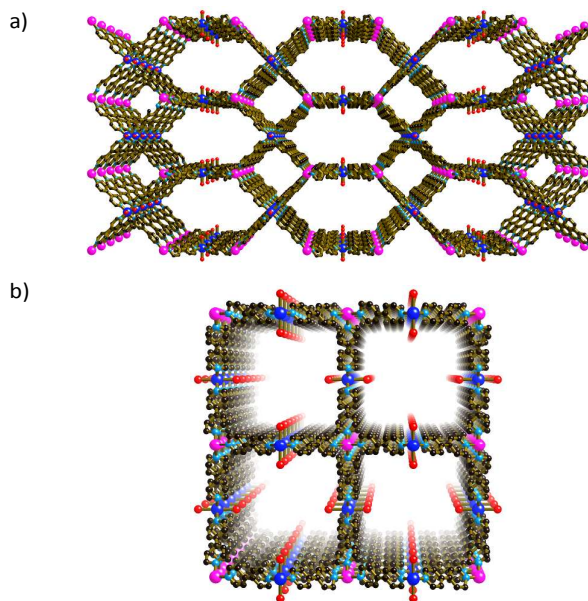


Fig. 2 A single network of the $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{-bipy})_4(\text{H}_2\text{O})_2]^{3+}$ network found in the orange crystals a) viewed along $[1\ 1\ 0]$ and b) viewed along $[0\ 0\ 1]$. Colour code: Cu(I) pink; Cu(II) blue O red; N light blue; C black. H atoms have been omitted for clarity.

As indicated by the structural descriptions presented above, the network connectivity within the orange and the blue crystals is clearly very different, however, the interpenetrating arrangements of the cationic frameworks (four 3D PtS networks in the case of $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{-bipy})_4(\text{H}_2\text{O})_2]^{3+}$ and infinite interpenetration in the case of the square grid, $[\text{Cu}^{\text{II}}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2]^{2+}$ networks) leads to a remarkable similarity when the crystals are viewed along a direction parallel to the *c* axis (Fig 4a and 4b). In each case, a similar arrangement of parallel square channels occupied by counteranions is found. In the case of $[\text{Cu}^{\text{II}}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2]^{2+}$

the dithionate anions appear at regular intervals (every 7.714 Å) along the length of the channels whereas for $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{bipy})_4(\text{H}_2\text{O})_2]^{3+}$ the dithionate anions appear at intervals almost twice as long (15.28 Å). The space between each successive pair of dithionate anions in the Cu(I)-Cu(II) network is occupied by a non-coordinated water molecule and a nitrate anion. A representation of the channel contents in each structure is presented in Figure S1 (see ESI).

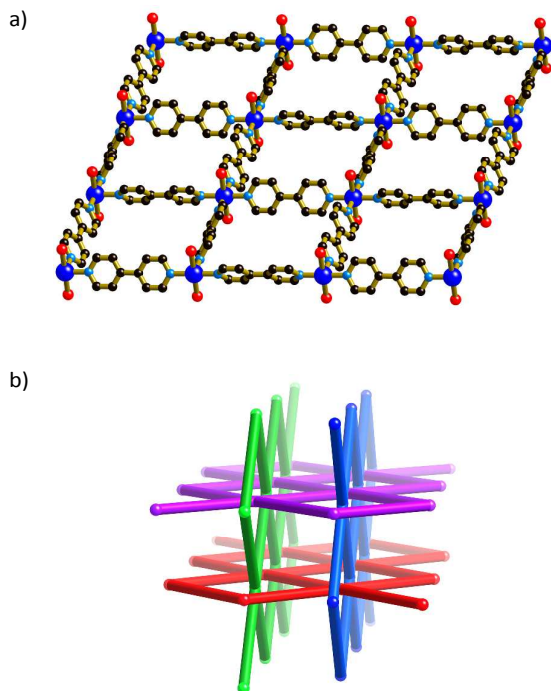


Fig. 3 The structure of $[\text{Cu}^{\text{II}}(4,4'\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$ showing a) a single $[\text{Cu}^{\text{II}}(4,4'\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$ 2D network and b) a schematic representation of the interpenetration; Cu(II) centres and 4,4'bipy ligands are represented by spheres and rods respectively.

The resemblance in the arrangement of the anion-filled channels reflects an underlying similarity in the location of the Cu centres that serve as the 4-connecting nodes in each of the crystals. If only the Cu centres are considered then in each case a primitive tetragonal lattice is formed with dimensions of $a' = 8.139$ ($a/\sqrt{2}$) and $c' = 7.639$ ($c/4$) Å for $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{bipy})_4(\text{H}_2\text{O})_2]^{3+}$ $a' = 8.138$ ($a/\sqrt{2}$) and $c' = 7.714$ ($c/2$) Å for $[\text{Cu}^{\text{II}}(4,4'\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$ (where a' and c' are "unit cell" dimensions of a primitive tetragonal cell defined by the Cu centres only).

Inspection of Fig. 1 reveals that the blue crystal grows on the surface of orange crystals and thus it would appear that when the ratio of Cu(I) to Cu(II) in the solution becomes too low to sustain crystal growth of $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{bipy})_4(\text{H}_2\text{O})_2](\text{S}_2\text{O}_6)(\text{NO}_3)\cdot\text{H}_2\text{O}$ the crystals provide a templating surface for the growth of the blue $[\text{Cu}^{\text{II}}(4,4'\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$ crystals. This phenomenon of templating crystal growth on crystals has been previously reported and used in the preparation of composite materials.²¹

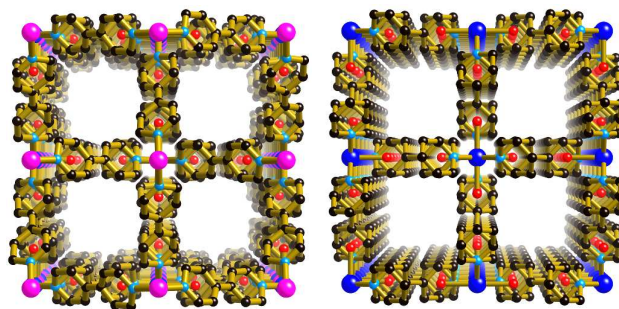


Fig. 4 The interpenetrating arrangements of the cationic a) 3D network, $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{bipy})_4(\text{H}_2\text{O})_2]^{3+}$ and b) 2D network $[\text{Cu}^{\text{II}}(4,4'\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}$, viewed down [001].

The structure of $\text{Cu}^{\text{I}}(4,4'\text{bipy})_2\text{PF}_6$, reported by MacGillivray, Subramanian and Zaworotko,⁴ provides an interesting comparison with the structures described above. As with the other structures the crystals are tetragonal but with space group PA/n . All Cu(I) centres in $\text{Cu}(4,4'\text{bipy})_2\text{PF}_6$ are tetrahedral, bound to the nitrogen atoms of 4,4'bipy ligands that form links to equivalent Cu(I) centres. The crystal structure consists of four interpenetrating $\text{Cu}^{\text{I}}(4,4'\text{bipy})_2$ networks and possesses square channels of remarkably similar dimensions and arrangement to that seen in $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{bipy})_4(\text{H}_2\text{O})_2](\text{S}_2\text{O}_6)(\text{NO}_3)\cdot\text{H}_2\text{O}$ and $[\text{Cu}^{\text{II}}(4,4'\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}\text{S}_2\text{O}_6$. The Cu(I) centres form a primitive tetragonal lattice of dimensions, $a' = 8.715$ Å and $c' = 6.981$ Å, similar to that found for $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{bipy})_4(\text{H}_2\text{O})_2](\text{S}_2\text{O}_6)(\text{NO}_3)\cdot\text{H}_2\text{O}$ and $[\text{Cu}^{\text{II}}(4,4'\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}\text{S}_2\text{O}_6$.

Although each of the three compounds considered, including Zaworotko's diamond net, involves polymeric structures of composition $[\text{Cu}(4,4'\text{bipy})_2]^{n+}$ ($n = 1, 1.5$ or 2 , depending on the oxidation states of the Cu centres) the topologies of the three networks are all very different. When all the Cu centres are Cu(I) the metal centres act as tetrahedral nodes within a diamond network. When there is an equal mix of Cu(I) and Cu(II) a 3D PtS-type network is obtained and when all Cu centres are Cu(II) a 2D square grid network is obtained. Whilst the mode of interpenetration in each of the three examples is also very different the interpenetration has the effect of generating copper ion lattices in each crystal that are remarkably similar. This similarity extends to the formation of square anion-filled channels that run parallel to the c -axes. It is presumably this structural similarity that allows the orange, $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{bipy})_4(\text{H}_2\text{O})_2](\text{S}_2\text{O}_6)(\text{NO}_3)\cdot\text{H}_2\text{O}$ crystals to serve as templates for the growth of the blue $[\text{Cu}^{\text{II}}(4,4'\text{bipy})_2(\text{H}_2\text{O})_2]^{2+}\text{S}_2\text{O}_6$ crystals.

Ms Monica Ivanyi is thanked for her kind assistance with the photographs of the crystals. We gratefully acknowledge the support of the Australian Research Council.

Notes and references

† Synthesis of $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{-bipy})_4(\text{H}_2\text{O})_2](\text{S}_2\text{O}_6)(\text{NO}_3)\cdot\text{H}_2\text{O}$: 4,4'-bipy 14.4 mg, 0.092 mmol) dissolved in 1 mL ethanol was added to a 5 mL aqueous solution of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (5.56 mg, 0.023 mmol) to produce a blue solution. 2 ml solution of an aqueous $\text{NaHSO}_3/\text{Na}_2\text{SO}_3$ (2.4/2.9 mg, 0.023/0.023 mmol). The resulting khaki suspension was left to stand for several weeks. A small number of discrete orange crystals as well as orange-blue crystals were isolated from a clear solution. Orange crystals and blue crystals, manually separated from the mixture of crystalline products were shown to be identical to single crystals that were used in the structure determination (see ESI). Synthesis of $[\text{Cu}^{\text{II}}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2](\text{S}_2\text{O}_6)$: 4,4'-bipy (19.4 mg, 0.124 mmol) dissolved in 2.5 mL of ethanol was added to a solution prepared by mixing a 10 mL aqueous solution of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (15.0 mg, 0.0621 mmol) with a 3 mL aqueous solution of $\text{Na}_2\text{S}_2\text{O}_6\cdot 2\text{H}_2\text{O}$ (15.0 mg, 0.0620 mmol). The mixture was placed in a microwave oven at 100 °C for 6 hours followed by a further 8 hours at 110 °C to yield homogenous small blue needles (14.5 mg, 41%).

‡ Crystal data for $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(4,4'\text{-bipy})_4(\text{H}_2\text{O})_2](\text{S}_2\text{O}_6)(\text{NO}_3)\cdot\text{H}_2\text{O}$ $M = 1027.99$, tetragonal, $a = 11.4766(3)$, $c = 30.5554(11)$ Å, $U = 4024.5(2)$ Å³, $T = 130$ K, space group $P4/ncc$, $Z = 4$, 7510 reflections measured, 1917 unique ($R_{\text{int}} = 0.0252$) which were used in all calculations. Final R values: $wR2 = 0.2237$ (all data), $R1 = 0.0650$ ($I > 2\sigma(I)$). Crystal data for $[\text{Cu}^{\text{II}}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2](\text{S}_2\text{O}_6)$ $M = 535.85$, tetragonal, $a = 11.5095(5)$, $c = 15.4286(7)$ Å, $U = 2043.8(2)$ Å³, $T = 240$ K, space group $P4/ncc$, $Z = 4$, 3647 reflections measured, 1023 unique ($R_{\text{int}} = 0.0284$) which were used in all calculations. Final R values: $wR2 = 0.1660$ (all data), $R1 = 0.0604$ ($I > 2\sigma(I)$). Crystal structures were solved using direct methods and refined using a full matrix least squares procedure based on F^2 within the WinGX program system.²³

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