

Stacked ring-like coordination complex molecules threaded by infinite water tapes



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ABSTRACT

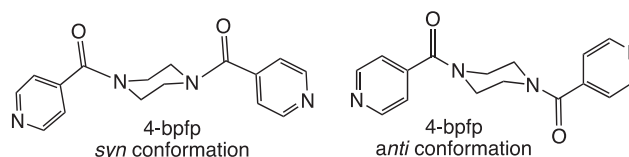
Crystals of $[\text{Cu}_2(\text{mal})_2(\text{bpfp})_2(\text{H}_2\text{O})_2] \cdot 10\text{H}_2\text{O}_n$ (**1**, mal = malonate, bpfp = bis(4-pyridylformyl)piperazine) were prepared by slow diffusion of an ethanolic solution of bpfp into an aqueous solution of copper malonate. Single-crystal X-ray diffraction showed the presence of supramolecular stacks of ring-like $[\text{Cu}_2(\text{mal})_2(\text{bpfp})_2(\text{H}_2\text{O})_2]$ neutral coordination complex molecules threaded by unique infinite water molecule tapes with a T6(6)4(4)4(3)4(3) A(2) classification. These feature six-membered chair conformation rings, four-membered rings, and are decorated by single water molecules. Hydrogen bonding acceptance by the formyl groups of the bpfp ligands proved critical in stabilizing the water molecule tapes within the nanotubular incipient channels.

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Divalent metal cations with dicarboxylate and dipyridyl ligands often form extended phase coordination polymer solids, which are being investigated for their potential applications [1], including gas storage [2], selective separation [3], ion exchange [4], heterogeneous catalysis [5], explosives detection [6], and laser frequency doubling [7]. Additionally, crystalline coordination polymers and coordination complexes can provide cavities and channels efficacious for trapping co-crystallized water molecule aggregations, which can model similar aggregations important in various biochemical pathways [8]. Within these crystals, oxoanion, aqua, amine or carboxylate ligands provide specific hydrogen bonding points of contact, thereby stabilizing numerous possible water molecule aggregations. For example, coordination complexes have been reported to entrap water molecule tetramers [9], hexamers [10], octamers [11,12], decamers [13], helices [14] or pipes [15]. The use of dipyridyl-type ligands with hydrogen-bonding capable functional groups has afforded some novel water molecule aggregations, for instance the infinite C(14) [16] water chain in $[\text{Cu}(\text{SO}_4)(\text{dpmd})_2] \cdot 8\text{H}_2\text{O}$ (dpmd = 4,4'-dipyridylmethanediol) [17] and the *twist-chair-chair* R(8) cyclic water molecule octamer in $[\text{Cu}(\text{bpfp})_2(\text{NO}_3)](\text{NO}_3) \cdot 8\text{H}_2\text{O}_n$ (bpfp = bis(4-pyridylformyl)piperazine, Scheme 1) [12]. In the latter material, the formyl group oxygen atoms of the bpfp ligands play a critical role in stabilizing the water octamer formation via hydrogen-bonding acceptance. In the present work, we report the synthesis, crystal structure, and dehydration properties of $[\text{Cu}_2(\text{mal})_2(\text{bpfp})_2(\text{H}_2\text{O})_2] \cdot 10\text{H}_2\text{O}_n$ (**1**, mal = malonate), which manifests ring-like coordination complex neutral molecules that entrap a unique water molecule tape morphology.

Blue crystals of **1** were prepared in moderate yield [18] by the slow diffusion of an ethanolic solution of bpfp into an aqueous solution of copper malonate, over the course of a 14 day period. Bands at 1618 cm^{-1} and 1420 cm^{-1} in the infrared spectrum of **1** (Fig. S1) denote the presence of ligated, deprotonated malonate carboxylate groups. The formyl groups of the bpfp ligands are indicated by a strong C=O stretching band at 1638 cm^{-1} . The broad spectral band with a maximum absorption at 3400 cm^{-1} is indicative of the aqua ligands and the water molecules of crystallization.

Single crystal X-ray diffraction [19] revealed that **1** crystallizes in the centrosymmetric monoclinic space group $C2/c$ with an asymmetric unit containing a divalent copper atom, one completely deprotonated mal ligand, a bpfp ligand in a curled *syn* conformation, an aqua ligand, and five water molecules of crystallization. Operation of the crystallographic two-fold rotation axis produces a complete $[\text{Cu}_2(\text{mal})_2(\text{bpfp})_2(\text{H}_2\text{O})_2]$ molecule (Fig. 1), featuring a 32-membered cycle around its center constructed from two *syn* conformation (Scheme 1) bpfp ligands. The presence of the *syn* conformation is averred by the O–C–O torsion angle of 6.9° ; the central piperazinyl rings of the bpfp ligands adopt the usual chair conformation. The Cu–Cu through-space distance across the cycle measures 13.253 \AA .



Scheme 1. Conformations of bpfp.

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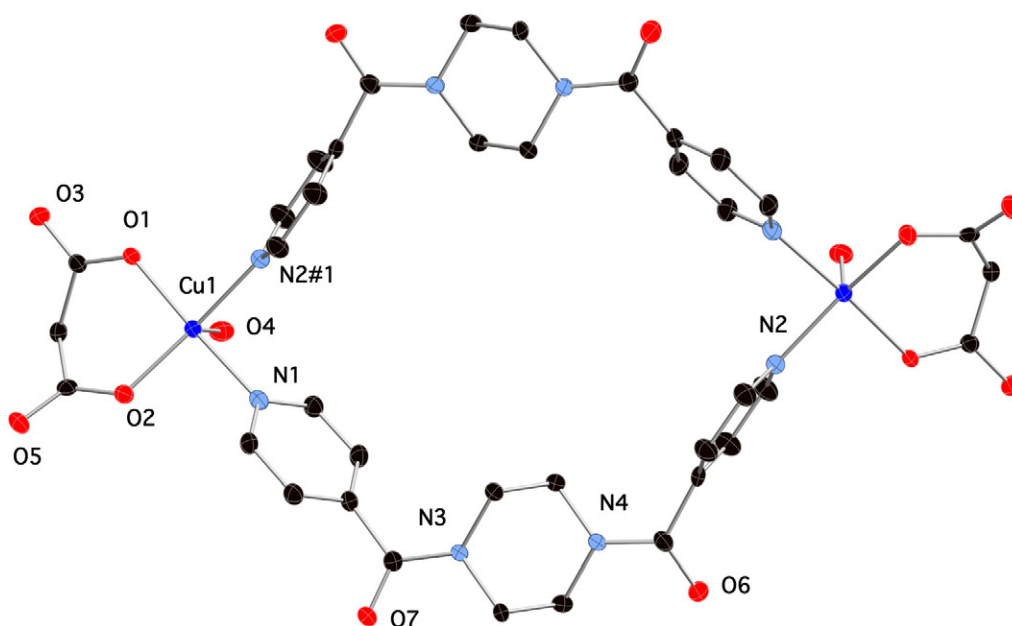


Fig. 1. A complete $[\text{Cu}_2(\text{mal})_2(\text{bpfp})_2(\text{H}_2\text{O})_2]$ molecule, featuring a ring motif measuring ~ 13 Å across.

Table 1

Selected bond distance (Å) and angle ($^\circ$) data for 1.

Cu1 – N1	2.005(2)	O2 – Cu1 – N2 ^{#1}	163.60(10)
Cu1 – N2 ^{#1}	2.018(2)	O1 – Cu1 – N2 ^{#1}	86.68(8)
Cu1 – O1	1.9530(18)	N1 – Cu1 – N2 ^{#1}	90.30(9)
Cu1 – O2	1.9207(19)	O2 – Cu1 – O4	101.97(8)
Cu1 – O4	2.316(2)	O1 – Cu1 – O4	89.73(8)
O1 – Cu1 – N1	176.72(9)	N1 – Cu1 – O4	91.79(9)
O2 – Cu1 – O1	93.75(8)	N2 ^{#1} – Cu1 – O4	94.42(9)
O2 – Cu1 – N1	88.78(9)		

Transformation for symmetry equivalent position: #1: $-x + 2, y, -z + 3/2$.

The symmetry related copper atoms display a distorted $\{\text{CuN}_2\text{O}_3\}$ square pyramidal coordination geometry, with an Addison τ factor [20] of 0.22. Pyridyl nitrogen donor atoms from two bpfp molecules are located in *cis* basal positions, as are two oxygen donors from the

1,3-chelating mal ligand. The aqua ligand is located in the Jahn–Teller elongated axial coordination site. Bond lengths and angles within the coordination environment are listed in Table 1.

Neighboring $[\text{Cu}_2(\text{mal})_2(\text{bpfp})_2(\text{H}_2\text{O})_2]$ molecules interact in a ‘head to tail’ fashion by means of hydrogen bonding donation from the aqua ligands to unligated malonate carboxylate oxygen atoms ($\text{O} \cdots \text{H} \cdots \text{O}$ distance = 2.679(3) Å), and also to bpfp formyl oxygen atoms ($\text{O} \cdots \text{H} \cdots \text{O}$ distance = 2.808(3) Å). These two supramolecular interactions cause the $[\text{Cu}_2(\text{mal})_2(\text{bpfp})_2(\text{H}_2\text{O})_2]$ molecules to align along the *b* crystal direction, where the $[\text{Cu}(\text{mal})(\text{H}_2\text{O})]$ fragments pack together quite closely (Fig. 2). In turn the 32-membered ring $[\text{Cu}_2(\text{bpfp})_2]$ moieties of next-nearest neighbor $[\text{Cu}_2(\text{mal})_2(\text{bpfp})_2(\text{H}_2\text{O})_2]$ molecules also align parallel to the *b* crystal direction (Fig. 3), forming incipient nanotubular channels that contain all of the water molecules of crystallization, with the solvent accessible volume occupying 22.8% of the unit cell volume

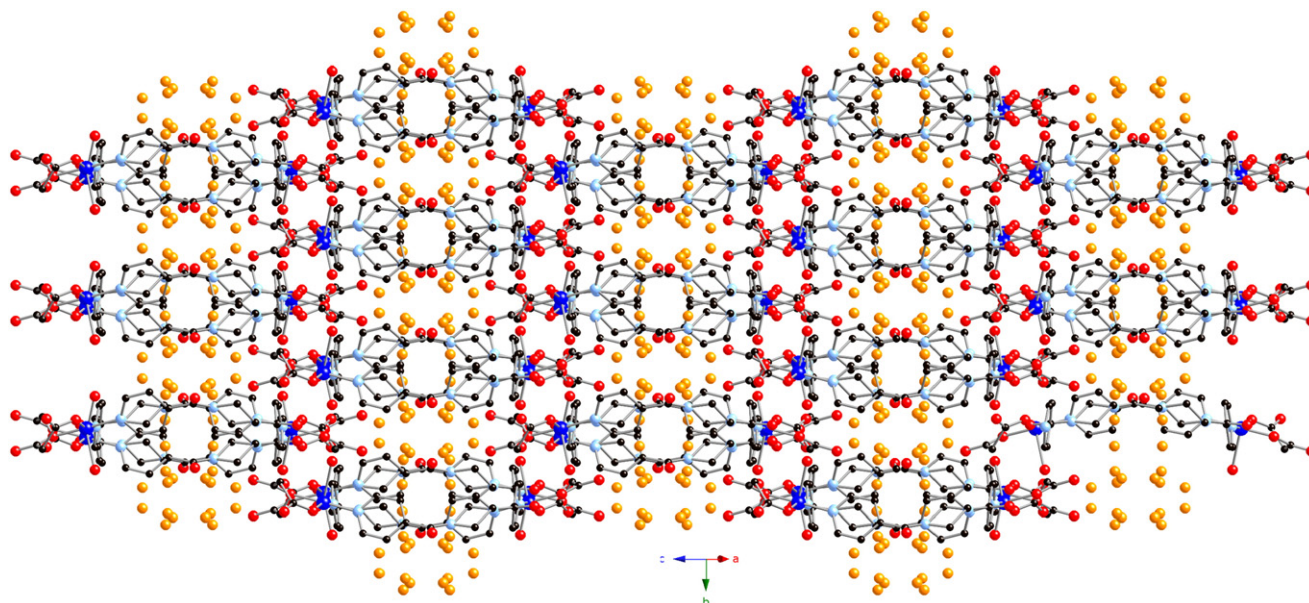


Fig. 2. Stacking of $[\text{Cu}_2(\text{mal})_2(\text{bpfp})_2(\text{H}_2\text{O})_2]$ molecules via hydrogen bonding. The water molecules of crystallization are indicated as orange spheres in the online version of this article.

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