

Poly[diacquabis(μ -4,4'-bipyridine- κ^2 N:N')bis(ethane-1,2-diol)di- μ -sulfato-dicopper(II)]

Kai-Long Zhong,* Li Chen and Lin Chen

 Department of Applied Chemistry, Nanjing College of Chemical Technology,
Nanjing 210048, People's Republic of China

Correspondence e-mail: zklong@tom.com

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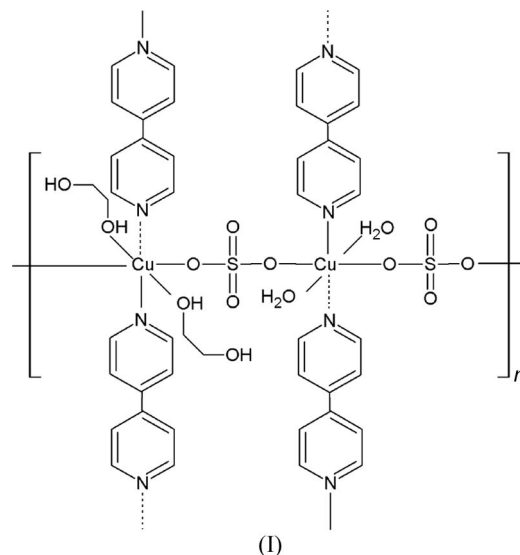
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The title compound, $[\text{Cu}_2(\text{SO}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{C}_2\text{H}_6\text{O}_2)_2(\text{H}_2\text{O})_2]_n$, contains two crystallographically unique Cu^{II} centres, each lying on a twofold axis and having a slightly distorted octahedral environment. One Cu^{II} centre is coordinated by two bridging 4,4'-bipyridine (4,4'-bipy) ligands, two sulfate anions and two aqua ligands. The second is surrounded by two 4,4'-bipy N atoms and four O atoms, two from bridging sulfate anions and two from ethane-1,2-diol ligands. The sulfate anion bridges adjacent Cu^{II} centres, leading to the formation of linear $\cdots\text{Cu1}-\text{Cu2}-\text{Cu1}-\text{Cu2}\cdots$ chains. Adjacent chains are further bridged by 4,4'-bipy ligands, which are also located on the twofold axis, resulting in a two-dimensional layered polymer. In the crystal structure, extensive $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions between water molecules, ethane-1,2-diol molecules and sulfate anions lead to the formation of a three-dimensional supramolecular network structure.

Comment

The self-assembly of coordination polymers and the crystal engineering of metal-organic coordination frameworks have recently received much attention because of their interesting molecular topologies and potential applications as functional materials (Batten & Robson, 1998; Eddaoudi *et al.*, 2001; Li *et al.*, 2003; Dietzel *et al.*, 2005; Liu *et al.*, 2007; Zhang *et al.*, 2010). It is still challenging to construct metal-organic coordination frameworks of mixed ligands with metal salts in crystal engineering. 4,4'-Bipyridine (4,4'-bipy) has been used as a bridging ligand, owing to its rod-like rigidity and length, and has been widely applied in constructing interesting coordination polymers (Tong *et al.*, 1998; Lu *et al.*, 1998; Kondo *et al.*, 1999; Greve *et al.*, 2003; Lah & Leban, 2006; Díaz de Vivar *et al.*, 2007; Bo *et al.*, 2008; Li *et al.*, 2009; Xu *et al.*, 2010; Wang *et al.*, 2010; Guo *et al.*, 2010). It is well known that hydrothermal (solvothermal) synthesis is an effective method for the construction of new metal-organic coordination polymers because it can provide ideal conditions for crystal growth,

owing to the enhanced transport ability of solvents in superheated systems. We have focused on the synthesis of complexes with 4,4'-bipy as an auxiliary ligand, while retaining some of the solvent molecules capable of hydrogen bonding to form higher-dimensional supramolecular networks. The title compound, (I), a new three-dimensional supramolecular network with two-dimensional layers, was obtained *via* a solvothermal reaction.



Part of the layer structure of (I) is shown in Fig. 1. There are two types of crystallographically independent Cu^{II} centres, both on twofold axes with a slightly distorted octahedral CuN_2O_4 environment. Atom Cu1 is coordinated by two N atoms (N3 and N4) from bridging 4,4'-bipy ligands occupying the axial positions, two O atoms (O2) from two bridging sulfate anions and two O atoms from water molecules (O1W) occupying the equatorial sites (Table 1). Atoms Cu1, O2, O2', O1W and O1W' [symmetry code: (i) $-x, y, -z + \frac{3}{2}$] are almost coplanar, the mean deviation from the plane being 0.042 Å. The *cis* bond angles around each Cu1 centre are in the range 87.37 (5)–92.63 (5)° (Table 1). The coordination environment

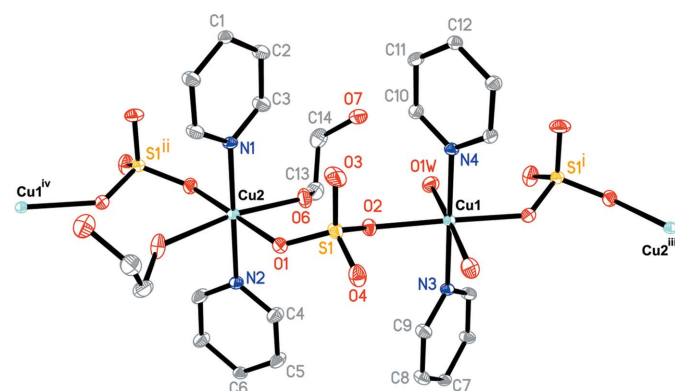
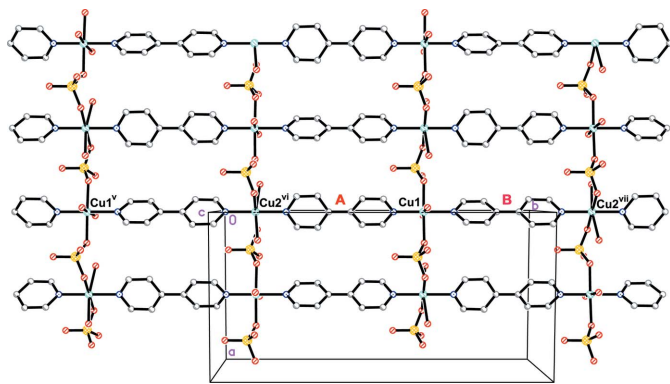
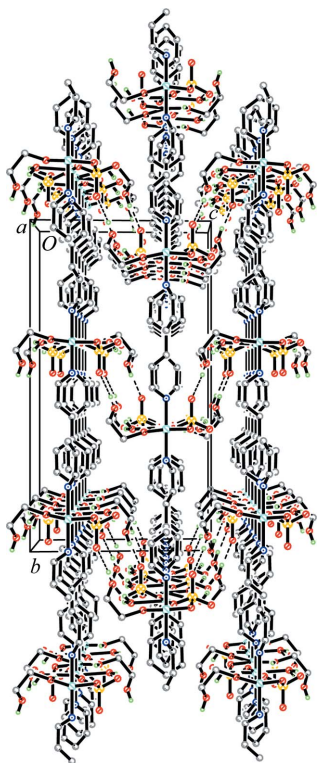


Figure 1
Part of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, y, -z + \frac{3}{2}$; (ii) $-x + 1, y, -z + \frac{3}{2}$; (iii) $x - 1, y, z$; (iv) $x + 1, y, z$.]


Figure 2

The crystal structure of (I), viewed along the *c* axis. The C and uncoordinated O atoms of the ethane-1,2-diol ligands and H atoms have been omitted for clarity. [Symmetry codes: (v) $x, y - 1, z$; (vi) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (vii) $x - \frac{1}{2}, y + \frac{1}{2}, z$.]


Figure 3

Hydrogen-bonding interactions between adjacent layers of (I), viewed along the *a* axis. Hydrogen bonds are represented by dashed lines and H atoms not involved in hydrogen bonds have been omitted for clarity.

of each Cu2 centre is very similar to that of Cu1, with ethane-1,2-diol ligands replacing the water ligands. The *cis* bond angles around Cu2 lie in the range 84.67 (6)–95.33 (6) $^\circ$ (Table 1).

The sulfate anion acts as an O–S–O bridging link between two different Cu^{II} cations, giving rise to the formation of linear $\cdots\text{Cu1-O-SO}_2\text{-O-Cu2-O-SO}_2\text{-O}\cdots$ chains running parallel to the *a* axis; the Cu1 \cdots Cu2 and Cu1 \cdots Cu1^{iv} [symmetry code: (iv) $x + 1, y, z$] distances are 5.5300 (10) and 11.060 (2) Å, respectively (Fig. 1). The dihedral angles between the two half-bipy rings coordinated to Cu1 and Cu2 are 82.23 (9) and

74.34 (10) $^\circ$, respectively. The Cu1 and Cu2 centres of adjacent $\cdots\text{Cu1-O-SO}_2\text{-O-Cu2-O-SO}_2\text{-O}\cdots$ chains are further cross-linked by the bridging 4,4'-bipy ligands, leading to the formation of linear $\cdots\text{Cu1-bipy-Cu2-bipy}\cdots$ chains along the *b* axis, in which the Cu1 \cdots Cu2^{vii} and Cu1 \cdots Cu2^{vi} [symmetry codes: (vi) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (vii) $x - \frac{1}{2}, y + \frac{1}{2}, z$] separations are 11.093 (2) and 11.127 (2) Å, respectively (Fig. 2). Each bridging 4,4'-bipy ligand lies on a twofold axis, with dihedral angles between the two pyridine rings within each independent 4,4'-bipy ligand of 7.97 (9) (4,4'-bipy A) and 15.46 (10) $^\circ$ (4,4'-bipy B) (Fig. 2). The $\cdots\text{M-O-SO}_2\text{-O-M}\cdots$ and $\cdots\text{M-bipy-M}\cdots$ chains are almost orthogonal, leading to a layered structure (Fig. 2). Intermolecular O1W–H5C \cdots O7 and O6–H6 \cdots O2 hydrogen bonds help to further stabilize the layered structure (Table 2).

In the crystal structure of (I), the two-dimensional polymeric layers are linked by classical hydrogen bonding, namely O–H \cdots O interactions involving the water molecules, sulfate anions and ethane-1,2-diol molecules, resulting in a three-dimensional supramolecular network (Table 2 and Fig. 3).

Experimental

4,4'-Bipyridine (0.2 mmol), CuSO₄·5H₂O (0.1 mmol), ethane-1,2-diol (2.0 ml) and water (1.0 ml) were mixed and placed in a thick Pyrex tube, which was sealed and heated to 383 K for 72 h. After this time, the tube was allowed to cool to room temperature and blue prisms of (I) were obtained. Analysis found: C 36.41, H 4.05, N 7.08%; calculated for C₂₄H₃₂Cu₂N₄O₁₄S₂: C 36.32, H 3.93, N 6.74%.

Crystal data

[Cu ₂ (SO ₄) ₂ (C ₁₀ H ₈ N ₂) ₂ (C ₂ H ₆ O ₂) ₂ ·(H ₂ O) ₂]	$\beta = 95.87$ (3) $^\circ$
$M_r = 791.74$	$V = 2984.5$ (10) Å ³
Monoclinic, <i>C2/c</i>	$Z = 4$
$a = 11.060$ (2) Å	Mo $K\alpha$ radiation
$b = 22.220$ (4) Å	$\mu = 1.64$ mm ⁻¹
$c = 12.208$ (2) Å	$T = 223$ K
	$0.65 \times 0.20 \times 0.18$ mm

Data collection

Rigaku Mercury CCD area-detector diffractometer	8511 measured reflections
Absorption correction: multi-scan (REQAB; Jacobson, 1998)	3390 independent reflections
$T_{\min} = 0.823, T_{\max} = 1.000$	2730 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.094$	
$S = 1.10$	$\Delta\rho_{\max} = 0.52$ e Å ⁻³
3390 reflections	$\Delta\rho_{\min} = -0.40$ e Å ⁻³
225 parameters	

The aromatic and methylene H atoms were positioned geometrically and allowed to ride on their parent atoms, with C–H = 0.93 and 0.97 Å, respectively, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The hydroxy and water H atoms were located in a difference Fourier map and their positions were refined freely, but with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine

Table 1

Selected geometric parameters (Å, °).

Cu1—N3	2.016 (3)	Cu2—O1	2.095 (2)
Cu1—N4	1.986 (3)	Cu2—O6	2.242 (2)
Cu1—O1W	2.324 (2)	S1—O1	1.4805 (19)
Cu1—O2	2.0637 (18)	S1—O2	1.5085 (19)
Cu2—N1	2.007 (3)	S1—O3	1.4544 (19)
Cu2—N2	2.019 (3)	S1—O4	1.461 (2)
N3—Cu1—N4	180	N1—Cu2—N2	180
N3—Cu1—O1W	87.37 (5)	N1—Cu2—O1	90.22 (4)
N3—Cu1—O2	89.26 (4)	N1—Cu2—O6	95.33 (6)
N4—Cu1—O1W	92.63 (5)	N2—Cu2—O1	89.78 (4)
N4—Cu1—O2	90.74 (4)	N2—Cu2—O6	84.67 (6)
O1W ⁱ —Cu1—O1W	174.75 (10)	O1—Cu2—O1 ⁱⁱ	179.55 (9)
O1W—Cu1—O2	89.91 (8)	O1—Cu2—O6	89.53 (8)
O2 ⁱ —Cu1—O2	178.53 (9)	O6 ⁱⁱ —Cu2—O6	169.34 (12)

 Symmetry codes: (i) $-x, y, -z + \frac{3}{2}$; (ii) $-x + 1, y, -z + \frac{3}{2}$.

structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3145). Services for accessing these data are described at the back of the journal.

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Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H5B ⁱ ···O4 ⁱ	0.84 (4)	1.94 (4)	2.741 (3)	159 (3)
O7—H7A ⁱ ···O3 ⁱⁱⁱ	0.80 (4)	1.92 (4)	2.693 (3)	164 (4)
O1W—H5C ⁱ ···O7	0.83 (3)	1.91 (4)	2.726 (3)	170 (3)
O6—H6 ⁱ ···O2	0.78 (4)	1.99 (4)	2.668 (3)	145 (4)

 Symmetry codes: (i) $-x, y, -z + \frac{3}{2}$; (iii) $x, -y + 1, z - \frac{1}{2}$.

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