

Di- μ -sulfato-bis[aqua(dipyridophenazine)-copper(II)] dihydrate

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The title compound, $[\text{Cu}_2(\text{SO}_4)_2(\text{C}_{18}\text{H}_{10}\text{N}_4)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, has a discrete binuclear structure lying on a centre of symmetry. The Cu atom shows a square-pyramidal coordination geometry. There exist π - π stacking interactions and hydrogen bonds between the complex molecules.

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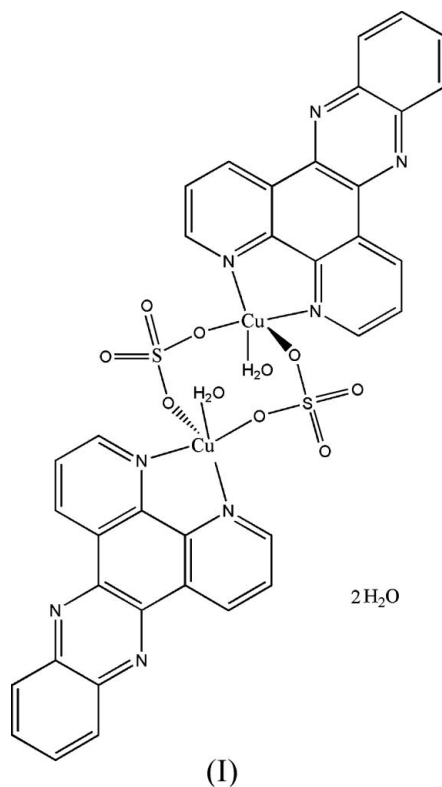
Key indicators

Single-crystal X-ray study
 $T = 293 \text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
 R factor = 0.039
 wR factor = 0.117
 Data-to-parameter ratio = 12.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

Dipyridophenazine derivatives are usually used as molecular light switches for DNA (Hartshorn & Barton, 1992) and for the study of fast electron transfer through DNA (Murphy *et al.*, 1993). A ruthenium(II) complex with dipyridophenazine has been found to be a good cleavage agent with high affinity for DNA (Gupta *et al.*, 1992). In our previous work, we reported a binuclear copper(II) complex of dipyridophenazine bridged by two Cl atoms (Han, 2006). We report here a new binuclear copper(II) complex, (I), of dipyridophenazine bridged by two sulfate groups.



Complex (I) has a discrete binuclear structure lying on a centre of symmetry. The asymmetric unit consists of one dipyridophenazine ligand, one sulfate ion, one coordinated aqua ligand, one Cu atom and one uncoordinated water

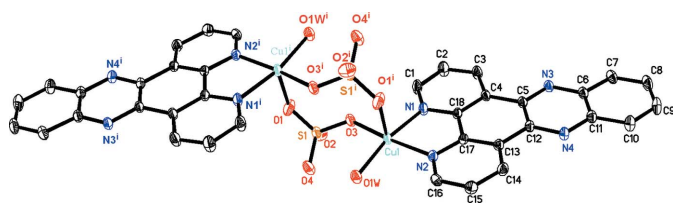


Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms and the uncoordinated water molecules have been omitted for clarity. [Symmetry code: (i) $1 - x, -y, 1 - z$.]

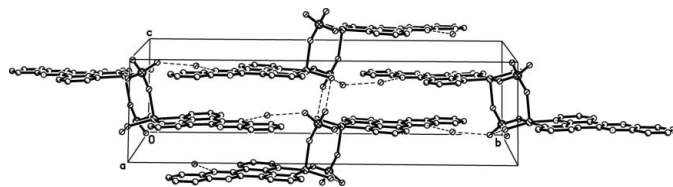


Figure 2

Crystal packing in (I), showing π - π stacking interactions and hydrogen bonds (dashed lines).

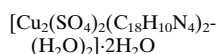
molecule (Table 1 and Fig. 1). Two μ -sulfato groups bridge two Cu atoms to form a binuclear complex unit.

The planar dipyridophenazine ligands from adjacent binuclear units at (x, y, z) and $(x, -y + \frac{1}{2}, z - \frac{1}{2})$ furnish strong π - π stacking interactions, with an average plane-to-plane separation of 3.36 Å (Zheng *et al.*, 2001). In addition, there are intra- and intermolecular hydrogen bonds involving the water molecules, the O atoms of sulfates and the N atoms of dipyridophenazine ligands (Table 2). The π - π interactions and hydrogen bonds stabilize the complex and link the binuclear units to form a supramolecular framework (Fig. 2).

Experimental

A mixture of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.5 mmol, 0.125 g), dipyridophenazine (0.5 mmol, 0.141 g) and water (10 ml) was sealed in a 23 ml Teflon-lined reactor, which was heated at 453 K for 6 d and then cooled to room temperature at a rate of 5 K h^{-1} (yield 42%). Analysis, calculated for $\text{C}_{36}\text{H}_{28}\text{Cu}_2\text{N}_8\text{O}_{12}\text{S}_2$: C 45.23, H 2.95, N 11.72%; found: C 45.58, H 2.86, N 11.83%.

Crystal data



$M_r = 955.86$

Monoclinic, $P2_1/c$

$a = 9.6401$ (9) Å

$b = 26.670$ (3) Å

$c = 7.0304$ (7) Å

$\beta = 105.145$ (2)°

$V = 1744.8$ (3) Å³

$Z = 2$

$D_x = 1.819$ Mg m^{-3}

Mo $K\alpha$ radiation

$\mu = 1.42$ mm^{-1}

$T = 293$ (2) K

Block, green

$0.47 \times 0.32 \times 0.12$ mm

Data collection

Bruker SMART APEX area-

detector diffractometer

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.558$, $T_{\max} = 0.845$

8062 measured reflections

3391 independent reflections

3041 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\text{max}} = 26.0^\circ$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.118$

$S = 1.04$

3391 reflections

283 parameters

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.072P)^2 + 1.1351P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\text{max}} < 0.001$$

$$\Delta\rho_{\text{max}} = 0.53 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.43 \text{ e } \text{Å}^{-3}$$

Table 1

Selected geometric parameters (Å, °).

Cu1—O3	1.949 (2)	Cu1—N2	2.021 (2)
Cu1—O1W	1.963 (2)	Cu1—O1 ⁱ	2.218 (3)
Cu1—N1	2.014 (2)		
O3—Cu1—O1W	94.22 (9)	N1—Cu1—N2	81.26 (9)
O3—Cu1—N1	90.09 (10)	O3—Cu1—O1 ⁱ	98.98 (10)
O1W—Cu1—N1	167.94 (10)	O1W—Cu1—O1 ⁱ	92.55 (10)
O3—Cu1—N2	170.56 (10)	N1—Cu1—O1 ⁱ	97.90 (11)
O1W—Cu1—N2	93.53 (9)	N2—Cu1—O1 ⁱ	86.03 (9)

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H1WA \cdots O2 ⁱⁱ	0.864 (18)	1.745 (19)	2.608 (3)	177 (4)
O1W—H1WB \cdots O4	0.859 (18)	1.81 (2)	2.649 (3)	164 (4)
O2W—H2WA \cdots N3	0.85 (2)	2.28 (3)	3.098 (4)	160 (7)
O2W—H2WB \cdots O4 ⁱⁱⁱ	0.85 (2)	1.97 (3)	2.806 (4)	168 (7)

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

H atoms of the aromatic rings were positioned geometrically and refined as riding, with $C-H = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms of water molecules were located in difference Fourier maps and refined with a single isotropic displacement parameter for each water molecule [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$], with distance restraints of $O-H = 0.85$ (1) Å and $H \cdots H = 1.39$ (1) Å.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2001); software used to prepare material for publication: SHELXTL.

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