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Key indicators

Single-crystal X-ray study
 T = 298 K
 Mean $\sigma(C-C)$ = 0.010 Å
 H-atom completeness 67%
 Disorder in solvent or counterion
 R factor = 0.066
 wR factor = 0.221
 Data-to-parameter ratio = 12.6

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

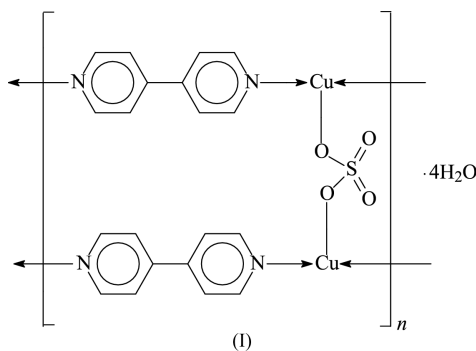
catena-Poly[[[μ -sulfato-dicopper(I)]-di- μ -4,4'-bipyridine-1:1' κ^2 N,N';2:2' κ^2 N,N'] tetrahydrate]

In the crystal structure of the yellow copper(I) compound, $\{[Cu_2(SO_4)(C_{10}H_8N_2)_2] \cdot 4H_2O\}_n$, one $[(C_{10}H_8N_2)_2Cu]_n$ chain is stacked over another $[Cu \cdots Cu = 3.180(1) \text{ \AA}]$; the two chains are bridged by SO_4 groups through two Cu—O bonds into a double-chain motif. The SO_4 groups are located alternately on opposite sides of the double chain and lie on twofold rotation axes. The disordered solvent water molecules occupy the space between the double chains. The Cu^I atom exists in a T-shaped environment.

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Comment

The reaction of copper(II) sulfate and the spacer heterocycle 4,4'-bipyridine affords a compound in which adjacent Cu atoms are linked to four of these ligands in a rhombic grid; water occupies the cavities within the grid. The compound $[(C_{10}H_8N_2)(SO_4)(H_2O)_3Cu] \cdot 2H_2O$ exists in a monoclinic (Tong & Chen, 2000) and a hexagonal (Hagman *et al.*, 1998; Cheng & Hu, 2003) modification. The chemistry of some metal complexes of 4,4'-bipyridine has been reviewed (Abu-Shandi *et al.*, 2001), but the review did not mention copper(I) complexes, such as, for example, the $[W_{12}O_{36}PO_4]^{3-}$ derivative (Inman *et al.*, 2002). The copper(I) chloride and bromide complexes are synthesized indirectly from the copper(II) salts, under hydrothermal conditions (Lu *et al.*, 1999). At high temperatures, 4,4'-bipyridine probably assists in the reduction of Cu^{II} to Cu^I ; this heterocycle and alcohols function in this manner in the formation of the mixed-valence complex $Cu^I Cu^II_2$ -malate/sulfate (Lah *et al.*, 2002). Our own studies have also confirmed the role of amines and alcohols (Zhang *et al.*, 2002, 2004; Zhang & Chen, 2003) in the synthesis of copper(I) and mixed-valence copper(I)/copper(II) compounds.



The reaction between copper(II) sulfate and 4,4'-bipyridine under hydrothermal conditions, but without an alcohol as co-solvent, surprisingly furnished a copper complex with the

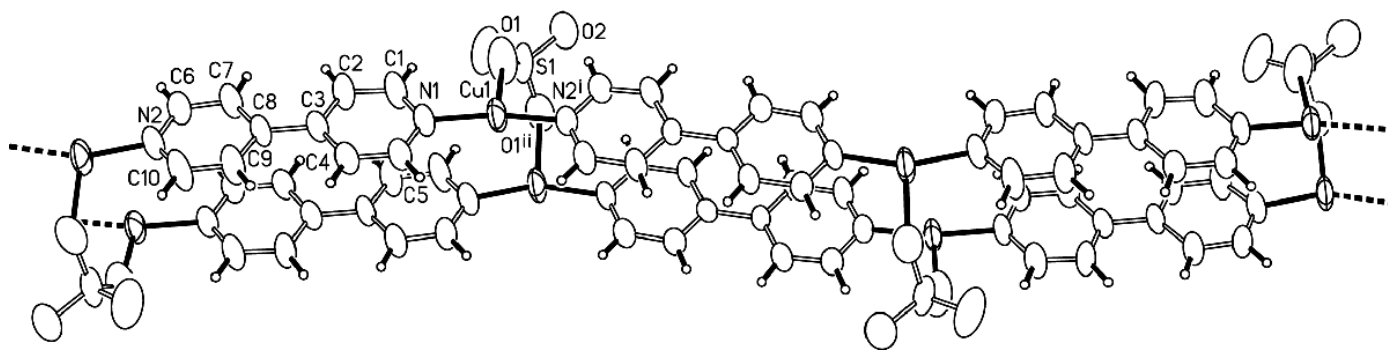


Figure 1

ORTEP (Johnson, 1976) plot of (I), illustrating the T-shaped geometry of the Cu^I atom, with ellipsoids drawn at the 50% probability level; the disordered water molecules are not shown. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $x - 1, -y, z - \frac{1}{2}$; (ii) $1 - x, y, \frac{1}{2} - z$.]

metal atom in the +1 oxidation state. The yellow color, in contrast to the typical blue color of copper(II) compounds, implies the presence of copper(I) in (SO₄)[(C₁₀H₈N₂)₂Cu]₂·4H₂O, (I) (Fig. 1). The compound has a [(C₁₀H₈N₂)₂Cu]_n chain that is stacked over another. The two chains are bridged by SO₄ groups, giving rise to a double-chain motif. However, as the SO₄ groups, on twofold rotation axes, are located alternately on alternate sides of the double chain, the structure does not resemble a ladder. The water molecules occupy the space between the chains, and are hydrogen bonded to them. Unfortunately, the hydrogen-bonding scheme could not be ascertained because of the disorder in the water molecules. The bridging modes of the spacer heterocycle and the sulfate anion confer a T-shaped geometry on the Cu^I atom. The N—Cu—N skeleton is somewhat bent [160.0 (2)°].

Experimental

A solution of copper sulfate pentahydrate (0.25 g, 1 mmol) and 4,4'-bipyridine (0.12 g, 0.8 mmol) in water (7 ml) was treated with 2 M sodium hydroxide to give a pH of 7. The mixture was then placed in a 15 ml Teflon-lined stainless-steel bomb. The bomb was heated at 433 K for 48 h, after which it was cooled slowly to room temperature. Yellow prismatic crystals were isolated in about 50% yield. Elemental analysis found: C 39.23, H 4.06, N 9.16, S 5.26%; calculated for C₂₀H₂₄Cu₂N₄O₈S: C 39.53, H 3.98, N 9.22, S 5.28%.

Crystal data

[Cu₂(SO₄)(C₁₀H₈N₂)₂]_n·4H₂O
M_r = 607.57
 Monoclinic, *C*2/*c*
a = 10.825 (1) Å
b = 17.316 (1) Å
c = 14.428 (1) Å
 β = 109.907 (1)°
V = 2542.8 (4) Å³
Z = 4

D_x = 1.587 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 2789 reflections
 θ = 2.3–24.7°
 μ = 1.81 mm⁻¹
T = 298 (2) K
 Block, yellow
 0.30 × 0.15 × 0.10 mm

Data collection

Bruker SMART APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
T_{min} = 0.675, *T_{max}* = 0.840
 11348 measured reflections

2234 independent reflections
 1449 reflections with *I* > 2σ(*I*)
R_{int} = 0.039
 θ_{\max} = 25.0°
h = -12 → 12
k = -20 → 20
l = -17 → 17

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.066
wR(*F*²) = 0.221
S = 1.11
 2234 reflections
 177 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.1121P)^2 + 9.1371P]$$

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

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

$$\Delta\rho_{\max} = 1.27 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.41 \text{ e } \text{Å}^{-3}$$

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	1.905 (5)	Cu1—O1	2.266 (6)
Cu1—N2 ⁱ	1.897 (5)		
N1—Cu1—N2 ⁱ	160.0 (2)	N2 ⁱ —Cu1—O1	101.0 (2)
N1—Cu1—O1	98.3 (2)		

Symmetry code: (i) $x - 1, -y, z - \frac{1}{2}$.

The two solvent water molecules are disordered over two positions; as the occupancies refined to almost 0.5, they were fixed as 0.5. The two unprimed atoms, O1_w and O2_w, comprise one set and the primed atoms, O1_{w'} and O2_{w'}, the other set. The disorder precluded the assignment of the H atoms. The displacement parameters of the O atoms of the SO₄ unit (as well as the water O atoms) were restrained to be approximately isotropic. The resolved and unresolved disorder also affected the 4,4'-bipyridine ligand. Ring C—C distances were restrained to 1.39 (1) Å as some of the distances were somewhat too short. The H atoms of the ligand were positioned geometrically [C—H = 0.93 Å and *U*_{iso} = 1.2*U*_{eq}(C)] and they were included in the refinement in the riding-model approximation. The final difference Fourier map had a large peak 1.7 Å from O1_w, but was otherwise featureless. The crystal structure has no solvent-accessible voids, as noted by PLATON (Spek, 2003).

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP (Johnson, 1976); software used to prepare material for publication: SHELXL97.

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