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catena-Poly[[tetrapyridinecopper(II)]-μ_2-naphthalene-1,5-disulfonato]

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The disordered naphthalene-1,5-disulfonate unit in the title compound, $[Cu(C_{10}H_6O_6S_2)(C_5H_5N)_4]_n$, connects adjacent $(C_5H_5N)_4Cu$ units into a linear chain; the Cu atom shows octahedral coordination. Both units lie on special positions of $\overline{1}$ site symmetry.

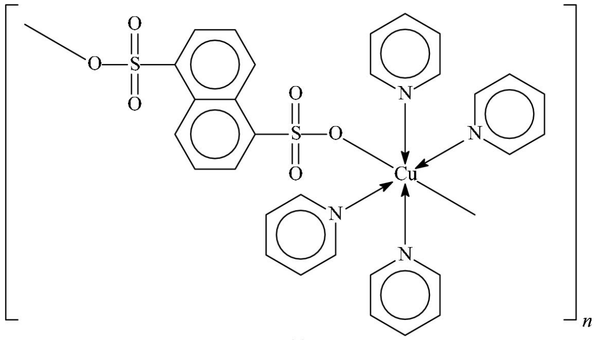
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.047
wR factor = 0.133
Data-to-parameter ratio = 14.9

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

Comment

In the crystal structure of the tetrapyridinecopper(II) complex that has the sulfate dianion as counter-ion, (I), the Cu atom exists in a square-pyramidal environment in which the basal plane is made up of the N atoms of the pyridine ligands; the Cu—O distance [2.105 (4) Å] is normal (Kožíšek *et al.*, 1989). Only a small number of tetrapyridinecopper(II) complexes of sulfonic acids have been structurally verified; these are the dicarboxybenzenesulfonate, whose Cu atom is involved in bonding to the sulfonate and carboxyl portions (Kulynych & Shimizu, 2002), the trifluorosulfonate (Haynes *et al.*, 1988) and the benzenesulfonate (Jedrzejas *et al.*, 1993). The benzenesulfonate has a rather long Cu—O bond [2.471 (8) Å].



(I)

The naphthalene-1,5-disulfonate in (I) displays a much longer Cu—O bond [2.602 (2) Å]; the length can be ascribed to the difficulty of accommodating the rigid dianion on a center of inversion, a feature that is sometimes found in such symmetrical naphthalenedisulfonates (Cai, 2004). The N atoms of the pyridine ligand constitute a square around the Cu atom and the O atoms of the dianion are located above and below this plane to give rise to a distorted octahedral geometry for the metal atom. The bridging mode of the dianion gives rise to a chain motif (Fig. 1).

Experimental

Copper(II) dichloride dihydrate (0.34 g, 2 mmol) was reacted with an excess of pyridine (1 ml) in methanol to give the deep-blue pyridine adduct. The adduct was then reacted with naphthalene-1,5-disulfonic acid (0.66 g, 2 mmol) in water. The pH was adjusted to 6 by the addition of drops of 0.2 *M* sodium hydroxide. Blue prismatic crystals were obtained after some days. Analysis calculated for $C_{30}H_{26}N_4CuO_6S_2$: C 54.09, H 3.93, N 8.41%; found: C 54.12, H 3.89; N 8.44%.

Crystal data

$[Cu(C_{10}H_6O_6S_2)(C_5H_5N)_4]$
M_r = 666.21
Triclinic, $P\overline{1}$
a = 8.9105 (7) Å
b = 9.0601 (7) Å
c = 10.5488 (8) Å
α = 66.158 (1)°
β = 68.752 (1)°
γ = 88.391 (1)°
V = 718.9 (1) Å^3
Z = 1
D_x = 1.539 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6473 reflections
θ = 2.3–28.3°
μ = 0.96 mm^{-1}
T = 295 (2) K
Prism, dark blue
0.35 × 0.24 × 0.19 mm

Data collection

Rigaki R-AXIS RAPID IP diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.531, T_{max} = 0.839
7482 measured reflections
3552 independent reflections
2989 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 28.3°
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.133
S = 1.07
3552 reflections
239 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0757P)^2 + 0.2705P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.91 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	2.602 (2)	Cu1—N2	2.039 (2)
Cu1—N1	2.015 (3)		
O1—Cu1—O1^i	180	N1—Cu1—N1^i	180
O1—Cu1—N1	90.7 (1)	N1—Cu1—N2	90.0 (1)
O1—Cu1—N1^i	89.3 (1)	N1—Cu1—N2^i	90.0 (1)
O1—Cu1—N2	89.9 (1)	N2—Cu1—N2^i	180
O1—Cu1—N2^i	90.2 (1)		

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

The napthalenedisulfonate unit is disordered over two sites on a center of inversion. For each component, the naphthalene fused ring was refined as a five-carbon species with a restrained C—C distance of 1.390 (5) Å; the 1,4-related distance was restrained to 2.780 (5) Å. The five atoms were restrained to being approximately coplanar within 0.01 Å. The $-SO_3$ portion is also disordered, but the two components share a common O atom; this atom is the atom that forms a bond to the Cu atom. The six S—O distances were restrained to within 0.005 Å of each other, as were the two S—C distances. Additionally, the six C···O distances, as well as the six O···O distances, were restrained to be equal. A somewhat tighter restraint was used to avoid a spread of the bond distances. The carbon-bound H atoms were placed at calculated positions [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$] and were included in the refinement in the riding-model approximation.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

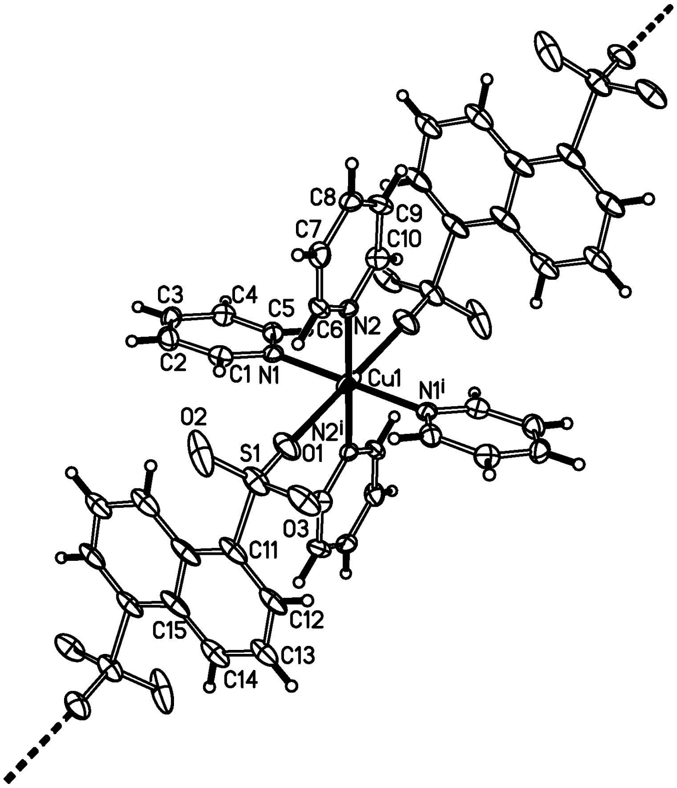


Figure 1
ORTEPII plot (Johnson, 1976) of a fragment of the polymeric chain in (I). Displacement ellipsoids are drawn at the 50% probability level. The Cu atom lies on a center of inversion at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). Only one disorder component of the naphthalenedisulfonate is shown.

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