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Bis(μ-2,2′-bipyridin-6-olato)-κ^3N,N':O;κ^3O:N,N'-dicopper(I,II) dichlorocuprate(II)

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Key indicators

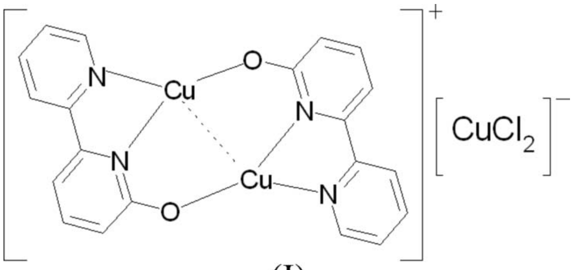
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.045
wR factor = 0.144
Data-to-parameter ratio = 16.4

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

The title compound, $[Cu_2(C_{10}H_7N_2O)_2][CuCl_2]$, is formulated as containing a mixed-oxidation-state $[Cu_2(obpy)_2]^+$ cation (Hobpy is 2,2′-bipyridin-6-ol) and a $[CuCl_2]^-$ anion, both of which lie on inversion centres. The mixed-valence $Cu^{I,II}$ is coordinated by one O and two N atoms of two obpy ligands. The Cu···Cu interaction [2.3805 (9) Å] results in a square-planar environment for the $Cu^{I,II}$ atoms. The Cu^{II} atom in the anion is coordinated by two chloride ions in a linear geometry.

Comment

Although many complexes with 2,2′-bipyridine (bpy) and a halogen have been reported, the hydroxylation of bpy is not very common as only a few compounds have been obtained until now (Chen *et al.*, 2002; Zhang, Tong & Chen, 2002; Zhang, Tong, Gong *et al.*, 2002; Zheng *et al.*, 2003). The key to the Gillard mechanism is the nucleophilic attack of the α-C atom of pyridine by a hydroxide ion to form a covalent hydrate (Gillard, 1975). Such complexes may provide more useful structural evidence for the study of the Gillard mechanism, which has been debated for a long time and is not only important in organic heterocyclic chemistry, but also in coordination chemistry. On the other hand, compounds with chloride as a bridging ligand, forming an open framework, are relatively rare. We are currently interested in pursuing synthetic strategies by using chloride, a versatile ligand, for the synthesis of complexes with transition metal cations. We report here the crystal structure of $[Cu_2(obpy)_2][CuCl_2]$ (Hobpy is 2,2′-bipyridin-6-ol), (I), with hydroxylated heterocyclic ligands.



(I)

Compound (I) is formulated as a mixed-oxidation-state $[Cu_2(obpy)_2]^+$ cation and a$[CuCl_2]^-$ anion (Fig. 1), both of which lie on crystallographic inversion centres. Each Cu atom of the binuclear cation, in which the oxidation states are disordered, is coordinated by two N atoms of the obpy ligand and the O atom of the inversion-related obpy ligand. The Cu···Cu interaction [2.3805 (9) Å] results in a square-planar environment for these Cu atoms. The Cu···Cu distance in (I) is shorter than that observed in $[Cu_4(obpy)_4(fumarate)]\cdot 6H_2O$ [2.4027 (5) Å; He *et al.*, 2004]. The *trans* angles in the Cu_2N_2O square plane are 171.85 (13) and 167.31 (9)°, and the other angles subtended at Cu1 range from 82.67 (13) to 100.19 (12)° (Table 1). The Cu^I ion of the anion is coordinated by two chloride ions in a linear geometry.

Experimental

A mixture of $CuCl_2\cdot 2H_2O$ (0.1875 g, 1.1 mmol), 2,2′-bipyridine (0.1874 g, 1.2 mmol), KOH (0.0345 g, 0.65 mmol) and water (15 ml) was stirred for 30 min in air, then transferred and sealed in a 23 ml Teflon reactor, which was heated in an oven to 443 K for 4 d. The oven was cooled to room temperature at a rate of 5 K h^{-1}. The resulting grey prismatic crystals were filtered, washed and dried in air (yied 47% based on Cu). No other characterization data are available for this product. The assignment of oxidation states, including the disordered mixed I/II states in the cation, is based on the sample colour, coordination geometry, and comparison with commonly observed $[CuCl_2]^-$ anions.

Crystal data

$[Cu_2(C_{10}H_7N_2O)_2][CuCl_2]$
$M_r = 603.90$
Monoclinic, $P2_1/n$
$a = 7.3583$ (6) Å
$b = 16.1779$ (8) Å
$c = 9.1962$ (6) Å
$\beta = 111.621$ (3)°
$V = 1017.71$ (12) Å^3
$Z = 2$
$D_x = 1.971$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 3.40$ mm^{-1}
$T = 293$ (2) K
Prism, grey
0.32 × 0.15 × 0.11 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.548$, $T_{max} = 0.688$
7777 measured reflections
2331 independent reflections
1858 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.144$
$S = 1.00$
2331 reflections
142 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.096P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1^i	1.886 (3)	Cu1—Cu1^i	2.3805 (9)
Cu1—N2	1.910 (3)	Cu2—Cl1	2.1134 (12)
Cu1—N1	2.030 (3)		
O1^i—Cu1—N2	171.85 (13)	N2—Cu1—Cu1^i	85.71 (10)
O1^i—Cu1—N1	100.19 (12)	N1—Cu1—Cu1^i	167.31 (9)
N2—Cu1—N1	82.67 (13)	Cl1^{ii}—Cu2—Cl1	180
O1^i—Cu1—Cu1^i	90.66 (8)		

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x-1, -y, -z$.

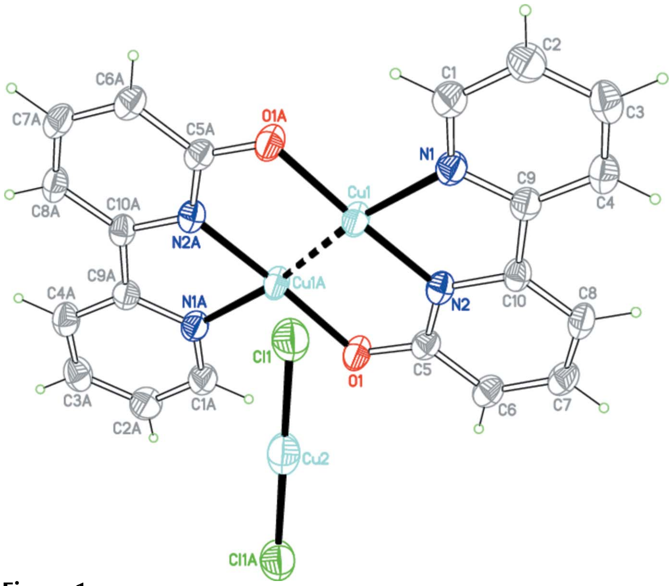


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level. Atoms labelled with the suffix A are generated by the symmetry operation ($-x$, $-y$, $-z$) in the binuclear cation and ($-x-1$, $-y$, $-z$) in the anion.

H atoms were positioned geometrically (C—H = 0.93 Å) and included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); 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, 1997); software used to prepare material for publication: *SHELXL97*.

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