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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean $\sigma(\text{C}-\text{C}) = 0.013$ Å

R factor = 0.060

wR factor = 0.173

Data-to-parameter ratio = 12.4

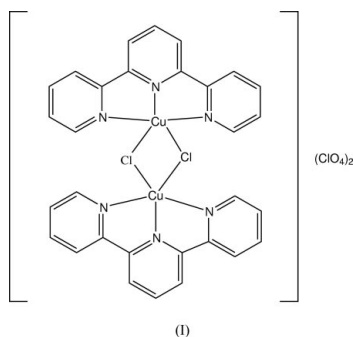
For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Di- μ -chloro-bis[(2,2':6,2''-terpyridine)- copper(II)] diperchlorate

The asymmetric unit of the title compound, $[\text{Cu}_2\text{Cl}_2(\text{C}_{15}\text{H}_{11}\text{N}_3)_2](\text{ClO}_4)_2$, consists of a centrosymmetric binuclear dication, $[\text{Cu}_2(\text{terpyridine})_2\text{Cl}_2]^{2+}$, and two perchlorate anions. In the dication, both Cu atoms have a 4+1 coordination, in an approximate square-pyramidal geometry.

Comment

The introduction of transition metals into a supramolecular structure provides access to properties and geometries that are not readily accessible through crystal engineering of organic molecular solids; for example, it is possible to obtain square-planar geometries and magnetic, electronic and catalytic properties through the presence of transition metal ions (Aakeröy & Beatty, 2001).



Any good supramolecular synthesis requires control at a molecular and a supramolecular level; usually the control at a molecular level is attainable. This is not the case with the Cu^{II} ion, which presents in one oxidation state a greater diversity in its stereochemical behavior than any other element (Wells, 1984). Due to its possible use in magnetic supramolecular materials, it is necessary to find a system where it is possible to have control of the geometry of this ion. A successful approach to controlling the geometry of transition metal ions has been the use of blocking ligands that leave only specific coordination sites available to incoming ligands (Holliday & Mirkin, 2001). Terdentate amines are possible blocking ligands for Cu^{II} when square-pyramidal geometry is required. This geometry has been observed for Cu compounds with the general formula $[\text{Cu}_2(\text{NNN})_2\text{Cl}_2]^{2+}$, where NNN is terpyridine (terpy) (Rojo *et al.*, 1987), NNN is propylenetriamine or diethylenetriamine (Urriaga *et al.*, 1996). Also, a non-centrosymmetric compound, in which water molecules are coordinated axially to one of the Cu^{II} ions, has been reported (Willet, 2001). In this compound, one of the Cu^{II} ions has a square-pyramidal geometry, but the other is hexacoordinated. In this paper, we report the structure of $[\text{Cu}_2(\text{terpy})_2\text{Cl}_2]^{2+}$ as a diperchlorate.

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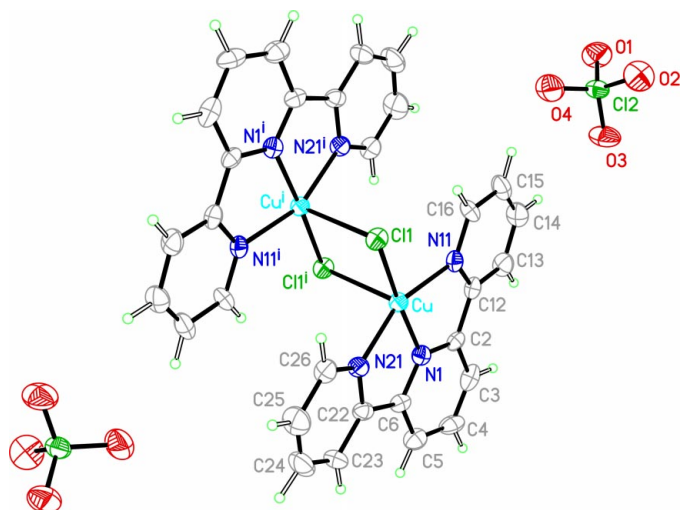


Figure 1

The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level [symmetry code: (i) is $-x, -y, -z$].

Compound (I) consists of centrosymmetric dinuclear $[\text{Cu}_2(\text{terpy})_2\text{Cl}_2]$ dications and ClO_4^- anions (see Fig. 1). The Cu^{II} ions have a $4 + 1$ coordination, in an approximate square-pyramidal geometry, according to the τ -descriptor value of 0.27 for five-coordination geometry (Addison & Reedijk, 1984). The three N atoms of the terpy ligand and a Cl^- anion coordinate to the Cu atom in a pseudo-planar primary coordination sphere, with the Cu atom 0.135 Å out of the N1/N11/N21/Cl1 mean plane. The Cl^- semicoordinates to a second Cu atom in the apical position of the pyramid, thereby producing dimers.

In the crystal structure of (I), a π - π interaction between the pyridine rings containing N11 and N21 ($1-x, -y, -z$) is observed. The pyridine rings are parallel (within experimental error), with a centroid-centroid distance of 3.66 Å and a perpendicular separation of 3.4 Å.

Compound (I) has the expected square-pyramidal structure, with no water or perchlorate molecules coordinated in the sixth position. Compound (I) may be a good starting material in the synthesis of supramolecular structures where Cu^{II} building blocks with two available sites are desired *cis* to each other.

Experimental

$\text{CuCl}_2(\text{H}_2\text{O})_2$ (1.0 mmol) and NaClO_4 (2.0 mmol) were dissolved in distilled H_2O and added to a solution of 2,2':6',2''-terpyridine (1.0 mmol) in acetonitrile (25 ml). The mixture was stirred for 1 h and left to evaporate slowly until blue crystals were obtained.

Crystal data

$[\text{Cu}_2\text{Cl}_2(\text{C}_{15}\text{H}_{11}\text{N}_3)_2](\text{ClO}_4)_2$
 $M_r = 863.42$
 Monoclinic, $P2_1/n$
 $a = 7.439$ (1) Å
 $b = 24.387$ (4) Å
 $c = 9.196$ (1) Å
 $\beta = 105.76$ (1)°
 $V = 1605.6$ (4) Å³
 $Z = 2$

$D_x = 1.786$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 46 reflections
 $\theta = 4.7$ – 12.5°
 $\mu = 1.72$ mm⁻¹
 $T = 293$ (2) K
 Truncated pyramid, blue
 $0.32 \times 0.20 \times 0.18$ mm

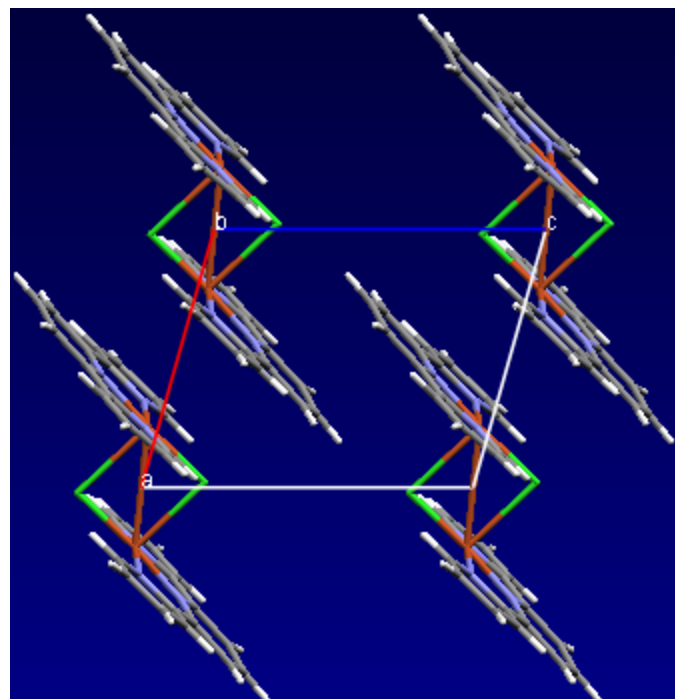


Figure 2

The crystal packing of (I), viewed down the b axis.

Data collection

Siemens P4/PC diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\text{min}} = 0.435, T_{\text{max}} = 0.533$
 3043 measured reflections
 2818 independent reflections
 1856 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.078$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = 0 \rightarrow 8$
 $k = 0 \rightarrow 29$
 $l = -10 \rightarrow 10$
 3 standard reflections
 every 97 reflections
 intensity decay: 3.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.173$
 $S = 1.07$
 2818 reflections
 227 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.067P)^2 + 2.0508P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.46$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.65$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0094 (11)

Table 1

Selected geometric parameters (Å, °).

Cu—N1	1.938 (6)	Cu—Cl1	2.227 (2)
Cu—N21	2.008 (6)	Cu—Cl1 ⁱ	2.698 (2)
Cu—N11	2.028 (6)		
N1—Cu—N21	80.3 (3)	N11—Cu—Cl1	98.5 (2)
N1—Cu—N11	80.7 (3)	N1—Cu—Cl1 ⁱ	93.2 (2)
N21—Cu—N11	158.8 (3)	Cl1—Cu—Cl1 ⁱ	91.80 (7)
N1—Cu—Cl1	174.9 (2)	Cu—Cl1—Cu ⁱ	88.20 (7)
N21—Cu—Cl1	99.6 (2)		
N1—C2—C12—N11	5.0 (10)	N1—C6—C22—N21	−2.5 (11)

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

Data collection: XSCANS (Siemens, 1993); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics:

PLATON (Spek, 1999) and *MERCURY* (Version 1.1; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 1999).

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