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Bis(2,2′:6′,2″-terpyridine)copper(II) diperchlorate hemihydrate

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Key indicators

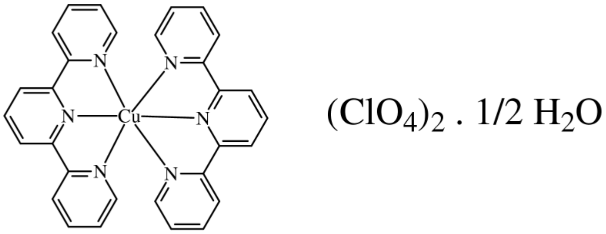
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
Disorder in solvent or counterion
R factor = 0.063
wR factor = 0.191
Data-to-parameter ratio = 11.6

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

In the title compound, $[Cu(C_{15}H_{11}N_3)_2](ClO_4)_2\cdot0.5H_2O$, the 2,2′:6′,2″-terpyridine (terpy) ligand coordinates to the Cu^{II} ion as a terdentate chelating ligand, giving a complex cation with compressed octahedral geometry. The $[Cu(terpy)_2]^{2+}$ cations have crystallographically imposed C_2 symmetry.

Comment

Several studies have been carried out on the structures and magnetic properties of copper(II) complexes with 2,2′:6′,2″-terpyridine (terpy) (Allmann *et al.*, 1978; Folgado *et al.*, 1990). In one of these studies (Folgado *et al.*, 1990), the crystal structures and/or magnetic properties of some $[Cu(terpy)_2]^{2+}$ salts were determined. Although the X-ray and EPR study revealed that the high-temperature phase of $[Cu(terpy)_2](PF_6)_2$, (II), was compressed octahedral, at low temperature, the structure contains elongated CuN_6 octahedra with an orthorhombic component. The EPR powder data for $[Cu(terpy)_2](ClO_4)_2$, (I), show the same magnetic behavior as (II), but the crystal structure of the former was not determined. In this paper, we report the crystal structure of $[Cu(terpy)_2]^{2+}(ClO_4)_2\cdot0.5\ H_2O$, (I), at 273 K.



(I)

Compound (I) consists of octahedral $[Cu(terpy)_2]^{2+}$, with Cu, N1′, C4′, H4′, N11′, C14′ and H14′ in sites with a twofold symmetry axis, two $[ClO_4]^-$ anions in general positions, and a water molecule with half occupancy. The terpy ligand coordinates to the metal ion as a meridional terdentate ligand. As a consequence of the rigid structure of the terpy ligand the Cu—N distances with the central pyridine ring are significantly shorter, giving a compressed octahedral geometry in agreement with the high-temperature structure expected by the previous EPR study.

Experimental

1.0 mmol of $[Cu(H_2O)_6](ClO_4)_2$ was dissolved in distilled H_2O and added to a solution of 1.0 mmol of 2,2′:6′,2″-terpyridine in 25 ml of

DMSO. The mixture was stirred for 1 h and left to evaporate until blue crystals were obtained.

Crystal data

$[Cu(C_{15}H_{11}N_3)_2](ClO_4)_2 \cdot 0.5H_2O$
$M_r = 746.99$
Tetragonal, $I4_1/a$
$a = 12.551$ (2) Å
$c = 40.418$ (5) Å
$V = 6367.0$ (16) Å^3
$Z = 8$
$D_x = 1.559$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 30 reflections
$\theta = 3.5$–12.5°
$\mu = 0.92$ mm^{-1}
$T = 293$ (2) K
Prism, green
0.6 × 0.5 × 0.4 mm

Data collection

Siemens *P*4/PC diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.637$, $T_{\max} = 0.693$
3081 measured reflections
2808 independent reflections
1368 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.062$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 48$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.191$
$S = 0.88$
2808 reflections
243 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.1064P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.019$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: none

Table 1
Selected geometric parameters (Å, °).

Cu—N1′	1.994 (7)	Cu—N1	2.178 (5)
Cu—N11′	2.009 (6)	Cu—N11	2.210 (5)
N1′—Cu—N11′	180.0	N1—Cu—N11	93.78 (18)
N1′—Cu—N1	77.37 (14)	N11—Cu—N11$^{\rm i}$	153.5 (3)
N11′—Cu—N1	102.63 (14)	N1—C2—C2′	115.3 (5)
N1—Cu—N1$^{\rm i}$	154.7 (3)	N1′—C2′—C2	115.0 (5)
N1′—Cu—N11	103.26 (14)	N11—C12—C12′	115.5 (5)
N11′—Cu—N11	76.74 (14)	N11′—C12′—C12	114.8 (5)
N1—C2—C2′—N1′	2.3 (7)	N11—C12—C12′—N11′	−1.9 (7)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*A*···O3*B*$^{\rm i}$	0.85	1.74	2.55 (4)	158
O5—H5*B*···O2	0.85	2.32	3.032 (19)	142

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

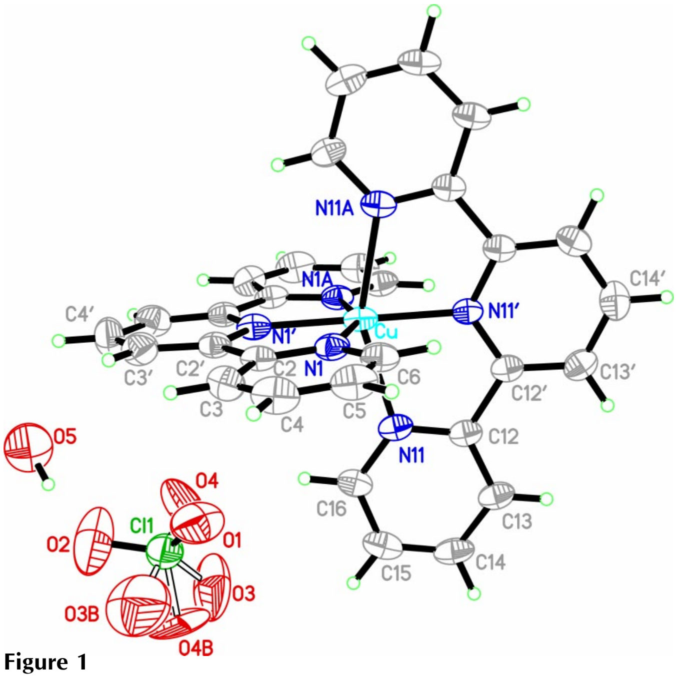


Figure 1
A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

H atoms were located in a difference Fourier map and made to ride on C or O atoms (C—H = 0.96 Å and O—H = 0.85 Å) with a fixed isotropic displacement parameter 1.2 times that of the parent atom. The perchlorate anion is disordered over at least two orientations, related approximately by twofold rotation about the Cl1—O1 bond. Half-occupancy sites were refined for two positions of O3 and O4, without geometrical constraints. A broad range of Cl—O distances was obtained, with average close to accepted values; angles at Cl are not all close to normal tetrahedral values, but no further disorder was resolved. Refinement of the site-occupation factor for the water O atom revealed a partial occupation close to 0.5, which was then kept fixed to this value in the final refinement.

Data collection: *XSCANS* (Siemens, 1993); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

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References

Allmann, R., Henke, W. & Reinen, D. (1978). *Inorg. Chem.* **17**, 378–382.
Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Folgado, J.-V., Henke, W., Allmann, R., Stratemeier, H., Betrán-Porter, D., Rojo, T. & Reinen, D. (1990). *Inorg. Chem.* **29**, 2035–2042.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual.* Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Siemens (1993). *XSCANS User's Manual.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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