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Key indicators

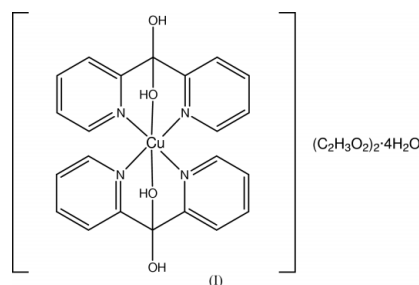
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.049
 wR factor = 0.115
Data-to-parameter ratio = 21.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis(di-2-pyridylmethanediol- κ^3N,O,N')-
copper(II) diacetate tetrahydrateThe crystal structure of $[\text{Cu}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2)_2](\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ reveals an extended $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bond network between helicoidal chains of water molecules and layers of $[\text{Cu}(\text{N},\text{O},\text{N}'\text{-dpkdiol})_2]^{2+}$ complex cations and acetate anions held together by means of carboxylate–diol hydrogen bonds. The cation has crystallographic inversion symmetry.

Received 19 June 2003

Accepted 27 June 2003

Online 30 June 2003

Comment

The di-2-pyridyl-ketone ligand (dpk) has been observed to undergo hydration of the ketocarbonyl group, forming a *gem*-diol after initial N,N' -coordination to a transition metal (Wang *et al.*, 1986). This *gem*-diol ligand (dpkdiol) can coordinate both as an N,N' -bidentate ligand (Parker *et al.*, 2000) or as an N,O,N' -tridentate ligand, either protonated (Sommerer *et al.*, 1993; Tangoulis *et al.*, 1997; Yang *et al.*, 1998; Serna *et al.*, 1999) or deprotonated (Sommerer *et al.*, 1990; Breeze *et al.*, 1996; Tong *et al.*, 1998; Hemmert *et al.*, 1999; Woltz *et al.*, 2002). The title complex, (I), which was obtained in an attempt to prepare a copper-dpk–Keggin complex, consists of $[\text{Cu}(\text{N},\text{O},\text{N}'\text{-dpkdiol})_2]^{2+}$ complex cations, acetate anions and uncoordinated water molecules.The Cu atom lies in a distorted elongated octahedral CuN_4O_2 environment. The equatorial coordination positions are occupied by the N atoms of the dpkdiol ligands, while two hydroxyl groups occupy the axial ones. The two hydroxyl groups of the ligands and the acetate anions form two strong face-to-face carboxylate–diol hydrogen bonds, leading to trimolecular entities built up of one cationic complex and two acetate anions (Fig. 1). These entities are placed in layers parallel to the (001) plane, which are connected by an extended $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bond network between the O atoms of the acetate anions and helicoidal chains of water running parallel to the b axis (Fig. 2).

Experimental

A solution containing 68 mg of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 25 mg of oxalic acid and 74 mg of dpk in 30 ml of water and 10 ml of methanol was added to a solution of 667 mg of $\text{K}_4\text{SiW}_{12}\text{O}_{40}$ in 50 ml of water and a violet

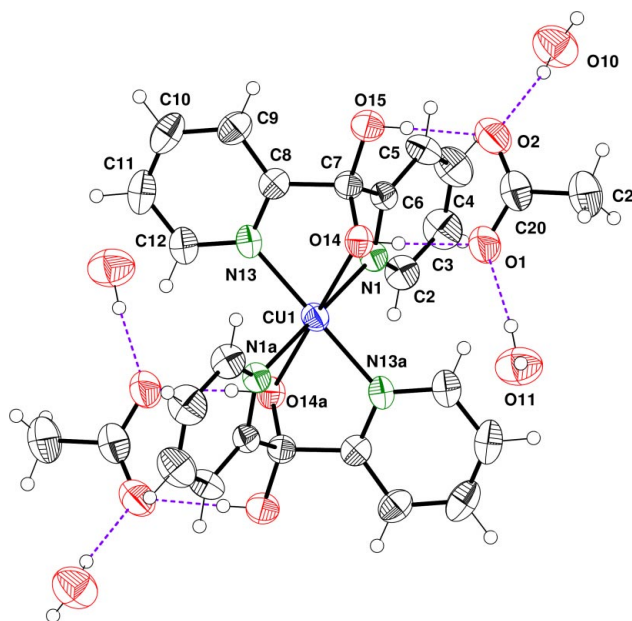


Figure 1
View of the molecular structure of (I) (twice the asymmetric unit), with 50% probability displacement ellipsoids. The suffix *a* on atom labels represents symmetry operation $-x, -y, -z$.

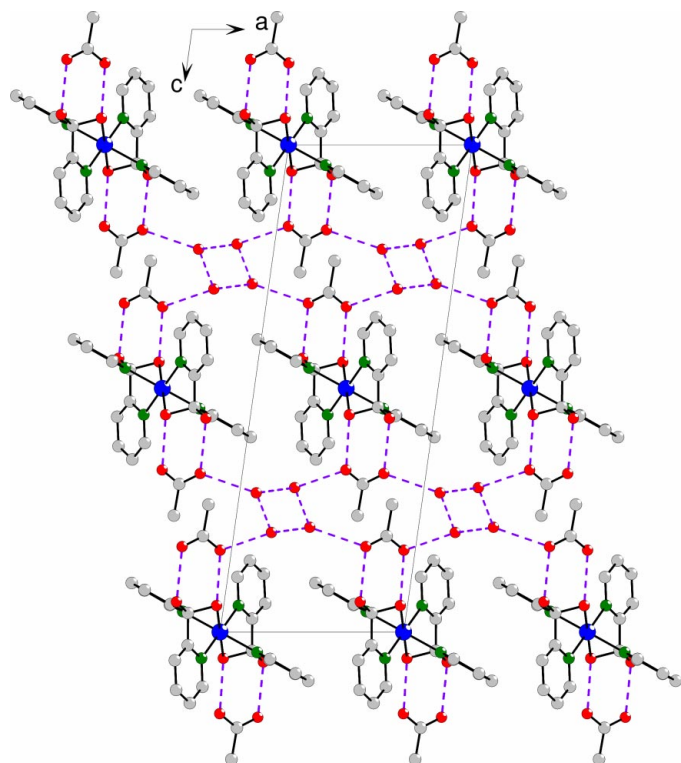


Figure 2
View of the crystal packing along the *b* axis.

precipitate was formed. The title compound was obtained upon recrystallization of the precipitate from a 2:1 mixture of an acetate buffer and DMF. Elemental analysis (%): found (C, H, N) 46.76, 5.16, 8.42; calculated for $C_{26}CuH_{26}N_4O_8 \cdot 4H_2O$: 47.45, 5.21, 8.51. IR (cm^{-1}): 1523, 1427, 1230, 1217, 1032.

Crystal data

$[Cu(C_{11}H_{10}N_2O_2)_2] \cdot (C_2H_3O_2)_2 \cdot 4H_2O$
 $M_r = 658.11$
Monoclinic, $P2_1/n$
 $a = 8.617(1) \text{ \AA}$
 $b = 7.8765(9) \text{ \AA}$
 $c = 23.103(3) \text{ \AA}$
 $\beta = 98.00(1)^\circ$
 $V = 1552.8(3) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.408 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 6500 reflections
 $\theta = 3.5\text{--}25^\circ$
 $\mu = 0.77 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
Prism, purple
 $0.37 \times 0.23 \times 0.10 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur diffractometer
 ω scans
Absorption correction: analytical (*CrysAlisRED*; Oxford Diffraction, 2002)
 $T_{min} = 0.793, T_{max} = 0.931$
12971 measured reflections

4484 independent reflections
2765 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.044$
 $\theta_{max} = 30^\circ$
 $h = -12 \rightarrow 12$
 $k = -11 \rightarrow 8$
 $l = -32 \rightarrow 32$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.115$
 $S = 0.96$
4480 reflections
211 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0588P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.47 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.34 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Cu1—N1 ⁱ	1.9918 (17)	O14—C7	1.408 (3)
Cu1—N13 ⁱ	2.0257 (18)	O15—C7	1.381 (2)
Cu1—O14 ⁱ	2.3990 (14)		
N1 ⁱ —Cu1—N13 ⁱ	87.86 (7)	N13—Cu1—O14 ⁱ	106.14 (6)
N1 ⁱ —Cu1—N13	92.14 (7)	C2—N1—Cu1	124.37 (15)
N1—Cu1—N13	87.86 (7)	C6—N1—Cu1	116.25 (13)
N1 ⁱ —Cu1—O14 ⁱ	75.63 (6)	C12—N13—Cu1	125.69 (16)
N1—Cu1—O14 ⁱ	104.37 (6)	C8—N13—Cu1	114.77 (14)
N13 ⁱ —Cu1—O14 ⁱ	73.86 (6)		

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

Table 2

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O14—H14 \cdots O1	0.82	1.78	2.603 (2)	178
O15—H15 \cdots O2	0.82	1.79	2.607 (3)	177
O10—H10A \cdots O2	0.848 (10)	1.958 (13)	2.788 (3)	166 (3)
O10—H10B \cdots O11 ⁱⁱ	0.845 (10)	1.906 (12)	2.741 (3)	169 (3)
O11—H11A \cdots O1	0.848 (10)	1.915 (14)	2.741 (3)	164 (3)
O11—H11B \cdots O10 ⁱⁱⁱ	0.842 (10)	1.910 (11)	2.748 (3)	173 (4)

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

The H atoms of the water molecules and hydroxyl groups of the dpkdol ligand were located in a Fourier difference map. The positions of all remaining H atoms were calculated geometrically. Water molecule H atoms were refined with the O—H distance constrained to 0.85 (1) \AA . All remaining H atoms were refined as riding, with isotropic displacement parameters fixed at 1.2 (aromatic C) or 1.5 (methyl and hydroxyl groups) times the equivalent isotropic displacement parameters of their parent atoms.

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlisRED* (Oxford Diffraction, 2002); data reduction: *CrysAlisRED*; program(s) used to solve structure: *DIRDIF99.2* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by MCT (MAT2002-03166). SR thanks Gobierno Vasco for his Doctoral Fellowship.

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