Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Aqua(di-2-pyridylamine)oxalatocopper(II) monohydrate

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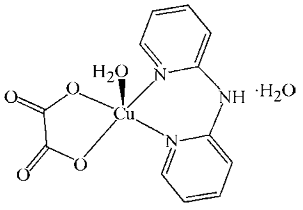
Received 4 April 2006
Accepted 4 May 2006
Online 24 May 2006

In the structure of the title complex, $[Cu(C_2O_4)(C_{10}H_9N_3)(H_2O)]\cdot H_2O$, the Cu^{II} atom displays a square-pyramidal geometry, being coordinated by two N atoms from the di-2-pyridylamine ligand, two O atoms from the oxalate group and one O atom of a water molecule. The complex molecules are linked to form a three-dimensional supramolecular array by hydrogen-bonding interactions between coordinated/uncoordinated water molecules and the uncoordinated oxalate O atoms of neighboring molecules.

Comment

There has been considerable interest in the design and syntheses of transition metal complexes with the oxalate ligand in coordination chemistry, owing to the fact that this type of complex has potential applications in molecular-based magnets. Furthermore, such complexes could have potential applications as precursors for the synthesis of, for instance, copper-containing superconducting ceramics (Bouayad *et al.*, 1995). Self-assembly of metal compounds by hydrogen bonds into one-, two- and three-dimensional supramolecular architectures connects with biological chemistry, materials chemistry (such as organic films and magnetic materials) and supramolecular chemistry (Chen *et al.*, 2001). Hydrogen bonds play vital roles in highly efficient and specific biological reactions, and are essential for molecular recognition and self-organization of molecules in supramolecular chemistry. We report here the crystal structure of one such complex, aqua(di-2-pyridylamine)oxalatocopper(II) monohydrate, (I). The di-2-pyridylamine (dpyam) ligand has been selected primarily because of the fact that it also has an NH hydrogen-bond donor function that might contribute to the formation of one-, two- or three-dimensional supramolecular architectures.



(I)

The molecular structure of (I), shown in Fig. 1, consists of discrete monomers. The Cu atom has a five-coordinate CuN_2O_2O' environment, with a distorted square-pyramidal structure ($\tau = 0.10$). [The structure index is defined as $\tau = (\beta - \alpha)/60$, where *b* and *a* are the largest coordination angles (Addison *et al.*, 1984).] The dpyam ligand and oxalate anion are both symmetrically coordinated to the Cu atom in the basal plane of the square pyramid, with a water molecule occupying the fifth coordinated position (Fig. 1 and Table 1). The dihedral angle between the planes of the pyridine rings is 16.8 (1)°, and that between the CuO_2 and CuN_2 planes is 18.3 (1)°. The Cu atom lies 0.2197 Å above the basal plane, towards the coordinated water molecule. Other related examples of oxalate compounds are $[Cu(bipy)(C_2O_4)(H_2O)]\cdot 2H_2O$, (II) (bipy is 2,2′-bipyridine), $[Cu(nphen)(C_2O_4)(H_2O)]\cdot 2H_2O$, (III) (nphen is 5-nitro-1,10-phenanthroline), and $[Cu(phen)(C_2O_4)(H_2O)]\cdot H_2O$, (IV) (phen is 1,10-phenanthroline) (Chen *et al.*, 2001). The Cu^{II} atoms in these compounds likewise exhibit distorted square-pyramidal geometry, with τ values of 0.21 for (II), 0.01 for (III) and 0.02 for (IV). The Cu—O(oxalate) bond distances are 1.958 (2) and 1.938 (2) Å for (II), 1.936 (6) and 1.935 (7) Å for (III), and 1.937 (1) and 1.944 (2) Å for (IV); the difference between these and the corresponding distances in (I) (Table 1) is probably due to the effect of the chelating coordination in (I). The Cu—O(water) distance is comparable to those of 2.175 (4) Å in (II), 2.175 (4) Å in (III) and 2.175 (4) Å in (IV) (Chen *et al.*, 2001). The Cu—N bond lengths are somewhat longer than those in $[Cu(dpyam)(H_2O)(CO_3)]\cdot 2H_2O$ [1.970 (3) and 1.972 (3) Å; Akhter *et al.*, 1991].

In (I), hydrogen bonds are observed between atom O5 and the uncoordinated water molecule, and between atom O5 and atom O4 of the oxalate group in an adjacent [Cu(dpyam)-

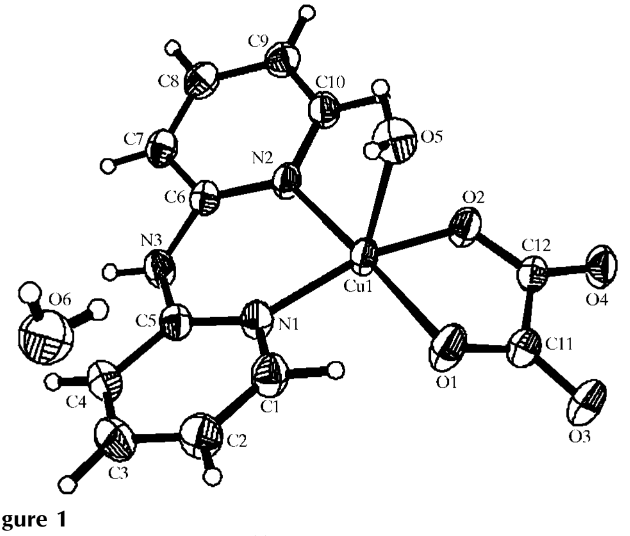


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 50% probability level.

DOI: 10.1107/S0108270106016398

$(C_2O_4)(H_2O)]$ unit (Table 2). These hydrogen bonds form a one-dimensional chain structure. Additional hydrogen bonds between the uncoordinated water molecule and atoms O3 and O4 of the oxalate group in an adjacent chain link the molecules into a three-dimensional array (Fig. 2 and Table 2).

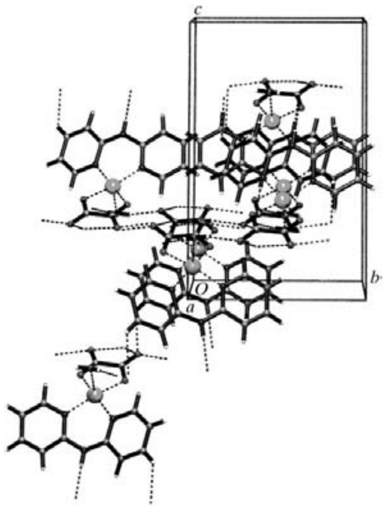


Figure 2
The molecular packing of (I), showing the three-dimensional structure along the *c* axis.

Experimental

The title compound was obtained as blue blocks by slow evaporation of a concentrated aqueous ethanol solution (1:2) containing stoichiometric amounts of $K_2[Cu(C_2O_4)_2]\cdot 2H_2O$ and di-2-pyridylamine. Crystals of (I) suitable for single-crystal X-ray diffraction were selected directly from the sample as prepared.

Crystal data

$[Cu(C_2O_4)(C_{10}H_9N_3)(H_2O)]\cdot H_2O$
$M_r = 358.79$
Monoclinic, $P2_1/n$
$a = 9.3814$ (1) Å
$b = 9.7427$ (1) Å
$c = 15.510$ (1) Å
$\beta = 103.487$ (1)°
$V = 1378.49$ (2) Å^3
$Z = 4$
$D_x = 1.729$ Mg m^{-3}
$D_m = 1.732$ Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
$\mu = 1.62$ mm^{-1}
$T = 293$ (2) K
Block, blue
0.63 × 0.48 × 0.40 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000*a*)
$T_{min} = 0.817$, $T_{max} = 1.000$ (expected range = 0.428–0.523)
9853 measured reflections
3924 independent reflections
3456 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 30.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.069$
$S = 1.04$
3924 reflections
251 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 0.1326P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9623 (10)	O3—C11	1.2309 (16)
Cu1—O2	1.9634 (9)	O4—C12	1.2331 (15)
Cu1—N2	1.9861 (10)	O2—C12	1.2721 (15)
Cu1—N1	1.9863 (10)	O1—C11	1.2700 (16)
Cu1—O5	2.2901 (12)		
O1—Cu1—O2	83.37 (4)	N2—Cu1—N1	91.67 (4)
O1—Cu1—N2	169.41 (5)	O1—Cu1—O5	96.40 (5)
O2—Cu1—N2	91.39 (4)	O2—Cu1—O5	93.32 (4)
O1—Cu1—N1	90.87 (4)	N2—Cu1—O5	93.07 (4)
O2—Cu1—N1	163.65 (4)	N1—Cu1—O5	102.55 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H5···O6^{i}	0.81 (2)	2.23 (2)	3.037 (1)	172 (2)
O5—H13···O4^{ii}	0.78 (3)	2.04 (3)	2.811 (1)	166 (2)
O5—H14···O6^{iii}	0.82 (2)	2.10 (3)	2.915 (1)	177 (2)
O6—H12···O3^{iv}	0.78 (2)	2.36 (3)	2.973 (1)	137 (2)
O6—H12···O4^{iv}	0.78 (2)	2.43 (3)	2.997 (1)	131 (2)

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

All H-atom parameters were refined freely. The resulting C—H distances are in the range 0.926 (19)–1.01 (2) Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000*b*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2001).

The authors gratefully acknowledge the TRF Senior Research Scholar program (agreement No. RTA 4880008) and the Higher Education Development Project: Postgraduate Education and Research Program in Chemistry, Thailand, for support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3005). Services for accessing these data are described at the back of the journal.

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