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μ-Oxalato-bis[(2,2′-bipyridine)(*N*,*N*-dimethylformamide)copper(II)] bis(perchlorate)

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Key indicators

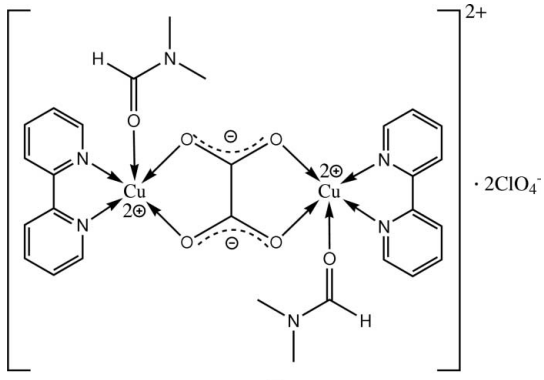
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.037
wR factor = 0.093
Data-to-parameter ratio = 12.9

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

In the title compound, $[Cu_2(C_2O_4)(C_{10}H_8N_2)_2(C_3H_7NO)_2](ClO_4)_2$, the oxalate-bridged binuclear copper(II) complex cation is centrosymmetric. The Cu^{II} atom has a distorted square-pyramidal geometry with two O and two N atoms from oxalate and bipyridine ligands in the basal plane, and with a dimethylformamide O atom in the apical position. The Cu···Cu distance is 5.1492 (18) Å.

Comment

In the last few decades, the chemistry of bisbidentate oxalate complexes has become an active area of research, with interest arising from the various structural features of these compounds (Román *et al.*, 1996; Girerd *et al.*, 1980; Pellaux *et al.*, 1997; Coronado *et al.*, 1996) and their applications in areas such as biological chemistry (Cleare, 1974), catalysis (Sinha & Shankar, 1993; Díaz-Guemes *et al.*, 1987), photochemistry (Hauser *et al.*, 1996) and magnetochemistry (Larionova *et al.*, 1998; Decurtins *et al.*, 1996; Kahn, 1993). In the process of fabricating these kinds of complexes, some organic N-donors, such as 2,2′-bipyridine and related species (Hagrman *et al.*, 1999; Fu *et al.*, 2001), have often been chosen as rigid ligands to bind the metal centres. In particular, binuclear Cu^{II} complexes with bis(bidentate) bridging ligands have been investigated, both experimentally and theoretically (Kahn, 1985; Charlot *et al.*, 1984; Julve *et al.*, 1984). However, there is only one paper to date describing a compound with *N*,*N*-dimethylformamide (DMF) coordinating to the Cu centre (Foxon *et al.*, 2004), among the many crystal structures of oxalate-bridged binuclear complexes. Here, we report the structure of the title compound, (I).



(I)

Compound (I) consists of a $[Cu_2(ox)(bpy)_2(DMF)_2]^{2+}$ (bpy is 2,2′-bipyridine and ox is oxalate) cation and two perchlorate anions (Fig. 1). The binuclear complex cation has an inversion

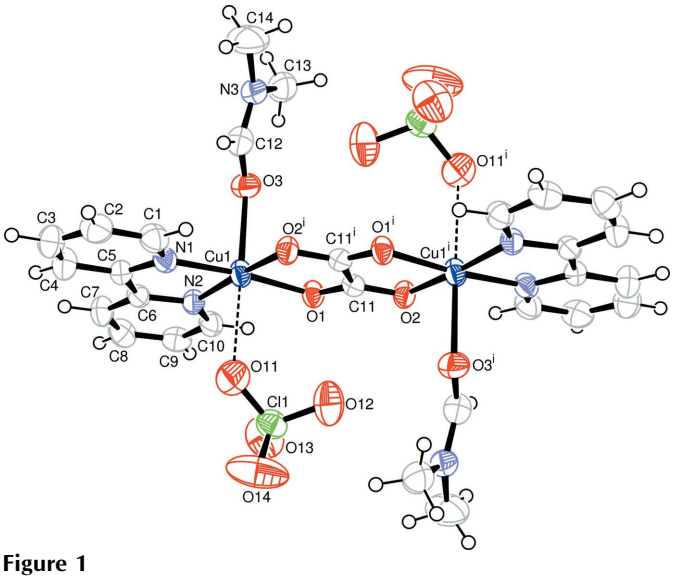


Figure 1
The molecular structure of (I), with 50% probability displacement ellipsoids. Dashed lines indicate weak bonds. [Symmetry code: (i) $2-x$, $-y$, $-z$.]

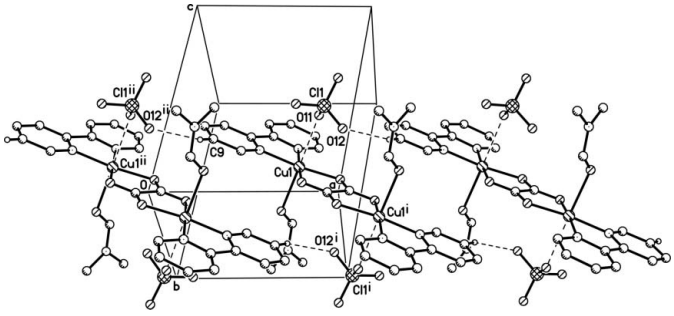


Figure 2
The one-dimensional structure of (I) extending along the *a* axis, with the complexes bridged by perchlorate anions *via* weak bond interactions and non-classical hydrogen bonds. Dashed lines indicate weak interactions. [Symmetry codes: (i) $2-x$, $-y$, $-z$; (ii) $x-1$, y, z.]

centre at the midpoint of the C11—C11^{i} [symmetry code: (i) $2-x$, $-y$, $-z$] bond of the ox ligand. The Cu1···Cu1^{i} distance is 5.1492 (18) Å, which compares well with similar types of reported binuclear oxalate-bridged complexes (Kahn, 1985; Charlot *et al.*, 1984; Julve *et al.*, 1984). The coordination geometry of the Cu atom is square-pyramidal, with atoms O1/O2^{i}/N1/N2 from the ox and bpy ligands in the basal plane and atom O3 from DMF in the apical position. The Cu atom is displaced 0.0988 (11) Å from the basal plane towards atom O3. The in-plane Cu—O bond distances average 1.974 (2) Å and the Cu—N bond distances average 1.980 (3) Å, while the apical Cu—O3 bond distance is 2.335 (2) Å (Table 1). A longer Cu—O distance of 2.653 (3) Å between atom Cu1 and perchlorate atom O11 *trans* to O3 implies a weak bonding interaction.

The perchlorate anions play an important role in the crystal structure of (I). As well as the weak bonding interactions with Cu atoms mentioned above, they are involved in non-classical hydrogen bonds (Table 2) with neighbouring bpy ligands, and thus they bridge the complexes into one-dimensional chains extending along the *a* axis (Fig. 2). There is offset π–π stacking between the two bpy ligands related by an inversion centre, the nearest separation being 3.485 (5) Å for C3···C3($1-x$, $-y$, $1-z$). These stacking and dipole attractions between the DMF ligands dominate the interchain interactions.

Experimental

All chemicals and solvents used for the synthesis were of reagent grade. A methanol solution (5 ml) of $Cu(ClO_4)_2\cdot 6H_2O$ (0.0742 g, 0.2 mmol) was added to a stirred aqueous solution (10 ml) of $K_2C_2O_4\cdot H_2O$ (0.184 g, 1 mmol). The mixture was heated at 333 K for 1 h. Then, a methanol solution (5 ml) of bpy (0.0312 g, 0.2 mmol) and DMF (5 ml) were added to the above mixture in turn. The resulting solution was heated at 333 K for 4 h. The precipitate was filtered off, washed with cold water, methanol and diethyl ether in turn, and then redissolved in water. Blue crystals of (I) were obtained from the solution by slow evaporation (yield 0.0174 g, 60%).

Crystal data

$[Cu_2(C_2O_4)(C_{10}H_8N_2)_2(C_3H_7NO)_2](ClO_4)_2$
$M_r = 872.58$
Triclinic, $P\overline{1}$
$a = 8.518$ (4) Å
$b = 9.361$ (4) Å
$c = 11.056$ (5) Å
$\alpha = 82.932$ (7)°
$\beta = 78.760$ (7)°
$\gamma = 83.165$ (6)°
$V = 853.9$ (7) Å^3
$Z = 1$
$D_x = 1.697$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.48$ mm^{-1}
$T = 293$ (2) K
Block, blue
0.30 × 0.20 × 0.15 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.665$, $T_{max} = 0.809$
4593 measured reflections
3046 independent reflections
2395 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 25.2°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.093$
$S = 1.05$
3046 reflections
237 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.7011P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.974 (2)	Cu1—N2	1.977 (3)
Cu1—O2^{i}	1.973 (2)	Cu1—O3	2.335 (2)
Cu1—N1	1.983 (3)	C11—C11^{i}	1.525 (6)
N2—Cu1—N1	82.11 (11)	N2—Cu1—O3	92.17 (10)
O2^{i}—Cu1—O1	84.91 (8)	O1—Cu1—O3	90.66 (9)
O1—Cu1—N1	174.36 (10)	O2^{i}—Cu1—O3	93.69 (9)
O2^{i}—Cu1—N2	173.75 (10)	C12—O3—Cu1	122.0 (2)
N1—Cu1—O3	94.95 (10)	O3—C12—N3	125.9 (3)
Cu1—O3—C12—N3	163.9 (3)		

Symmetry code: (i) $-x+2$, $-y$, $-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9···O12^{ii}	0.93	2.60	3.465 (5)	155

Symmetry code: (ii) $x-1, y, z$.

All H atoms were placed in calculated positions, with C—H distances of 0.93 Å (Csp^2—H) or 0.96 Å (CH_3), and were included in the final cycles of refinement as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}$(methyl C).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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