metal-organic papers

μ-Oxalato-$\kappa^4O^1,O^2:O^{1'},O^{2'}$-bis{[N,N′-bis(pyridin-2-ylmethylene)propane-1,2-diamine-κ^4-N,N′,N″,N‴]-copper(II)} bis(perchlorate)

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In the centrosymmetric dinuclear title complex, $[Cu_2(C_2O_4)(C_{15}H_{16}N_4)_2](ClO_4)_2$, each Cu^{II} ion is in an elongated octahedral environment, coordinated by two oxalate O atoms and four N atoms from the tetradentate ligand. One O atom and three N atoms are in the equatorial plane, and another O atom and one N atom are in axial sites. Each copper ion is bound to two O atoms from the two different carboxylate groups of the oxalate ligands, with a Cu···Cu distance of 5.6623 (16) Å. The anions lie on twofold rotation axes.

Comment

Dinuclear Cu^{II} compounds are of considerable current interest in relation to the nature of magnetic exchange interactions between metal ions through extended bridging ligands, since they provide the simplest case of magnetic interaction involving only two unpaired electrons (Kahn, 1993), and also as models for the active sites of some metalloenzymes (Holm et al., 1996). Owing to the proven ability of the oxalate ligand to propagate magnetic interactions and its varied bridging modes for the construction of new topologies, the oxalato-bridged Cu^{II} dinuclear system has been one of the most actively pursued topics (Tuero et al., 1991; Oshio & Nagashima, 1992; Chattopadhyay et al., 1995; Mandal et al., 2005). Employing a Schiff base compound N,N′-bis(pyridin-2-ylmethylene)propane-1,2-diamine, BPM, we obtained the title oxalato-bridged dicopper complex, (I).
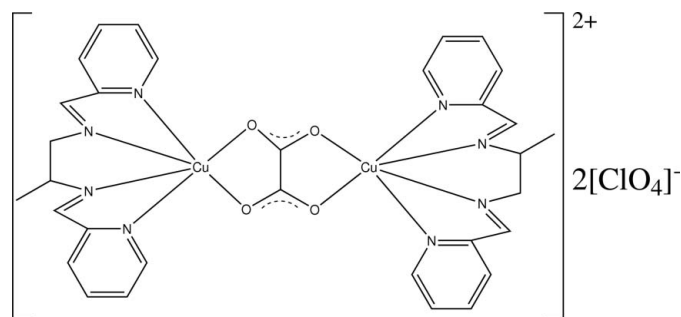
(I)

The structure of (I) consists of $[Cu_2(L)_2(ox)]^{2+}$ cations and uncoordinated perchlorate anions (Fig. 1). The cation is centrosymmetric, while both anions lie on crystallographic twofold rotation axes. The geometry about each copper(II) center is approximately octahedral, the coordinating atoms being two atoms of the oxalate bridge and the four N atoms of
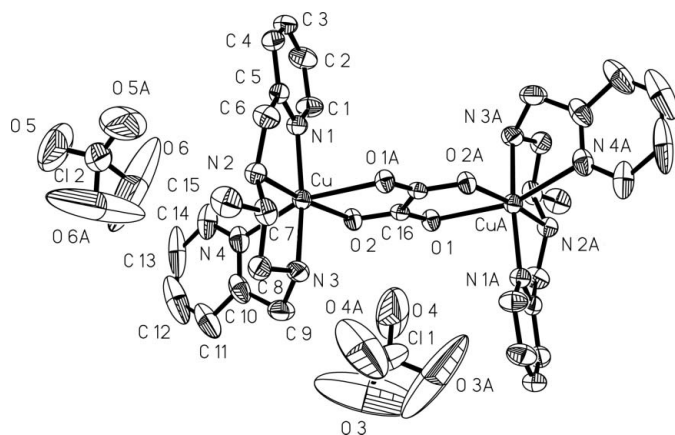
Figure 1
The molecular structure of the title complex. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been excluded for clarity. [Symmetry code: (A) $-x$, $1 - y$, $1 - z$.]

the pyridyl and amino groups of the BPM ligand. The isomer isolated is the α,α form in which the pyridine N atoms are *trans* at both metal centers.

The Cu···Cu separation of 5.6623 (16) Å is slightly longer than the values of 5.244–5.52 Å found in analogous dicopper(II) complexes (Tamaki *et al.*, 1992; Bu *et al.*, 2000; Coronado *et al.*, 2006; Wong *et al.*, 2006).

The axial bonds, at 2.309 (4) and 2.405 (3) Å, are markedly longer than the equatorial bonds (Table 1). Since this complex contains a d^9 ion, this observed lengthening of the axial bonds is attributable to a Jahn–Teller distortion, with an axially compressed (2+4) geometry rather than the more common axially elongated (4+2) structure (Glerup *et al.*, 1995).

Experimental

The Schiff base compound, BPM, was synthesized according to the literature method (Fischer *et al.*, 1984). Copper(II) perchlorate hexahydrate (2.3 mmol), BPM (2.3 mmol) and sodium oxalate (1.2 mmol) were mixed in water (15 ml). After 30 min a blue microcrystalline precipitate of complex (I) was filtered off. From the mother liquor, blue single crystals suitable for X-ray crystallography were collected two weeks later.

Crystal data

[Cu2(C2O4)(C15H16N4)2](ClO4)2	$V = 2026.3$ (7) Å³
$M_r = 918.64$	$Z = 2$
Monoclinic, $P2/c$	Mo $K\alpha$ radiation
$a = 11.339$ (2) Å	$\mu = 1.25$ mm⁻¹
$b = 9.2995$ (19) Å	$T = 293$ K
$c = 19.395$ (4) Å	$0.40 \times 0.25 \times 0.15$ mm
$\beta = 97.79$ (3)°	

Data collection

Rigaku R-AXIS RAPID IP diffractometer	16951 measured reflections
	4599 independent reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	2290 reflections with $I > 2\sigma(I)$
$T_{min} = 0.694$, $T_{max} = 0.829$	$R_{int} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$	255 parameters
$wR(F^2) = 0.147$	H-atom parameters constrained
$S = 0.86$	$\Delta\rho_{max} = 0.64$ e Å⁻³
4599 reflections	$\Delta\rho_{min} = -0.45$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Cu—O2	1.979 (3)	Cu—O1ⁱ	2.405 (3)
Cu—N2	2.013 (3)	O1—C16	1.227 (4)
Cu—N1	2.021 (3)	O2—C16	1.284 (4)
Cu—N3	2.051 (3)	C16—C16ⁱ	1.549 (7)
Cu—N4	2.309 (4)		
O2—Cu—N2	171.47 (12)	N3—Cu—N4	77.26 (16)
O2—Cu—N1	97.43 (12)	O2—Cu—O1ⁱ	75.88 (10)
N2—Cu—N1	81.31 (13)	N2—Cu—O1ⁱ	95.65 (12)
O2—Cu—N3	95.76 (13)	N1—Cu—O1ⁱ	89.51 (12)
N2—Cu—N3	85.18 (14)	N3—Cu—O1ⁱ	90.62 (12)
N1—Cu—N3	166.43 (14)	N4—Cu—O1ⁱ	161.76 (13)
O2—Cu—N4	91.63 (12)	O1—C16—O2	124.6 (3)
N2—Cu—N4	96.84 (13)	O1—C16—C16ⁱ	119.3 (4)
N1—Cu—N4	105.48 (16)	O2—C16—C16ⁱ	116.1 (4)

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

H atoms were positioned geometrically (aromatic C—H = 0.93 Å, aliphatic C—H = 0.96–0.98 Å) and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$ [$1.5U_{eq}(C)$ for methyl H].

Data collection: *PROCESS-AUTO* (Molecular Structure Corporation, 1994); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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