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Heptapyridinebis(μ-dimethylglyoximato)-tricopper(II) diperchlorate: a novel trinuclear copper complex bridged by glyoximate groups

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Key indicators

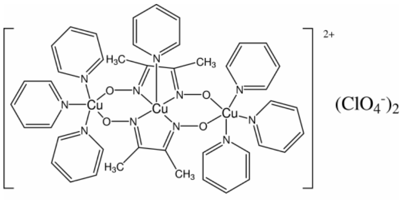
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.051
wR factor = 0.082
Data-to-parameter ratio = 22.8

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

The title compound, $[Cu_3(C_4H_6N_2O_2)_2(C_5H_5N)_7](ClO_4)_2$, is a trinuclear Cu^{II} complex bridged by two glyoximate groups. The central Cu and the pyridine N atom bonded to it lie on a twofold axis. The geometry around each Cu atom is a distorted square pyramid.

Comment

Current research concerning the structures and properties of polynuclear transition-metal compounds is aimed at understanding the structural and chemical features governing electronic exchange coupling through multi-atom bridging ligands (Zhan *et al.*, 1999; Cervera *et al.*, 1997; Ruiz *et al.*, 1997, 1998; Zhang *et al.*, 1996). This problem has important implications for research topics such as the nature of orbital interactions, electron transfer in redox reaction precursors and biological electron-transport chains (Vernik & Stynes, 1998; Burdinski *et al.*, 1998).



(I)

The chemistry of bis-dioximate complexes of transition metal ions has been attracting continuous attention because of their importance with reference to models for vitamin B12 (Polson *et al.*, 1997), hydrogen bonding between molecules and metal–metal interactions (Ruiz *et al.*, 1993). The oximate group can behave as a bridge binding one metal atom through the imine N atom and another one through the deprotonated O atom to generate dinuclear, trinuclear, tetranuclear and polymeric chain metal complexes (Chen *et al.*, 2003; Liu *et al.*, 2002; Li *et al.*, 2002). Although many bidentate and tridentate ligands are utilized as terminal ligands to synthesize these complexes (Burdinski *et al.*, 2001; Birkelbach *et al.*, 1998), the chemistry of bis-dioximate complexes with monodentate ligands has not been much explored (Fraser *et al.*, 1994; Kubiak *et al.*, 1995; Solans *et al.*, 1996). With this idea in mind, we designed and synthesized a copper(II) trinuclear complex, (I), with the double oximate bridges in *cis* arrangement, and pyridine as the terminal ligands. To the best of our knowledge, it is the first structurally characterized copper compound bridged by glyoximate groups in which a monodentate ligand is employed as terminal ligand. Here we report the synthesis and molecular structure of (I).

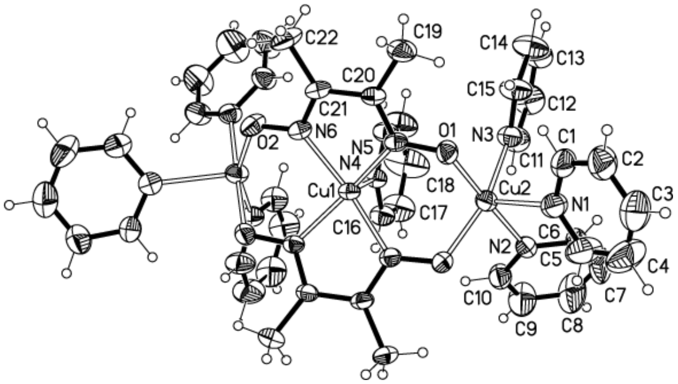


Figure 1
A view of the complex cation in (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

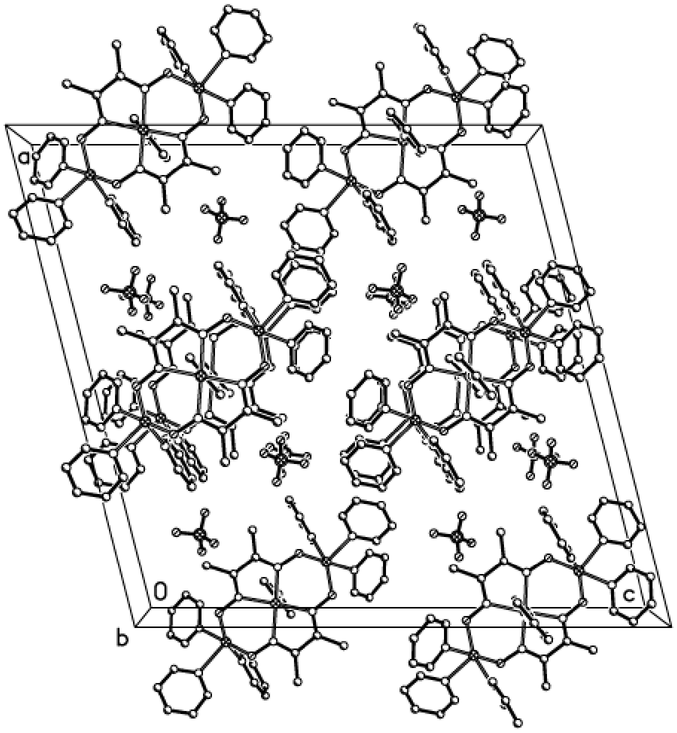


Figure 2
The packing of (I), viewed along the *b* axis.

The crystal structure of (I) consists of a discrete dicationic trinuclear unit (Fig. 1) and two uncoordinated perchlorate anions (Fig. 2), the asymmetric unit consisting of half the chemical formula unit; the cation has crystallographic twofold rotation symmetry. The $[Cu(dmg)_2]^{2-}$ dianion bridges two terminal copper ions through its deprotonated oxime O atoms, with a Cu1$\cdots$Cu2 separation of 3.470 (1) Å. The coordination geometry around the three Cu ions can best be described as distorted square pyramidal. For Cu1, four oxime N atoms comprise the basal plane, and pyridine atom N4 occupies the apical position [2.124 (4) Å for Cu1—N4]. For Cu2, two pyridine N atoms and two oximate O atoms comprise the corresponding basal plane, and the apical position of the square pyramid is occupied by weakly bound atom N1 [2.290 (3) Å for Cu2—N1]. For the basal plane of Cu2, the Cu—O bond distances [1.919 (2)–1.929 (2) Å] are slightly shorter than those of Cu—N [2.045 (3)–2.085 (3) Å], as expected from electronegativity considerations. The four basal donor atoms around each Cu atom are nearly coplanar [maximum deviations are 0.03 Å at N5 and N6, and 0.20 Å at O2($1 - x, y, \frac{1}{2} - z$), respectively]. The dihedral angle between the basal planes of Cu1 and Cu2 is 63.09 (8)°. The atoms Cu1 and Cu2 lie out of their least-squares basal planes by 0.37 (2) and 0.22 (2) Å, respectively.

Experimental

A solution (10 ml) of dimethylglyoxime (70 mg, 0.6 mmol) in water was added to an aqueous solution (5 ml) of $Cu(ClO_4)_2.6H_2O$ (111 mg, 0.3 mmol) under vigorous stirring in a round-bottomed flask. After 0.5 h of stirring, a blue aqueous solution (10 ml) containing $Cu(ClO_4)_2\cdot6H_2O$ (222 mg, 0.6 mmol) and several drops of pyridine was added. The mixture was filtered and slowly evaporated to generate black single crystals of (I) suitable for X-ray diffraction analysis (yield 30% based on copper).

Crystal data

$[Cu_3(C_4H_6N_2O_2)_2(C_5H_5N)_7](ClO_4)_2$
$M_r = 1171.47$
Monoclinic, $C2/c$
$a = 24.615\ (5)$ Å
$b = 8.3158\ (17)$ Å
$c = 25.469\ (5)$ Å
$\beta = 104.48\ (3)°$
$V = 5047.7\ (19)$ Å^3
$Z = 4$
$D_x = 1.541$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3680 reflections
$\theta = 2.6$–$25.2°$
$\mu = 1.43$ mm^{-1}
$T = 293\ (2)$ K
Prism, black
0.25 × 0.20 × 0.15 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.717$, $T_{max} = 0.807$
19837 measured reflections
7370 independent reflections
2919 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 30°$
$h = -34 \rightarrow 34$
$k = -10 \rightarrow 11$
$l = -35 \rightarrow 34$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.082$
$S = 1.07$
7345 reflections
322 parameters
H-atom parameters constrained
$w = \{\exp[1.50(\sin\theta/\lambda)^2]\}/[\sigma^2(F_o^2) + (0.001P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N5	1.986 (3)	Cu2—O2^i	1.929 (2)
Cu1—N6	1.999 (3)	Cu2—N2	2.045 (3)
Cu1—N4	2.124 (4)	Cu2—N3	2.085 (3)
Cu2—O1	1.919 (2)	Cu2—N1	2.290 (3)
N5—Cu1—N5^i	156.84 (17)	O1—Cu2—O2^i	94.37 (11)
N5—Cu1—N6	80.65 (12)	O1—Cu2—N3	88.86 (12)
N5^i—Cu1—N6	95.48 (12)	O2^i—Cu2—N3	155.43 (12)
N6—Cu1—N6^i	160.75 (17)	N2—Cu2—N3	88.50 (13)
N5—Cu1—N4	101.58 (8)	O1—Cu2—N1	87.55 (12)
N6—Cu1—N4	99.62 (9)		

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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