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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.013 \text{ \AA}$
H-atom completeness 92%
Disorder in solvent or counterion
R factor = 0.056
wR factor = 0.159
Data-to-parameter ratio = 11.9

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

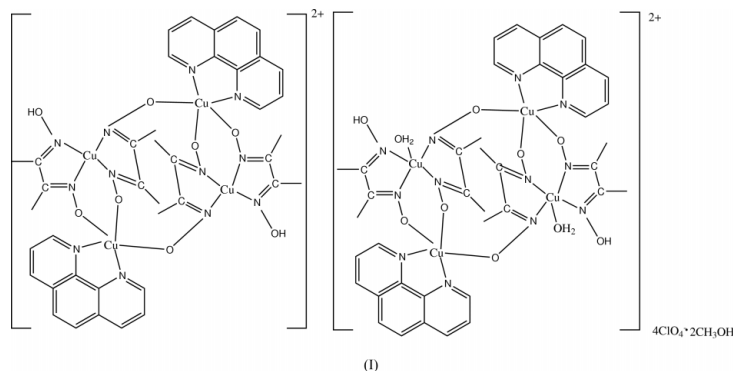
A new tetranuclear copper(II) complex bridged by dimethylglyoxime

The title tetranuclear copper(II) complex, diaquabis[dimethylglyoximato(2-)]bis[dimethylglyoximato(1-)]bis(phenanthroline) tetracopper(II)bis[phenanthroline] tetraperchlorate methanol disolvate, $[\text{Cu}_4(\text{dmg})_2(\text{Hdmg})_2(\text{phen})_2(\text{H}_2\text{O})_2][\text{Cu}_4(\text{dmg})_2(\text{Hdmg})_2(\text{phen})_2](\text{ClO}_4)_4 \cdot 2\text{CH}_3\text{OH}$ (dmg = dimethylglyoximate and phen = 1,10-phenanthroline) or $[\text{Cu}_4(\text{C}_4\text{H}_6\text{N}_2\text{O}_2)_2(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2][\text{Cu}_4(\text{C}_4\text{H}_6\text{N}_2\text{O}_2)_2(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]_4 \cdot 2\text{CH}_3\text{O}$, with cations containing dimethylglyoximate bridges, has been synthesized and its structure determined by X-ray single-crystal diffraction methods. The Cu atoms have two different coordination geometries, distorted square pyramidal and distorted square planar. There are two different cations, each lying on an inversion centre; one contains water molecules coordinated to two of the Cu atoms.

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Comment

It is well known that dioxime ligands have a remarkable capability to bind metal ions through the imino N atom and the deprotonated O atom, which can coordinate to metal ions in versatile ways as a bridging ligand. Dimethylglyoxime has the potential to form tridentate as well as tetradentate ligands. Recent studies have shown that dimethylglyoxime is more likely to act as a bridge between two metal ions than as a terminal ligand (Liu *et al.*, 2002; Birkelbach *et al.*, 1998; Burdinski *et al.*, 1998). In addition, 1,10-phenanthroline has received much attention owing to its strong coordination capability and simple coordination mode derived from two N



atoms. Recent reports include those by Chen *et al.* (2003), Wang *et al.* (2002), Devi & Zubieta (2003), Clarke *et al.* (2003) and Guo *et al.* (2002). In order to investigate further the versatility of oximes in coordination chemistry and throw further light on such co-ligand systems, we designed and successfully synthesized a new tetranuclear copper(II) complex bridged by dimethylglyoxime. We report in this paper the crystal structure of the title compound, (I).

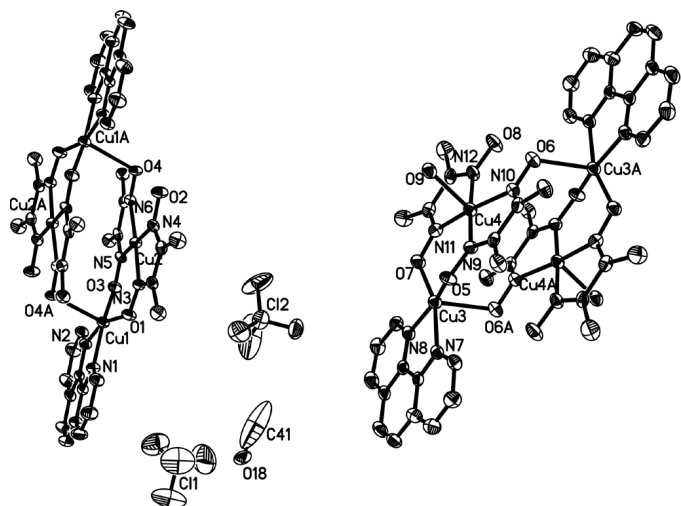


Figure 1
ORTEP (Johnson, 1976) drawing of (I), with 35% probability displacement ellipsoids, showing the atomic numbering scheme. The suffix *A* denotes symmetry code (i) of Table 1 for the left-hand cation and symmetry code (ii) for the right-hand cation.

Single-crystal X-ray diffraction results show that complex (I) consists of two tetranuclear cations, *viz.* $[\text{Cu}_4(\text{dmg})_2(\text{Hdmg})_2(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Cu}_4(\text{dmg})_2(\text{Hdmg})_4(\text{phen})_2]^{2-}$, four uncoordinated perchlorate anions, and two uncoordinated CH_3OH molecules in the unit cell, the asymmetric unit consisting of half of the total chemical formula. Complex (I) is shown in Fig. 1. The two tetranuclear complex cations are on centres of symmetry. Atoms Cu3 and Cu4 are both five-coordinate; their coordination geometry can be described as distorted square-pyramidal, but the coordination environments are very different. Cu3 is coordinated by two phen N atoms and three O atoms of three different dmg groups, with the apex of the pyramid occupied by an O atom from a dmg group. In contrast, Cu4 is coordinated by four N atoms from two dmg groups, the apex of the pyramid being an aqua O atom. The Cu3–O6ⁱⁱ bond distance is 2.372 (5) Å (symmetry code as in Table 1). The bond distances between Cu3 and O7, O5, N8 and N7 are 1.919 (5), 1.947 (5), 2.066 (5) and 2.033 (6) Å, respectively. The Cu3–O5 bond distance is not significantly different from that of Cu3–O7, and the other two bond distances are very similar. The bond distances between Cu4 and N9, N10, N11, N12, and O9 are 1.961 (6), 1.963 (6), 1.977 (6), 1.967 (6) and 2.287 (5) Å, respectively. The Cu4–N9 bond distance is not significantly different from that of Cu4–N10, and the Cu4–N11 bond distance is not significantly different from that of Cu4–N12. In this tetranuclear cation, all four Cu^{2+} ions have the coordination number 5, which is normal for Cu(II).

It is interesting that there are two coordination modes for the Cu^{2+} ion in the other tetranuclear unit $[\text{Cu}_4(\text{dmg})_2(\text{Hdmg})_2(\text{phen})_2]$ (shown in the left of Fig. 1). From Fig. 1, it can be observed that there is also a centre of symmetry in this cation. The coordination of Cu1 is like that of Cu3. However, unusually, Cu2 has a completely different coordination geometry from the aforementioned atoms, which can be

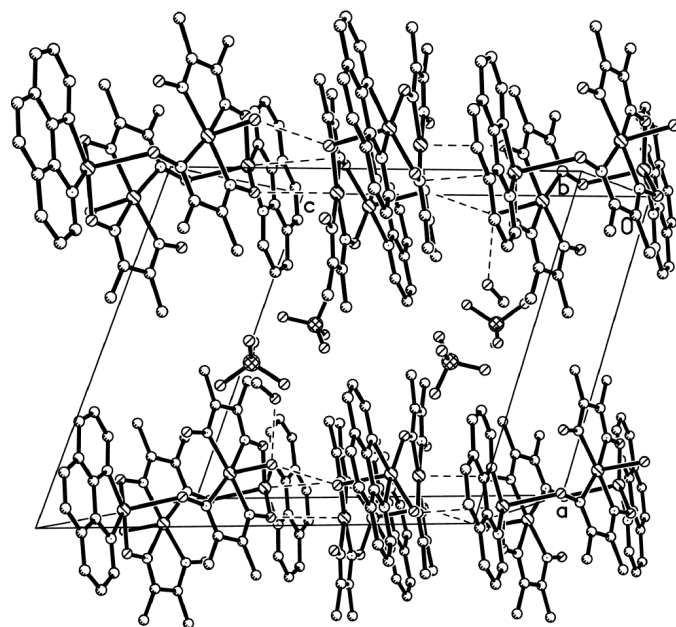


Figure 2
The packing, viewed along the *b* direction.

described as distorted square planar, with the Cu^{2+} ion coordinated by four N atoms from two dmg groups. The Cu1–O4ⁱ distance is 2.453 (5) Å. All four Cu^{2+} ions of this tetranuclear unit have normal coordination numbers for Cu (4 or 5); this along with the bond distances suggests that cation Cu1A is coordinated by O4.

Fig. 2 shows the packing arrangement of the complex in unit cell. The two cations are arranged alternately.

In summary, the most notable features of complex (I) are the versatile coordination modes of the dmg groups and their strong bridging coordination capability. In this complex, the dmg groups display two kinds of coordination modes, *viz.* as tri-dentate (two N atoms and one O atom) and tetradentate (two N atoms and two O atoms) ligands. In the structure, tridentate dmg groups serve as bridging ligands, connecting two Cu^{2+} ions, while tetradentate dmg groups serve as bridging ligands connecting three Cu^{2+} ions. It has long been known that the NO oxime group has a remarkable efficiency in mediating magnetic interactions when it acts as a bridging ligand (Ruiz *et al.*, 1997). It is therefore no surprise that this complex encourages us to find a new approach for the design of inorganic ferromagnetic materials.

Experimental

To a solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) and phen (0.3 mmol) in water and methanol (20 ml) (water:methanol ratio 0.6:1), H_2dmg (0.6 mmol) was added. The mixture was stirred for 2 h in air before standing at room temperature for 30 min. The resulting dark-blue solution was then filtered. The final solution was allowed to evaporate at room temperature. After one day, blue crystals of the complex suitable for X-ray analysis were obtained. They were collected by filtration and air-dried. All chemicals used in this experiment were purchased commercially and used without further purification.

Crystal data

$[\text{Cu}_4(\text{C}_4\text{H}_6\text{N}_2\text{O}_2)_2(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{-}(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{-}[\text{Cu}_4(\text{C}_4\text{H}_6\text{N}_2\text{O}_2)_2(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{-}(\text{C}_{12}\text{H}_8\text{N}_2)_2](\text{ClO}_4)_4\cdot 2\text{CH}_4\text{O}$	$V = 2545.8 (11) \text{ \AA}^3$
$M_r = 2643.94$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.725 \text{ Mg m}^{-3}$
$a = 13.922 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 14.841 (4) \text{ \AA}$	Cell parameters from 995 reflections
$c = 15.024 (4) \text{ \AA}$	$\theta = 2.9\text{--}24.4^\circ$
$\alpha = 65.547 (5)^\circ$	$\mu = 1.84 \text{ mm}^{-1}$
$\beta = 70.265 (5)^\circ$	$T = 293 (2) \text{ K}$
$\gamma = 67.182 (4)^\circ$	Plate, blue
	$0.32 \times 0.18 \times 0.04 \text{ mm}$

Data collection

Bruker SMART CCD diffractometer	8911 independent reflections
φ and ω scans	5441 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$R_{\text{int}} = 0.040$
$T_{\text{min}} = 0.675, T_{\text{max}} = 0.929$	$\theta_{\text{max}} = 25.0^\circ$
13013 measured reflections	$h = -16 \rightarrow 16$
	$k = -9 \rightarrow 17$
	$l = -14 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 4P]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.159$	$(\Delta/\sigma)_{\text{max}} = 0.119$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.96 \text{ e \AA}^{-3}$
8911 reflections	$\Delta\rho_{\text{min}} = -0.83 \text{ e \AA}^{-3}$
749 parameters	
H-atom parameters constrained	

Table 1

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

Cu1—O1	1.900 (5)	Cu3—O5	1.947 (5)
Cu1—O3	1.917 (5)	Cu3—N7	2.033 (6)
Cu1—N2	2.037 (5)	Cu3—N8	2.066 (5)
Cu1—N1	2.042 (6)	Cu3—O6 ⁱⁱ	2.372 (5)
Cu1—O4 ⁱ	2.453 (5)	Cu4—N9	1.961 (6)
Cu2—N5	1.957 (5)	Cu4—N10	1.963 (6)
Cu2—N6	1.959 (5)	Cu4—N12	1.967 (6)
Cu2—N3	1.962 (5)	Cu4—N11	1.977 (6)
Cu2—N4	1.962 (5)	Cu4—O9	2.287 (5)
Cu3—O7	1.919 (5)		
O1—Cu1—O3	103.55 (19)	O5—Cu3—N7	88.5 (2)
O1—Cu1—N2	160.4 (2)	O7—Cu3—N8	85.6 (2)
O3—Cu1—N2	86.7 (2)	O5—Cu3—N8	161.3 (2)
O1—Cu1—N1	86.1 (2)	N7—Cu3—N8	80.6 (2)
O3—Cu1—N1	165.0 (2)	O7—Cu3—O6 ⁱⁱ	102.5 (2)
N2—Cu1—N1	80.9 (2)	O5—Cu3—O6 ⁱⁱ	96.1 (2)
O1—Cu1—O4 ⁱ	97.27 (19)	N7—Cu3—O6 ⁱⁱ	90.8 (2)
O3—Cu1—O4 ⁱ	93.24 (18)	N8—Cu3—O6 ⁱⁱ	99.1 (2)
N2—Cu1—O4 ⁱ	98.8 (2)	N9—Cu4—N10	81.4 (2)
N1—Cu1—O4 ⁱ	96.9 (2)	N9—Cu4—N12	176.6 (3)
N5—Cu2—N6	81.2 (2)	N10—Cu4—N12	95.8 (2)
N5—Cu2—N3	102.4 (2)	N9—Cu4—N11	102.7 (2)
N6—Cu2—N3	174.5 (2)	N10—Cu4—N11	169.4 (2)
N5—Cu2—N4	176.6 (2)	N12—Cu4—N11	79.7 (2)
N6—Cu2—N4	96.4 (2)	N9—Cu4—O9	94.3 (2)
N3—Cu2—N4	80.2 (2)	N10—Cu4—O9	91.4 (2)
O7—Cu3—O5	101.6 (2)	N12—Cu4—O9	87.7 (2)
O7—Cu3—N7	162.2 (2)	N11—Cu4—O9	98.0 (2)

Symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $-x, -y, -z$.

Table 2

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

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O2—H2A \cdots O4	0.82	1.79	2.575 (7)	161
O8—H8A \cdots O6	0.82	1.76	2.549 (7)	162
C13—H13A \cdots O1	0.96	2.34	2.762 (9)	106
C16—H16A \cdots O2	0.96	2.35	2.775 (9)	106
C17—H17A \cdots O3	0.96	2.40	2.742 (9)	101
C33—H33C \cdots O5	0.96	2.38	2.795 (9)	105
C40—H40A \cdots O8	0.96	2.39	2.794 (10)	105
C22—H22 \cdots O16 ⁱⁱ	0.93	2.35	3.198 (15)	152
O9—H109 \cdots O4 ⁱⁱⁱ	0.85	1.94	2.788 (7)	178
O9—H209 \cdots O18 ⁱⁱⁱ	0.85	1.92	2.754 (10)	168

Symmetry codes: (ii) $x - 1, y, z$; (iii) $x, y - 1, z$.

H atoms of organic legends were positioned geometrically and the coordinates for water H atoms were calculated using the program *HYDROGEN* (Nardelli, 1999). They were allowed to ride on their parent atoms in the final refinement. One of the perchlorates is orientationally disordered and the solvent molecule, methanol, is positionally disordered so that the displacement parameters of the involved atoms are somewhat large and the distance between C41 and C42 is too short. The H atoms of the disordered methanol were not included in the structure refinement. The largest 10 peaks in the final difference Fourier map were located around the disordered methanol and perchlorate moieties, except one which was located near O6, to show another potential position of H8A.

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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