

A novel one-dimensional zigzag coordination polymer of copper(II) with dimethylglyoxime

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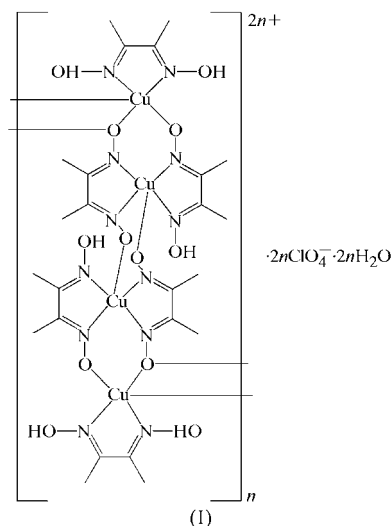
A novel metal-organic based polymeric complex, namely *catena*-poly[[bis(μ_4 -dimethylglyoximate)bis(μ_2 -dimethylglyoximate)bis(dimethylglyoximate)tetracopper(II)] diperchlorate dihydrate], $\{[\text{Cu}_4(\text{dmg})_2(\text{Hdmg})_2(\text{H}_2\text{dmg})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}\}_\infty$ (H_2dmg is dimethylglyoxime, $\text{C}_2\text{H}_8\text{N}_2\text{O}_2$), has been synthesized and characterized by single-crystal X-ray diffraction methods. The complex is a one-dimensional zigzag chain coordination polymer, in which the tetranuclear repeat unit is a centrosymmetric Cu_4 moiety coordinated to dimethylglyoxime ligands only. These units are linked by double $\text{Cu}-\text{O}-\text{Cu}$ bridges in a centrosymmetric rectangular junction.

Comment

Self-assembly processes involving metal ions have attracted much attention in the past few years because a metal ion together with its ligand contains a variety of structural information to guide the self-assembly reaction (Lehn, 1995). Recent attention has been focused particularly on the construction of various supramolecular structures. In these structures, the very simple topological types of coordination arrays are one-dimensional architectures, such as one-dimensional zigzag chains (Mimura *et al.*, 1998; Colacio *et al.*, 1999) and a one-dimensional helix (Ranford *et al.*, 1999). The most commonly used strategy to obtain these extended structures is to employ appropriate bridging ligand which are capable of linking to several metal centers through direct bond formation.

It is well known that the oximate group ($=\text{N}-\text{O}-$) can function as a bridging ligand to link two metal ions through the imine N atom and the deprotonated O atom, and this group can coordinate with metal ions in versatile ways. Dimethylglyoxime (H_2dmg) has four potential donor sites. Framework molecular models show that it is more likely to act as a bridging ligand between two metal ions than as a terminal ligand

(Cervera *et al.*, 1997; Ruiz *et al.*, 1997). Recently, several groups, including our own, have reported the syntheses, X-ray crystal structure analyses and SQUID (superconducting quantum interference device) measurements of complicated complexes of transition metals using this bridging ligand (Chen *et al.*, 2003; Li *et al.*, 2002; Liu *et al.*, 2002; Zhang *et al.*, 2003). In this present contribution, we have extended our work, using this ligand to form one-dimensional zigzag chains containing multidentate dimethylglyoxime. In this paper, we report the synthesis, structure and spectroscopic properties of the title compound, *viz.* $\{[\text{Cu}_4(\text{dmg})_2(\text{Hdmg})_2(\text{H}_2\text{dmg})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}\}_\infty$ (I).



Selected geometric parameters are listed in Table 1. The principal feature of the structure of (I) is polymeric chains extending along $[\bar{1}10]$. The translationally repeating unit of these chains is a centrosymmetric sequence of four square-pyramidally coordinated Cu^{II} ions (Fig. 1). Atoms Cu1 and Cu1^{i} [symmetry code: (i) $-x, 2-y, 1-z$] are at the 1,4-positions of a centrosymmetric six-membered ring that is in a chair conformation. The two unique Cu atoms (Cu1 and Cu2) are also bridged in a six-membered ring but in a half-chair conformation. This tetranuclear unit is repeated by lattice translation, incorporating another center of symmetry, this time involving an oxo bridge (O3) between atoms Cu2 and Cu2^{ii} [symmetry code: (ii) $1-x, 1-y, 1-z$], giving a four-membered ring. This linking style forms an interesting Cu_2O_2 rectangular junction. To our knowledge, it is rare for metal coordination polymers to be connected through double bridges in a rectangular junction.

A remarkable feature of this coordination environment is that all ligands are either H_2dmg or one of its ions, and there are no coordinated water molecules; in this respect, compound (I) differs from all previously reported complexes containing dimethylglyoxime ligands. Among the six ligands in each tetranuclear moiety, two (H_2dmg) are bidentate terminal ligands, two (Hdmg^-) are tridentate bridging ligands within the moiety, and the other two (dmg^{2-}) are tetradentate but are bound to five different Cu atoms, because atom O3 bridges two Cu atoms.

As can be seen from Fig. 2, the entire polymer is a one-dimensional zigzag chain, which is built from Cu_4 moieties. In order to form double Cu—O—Cu bonding bridges, the symmetrical dinuclear Cu^{II} unit in the Cu_4 moiety adopts a chair form. The zigzag chain is further stabilized by intrachain hydrogen bonding by all three OH groups (Fig. 1 and Table 2). Both bonds of the bifurcated O6—H hydrogen bonds are intrachain, as is one of the bifurcated O5—H hydrogen bonds. The other component of the latter is to the uncoordinated water molecule (O11).

There are weak and ill-defined interactions between O atoms of the disordered perchlorate ion and both Cu atoms

near the sixth (vacant) octahedral coordination site of the Cu atoms. The uncoordinated water molecule is located in the interchain region.

The crystal structure of (I) exhibits some characteristics that differ from those of previously reported structures, *viz.* all coordination sites are occupied by dimethylglyoxime ligands, and double Cu—O—Cu bridges are connected in a rectangular form. This polymeric structure shows the amazing bridging ability and the fantastic coordinating versatility of the dimethylglyoxime ligand, which can play an important role in the direct assembly of coordination polymers. Further investigation is in progress.

Experimental

To prepare (I), H_2dmg (0.058 g, 0.5 mmol) and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.270 g, 0.75 mmol) were dissolved in methanol (10 ml) and a 0.5 M NaOH aqueous solution (1 ml) was added in order to deprotonate the oxime groups. The resulting mixture was stirred for 1 h at room temperature, and then filtered and evaporated also at room temperature. After 4 d, dark-red crystals of the complex suitable for single-crystal X-ray analysis were obtained. These were collected by suction filtration and dried in air (yield 60%). All chemicals used in this experiment were purchased commercially and used without further purification. Analysis found: C 25.56, H 3.77, N 14.10%; calculated: C 24.43, H 3.90, N 14.25%. IR (cm^{-1}): ν 1589 (s, C=N), 1201 (s, N—O), 1090 (s, Cl=O). The room-temperature value of $\chi_M T$ for (I) (χ_M is the molar magnetic susceptibility for a one-dimensional copper chain; *ca.* $0.454 \text{ cm}^3 \text{ K mol}^{-1}$) is higher than the expected value for a one-dimensional chain of copper(II) ions (*ca.* $0.374 \text{ cm}^3 \text{ K mol}^{-1}$), so the $\chi_M T$ value of (I) reveals a ferromagnetic coupling between the copper(II) ions.

Crystal data

$[\text{Cu}_4(\text{C}_2\text{H}_8\text{N}_2\text{O}_2)_2(\text{C}_2\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_2\text{H}_6\text{N}_2\text{O}_2)_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$
 $M_r = 1179.78$
 Triclinic, $P\bar{1}$
 $a = 9.458(3) \text{ \AA}$
 $b = 10.381(3) \text{ \AA}$
 $c = 12.838(3) \text{ \AA}$
 $\alpha = 88.402(5)^\circ$
 $\beta = 74.831(4)^\circ$
 $\gamma = 63.064(4)^\circ$
 $V = 1078.5(5) \text{ \AA}^3$

$Z = 1$
 $D_x = 1.817 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 1006 reflections
 $\theta = 2.5\text{--}26.4^\circ$
 $\mu = 2.16 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Prism, red
 $0.12 \times 0.10 \times 0.06 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.762$, $T_{\max} = 0.878$
 6254 measured reflections
 4356 independent reflections

3341 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\max} = 26.4^\circ$
 $h = -11 \rightarrow 11$
 $k = -9 \rightarrow 12$
 $l = -14 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.093$
 $S = 1.07$
 4356 reflections
 305 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.005P)^2 + 2.5P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.66 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.66 \text{ e \AA}^{-3}$

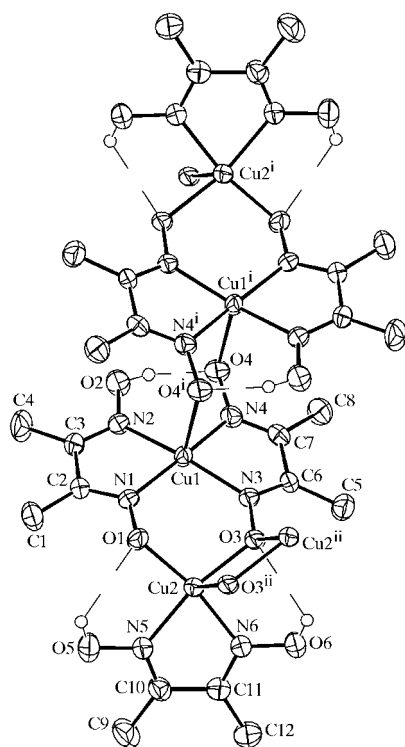


Figure 1

The centrosymmetric tetranuclear unit of (I), also showing one rectangular junction. Intrachain hydrogen-bond interactions ($\text{O6—H} \cdots \text{O1}^{\text{ii}}$ omitted) are shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level and the atom-numbering scheme is shown. Methyl-group H atoms, perchlorate ions and uncoordinated water molecules have been omitted. [Symmetry codes: (i) $-x, 2-y, 1-z$; (ii) $1-x, 1-y, 1-z$.]

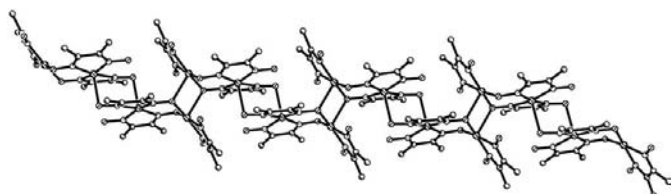


Figure 2

An extended view of the polymeric chain in (I). The rectangular junctions are one lattice repeat apart along $[\bar{1}10]$.

Table 1
Selected geometric parameters (Å, °).

Cu1—N4	1.965 (3)	Cu2—O1	1.941 (3)
Cu1—N2	1.966 (3)	Cu2—O3	1.961 (3)
Cu1—N3	1.973 (3)	Cu2—N6	1.997 (4)
Cu1—N1	1.984 (3)	Cu2—N5	2.019 (4)
Cu1—O4 ⁱ	2.400 (3)	Cu2—O3 ⁱⁱ	2.308 (3)
N4—Cu1—N2	94.38 (14)	O1—Cu2—O3	102.47 (12)
N4—Cu1—N3	79.96 (14)	O1—Cu2—N6	169.22 (13)
N2—Cu1—N3	164.17 (15)	O3—Cu2—N6	88.16 (13)
N4—Cu1—N1	170.67 (14)	O1—Cu2—N5	91.93 (14)
N2—Cu1—N1	79.64 (14)	O3—Cu2—N5	163.92 (14)
N3—Cu1—N1	103.92 (13)	N6—Cu2—N5	77.30 (14)
N4—Cu1—O4 ⁱ	87.32 (13)	O1—Cu2—O3 ⁱⁱ	89.98 (12)
N2—Cu1—O4 ⁱ	96.35 (13)	N6—Cu2—O3 ⁱⁱ	94.10 (13)
N3—Cu1—O4 ⁱ	98.12 (12)	N5—Cu2—O3 ⁱⁱ	109.59 (13)
N1—Cu1—O4 ⁱ	100.38 (12)		

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

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2...O4	0.82	1.73	2.525 (5)	161
O5—H5...O1	0.82	2.53	3.046 (4)	122
O5—H5...O11	0.82	2.38	2.984 (9)	131
O6—H6...O3	0.82	2.43	2.897 (4)	117
O6—H6...O1 ⁱⁱ	0.82	2.12	2.885 (4)	154
O11—H11A...O8 ⁱⁱⁱ	0.85	2.11	2.92 (3)	159
O11—H11B...O9 ^{iv}	0.85	2.04	2.885 (12)	171

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

The O atoms of the perchlorate ion occupy two positions. They were refined freely but with a parameter constraining their populations to 1.0. Consequently, the $U_{eq}(\text{max})/U_{eq}(\text{min})$ ratio for the perchlorate group is larger than usual. Hydroxy H atoms were positioned geometrically, and the coordinates of water H atoms were calculated using *HYDROGEN* (Nardelli, 1999) (O—H = 0.85 Å). All of these H atoms were allowed to ride on their parent atoms in the final refinement. H atoms attached to C atoms were placed in

calculated positions (C—H = 0.93 Å) and allowed to ride on the parent atoms.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1453). Services for accessing these data are described at the back of the journal.

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