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dicopper(II)} tetrahydrate, $[Cu_4(C_{12}H_{24}N_4O_2)_2(C_5O_5)_2]$·-$4H_2O$, comprises two μ-oxamidato-dicopper(II) units bridged by croconate ligands to give a tetracopper(II) ring system with crystallographic $\bar{1}$ symmetry; all the copper centres are five-coordinate.

Comment

In the course of our work on copper(II) compounds with the general formula $Cu_2(L)X_2$, where L is N,N'-bis(3-amino-2,2-dimethylpropyl)oxamidate (Cornia *et al.*, 1993), we have found that the complex $Cu_2(L)(croc)$ (croc is croconate) has an unusual structure compared with the chain-like structures of $Cu_2(L)(OAc)_2$, $Cu_2(L)Cl_2$ and $Cu_2(L)Br_2$.

The title compound, di-μ-croconato-bis$\{\mu$-[N,N'-bis-(3-amino-2,2-dimethylpropyl)oxamidato(2−)-N,O':-N',O]dicopper(II)} tetrahydrate, (I), has the molecular formula $[Cu_2(L)(C_5O_5)]_2$ and can be described as two $Cu_2(L)$ units bridged by croconate ligands to give a tetracopper(II) ring system with crystallographic inversion symmetry. Whereas the oxamidate ligand adopts the common *trans*-bridging mode [Cu1···Cu2 = 5.1919(9) Å], the croconate dianion exhibits an unprecedented coordination mode involving three adjacent donor O atoms [Cu1···Cu2^i = 4.9925(7) Å; symmetry code: (i) $1-x$, $1-y$, $1-z$], which leads to a marked inequivalence of the two independent copper(II) ions.

(I)
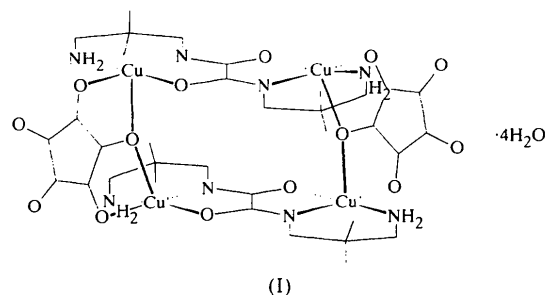
An almost perfectly square-planar geometry is formed around the Cu1 atom by the N1/N3/O4 donor set of the bridging oxamidate and the O1 donor of the croconate dianion [maximum deviation from the best plane is 0.057 Å and Cu1 deviates from this plane by 0.0749(9) Å]. However, the O6 atom provides a longer axial contact [2.619(2) Å], completing a square-pyramidal coordination.

The basal plane at Cu1 is coplanar with the central oxamidate moiety [4.0(1)°]. In contrast, the coordination geometry around Cu2 is approximately square pyramidal, with notable distortions.

The croconate dianion provides two O-atom donors, O2 and O6, in basal and apical coordination sites, respectively. The Cu2 atom is displaced from the average basal plane towards the apical O6 atom by 0.1496(9) Å. The basal plane is affected by a twist-like distortion, with a dihedral angle of 22.07(6)° between

A tetracopper(II) complex containing two μ-oxamidato-dicopper(II) units linked by croconate anions

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Abstract

The title compound, di-μ-croconato-bis$\{\mu$-[N,N'-bis(3-amino-2,2-dimethylpropyl)oxamidato(2−)-N,O':N',O]-
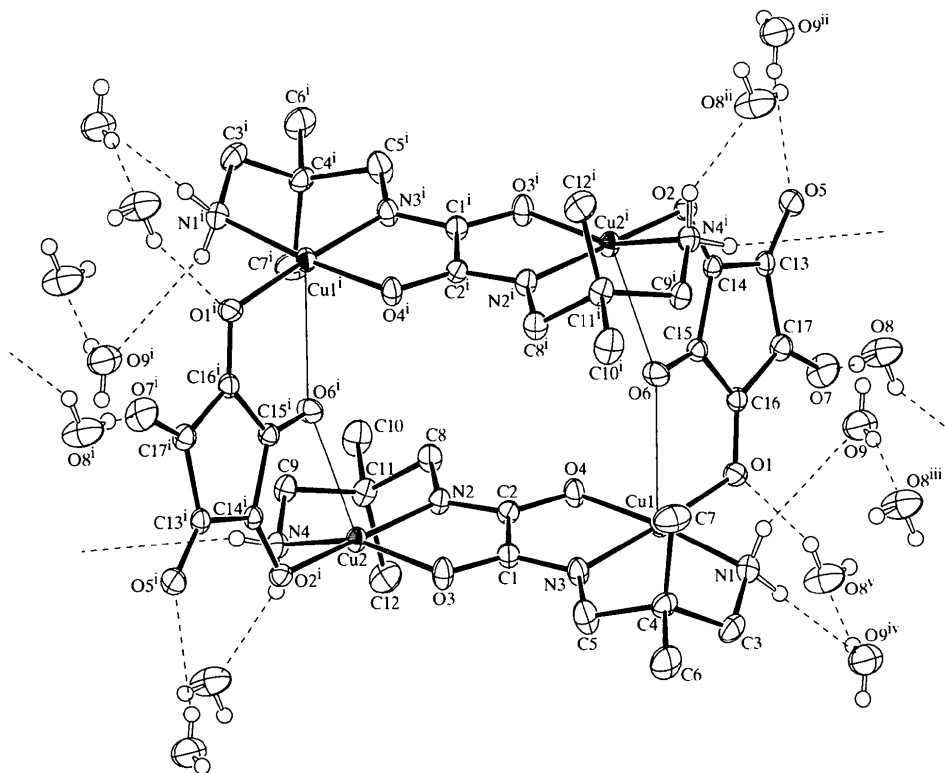
Fig. 1. The molecular structure of (I) showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

the Cu2/O2^i/N4 plane and the rest of the oxamidate bridge.

The two water molecules are involved in hydrogen-bonding interactions with N1, N4, O7 and O5. An additional hydrogen bond involving N4 and O5 links the tetranuclear complexes parallel to the y axis.

The magnetic behavior is dominated by antiferromagnetic exchange-coupling interactions through the oxamidate bridges. In the temperature range 2.4–280.0 K and in a 0.5 T magnetic field, the magnetic susceptibility per Cu2 unit follows the Bleaney–Bowers equation, with $J = 376\,(2)\,\text{cm}^{-1}$. The observed J values correlate well with the extent of twist-like distortion of the basal plane of Cu2 (Cornia, 1995).

Experimental

The copper(II) complex [CuL] (1 mmol), prepared according to the method of Fabretti et al. (1991), was suspended in water (30 ml) and treated under stirring with solid copper(II) chloride dihydrate (1 mmol) and dipotassium croconate (1 mmol) in water (20 ml). The resulting solution was filtered and left under vacuum over P_2O_5. Within a few days, crystals of the title compound formed. Found: C 36.52, H 5.15, N 10.02%; calculated for $C_{34}H_{56}Cu_4N_8O_{18}$: C 36.49, H 5.04, N 10.01%.

Crystal data

$[Cu_4(C_{12}H_{24}N_4O_2)_2$-$(C_5O_5)_2]\cdot4H_2O$
$M_r = 1119.02$
Triclinic
$P\bar{1}$
$a = 9.496\,(1)$ Å
$b = 10.6620\,(8)$ Å
$c = 12.966\,(2)$ Å
$\alpha = 71.481\,(8)°$
$\beta = 75.780\,(10)°$
$\gamma = 66.160\,(10)°$
$V = 1128.1\,(3)$ Å^3
$Z = 1$
$D_x = 1.647$ Mg m^{-3}
$D_m = 1.65\,(1)$ Mg m^{-3}
D_m measured by flotation in $CHCl_3/CHBr_3$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.3–13.7°$
$\mu = 1.940$ mm^{-1}
$T = 293\,(2)$ K
Prism
$0.35 \times 0.35 \times 0.30$ mm
Translucent intense blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction:
ψ scan (North et al., 1968)
$T_{min} = 0.820$, $T_{max} = 0.840$
6504 measured reflections
6246 independent reflections

4736 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 29.45°$
$h = -12 \rightarrow 13$
$k = -13 \rightarrow 14$
$l = 0 \rightarrow 17$
2 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.032$
$wR(F^2) = 0.087$
$S = 1.065$
6246 reflections
373 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.406$ e Å^{-3}
$\Delta\rho_{min} = -0.620$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—N3	1.9401 (17)	Cu2—N2	1.9417 (17)
Cu1—O4	1.9620 (15)	Cu2—O3	1.9728 (15)
Cu1—N1	1.975 (2)	Cu2—N4	1.9870 (18)
Cu1—O1	1.9888 (15)	Cu2—O2^i	2.0146 (14)
Cu1—O6	2.6188 (15)	Cu2—O6^i	2.4380 (15)
N3—Cu1—O4	85.16 (7)	O3—Cu2—N4	159.27 (8)
N3—Cu1—N1	96.03 (8)	N2—Cu2—O2^i	171.77 (6)
O4—Cu1—N1	172.20 (8)	O3—Cu2—O2^i	88.55 (6)
N3—Cu1—O1	174.32 (7)	N4—Cu2—O2^i	93.26 (7)
O4—Cu1—O1	89.20 (6)	N2—Cu2—O6^i	98.06 (6)
N1—Cu1—O1	89.48 (8)	O3—Cu2—O6^i	106.94 (6)
N2—Cu2—O3	84.64 (6)	N4—Cu2—O6^i	93.68 (7)
N2—Cu2—N4	94.75 (7)	O2^i—Cu2—O6^i	79.49 (5)

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

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
O8—H108$\cdots$O7	0.78 (4)	1.95 (4)	2.700 (3)	160 (4)
O8^i—H2O8$^i\cdots$O1	0.69 (4)	2.16 (4)	2.803 (2)	156 (5)
O9^{ii}—H2O9$^{ii}\cdots$O5	0.66 (4)	2.23 (4)	2.867 (3)	162 (5)
O9—H1O9$\cdots$O8^{iii}	0.75 (4)	1.99 (4)	2.726 (3)	164 (4)
N1—H2N1$\cdots$O9^{iv}	0.83 (3)	2.15 (3)	2.979 (3)	176 (3)
N1—H1N1$\cdots$O9	0.78 (3)	2.41 (3)	3.114 (3)	150 (3)
N4^v—H2N4$^v\cdots$O8^{ii}	0.82 (3)	2.40 (3)	3.107 (3)	144 (2)
N4—H1N4$\cdots$O5^{vi}	0.83 (3)	2.25 (3)	3.074 (2)	173 (3)

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

All H atoms were located in ΔF maps, were refined isotropically and assigned isotropic displacement parameters $U(H) = 1.5U_{eq}(C$ or $N)$.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (Enraf-Nonius, 1985). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *OR-TEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL97*.

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[(2S,4S)-4-Hydroxymethyl-1,3-dioxan-2-yl]-ferrocene

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Abstract

The structure of the title complex, [Fe(C$_5$H$_5$)(C$_{10}$H$_{13}$O$_3$)], shows the occurrence of two stereogenic centres in the hydroxymethyl-1,3-dioxane fragment. The S configuration found for these chiral C atoms agrees with the synthetic route. The dioxane ring has a nearly perfect chair conformation. O—H$\cdots$O hydrogen bonds result in the formation of an eight-membered ring built from the arrangement of four complex molecules around a fourfold axis.

Comment

For many years, owing to their involvement in numerous fields (catalysis, materials *etc.*; Togni & Hayashi, 1995), ferrocene derivatives have continued to create growing interest. Some of these applications require the use of chiral enantiomerically pure compounds, so much effort has been devoted to finding an efficient way to obtain these molecules (Batelle *et al.*, 1973; Ganter & Wagner, 1995; Riant *et al.*, 1993; Rebière *et al.*, 1993; Sammakia & Latham, 1996; Tsukazaki *et al.*, 1996). The title compound, [(2S,4S)-4-hydroxymethyl-