

Tetra- μ_2 -acetato-diacetatodi- μ_3 -hydroxido-tetrakis[piperidine-copper(II)] dihydrate

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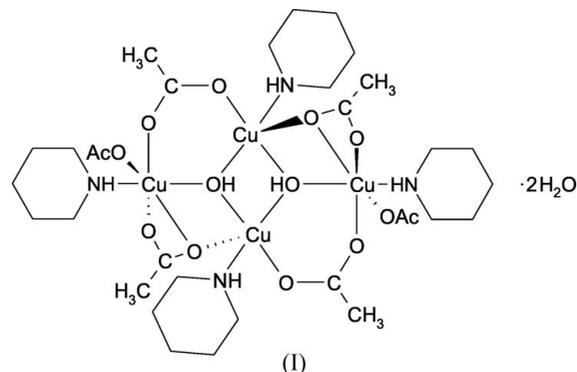
The title complex, $[\text{Cu}_4(\text{C}_2\text{H}_3\text{O}_2)_6(\text{OH})_2(\text{C}_5\text{H}_{11}\text{N})_4]\cdot 2\text{H}_2\text{O}$, possesses an unusual inversion-symmetric tetranuclear copper framework, with each Cu^{II} atom displaying a square-pyramidal geometry and one additional long $\text{Cu}\cdots\text{O}$ contact. The four piperidine ligands are terminal, one at each Cu^{II} atom, and the two hydroxide ligands are triply bridging. The six acetate ligands exhibit two distinct coordination modes, namely as two monodentate acetates and four bridging acetates that bridge the two inequivalent copper centres. The noncoordinating acetate O atom is involved in intramolecular hydrogen bonding with H atoms from the hydroxide and one piperidine ligand. In addition, extensive intermolecular hydrogen bonding involving the solvent water molecules is observed.

Comment

We have recently been interested in the preparation of oxoindoles using copper catalysis (Klein *et al.*, 2010). In the course of this investigation, we found that the addition of piperidine assisted turnover of the catalyst under certain reaction conditions. In an attempt to isolate the active copper species, we treated $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ (Ac is acetyl) with piperidine in dimethylformamide (or toluene), which resulted in the formation of a dark-blue solution. After solvent removal and crystallization, we reproducibly obtained the title complex, tetra- μ_2 -acetato-diacetatodi- μ_3 -hydroxido-tetrakis[piperidine-copper(II)] dihydrate, (I). Tetrameric complexes of copper that possess bridging O atoms have been reported previously. Most of these complexes display a cubane-type structure [for a recent example containing μ_3 -hydroxide O atoms, see Eberhardt *et al.* (2005)].

The title complex, (I) (Fig. 1), is inversion symmetric; the asymmetric unit contains the bis-copper(II) moiety $[\text{Cu}_2(\text{OAc})_3(\text{OH})(\text{C}_5\text{H}_{11}\text{N})_2]$ and a water of crystallization. Ignoring weak $\text{Cu}\cdots\text{O}$ contacts $> 2.5 \text{ \AA}$ (see below), the acetate ligand based on atoms O1 and O2 is monodentate *via*

O1 at Cu1, the bridging acetate based on atoms O3 and O4 bridges Cu1 and Cu2ⁱ, and the bridging acetate based on atoms O5 and O6 bridges Cu1 and Cu2 within the asymmetric unit. Hydroxide atom O7 bridges Cu1, Cu2 and Cu2ⁱ [symmetry code: (i) $-x + 1, -y + 1, -z + 1$]. Each piperidine ligand is coordinated to one copper centre *via* the N atom.



The geometry about both Cu1 and Cu2 is, in both cases, a distorted square-based pyramid with an additional long contact that completes a highly distorted octahedron. For Cu1 (Table 1), the principal coordinating atoms are N1, O1, O3 and O7, which are approximately coplanar (r.m.s. deviation = 0.20 \AA) and form the base of the square pyramid. Atom O6 lies at the apex of the square pyramid with a longer $\text{Cu}-\text{O}$ bond of $2.2434(10) \text{ \AA}$ associated with Jahn–Teller distortion. On the other side of the pyramid base, atom O4 has a weak contact of $2.6905(11) \text{ \AA}$ to Cu1, although the $\text{Cu}-\text{O}$ distance is long and the angle of 60.6° of $\text{Cu1}\cdots\text{O4}$ to the basal plane deviates significantly from an ideal right angle. Similarly, for Cu2, the pyramid base is formed by N2, O5, O7 and O7ⁱ (Table 2; r.m.s. deviation from the plane = 0.21 \AA). Atom O4ⁱ

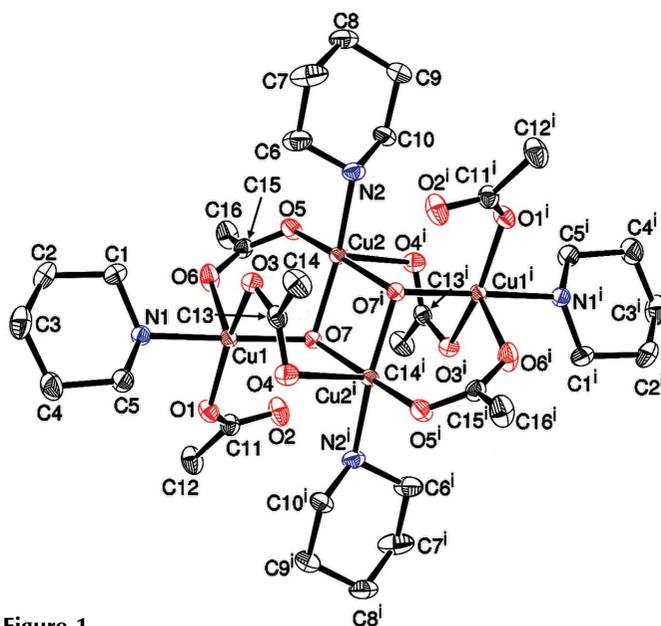
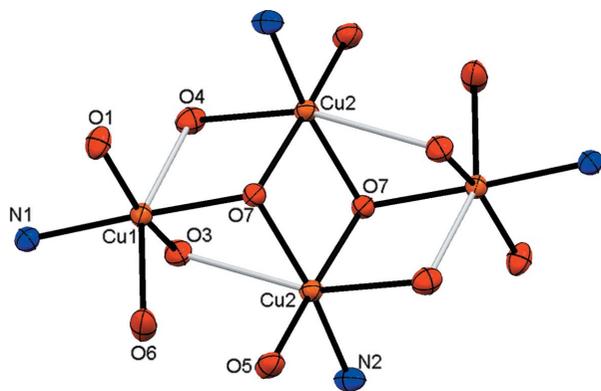


Figure 1

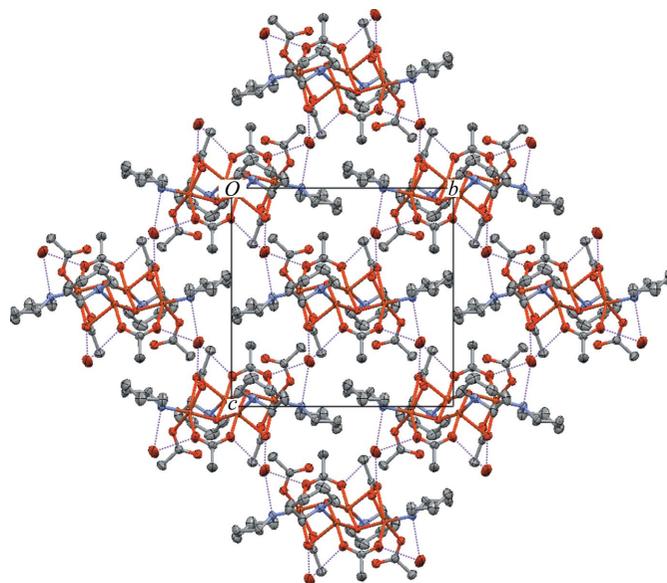
A view of the title tetranuclear copper complex. H atoms and solvent water molecules have been omitted, as have $\text{Cu}\cdots\text{O}$ contacts $> 2.5 \text{ \AA}$. The asymmetric unit corresponds to half the complex. Ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

**Figure 2**

A simplified view of the central core of the title complex showing ligand atoms coordinating to the Cu atoms. Long Cu...O contacts are indicated as pale bonds. Ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

lies at the apex and is approximately perpendicular to the plane, whereby again the Cu2...O3 interaction lies on the opposite side of the pyramid base with a still weaker contact of 2.8452 (10) Å.

The simplified framework of the tetranuclear unit is shown in Fig. 2. If the more distant apical ligands with Cu...O > 2 Å are ignored, the overall geometry within the tetracopper structure can be regarded as consisting of a central planar dimeric copper complex based on two Cu2 units, with two planar monocopper complexes based on Cu1 to either side. The dimeric complex centres about the inversion-symmetric four-membered ring formed by two Cu2 atoms and two hydroxide O7 atoms. The angle between the basal planes of the coordination polyhedra about atoms Cu1 and Cu2 is 75.40 (3)°. The three components are joined not only by the shared hydroxide ligands, but also by acetate O atoms, *viz.* Cu1...O4—Cu2ⁱ and Cu1—O3...Cu2 (Fig. 2). This construction differs from that of a previously reported tetrameric Cu-Schiff base complex (Pradeep *et al.*, 2006), which can be

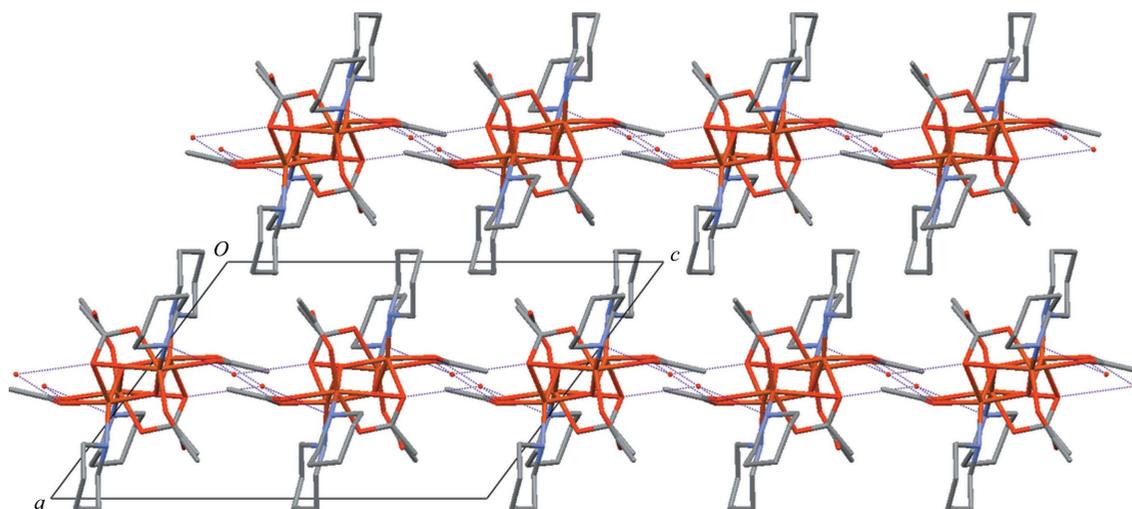
**Figure 3**

Packing diagram for the tetranuclear complex (H atoms omitted), viewed perpendicular to (100). Hydrogen bonds are indicated by thin lines.

regarded as consisting of a pair of planar dimeric copper complexes that are parallel and linked by four long axial Cu—O bridges.

Acetate atom O2 is not involved in coordination to the metal centres. Instead, it accepts two intramolecular hydrogen bonds, one from a hydroxide H atom and one from the H atom at N2ⁱ. The water of crystallization, O8, forms four hydrogen bonds, acting as an acceptor for N1, a donor to O6 and forming a three-centre hydrogen bond from H8D to O4ⁱⁱ and O5ⁱⁱⁱ (for details and symmetry codes, see Table 3).

The packing is largely governed by the hydrogen-bonding framework with each complex bonding to four water molecules which, in turn, hydrogen bond to four adjacent complexes. This produces a two-dimensional hydrogen-

**Figure 4**

Packing of the tetranuclear complex (H atoms omitted), viewed parallel to the *b* axis, showing hydrogen-bonded layers with intercalation of piperidine rings between these layers.

bonded layer of the complexes parallel to (100) (Fig. 3), and concomitantly a hydrophobic region where the methylenes of the piperidines from adjacent layers are in close proximity and are partially interleaved (Fig. 4).

Experimental

Piperidine (9.90 ml, 10 mmol, 10 equivalents) was added dropwise to a stirred suspension of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2.00 g, 10 mmol, 1 equivalent) in dimethylformamide or toluene (10 ml). The resulting mixture was stirred for 15 min at room temperature, filtered through a plug of cotton wool and the solvent was removed under reduced pressure at room temperature followed by co-evaporation with *n*-pentane (2 × 5 ml). Trituration with *n*-pentane (25 ml) resulted in a blue solid, which was filtered off and washed with *n*-pentane (2 × 50 ml). This solid was dissolved in a minimum amount of CH_2Cl_2 and layered with *n*-pentane to give crystals suitable for X-ray analysis. Repeated preparation of the complex resulted in samples with the same unit cell, confirming the reproducibility of the above procedure. Attempts to record the ^1H and ^{13}C NMR spectra of the complex proved impossible, consistent with its paramagnetic nature.

Crystal data

$[\text{Cu}_4(\text{C}_2\text{H}_3\text{O}_2)_6(\text{OH})_2(\text{C}_5\text{H}_{11}\text{N})_4] \cdot 2\text{H}_2\text{O}$	$\beta = 126.970 (1)^\circ$
$M_r = 1019.06$	$V = 2238.3 (2) \text{ \AA}^3$
Monoclinic, $P2_1/c$	$Z = 2$
$a = 11.6024 (6) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 14.0371 (7) \text{ \AA}$	$\mu = 1.94 \text{ mm}^{-1}$
$c = 17.2020 (9) \text{ \AA}$	$T = 110 \text{ K}$
	$0.45 \times 0.30 \times 0.15 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	33084 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	6505 independent reflections
$T_{\min} = 0.600$, $T_{\max} = 0.747$	5935 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.067$	$\Delta\rho_{\text{max}} = 0.84 \text{ e \AA}^{-3}$
$S = 1.05$	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$
6505 reflections	
276 parameters	
2 restraints	

The methylene H atoms were placed at calculated positions, with $\text{C}-\text{H} = 0.99 \text{ \AA}$ and $\text{H}-\text{C}-\text{H} = 109.5^\circ$, and refined using a riding model. Methyl groups of the acetate ligands were modelled as rigid groups ($\text{C}-\text{H} = 0.98 \text{ \AA}$ and $\text{H}-\text{C}-\text{H} = 109.5^\circ$) that were allowed to rotate but not tip. $U_{\text{iso}}(\text{H})$ values were fixed to $mU_{\text{eq}}(\text{C})$, with $m = 1.2$ for methylene and 1.5 for methyl H atoms. The hydroxide and amine H atoms were located in difference maps and refined freely. The water H atoms were also located in difference maps and were refined with $\text{O}-\text{H}$ bond lengths restrained to $0.80 (1) \text{ \AA}$.

Data collection: SMART (Bruker, 2003); cell refinement: SMART; data reduction: SAINT (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-32 for Windows (Farrugia, 1998) and Mercury (CCDC, 2010); software used to prepare material for publication: SHELXTL (Bruker, 2003).

Table 1

Cu1–ligand distances (Å) and angles (°).

Cu1–N1	1.9952 (10)	Cu1–O7	1.9908 (8)
Cu1–O1	1.9833 (9)	Cu1–O6	2.2434 (10)
Cu1–O3	1.9951 (9)	Cu1–O4	2.6905 (11)
N1–Cu1–O1	85.72 (4)	O1–Cu1–O7	93.36 (4)
N1–Cu1–O3	92.43 (4)	O3–Cu1–O4	54.15 (5)
N1–Cu1–O4	104.69 (4)	O3–Cu1–O6	104.89 (4)
N1–Cu1–O6	88.41 (4)	O3–Cu1–O7	89.60 (4)
N1–Cu1–O7	176.48 (4)	O4–Cu1–O6	154.92 (4)
O1–Cu1–O3	159.93 (4)	O4–Cu1–O7	78.83 (3)
O1–Cu1–O4	107.02 (4)	O6–Cu1–O7	88.29 (4)
O1–Cu1–O6	95.04 (4)		

Table 2

Cu2–ligand distances (Å) and angles (°).

Cu2–N2	1.9961 (11)	Cu2–O7	1.9735 (9)
Cu2–O3	2.8452 (10)	Cu2–O7 ⁱ	1.9737 (8)
Cu2–O4 ⁱ	2.4198 (10)	Cu2···Cu2 ⁱ	3.0262 (3)
Cu2–O5	1.9289 (9)		
N2–Cu2–O3	94.16 (4)	O3–Cu2–O7 ⁱ	82.31 (3)
N2–Cu2–O4 ⁱ	98.56 (4)	O4 ⁱ –Cu2–O5	85.63 (4)
N2–Cu2–O5	92.69 (6)	O4 ⁱ –Cu2–O7	97.49 (3)
N2–Cu2–O7	161.94 (4)	O4 ⁱ –Cu2–O7 ⁱ	86.26 (3)
N2–Cu2–O7 ⁱ	92.96 (5)	O5–Cu2–O7	96.71 (4)
O3–Cu2–O4 ⁱ	163.28 (4)	O5–Cu2–O7 ⁱ	170.71 (5)
O3–Cu2–O5	104.63 (4)	O7–Cu2–O7 ⁱ	79.89 (4)
O3–Cu2–O7	68.56 (4)	Cu2–O7–Cu2 ⁱ	100.11 (4)

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

Table 3

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1–H1···O8	0.838 (19)	2.206 (19)	2.9718 (17)	152.0 (16)
N2–H2···O2 ⁱ	0.83 (2)	2.34 (2)	3.1523 (16)	166.8 (19)
O7–H7···O2	0.78 (2)	1.92 (2)	2.6678 (13)	161 (2)
O8–H8C···O6	0.81 (1)	2.06 (2)	2.7994 (16)	153 (3)
O8–H8D···O4 ⁱⁱ	0.79 (3)	2.33 (2)	3.0539 (17)	154 (3)
O8–H8D···O5 ⁱⁱⁱ	0.79 (3)	2.46 (2)	3.0206 (16)	129 (2)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $-x + 1, y + \frac{3}{2}, -z + \frac{3}{2}$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3201). Services for accessing these data are described at the back of the journal.

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