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The compound described as tetra-μ-nitroaminato-bis[aquacopper(II)] is tetra-μ-acetato-bis[aquacopper(II)]

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The compound reported as tetra-μ-nitroaminato-bis[aquacopper(II)] [Öztürk *et al.* (2003). *Acta Cryst.* E**59**, i107–i109] is shown to be tetra-μ-acetato-bis[aquacopper(II)], $[Cu_2(C_2H_3O_2)_4(H_2O)_2]$, based on a new refinement using the original reflection data.

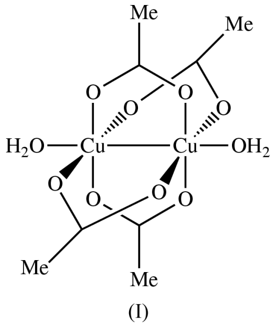
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.048
wR factor = 0.096
Data-to-parameter ratio = 16.2

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

Comment

The structure of a centrosymmetric binuclear copper(II) complex described as tetra-μ-nitroaminato-bis[aquacopper(II)], $[(H_2NNO_2)_2Cu(H_2O)]_2$, has recently been reported (Öztürk *et al.*, 2003). Our interest in this material was kindled by the fact that, while the coordinated water molecule acts as a double donor in O—H···O hydrogen bonds, neither of the supposed amino groups participates in the hydrogen bonding. We note that no elemental analysis was reported for this complex and that identification as a nitramine derivative was based solely on the IR spectrum. We note further that nitramine H_2NNO_2 is a neutral compound, so that the description of the neutral complex in question as a copper(II) complex of nitramine cannot possibly be correct. Moreover, the reported N—N distances in this complex [1.505 (7) and 1.477 (6) Å] are both very long for bonds of this type. In 1-nitroindazole, for example, the N—NO_2 distance is 1.336 (1) Å (Zaleski *et al.*, 2001); on the other hand, such distances are typical of C—CO_2 distances in carboxylate anions.



(I)

We report here that the material described as a nitramine complex (Öztürk *et al.*, 2003) is, in fact, the well known tetra-μ-acetato-bis[aquacopper(II)], (I), whose structure has been extensively documented (van Niekerk & Schoening, 1953; de Meester *et al.*, 1973; Brown & Chidambaram, 1973; Kita *et al.*, 1992; Shamuratov *et al.*, 1994). We base this diagnosis on (*a*) the unit-cell dimensions and space group, identical with those reported earlier; (*b*) the method of production, where an unidentified copper complex, obtained adventitiously

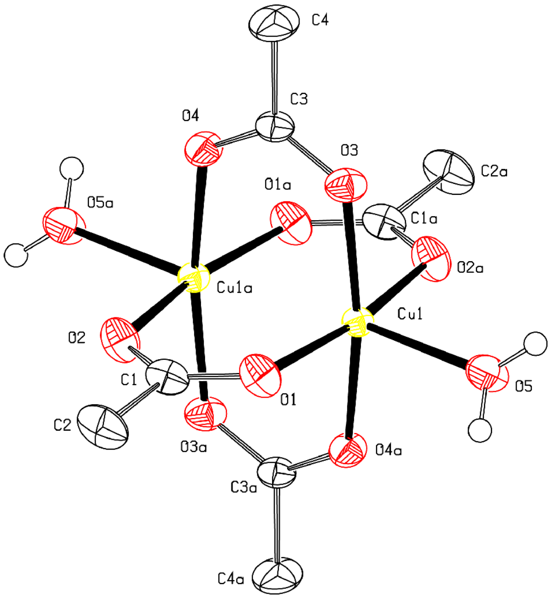


Figure 1
The molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level, and the atoms marked '*a*' are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

following decomposition of a substituted triazolone, intended to act as a ligand, but containing no nitro group or indeed any N—O bonds, was recrystallized from hot glacial acetic acid, *i.e.* conditions in which nitramine readily undergoes decomposition to nitrous oxide N_2O (Stedman, 1979); and (*c*) a new refinement based upon the original reflection data, but using the correct composition $C_8H_{16}Cu_2O_{10}$ (Fig. 1), rather than the erroneous formulation $H_{12}Cu_2N_8O_{10}$. This new refinement gave a lower *R* factor, *viz*. 0.048 as opposed to the 0.051 obtained using the same data set and the wrong composition, and detailed scrutiny of an extensive series of difference-map sections showed plainly the presence of disordered methyl groups, both modelled using six sites with 0.5 occupancy each, rather than amino groups. Similar scrutiny of difference-map sections based on the original refinement model allowed us to reject definitively the presence of NH_2 groups. The C—C and C—O distances obtained (Table 1), while essentially the same as those reported as N—N and N—O distances, agree with those found in previous determinations of the structure of this acetate complex, as do the hydrogen bonds (Table 2).

We conclude that the identification reported for this material by Öztürk *et al.* (2003), in terms of both the chemical composition and the X-ray structure, is incorrect.

Experimental

Crystal data

$[Cu_2(C_2H_3O_2)_4(H_2O)_2]$
$M_r = 399.31$
Monoclinic, $C2/c$
$a = 13.1677$ (18) Å
$b = 8.5716$ (12) Å
$c = 13.8499$ (19) Å
$\beta = 117.024$ (2)°
$V = 1392.5$ (3) Å^3
$Z = 4$

$D_x = 1.905$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2792 reflections
$\theta = 2.9$–28.3°
$\mu = 3.12$ mm^{-1}
$T = 293$ (2) K
Slab, blue
0.36 × 0.28 × 0.22 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.368$, $T_{max} = 0.504$
3874 measured reflections

1624 independent reflections
1391 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 28.3°$
$h = -17 \rightarrow 15$
$k = -11 \rightarrow 11$
$l = 14 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.096$
$S = 1.36$
1624 reflections
100 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2 + 2.7917P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

C1—C2	1.506 (5)	C3—C4	1.486 (5)
O1—C1	1.239 (5)	O3—C3	1.260 (4)
O2—C1	1.275 (5)	O4—C3	1.261 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H50···O3^{i}	0.84 (4)	2.12 (4)	2.931 (4)	166 (5)
O5—H51···O4^{ii}	0.84 (4)	1.99 (4)	2.825 (4)	179 (5)

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

The refinement of the title compound employed the data associated with the publication of Öztürk *et al.* (2003). The coordinates were adjusted such that the asymmetric unit now forms a connected set, with the dimeric complex centred at (0.5, 0.5, 0.5). The two water H atoms were clearly visible in a difference map and the O—H distances were restrained to 0.84 (4) Å during subsequent refinement. The H atoms of the two independent methyl groups were clearly disordered and each group was modelled using six sites of 0.5 occupancy and a constrained common C—H distance of 0.99 Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); method used to prepare material for publication: manual editing of CIF.

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