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The Structure of Bis[μ-acetato-(*O*,*O'*)-diacetato-μ_3-(2-diethylaminoethanolato-*N*,μ_3-*O*)-μ-(2-diethylaminoethanolato-*N*,μ-*O*)-μ_3-hydroxo-tricopper(II)] Hydrate

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Abstract

$[Cu_6(C_6H_{14}NO)_4(C_2H_3O_2)_6(OH)_2].H_2O$, $C_{36}H_{76}Cu_6N_4O_{18}.H_2O$, is triclinic, space group $P\bar{1}$, with a = 9·070 (6), b = 11·944 (6), c = 13·081 (9) Å, α = 107·23 (5), β = 96·94 (6), γ = 76·76 (5)°, Z = 1. The structure determination was based on 2051 reflections collected by counter methods and refined to R = 0·071. The crystal structure is composed of centrosymmetric hexanuclear complexes and H_2O molecules. The Cu atoms are linked by triply bridging ethanolato O atoms and OH^- ions, and by carboxylate and ethanolato O bridges. The H_2O molecule is disordered with a site-population parameter of 0·5 and is weakly bonded to two Cu atoms within the hexamer. The coordination number of Cu^{II} ions varies from four to six, the coordination polyhedra being square-planar, square-pyramidal and octahedral. Two of the three independent carboxylate groups are unidentate; the third acetate group forms a triatomic bridge from a basal coordination site of one Cu atom to the apical site of another.

Introduction

Cu^{II} acetate and halogen-substituted acetates form polynuclear complexes with 2-dialkylaminoethanol. According to Estes & Hodgson (1975), the structure of acetato(2-dibutylaminoethanolato)copper(II) is built up of dimeric units in which the aminoalcohol acts as a chelating bridge. Haloacetate complexes of the general formula $[Cu(R_2NCH_2CH_2O)(R'COO)]_4$ are tetrameric, with the Cu and bridging ethanolato O atoms forming a cubane-type structure (Ahlgrén, Hämäläinen, Turpeinen & Smolander, 1979; Turpeinen, Hämäläinen & Ahlgrén, 1980). To investigate further the structural properties of 2-dialkylaminoethanolato complexes of Cu^{II} carboxylates we have prepared bis[μ-acetato-(*O*,*O'*)-diacetato-μ_3-(2-diethylaminoethanolato-*N*,μ_3-*O*)-μ-(2-diethylaminoethanolato-*N*,μ-*O*)-μ_3-hydroxo-tricopper(II)] hydrate, and report here its crystal structure.

Experimental

The compound was prepared by dissolving 0·05 mol of Cu^{II} acetate (E. Merck AG) in methanol and adding 0·1 mol of redistilled 2-diethylaminoethanol (Fluka AG). The solution was concentrated and after the addition of ether yielded blue crystals suitable for X-ray studies.

Weissenberg photographs showed the crystals to be triclinic. Solution of the structure was successfully

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Table 1. *Crystal data*

$C_{36}H_{78}Cu_6N_4O_{19}$	FW = 1252·31
$a = 9{\cdot}070\ (6)$ Å	Triclinic $P\bar{1}$
$b = 11{\cdot}944\ (6)$	$Z = 1$
$c = 13{\cdot}081\ (9)$	$D_m = 1{\cdot}59\ (1)\ \mathrm{Mg\ m^{-3}}$
$\alpha = 107{\cdot}23\ (5)°$	$D_c = 1{\cdot}581$
$\beta = 96{\cdot}94\ (6)$	$\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å
$\gamma = 76{\cdot}76\ (5)$	$\mu(\mathrm{Mo}\ K\alpha) = 2{\cdot}54\ \mathrm{mm^{-1}}$

achieved in the centrosymmetric space group $P\bar{1}$. Cell dimensions were determined by least squares from 25 reflections measured on a Syntex $P2_1$ diffractometer. The crystal data are shown in Table 1.

The crystal used for data collection was 0·32 × 0·12 × 0·07 mm. Intensities were collected ($3{\cdot}0 < 2\theta < 50°$) at room temperature on a Syntex $P2_1$ diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The ω-scan technique was employed with a scan range of 1·0°. The scan rate varied from 2·55 to 29·3° $\mathrm{min^{-1}}$, depending on the number of counts accumulated in a preliminary scan. Background measurements were taken at both ends of the scan with ω displaced by 1·0° from the $K\alpha$ peak; each background was measured for half the scan time. The intensity of a standard reflection, recorded after every 99 measurements, remained essentially constant. The intensities were corrected for Lorentz and polarization effects and for absorption from empirical φ-scan data. Of the 4721 reflections collected, 2051 had $F_o > 4\sigma(F_o)$ and were used in subsequent calculations.

Table 2. *Fractional atomic coordinates* (×10^4) *with e.s.d.'s in parentheses*

	x	y	z
Cu(1)	1264 (2)	588 (2)	−101 (1)
Cu(2)	2002 (2)	−174 (2)	1862 (2)
Cu(3)	−896 (2)	1822 (2)	2326 (2)
O(1)	985 (11)	1286 (9)	1511 (8)
O(w)*	4058 (28)	140 (23)	638 (22)
O(11)	1251 (12)	2145 (10)	−279 (9)
O(12)	3652 (17)	2109 (14)	237 (11)
C(11)	2364 (21)	2619 (15)	46 (13)
C(12)	2067 (31)	4003 (19)	177 (21)
O(21)	2820 (14)	524 (10)	3273 (9)
O(22)	543 (13)	1392 (13)	3849 (10)
C(21)	1923 (20)	1158 (15)	4007 (15)
C(22)	2696 (26)	1637 (26)	5116 (16)
O(31)	−721 (14)	3510 (12)	2788 (11)
O(32)	1743 (16)	3333 (11)	2615 (12)
C(31)	480 (26)	3907 (16)	2929 (16)
C(32)	211 (29)	5260 (19)	3402 (25)
O(23)	1407 (11)	−858 (8)	390 (8)
C(23)	2310 (19)	−2012 (13)	−1 (13)
C(24)	2418 (19)	−2638 (13)	902 (13)
N(2)	2940 (15)	−1899 (12)	1928 (10)
C(25)	4626 (21)	−1929 (17)	2025 (17)
C(26)	5565 (28)	−3093 (23)	2192 (23)
C(27)	2457 (24)	−2179 (20)	2879 (16)
C(28)	704 (23)	−1759 (22)	3020 (18)
O(33)	−1468 (12)	302 (9)	1606 (8)
C(33)	−2607 (19)	71 (14)	2130 (12)
C(34)	−2855 (18)	993 (15)	3210 (14)
N(3)	−2863 (14)	2173 (11)	3134 (10)
C(35)	−4288 (19)	2578 (15)	2473 (14)
C(36)	−4405 (23)	3867 (16)	2357 (18)
C(37)	−2777 (22)	3068 (18)	4208 (14)
C(38)	−4130 (25)	3299 (20)	4870 (15)

* Population parameter 0·5.

Structure determination

The positions of the three independent Cu atoms were determined from a sharpened Patterson map, and least-squares refinement of these positions was run. All refinements of this structure were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$ with unit weights used in the beginning and $1/(60 + |F_o| + 0{\cdot}003|F_o|^2)$ in the final refinement. The scattering factors of Cromer & Mann (1968) were used for Cu, O, N and C. The effects of the anomalous dispersion of Cu were included, the values of f' and f'' being taken from *International Tables for X-ray Crystallography* (1974). The remaining non-hydrogen atoms of the structure were all apparent in a Fourier synthesis based on phases calculated from the Cu atoms alone. The water O atom was found to be represented by a peak half as high as those of the other O atoms. Isotropic refinement of all non-hydrogen atoms converged at $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0{\cdot}11$.

At this stage we checked our model. O(w) with a site-population parameter of 1·0 was found to have about twice as much thermal motion as the other atoms and it formed a very short contact of 2·43 Å with the centrosymmetrically related O(w) at equivalent position $1 - x, -y, -z$. Hydrogen bonds between normal H_2O molecules are about 2·7–2·8 Å. An attempt was made to refine the structure in the space group $P1$, but the atomic parameters obtained were essentially the same as in $P\bar{1}$, with more uneven bond lengths and angles. The refinement was thus continued in $P\bar{1}$ and the water O atom was assigned a site-population parameter of 0·5.

Full-matrix least-squares refinement with anisotropic thermal parameters reduced R to 0·071. The largest parameter shift in the last cycle was $0{\cdot}15\sigma$ and the average shift/error ratio was 0·02. A difference map was then computed. Distorted peaks between 0·2 and 0·6 e Å^{-3} were found at the expected positions of H atoms but some spurious peaks as high as 0·7 e Å^{-3} were also present. Further calculations to include the H atoms were therefore not made.

The calculations were performed on a Univac 1108 computer with XRAY 76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Final atomic positional parameters are given in Table 2. Interatomic distances

Table 3. *Intramolecular distances (Å) with e.s.d.'s in parentheses*

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

Cu(1)···Cu(2)	2·926 (4)	C(11)–O(11)	1·24 (2)
Cu(1)···Cu(3)	3·675 (4)	C(11)–O(12)	1·22 (2)
Cu(1)···Cu(1$^{\text{i}}$)	3·024 (4)	C(11)–C(12)	1·57 (3)
Cu(1)···Cu(2$^{\text{i}}$)	3·559 (4)		
Cu(1)···Cu(3$^{\text{i}}$)	3·480 (4)	C(21)–O(21)	1·28 (2)
Cu(2)···Cu(3)	3·102 (3)	C(21)–O(22)	1·22 (2)
Cu(2)···Cu(2$^{\text{i}}$)	5·772 (5)	C(21)–C(22)	1·54 (3)
Cu(2)···Cu(3$^{\text{i}}$)	5·299 (5)		
Cu(3)···Cu(3$^{\text{i}}$)	6·487 (6)	C(31)–O(31)	1·26 (3)
		C(31)–O(32)	1·24 (2)
Cu(1)–O(1)	2·048 (10)	C(31)–C(32)	1·52 (3)
Cu(1)–O(11)	1·938 (13)		
Cu(1)–O(23)	1·987 (11)	O(23)–C(23)	1·41 (2)
Cu(1)–O(33$^{\text{i}}$)	1·949 (10)	C(23)–C(24)	1·56 (3)
Cu(1)–O(23$^{\text{i}}$)	2·369 (10)	C(24)–N(2)	1·46 (2)
Cu(1)–O(*w*)	2·595 (24)	C(25)–N(2)	1·51 (2)
		C(25)–C(26)	1·52 (3)
Cu(2)–O(1)	1·934 (11)	C(27)–N(2)	1·52 (3)
Cu(2)–O(21)	1·923 (11)	C(27)–C(28)	1·57 (3)
Cu(2)–O(23)	1·919 (10)		
Cu(2)–N(2)	2·063 (14)	O(33)–C(33)	1·42 (2)
Cu(2)–O(*w*)	2·754 (31)	C(33)–C(34)	1·52 (2)
		C(34)–N(3)	1·44 (2)
Cu(3)–O(1)	1·999 (11)	C(35)–N(3)	1·53 (2)
Cu(3)–O(31)	1·964 (14)	C(35)–C(36)	1·57 (3)
Cu(3)–O(33)	1·937 (11)	C(37)–N(3)	1·50 (2)
Cu(3)–N(3)	2·079 (14)	C(37)–C(38)	1·51 (3)
Cu(3)–O(22)	2·367 (13)		
O(12)···O(*w*)	2·50 (3)	O(1)···O(32)	2·64 (2)

Table 4. *Intramolecular angles (°) with e.s.d.'s in parentheses*

O(1)–Cu(1)–O(11)	92·2 (5)	Cu(1)–O(11)–C(11)	120 (1)
O(1)–Cu(1)–O(23)	77·1 (4)	O(11)–C(11)–O(12)	126 (2)
O(1)–Cu(1)–O(33$^{\text{i}}$)	171·1 (5)	O(11)–C(11)–C(12)	116 (2)
O(11)–Cu(1)–O(23)	168·3 (4)	O(12)–C(11)–C(12)	118 (2)
O(11)–Cu(1)–O(33$^{\text{i}}$)	96·5 (5)		
O(23)–Cu(1)–O(33$^{\text{i}}$)	94·4 (4)	Cu(2)–O(21)–C(21)	120 (1)
O(23$^{\text{i}}$)–Cu(1)–O(1)	88·8 (4)	O(21)–C(21)–O(22)	123 (2)
O(23$^{\text{i}}$)–Cu(1)–O(11)	91·9 (4)	O(21)–C(21)–C(22)	115 (2)
O(23$^{\text{i}}$)–Cu(1)–O(23)	92·5 (4)	O(22)–C(21)–C(22)	122 (2)
O(23$^{\text{i}}$)–Cu(1)–O(33$^{\text{i}}$)	89·3 (4)	Cu(3)–O(22)–C(21)	129 (1)
O(23$^{\text{i}}$)–Cu(1)–O(*w*)	165·3 (8)		
O(*w*)–Cu(1)–O(1)	79·8 (7)	Cu(3)–O(31)–C(31)	127 (1)
O(*w*)–Cu(1)–O(11)	97·6 (7)	O(31)–C(31)–O(32)	126 (2)
O(*w*)–Cu(1)–O(23)	76·1 (7)	O(31)–C(31)–C(32)	113 (2)
O(*w*)–Cu(1)–O(33$^{\text{i}}$)	100·6 (6)	O(32)–C(31)–C(32)	120 (2)
O(1)–Cu(2)–O(21)	98·5 (5)	O(1)–Cu(3)–O(31)	93·7 (5)
O(1)–Cu(2)–O(23)	81·4 (4)	O(1)–Cu(3)–O(33)	89·7 (4)
O(1)–Cu(2)–N(2)	168·5 (4)	O(1)–Cu(3)–N(3)	173·5 (5)
O(21)–Cu(2)–O(23)	173·1 (5)	O(31)–Cu(3)–O(33)	164·9 (5)
O(21)–Cu(2)–N(2)	93·0 (5)	O(31)–Cu(3)–N(3)	92·9 (5)
O(23)–Cu(2)–N(2)	87·1 (4)	O(33)–Cu(3)–N(3)	84·2 (5)
O(*w*)–Cu(2)–O(1)	77·6 (6)	O(22)–Cu(3)–O(1)	89·9 (4)
O(*w*)–Cu(2)–O(21)	100·0 (7)	O(22)–Cu(3)–O(31)	93·3 (5)
O(*w*)–Cu(2)–O(23)	73·2 (6)	O(22)–Cu(3)–O(33)	101·4 (5)
O(*w*)–Cu(2)–N(2)	99·8 (7)	O(22)–Cu(3)–N(3)	89·2 (5)
Cu(1)–O(*w*)–Cu(2)	66·2 (6)	Cu(1)–O(1)–Cu(2)	94·5 (4)
		Cu(1)–O(1)–Cu(3)	130·4 (5)
Cu(1)–O(23)–Cu(1$^{\text{i}}$)	87·5 (3)	Cu(2)–O(1)–Cu(3)	104·1 (6)
Cu(2)–O(23)–Cu(1$^{\text{i}}$)	111·8 (4)		
C(23)–O(23)–Cu(1$^{\text{i}}$)	119·1 (9)		
Cu(2)–O(23)–Cu(1)	97·0 (4)	Cu(3)–O(33)–Cu(1$^{\text{i}}$)	127·2 (7)
Cu(2)–O(23)–C(23)	110·1 (9)	Cu(3)–O(33)–C(33)	112·8 (8)
C(23)–O(23)–Cu(1)	128·3 (11)	C(33)–O(33)–Cu(1$^{\text{i}}$)	115·9 (9)
O(23)–C(23)–C(24)	106 (1)	O(33)–C(33)–C(34)	110 (1)
C(23)–C(24)–N(2)	111 (1)	C(33)–C(34)–N(3)	111 (2)
C(24)–N(2)–C(25)	114 (1)	C(34)–N(3)–C(35)	109 (1)
C(24)–N(2)–C(27)	112 (2)	C(34)–N(3)–C(37)	113 (1)
Cu(2)–N(2)–C(24)	103 (1)	Cu(3)–N(3)–C(34)	100 (1)
Cu(2)–N(2)–C(25)	103 (1)	Cu(3)–N(3)–C(35)	112 (1)
Cu(2)–N(2)–C(27)	113 (1)	Cu(3)–N(3)–C(37)	112 (1)
C(25)–N(2)–C(27)	111 (1)	C(35)–N(3)–C(37)	111 (1)
N(2)–C(25)–C(26)	113 (2)	N(3)–C(35)–C(36)	113 (1)
N(2)–C(27)–C(28)	113 (2)	N(3)–C(37)–C(38)	114 (2)

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

and angles are tabulated in Tables 3 and 4, respectively.*

Description of the structure and discussion

The crystal structure of $Cu_6(C_6H_{14}NO)_4(C_2H_3O_2)_6(OH)_2.H_2O$ is built up from centrosymmetric hexanuclear complexes and disordered H_2O molecules which link the hexamers into chains along *a*. The molecular structure is shown in Fig. 1 and a stereoscopic view of the structure in Fig. 2. Intermolecular contacts <3·8 Å are listed in Table 5.

A point of interest is the ordering of H_2O molecules. The X-ray analysis indicates that the H_2O molecule has a site-population parameter of 0·5. This finding is also supported by geometrical features. If H_2O occupies half of the sites so that there is only one H_2O in the hole between adjacent hexamers (Fig. 2), it forms two weak bonds of 2·60 (2) and 2·75 (3) Å with Cu(1) and Cu(2) and two short contacts of 2·50 (3) and 3·01 (3) Å with O(12) and O(12$^{\text{v}}$), respectively. The latter two dis-

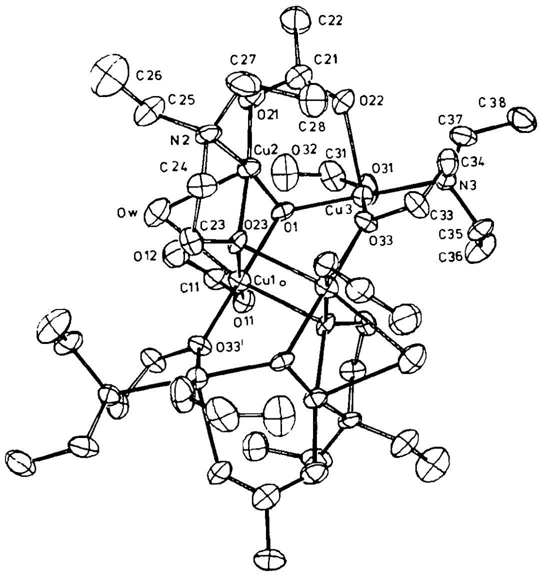

Fig. 1. View of the molecular structure omitting the methyl C atom of the unidentate acetate groups.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35087 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Intermolecular contacts < 3·8 Å with e.s.d.'s in parentheses*

O(*w*)···C(33$^{\mathrm{ii}}$)	3·39 (3)	C(22)···C(26$^{\mathrm{iv}}$)	3·77 (3)
O(*w*)···C(35$^{\mathrm{ii}}$)	3·67 (3)	O(*w*)···O(12$^{\mathrm{v}}$)	3·01 (3)
O(12)···C(35$^{\mathrm{ii}}$)	3·25 (2)	O(12)···C(23$^{\mathrm{v}}$)	3·69 (2)
O(12)···C(36$^{\mathrm{ii}}$)	3·50 (2)	O(12)···C(25$^{\mathrm{v}}$)	3·44 (3)
O(32)···C(35$^{\mathrm{ii}}$)	3·52 (2)	C(12)···C(26$^{\mathrm{v}}$)	3·73 (4)
O(32)···C(36$^{\mathrm{ii}}$)	3·76 (3)	C(27)···C(38$^{\mathrm{vi}}$)	3·62 (3)
C(26)···C(36$^{\mathrm{iii}}$)	3·69 (4)		

Symmetry code

(ii) $x + 1, y, z$
(iii) $x + 1, y - 1, z$
(iv) $1 - x, -y, 1 - z$
(v) $1 - x, -y, -z$
(vi) $-x, -y, 1 - z$

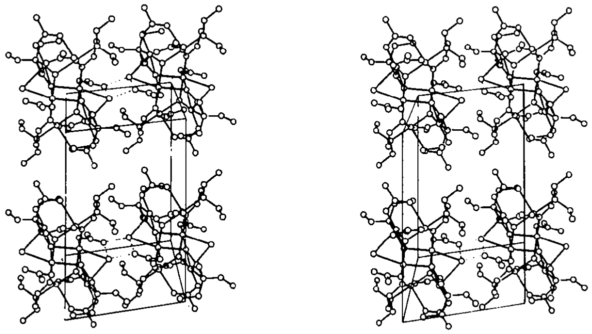

Fig. 2. Stereoview of the structure.

tances suggest the presence of hydrogen-bonded interactions, if we assume a distorted tetrahedral geometry about O(*w*). Similar hydrogen bonds are found in Ni$^{\mathrm{II}}$ and Cu$^{\mathrm{II}}$ complexes containing bridging $\mathrm{H_2O}$ molecules (Cotton & Winquist, 1969; Prout, Carruthers & Rossotti, 1971; Komson, McPhail, Mabbs & Porter, 1971; Ahlgrén, Turpeinen & Hämäläinen, 1978). If $\mathrm{H_2O}$ were to occupy all sites (p.p. 1·0), it would form one additional contact, a very strong, crystallographically symmetric hydrogen bond (Catti & Ferraris, 1976) of 2·43 (4) Å, with O(w^{v}), leading to a disordered H(*w*) atom position. Thus every other $\mathrm{H_2O}$ molecule would coordinate three cations. But from known crystal structures it appears that this kind of coordination is possible only with H and alkali atoms (Ferraris & Franchini-Angela, 1972). Therefore, we believe that only half of the sites are occupied by $\mathrm{H_2O}$.

The coordination number of the Cu$^{\mathrm{II}}$ ions varies from four to six. The coordination sphere of Cu(1) is either distorted octahedral with unequal axial bonds, or square-pyramidal depending on the site population of $\mathrm{H_2O}$. Similarly the coordination sphere of Cu(2) depends on the site population of $\mathrm{H_2O}$ and is either square-pyramidal or square-planar. Cu(3) is five-coordinate, the apical site of square-pyramidal coordination being occupied by the second carboxyl O atom of the acetate group coordinated to Cu(2). The other linkages between the Cu atoms are monoatomic O bridges so that the coordination polyhedra of Cu(1) and Cu(2) share a face or a basal edge; Cu(1) and Cu(1$^{\mathrm{i}}$) share an apical edge; Cu(1) and Cu(3$^{\mathrm{i}}$), like Cu(2) and Cu(3), share a single coordination site. The basal coordination planes of Cu(1) and Cu(1$^{\mathrm{i}}$) are parallel as required by the molecular centre of symmetry. The angle between the Cu(1) and Cu(2) basal planes is 145·5°, between Cu(2) and Cu(3) 91·0° and between Cu(3) and Cu(1$^{\mathrm{i}}$) 125·4°.

The displacements of Cu(1), Cu(2) and Cu(3) from their basal coordination planes are 0·021 (2), 0·057 (2) and 0·112 (3) Å, respectively. The atoms occupying the four basal sites of each Cu atom are not strictly coplanar, as is evident from the data tabulated in Table 6. The interatomic angles about Cu(1) and Cu(2) vary up to 13° from idealized values; about Cu(3) they vary less but still considerably. The Cu–ligand distances are in the range normally observed for Cu$^{\mathrm{II}}$ complexes having similar coordination spheres (Näsäkkälä, 1977;

Table 6. *Least-squares planes and deviations* (Å) *of some atoms of interest from the planes*

(*a*) Plane defined by O(1), O(11), O(23), O(33$^{\mathrm{i}}$)

$(8{\cdot}824x + 0{\cdot}658y + 1{\cdot}007z = 1{\cdot}165)$

O(1)	−0·059 (10)	Cu(1)	−0·021 (2)
O(11)	0·051 (11)	O(23$^{\mathrm{i}}$)	−2·390 (10)
O(23)	0·059 (10)	O(*w*)	2·489 (25)
O(33$^{\mathrm{i}}$)	−0·051 (11)		

(*b*) Plane defined by O(1), O(21), O(23), N(2)

$(8{\cdot}419x + 4{\cdot}337y - 6{\cdot}245z = 0{\cdot}505)$

O(1)	−0·061 (10)	N(2)	−0·056 (14)
O(21)	0·052 (12)	Cu(2)	−0·058 (2)
O(23)	0·065 (10)	O(*w*)	2·575 (27)

(*c*) Plane defined by O(1), O(31), O(33), N(3)

$(3{\cdot}486x - 4{\cdot}765y + 10{\cdot}877z = 1{\cdot}237)$

O(1)	0·136 (10)	N(3)	0·138 (13)
O(31)	−0·128 (14)	Cu(3)	0·112 (3)
O(33)	−0·147 (11)	O(22)	2·475 (13)

(*d*) Plane defined by O(11), O(12), C(11), C(12)

$(-2{\cdot}741x - 1{\cdot}888y + 12{\cdot}643z = -1{\cdot}096)$

O(11)	−0·004 (12)	C(12)	−0·003 (27)
O(12)	−0·004 (14)	Cu(1)	0·510 (3)
C(11)	0·012 (17)	O(*w*)	0·763 (29)

(*e*) Plane defined by O(21), O(22), C(21), C(22)

$(2{\cdot}686x + 11{\cdot}558y - 6{\cdot}803z = -0{\cdot}866)$

O(21)	0·002 (12)	C(22)	0·002 (29)
O(22)	0·002 (15)	Cu(2)	−0·064 (2)
C(21)	−0·006 (18)	Cu(3)	1·148 (2)

(*f*) Plane defined by O(31), O(32), C(31), C(32)

$(0{\cdot}550x - 4{\cdot}733y + 12{\cdot}711z = 1{\cdot}858)$

O(31)	−0·015 (14)	C(32)	−0·011 (32)
O(32)	−0·016 (15)	Cu(3)	0·187 (3)
C(31)	0·042 (21)	O(1)	−0·493 (10)

Ahlgrén, Hämäläinen, Turpeinen & Smolander, 1979; Turpeinen, Hämäläinen & Ahlgrén, 1980).

Since H atoms were not located in this study, identification of the triply bridging O(1) as the O atom of a OH^- group rests on indirect evidence. The Cu—O—Cu angles about O(1) and the O(1) displacement of 0·63 (1) Å out of the Cu(1)—Cu(2)—Cu(3) plane towards the unbonded carboxylate O(32) are consistent with a distorted tetrahedral geometry. Furthermore, the O(1)···O(32) contact of 2·64 (2) Å and the O(1)···O(32)—C(31) angle of 99·2 (12)° indicate a probable hydrogen bond between O(1) and O(32). We see no alternative interpretation of O(1) that is both chemically feasible and consistent with the structural results.

Two of the three independent carboxylate groups are unidentate. The acetate group bonded to Cu(1) is nearly perpendicular to the basal coordination plane of Cu(1) (dihedral angle 82·4°) and is involved in a probable hydrogen bond of 2·50 (3) Å with the axial H_2O molecule. O(12) lies 3·05 (2) Å from Cu(1) and off the axial position. A similar non-bonded interaction of 3·21 Å occurs in the crystal structure of diacetatobis(*p*-toluidine)copper(II) trihydrate (Komson, McPhail, Mabbs & Porter, 1971). The acetate group bonded to Cu(3) is roughly coplanar with the basal coordination plane of Cu(3), the dihedral angle being 20·6°. A probable hydrogen bond of 2·64 (2) Å is formed with O(1). A similar hydrogen bond of 2·550 (10) Å between the triply bridging OH^- group and a monodentate carboxylate group is found in a tetrameric basic quinoline adduct of Cu^{II} trifluoroacetate (Little, Moreland, Yawney & Doedens, 1974). The third acetate group is bidentate, bridging from a basal coordination site of Cu(2) to the apical site of Cu(3) in *syn–syn* configuration. This coordination type is common in carboxylato(2-dialkylaminoethanolato)-copper(II) tetramers (Ahlgrén, Hämäläinen, Turpeinen & Smolander, 1979; Turpeinen, Hämäläinen & Ahlgrén, 1980) although their axial Cu–O(carboxylate) distances are longer, partly owing to distorted octahedral environments of Cu atoms.

The bond distances and angles of the 2-diethylaminoethanolato ligands are as expected. The two five-membered aminoethanolato chelate rings have the *gauche* form. In one chelate ring C(23) and C(24) lie 0·48 (2) Å above and −0·21 (2) Å below the plane defined by O(23)—Cu(2)—N(2) and in the other chelate ring C(33) and C(34) deviate 0·33 (2) and 0·81 (2) Å to the same side from the plane defined by O(33)—Cu(3)—N(3). The ethanolato O(23) is tetracoordinate, while O(33) is tricoordinate. The angles about O(23) are approximately tetrahedral as in carboxylato(2-dialkylaminoethanolato)copper(II) tetramers and O(23) deviates 0·48 (1) Å from the plane defined by Cu(1)—Cu(2)—C(23). The angles about O(33) are between 112·8 (8) and 127·2 (7)° and O(33) deviates 0·20 (1) Å from the plane defined by Cu(3)—Cu(1^i)—C(33) suggesting trigonal-planar rather than tetrahedral geometry for O(33).

Of principal interest is the array of the Cu and bridging O atoms. This can be thought of as built up of two distorted cubes with the common face Cu(1)—O(23)—Cu(1^i)—O(23^i). These cubes resemble the Cu_4O_4 core of carboxylato(2-dialkylaminoethanolato)-copper(II) tetramers, except in the arrangement of the short and long Cu—O distances. In the tetrameric complexes, two pairs of long Cu—O distances are perpendicular to each other so that the Cu_4O_4 framework is best described as an eight-membered ring folded in boat-like conformation with short Cu—O distances of 1·85 (2)–2·02 (2) Å defining the ring and four long Cu—O distances of 2·52 (1)–3·01 (1) Å defining the approach of folded portions. The coordination of each Cu is square-pyramidal or octahedral. In the Cu_4O_4 cubes of the present compound the short Cu—O distances range from 1·919 (10) to 2·048 (10) Å and the long ones from 2·369 (10) to 3·404 (10) Å, of which the Cu(2)—O(33) and Cu(3)—O(23^i) distances of 3·063 (11) and 3·404 (10) Å are non-bonded interactions. The short Cu—O distances do not form an eight-membered ring in one Cu_4O_4 core, but rather a chair-like eight-membered Cu_4O_4 ring, to which two additional four-membered rings are connected, forming a Cu_6O_6 core.

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