

## The Crystal Structure of Tetrakis[chloroacetato- $\mu$ -(2-dimethylaminoethanolato)copper(II)]

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The crystal structure of the title compound has been determined from three-dimensional X-ray data and refined by full-matrix least-squares methods to an  $R$  value of 0.044 for 1242 independent reflections. The blue crystals belong to the tetragonal space group  $I4_1/a$  with  $a = 17.256(9)$ ,  $c = 13.053(7)$  Å and  $Z = 4$ . The compound consists of tetrameric cubane-type units formed by four copper and four bridging ethanolato oxygen atoms with Cu–Cu distances of 3.182 and 3.766 Å. Each copper atom has a distorted octahedral environment, two ethanolato oxygen atoms, a carboxyl oxygen atom and an amino nitrogen atom forming the equatorial coordination plane with Cu–O bonds of 1.937, 1.946 and 1.946 Å and a Cu–N bond of 2.060 Å. The axial sites are occupied by a carboxyl oxygen atom and an ethanolato oxygen atom with Cu–O distances of 2.712 and 2.737 Å, respectively.

Several halogeno- and pseudohalogeno(2-dialkylaminoethanolato)copper(II) complexes have been investigated in the solid state and shown to be built up of dimeric, polymeric or tetrameric structures. A summary of known structures up to 1977 is given by Mergehenn and Haase.<sup>1</sup> There are two extreme types of tetrameric structures, both derived from an idealized  $Cu_4O_4$  cube by stretching four edges; in one the four stretched edges are parallel and in the other, two of the stretched edges are perpendicular to the other two. In addition to these extreme types, in which Cu–Cu distances range between 2.91 and 3.54 Å, there are intermediate types where Cu–Cu distances are approximately equal. The structure of such a complex, having all Cu–Cu distances equal (3.19 Å), has recently been determined.<sup>2</sup>

As part of our studies on the effects of halogen substitution in the carboxylate ligand on the

stereochemistry of nickel(II) and copper(II) complexes, we have prepared several copper(II) complexes with 2-dialkylaminoethanol as the second ligand. The crystal structures of tetrakis[chlorocarboxylato- $\mu$ -(2-diethylaminoethanolato)copper(II)], where chlorocarboxylato is dichloroacetato<sup>3</sup> or chloroacetato,<sup>4</sup> have already been published. These two complexes contain a  $Cu_4O_4$  cube having two stretched edges approximately perpendicular to the other two, but because the Cu–Cu distances range from 3.18 to 4.02 Å they represent new examples of the variability of  $Cu_4O_4$  cores. To study further the structural properties of this class of complexes, we have now examined the crystal structure of tetrakis[chloroacetato- $\mu$ -(2-dimethylaminoethanolato)copper(II)].

### EXPERIMENTAL

Blue crystals were obtained by slow concentration of an ethanol solution containing copper(II) chloroacetate and 2-dimethylaminoethanol in the molar ratio 9:10. A single square-bipyramidal crystal of dimensions  $0.5 \times 0.5 \times 0.3$  mm was selected for X-ray investigation.

Lattice parameters were obtained from a least-squares refinement of seventeen well-centered reflections measured on a Syntex  $P2_1$  diffractometer using graphite monochromatized  $MoK\alpha$  radiation ( $\lambda = 0.71069$  Å). Crystal data:  $a = 17.256(9)$ ,  $c = 13.053(7)$  Å,  $Z = 4$ ,  $D_m = 1.67$  g cm<sup>-3</sup>,  $D_x = 1.680$  g cm<sup>-3</sup>, space group  $I4_1/a$ ,  $\mu(MoK\alpha) = 25.6$  cm<sup>-1</sup>.

Intensity data were collected ( $5^\circ < 2\theta < 55^\circ$ ) at room temperature using the  $\omega$ -scan technique and a scan rate varying from 2.5 to 30.0° min<sup>-1</sup> depending upon the peak intensity. The intensity of one check reflection, recorded after every 99 measurements, remained essentially constant

throughout the data collection. Out of 2180 independent reflections measured, 1242 had  $I > 3\sigma(I)$ , and were used in the structure analysis. The data were corrected for Lorentz and polarization factors and for absorption from  $\phi$ -scan data.

## STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by direct and Fourier methods, and refined by full-matrix least-squares

techniques. The function minimized was  $\sum w(|F_o| - |F_c|)^2$  with  $w = 1/(40.0 + |F_o| + 0.05|F_o|^2)$ . Scattering factors for neutral nonhydrogen atoms were taken from Cromer and Mann,<sup>5</sup> and those for H from Stewart *et al.*<sup>6</sup> Real and imaginary anomalous dispersion corrections were included for the Cu and Cl atoms.<sup>7</sup> Refinement of a model including isotropic thermal parameters led to an  $R$  value of 0.091 ( $R = \sum \|F_o| - |F_c|\| / \sum |F_o|$ ). Further refinement with anisotropic thermal parameters reduced the  $R$  factor to 0.053. At this stage hydrogen atoms

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and thermal parameters ( $\times 10^3$ ).

	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cu	6065(1)	7737(1)	5583(1)	39(1)	42(1)	45(1)	6(1)	8(1)	8(1)
O1	5111(2)	8327(2)	5535(3)	44(2)	33(2)	45(2)	6(1)	4(2)	6(2)
O2	6988(3)	7100(3)	5422(4)	62(3)	73(3)	66(3)	24(2)	19(2)	17(3)
O3	6507(3)	5931(3)	5890(6)	65(3)	62(3)	148(6)	3(3)	-4(4)	-13(4)
N	6304(3)	8248(3)	4192(4)	54(3)	62(3)	49(3)	1(2)	13(2)	18(3)
C1	5585(6)	8626(7)	3862(9)	96(7)	130(9)	92(7)	41(6)	32(6)	60(7)
C2	5151(5)	8906(4)	4771(6)	87(6)	55(4)	51(4)	26(4)	8(4)	13(3)
C3	7013(7)	8700(7)	4247(9)	80(7)	89(7)	103(8)	-31(6)	26(6)	23(6)
C4	6483(9)	7625(8)	3368(9)	140(9)	116(9)	72(6)	17(8)	33(7)	-2(6)
C5	7013(4)	6362(4)	5536(6)	63(4)	66(4)	60(4)	21(3)	-4(3)	1(4)
C6	7795(7)	5994(7)	5332(9)	77(6)	83(6)	93(7)	37(5)	7(5)	-3(5)
Cl	8371(2)	6463(2)	4411(2)	91(2)	122(2)	88(2)	38(1)	24(1)	2(1)

Table 2. Interatomic distances (Å) and angles ( $^\circ$ ).<sup>a</sup>

The copper(II) environment					
Cu-O1	1.937(4)	O1-Cu-N	85.2(2)	O1 <sup>III</sup> -Cu-O1 <sup>I</sup>	70.0(1)
Cu-O2	1.946(5)	O1-Cu-O1 <sup>I</sup>	90.7(2)	O3 <sup>III</sup> -Cu-O1	82.2(2)
Cu-N	2.060(6)	O2-Cu-N	89.0(2)	O3 <sup>III</sup> -Cu-N	91.5(2)
Cu-O1 <sup>I</sup>	1.946(4)	O2-Cu-O1 <sup>I</sup>	95.7(2)	O3 <sup>III</sup> -Cu-O2	104.3(2)
Cu-O1 <sup>II</sup>	2.737(4)	O1 <sup>II</sup> -Cu-O1	73.8(1)	O3 <sup>III</sup> -Cu-O1 <sup>I</sup>	81.9(2)
Cu-O3 <sup>III</sup>	2.712(7)	O1 <sup>II</sup> -Cu-N	114.5(2)	O3 <sup>III</sup> -Cu-O1 <sup>II</sup>	142.3(2)
		O1 <sup>II</sup> -Cu-O2	103.0(2)		
The 2-dimethylaminoethanolato ligand					
N-C1	1.464(13)	C1-N-C3	119.3(8)	C3-N-Cu	110.7(6)
C1-C2	1.485(14)	C1-N-C4	105.8(8)	C4-N-Cu	110.8(6)
C2-O1	1.413(8)	C3-N-C4	103.8(8)	C2-O1-Cu	110.6(4)
N-C3	1.453(14)	N-C1-C2	109.7(8)	C2-O1-Cu <sup>III</sup>	121.3(4)
N-C4	1.553(14)	C1-C2-O1	111.0(7)	Cu-O1-Cu <sup>III</sup>	110.1(2)
		C1-N-Cu	106.3(5)		
The chloroacetate ligand					
O2-C5	1.284(9)	C6-C1	1.758(12)	O3-C5-C6	116.3(7)
O3-C5	1.237(9)	O2-C5-O3	128.0(7)	C5-C6-C1	115.6(8)
C5-C6	1.514(14)	O2-C5-C6	115.2(7)	C5-O2-Cu	125.2(5)

<sup>a</sup> I =  $y - 1/4$ ,  $-x + 5/4$ ,  $-z + 5/4$ ; II =  $-x + 1$ ,  $-y + 2/3$ ,  $z$ ; III =  $-y + 5/4$ ,  $x + 1/4$ ,  $-z + 5/4$ .

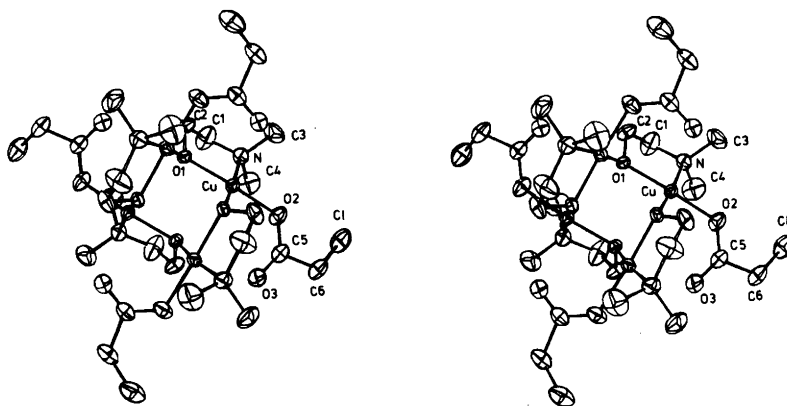


Fig. 1. Stereoscopic view of the molecule.

were included in calculated positions ( $C-H=1.0$  Å). The final least-squares refinement (positional parameters of H atoms were not refined) yielded  $R=0.044$ , the average shift/error ratio in the last cycle being 0.07. A final difference synthesis showed only one peak above  $0.40 e \text{ \AA}^{-3}$ . With an electron density of  $0.68 e \text{ \AA}^{-3}$ , at fractional coordinates (0.860, 0.699, 0.450), this peak is of no chemical significance, and lies close to the chlorine atom. The computations were performed on a UNIVAC 1108 computer with the X-Ray 76 program system.<sup>8</sup>

## RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters with their standard deviations are given in Table 1.

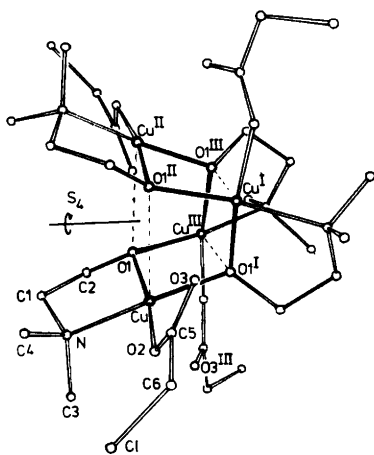


Fig. 2. A view of the molecule.

A list of observed and calculated structure factors can be obtained from the authors. The interatomic distances and angles are listed in Table 2 and the geometry and numbering schemes are shown in Figs. 1 and 2.

The unit cell contains four discrete tetrameric  $Cu_4(Me_2NC_2H_4O)_4(ClC_2H_2O_2)_4$  molecules, the shortest intermolecular distances being between the chlorine and methyl carbon atoms:  $Cl \cdots C4$  ( $y+1/4, -x+5/4, z+1/4$ ) = 3.65 Å and  $Cl \cdots C3$  ( $-y+7/4, x-1/4, -z+3/4$ ) = 3.76 Å. These contacts are close to the sum of the appropriate van der Waals distances.

The symmetry of the molecules is  $S_4$  and thus the same as in the previously reported  $Cu_4(Et_2NC_2H_4O)_4(ClC_2H_2O_2)_4$  complex.<sup>4</sup> Each molecule consists of an eight-membered  $Cu_4O_4$  ring of cubane-type formed by four copper and four ethanolate oxygen atoms with  $Cu-Cu$  distances of 3.182 ( $4 \times$ ) and 3.766 ( $2 \times$ ) Å. The array of the oxygen atoms in the  $Cu_4O_4$  core is nearly tetrahedral, the  $O-O$  distances being 2.762 ( $4 \times$ ) and 2.879 ( $2 \times$ ) Å. The angles between the limiting least-squares planes of the cube are 0, 26, 77, 87, 93 and 103°. In the two limiting planes perpendicular to the  $S_4$ -axis the  $Cu, O, Cu, O$  atoms deviate 0.03 Å from the plane (*cf.* Fig. 2); in the other four planes the deviations of the atoms are between 0.12 and 0.18 Å.

The difference of 0.584 Å between the longest and the shortest copper-copper atom distances in the present compound is nearly the same as in  $Cu_4(Et_2NC_2H_4O)_4(ClC_2H_2O_2)_4$  (0.546 Å)<sup>4</sup> but is much less than in  $Cu_4(Et_2NC_2H_4O)_4(Cl_2C_2HO_2)_4$  (0.848

$\text{Å})^3$  and  $\text{Cu}_4(\text{Et}_2\text{NC}_2\text{H}_4\text{O})_4(\text{Cl}_3\text{C}_2\text{O}_2)_4$  (0.902 Å).<sup>9</sup> Thus the distortion of the cube increases and the symmetry of the molecules decreases on going from chloroacetate *via* dichloroacetate to trichloroacetate. The trend can be attributed to the larger steric hindrance and unfavourable packing effects when the number of the chloro-substituents is increased. On the other hand the substitution of ethyl groups for methyl groups in 2-dialkylaminoethanol changes the molecular structure very little, and the symmetry remains unchanged in the two chloroacetate complexes.

Each copper atom has a distorted octahedral environment, two ethanolato oxygen atoms, a carboxyl oxygen atom and an amino nitrogen atom forming a nearly square-planar arrangement with Cu—O bonds of 1.937, 1.946 and 1.946 and Cu—N bond of 2.060 Å. The Cu atom lies in the least-squares plane through O1, O2, O1<sup>I</sup> and N; O1 and O2 are 0.1 Å below and O1<sup>I</sup> and N are 0.1 Å above this plane. The deviations of these atoms from the plane and the dihedral angle of 8.4° between the Cu, O1, N and Cu, O1<sup>I</sup>, O2 planes indicate slight tetrahedral distortion. The axial sites of the Cu complex are occupied by an oxygen atom of the carboxylate group bonded to the adjacent Cu atom (*cf.* Fig. 2) and by an ethanolato oxygen atom, with Cu—O distances of 2.712 and 2.737 Å, respectively. The axial Cu—O3<sup>III</sup> and Cu—O1<sup>II</sup> directions make angles of 12.3 and 26.9° with the normal to the O1, O2, O1<sup>I</sup>, N plane. These values for the angles between axial coordination directions and the copper atom z-axis are similar to the values 13.0 and 26.3° found in  $\text{Cu}_4(\text{Et}_2\text{NC}_2\text{H}_4\text{O})_4(\text{ClC}_2\text{H}_2\text{O}_2)_4$ .<sup>4</sup>

The bond distances and angles of the 2-dimethylaminoethanolato ligand are as expected. The average value of the interbond angles around the ethanolato oxygen atom is 108.6°, indicating  $sp^3$  hybridization. The observed angle of 110.1° for Cu—O—Cu in the eight-membered  $\text{Cu}_4\text{O}_4$  ring is close to the corresponding value of 111.0° reported earlier for the chloroacetate complex.<sup>4</sup>

The acetate group is almost planar, the maximum deviation (C5) from the least-squares plane being 0.04 Å. The copper and chlorine atoms are displaced 0.08 and 0.69 Å from the plane. The Cu—O2—C5 angle of 125.2° is close to the value of 127° found in  $\text{Cu}_4(\text{Et}_2\text{NC}_2\text{H}_4\text{O})_4(\text{ClC}_2\text{H}_2\text{O}_2)_4$ ,<sup>4</sup> and the O2—C5—O3 angle of 128.0° in the carboxylate group is in good agreement with the values found in other chlorocarboxylates.<sup>3,4,10,11</sup> The C—O distances are

1.237 and 1.284 Å. On the basis of simple valence bond arguments the longer C—O bond length of the carboxylate group would be expected to involve the oxygen atom that is more strongly coordinated to the metal atom and this is consistent with the observed C—O distances.

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