

Crystal Structures of (2-Amino-2-methyl-1-propanolato)chloro-copper(II) and -bromocopper(II) Tetramers

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The crystal and molecular structure of $[\text{CuCl}(\text{C}_4\text{H}_{10}\text{NO})]_4$ has been determined from 756 independent reflections collected on an automatic four-circle diffractometer. The compound crystallizes in the tetragonal space group $P4_2/n$, with $a=b=12.604(8)$ Å, $c=8.998(3)$ Å and $Z=2$. The structure was solved by direct and Fourier methods and refined by least-squares techniques to a conventional R -value of 0.050.

Tetrameric oxygen-bridged cubane-type molecules with a Cu_4O_4 core and 4 (S_4) point symmetry are present in the solid state. The Cu–Cu separations in the tetranuclear cluster are 3.036(2) Å ($\times 2$) and 3.302(2) Å ($\times 4$). The tetramers can be considered as composed of two dimers, the intervening long Cu–O distance being 2.461(9) Å ($\times 4$). The two short independent Cu–O distances within the “dimer” are 1.970(7) Å (chelated) and 1.959(7) Å (non-chelated). The Cu–N and Cu–Cl distances are 1.984(9) and 2.230(3) Å, respectively. Copper(II) has an approximately square-pyramidal coordination involving the amine nitrogen, chlorine and three triply bridging alkoxo-oxygen atoms.

$[\text{CuBr}(\text{C}_4\text{H}_{10}\text{NO})]_4$ is isomorphous with the chloro compound. The lattice dimensions are $a=b=12.954(13)$ Å and $c=9.248(6)$ Å.

A summary of the known crystal structures of alkoxo-bridged copper(II) complexes $[\{\text{CuX}(\text{OCH}_2\text{CH}_2\text{NR}_2)\}_n]$ ($R=\text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$ or $n\text{-C}_4\text{H}_9$; $X=\text{Cl}$, Br , NCO or NCS) has recently been published and the existence of di-, tetra- and polymeric structures reported.¹ Our earlier work with a 2-amino-2-methyl-1-propanol compound where the counter ion was the large organic benzoate group rather than a small inorganic ion, demonstrated the formation of a mononuclear copper(II) aminoalcohol complex.² Further we

know that copper(II) forms trinuclear complex with 2-dibutylaminoethanol when the benzoate group acts as a counter ion.³ When it is remembered that the same counter ion may produce different structural types, even under the same conditions, one is prepared for great variations in the behaviour of aminoalcohols upon coordination. For this work the widely used halogeno ions were selected so that structural comparisons with known structures formed by N,N -dialkylaminoalcohols could be made. Through systematic study of complexes formed by $\text{C}_4\text{H}_{11}\text{NO}$ we aim at elucidating the coordination behaviour of aminoalcohols with different counter ions and in various environments.

EXPERIMENTAL

The chloro compound was prepared by treating a hot solution of 2-amino-2-methyl-1-propanol in methanol with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (molar ratio 2:1). The solution was filtered and left to stand for several days in a closed Erlenmeyer flask. Green needle-shaped crystals were precipitated.

The bromo compound was prepared in the same way from CuBr_2 . Crystals were smaller and a bit lighter green than those of the chloro compound.

Densities were determined by flotation method in a mixture of carbon tetrachloride and methyl iodide. Values are given in Table 1.

Preliminary oscillation and Weissenberg photographs taken with $\text{CuK}\alpha$ radiation showed that both compounds belong to the tetragonal system and systematic absences were recognized for the reflections $00l$ and $hk0$, with l and $h+k$ odd, respectively. The space group is thus $P4_2/n$ (No. 86). This was further confirmed by dividing the reflections into classes on the basis of the limiting conditions and the magnitude of the intensity. For the

Table 1. Crystal data of $[\text{CuCl}(\text{C}_4\text{H}_{10}\text{NO})]_4$ and $[\text{CuBr}(\text{C}_4\text{H}_{10}\text{NO})]_4$ and details of data collection for the former compound.

CRYSTAL DATA

Compound	$[\text{CuCl}(\text{C}_4\text{H}_{10}\text{NO})]_4$	$[\text{CuBr}(\text{C}_4\text{H}_{10}\text{NO})]_4$
Space group	$P4_2/n$ (No. 86)	$P4_2/n$ (No. 86)
$a=b$ (Å)	12.604(8)	12.954(13)
c	8.998(3)	9.248(6)
V (Å ³)	1429.4	1552.1
M	748.49	926.31
Z	2	2
D_m (g cm ⁻³)	1.76	1.98
D_c (g cm ⁻³)	1.74	1.98
μ (cm ⁻¹)	19.8	41.8

DATA COLLECTION

Crystal size: $\sim 0.33 \times 0.08 \times 0.05$ mm

Radiation: $\text{MoK}\alpha$ ($\lambda = 0.71069$ Å)

Monochromator: highly oriented graphite

Scan type: $\theta - 2\theta$

2θ range: $4 - 55^\circ$

Scan speed: intensity dependent variable (150–4000 counts s⁻¹) 2.5–25° min⁻¹

Scan length: from $[2\theta(K\alpha_1) - 1.0]$ to $[2\theta(K\alpha_2) + 1.0]^\circ$

Background measurement: at the beginning and end of each scan, each for half of the total scan time

Standards: 1 every 99 reflections

Reflections collected: one octant (*i.e.*, $+h$, $+k$, $+l$), giving a total of 1765 independent measurements of which 113 were systematic absences

bromo compound, which can be verified to be isomorphous with the chloro compound, only the lattice parameters and density were determined.

The intensity data were collected on a Syntex P2₁ four-circle, computer controlled diffractometer. The crystal was mounted in an arbitrary orientation relative to the instrument coordinate system. Calculation of the orientation matrix and refinement of cell parameters were carried out by least-squares method from 12 centred and indexed reflections. For the bromo compound the lattice dimensions were determined from five Friedel pairs and two other reflections on the same diffractometer. Crystal data and intensity collection details appear in Table 1.

The intensity of the standard reflection showed only statistical fluctuation throughout the data collection. Of the 1765 measured intensities, 756 with $I > 3\sigma(I)$ were used in the final refinement. Data were corrected for Lorentz and polarization factors and for absorption by an empirical method. In the absorption correction five fairly intense reflections, with χ values close to 90° and 2θ values evenly distributed over the 2θ range used, were measured at 36 points around the diffraction vector (from $\psi = 0^\circ$ to $\psi = 350^\circ$, $\Delta\psi = 10^\circ$). Each reflection was used to define an absorption curve, I vs. ϕ ,

corrected for ω and χ .^{4,5} The curves bracketing the 2θ value of the reflection under consideration were interpolated both in 2θ and in ϕ to derive the absorption correction for the intensity of that reflection. The largest relative intensity drop (I_{\min}/I_{\max}) was 0.63.

STRUCTURE DETERMINATION AND REFINEMENT

The phase problem was solved by SINGEN and PHASE programs of the X-RAY 76 program system.⁶ At this stage 1382 reflections were included. In the space group representation the origin is at $\bar{1}$. The copper atom position could be determined from the first Fourier map, the signs of F having been derived from the output of the PHASE program. Two successive Fourier syntheses gave the positions of all non-hydrogen atoms.

An initial refinement of the structure was carried out by block-diagonal least-squares technique and continued by full-matrix method with anisotropic thermal parameters. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the final weighting scheme

Table 2a. Fractional atomic coordinates ($\times 10^4$) and anisotropic thermal parameters^a ($\times 10^3$) for non-hydrogen atoms. Standard deviations are given in parentheses.

	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cu1	1589(1)	3288(1)	6106(2)	15(1)	16(1)	37(1)	0(1)	-1(1)	4(1)
Cl1	-165(2)	3293(2)	5776(4)	14(1)	32(1)	57(2)	0(1)	-8(1)	7(1)
N1	1880(6)	4826(7)	5883(12)	13(4)	18(4)	40(7)	2(3)	6(4)	-1(4)
O1	3150(5)	3244(5)	6176(10)	18(3)	16(4)	51(4)	3(3)	4(4)	3(4)
C1	3641(8)	4137(8)	5472(16)	7(4)	23(5)	50(7)	7(4)	8(5)	-5(5)
C2	2817(9)	4885(8)	4846(14)	24(6)	23(5)	45(8)	9(5)	1(5)	17(5)
C3	2422(12)	4524(14)	3337(17)	40(8)	71(11)	35(8)	10(8)	8(7)	3(8)
C4	3221(12)	6021(11)	4694(25)	34(7)	30(7)	90(15)	1(6)	15(9)	25(8)

^a The anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$.

Table 2b. Fractional atomic coordinates ($\times 10^3$) and isotropic temperature factors^b ($\times 10^2$) for hydrogen atoms.

	x	y	z	U	x	y	z	U	
H1(C1)	408(10)	392(10)	483(15)	3	H6(C4)	266(13)	647(12)	473(19)	9
H2(C1)	400(10)	455(10)	631(16)	5	H7(C4)	337(9)	620(9)	574(14)	2
H3(C3)	296(9)	449(9)	270(13)	2	H8(C4)	376(11)	597(11)	386(16)	6
H4(C3)	223(8)	365(9)	334(13)	2	H9(N1)	207(12)	511(12)	682(18)	7
H5(C3)	178(11)	482(10)	301(14)	4	H10(N1)	141(8)	533(8)	553(12)	1

^b The isotropic temperature factors are of the form $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$.

$w = 1/\{1 + [(F_o - 60)/75]^2\}$. With all non-hydrogen atoms included an *R*-value of 0.058 ($R = \sum \|F_o\| - |F_c| / \sum \|F_o\|$) was reached. A difference Fourier synthesis then revealed the positions of all hydrogen atoms. Continued refinement in which hydrogen atoms were assigned isotropic thermal parameters led to final convergence with *R* = 0.050 and *R*_w = 0.060 ($[\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$). A difference map calculated from the final parameter values showed eight spurious peaks around the copper atom, varying in height from 0.84 e/Å³ down to 0.55 e/Å³. Since all other peaks were lower than 0.50 e/Å³, the analysis was considered complete. Calculations were performed on a Univac 1108 computer. Scattering factors were those stored in the program system.⁶ An anomalous dispersion correction was applied to the copper atom.⁷

The final atomic parameters are given in Tables 2a and b. A list of the observed and calculated structure factors is obtainable on request from the author.

RESULTS AND DISCUSSION

Interatomic distances and angles together with their estimated standard deviations are given in Table 3.

The unit cell contains two tetrameric molecules [CuCl(C₄H₁₀NO)]₄ of cubane-type clusters (Fig. 1) with a Cu₄O₄ core. The shortest distances between the tetramers N \cdots Cl ($-x, 1-y, 1-z$) and C4 \cdots Cl ($x + \frac{1}{2}, y + \frac{1}{2}, 1-z$) are 3.54 Å. There are two short 3.036(2) Å (within a "dimer") and four long 3.302(2) Å (between two "dimers") Cu-Cu separations in the Cu₄ tetrahedron. The geometry of the Cu₄O₄ core is highly symmetric. The Cu-O bonds inside the "dimer" are 1.970(7) Å (chelated) and 1.959(7) Å (non-chelated) and within standard deviations they are equal. The least-squares planes through the Cu₂O₂ four-membered rings (Table 4) constitute a nearly rectangular parallelepiped which has a rhombus top and bottom. Thus the symmetry of the Cu₄O₄ core can well be described by the notation $42m (D_{2d})$, although the exact point symmetry of the whole cubane-type cluster is 4

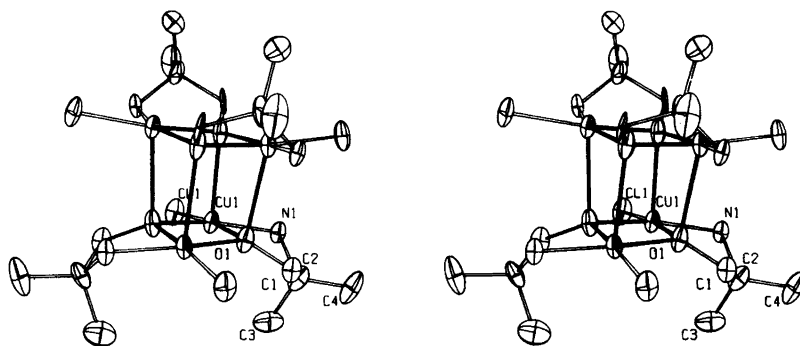


Fig. 1. A stereo view of the tetrameric molecule.

(S_4). The [(2-diethylaminoethanolato)isocyanato-copper(II)] tetramer also has 4 point symmetry, but possesses a less symmetric Cu_4O_4 core.⁸ The tetramer may be considered as composed of two dimers held together by out-of-plane Cu–O bonds of 2.461(9) Å ($\times 4$). The extent of bending of the Cu_2O_2 ring within the “dimer” is described by the dihedral angle of 4.8° between the O–Cu–O planes. The same dihedral angle for the 2-diethylaminoethanol compound, mentioned above, is 12.4°. Mergehenn and Haase¹ have classified tetrameric Cu_4O_4 core complexes on the basis of their investigations on *N,N*-dialkylaminoethanols and suggest that their classification is applicable also to other compounds containing the Cu_4O_4

core. The compound described here falls into their classification scheme, representing the extreme type they describe by the symbol I.

The coordination around each Cu atom is distorted square pyramidal with the amine nitrogen, chlorine and two alkoxo-oxygens in the basal plane and the out-of-plane alkoxo-oxygen at the top of the pyramid (*cf.* Tables 3 and 4). The mean value for the angles $O1''-Cu1-L$ ($L=O1, O1', N1, Cl1$) is 92.0° and the mean values for the basal angles are 89.9° ($\times 4$) and 166.7° ($\times 2$).

The bridging O atoms of the aminoalcohol have sp^3 hybridization. This is confirmed by the fact that the mean value of the interbond angles at O is 108.3°, though the individual values range from

Table 3. Interatomic distances (Å) and angles (°). The symmetry codes are (') = $\frac{1}{2} - x, \frac{1}{2} - y, z$; (") = $\frac{1}{2} - y, x, \frac{3}{2} - z$; (""') = $y, \frac{1}{2} - x, \frac{3}{2} - z$. Distances involving hydrogen atoms vary between 0.85 and 1.12 Å.

The Cu and O atom environments

Cu1–Cu1'	3.036(2)	O1–Cu1–O1'	78.7(3)	N1–Cu1–O1''	98.8(4)
Cu1–Cu1''	3.302(2)	O1–Cu1–Cl1	174.0(3)	Cu1–O1–Cu1'	101.2(3)
Cu1–Cl1	2.230(3)	O1–Cu1–N1	81.1(3)	Cu1–O1–C1	113.3(6)
Cu1–O1	1.970(7)	O1–Cu1–O1''	83.2(3)	Cu1–O1–Cu1'''	95.7(3)
Cu1–O1'	1.959(7)	O1'–Cu1–Cl1	100.0(2)	Cu1'–O1–C1	133.4(7)
Cu1–O1''	2.461(9)	O1'–Cu1–N1	159.3(3)	Cu1'–O1–Cu1'''	96.0(3)
Cu1–N1	1.984(9)	O1'–Cu1–O1''	83.4(3)	C1–O1–Cu1'''	110.0(7)
O1–O1'	2.491(10)	Cl1–Cu1–N1	99.6(3)		
O1–O1''	2.963(12)	Cl1–Cu1–O1''	102.6(2)		

The aminoalcohol skeleton

C1–O1	1.431(13)	O1–C1–C2	111.0(8)	C3–C2–N1	106.4(10)
C1–C2	1.511(16)	C1–C2–C3	111.8(11)	C4–C2–N1	111.3(10)
C2–C3	1.516(20)	C1–C2–C4	113.0(10)	Cu1–N1–C2	104.8(6)
C2–C4	1.526(18)	C1–C2–N1	106.1(10)		
C2–N1	1.507(15)	C3–C2–C4	108.1(13)		

Table 4. Deviations (Å) of atoms from least-squares planes.

Plane I: Cu1, Cu1', O1, O1'							
Cu1	-0.032	Cu1'	-0.032	O1	0.032	O1'	0.032
Plane II: Cu1, Cu1'', O1, O1''							
Cu1	0.096	Cu1''	0.097	O1	-0.096	O1''	-0.097
Plane III: Cu1, Cu1''', O1', O1'''							
Cu1	-0.097	Cu1'''	-0.096	O1'	0.097	O1'''	0.096
Plane IV: O1, O1', N1, Cl1							
O1	-0.006	O1'	0.005	N1	0.005	Cl1	-0.004
Cu1	0.103						

The angles (°) between the planes: I, II=89.9; I, III=89.9; II, III=90.0

95.7 to 133.4°, with only the angles C1–O1–Cu1''' and C1–O1–Cu1 (110.0, 113.3°) of normal magnitude.

Comparison of bond lengths and interbond angles of the aminoalcohol skeleton with those in bis(2-amino-2-methyl-1-propanol)copper(II) dibenzoate² shows good agreement to prevail. However, the chelated Cu–O bond has increased from 1.933(5) in the monomer to 1.970(7) Å. A second change has occurred in the conformation. The monomer has unsymmetrical *gauche* conformation with the C1 and C2 atoms lying on opposite sides of the N–Cu–O plane. This form of conformation is common for five-membered chelate rings of diamines and substituted diamines. The present complex, on the other hand, exists in another form with the C1 and C2 atoms both below the plane, at distances from the plane of 0.525 and 0.953 Å, respectively. The dihedral angle between the planes O1–C1–C2 and N1–C2–C1 is 33.2°, whereas the same angle for the benzoate compound is 50.0°.

Acknowledgement. Financial aid from The Finnish Academy of Science is gratefully acknowledged.

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Received August 20, 1979.