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Crystal and Molecular Structure of a Cubane Type Tetrameric Copper(II) Chloride–Thiodiethanol Complex

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The crystal and molecular structure of tetrameric copper(II) chloride–thiodiethanol, $[CuClOC_2H_4SC_2H_4OH]_4$ *was determined from three-dimensional X-ray diffraction studies and was refined by least squares methods to R = 0.057 for 1837 reflections. The compound is monoclinic, space group C2/c, the unit cell parameters being* a = *20.836(3),* b = *9.963 (2),* c = *17.793(3)* Å, β = *122.57(2)°, V = 3112.8* Å^3, Z = *4 tetramers per cell.*

Within the single $CuClOC_2H_4SC_2H_4OH$ *unit, the copper atom is bonded to the S and O atoms of the ligand, and to the chlorine atom. The average Cu–S, Cu–Cl, Cu–O(alkoxide) and Cu–OH distances are 2.336, 2.280, 1.980 and 2.506* Å, *respectively. The alkoxide oxygen atom in each unit is further bonded to two other copper atoms at distances (av.) of 1.945 and 2.440* Å, *resulting in a cubane type tetramer with* C_2 *symmetry. The geometry around each copper in the tetramer is distorted octahedral, the long bonds being* trans *to each other. The Cu...Cu distances within the tetramer are between 3.158 and 3.364* Å.

Introduction

Though a number of metal complexes of aminoalcohols are known [1], studies on thioalcohols are very sparse. This may partly be due to the poor coordinating ability of both the thioether and the alcohol groups. Sen and Johnson [2] have reported the coordinating behaviour of potentially tridentate thiodiethanol, and recently several transition metal complexes of this ligand have been prepared and characterized [3]. Though the alcoholic proton in the ligand is not acidic, the proton may be lost on bonding to a metal, resulting in an alkoxide anion. Further, as in the case of iminoalcohols [1], the alkoxide groups may be involved in bridge bonds to give polynuclear complexes.

Recently Udupa and Krebs [4] have reported the crystal structure of dichloro(thiodiethanol)–copper (II), and in this communication we report the crystal structure of the deprotonated thiodiethanol–copper (II) chloride complex, $[CuClOC_2H_4SC_2H_4OH]$.

Experimental

The title compound was prepared by adding dropwise 20 mmol of thiodiethanol to 100 ml of an alcoholic solution containing 20 mmol of copper(II) chloride. The solution was stirred on a magnetic stirrer and the pH was adjusted to 10 by the addition of 1N aqueous KOH solution. Tiny, needle-like green coloured crystals were separated out on standing overnight. The crystals were collected on a filter, washed with acetone and dried.

Anal. Found, C 21.18, H 4.36, S 14.18, Cl 15.49, Cu 28.67%; required for $C_4H_9O_2SClCu$, C 21.82, H 4.13, S 14.56, Cl 16.10, Cu 28.86%.

A satisfactory crystal of dimension 0.08 × 0.15 × 0.09 mm was chosen for the preliminary Weissenberg and precession photographs. They indicated the crystal to be monoclinic. The systematic absences hkl, h + k = 2n + 1 and h0l, l = 2n + 1 suggested two possible space groups, C2/c – C_{2h}^6 and Cc – C_s^4. The unit cell constants obtained from the photographs were refined by least-squares from diffractometer coordinates of 15 high angle reflections to be *a* = 20.836(3), *b* = 9.963(2), *c* = 17.793(3) Å, β = 122.57 (2)°, V = 3112.8 Å^3. The calculated density of 1.879 g cm^{-3} agreed with the measured value of 1.86(1) g cm^{-3}. There are 16 formula units of $CuClOC_2H_4SC_2H_4OH$ or four tetramers per unit cell. From the two possible space groups, the statistical distribution of the normalized structure factors suggested the centrosymmetric C2/c – C_{2h}^6 (No. 15) to be the correct choice which was later confirmed by the successful completion of the structure determination.

Data Collection and Reduction

The X-ray diffraction intensity data were collected at 22 °C, by making use of the same crystal on a

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Syntex P2$_1$ four-circle diffractometer using a graphite monochromator (MoKα radiation, λ = 0.71069 Å, ω–2θ scan, scintillation counter, scan range 2° in 2θ, scan rate 2° min^{-1} to 30° min^{-1} depending on the intensity, reference reflection for every 50 reflections). A complete set of 3159 unique reflections were measured in the range up to $(\sin\theta)/\lambda$ = 0.64 Å^{-1} out of which only 1837 were accepted as being statistically above background on the basis of $I > 1.96\ \sigma(I)$. The rest of the reflections were assigned zero weight. The data were reduced to structure factors by Lorentz and polarization corrections, including a Wilson plot. The linear absorption coefficient of the crystal was calculated to be 34.3 cm^{-1}; no absorption correction was applied.

Structure Determination and Refinement

The structure could be solved from direct methods [5], using the MULTAN programme system. Besides the origin defining reflections, the starting set consisted of three reflections and two others phased by Σ_1 relations. The figures of merit readily suggested the correct solution. From the E-map the Cu, Cl, S, O and some of the C atoms were located. The remaining atoms including the H atoms were identified from subsequent ΔF maps after isotropic refinement of the heavy atoms. Full-matrix least-squares refinement with anisotropic temperature factors for the non-hydrogen atoms and isotropic ones fixed at 5.0 Å^3 for the H atoms resulted in residuals of R_1 = 0.057, R_2 = 0.053 for 1837 observed data, where $R_1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$ and $R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma wF_0^2]^{1/2}$. The atomic scattering factors for Cu, Cl, S, O, C and H were taken from the International Tables [6]. The weighting scheme was based on the counting statistics. The final coordinates and thermal parameters of all atoms except the methylene hydrogens are given in Tables I and II. A Table of the calculated and observed strucure factors is available from the Editor.

TABLE I. $[CuClOC_2H_4SC_2H_4OH]_4$: Coordinates of the Atoms of One Asymmetric Unit in the Cell[a].

Cu1	0.09501(6)	0.47111(13)	0.30337(8)
Cu2	0.00760(7)	0.26053(14)	0.34904(8)
Cl1	0.18232(14)	0.50626(30)	0.45131(17)
Cl2	−0.08428(15)	0.22448(35)	0.37917(20)
S1	0.10530(16)	0.69143(30)	0.26721(21)
S2	0.04939(16)	0.03770(32)	0.38143(22)
O1	0.0109(3)	0.4513(7)	0.1761(4)
O2	0.1923(4)	0.4378(8)	0.2615(5)
O3	0.0810(3)	0.2799(6)	0.3125(4)
O4	0.1093(4)	0.2847(10)	0.5091(5)
C1	0.0148(6)	0.5393(15)	0.1150(7)
C2	0.0336(7)	0.6818(13)	0.1487(9)
C3	0.1964(8)	0.6813(18)	0.2783(9)
C4	0.2068(7)	0.5612(16)	0.2319(10)
C5	0.1461(9)	0.1890(16)	0.3559(8)
C6	0.1209(6)	0.0480(12)	0.3534(9)
C7	0.1043(8)	0.0448(15)	0.5060(10)
C8	0.1502(8)	0.1646(20)	0.5450(10)
H(O2)	0.153(5)	0.387(9)	0.194(6)
H(O4)	0.145(5)	0.341(9)	0.508(7)

[a] Estimated standard deviations are given in all tables in units of the least significant digits.

TABLE II. Coefficients of the Anisotropic Temperature Factors.[a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu1	2.58(5)	3.15(6)	2.75(6)	−0.28(5)	1.15(5)	0.02(5)
Cu2	2.68(5)	4.06(7)	3.06(6)	−0.28(5)	1.32(5)	0.81(6)
Cl1	3.61(13)	5.50(18)	3.33(13)	−0.84(17)	0.94(11)	−0.65(12)
Cl2	3.92(14)	8.49(23)	5.71(17)	−0.39(15)	2.90(13)	2.63(17)
S1	4.55(15)	3.85(15)	5.28(18)	−0.66(12)	2.17(14)	0.31(14)
S2	3.62(14)	4.00(16)	5.93(18)	−0.67(12)	0.90(13)	1.66(15)
O1	2.9(3)	4.6(4)	3.0(3)	0.4(3)	1.6(3)	1.2(3)
O2	4.3(4)	7.4(6)	4.2(4)	−0.4(4)	2.1(3)	0.1(4)
O3	1.7(3)	3.5(4)	3.2(3)	0.3(3)	0.7(2)	0.1(3)
O4	4.3(4)	7.8(6)	4.4(4)	0.2(4)	2.0(4)	1.0(4)
C1	4.0(6)	6.1(7)	3.1(6)	1.6(6)	1.5(4)	2.2(6)
C2	5.6(6)	4.3(7)	4.9(6)	0.3(5)	3.0(5)	2.1(5)
C3	5.5(7)	5.9(9)	6.8(9)	−2.1(7)	3.0(7)	0.4(7)
C4	3.4(6)	7.4(9)	7.4(9)	−0.1(6)	2.4(6)	3.0(8)
C5	4.7(6)	4.4(6)	3.4(6)	1.1(5)	1.3(6)	1.4(6)
C6	4.4(6)	2.2(6)	6.0(7)	1.0(4)	1.2(5)	1.0(5)
C7	5.8(8)	5.6(8)	7.8(9)	−0.4(7)	3.5(7)	2.4(8)
C8	5.6(9)	12.6(14)	4.0(7)	1.5(9)	3.0(7)	3.3(8)

[a] The anisotropic temperature factors are expressed in the form exp $[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}{}^{2c^{*2}} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

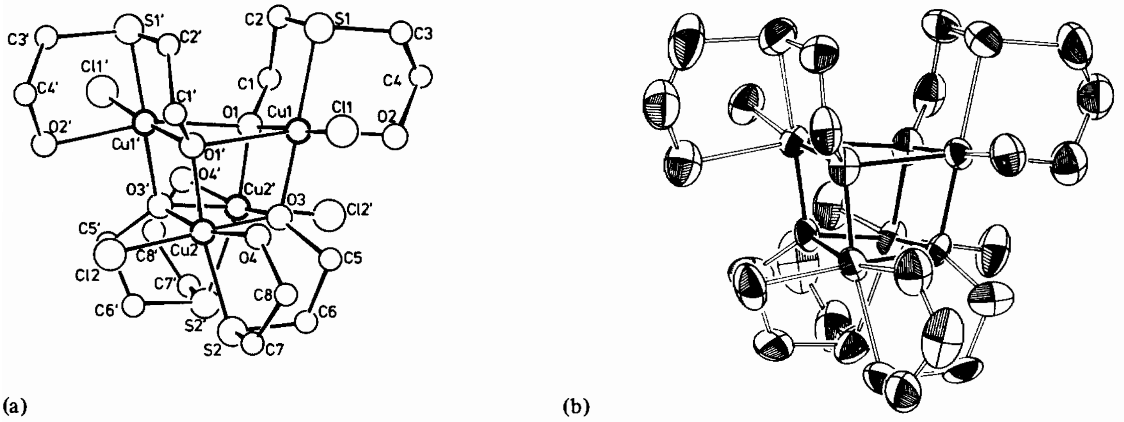

Fig. 1. Tetrameric copper(II) chloride–thiodiethanol [$CuClOC_2H_4SC_2H_4OH]_4$. (a): molecule with atom designations; (b): ORTEP plot (ellipsoids are drawn to 50% probability).

Results and Discussion

The structure consists of [$CuClOC_2H_4SC_2H_4OH$] units in which copper is bonded to one chlorine, one sulfur and two oxygen atoms of the thiodiethanol anion. Each alkoxide oxygen further bridges to two more copper atoms resulting in a tetramer with C_2 symmetry. The configuration of the tetranuclear complex with all non-hydrogen atoms, including the atom designations, is given in Fig. 1a; the ORTEP plot of the molecule is reproduced in Fig. 1b. As can be seen from the Figure, four copper and four oxygen atoms occupy the alternate corners of a highly distorted cube resulting in a cubane type structure. The interatomic distances and the bond angles involving all the non-hydrogen atoms are given in Table III.

The copper atom in each unit is bonded to one chlorine atom at distances of 2.282(3) (Cu1–Cl1) and 2.277(3) Å (Cu2–Cl2). These bond distances are very close to the sum of the Pauling covalent radii [7] and are comparable to those found in the literature for several copper(II) chloro complexes [8–13]. The uninegative thiodiethanol is bonded to the copper atom in each unit through the S (Cu1–S1 2.330(3), Cu2–S2 2.341(3) Å) and the alkoxide oxygen atoms (Cu1–O1 1.992(6), Cu2–O3 1.968(7) Å). In several S-ligated copper(II) complexes [14–19] the Cu–S distances fall in the range 2.17 to 2.33 Å. The observed values in the present complex are in accordance with the reported ones. The Cu–O bond lengths are generally found [20] within the limits of 1.89 to 2.04 Å in Cu(II) complexes of oxygen ligands. The alcoholic oxygen atoms of the ligand are in contact with the copper centers at 2.528(9) and 2.483(8) Å. Though these values are significantly larger than the normal single bond length, these are considered as (fairly weak) bonds; Cu–O effective bonding contact distances up to 2.65 Å are known in the literature [20]. Thus, the ligand is tridentate, forming two five-membered rings with the same copper atom. This is similar to the coordination in dichloro(thiodiethanol)copper(II), as observed previously [4]. The angle between the normals to the average planes consisting of the atoms in the two five-membered rings is 91.4° for Cu1 and 91.3° for Cu2.

The association of the monomeric $CuClOC_2H_4$·SC_2H_4OH subunits in the highly distorted cubane skeleton is such that the very weak Cu–O bonds are in directions perpendicular to the molecular C_2 axis (C_2 is vertical in Fig. 1), resulting in rectangular Cu1–O1–Cu1'–O1' and Cu2–O3–Cu2'–O3' faces with alternating short and long edges and being turned 90° relative to each other around the molecular C_2 axis. The faces of the cube parallel to C_2 (Cu1–O3–Cu2–O1', Cu1–O1–Cu2'–O3 and the symmetric equivalents), in contrast, have only one long together with three short edges. The Cu...Cu distances across the cube are Cu1–Cu2 3.158(2), Cu1–Cu2' 3.176(2), Cu1–Cu1' 3.345(2), Cu2–Cu2' 3.364 (2) Å, excluding, as expected, any Cu–Cu bonding. In the tetramer each copper is thus bonded to one Cl, one S and two alkoxide oxygen atoms in an approximately planar arrangement. An alcoholic oxygen and the third neighbouring alkoxide oxygen approach the copper in the axial positions. These axial bond distances are, as expected for copper(II), longer than the planar distances due to Jahn–Teller distortions. Thus the stereochemistry around copper can be described as a tetragonal bipyramid.

The bond distances have normal values and are almost identical [4] with those of dichloro(thiodiethanol)–copper(II). The S atoms have a trigonal pyramidal coordination with Cu1, C2, C3 and Cu2, C6, C7, respectively, as ligands. The alkoxide oxygen atoms are coordinated in a distorted tetrahedral arrangement with one C and three Cu atoms as neighbours. Among the tetrameric oxygen bridged

TABLE III. $[CuClOC_2H_4SC_2H_4OH]_4$: Interatomic Distances (Å) and Bond Angles (°).[a]

Cu Coordination

Cu1–Cl1	2.282(3)	Cu1	Cl1	S1	O1	O1'	O2
Cu1–S1	2.330(3)	S1	92.3(1)				
Cu1–O1	1.992(6)	O1	173.8(2)	86.3(2)			
Cu1–O1'	2.431(8)	O1'	93.6(2)	110.1(2)	81.3(3)		
Cu1–O2	2.528(9)	O2	95.3(2)	80.5(2)	90.4(3)	165.9(3)	
Cu1–O3	1.947(6)	O3	96.7(2)	170.1(2)	85.3(3)	73.7(3)	94.3(3)
Cu2–Cl2	2.277(3)	Cu2	Cl2	S2	O1'	O3	O3'
Cu2–S2	2.341(3)	S2	92.3(1)				
Cu2–O1'	1.943(7)	O1'	96.9(2)	170.4(2)			
Cu2–O3	1.968(7)	O3	174.2(2)	85.5(2)	85.5(3)		
Cu2–O3'	2.448(6)	O3'	95.2(2)	108.0(2)	73.9(3)	80.4(2)	
Cu2–O4	2.483(8)	O4	93.0(2)	80.5(2)	96.3(3)	92.0(3)	167.9(3)

Thiodiethanol Ligands

S1–C2	1.816(12)	Cu1–S1–C2	97.5(5)	Cu1–O1–Cu1'	97.8(3)
S1–C3	1.803(18)	Cu1–S1–C3	99.5(6)	Cu1–O1–Cu2'	107.6(3)
C1–C2	1.508(18)	C2–S1–C3	106.4(7)	Cu1'–O1–Cu2'	91.8(3)
C1–O1	1.432(14)	C2–C1–O1	112.7(9)	Cu1–O1–C1	115.3(6)
C3–C4	1.534(22)	C1–C2–S1	112.7(9)	Cu1'–O1–C1	119.4(7)
C4–O2	1.433(18)	C4–C3–S1	115.5(11)	Cu2'–O1–C1	120.7(6)
		C3–C4–O2	110.7(12)		
S2–C6	1.810(16)	Cu2–S2–C6	97.5(5)	Cu2–O3–Cu2'	98.7(3)
S2–C7	1.870(16)	Cu2–S2–C7	99.5(6)	Cu1–O3–Cu2	107.5(3)
C5–C6	1.492(20)	C6–S2–C7	104.8(6)	Cu1–O3–Cu2'	91.8(3)
C5–O3	1.458(18)	C6–C5–O3	110.9(11)	Cu2–O3–C5	115.5(7)
C7–C8	1.452(24)	C5–C6–S2	112.0(9)	Cu2'–O3–C5	118.2(7)
C8–O4	1.407(22)	C8–C7–S2	115.0(12)	Cu1–O3–C5	120.9(7)
		C7–C8–O4	113.6(14)		

[a] The primed atoms are related to the unprimed ones (coordinates of Table I) by a twofold axis through the center of the tetrameric unit.

copper(II) complexes four- and five-coordinated copper is found [22] in acetylacetone-mono-(O-hydroxy anil)copper(II), and a cubane type structure with five-coordination of Cu(II) is observed in $[Cu(OCH_2CH_2NC(CH_3)CHC(O)CH_3)]_4$ [23]. The present complex is a novel example of 6-coordinated cubane type tetramer of a copper(II) complex.

It is interesting to note that the hydroxyl hydrogen atoms form fairly strong intramolecular H bridge bonds to neighbouring Cl atoms: within the almost linear system O2–H....Cl2' the O2....Cl2' O2–H and H...Cl2' distances are 3.128(9), 1.14(9) and 2.09(9) Å, respectively (Fig. 1). A very similar arrangement is observed in the O4–H....Cl1 system: the O4...Cl1, O4–H and H...Cl1 distances are 3.151(9), 0.94(11) and 2.28(10) Å.

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