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Crystal and Molecular Structure of Dichloro(β-thiodiglycol)copper(II)

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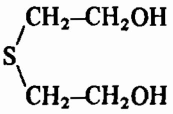
The preparation and the crystal and molecular structure of dichloro(β-thiodiglycol)copper(II) are reported. The structure has been determined by X-ray diffraction studies and refined by least-squares methods to R = 0.034 for 1111 reflections measured. The compound is orthorhombic, space group $P2_12_12_1$. *The cell dimensions are* a = *10.036(3),* b = *12.882(3),* c = *6.696(2)* Å, V = *865.7* Å^3, d_c = *1.968 and* d_m = *1.96 g cm*$^{-3}$, *Z = 4. β-Thiodiglycol behaves as a terdentate ligand through bonding of two oxygens and a sulphur atom to copper (Cu–O1 2.429(4), Cu–O2 2.024(4), Cu–S 2.322(2)* Å*). The tetragonal pyramidal geometry (distorted towards trigonal bipyramidal) around copper is completed by the bonding of two chlorine atoms (Cu–Cl1 2.259(2), Cu–Cl2 2.258(1)* Å).

Introduction

2,2′-Thiodiethanol, also known as β-thiodiglycol,



$$S(CH_2–CH_2OH)_2$$

is of interest for complexation studies, as it contains three possible binding sites, namely S and two O atoms and may form polynuclear complexes. However, not much information is available in the literature on its binding nature to metals, except for reports on stability constant determinations [1] of its metal derivatives. This is possible due to the poor ligating capacity of thioether and alcoholic groups. In order to investigate the coordination site in β-thiodiglycol and to compare its complexation tendencies with that of 2,2′-iminodiethanol [2] we prepared several complexes of β-thiodiglycol and report in this communication the crystal and molecular structure of dichloro(β-thiodiglycol)copper(II).

Experimental

Preparation of dichloro(β-thiodiglycol)copper(II)

To an ethanolic solution of copper(II) chloride β-thiodiglycol was added in a 1:2 molar ratio. The mixture was then stirred for an hour during which the pale green complex crystallized. The crystals were filtered and washed with acetone and ether. *Anal.* Found: C 18.16, H 4.24, Cl 26.91, Cu 24.18; Calcd. for $C_4H_{10}O_2SCl_2Cu$, C 18.71, H 3.93, Cl 27.63, Cu 24.75%.

Crystal Data

The unit cell parameters determined by preliminary Weissenberg and precession photographs were refined by least-squares from diffractometer coordinates of 15 high-order reflections. The crystals are orthorhombic with a = 10.036(3), b = 12.882(3), c = 6.696(2) Å, V = 865.7 Å^3. The measured and calculated densities are 1.96(1) and 1.968 g cm^{-3} for four molecules per unit cell. The systematic absences observed from the photographs, h00, h = 2n +1, 0k0, k = 2n + 1 and 00l, l = 2n + 1 suggested the space group $P2_12_12_1$ (D_2^4, No. 19).

Data Collection and Reduction

The X-ray intensity data for a crystal of approximate dimensions 0.11 × 0.15 × 0.21 mm^3 were collected at 22 °C on a Syntex $P2_1$ four-circle diffractometer using graphite monochromated MoKα radiation (Kα$_1$ = 0.70926 Å, Kα$_2$ = 0.71354 Å, ω–2θ scan, scintillation counter, take-off angle 6°). The sampling interval in 2θ for each reflection was 1.0° below the calculated MoKα$_1$ maximum to 1.0° above the calculated MoKα$_2$ maximum. The scan rate, depending on the intensity of the reflection, varied from 2° min^{-1} to 15° min^{-1} (in 2θ). The background measurements with the total time for background counts being equal to the scan time were made both at the start and end of each scan with the counter stationary. A standard reflection was measured for every 50 reflections. A complete set of 1111 unique reflections was measured up to (sinθ)/λ = 0.64 Å^{-1}, out of which 1068 reflections were accepted as statistically above the background on the

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TABLE I. Coordinates of the Atoms in the Structure of Dichloro(2,2′-thiodiethanol)copper(II).

	x	y	z
Cu	0.38587(6)	0.47981(5)	0.41475(9)
Cl1	0.50046(13)	0.60045(11)	0.58920(22)
Cl2	0.22532(13)	0.58983(9)	0.30994(20)
S	0.54587(14)	0.35359(12)	0.47614(24)
O1	0.50973(47)	0.48531(40)	0.10328(60)
O2	0.27366(38)	0.35761(29)	0.32634(61)
C1	0.60195(69)	0.40235(58)	0.07667(117)
C2	0.66098(60)	0.37229(58)	0.27143(126)
C3	0.45100(64)	0.23943(46)	0.40454(108)
C4	0.33939(60)	0.26379(45)	0.26121(91)
H1	0.459(7)	0.491(6)	0.004(11)
H2	0.563(7)	0.345(6)	0.020(11)
H3	0.667(7)	0.434(6)	0.007(11)
H4	0.751(7)	0.315(5)	0.256(10)
H5	0.715(7)	0.422(6)	0.321(12)
H6	0.415(7)	0.212(5)	0.541(11)
H7	0.512(7)	0.193(6)	0.340(11)
H8	0.284(7)	0.210(6)	0.270(10)
H9	0.353(6)	0.267(5)	0.104(10)
H10	0.246(6)	0.423(6)	0.241(11)

basis that $I > 1.96\sigma(I)$. The data reduction was done applying Lorentz and polarization corrections and a Wilson plot. The linear absorption coefficient was calculated to be 33.9 cm^{-1}; no absorption correction was applied.

Solution and Refinement of the Structure

The structure was solved by direct methods using the MULTAN programme system [3]. The correct solution was readily apparent from the combined figure of merit. The Cu, Cl, S and O atoms were located from the E-map. The C atoms were found from the subsequent difference Fourier map after some isotropic refinement. All H atoms were located from ΔF Fourier maps after anisotropic refinement of the non-hydrogen atoms. The atomic scattering factors for Cu, Cl, S, O, C and H were taken from the International Tables [4]. Full-matrix least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors fixed at 5.0 for the hydrogen atoms converged to residuals of $R_1 = 0.033$ (including unobserved data: 0.034), $R_2 = 0.042$, where $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics of the intensities. The shifts in the final cycle were below 0.02σ. The final difference Fourier map had no significant features. The final positional and thermal parameters are given in Tables I and II. A Table of calculated and observed structure factors is available from the Editor.

Results and Discussion

The crystal structure consists of $[CuCl_2 \cdot \beta$-thiodiglycol$]$ molecular units. One of the chlorine atoms in the unit (Cl2) is linked to one adjacent unit through a Cl···H–O hydrogen bond. An ORTEP plot of the structure is reproduced in Figure 1 with the atom numbering.

The copper atom in the molecule is strongly bonded to both chlorine atoms. The geometrical arrangement around copper is completed by the sulphur and the two oxygen atoms of the ligand resulting in two 5-membered rings. The penta-coordination around copper may be described either as square pyramidal or trigonal bipyramidal. Using the first description, S and Cl2, and O2 and Cl1 are trans to each other and constitute an approximate square. The least-squares equation for the plane containing these atoms together with Cu is $0.5103x + 0.2278y - 0.8293z - 1.0939 = 0$, where x, y and z are related

TABLE II. Anisotropic Temperature Factors.[a]

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2.03(2)	2.44(2)	2.67(2)	0.19(2)	−0.41(2)	−0.40(2)
Cl1	2.71(4)	3.64(6)	3.15(5)	−0.96(4)	−0.97(5)	−0.62(5)
Cl2	2.76(5)	2.88(5)	2.82(5)	0.59(4)	−0.36(4)	−0.11(4)
S	2.66(5)	3.42(6)	3.33(6)	0.67(5)	−0.69(5)	−0.13(5)
O1	4.84(22)	3.98(18)	2.88(16)	0.67(17)	−0.10(16)	−0.24(17)
O2	2.78(14)	2.82(14)	3.06(15)	0.02(13)	−0.33(14)	−0.50(14)
C1	3.64(27)	4.56(31)	4.81(32)	−0.05(24)	1.45(31)	−1.04(28)
C2	2.23(20)	4.16(29)	6.48(40)	0.32(21)	0.86(26)	0.19(29)
C3	4.15(26)	2.66(22)	3.96(26)	0.08(20)	−0.09(26)	0.74(22)
C4	3.27(22)	2.52(20)	3.34(23)	−0.60(19)	0.37(20)	−0.11(18)

[a] The isotropic temperature factors for the hydrogen atoms are fixed at 5.0. Definition of the anisotropic temperature factors: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

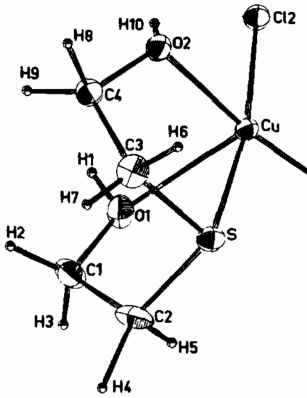

Fig. 1. Dichloro(β-thiodiglycol)copper(II): molecular structure in the crystal with atomic designations. Thermal ellipsoids are scaled to 50% probability.

TABLE III. Interatomic Distances and Bond Angles in the Crystal Structure of Dichloro(2,2'-thiodiethanol)copper(II).

Distances (A)			Angles (°)
Cu Coordination			
Cu–Cl1	2.259(2)	Cl1–Cu–Cl2	95.3(1)
Cu–Cl2	2.258(1)	Cl1–Cu–O1	99.4(1)
Cu–S	2.322(2)	Cl1–Cu–S	92.2(1)
Cu–O1	2.429(4)	Cl1–Cu–O2	165.8(1)
Cu–O2	2.024(4)	Cl2–Cu–O1	94.6(1)
		Cl2–Cu–S	171.2(1)
		Cl2–Cu–O2	90.0(1)
		O1–Cu–S	79.5(1)
		O1–Cu–O2	93.2(2)
		S–Cu–O2	83.8(1)
Thiodiethanol Molecule			
C1–C2	1.484(11)	C1–O1–Cu	114.7(4)
C1–O1	1.425(9)	C4–O2–Cu	119.0(3)
C2–S	1.809(8)	C2–C1–O1	110.2(6)
C3–S	1.816(6)	C1–C2–S	116.5(5)
C3–C4	1.508(9)	C2–S–C3	104.1(3)
C4–O2	1.444(7)	C2–S–Cu	102.4(2)
		C3–S–Cu	99.1(2)
		S–C3–C4	112.9(4)
		C3–C4–O2	108.7(5)

to the crystal axes. The Cu–O1 line is exactly perpendicular to this plane (90.2°). However, the atom O2 deviates from the mean plane by 0.45 Å. This deviation suggests to consider the alternative trigonal bipyramidal arrangement. In this description, atoms Cl1, O1 and O2 constitute a triangular plane, with Cl2 and S approaching in the axial positions. The least-squares equation for the triangular plane containing copper is $-0.6337x + 0.6980y - 0.3259z - 0.9309 = 0$. The S–Cu–Cl2 line is almost perpendicular to this plane (84.3°). However, the angles of the triangular plane are not 120° (Table III). Thus, the geometry around copper is best described as tetragonal pyramidal distorted towards trigonal bipyramidal. Similar observations were reported [5] in the literature, *e.g.* for [CuCl$_2$(coffeine)OH$_2$].

The interatomic distances and bond angles are given in Table III. The bond distances, Cu–Cl1 and Cu–Cl2 (2.259(2) and 2.258(1) Å respectively) are almost equal to the sum of the covalent radii (2.27 Å) given by Pauling [6]. Cu–S bond distances are found in the range 2.17–2.32 Å in S-ligated copper(II) complexes [7–14]. The bond length, 2.322(2) Å, observed in the present complex is in agreement with reported values of similar complexes. Single bond Cu–O distances are generally found within the limits 1.89 to 2.04 Å [15]. The Cu–O2 bond (2.024(4) Å) is of normal length, however, Cu–O1 (2.429(4) Å) suggests significantly weaker bonding. This may be due to the greater strain induced in the ligand due to the formation of two 5-membered rings.

Bond distances within the ligand molecule have normal values. The sulphur atom assumes a pyramidal arrangement with Cu, C2 and C3 as neighbours, the S–C2 and S–C3 distances being as expected for C(sp^3)–S. The C–C bond distances are slightly shorter than undisturbed C(sp^3)–C(sp^3) values; the possibly significant shortening of C1–C2 and C1–O1 compared with C3–C4 and C4–O2 seems to be a result of the much weaker Cu–O1 bonding compared to Cu–O2. The intermolecular hydrogen bonding links a O1–H1 group to a Cl2 of a neighbouring molecule (O–H 0.85(7), O···Cl 3.221(5), H···Cl 2.49(7) Å. O–H···Cl 144(8)°).

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