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Crystal and Molecular Structure of Dichlorobis(2,2'-Thiodiethanol)Cobalt(II)

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The crystal and molecular structure of dichlorobis-(2,2'-thiodiethanol)cobalt(II) was determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes as prismatic pink plates and belongs to space group $P2_1/c$. The unit cell dimensions are a = *6.786(2),* b = *11.270(3),* c = *10.331(3) Å, β = 109.24(2)°, and Z = 2. The structure was solved by direct methods from 1496 reflections and was refined by least-squares to an R value of 0.028. The complex is centrosymmetric, and each thiodiethanol molecule is bonded to cobalt through a sulphur (Co–S 2.508 Å) and an oxygen atom (Co–O 2.066 Å), resulting in a five-membered chelating ring. The six-coordination around cobalt is completed by the two chlorine atoms occupying the apical positions* trans *to each other (Co–Cl 2.423 Å). There is extensive hydrogen bonding involving the hydroxyl groups and chlorine atoms.*

Introduction

2,2'-Thiodiethanol, $S(CH_2CH_2OH)_2$, is potentially a terdentate ligand, capable of bonding through the sulphur and hydroxy groups. Several 1:1 and 1:2 transition metal halide and thiodiethanol complexes have been isolated and their bonding properties have been discussed based on magnetic and spectroscopic studies [1, 2]. Similar to 2,2'-iminodiethanol [3], thiodiethanol also functions as an anionic ligand which favours the formation of polynuclear complexes through bridging alkoxide groups. Recently Udupa and Krebs [4, 5] have reported the crystal structures of copper(II) complexes of this ligand. In this paper, we report the crystal and molecular structure of dichlorobis(2,2'-thiodiethanol)cobalt(II).

Experimental

Dichlorobis(thiodiethanol)cobalt(II) was prepared by mixing alcoholic solutions of cobalt(II) chloride and thiodiethanol taken in a 1:2 molar ratio. The resultant solution was stirred for some time and was diluted with diethyl ether. The pink crystalline product separated was filtered and washed with ether. Single crystals were obtained by slow evaporation of the acetone solution of the complex. *Anal.*: found, C 25.16, H 5.66, Cl 19.33%; calculated for $C_8H_{20}O_4S_2Cl_2Co$: C 25.68, H 5.39, Cl 18.95%.

The unit cell parameters were determined by preliminary Weissenberg and precession photographs and were refined by least-squares from diffractometer coordinates of 15 high-order reflections. The crystals are monoclinic with a = 6.786(2), b = 11.270(3), c = 10.331(3) Å, β = 109.24(3)°, V = 746.0 Å^3. The measured density of 1.65(1) g cm^{-3} is in agreement with 1.667 g cm^{-3} obtained for two formula units of the complex per unit cell. The systematic absences observed from the photographs, 0k0 with k = 2n + 1, h0l with l = 2n + 1 indicated the space group $P2_1/c$ (C_{2h}^5, No. 14).

The X-ray intensity data of a prismatic crystal of approximate dimensions 0.02 × 0.1 × 0.15 mm^3 were collected at 22 °C on a Syntex $P2_1$ four-circle diffractometer using graphite monochromated MoKα radiation ($\lambda(\alpha_1)$ 0.70926, $\lambda(\alpha_2)$ 0.71354 Å, ω–2θ scan, scintillation counter, take-off angle 6°). The sampling interval in 2θ was 1° below the calculated MoKα_1 maximum to 1.0° above the calculated MoKα_2 maximum. Depending on the intensity of reflections, the scan rate was varied from 2° min^{-1} to 15° min^{-1}. A standard reflection was measured for every 50 reflections. A complete set of 1634 unique reflections was measured up to $(\sin\theta)/\lambda = 0.64$ Å^{-1}, out of which 1496 were accepted as statistically above background based on $I > 1.96\sigma(I)$. No absorption correction was made (μ = 18.2 cm^{-1}). The data reduction was done by applying Lorentz and polarization corrections including a Wilson plot.

Determination and Refinement of the Structure

The structure was solved by direct methods, employing the MULTAN programme system*. The

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*The calculations were carried out on a Data General Eclipse computer, using, besides own programmes, the programmes of the Syntex EXTL system, and on an IBM 360/50 using the ORTEP programme of C. Johnson.

programme was allowed to select origin-defining reflections. The correct solution was readily apparent from the combined figure of merit values. An E map, calculated with phases having the highest figure of merit, revealed the positions of most of the non-hydrogen atoms. After isotropic refinement of the Co, Cl and S atoms, the remaining non-hydrogen atoms were located from the difference Fourier map. All the hydrogen atoms were found, after anisotropic refinement of the non-hydrogen atoms, from a subsequent difference Fourier map. The atomic scattering factors for Co, Cl, S, O, C and H were taken from the International Tables [6]. Full-matrix least-squares refinement with anisotropic temperature factors for the non-hydrogen atoms and isotropic ones for hydrogen converged to residuals of $R_1 = 0.028$, $R_2 = 0.033$ where $R_1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$ and $R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2]^{1/2}$. The quantity minimized was $\Sigma w(|F_0| - |F_c|)^2$. The weighting scheme was based on counting statistics of the intensities. The shifts in the final cycle were below 0.02σ and the ΔF map had no significant features. The final positional and thermal parameters of the atoms are given in Tables I and II. A Table of the calculated and the observed structure factors is available from the Editor.

TABLE II. Experimental Coordinates and Temperature Factors of the Hydrogen Atoms.

	x	y	z	B
H(1)	0.808(4)	0.072(3)	0.422(3)	4.6(7)
H(2)	0.771(4)	−0.001(2)	0.232(3)	4.7(7)
H(3)	0.674(4)	−0.118(2)	0.273(3)	4.1(6)
H(4)	0.452(4)	0.104(2)	0.174(3)	3.6(6)
H(5)	0.400(4)	−0.013(2)	0.092(3)	4.1(7)
H(6)	0.125(4)	−0.197(3)	0.263(3)	4.8(7)
H(7)	0.322(4)	−0.212(2)	0.221(3)	4.3(7)
H(8)	−0.063(4)	−0.139(2)	0.037(3)	3.8(6)
H(9)	0.152(4)	−0.155(2)	0.005(3)	3.8(6)
H(10)	−0.097(4)	−0.321(3)	0.026(3)	4.3(7)

Results and Discussion

The crystal structure consists of centrosymmetric dichlorobis(2,2′-thiodiethanol)cobalt(II), $[CoCl_2 \cdot 2S(CH_2CH_2OH)_2]$, units which are linked through hydrogen bonds involving the Cl atoms and the hydroxyl groups. The geometrical arrangement of the atoms in the molecule is shown in the ORTEP plot reproduced in Fig. 1. The cobalt atom in the mole-

TABLE I. Coordinates and Anisotropic Temperature Factor Coefficients of the Atoms other than Hydrogen in the Unit Cell of Dichlorobis(2,2′-thiodiethanol)cobalt(II).

	x	y	z
Co	0.50000	0.00000	0.50000
Cl	0.43931(9)	0.21167(5)	0.47001(6)
S	0.25460(9)	−0.01733(5)	0.25870(6)
O(1)	0.72603(24)	0.00933(14)	0.40664(17)
O(2)	0.02096(26)	−0.30633(16)	0.02688(19)
C(1)	0.66753(40)	−0.02707(25)	0.26604(27)
C(2)	0.45502(42)	0.01825(24)	0.18347(27)
C(3)	0.19790(40)	−0.17147(20)	0.20974(26)
C(4)	0.06843(40)	−0.18400(22)	0.06080(27)

	B_{11} [a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	2.05(2)	1.81(2)	1.80(2)	0.08(1)	0.79(1)	−0.06(1)
Cl	2.94(2)	1.85(2)	2.91(2)	0.13(2)	1.17(2)	0.17(2)
S	2.54(2)	2.11(2)	2.24(2)	0.86(2)	0.48(2)	−0.11(2)
O(1)	2.43(6)	2.38(7)	2.59(7)	−0.30(5)	1.13(5)	−0.20(6)
O(2)	2.39(7)	2.51(7)	4.38(9)	−0.30(5)	0.64(7)	−0.89(6)
C(1)	3.46(11)	3.63(12)	2.97(11)	−0.60(9)	1.93(10)	−0.83(9)
C(2)	4.24(12)	3.33(12)	2.10(10)	−1.06(10)	1.08(9)	0.06(9)
C(3)	2.94(10)	2.16(9)	2.72(10)	−0.23(8)	0.83(9)	−0.02(8)
C(4)	2.79(10)	2.41(10)	3.13(12)	−0.18(8)	0.25(9)	−0.27(9)

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

TABLE III. Dichlorobis(2,2'-thiodiethanol)cobalt(II): Interatomic Distances [Å] and Bond Angles [°] with Standard Deviations[a].

Co-Coordination			A–B–C	∢ A–B–C	d(A...C)
Co–Cl	(–Cl')	2.423(1)	Cl–Co–S	85.43(3)	3.346(2)
Co–S	(–S')	2.508(1)	Cl–Co–S'	94.57(3)	3.624(2)
Co–O(1)	(–O(1'))	2.066(2)	Cl–Co–O(1)	90.64(5)	3.202(3)
			Cl–Co–O(1')	89.36(5)	3.167(3)
			S–Co–O(1)	83.79(5)	3.072(3)
			S–Co–O(1')	96.21(5)	3.418(3)
Thiodiethanol Molecule					
S–C(2)		1.820(3)	Co–S–C(2)	93.6(1)	
S–C(3)		1.815(2)	Co–S–C(3)	111.2(1)	
C(1)–C(2)		1.502(4)	C(2)–S–C(3)	102.2(1)	
C(3)–C(4)		1.506(4)	C(2)–C(1)–O(1)	111.8(2)	
C(1)–O(1)		1.434(3)	S–C(2)–C(1)	113.3(2)	
C(4)–O(2)		1.433(3)	S–C(3)–C(4)	111.9(2)	
			C(3)–C(4)–O(2)	110.4(2)	
O(1)–H(1)		0.88(3)	Co–O(1)–C(1)	117.3(1)	
C(1)–H(2)		0.93(3)	Co–O(1)–H(1)	118(2)	
C(1)–H(3)		1.03(3)	C(1)–O(1)–H(1)	112(2)	
C(2)–H(4)		0.97(3)	C(4)–O(2)–H(10)	110(2)	
C(2)–H(5)		0.97(3)			
C(3)–H(6)		0.90(3)			
C(3)–H(7)		0.93(3)			
C(4)–H(8)		0.98(3)			
C(4)–H(9)		0.99(3)			
O(2)–H(10)		0.82(3)			

[a] The primed atoms are related to the unprimed by a centre of inversion at the Co site.

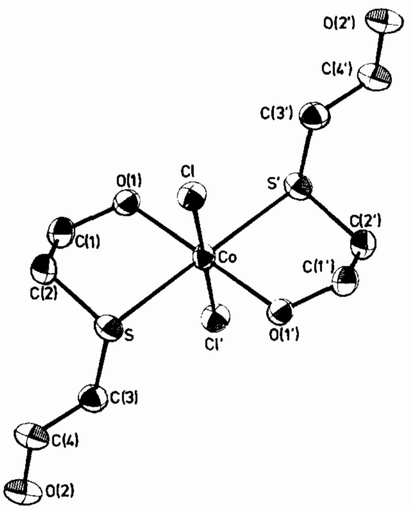

Fig. 1. Dichlorobis(2,2'-thiodiethanol)cobalt(II): ORTEP plot of the complex molecule with atom numbering (50% probability ellipsoids).

cule is strongly bonded to two chlorine, two sulphur and two oxygen atoms of the two ligand molecules. The *trans* coordination of the two thiodiethanol molecules per cobalt(II) produces an equatorial S_2O_2 ligand set forming a tetragonal plane with the cobalt atom at the centre. Thus, the ligand is bidentate chelating to a 5-membered non-planar ring. The apical positions of the tetragonal plane are occupied by the chlorine atoms resulting in a distorted octahedral arrangement around cobalt.

The interatomic bond distances and the bond angles are given in Table III. In typical O-ligated octahedral Co(II) complexes [*e.g.* 7–10] the average Co–O distance is found to be 2.09 Å. In the present complex, the bond distance of 2.066 Å (Co–O (1)) is of normal value, suggesting strong interaction of Co(II) with the hydroxyl oxygen of the ligand. Though Co–S distances are in the range 2.144–2.382 Å for several S-bonded cobalt complexes (S being two- or three-coordinated) [11–14], the bond distance of 2.508 Å observed for the present complex is significantly larger than the expected value of 2.31 Å, derived from the sum of the covalent radii [15] of Co(II) (octah.) and S (tetrah.). However, it has been reported [16] that in *trans*-Co(thiourea)$_4$Cl$_2$, where cobalt is 6-coordinated, the Co–S bond lengths are 2.502(6) and 2.553(6) Å, which are very close to that found for the present complex. A Co–Cl bond length of 2.405 Å is observed in dichlorobis(pyrazine)cobalt(II) [17], and 2.469 Å in dichlorotetrathiourea

TABLE IV. Hydrogen Bonding in the Dichlorobis(2,2'-thiodiethanol)cobalt(II) Structure[a].

Distances [Å]						Angles [°]	
O(1)–H(1)	0.88(3)	H(1)...O(2'')	1.77(3)	O(1)...O(2'')	2.638(2)	O(1)–H(1)...O(2'')	174(3)
O(2)–H(10)	0.82(3)	H(10)...Cl'''	2.36(3)	O(2)...Cl'''	3.141(2)	O(2)–H(10)...Cl'''	160(3)

[a] The indices refer to the following transformations of the coordinates in Table I:

O(2''): 1 – x, 1/2 + y, 1/2 – z
Cl''': –x, y – 1/2, 1/2 – z

cobalt(II) [16]. The value of 2.423 Å found for $CoCl_2 \cdot 2S(CH_2CH_2OH)_2$ is close to the reported values.

The bond distances within the ligand molecule have normal values. The sulphur atom assumes pyramidal geometry, as found in dichlorothiodiethanolcopper(II) [4], with Co, C(2) and C(3) as the nearest neighbours. The C(2)–S and C(3)–S bond lengths are the expected values for $C(sp^3)$–S. The C–C distances in both the coordinated and the free alcoholic groups are almost the same, equal to the normal C–C single bond length values.

The five-membered chelate ring formed by the atoms Co, S, C(2), C(1) and O(1) has half-chair configuration with C(1) and C(2) being 0.34 Å, and 0.30 Å below and above the plane $-0.0954x + 0.9952y - 0.0228z + 0.3979 = 0$ through Co, S and O(1), where x, y, z are related to the monoclinic axes of the crystal. The atoms S, C(3), C(4) and O(2) constitute a plane the least-squares equation of it being $-0.8329x + 0.0639y + 0.5497z + 0.2159 = 0$. The maximum deviation from the mean plane is 0.002 Å for C(1).

In Table IV data on the intermolecular hydrogen bonding are given. It is clearly seen that the O(1)–H(1) group is linked to the O(2)–H(10) group of a neighbouring molecule which is also hydrogen-bonded to the Cl atom of an adjacent molecule.

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