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Crystal and Molecular Structure of Dibromobis(2,2′-Thiodiethanol)Nickel(II)

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The crystal and molecular structure of dibromobis(2,2′-thiodiethanol)nickel(II), $[NiBr_2(S(CH_2CH_2OH)_2)_2]$ *was determined from single-crystal three-dimensional X-ray data collected by counter methods at −120 °C. The compound is monoclinic with space group* $P2_1/c$. *The unit cell parameters are* $a = 6.889(2)$, $b = 11.498(3)$, $c = 10.328(3)$ Å, $\beta = 112.21(2)^\circ$ *and* $Z = 2$.

The structure was solved by direct methods, and the least-squares refinement of 1469 reflections yielded a final R value of 0.025. The complex consists of a centrosymmetric unit in which the central nickel(II) is bonded to the sulphur (Ni–S 2.431 Å) and one of the hydroxyl oxygen (Ni–O 2.046 Å) atoms of the thiodiethanol molecules, resulting in two five-membered chelate rings. Two bromine atoms are strongly bonded to nickel (Ni–Br 2.548 Å) in axial positions trans *to each other, giving a distorted octahedral geometry around nickel. The hydroxy groups of the ligand are involved in intermolecular hydrogen bonding.*

Introduction

The potentially tridentate ligand 2,2′-thiodiethanol is capable of coordinating through the thioether S and hydroxy O atoms in its metal complexes [1]. One of the hydroxy groups may even deprotonate to form polynuclear anionic complexes as observed in the case of 2,2′-iminodiethanol [2]. Furthermore, the geometry of the ligand is such that it may sterically adjust to form five-coordinate square pyramidal or trigonal bipyramidal metal complexes [1, 3]. We have been interested in finding out the bonding capability of S-ligands containing thioether groups towards metal atoms. Recently we have reported the crystal structures of Cu(II) [4, 5] and Co(II) [6] complexes of thiodiethanol and a Cu(II) complex [7] of thiodipropionic acid. In this paper the results of the crystal and molecular structure of dibromobis(2,2′-thiodiethanol)nickel(II) are reported.

Experimental

Dibromobis(thiodiethanol)nickel(II) was prepared by interaction of alcoholic solutions of nickel(II) bromide and thiodiethanol taken in a 1:2 molar ratio. The resultant solution was stirred and diluted with diethyl ether, when the green crystalline product separated out. Single crystals suitable for X-ray studies were obtained by slow evaporation of the alcoholic solution of the complex. *Anal.:* found, C 21.21, H 4.68, Br 34.13, Ni 12.38; calcd. for $C_8H_{20}O_4S_2Br_2Ni$: C 20.76, H 4.36, Br 34.53, Ni 12.68%.

X-ray Data

Preliminary Weissenberg and precession photographs of a crystal of the title compound suggested the crystal belonging to the monoclinic system. The systematic absences as seen from the photographs, 0k0, k = 2n + 1 and h0l, l = 2n + 1 indicated the space group being $P2_1/c$ (C_{2h}^5, No. 14). The unit cell parameters of the crystal after least-squares refinement from diffractometer coordinates of 15 high-order reflections are $a = 6.889(2)$, $b = 11.498(3)$, $c = 10.328(3)$ Å, $\beta = 112.21(2)^\circ$, $V = 757.4$ Å^3. The measured density 2.02(2) g cm^{-3} is in agreement with the calculated value of 2.029 g cm^{-3} for 2 formula units of the complex per unit cell.

The X-ray intensity data were collected at −120 °C using a Syntex $P2_1$ four-circle diffractometer and graphite monochromated MoKα radiation (Kα_1 0.070926, Kα_2 0.71354 Å, θ–2θ scan, take-off angle 6°, scintillation counter). The sampling interval in 2θ for each reflection was 2.1–2.3°. The rate of scanning was varied from 2–15° per min, depending on the intensity of the reflection. The background counts at the start and end of the measurement were recorded with the total time for background counts being equal to the scan time. A standard reflection was measured for every 50 reflections. A complete set of 1665 unique reflections was recorded up to $(\sin\theta)/\lambda = 0.64$ Å^{-1}, out of which 1469 reflections were accepted satisfactory above the background on the basis of $I > 1.96\sigma(I)$. The data reduction was done by applying Lorentz and polarization corrections. An

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empirical absorption correction was made, employing ψ scans around the diffraction vectors for 8 reflections (μ = 71.3 cm^{-1}). The size of the crystal investigated was 0.02 × 0.12 × 0.04 mm^3.

Solution and Refinement of the Structure

The structure was solved by direct methods using the MULTAN programme system*. The atoms Ni, Br and S were located from the first E map obtained using the phases for the set of best figures of merit. The other non-hydrogen atoms were located from subsequent Fourier and difference Fourier syntheses. The hydrogen atoms were obtained from the difference Fourier maps obtained after the anisotropic refinement of the non-hydrogen atoms. The atomic scattering factors for Ni, Br, S, O, C and H were taken from the International Tables [8]. Full-matrix least-squares refinement with anisotropic temperature factors for all the non-hydrogen atoms and isotropic ones for the hydrogen atoms converged to residuals $R_1 = 0.025$ and $R_2 = 0.028$, 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. The shifts in the final cycle were below 0.02σ and the final difference Fourier map revealed no significant features. The final coordinates and the temperature factors 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 of dibromobis(2,2′-thiodiethanol)nickel(II) consists of centrosymmetric $[NiBr_2(S(CH_2CH_2OH)_2)_2]$ units in which the nickel atom is coordinated by the sulphur atom and one of the hydroxyl oxygen atoms of each ligand molecule, forming a NiS_2O_2 tetragonal plane. The ligand molecules are *trans* to each other and bidentate, forming five-membered non-planar rings with the nickel atom. The axial positions of the tetragonal plane are occupied by the two bromine atoms, resulting in a distorted octahedral geometry around nickel. An ellipsoid plot of the structure of the complex is given in Fig. 1. The structure is found to be isostructural with that of dichlorobis(diethanol)-cobalt(II) [6].

The interatomic bond lengths and bond angles are given in Table III. The Ni–O distances fall in the range 2.01–2.19 Å with a mean value of 2.06 Å in six-coordinated nickel(II) complexes [9–18]. The value of 2.046 Å observed for the present compound is normal and is slightly less than the sum of the covalent radii of the Ni(oct) and O atoms (2.13 Å). [19] suggesting a strong interaction of nickel and the hydroxy group. In several S-ligated Ni(II) complexes the crystal structures of which are known [20–29], the Ni–S bond distances vary from 2.22 to

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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 of the SHELXTL system of G. M. Sheldrick.

TABLE I. Coordinates of the Atoms in the Unit Cell of Dibromobis(2,2′-thiodiethanol)nickel(II) with Standard Deviations.

	x	y	z	B
Ni	0.5	0.0	0.5	
Br	0.42777(4)	0.21682(2)	0.45701(3)	
S	0.25928(11)	−0.02014(6)	0.25822(7)	
O(1)	0.73189(32)	0.00818(17)	0.42180(22)	
O(2)	0.02774(33)	−0.30445(19)	0.01849(23)	
C(1)	0.67373(50)	−0.02839(28)	0.27937(33)	
C(2)	0.45763(50)	0.01599(27)	0.18778(32)	
C(3)	0.20429(50)	−0.17085(26)	0.20781(31)	
C(4)	0.07357(49)	−0.18386(27)	0.05371(32)	
H(1)	0.789(7)	0.056(4)	0.434(5)	1.9(9)
H(2)	0.775(6)	0.002(3)	0.246(4)	1.7(7)
H(3)	0.681(6)	−0.114(3)	0.276(4)	2.3(8)
H(4)	0.454(6)	0.094(3)	0.184(4)	2.2(8)
H(5)	0.417(6)	−0.013(3)	0.095(4)	0.6(6)
H(6)	0.133(7)	−0.191(4)	0.252(4)	3.8(11)
H(7)	0.337(7)	−0.208(3)	0.235(4)	1.3(7)
H(8)	−0.057(6)	−0.140(3)	0.030(4)	1.6(7)
H(9)	0.163(6)	−0.155(3)	0.000(4)	1.5(7)
H(10)	−0.086(7)	−0.320(4)	0.026(4)	2.3(9)

TABLE II. Temperature Factor Coefficients[a] of Atoms in the Unit Cell of Dibromobis(2,2′-thiodiethanol)nickel(II).

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.86(2)	0.77(2)	0.92(2)	0.03(2)	0.43(2)	0.02(2)
Br	1.22(1)	0.78(1)	1.33(1)	0.09(1)	0.64(1)	0.13(1)
S	1.08(3)	0.91(3)	1.09(3)	0.07(2)	0.35(2)	0.00(2)
O(1)	1.03(8)	0.89(8)	1.17(8)	−0.22(6)	0.49(7)	−0.20(7)
O(2)	0.97(9)	1.09(8)	2.01(10)	−0.14(6)	0.44(8)	−0.38(7)
C(1)	1.50(12)	1.38(12)	1.53(12)	−0.25(9)	1.03(10)	−0.49(10)
C(2)	1.67(12)	1.46(12)	1.00(11)	−0.33(10)	0.61(10)	0.07(10)
C(3)	1.31(12)	0.99(11)	1.25(12)	−0.11(9)	0.44(10)	0.06(9)
C(4)	1.19(11)	0.99(11)	1.38(12)	0.09(9)	0.23(9)	−0.04(9)

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

TABLE III. Interatomic Distances (Å) and Bond Angles (°) with Standard Deviations.[a]

Ni Coordination			
Ni–Br (–Br′)	2.548(1)	Br–Ni–S	95.64(2)
Ni–S (–S′)	2.431(1)	Br–Ni–S′	84.36(2)
Ni–O(1) (–O(1′))	2.046(2)	Br–Ni–O(1)	90.94(6)
		Br–Ni–O(1′)	89.06(6)
		S–Ni–O(1)	86.00(6)
		S–Ni–O(1′)	94.00(6)
Thiodiethanol Molecule			
S–C(2)	1.822(4)	Ni–S–C(2)	93.7(1)
S–C(3)	1.808(3)	Ni–S–C(3)	112.0(1)
C(1)–C(2)	1.519(5)	C(2)–S–C(3)	102.2(2)
C(3)–C(4)	1.511(4)	C(2)–C(1)–O(1)	111.6(3)
C(1)–O(1)	1.434(4)	S–C(2)–C(1)	112.4(2)
C(4)–O(2)	1.438(4)	S–C(3)–C(4)	112.0(2)
		C(3)–C(4)–O(2)	110.4(3)
O(1)–H(1)	0.67(4)	Ni–O(1)–C(1)	115.7(2)
C(1)–H(2)	0.95(4)		
C(1)–H(3)	0.98(4)	Ni–O(1)–H(1)	117(4)
C(2)–H(4)	0.90(4)	C(1)–O(1)–H(1)	111(4)
C(2)–H(5)	0.95(4)	C(4)–O(2)–H(10)	108(3)
C(3)–H(6)	0.82(5)		
C(3)–H(7)	0.95(5)		
C(4)–H(8)	0.98(4)		
C(4)–H(9)	1.03(4)		
O(2)–H(10)	0.84(5)		

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

2.59 Å with a mean value of 2.48 Å. The bond distance of 2.431 Å noticed in the present compound is in accordance with the reported value and is almost equal to the sum of the covalent radii (2.43 Å) of Ni(oct) and S [19]. The corresponding sum for Ni–Br is found to be 2.53 Å [19] and the experimental value of 2.548 Å, though slightly greater, is comparable with the literature values found in six-coordinated bromocomplexes of nickel(II) [18, 20].

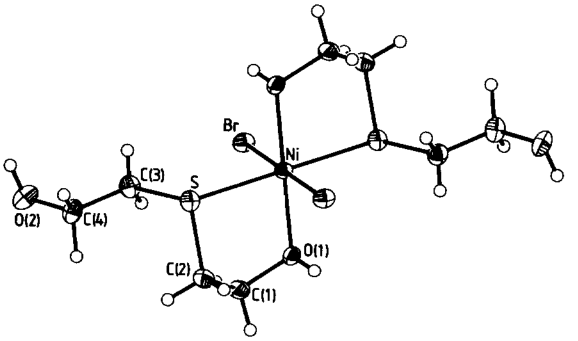

Fig. 1. Dibromobis(2,2′-thiodiethanol)nickel(II). Plot of the molecule with atomic designations and thermal ellipsoids (75% probability at −120 °C).

Within the ligand molecule, the bond distances are found to be normal. The bond length C(1)–O(1) (1.434 Å) is not significantly different from C(4)–O(2) in spite of the bonding of O(1) to nickel. Due to the chelate effect, the S–C(2) bond length is slightly larger than that of S–C(3). The sulphur atom assumes pyramidal geometry as found in dichlorobis(thiodiethanol)cobalt(II) [6], with Ni, C(2) and C(3) as the nearest neighbours. The chelate ring with Ni, S, C(2), C(1) and O(1) has half chair configuration with C(1) and C(2) atoms being 0.33 and 0.29 Å below and above the plane $-0.0828x + 0.9964y - 0.0204z + 0.3397 = 0$ through Ni, S and O(1), where x, y and z are related to the monoclinic axes of the crystal.

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

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TABLE IV. Hydrogen Bonding in the Structure of Dibromobis(2,2′-thiodiethanol)nickel(II).

A–H…B	Distance (Å)			Angle (°) AHB
	A–H	H…B	A…B	
O(1)–H(1)…O(2)	0.67(4)	1.99(5)	2.644(3)	177(5)
O(2)–H(10)…Br	0.84(5)	2.46(5)	3.251(2)	158(4)

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