

Crystal Structure of the Complex of Dibenzo-30-crown-10 with Dysprosium Isothiocyanate

YAN SHIPING, JIANG ZONGHUI, LIAO DIAZHENG and WANG GENGLIN
Department of Chemistry, Nankai University, Tianjin, China

and

WANG RUJI, WANG HONGGEN and YAO XINKAN
Central Laboratory, Nankai University, Tianjin, China

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Abstract. Crystalline $[\text{Dy}(\text{NCS})_3(\text{dibenzo-30-crown-10})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \cdot \text{MeCN}$ can be obtained by slowly evaporating a reaction mixture of $\text{Dy}(\text{NCS})_3 \cdot n\text{H}_2\text{O}$ with dibenzo-30-crown-10 in a solution of acetonitrile. The material crystallizes in the monoclinic space group $P2_1/n$, the cell parameters are $a = 11.450(5)$, $b = 23.284(4)$, $c = 18.424(6)$ Å, $\beta = 106.28(4)^\circ$, $V = 4715$ Å³, $M = 968.47$, $D_x = 1.36$ g cm⁻³, $\mu = 17.80$ cm⁻¹, $F(000) = 1972$, $Z = 4$. 2740 independently observed [$I \geq 3\sigma I$] reflections were used in the final least-squares refinement leading to an agreement index of $R = 0.085$. The Dy(III) ion coordination geometry approximates a square antiprism, involving two water oxygens and three dibenzo-30-crown-10 oxygen atoms and three isothiocyanate nitrogens. Hydrogen bonds are formed between the two water molecules and four uncoordinated crown ether oxygen atoms.

Key words: Dibenzo-30-crown-10, crystal structure, complexation, dysprosium isothiocyanate.

Supplementary Data relevant to this paper have been deposited with the British Library as Supplementary Publication No. SUP 82148 (22 pp.)

1. Introduction

The coordination chemistry of crown ethers has been extensively studied since their initial discovery [1, 2]. Complexes formed were found to depend not only on the size of the cation and crown ether cavity but also the choice of anion and solvent. Dibenzo-30-crown-10 (hereinafter named L) is a large cyclic ether (its diameter is about 4 Å). Very few solid complexes of this ligand with metal ions have been reported [3–5]. Bush and Truter [3] determined the crystal structure of the complex of potassium with dibenzo-30-crown-10 and found the ligand was wrapped around the potassium ion. Ciampolini and Nardi [5] synthesized compounds of lanthanide perchlorate with dibenzo-30-crown-10 by using anhydrous salts and anhydrous acetonitrile. Recently, the crystal structure of $\text{Gd}(\text{NCS})_3 \cdot \text{L} \cdot 2\text{H}_2\text{O}$ has been reported [6]. The synthesis and structural characterization of the title complex is the subject of this report. This complex bears a striking similarity to the $\text{Gd}(\text{NCS})_3 \cdot \text{L} \cdot 2\text{H}_2\text{O}$ structure.

2. Experimental

2.1. SYNTHESIS AND CRYSTALLIZATION OF $[\text{Dy}(\text{NCS})_3(\text{DIBENZO-30-CROWN-10})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \cdot \text{MeCN}$

Dibenzo-30-crown-10 (1 mmol) in 10 mL anhydrous acetonitrile was added to a stirred solution of 1 mmol of $\text{Dy}(\text{NCS})_3 \cdot \text{H}_2\text{O}$ in 5 mL of the same solvent. The reaction mixture was heated to about 80 °C for 2 h. The colorless precipitate was isolated, washed with cooled acetonitrile three times, filtrated and dried *in vacuo*. The solid was recrystallized in anhydrous acetonitrile. The transparent crystals formed over a period of approximately five days at room temperature: *Analysis: Calcd.* for $\text{C}_{33}\text{H}_{49}\text{N}_4\text{O}_{13}\text{S}_3\text{Dy}$: C, 40.89; H, 5.06; N, 5.78; *Found:* C, 41.02; H, 5.31; N, 5.49.

2.2. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION AND REFINEMENT FOR $[\text{Dy}(\text{NCS})_3\text{L}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \cdot \text{MeCN}$

A transparent single crystal of the title complex having approximate dimensions of $0.2 \times 0.2 \times 0.3$ mm was mounted on a glass fibre in a random orientation. The determination of the unit cell and the data collection were performed with Mo K_α radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 diffractometer. A total of 6799 independent reflections were collected in the range of $2^\circ < \theta < 23^\circ$ by the $\omega - 2\theta$ scan technique at room temperature, of which 2740 reflections (with $I > 3\sigma I$) were considered to be observed and used in the refinement. The corrections for L_p effects and empirical absorption were applied to the data.

Crystals are monoclinic, space group $P2_1/n$, with $a = 11.450(5)$, $b = 23.284(4)$, $c = 18.424(6)$ Å, $\beta = 106.28(4)$, $V = 4715$ Å³, $M_w = 968.47$, $Z = 4$, $D_x = 1.36$ g cm⁻³, $\mu = 17.80$ cm⁻¹, $F(000) = 1972$.

The structure was solved by the heavy atom techniques. Positions for all of the other non-hydrogen atoms were obtained from successive difference Fourier syntheses.

The final refinement using a full-matrix least-squares procedure with anisotropic thermal parameters for non-hydrogen atoms converged with agreement factors of $R = \Sigma|\Delta F|/\Sigma|F_0| = 0.085$ and $R_w = [\Sigma W|\delta F|^2/\Sigma W|F_0|^2]^{1/2} = 0.098$ (unit weights for all observed reflections). The largest peak in the final difference Fourier map had a magnitude of $0.98 \text{ e} \text{ \AA}^{-3}$.

All calculations were performed on a PDP 11/44 computer using the SDP-PLUS program system.

Tables of final atomic positional and thermal parameters, full lists of bond lengths and angles, equations of least-squares planes have been deposited as supplementary material with the *British Library*.

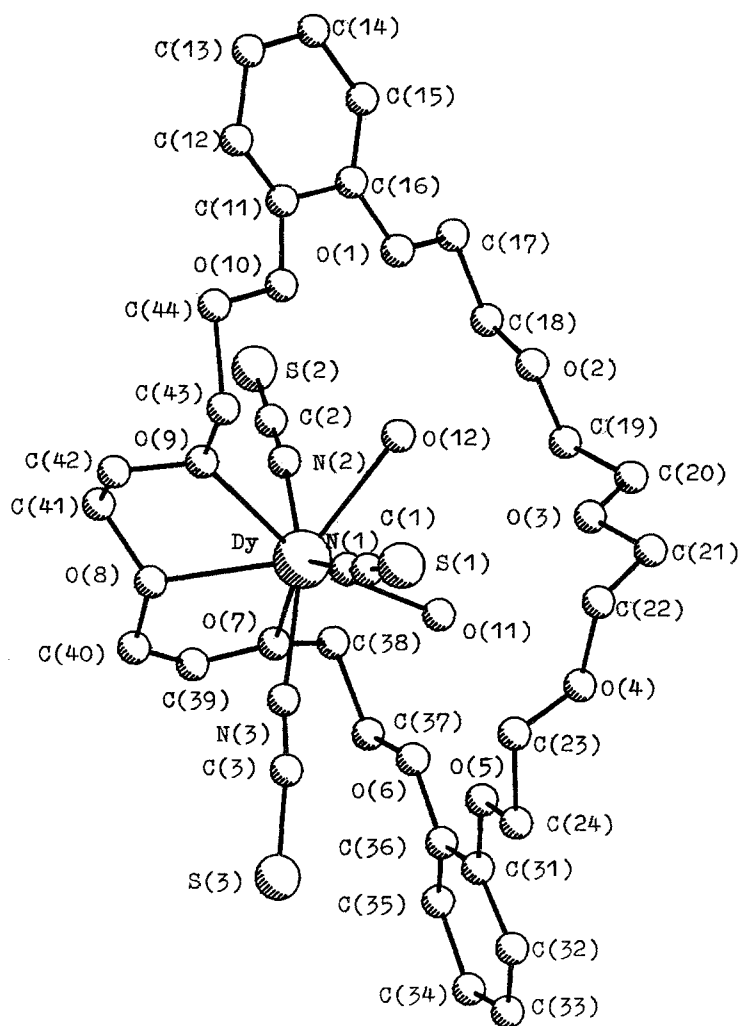


Fig. 1. Perspective view of the Dy(NCS)₃·L·(H₂O)₂ showing the atom numbering.

3. Results and Discussion

The crystal structure of the complex is shown with crystallographic numbering of the atoms in Figure 1. The final values of the positional parameters are given in Table I, and some bond lengths and bond angles are given in Tables II and III.

Reaction of Dy(NCS)₃·nH₂O with dibenzo-30-crown-10 in anhydrous acetonitrile produces a complex which is structurally similar to that observed in our previous work [6]. In the title complex, only three oxygen atoms O(7), O(8), O(9) of the cyclic ether interact with the Dy(III) ion with the Dy—O distances ranging from 2.370(6) Å to 2.546(5) Å. The average of all three Dy—O (ether) separations is 2.477 Å. The nitrogen atoms of three isothiocyanate anions and two oxygen atoms

TABLE I

Fractional coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Dy	0.4718(1)	0.39090(6)	0.72993(7)	3.78(2)
S(1)	0.0808(7)	0.2803(5)	0.7325(6)	7.4(3)
S(2)	0.6441(9)	0.5757(5)	0.6531(5)	8.6(3)
S(3)	0.616(1)	0.1997(5)	0.8605(6)	9.0(3)
O(1)	0.257(2)	0.576(1)	0.643(1)	6.0(6)
O(2)	0.332(2)	0.572(1)	0.801(1)	7.3(7)
O(3)	0.318(2)	0.4783(9)	0.900(1)	5.9(5)
O(4)	0.359(1)	0.3651(9)	0.965(1)	6.1(6)
O(5)	0.590(1)	0.3270(9)	0.979(1)	5.2(5)
O(6)	0.750(1)	0.389(1)	0.942(1)	5.7(5)
O(7)	0.701(1)	0.4022(8)	0.7847(9)	4.2(4)
O(8)	0.594(1)	0.3585(9)	0.648(1)	5.9(5)
O(9)	0.362(1)	0.3822(7)	0.5960(8)	3.9(4)
O(10)	0.211(1)	0.4878(8)	0.559(1)	5.1(5)
O(11)	0.501(1)	0.4137(7)	0.8592(9)	4.2(4)
O(12)	0.317(1)	0.462(1)	0.725(1)	6.9(6)
N(1)	0.295(2)	0.336(1)	0.734(1)	5.6(6)
N(2)	0.533(2)	0.479(1)	0.690(1)	5.8(6)
N(3)	0.541(2)	0.306(1)	0.783(1)	7.1(7)
C(1)	0.210(2)	0.312(1)	0.733(1)	4.9(7)
C(2)	0.577(2)	0.520(1)	0.673(1)	4.7(7)
C(3)	0.570(2)	0.265(1)	0.817(2)	6.1(8)
C(11)	0.170(2)	0.536(1)	0.520(2)	5.0(7)
C(12)	0.107(2)	0.539(1)	0.449(1)	4.6(7)
C(13)	0.067(2)	0.595(1)	0.416(2)	5.9(9)
C(14)	0.090(2)	0.644(1)	0.462(2)	6.4(9)
C(15)	0.153(3)	0.636(2)	0.538(2)	6.2(9)
C(16)	0.193(2)	0.585(1)	0.570(1)	5.5(8)
C(17)	0.299(3)	0.625(1)	0.686(1)	5.6(8)
C(18)	0.389(3)	0.609(2)	0.761(2)	7.2(9)
C(19)	0.416(3)	0.560(2)	0.871(2)	10(1)
C(20)	0.347(3)	0.535(2)	0.921(2)	8(1)
C(21)	0.245(3)	0.451(1)	0.944(2)	8(1)
C(22)	0.241(2)	0.391(2)	0.925(2)	6.6(8)
C(23)	0.380(2)	0.311(1)	0.938(2)	6.0(9)
C(24)	0.503(2)	0.291(1)	0.997(2)	5.4(8)
C(31)	0.709(2)	0.319(1)	1.025(2)	4.7(7)
C(32)	0.739(3)	0.284(1)	1.087(2)	6.4(9)
C(33)	0.863(3)	0.281(2)	1.131(2)	8(1)

Table I (continued)

C(34)	0.949(3)	0.315(2)	1.111(2)	8(1)
C(35)	0.917(2)	0.356(2)	1.047(2)	6.4(9)
C(36)	0.796(2)	0.356(1)	1.004(1)	5.4(7)
C(37)	0.833(2)	0.422(1)	0.916(2)	6.8(9)
C938)	0.755(2)	0.446(1)	0.839(2)	5.9(8)
C(39)	0.773(2)	0.381(2)	0.745(2)	11(1)
C(40)	0.723(3)	0.351(3)	0.685(3)	14(2)
C(41)	0.551(2)	0.379(2)	0.571(2)	8(1)
C(42)	0.415(2)	0.359(1)	0.544(1)	4.9(7)
C(43)	0.229(2)	0.381(1)	0.566(1)	4.4(7)
C(44)	0.186(2)	0.437(1)	0.512(2)	4.6(7)
C(51)	0.543(3)	0.036(2)	0.275(3)	11(1)
C(52)	0.526(3)	-0.020(2)	0.264(2)	9(1)
N(51)	0.509(3)	-0.076(2)	0.243(2)	13(2)
O	0.721(1)	0.0957(8)	0.6152(9)	5.3(4)*

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as:

$$(4/3 * [a^2 * B(1, 1) + b^2 * B(2, 2) + c^2 * B(3, 3) + ab(\cos \gamma) * B(1, 2) + ac(\cos \beta) * B(1, 3) + bc(\cos \alpha) * B(2, 3)]).$$

TABLE II

Bond distances (Å) for [Dy(NCS)₃·L·(H₂O)₂]·MeCN.

Atoms	Distance	Atoms	Distance
Dy—O(7)	2.546(5)	Dy—O(12)	2.423(7)
Dy—O(8)	2.444(8)	Dy—N(1)	2.402(9)
Dy—O(9)	2.442(6)	Dy—N(2)	2.34(1)
Dy—O(11)	2.370(6)	Dy—N(3)	2.26(2)

of coordinated water molecules are also bonded to the Dy(III) ion. The coordination number of the Dy(III) ion is eight.

It is possible that hydrogen bonds exist in the complex of [Dy(NCS)₃L(H₂O)₂]·H₂O·MeCN. The possible hydrogen bond contacts (Table IV) are between the two coordinated water molecules and uncoordinated oxygen atoms of dibenzo-30-crown-10. Because the positions of hydrogen atoms cannot be located, the hydrogen bonds listed in Table IV are only proposed in complex molecules.

The variation in Dy—O (ether) and Dy—N (anions) distances is quite large. The Dy—O(7) distance is the longest (2.546 Å) among the three Dy—O bonds. The Dy—N interatomic distances range from 2.26(2) Å to 2.402(9) Å.

The Dy(III) ion coordination in the title complex is best described as a square

TABLE III
Bond angles (deg.) for $[\text{Dy}(\text{NCS})_3 \cdot \text{L} \cdot (\text{H}_2\text{O})_2] \cdot \text{MeCN}$.

Atoms	Angle	Atoms	Angle
O(7)—Dy—O(8)	64.6(3)	O(9)—Dy—O(12)	81.9(2)
O(7)—Dy—O(9)	126.0(2)	O(9)—Dy—N(1)	78.0(3)
O(7)—Dy—O(11)	75.0(2)	O(9)—Dy—N(2)	82.5(3)
O(7)—Dy—O(12)	127.7(2)	O(9)—Dy—N(3)	112.6(3)
O(7)—Dy—N(1)	145.3(3)	O(11)—Dy—O(12)	77.0(2)
O(7)—Dy—N(2)	70.9(2)	O(11)—Dy—N(1)	88.3(3)
O(7)—Dy—N(3)	73.6(3)	O(11)—Dy—N(2)	98.5(3)
O(8)—Dy—O(9)	64.7(2)	O(11)—Dy—N(3)	80.1(3)
O(8)—Dy—O(11)	138.1(2)	O(12)—Dy—N(1)	75.5(3)
O(8)—Dy—O(12)	137.2(3)	O(12)—Dy—N(2)	70.8(3)
O(8)—Dy—N(1)	119.0(3)	O(12)—Dy—N(3)	114.8(3)
O(8)—Dy—N(2)	78.9(4)	N(1)—Dy—N(2)	142.9(3)
O(8)—Dy—N(3)	78.5(3)	N(1)—Dy—N(3)	73.7(3)
O(9)—Dy—O(11)	157.1(2)	N(2)—Dy—N(3)	143.4(3)

TABLE IV
Hydrogen bonding contact geometries (\AA , deg.).

Atoms	Distance	Atoms	Distance
O(11)—O(3)	2.85(1)	O(12)—O(1)	3.04(1)
O(11)—O(4)	3.07(1)	O(12)—O(2)	2.90(1)
O(11)—O(5)	2.96(1)	O(12)—O(3)	3.23(1)
O(11)—O(6)	2.89(1)	O(12)—O(10)	3.02(1)
Atoms	Angle	Atoms	Angle
O(3)—O(11)—O(5)	107(1)	O(1)—O(12)—O(3)	110(1)
O(4)—O(11)—O(5)	105(1)	O(2)—O(12)—O(10)	105(1)

antiprism (see Figure 2). The coordinated atoms N(1), N(3), O(8), and O(9) form one plane, while N(2), O(7), O(11) and O(12) form another plane of the square antiprism geometry. The dihedral angle between them is 6.64° .

Despite similar coordination environments and interatomic distances, the two complexes of Gd and Dy have different coordination polyhedra.

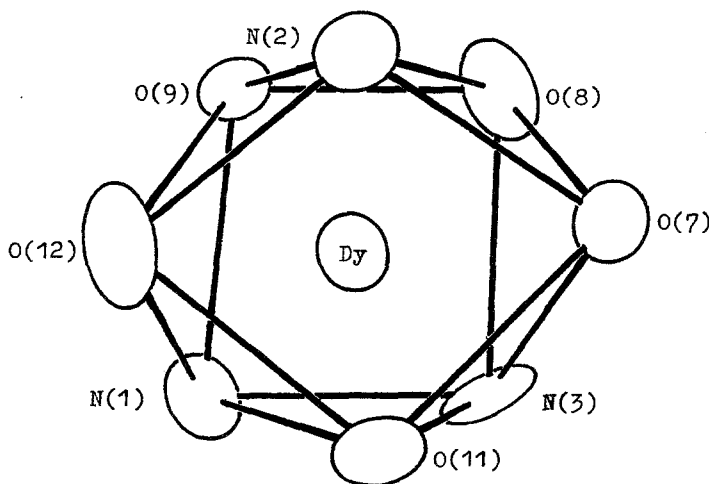


Fig. 2. The coordination polyhedron of the Dy(III) ion.

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