Crystal and Molecular Structure of Dysprosium(III) Nitrate with (2-Methoxy-1,3-xylyl)-15-crown-4

GIULIANA TOMAT*

Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Corso Stati Uniti, 35100 Padua, Italy

GIOVANNI VALLE

Centro di Ricerche sui Biopolimeri del C.N.R., Via Marzolo 1, 35131 Padua, Italy

PLINIO DI BERNARDO and PIER LUIGI ZANONATO

Dipartimento di Chimica Inorganica Metallorganica ed Analitica dell'Università, Via Marzolo 1, 35131 Padua, Italy

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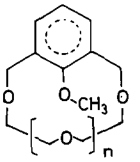
Abstract

The crystal and molecular structure of the compound $[Dy(NO_3)_3(H_2O)_3]L$ (L = (2-methoxy-1,3-xylyl)-15-crown-4) was determined from three-dimensional X-ray diffraction analysis. The crystals are triclinic, space group $P\bar{1}$; the unit cell has a = 12.312(5), b = 10.193(4), c = 10.264(4) Å, α = 95.1(3), β = 94.5(3), γ = 92.5(3), and Z = 2. The structure was refined by least-squares techniques to R = 4.2% for 3829 independent reflections. The coordination polyhedron around the Dy atom is a quasi-ideal tricapped trigonal prism formed by six oxygen atoms of the bidentate nitrate groups and by three oxygen atoms of the coordinated water molecules. The crown ether L is linked to the $[Dy(NO_3)_3(H_2O)]$ moiety through hydrogen bonds which favour also the formation of an extensive three-dimensional H-bonding network.

Introduction

Structural studies play an important role in understanding the interaction of lanthanoid ions with macrocyclic crown-ethers. A variety of coordination compounds can be obtained from these metal–ligand systems as a consequence of various factors affecting the complexation: the conformation of the crown-ethers, the size of the metal ions, the complexing properties of the anions, the nature and water content of the solvent, and, in some cases, even the experimental conditions of the preparation (temperature and period of crystallisation) [1–7].

The growing interest in host-guest complexation has led to the synthesis of several crown-ethers containing different functional groups. Among these, some macrocyclic polyethers with convergent methoxyaryl groups have been reported and their ligating properties towards alkali and ammonium cations have been studied in chloroform [8, 9]. Due to some similarities in the coordination behaviour of alkali metals and rare earths [10] we have thought it may be interesting to study some complexes of lanthanoid ions with these new ligands. Recently we have reported the crystal and molecular structure of the adduct between $Sm(NO_3)_3$ and the ligand 2 [11]. We now report a crystallographic investigation on the compound formed by $Dy(NO_3)_3$ with the smaller crown ether 1.



1, n = 2
2, n = 3

Experimental

Preparation of the Compound

The crown ether was prepared according to the reported method [12]. The compound was obtained by adding a solution of the crown ether (1.1 mmol in 10 ml) in methyl cyanide to a solution of hydrated dysprosium nitrate (1.0 mmol in 10 ml) in the same solvent. The resulting mixture was refluxed for 2–3 h and the crystals were obtained after partial

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*Author to whom correspondence should be addressed.

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TABLE I. Atomic Fractional Coordinates and Equivalent Isotropic Thermal Parameters with e.s.d.s in Parentheses.

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
Dy	0.2412(0)	0.0756(0)	1.0427(0)	0.035
O(1)	0.4364(4)	0.0983(6)	1.1209(6)	0.049
O(2)	0.3242(5)	0.1812(7)	1.2513(6)	0.054
O(3)	0.4969(5)	0.1809(7)	1.3159(6)	0.061
O(4)	0.0779(5)	0.0698(6)	1.1593(6)	0.048
O(5)	0.1314(5)	0.2634(6)	1.1182(7)	0.057
O(6)	−0.0108(5)	0.2368(7)	1.2289(7)	0.065
O(7)	0.1562(5)	−0.1485(6)	1.0201(6)	0.056
O(8)	0.2725(6)	−0.0986(7)	1.1851(7)	0.069
O(9)	0.1858(7)	−0.2893(7)	1.1631(9)	0.099
O(10)	0.0914(5)	0.1607(6)	0.6112(6)	0.050
O(11)	0.3040(5)	0.0577(7)	0.6449(6)	0.058
O(12)	0.4622(6)	0.2561(8)	0.7726(8)	0.081
O(13)	0.3937(5)	0.5079(7)	0.8632(7)	0.062
O(14)	0.1561(5)	0.3980(6)	0.8093(6)	0.047
N(1)	0.4217(6)	0.1545(7)	1.2330(7)	0.045
N(2)	0.0628(6)	0.1942(8)	1.1707(7)	0.047
N(3)	0.2037(6)	−0.1830(8)	1.1235(9)	0.060
C(1)	0.1417(8)	0.0988(10)	0.5041(9)	0.056
C(2)	0.2172(9)	−0.0018(10)	0.5546(10)	0.064
C(3)	0.3859(11)	0.1238(20)	0.5818(13)	0.111
C(4)	0.4645(15)	0.1995(21)	0.6567(18)	0.198
C(5)	0.5351(9)	0.3656(13)	0.8158(13)	0.078
C(6)	0.4872(8)	0.4932(12)	0.7895(13)	0.076
C(7)	0.3213(11)	0.6051(13)	0.8175(14)	0.063
C(8)	0.2548(10)	0.5524(11)	0.6930(12)	0.051
C(9)	0.2730(11)	0.6000(13)	0.5723(14)	0.063
C(10)	0.2163(11)	0.5492(14)	0.4582(14)	0.068
C(11)	0.1408(10)	0.4444(13)	0.4590(12)	0.057
C(12)	0.1193(9)	0.3945(11)	0.5775(11)	0.046
C(13)	0.0383(9)	0.2790(12)	0.5801(12)	0.050
C(14)	0.1757(8)	0.4492(10)	0.6912(11)	0.042
C(15)	0.0733(11)	0.4626(14)	0.8792(14)	0.066
O(W1)	0.1154(6)	0.0767(6)	0.8592(6)	0.016
O(W2)	0.3037(6)	0.2548(6)	0.9403(6)	0.019
O(W3)	0.3394(6)	−0.0355(6)	0.8799(7)	0.020

evaporation of the solvent and/or addition of dichloromethane. *Anal.* Calcd. for $Dy(NO_3)_3(H_2O)_3$-$(C_{15}H_{22}O_5)$: C = 26.30, H = 4.12, N = 6.14%; Found: C = 26.29, H = 4.08, N = 6.07%.

X-Ray Measurements and Structure Determination

$C_{15}H_{28}N_3O_{17}Dy$, MM = 684.9, triclinic, space group $P\bar{1}$; a = 12.312(5), b = 10.193(4), c = 10.264(4) Å; α = 95.1(3), β = 94.5(3), γ = 92.5(3); V = 1277.4 Å^3; D_c = 1.779, D_o = 1.77 g/cm^3 by flotation; Z = 2.

4506 reflections were collected from a crystal mounted on a Philips PW 1100 diffractometer with graphite monochromated MoKα radiation (λ = 0.7107 Å) in the range $4° < 2\theta < 50°$, using the $\theta-2\theta$ scan mode. The intensities of 3829 reflections with $I = 3\sigma(I)$, corrected for background, Lorentz and polarization effects, were used throughout the refinement. The structure was solved by the heavy atom method and refined by full-matrix least-squares with anisotropic temperature factors for all non-hydrogen atoms. The position of hydrogen atoms were calculated and not refined. The SHELX-76 system of programs was used [13]; the final value of R was 4.2%. Atomic coordinates and thermal parameters are reported in Table I.

Results and Discussion

Figure 1 represents a view of the $[Dy(NO_3)_3(H_2O)_3]$L molecule with the atom numbering scheme. The cation, which is nine-coordinated, is directly bonded to three bidentate nitrate groups and three water molecules. The metal ion, is not directly bonded to the crown ether which exhibits a folded structure with an angle of about 94° between the plane of the aryl group and the best plane of the ethereal oxygens.

The coordination polyhedron around the dysprosium atom is a quasi-ideal tricapped trigonal prism (*D3h*, Fig. 2). The two triangular bases are formed by the three water oxygens O(W1), O(W2), O(W3) and by oxygens of three different nitrate groups O(2), O(4), O(8). The two bases are also practically parallel to each other (their normals form an angle of 4.8 deg) and are 1.59 and 1.66 Å below and up the dysprosium atom respectively. Also the plane formed by the three caps O(1), O(5), O(7) of the polyhedron is nearly parallel to the bases and forms a dihedral angle of 7.7° with the upper base and 3.0° with the lower one; Dy atom is 0.45 Å out of this plane.

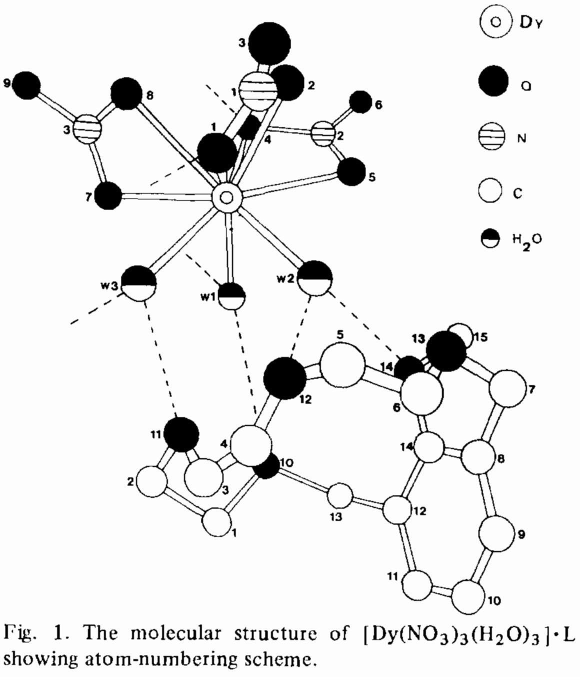

Fig. 1. The molecular structure of $[Dy(NO_3)_3(H_2O)_3]\cdot L$ showing atom-numbering scheme.

TABLE II. Selected Distances (Å) and Angles (°) Involving Dysprosium Atom and Coordinated Ligands.

Coordination sphere

(a) Distances

Dy–O(1) = 2.467(5)	Dy–O(2) = 2.436(6)	Dy–O(4) = 2.420(6)
Dy–O(5) = 2.495(7)	Dy–O(7) = 2.455(6)	Dy–O(8) = 2.422(7)
Dy–O(W1) = 2.345(7)	Dy–O(W2) = 2.319(7)	Dy–O(W3) = 2.374(7)

e.s.d.s in parentheses.

(b) Angles

O(1)–Dy–O(7) = 116.5	O(7)–Dy–O(5) = 118.8	O(5)–Dy–O(1) = 114.9
O(1)–Dy–O(W3) = 72.5	O(7)–Dy–O(W3) = 77.1	O(5)–Dy–O(W2) = 74.2
O(1)–Dy–O(W2) = 77.2	O(7)–Dy–O(W1) = 76.8	O(5)–Dy–O(W1) = 80.1
O(1)–Dy–O(8) = 73.8	O(7)–Dy–O(8) = 52.1	O(5)–Dy–O(2) = 70.4
O(1)–Dy–O(2) = 51.9	O(7)–Dy–O(4) = 69.7	O(5)–Dy–O(4) = 51.6
O(8)–Dy–O(W3) = 90.6	O(2)–Dy–O(W2) = 89.1	O(4)–Dy–O(W1) = 83.0
O(W3)–Dy–O(W1) = 79.9	O(W1)–Dy–O(W2) = 77.0	O(W2)–Dy–O(W3) = 80.3
O(8)–Dy–O(4) = 77.0	O(4)–Dy–O(2) = 83.4	O(2)–Dy–O(8) = 73.4
O(8)–Dy–O(W2) = 151.0	O(2)–Dy–O(W1) = 149.9	O(4)–Dy–O(W3) = 145.3
O(W3)–Dy–O(2) = 124.3	O(W2)–Dy–O(4) = 124.6	O(W1)–Dy–O(8) = 128.7

e.s.d.s = 0.2°.

Nitrate groups

(a) Distances

N(1)–O(1) = 1.27	N(2)–O(4) = 1.29	N(3)–O(7) = 1.26
N(1)–O(2) = 1.27	N(2)–O(5) = 1.26	N(3)–O(8) = 1.27
N(1)–O(3) = 1.21	N(2)–O(6) = 1.20	N(3)–O(9) = 1.21

e.s.ds. = 0.01 Å.

(b) Angles

O(1)–N(1)–O(2) = 115.7	O(1)–N(1)–O(3) = 121.4	O(3)–N(1)–O(2) = 122.9
O(4)–N(2)–O(5) = 114.5	O(4)–N(2)–O(6) = 120.7	O(6)–N(2)–O(5) = 124.8
O(7)–N(3)–O(8) = 115.8	O(7)–N(3)–O(9) = 122.8	O(9)–N(3)–O(8) = 121.4

e.s.d.s = 0.8°.

Other averaged distances (Å): C–C(crown) = 1.43(2); C–O(crown) = 1.41(2).

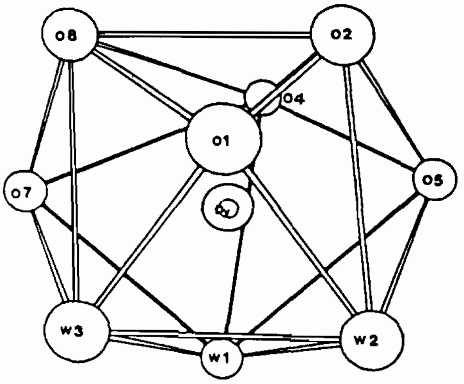

Fig. 2. Coordination polyhedron for the [Dy$(NO_3)_3(H_2O)_3$] molecule.

The water oxygen atoms are closer to the Dy atom than the nitrate oxygen atoms. The average Dy–O(water) distance is 2.35(2) Å while the average Dy–O(nitrate) distance is 2.45(3) Å. According to Addison *et al.* [14], the three nitrate groups appear to be symmetrically bound to the Dy atom since the distances between the central atom and the two oxygen atoms of the same nitrate group differ by less than 0.2 Å.

This structure, as most structures with coordinated bidentate nitrate groups, shows a remarkable change in the N–O bond lengths and O–N–O interbond angles with respect to the values in a regular C_{3v} nitrate ion [15] indicating a tendency of NO_3^- groups to assume a local C_{2v} symmetry. As reported in Table II the terminal N–O bond distances in the three nitrate groups are shorter than those reported in ref. 15 (average 1.21(1) *vs.* 1.245 Å) and the N–O bonds involving the chelating oxygen atoms are lengthened (average 1.27(1) Å). The O–N–O interbond angle involving both coordinated oxygen atoms is less than 120° (average 115.3 deg) and the other two angles are correspondingly larger (average 122.3 deg).

TABLE III. (a) Contact Distances in the Coordination Sphere (Å). (b) Contact Distances Involving Water Molecules (Å). E.s.d.s = 0.02 Å.

(a)	O(1)···O(8) = 2.94 O(2)···O(5) = 2.84 O(5)···O(W2) = 2.91	O(1)···O(W2) = 2.99 O(2)···O(8) = 2.90 O(7)···O(W1) = 2.98	O(1)···O(W3) = 2.86 O(4)···O(7) = 2.78 O(W2)···O(W1) = 2.90
(b)	O(W1)···O(10) = 2.76 O(W2)···O(14) = 2.73	O(W1)···O(4)″ = 2.74 O(W3)···O(11) = 2.68	O(W2)···O(12) = 2.70 O(W3)···O(1)′ = 2.86

Symmetry code: ′ 1 − x; y; 2 − z; ″x; y; 2 − z.

These values compare well with the distances Dy–O(water) already reported [16, 17] and, considering that the difference between the ionic radius of Dy^{3+} and Gd^{3+} is about 0.03 Å, they also agree well with the mean Gd–O (nitrate) and Gd–O (water) (2.45(4) and 2.39(6) Å respectively) found in the analogous nine-coordinated $[Gd(NO_3)_3(H_2O)_3]$ moiety in the complex with the 18-crown-6 [6]. It is worthwhile to compare the $[Dy(NO_3)_3(H_2O)_3]$ molecule with this gadolinium analogue. Both possess the same stoichiometric and coordination number but they differ considerably in their structures. In the Gd complex, in fact, the oxygen atoms of the nitrate ions and water molecules form an irregular coordination polyhedron while, as shown, the dysprosium coordination polyhedron is quite regular. The reason for these different conformations can be tentatively attributed to the different ability of the crown-ethers to form H-bridges. The regular, highly symmetrical and flexible structure of 18-crown-6 favours the formation of six hydrogen bonds between the polyether oxygen atoms and the coordination water molecules. The formation of these bonds probably conditions the position of the H_2O molecules in the coordination sphere of the gadolinium ion. The asymmetrical structure and the lower number of oxygen atoms of the title ligand, make the formation of these H-bonds less easy, so the nitrate ions and water molecules are free to place themself around the metal ion more ordinately. This causes a noticeable crowding in the coordination sphere: nine contact distances within the range 2.70–3.00 Å in the coordination sphere of dysprosium compared to the four in the gadolinium complex. The contact distances in the coordination sphere of the cation are reported in Table III,a.

As previously pointed out, there is no direct interaction between the crown and the metal ion in this case; a different arrangement was found in the samarium(III) complex with the ligand 2 containing one more $-CH_2-O-CH_2-$ group in the cycle [11]. In this complex, in fact, the metal ion is directly bonded to three oxygen atoms of the ligand, one of which is the methoxyarylic one. The reduced number of donor oxygen atoms, the consequent shrinkage of the macroring, and the disturbing steric effect of the methoxy group, may account for the complete loss of the host ligand properties of the crown-ether derivative in the compound considered herein.

Finally, the important role of hydrogen bonds in this compound should be emphasized. In fact, the water molecules coordinated to the metal ion form six rather strong hydrogen bonds: four with oxygen atoms of the ligand (one methoxylic and the other three ethereal) the remaining two with the nitrate oxygens O′(1) and O″(4) of two adjacent molecules. The hydrogen bond is, therefore, the driving force both for the formation of the 1:1 adduct and the association of the asymmetric units in a three-dimensional extensive H-bonding network as shown in Fig. 3. The hydrogen bond distances are reported

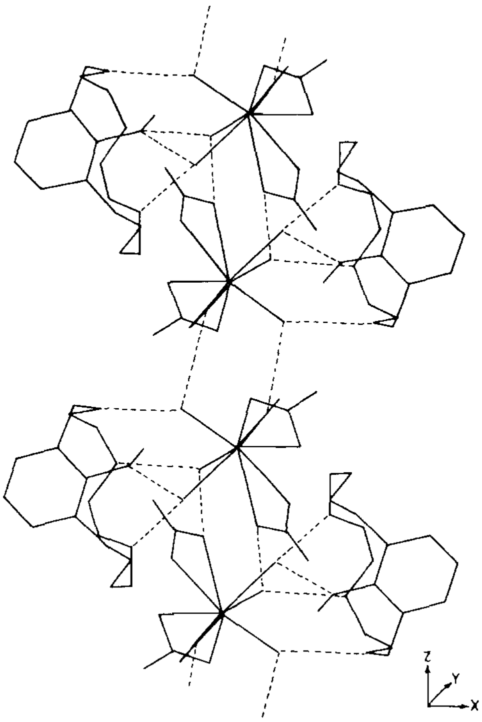

Fig. 3. Perspective of the molecular packing. Only the molecules involved in the hydrogen bonds are reported.

in Table III,b. Similar conclusions were reached by D. J. Baker-Dirks *et al.* in studying the crystal structure of the above mentioned complex of Gd^{3+} with 18-crown-6 [6].

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