

Crystal and Molecular Structure of Samarium(III) Nitrate with (2-Methoxy-1,3-xylyl)-18-Crown-5

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Introduction

Growing interest is being devoted to the study of coordination compounds between lanthanoid ions and macrocyclic ligands such as crown ethers and cryptands. In fact the selective metal binding properties of these macrocyclic molecules make them useful for the investigation of the coordinative properties of the lanthanoid ions.

Complexes of these ions with crown ethers containing from four to ten oxygen atoms were obtained by various workers [1–8], and for some the crystal and molecular structures have been established by X-ray diffraction [9–14]. Six of these structures refer to lanthanoid complexes with the three cyclic polyethers conventionally named dicyclohexyl-18-crown-6 [11], dibenzo-18-crown-6 [9], and 18-crown-6 [10, 12–14]. It should be noted that these molecules share the same 'crown' of atoms, that is a cycle formed by eighteen atoms including six oxygen donor atoms. In spite of this close similarity, the complexes formed by these three molecules with lanthanoid salts show some significant structural differences, such as the coordination number which may be ten [9, 10] or twelve [11–14], and the coordination polyhedron. On the other hand, complexes of different metal/crown-ether ratios were also obtained [3, 6]. All these remarks are indicative of a rather flexible behaviour of these metal–ligand systems.

Keeping the same framework of the cycle 18-crown-6, we have examined how the ability of a crown ether to bond lanthanoid ions is influenced by a convergent methoxy group. Interesting information on the binding properties towards alkali metal and ammonium cations of crowns modified in this way is available [17–19].

TABLE I. Fractional Atomic Coordinates of Non Hydrogen Atoms with e.s.d. s in Parentheses.

Atom	x/a	y/b	z/c	U
Sm	0.441(1)	0.934(1)	0.633(2)	^a
O(1)	0.349(2)	0.950(2)	0.834(3)	0.05
O(2)	0.417(2)	0.785(2)	0.735(3)	0.05
O(3)	0.557(2)	0.832(2)	0.649(3)	0.06
O(4)	0.666(2)	0.919(3)	0.810(4)	0.09
O(5)	0.614(2)	1.011(2)	1.025(3)	0.06
O(6)	0.460(1)	1.070(2)	1.023(2)	0.04
O(7)	0.516(2)	0.942(2)	0.434(2)	0.04
O(8)	0.542(2)	1.036(2)	0.572(3)	0.05
O(9)	0.593(2)	1.042(2)	0.390(3)	0.06
O(10)	0.397(2)	0.820(2)	0.472(3)	0.06
O(11)	0.310(2)	0.888(2)	0.578(3)	0.06
O(12)	0.281(2)	0.792(3)	0.441(4)	0.08
O(13)	0.388(2)	1.085(2)	0.664(3)	0.05
O(14)	0.387(2)	1.040(2)	0.476(4)	0.07
O(15)	0.348(3)	1.173(4)	0.517(5)	0.12
O(W)	0.507(2)	0.973(2)	0.816(3)	0.05
N(1)	0.547(2)	1.010(2)	0.461(3)	0.05
N(2)	0.327(2)	0.837(3)	0.497(4)	0.05
N(3)	0.374(3)	1.096(3)	0.553(5)	0.07
C(1)	0.268(3)	0.980(4)	0.819(5)	0.07
C(2)	0.359(3)	0.908(3)	0.945(4)	0.04
C(3)	0.369(3)	0.948(4)	1.044(5)	0.06
C(4)	0.377(3)	0.903(3)	1.170(5)	0.06
C(5)	0.380(5)	0.805(6)	1.185(8)	0.08
C(6)	0.365(5)	0.769(6)	1.074(8)	0.11
C(7)	0.358(3)	0.808(3)	0.941(5)	0.05
C(8)	0.353(3)	0.760(3)	0.823(5)	0.05
C(9)	0.484(2)	0.739(3)	0.757(4)	0.06
C(10)	0.536(2)	0.742(3)	0.670(4)	0.04
C(11)	0.632(3)	0.844(3)	0.612(5)	0.05
C(12)	0.684(3)	0.844(3)	0.732(5)	0.05
C(13)	0.717(5)	0.914(6)	0.930(7)	0.12
C(14)	0.696(5)	1.022(5)	0.964(7)	0.13
C(15)	0.593(3)	1.086(4)	1.093(6)	0.08
C(16)	0.508(3)	1.061(4)	1.125(5)	0.06
C(17)	0.382(3)	1.056(4)	1.050(4)	0.05

^aU₁₁ = 0.03, U₂₂ = 0.04, U₃₃ = 0.05, U₂₃ = 0.00, U₁₃ = 0.00, U₁₂ = 0.00.

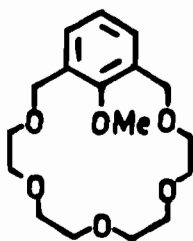


Fig. 1. (2-Methoxy-1,3-xylyl)-18-crown-5 (L).

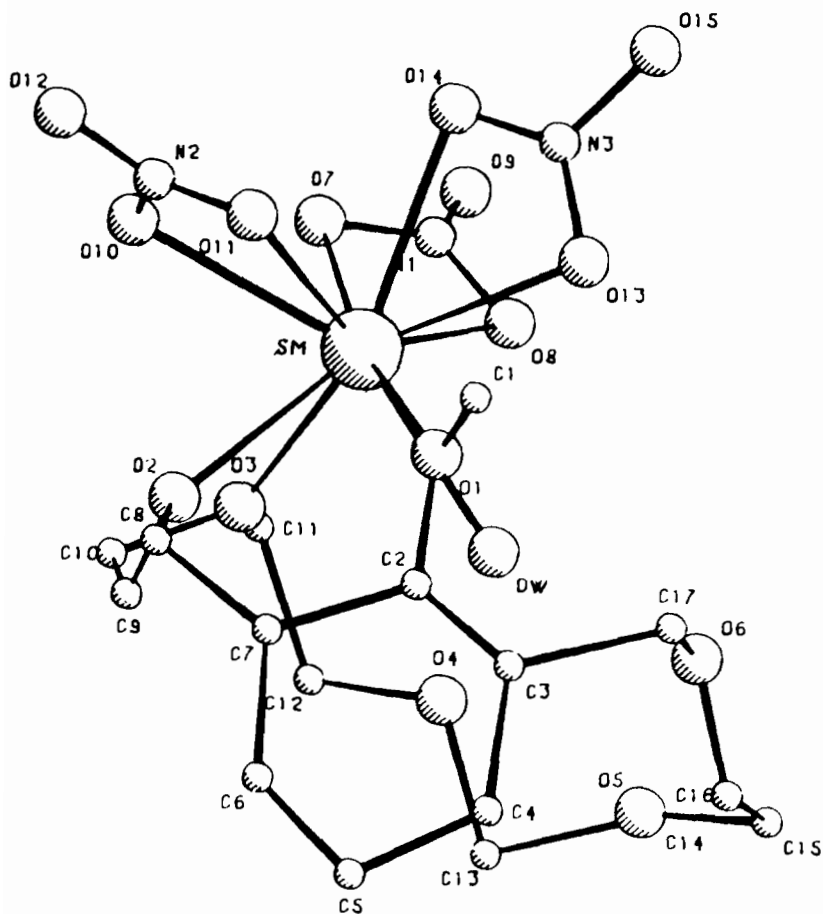


Fig. 2. The molecular structure of $[\text{Sm}(\text{NO}_3)_3 \cdot \text{L} \cdot \text{H}_2\text{O}]$ showing atom-numbering scheme.

Experimental

The crown ether was prepared according to previously reported method [17].

The complex was prepared adding a solution of $\text{Sm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in anhydrous methyl cyanide (1 mmol in 5 cm^3) to a solution of crown ether in the same solvent (1.1 mmol in 5 cm^3). Pale green crystals precipitate after partial evaporation of the solvent; they were filtered off, washed with a mixture of methyl cyanide and dichloromethane and dried *in vacuo* at room temperature. The compound is sensitive to moisture, so all operations were performed in dry nitrogen.

The elemental analysis agrees with the formula $\text{Sm}(\text{NO}_3)_3 \cdot \text{L} \cdot \text{H}_2\text{O}$ ($\text{C}_{17}\text{H}_{28}\text{N}_3\text{O}_{16}\text{Sm}$ requires C, 29.99; N, 6.17; H, 4.14; Sm, 22.08%. Found: C, 29.85; N, 6.23; H, 4.28; Sm, 22.03%).

Crystal Data

A crystal of dimensions $0.4 \times 0.3 \times 0.2 \text{ mm}$ was sealed in a closed glass capillary for X-ray

analysis. The unit cell belongs to the orthorhombic system, space group $P2_1P2_1P2_1$ with $a = 17.648(8)$, $b = 15.083(8)$, $c = 10.830(7) \text{ \AA}$; $D_c = 1.56$, $D_o = 1.55 \text{ g/cm}^3$ by flotation, $Z = 4$.

Intensity data were collected with a Philips PW1100 four-circle diffractometer up to $\theta = 23^\circ$ in the $\theta-2\theta$ scan mode using the graphite-monochromated $\text{MoK}\alpha$ radiation. Adopting the criterion $I \geq 3\sigma(I)$, 1506 of the 2088 recorded intensities were used throughout the refinement. The intensities of the standard reflections slowly decrease to *ca.* 60% of their initial values at the end of data collection. On the basis of the loss in intensity of the standard reflections the intensities of all the reflections were recalculated. The convergence obtained using these corrected data was not better than that with the uncorrected ones. The samarium atom was located from a Patterson synthesis; successive Fourier syntheses show the position of all the non-hydrogen atoms. The full-matrix least-squares refinement on F_o was computed minimizing the function $\sum w(|F_o| - |F_c|)^2$ ($w = 1$). The SHELX-76 system of programs

TABLE II. Bond Distances ($\delta = 0.03 \text{ \AA}$) and Angles ($\delta = 1^\circ$) Involving Sm Atom.

Sm-O(1) = 2.73	Sm-O(2) = 2.54	Sm-O(3) = 2.56
Sm-O(7) = 2.52	Sm-O(8) = 2.45	Sm-O(10) = 2.57
Sm-O(11) = 2.49	Sm-O(13) = 2.49	Sm-O(14) = 2.53
Sm-O(W) = 2.38		
O(2)-Sm-O(1) = 68	O(3)-Sm-O(1) = 118	
O(3)-Sm-O(2) = 65	O(7)-Sm-O(1) = 171	
O(7)-Sm-O(2) = 120	O(7)-Sm-O(3) = 71	
O(8)-Sm-O(1) = 126	O(8)-Sm-O(2) = 143	
O(8)-Sm-O(3) = 79	O(8)-Sm-O(7) = 50	
O(10)-Sm-O(1) = 115	O(10)-Sm-O(2) = 70	
O(10)-Sm-O(3) = 84	O(10)-Sm-O(7) = 67	
O(10)-Sm-O(8) = 118	O(11)-Sm-O(1) = 70	
O(11)-Sm-O(2) = 73	O(11)-Sm-O(3) = 126	
O(11)-Sm-O(7) = 107	O(11)-Sm-O(8) = 142	
O(11)-Sm-O(10) = 51	O(13)-Sm-O(1) = 66	
O(13)-Sm-O(2) = 133	O(13)-Sm-O(3) = 147	
O(13)-Sm-O(7) = 106	O(13)-Sm-O(8) = 75	
O(13)-Sm-O(10) = 126	O(13)-Sm-O(11) = 86	
O(14)-Sm-O(1) = 105	O(14)-Sm-O(2) = 142	
O(14)-Sm-O(3) = 137	O(14)-Sm-O(7) = 66	
O(14)-Sm-O(8) = 72	O(14)-Sm-O(10) = 82	
O(14)-Sm-O(11) = 70	O(14)-Sm-O(13) = 51	
O(W)-Sm-O(1) = 66	O(W)-Sm-O(2) = 86	
O(W)-Sm-O(3) = 73	O(W)-Sm-O(7) = 117	
O(W)-Sm-O(8) = 73	O(W)-Sm-O(10) = 152	
O(W)-Sm-O(11) = 136	O(W)-Sm-O(13) = 81	
O(W)-Sm-O(14) = 126		
Other averaged distances (\AA).		
C-C(crown) = 1.50(8)	C-O(crown) = 1.45(6)	N-O(nitrate) = 1.23(4)

[20] was used. The final fractional atomic coordinates and thermal parameters are reported in Table I; hydrogen atoms were not introduced. The final agreement factor R was 10.2%.

Results and Discussion

As shown in Fig.2, in which the structure is projected along an axis perpendicular to the plane through atoms Sm, O(10) and O(14), the compound consists of neutral molecules of $[\text{Sm}(\text{NO}_3)_3 \cdot \text{L} \cdot \text{H}_2\text{O}]$ in which the metal atom is deca-coordinated, being directly bonded to three ligand oxygen atoms, to three bidentate nitrate groups, and to one water molecule. The coordination polyhedron is a *quasi* regular bicapped square antiprism in which the methoxyarylic oxygen O(1) and the nitrate oxygen O(7) occupy axial positions, Fig. 3.

Metal-ligand interatomic distances fall in the limits 2.54–2.73 \AA for Sm–O (ether), 2.45–2.87 \AA for Sm–O(nitrate), and 2.38 \AA for Sm–O(water).

These bond distances are as expected from previously determined structures involving the samarium ion with etheral and nitrate oxygen atoms [9, 21]. Bond distances and angles concerning the coordination of the samarium ion and other averaged distances are given in Table II.

A swift glance at this structure makes clear some dramatic differences compared with the other structures referring to the lanthanoid-crown ether complexes above mentioned.

i) In the complex here examined the metal cation is not bound to all six oxygen atoms of the cyclic polyether, but only to three, one of which is the methoxyarylic oxygen, O(1), and the other two are contiguous oxygens, O(2) and O(3), of a group $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ bound to a benzylic carbon. In this way the samarium atom is not enclosed within the crown cavity.

ii) Since the metal is quite out of the best plane of the ethereal oxygens, all three bidentate nitrate groups are on the same side of this plane, which, in turn, is tilted out of the plane of the aryl by about 90° .

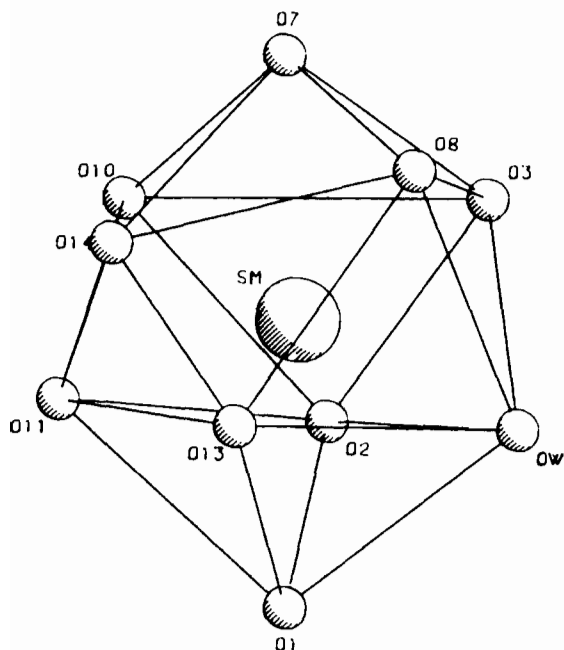


Fig. 3. The coordination polyhedron around the Samarium atom.

iii) In the coordination polyhedron of the metal there is a water molecule. Contacts between this molecule and some of the oxygen atoms suggest the possibility of some kind of intramolecular hydrogen bonding. In particular the atoms most probably involved seem to be the ethereal O(4) and O(6), for which the distances are $O(W)\cdots O(4) = 2.92 \text{ \AA}$, $O(W)\cdots O(6) = 2.80 \text{ \AA}$ and the $O(4)-O(W)-O(6)$ angle is 116.5° .

This structure as a whole shows that a convergent methoxy group in a crown ether hinders the formation of typical crown complexes with lanthanoid ions. This effect should be due to unfavourable steric and/or conformational conditions rather than to the poorer donor properties of the methoxy-arylic oxygen compared to purely aliphatic oxygens

because of the electron withdrawing effect of the attached aryl group.

Further work is in progress regarding the behaviour of the lanthanoids with similar crown ethers.

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