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Crystal and Molecular Structure of the 4:3 Complex of 18-Crown-6 Ether with Neodymium Nitrate*

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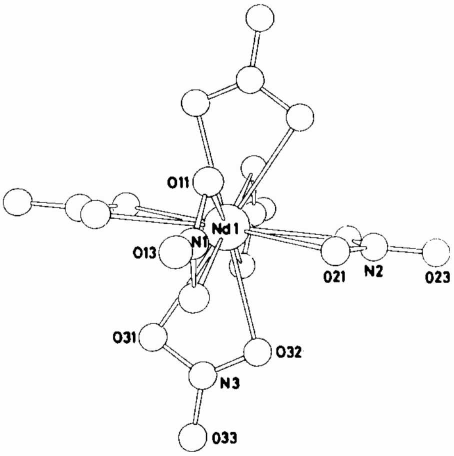

Fig. 1. View of the $[Nd(NO_3)_6]^{3-}$ ion.

In previous parts of this series we have reported the isolation of lanthanoid nitrate complexes with 15-crown-5, 18-crown-6 and 21-crown-7 ethers having two different Ln(III)/crown ratios, 1:1 and 4:3. The latter either precipitate directly from an acetonitrile solution containing equimolar quantities of salt and ligand [1, 2] or are formed by thermal decomposition of the corresponding 1:1 complexes [1, 3]. The 4:3 complexes form for Ln = Eu–Lu with the 15-crown-5 polyether [3], for Ln = Nd–Lu with the 18-crown-6 polyether [1, 3] and for Ln = La–Gd with the 21-crown-7 polyether [4]; such complexes appear also to form with lanthanoid chlorides [3]. We report here the determination of the crystal and molecular structure, at room temperature, of one of these complexes: $[Nd(NO_3)_3]_4(C_{12}H_{24}O_6)_3$.

Experimental

The complex was synthesized according to the procedure described in [1]. Recrystallization from acetonitrile yielded pale violet crystals suitable for X-ray analysis. A crystal of approximate dimensions 0.28 X 0.20 X 0.23 mm was measured. Precession photographs display the systematic extinction h + k = 2n + 1 for (hkl) and therefore the possible space groups are C_2, Cm or C2/m. A statistical analysis [5] of normalized structural factors $|E_{hkl}| < 2.0$ clearly points to a centrosymmetrical space group. Photographs of another crystal, synthesized independently, appeared to display extremely weak reflections which destroy the systematic extinction, pointing to a primitive cell. Numerous problems arose during the structure determination, either with the centered or with the primitive cell, and the structure was finally refined in C2/m.

X-ray data were collected up to $2\theta = 55°$ on a Syntex $P2_1$ four cycle diffractometer using Nb-filtered MoKα radiations and the θ–2θ scanning technique. Intensities were measured for 4369 reflections, of which 1780 were smaller than $3\sigma(I)$. Data collection and corrections were performed as described in [6] (linear absorption coefficient: 29.7 cm^{-1}). Interpretation of the Patterson map revealed that all the neodymium ions lie in special positions (0, 0, 0; 0, ½, ½; 0.27, ½, 0.26); successive Fourier syntheses revealed all the atoms surrounding the first two Nd(III) ions. The crown ether next to the (0.27, ½, 0.26) ion is disordered. A Fourier map revealed a superposition of two macrocycles which were individually refined with a weight of ½. The carbon atoms could however not be determined. Attempts to refine the structure in space groups C_2 or Cm failed to give better results. Final refinement with anisotropic factors for all atoms, except for the carbon and oxygen atoms of the polyethers, converged to $R_F = 0.061$ (weighted $R_F = 0.066$), with 16 observations per refined parameter. Bond distances and angles are reported in Table I. Tables of structural factors, positional parameters and temperature factors are available upon request.

Crystal data: $C_{36}H_{72}N_{12}O_{54}Nd_4$, FW = 2,113.96; monoclinic $a = 29.461(9)$, $b = 11.246(3)$, $c =$

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*Part 9 of the series 'Complexes of Lanthanoid Salts with Macrocyclic Ligands'. For part 8, see ref. [18].

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TABLE I. Bond Lengths (Å) and Angles (°); eds are given in parentheses.

$[Nd(NO_3)_6]^{3-}$, D_{2h}			
Nd(1)–O(11)	2.57(1)	Nd(1)–O(31)	2.61(1)
Nd(1)–O(21)	2.57(1)	Nd(1)–O(32)	2.66(2)
N(1)–O(11)	1.27(1)	O(11)–N(1)–O(11)	116(1)
N(1)–O(13)	1.23(2)	O(11)–N(1)–O(13)	122(1)
N(2)–O(21)	1.30(1)	O(21)–N(2)–O(21)	110(1)
N(2)–O(23)	1.24(2)	O(21)–N(2)–O(23)	125(1)
N(3)–O(31)	1.17(2)	O(31)–N(3)–O(32)	117(2)
N(3)–O(32)	1.25(2)	O(31)–N(3)–O(33)	123(1)
N(3)–O(33)	1.22(3)	O(32)–N(3)–O(33)	120(2)
$[Nd(NO_3)_2(C_{12}H_{24}O_6)]^+$, D_{2h}			
Nd(2)–O(41)	2.42(2)	O(41)–Nd(2)–O(41)′	43(1)
Nd(2)–O(101)	2.60(1)	O(101)–Nd(2)–O(101)′	53(1)
Nd(2)–O(102)	2.56(2)	O(101–Nd(2)–O(102)	64(1)
		O(41)–Nd(2)–O(101)	73(1)
		O(41)–Nd(2)–O(102)	88(1)
N(4)–O(41)	1.16(2)	O(41)–N(4)–O(43)	129(3)
N(4)–O(43)	1.18(3)	O(41)–N(4)–O(41)′	100(2)
C–C	1.42(10)	C–C–O	105(14)
C–O	1.47(6)	C–O–C	110(7)
$[Nd(NO_3)_2(C_{12}H_{24}O_6)]^+$, C_1			
Nd(3)–O(51)	2.57(2)	O(51)–Nd(3)–O(52)	49(1)
Nd(3)–O(52)	2.49(1)	O(61)–Nd(3)–O(61)′	49(1)
Nd(3)–O(61)	2.54(1)		
Nd(3)–O(201)	2.64(2)	Nd(3)–O(211)	2.71(2)
Nd(3)–O(202)	2.54(2)	Nd(3)–O(212)	2.68(2)
Nd(3)–O(203)	2.56(2)	Nd(3)–O(213)	2.59(2)
N(5)–O(51)	1.16(2)	O(51)–N(5)–O(52)	125(2)
N(5)–O(52)	1.21(3)	O(51)–N(5)–O(53)	116(2)
N(5)–O(53)	1.21(2)	O(52)–N(5)–O(53)	119(2)
N(6)–O(61)	1.23(1)	O(61)–N(6)–O(63)	119(1)
N(6)–O(63)	1.19(2)	O(61)–N(6)–O(61)′	121(1)

12.057(2) Å, β = 115.34(5)°, U = 3.610.4 Å^3, D_x = *1.942 (by flotation in* $CHBr_3/CHCl_3$ mixtures, at 22 °C), D_c = 1.947 for Z = 2, F(000) = 2,088.0, space group C2/m.

Results and Discussion

The structure contains three crystallographically distinct ions in the ratio 1:1:2: (i) $[Nd(NO_3)_6]^{3-}$ with D_{2h} symmetry, (ii) $[Nd(NO_3)_2(C_{12}H_{24}O_6)]^+$ with the same symmetry, and (iii) $[Nd(NO_3)_2(C_{12}H_{24}O_6)]^+$ with a disordered polyether on a C_1 symmetry site. An identical situation is described by Hart *et al.* for the complex of lanthanum nitrate with the [2.2.2] cryptand which contains dodecacoordinated $[La(NO_3)_6]^{3-}$ (C_i) and $[La(NO_3)_2(2.2.2)]^+$ (C_2 and C_1) ions [7]. Similarly, Burns reports that $[Sm(NO_3)_3]_2(2.2.2)\cdot H_2O$ contains eleven-coordinated $[Sm(NO_3)_6\cdot H_2O]^{2-}$ ions and dodecacoordinated $[Sm(NO_3)(2.2.2)]^{2+}$ ions [8]. Finally, similar behaviour has been observed for uranium complexes with 18-crown-6 ether: recrystallisation of $(UCl_4)_3(C_{12}H_{24}O_6)_2$ in nitromethane yields a product which includes $[UCl_3(C_{12}H_{24}O_6)]^+$ and $[UO_2Cl_3(OH)(H_2O)]^{2-}$ ions [9], whereas $[U(BH_4)_3]_4(C_{12}H_{24}O_6)_3$ contains octahedral $[U(BH_4)_6]^{3-}$ moieties in addition to $[U(BH_4)_2(C_{12}H_{24}O_6)]^+$ ions, two thirds of them having a disordered crown ether [10].

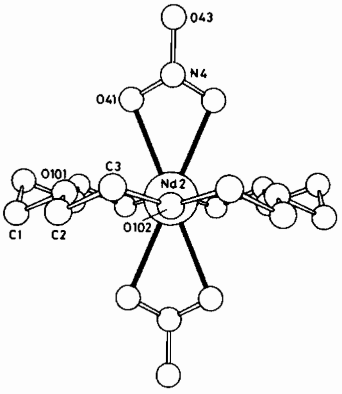

Fig. 2. View of the $[Nd(NO_3)_2(C_{12}H_{24}O_6)]^+$ ion.

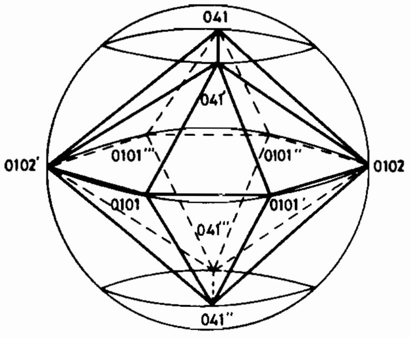

Fig. 3. Coordination polyhedron for the $[Nd(NO_3)_2(C_{12}H_{24}O_6)]^+$ ion.

A view of the hexanitrato anion of D_{2h} symmetry is given in Fig. 1. The neodymium ion is 12-coordinated to six bidentate and planar nitrato groups. The Nd–O bond lengths range from 2.57 to 2.66 Å with a mean value of 2.59(4) Å, a value identical to that found for $Nd–ONO_2$ bonds in the 1:1 complex $Nd(NO_3)_3(C_{12}H_{24}O_6)$ [11]. Ln–O distances in similar hexanitrato complexes, 2.65(3), 2.64(3), and 2.63(8) for Ln = La [12], Ce [13] and Pr [14], respectively, nicely reflect the contraction of the lanthanide ionic radii. The coordination polyhedron of each known structure of $[Ln(NO_3)_6]^{3-}$ may be described as a distorted icosahedron. The distortion mainly arises from the short 'bite' of the nitrato groups: for Ln = Nd, the mean distance between bonding oxygen atoms belonging to neighbouring nitrato groups is 2.90(3) Å and the mean O–Nd–O angle is 68(1)°; the corresponding distance and angle for oxygen atoms of the same nitrato group are 2.16(2) Å and 48(1)°. A regular icosahedron would require identical O–O distances and 60° angles. If bidentate ligands of small 'bite' are viewed as occupying one coordination site in a polyhedron, according to the suggestion of Bergman and Cotton [15], then the resulting lower coordination number polyhedron should closely approach the ideal geometry for that coordination number, here an octahedral geometry (N = 12/2). This is indeed true for $[Nd(NO_3)_6]^{3-}$, if we consider the structural arrangement of the nitrogen atoms around Nd(1). The neodymium ion and two pairs of nitrogen atoms lie exactly in three orthogonal planes: the only slight distortion arises from the N(2)–Nd(1)–N(3) angle which deviates by 0.3° from orthogonality. Slightly different Nd–N distances (3.01, 3.09, 3.05 Å) introduce a further small departure from the ideal octahedral arrangement.

Of special interest is the complex cation of D_{2h} symmetry in which one Nd(III) ion is enclosed in a crown ether molecule and held by one bidentate nitrato group on each side (Fig. 2). The coordination polyhedron of the lanthanide ion is different from the three polyhedra usually found for 10-coordination, namely, the bicapped square antiprism, the bicapped dodecahedron and the 4A, 6B-expanded dodecahedron [16]. It may rather be described as a tetracapped hexagon (Fig. 3). The O(ether)–Nd–O(ether) angles range from 53.0 to 63.7° with a mean value of 58.4(5)°. The vicinal O(ether)–O(ether) distances range from 2.62 to 2.64 Å. The best plane through the oxygen atoms of the crown ether (standard deviation: 0.12 Å) contains the noedymium ion and its dihedral angle with the plane containing the four bonded oxygen atoms of the NO_3^- groups and the metal ion is 88.2°. The Nd–O bond lengths are shorter than in the 1:1 complex $Nd(NO_3)_3(C_{12}H_{24}O_6)$ [11], which is consistent with the smaller coordination number: 2.42 Å for Nd–O(nitrate), as compared to 2.60 Å, and 2.59(2) Å for Nd–O(ether), as compared to 2.70 Å. Upon complexation, the crown ether is considerably flattened from its usual conformation [17]. The isotropic temperature factors of the C and O atoms are large (~0.18 Å^2), which can be interpreted as reflecting some disorder in the crown ether.

In the bisnitrato complex with C_1 symmetry, the two nitrato groups also lie above and under the mean plane of the macrocycle; $N(5)O_3^-$ lies in the plane of symmetry which bisects the O(61)–N(6)–O(61)' angle. The two positions of the disordered polyether are staggered by about 30° in such a way that the carbon atoms of one conformation are fairly exactly related to the carbon atoms of the other conformation by the plane of symmetry, which makes the disorder difficult to solve completely. The mean Nd–O bond lengths are 2.56(4) Å for the other position, as compared to 2.52(9) Å for one position of the polyether and 2.61(6) Å for the corresponding bis-nitrato complex cation with D_{2h} symmetry and to

Work is in progress in our laboratories to elucidate further this crystal structure and to solve the structure of other complexes between crown ethers and lanthanoid salts.

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