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Crystal and Molecular Structure of the 1:1 Complex of 18-crown-6 Ether with Neodymium Nitrate*

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Introduction

Rare earth salts are known to form complexes with crown ethers [1–9] and with cryptands [10, 11]. These complexes have recently received growing attention [12–18], especially since they may be used for lanthanide ion separation [2] and for stabilizing Ln(II) oxidation states [19]. However, few crystallographic data are available; to our knowledge, only the crystal structure of the 1:1 complex of lanthanum nitrate with dicyclohexyl-18-crown-6 ether [20] and of two cryptates [21, 22] have been reported so far. The 18-crown-6 ether forms both 1:1 and 4:3 complexes with lanthanoid nitrates [5, 18] and thus is an interesting ligand for structural investigations. We report here the crystal and molecular structure of the 1:1 complex of neodymium nitrate with this ligand, the 1,4,7,10,13,16-hexaoxacyclooctadecane.

Experimental

The complex was synthesized according to the procedure described in [5]. Recrystallization in acetonitrile yielded pale violet plate-like crystals which were suitable for X-ray analysis.

A crystal of approximate dimensions 0.31 X 0.15 X 0.25 mm was investigated. The unit cell is orthorhombic, with *a* = 12.232(2), *b* = 15.622(3), *c* = 21.799(3) Å, and *Z* = 8. The observed density is 1.891, as determined by flotation technique ($CHBr_3/CHCl_3$ mixtures), and it is in good agreement with the calculated density for *Z* = 8, 1.896. The space group, Pbca (ITC Nr. 61), was determined by systematic absences: 0kl: k = 2n, h0l: 1 = 2n, and hk0: h = 2n.

TABLE I. Bond Lengths (A) and Angles (°). The esd's are given in parentheses.

(a) *Coordination polyhedron*			
Nd–O1	2.598(5)	Nd–O11	2.615(4)
Nd–O2	2.699(5)	Nd–O12	2.580(4)
Nd–O3	2.788(4)	Nd–O21	2.607(6)
Nd–O4	2.632(4)	Nd–O22	2.590(5)
Nd–O5	2.719(4)	Nd–O31	2.602(4)
Nd–O6	2.771(5)	Nd–O32	2.615(4)
(b) *Nitrate ions*			
N1–O11	1.259(7)	O11–N1–O12	116.7(5)
N1–O12	1.250(8)	O11–N1–O13	120.8(5)
N1–O13	1.233(8)	O12–N1–O13	122.5(6)
N2–O21	1.252(8)	O21–N2–O22	115.1(7)
N2–O22	1.280(9)	O21–N2–O23	124.4(7)
N2–O23	1.21(1)	O22–N2–O23	120.5(6)
N3–O31	1.278(6)	O31–N3–O32	115.1(5)
N3–O32	1.263(8)	O31–N3–O33	121.5(5)
N3–O33	1.221(6)	O32–N3–O33	123.4(4)
(c) *Macrocycle*			
C1–C2	1.495(5)	O1–C12	1.452(7)
C3–C4	1.513(6)	O1–C1	1.454(7)
C5–C6	1.522(6)	O2–C2	1.448(6)
C7–C8	1.505(4)	O2–C3	1.444(6)
C9–C10	1.487(4)	O3–C4	1.427(8)
C11–C12	1.518(5)	O3–C5	1.446(7)
		O4–C6	1.441(6)
C12–O1–C1	112.8(5)	O4–C7	1.469(6)
C2–O2–C3	109.0(6)	O5–C8	1.454(7)
C4–O3–C5	109.9(6)	O5–C9	1.455(8)
C6–O4–C7	112.3(5)	O6–C10	1.447(6)
C8–O5–C9	112.2(4)	O6–C11	1.461(6)
C10–O6–C11	108.5(3)		

X-ray data were collected up to $2\theta = 50°$ on a Syntex $P2_1$ four cycle diffractometer using Nb-filtered MoK_α radiations ($\lambda = 0.71069$ Å), and the θ–2θ technique. Intensities were measured for 3,670 reflections, of which 1,236 were less than $3\sigma(I)$. Data correction and solution of the structure were performed as described in [23]. The final refinement converged to $R_F = 0.036$ (weighted $R_F = 0.041$), with 13 observations per refined parameter. Bond distances, positional parameters and temperature factors are given in Tables I and II. A table of structural factors is available upon request.

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TABLE II. Atomic Fractional Coordinates and Anisotropic Thermal Parameters.[a]

Atom	X	Y	Z	U22	U33	U12	U13	U23
Nd(1)	0.0107	0.1847	0.1176	0.0324	0.0330	−0.0044	0.0022	−0.0036
N(1)	0.2160	0.2917	0.1232	0.0442	0.0449	−0.0062	−0.0070	0.0042
N(2)	0.4146	0.0181	0.3336	0.0415	0.0473	−0.0022	0.0044	−0.0073
N(3)	0.2817	0.1490	0.4287	0.0373	0.0464	0.0073	0.0036	0.0016
O(1)	0.0855	0.0990	0.0245	0.0444	0.0439	−0.0040	0.0068	−0.0033
O(2)	0.0358	0.2676	0.0099	0.0459	0.0469	−0.0023	0.0004	0.0064
O(3)	0.4101	0.3423	0.4027	0.0398	0.0794	0.0045	−0.0095	0.0047
O(4)	0.4273	0.2685	0.2887	0.0585	0.0599	−0.0031	−0.0093	0.0159
O(5)	0.1198	0.1787	0.2262	0.0739	0.0419	−0.0117	−0.0013	−0.0097
O(6)	0.1656	0.0589	0.1393	0.0473	0.0547	−0.0025	−0.0090	0.0065
O(11)	0.1255	0.3226	0.1394	0.0463	0.0684	0.0009	0.0057	−0.0121
O(12)	0.2138	0.2198	0.0980	0.0376	0.0573	−0.0007	0.0014	−0.0037
O(13)	0.3020	0.3305	0.1331	0.0483	0.0871	−0.0171	−0.0098	−0.0025
O(21)	0.4419	0.0782	0.2988	0.0707	0.0396	−0.0072	−0.0021	0.0062
O(22)	0.4339	0.0306	0.3906	0.0447	0.0457	−0.0029	0.0043	−0.0021
O(23)	0.1285	0.4526	0.3165	0.0478	0.0855	0.0181	−0.0038	−0.0259
O(31)	0.2991	0.1730	0.3735	0.0576	0.0514	0.0025	−0.0078	0.0143
O(32)	0.3592	0.1630	0.4656	0.0618	0.0500	−0.0016	−0.0056	0.0023
O(33)	0.1975	0.1123	0.4432	0.0646	0.1119	−0.0084	0.0224	0.0143
C(1)	0.1344	0.3540	0.4739	0.0549	0.0469	0.0162	0.0194	0.0085
C(2)	0.0539	0.2862	0.4567	0.0644	0.0342	0.0026	−0.0016	−0.0050
C(3)	0.4627	0.1636	0.0067	0.0535	0.0790	−0.0013	0.0049	0.0287
C(4)	0.4536	0.3937	0.4510	0.0483	0.0796	0.0012	0.0002	−0.0226
C(5)	0.3903	0.3945	0.3491	0.0474	0.0905	0.0151	−0.0133	0.0253
C(6)	0.3475	0.3345	0.2997	0.0504	0.0923	0.0072	−0.0206	0.0188
C(7)	0.5035	0.2913	0.2392	0.1163	0.0523	−0.0191	−0.0079	0.0511
C(8)	0.0603	0.2099	0.2794	0.1100	0.0406	−0.0111	0.0031	−0.0148
C(9)	0.1760	0.1000	0.2432	0.0783	0.0601	0.0059	−0.0291	0.0204
C(10)	0.2413	0.0709	0.1896	0.0815	0.0517	0.0125	−0.0218	0.0107
C(11)	0.2247	0.0284	0.0853	0.0525	0.0528	0.0015	0.0028	−0.0041
C(12)	0.1387	0.0174	0.0357	0.0358	0.0640	0.0132	0.0044	−0.0158

[a] Exp(−T), with $T = 2\pi^2\Sigma(H_iH_jU_{ij}A_i^*A_j^*)$; the A* s are the reciprocal axial lengths and the H's are the Miller indices.

Results and Discussion

The neodymium ion is decacoordinated being bound to three bidentate nitrato groups and to the six oxygen atoms of the polyether. A stereographic view of the molecule and a simplified representation of the unit cell are presented in Figs. 1 and 2, respectively. Due to the short bite of the nitrato groups, the mean Nd–O(NO_3^-) bond length is shorter than the mean Nd–O (ether) distance: 2.60(2) Å as compared with 2.70(10) Å. The nitrato groups show a slight departure from the idealized C_{2v} local symmetry; compared with the data obtained for $[Eu(NO_3)_5]^{2-}$ [23], the mean N(i)–O(i3) bond length, 1.22 Å, is 0.02 Å shorter, whereas the mean N–O-(Ln) distance is exactly the same: 1.26 Å. The macrocycle adopts a boat conformation, with one nitrate on the more sterically hindered side and the two remaining ones on the opposite side. This arrangement is similar to the reported structure of two $La(NO_3)_3$ complexes with dicyclohexyl-18-crown-

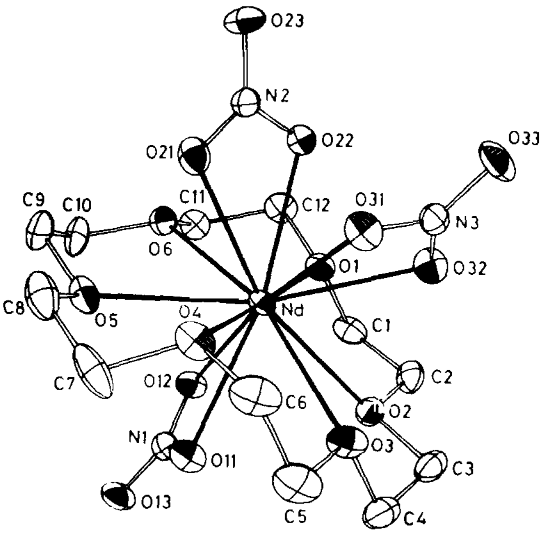

Fig. 1. View of the complex with thermal ellipsoids.

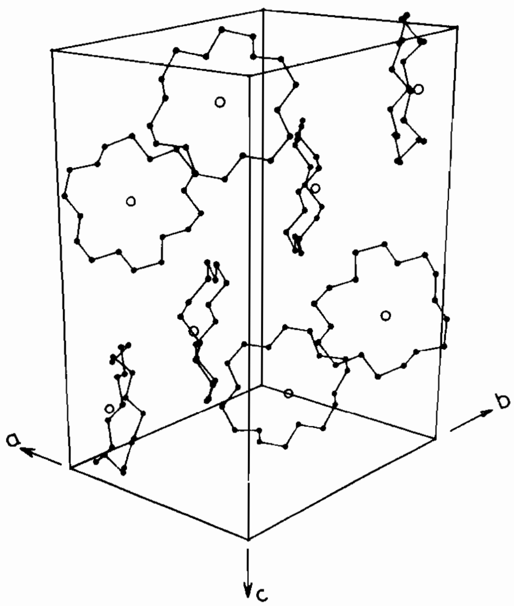

Fig. 2. Unit cell of $Nd(NO_3)_3\cdot$(18-crown-6). For the sake of clarity, the nitrato groups are not shown.

6-ether [20] and with a hexadentate nitrogen-donor macrocycle [24]. The mean C–C bond length, 1.507 Å, is identical with the mean bond length reported for the uncomplexed ligand [25], that is the C–C bonds remain unaffected by the complexation, contrary to the C–O bonds. Indeed, the mean C–O distance of the uncomplexed ligand, 1.41 Å [25], increases by 0.04 Å upon complexation with neodymium nitrate. This lengthening probably arises from the strong ion/dipole interaction between the trivalent Nd(III) ion and the oxygen atoms of the polyether. A comparable lengthening (0.05–0.06 Å) is found in a U(III) complex [26] whereas the C–O distance increases only by 0.01 Å upon complexation of the crown with monovalent alkaline ions [25].

The cavity diameter of the 18-crown-6 ether was evaluated by taking the smallest distance between two opposite atoms of the macrocycle and by substracting their covalent radii. Using Dunitz' data [25] we find 2.7 Å for the uncomplexed ether, a value which fits within the accepted 2.6–3.2 Å range obtained from molecular models [27]. The slight conformational change upon complexation results in a smaller cavity diameter; it is interesting to note that this shrinkage is cation-independent: the cavity diameter is 2.5 Å for both the four alkaline ion complexes [25] and for the 1:1 neodymium nitrate complex.

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