

16. Studies on Rare-Earth Complexes with Crown Ethers

Part XXV

Synthesis, Characterization, and Structure of the Complexes of Lanthanide Nitrates with 13-Crown-4¹⁾

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The lanthanide nitrate complexes with 13-crown-4(13-C-4) have been prepared in AcOEt. These new complexes with the general formula $\text{Ln}(\text{NO}_3)_3 \cdot (13\text{-C-4})$ ($\text{Ln} = \text{La-Nd, Sm-Lu}$) have been characterized by means of elemental analysis, IR and ¹H-NMR spectra, conductivity measurements, and TG-DTA techniques. The crystal and molecular structure of $\text{Nd}(\text{NO}_3)_3 \cdot (13\text{-C-4})$ has been determined by single crystal X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/a$ with $Z = 8$. Lattice parameters are $a = 15.393(1)$, $b = 12.578(1)$, $c = 19.279(2)$ Å, $\beta = 113.05(1)^\circ$, $V = 3435$ Å³, $D_c = 2.01$ g cm⁻³, $D_o = 2.03$ g cm⁻³, $\mu = 31.0$ cm⁻¹(MoK_α), $F(000) = 2056$. The structure was solved by *Patterson* and *Fourier* techniques and refined by least-squares to a final conventional R value of 0.032 for 5218 independent reflections with $I \geq 3\sigma(I)$. There are two independent $\text{Nd}(\text{NO}_3)_3 \cdot (13\text{-C-4})$ monomers in one asymmetrical unit. The coordination numbers are ten in these two independent monomers.

Introduction. – Recent studies [1] [2] demonstrated that the crown ethers of low symmetry, containing a trimethylene unit, have a lower coordination power towards most metal ions, but they have a selectivity to the best size-fitted metal ions than the corresponding symmetrical crown ethers. The enhanced cation selectivities have been assumed to be due to their enlarged cavity size and the favorable orientation of donor atoms. To study the selectivity and coordination pattern of these crown ethers to rare-earth ions, we synthesized the solid complexes of 13-C-4 with lanthanide nitrates in anhydrous medium, and investigated the composition, properties, and structure of these new complexes.

Experimental. – *Reagents.* Hydrated lanthanide nitrates were prepared by dissolving the corresponding oxides (*Anala R*) in 1:1 HNO₃. The ligand was prepared as reported in [1]. All other chemicals used were of *Anala R* grade.

¹⁾ The systematic name is 1,4,7,10-tetraoxacyclotridecane.

Chemical and Physical Measurements. The metal-ion contents was determined by EDTA titration using xylene-orange as an indicator. C, N, and H contents were determined using a *Carlo Erba 1106* elemental analyzer. The IR spectra were recorded in the 4000–200-cm⁻¹ region using KBr pellets and a *170SX-FTIR* spectrometer. The ¹H-NMR spectra were recorded on a *FT-80A* spectrophotometer using (D₆)acetone as a solvent and TMS as an internal standard. Thermal analyses (TG and DTA) were performed on a *Beijing PcT-2* thermobalance. The heating rate was 10° min⁻¹. Conductivity measurements were carried out with a *DDS-11A* type conductivity bridge for a freshly prepared soln. (10⁻³ M) in acetone at 25°. The crystal data were collected on an *Enraf-Nonius CAD-4* diffractometer by the ω -2 θ scan technique.

Preparation of the Complexes and the Single Crystal. A soln. of 0.3 mmol lanthanide nitrate in 2 cm³ of AcOEt was added dropwise to a soln. of 0.3 mmol of ligand in 2 cm³ of AcOEt. The mixture was stirred at r.t. for 12 h. The precipitated solid complex was filtered, washed with AcOEt, and dried in a desiccator (0.1 mm Hg) over P₄O₁₀ for 2 d. All the complexes are powdered solids with the characteristic color of the corresponding lanthanide nitrates.

The single crystals of Nd complex were obtained by dissolving the powdered solid complex in MeNO₂ and leaving the soln. in a desiccator over CaCl₂ at r.t. After about one month, the purplish red crystals formed from the soln. were used for X-ray analysis.

Results and Discussion. – **Composition of the Complexes.** The analytical data for the newly synthesized complexes, listed in *Table 1*, indicate that all of the complexes conform to a 1:1 stoichiometry of metal ion and crown ether.

IR Spectra. Upon complexation, the absorptions of $\nu(\text{R}-\text{O}-\text{R})$ shift from 1126 cm⁻¹ in free 13-C-4 to 1056–1063 cm⁻¹ region in the complexes. This provides evidence for the coordination of the crown ether with the metal ions.

The characteristic frequencies of coordinating NO₃ groups appear at 1752–1781 ($\nu_2+\nu_3$), 1729–1740 ($\nu_2+\nu_6$), 1499–1536 (ν_1), 1291–1315 (ν_4), 1018–1030 (ν_2), 811–849 (ν_3), 732–751 (ν_6), and 707–709 (ν_5) cm⁻¹ regions in the IR spectrum of the complexes; the difference between two strongest absorptions (ν_1 and ν_4) of NO₃ groups of ca. 200 cm⁻¹ indicate that the NO₃ groups in the complexes coordinate to the metal ions as bidentate ligand [3]. The absence of the absorptions around 1360 cm⁻¹ indicates that all of the NO₃ groups in the complexes coordinate to the lanthanide ions [3]. This result is consistent with that of the molar conductance values (*Table 1*). Moreover, weak bands assigned to the $\nu(\text{Ln}-\text{O}_{(\text{NO}_3)})$ [3] [4] are found in the 302–324 cm⁻¹ region, further supporting the above structure assignment.

Table 1. *Elemental-Analysis, Molar-Conductance, and Thermal-Analysis Data*

Compound	C [%] found (calc.)	H [%] found (calc.)	N [%] found (calc.)	Ln [%] found (calc.)	Molar conductance [ohm ⁻¹ cm ² mol ⁻¹]	Exothermic peaks [°C]
La(NO ₃) ₃ ·(13-C-4)	20.99 (20.96)	3.41 (3.49)	7.68 (8.15)	26.58 (26.96)	9.6	290
Ce(NO ₃) ₃ ·(13-C-4)	20.84 (20.93)	3.53 (3.49)	7.78 (8.14)	26.83 (27.15)	11.5	198, 282
Pr(NO ₃) ₃ ·(13-C-4)	20.77 (20.88)	3.47 (3.48)	7.95 (8.12)	26.88 (27.25)	14.2	313
Nd(NO ₃) ₃ ·(13-C-4)	21.12 (20.75)	3.37 (3.46)	7.61 (8.07)	27.43 (27.71)	14.1	326
Sm(NO ₃) ₃ ·(13-C-4)	20.67 (20.51)	3.31 (3.42)	7.42 (7.97)	28.34 (28.56)	14.0	310
Eu(NO ₃) ₃ ·(13-C-4)	20.85 (20.45)	3.41 (3.41)	7.60 (7.95)	28.45 (28.77)	10.7	299

Table 1 (cont.)

Compound	C [%] found (calc.)	H [%] found (calc.)	N [%] found (calc.)	Ln [%] found (calc.)	Molar conductance [ohm ⁻¹ cm ² mol ⁻¹]	Exothermic peaks [°C]
Gd(NO ₃) ₃ ·(13-C-4)	20.09 (20.24)	3.38 (3.37)	7.64 (7.87)	29.63 (29.48)	7.0	292
Tb(NO ₃) ₃ ·(13-C-4)	20.04 (20.18)	3.31 (3.36)	7.63 (7.85)	29.60 (29.69)	5.3	288
Dy(NO ₃) ₃ ·(13-C-4)	20.19 (20.05)	3.29 (3.34)	7.61 (7.79)	29.78 (30.16)	4.2	276
Ho(NO ₃) ₃ ·(13-C-4)	20.31 (19.96)	3.28 (3.33)	7.70 (7.76)	30.15 (30.47)	3.3	269
Er(NO ₃) ₃ ·(13-C-4)	19.68 (19.87)	3.20 (3.31)	7.58 (7.73)	30.49 (30.78)	2.9	252
Tm(NO ₃) ₃ ·(13-C-4)	20.06 (19.81)	3.23 (3.30)	7.44 (7.70)	30.81 (30.98)	2.8	277
Yb(NO ₃) ₃ ·(13-C-4)	19.77 (19.60)	3.47 (3.28)	7.42 (7.65)	31.32 (31.50)	2.6	233
Lu(NO ₃) ₃ ·(13-C-4)	19.47 (19.59)	3.32 (3.26)	7.77 (7.62)	32.04 (31.75)	8.5	190

¹H-NMR Spectra. The ¹H chemical shifts of the ligand and the La and Lu complexes are presented in Table 2.

Table 2. ¹H-NMR Chemical Shifts [ppm] for the Ligand and La^{III} and Lu^{III} Complexes

Compound	O–R–CH ₂ –R–O	CH ₂ O
13-C-4	1.58–1.71 (m, 2 H)	3.45–3.66 (m, 16 H)
La(NO ₃) ₃ ·(13-C-4)	1.83 (m, 2 H)	3.70–3.83 (m, 16 H)
Lu(NO ₃) ₃ ·(13-C-4)	1.71–1.78 (m, 2 H)	3.49–3.73 (m, 16 H)

All of the protons in the complexes show significant downfield shifts, indicating the metal-ligand complex formation. The δ values of the La complex ($\Delta\delta(\text{O–R–CH}_2\text{–R–O}) = 0.25$ ppm, $\Delta\delta(\text{O–CH}_2) = 0.17\text{--}0.25$ ppm) exhibit larger shifts compared with those of the Lu complex ($\Delta\delta(\text{O–R–CH}_2\text{–R–O}) = 0.07\text{--}0.13$ ppm, $\Delta\delta(\text{O–CH}_2) = 0.04\text{--}0.07$ ppm), indicating that the stronger binding between the La ion and the crown ether. This conclusion is consistent with that of thermal analytical data.

Thermal Analyses. The DTA curve of the ligand shows an exothermic peak at 186°, then an endothermic peak appears at 312°. The ligand decomposes completely when heated up to 630°.

The processes of thermal decomposition for all the complexes are almost the same (Table 1) and are different from that of the ligand. The complexes have no thermal change before decomposing, then decompose rapidly, producing high exothermic peaks. Above these temperature, there are no apparent endothermic or exothermic peaks. All the complexes decomposed completely into their corresponding lanthanide oxides when heated up to 850°. The total weight losses found were approximately consistent with those calculated.

From *Table 1*, one can find that the thermal stability of the complex increases firstly (except Ce complex), approaching the highest decomposing temperature for the Nd complex, and then decreases with increasing atomic number. Two exothermic peaks appear in the DTA curve of the Ce complex, and the decomposing temperature of the first exothermic peak is much lower than those of the other complexes (except Lu complex). The facile oxidation of Ce^{III} to Ce^{IV} must be responsible for this substantially low decomposing temperature.

By comparing the first exothermic peaks of the 13-C-4 complexes with those of the 12-crown-4 (12-C-4) complexes [5], one can find that the 13-C-4 complexes is thermally less stable than the 12-C-4 complexes. This indicates that the lanthanide ions are bound more weakly with less symmetrical 13-C-4 due to the existence of trimethylene unit.

Solubility and Molar Conductance. All the complexes are easily soluble in MeOH, EtOH, and acetone, partly soluble in MeCN, THF, and MeNO₂, and slightly soluble in AcOEt, CHCl₃, and Et₂O. The molar conductances of the complexes measured in acetone at 25° lie in the range 2.6–14.2 Ω⁻¹cm²mol⁻¹ (*Table 1*), indicating that all the complexes are essentially non-electrolytes [6]. This indicates that all the NO₃ groups in the complexes are coordinated to the lanthanide ions at least in acetone solution.

Crystal Structure of Nd Complex. Crystal data: C₉H₁₈N₃O₁₃Nd, *M* = 520.50, monoclinic space group *P*2₁/*a*, *a* = 15.393(1), *b* = 12.578(1), *c* = 19.279(2) Å, β = 113.05(1)°, *V* = 3435 Å³, *D*_c = 2.01 g cm⁻³, *D*_o = 2.03 g cm⁻³, μ = 31.0 cm⁻¹(MoK_α), *Z* = 8, *F*(000) = 2056.

Data Collection. A purplish red single crystal of 0.3 × 0.3 × 0.4 mm was selected for data collection on an *Enraf-Nonius CAD-4* diffractometer with graphite-monochromatized MoK_α radiation at 293 K, using ω/2θ scan technique. Some 6539 independent reflections were collected in the range 2° ≤ 2θ ≤ 50°. Of these, 5218 reflections with *I* ≥ 3σ(*I*) were used in the structure determination and refinement. The intensities were corrected for *Lorentz*, polarization effects, and for empirical absorption based on ψ scan. Three standard reflections that were monitored every 90 min during data collection showed negligible decay (< 2%).

The two Nd-atom positions were determined *via* inspection of a *Patterson* function map. A difference *Fourier* map phased on the Nd-atoms readily revealed the positions of the non-H-atoms and part of the crown-ether H-atoms, the other crown-ether H-atoms were placed in calculated positions. The refinements were carried out by full-matrix least-squares for the coordinates of all atoms, the anisotropic thermal parameters for the non-H-atoms (the isotropic thermal parameters for the H-atoms were fixed at 5 Å²) and scale factor *K*. The final refinement converged to *R* = 0.032, *R*_w = 0.049.

Table 3. Selected Bond Lengths [Å]

	Distance		Distance		Distance
Nd(1)–O(1)	2.591(3)	Nd(1)–O(22)	2.518(3)	Nd(2)–O(41)	2.527(3)
Nd(1)–O(2)	2.572(3)	Nd(1)–O(31)	2.577(3)	Nd(2)–O(42)	2.511(3)
Nd(1)–O(3)	2.580(3)	Nd(1)–O(32)	2.473(3)	Nd(2)–O(51)	2.525(3)
Nd(1)–O(4)	2.508(3)	Nd(2)–O(5)	2.569(3)	Nd(2)–O(52)	2.528(3)
Nd(1)–O(11)	2.535(3)	Nd(2)–O(6)	2.590(3)	Nd(2)–O(61)	2.564(3)
Nd(1)–O(12)	2.527(4)	Nd(2)–O(7)	2.571(4)	Nd(2)–O(62)	2.475(3)
Nd(1)–O(21)	2.508(4)	Nd(2)–O(8)	2.510(3)		

The selected bond lengths and bond angles are given in *Tables 3* and *4*, respectively. *Fig. 1* shows the structures of $\text{Nd(1)(NO}_3)_3 \cdot (13\text{-C-4})$ and $\text{Nd(2)(NO}_3)_3 \cdot (13\text{-C-4})$. *Fig. 2* illustrates the molecular packing arrangement in the unit cell.

It is very interesting to note that two independent $\text{Nd(NO}_3)_3 \cdot (13\text{-C-4})$ monomers exist in one asymmetrical unit (see *Fig. 1*). In each of the $\text{Nd(NO}_3)_3 \cdot (13\text{-C-4})$ monomer, the

Table 4. Selected Bond Angles [deg]

Angle		Angle	
O(1)–Nd(1)–O(2)	63.1(2)	O(3)–Nd(1)–O(21)	140.0(1)
O(1)–Nd(1)–O(3)	98.2(1)	O(3)–Nd(1)–O(22)	106.3(1)
O(1)–Nd(1)–O(4)	62.8(1)	O(3)–Nd(1)–O(31)	143.3(2)
O(1)–Nd(1)–O(11)	169.7(1)	O(3)–Nd(1)–O(32)	140.7(1)
O(1)–Nd(1)–O(12)	127.1(2)	O(4)–Nd(1)–O(11)	112.7(2)
O(1)–Nd(1)–O(21)	72.6(1)	O(4)–Nd(1)–O(12)	145.7(2)
O(1)–Nd(1)–O(22)	116.2(2)	O(4)–Nd(1)–O(21)	75.1(2)
O(1)–Nd(1)–O(31)	115.9(1)	O(4)–Nd(1)–O(22)	74.9(2)
O(1)–Nd(1)–O(32)	71.9(3)	O(4)–Nd(1)–O(31)	140.7(2)
O(2)–Nd(1)–O(3)	63.3(1)	O(4)–Nd(1)–O(32)	131.1(2)
O(2)–Nd(1)–O(4)	95.6(2)	O(11)–Nd(1)–O(12)	51.0(2)
O(2)–Nd(1)–O(11)	109.6(2)	O(11)–Nd(1)–O(21)	116.2(2)
O(2)–Nd(1)–O(12)	69.2(2)	O(11)–Nd(1)–O(22)	69.4(2)
O(2)–Nd(1)–O(21)	133.5(1)	O(11)–Nd(1)–O(31)	73.7(1)
O(2)–Nd(1)–O(22)	168.5(1)	O(11)–Nd(1)–O(32)	114.9(1)
O(2)–Nd(1)–O(31)	119.6(1)	O(12)–Nd(1)–O(21)	137.8(1)
O(2)–Nd(1)–O(32)	78.9(1)	O(12)–Nd(1)–O(22)	115.1(2)
O(3)–Nd(1)–O(4)	66.5(1)	O(12)–Nd(1)–O(31)	69.7(2)
O(3)–Nd(1)–O(11)	71.5(1)	O(12)–Nd(1)–O(32)	77.6(2)
O(3)–Nd(1)–O(12)	79.2(1)	O(21)–Nd(1)–O(22)	51.1(1)
O(21)–Nd(1)–O(31)	68.1(2)	O(7)–Nd(2)–O(51)	108.2(1)
O(21)–Nd(1)–O(32)	74.7(2)	O(7)–Nd(2)–O(52)	141.6(2)
O(22)–Nd(1)–O(31)	71.6(1)	O(7)–Nd(2)–O(61)	142.1(2)
O(22)–Nd(1)–O(32)	112.2(1)	O(7)–Nd(2)–O(62)	138.0(2)
O(31)–Nd(1)–O(32)	50.4(1)	O(8)–Nd(2)–O(41)	112.5(2)
O(5)–Nd(2)–O(6)	62.8(2)	O(8)–Nd(2)–O(42)	144.3(2)
O(5)–Nd(2)–O(7)	97.8(2)	O(8)–Nd(2)–O(51)	74.0(2)
O(5)–Nd(2)–O(8)	63.4(2)	O(8)–Nd(2)–O(52)	75.7(2)
O(5)–Nd(2)–O(41)	170.2(2)	O(8)–Nd(2)–O(61)	141.6(1)
O(5)–Nd(2)–O(42)	126.6(2)	O(8)–Nd(2)–O(62)	133.2(2)
O(5)–Nd(2)–O(51)	115.0(2)	O(41)–Nd(2)–O(42)	51.1(2)
O(5)–Nd(2)–O(52)	71.8(2)	O(41)–Nd(2)–O(51)	70.5(2)
O(5)–Nd(2)–O(61)	116.8(1)	O(41)–Nd(2)–O(52)	116.5(2)
O(5)–Nd(2)–O(62)	72.9(1)	O(41)–Nd(2)–O(61)	72.2(2)
O(6)–Nd(2)–O(7)	63.8(1)	O(41)–Nd(2)–O(62)	113.2(2)
O(6)–Nd(2)–O(8)	97.1(1)	O(42)–Nd(2)–O(51)	117.1(2)
O(6)–Nd(2)–O(41)	110.4(2)	O(42)–Nd(2)–O(52)	138.8(2)
O(6)–Nd(2)–O(42)	68.0(2)	O(42)–Nd(2)–O(61)	69.8(2)
O(6)–Nd(2)–O(51)	170.2(2)	O(42)–Nd(2)–O(62)	76.5(2)
O(6)–Nd(2)–O(52)	131.7(2)	O(51)–Nd(2)–O(52)	50.9(2)
O(6)–Nd(2)–O(61)	117.5(2)	O(51)–Nd(2)–O(61)	72.2(1)
O(6)–Nd(2)–O(62)	76.1(1)	O(51)–Nd(2)–O(62)	112.9(1)
O(7)–Nd(2)–O(8)	67.0(2)	O(52)–Nd(2)–O(61)	69.2(2)
O(7)–Nd(2)–O(41)	72.6(2)	O(52)–Nd(2)–O(62)	75.7(2)
O(7)–Nd(2)–O(42)	77.5(2)	O(61)–Nd(2)–O(62)	50.6(1)

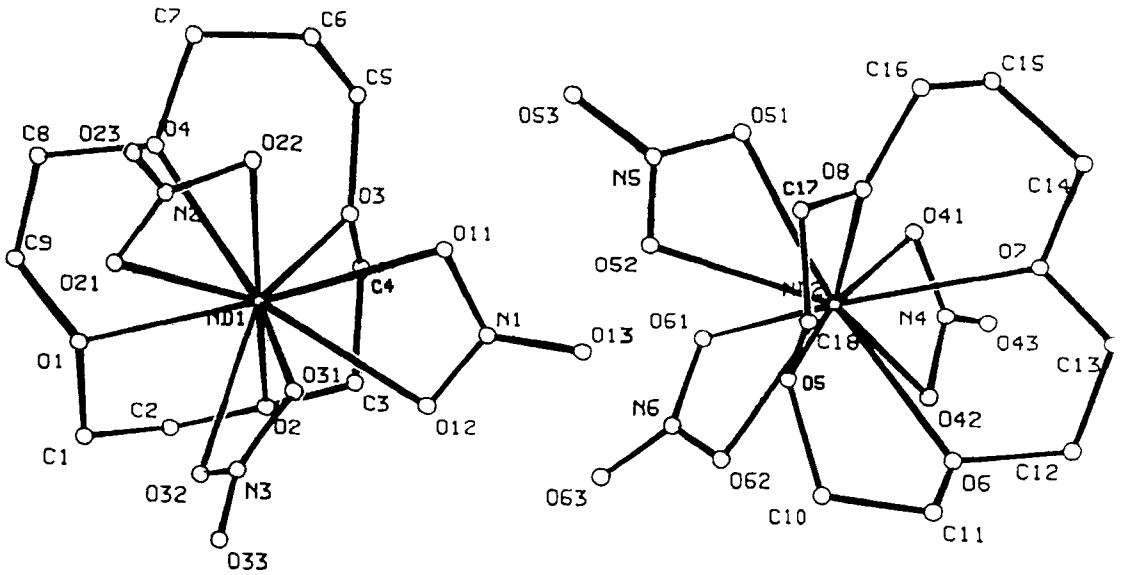


Fig. 1. The structure of $Nd(1)(NO_3)_3 \cdot (13-C-4)$
and $Nd(2)(NO_3)_3 \cdot (13-C-4)$

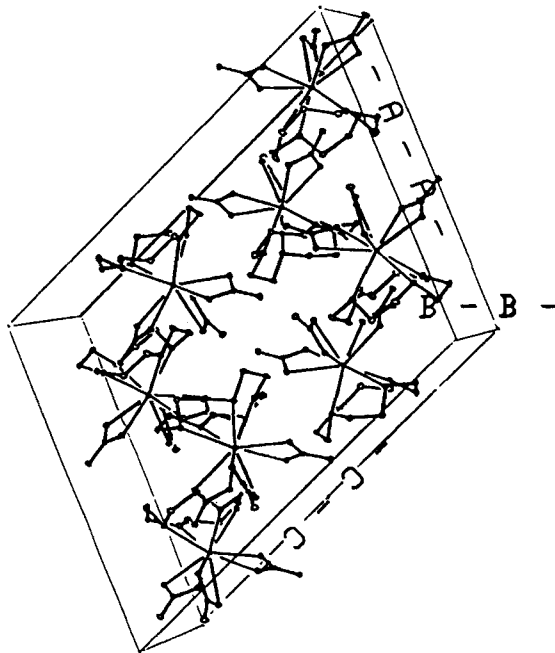


Fig. 2. Molecular packing in the unit cell

Nd^{III} ions is coordinated by all four crown-ether O-atoms on the one side and the six O-atoms of three bidentate NO₃ groups on the other side, the coordination number is ten. In the Nd(1)(NO₃)₃·(13-C-4) monomer, the mean Nd(1)–O distance is 2.54(4) Å, while the mean Nd(1)–O(nitrate) distance, 2.52(3) Å (range from 2.473(3) to 2.577(3) Å), is slightly shorter than the mean Nd(1)–O(ether) distance, 2.56(4) Å (range from 2.508(3) to 2.591(3) Å). In the Nd(2)(NO₃)₃·(13-C-4) monomer, the mean Nd(2)–O distance is 2.54(3) Å, while the mean Nd(2)–O(nitrate) distance, 2.52(3) Å (range from 2.475(3) to 2.564(3) Å), is also slightly shorter than the mean Nd(2)–O(ether) distance, 2.56(3) Å (range from 2.510(3) to 2.590(3) Å). After a correction [7] of *ca.* 0.04 Å for the differences in the ionic radius of Nd^{III} and Eu^{III} (coordination number 10), these values are comparable to those found in Eu(NO₃)₃·(12-C-4), in which the Eu–O(mean) distance is 2.49(5) Å, the Eu–O(nitrate) distance is 2.47 Å, and the Eu–O(ether) distances is 2.52 Å [8]. But the Nd–O(ether) distance is shorter than that of [Nd(NO₃)₂·(18-C-6)]₃Nd(NO₃)₆ complex [9], 2.60(5) Å; the reason is that the smaller size of the 13-membered ring allows it to sit closer to the metal ion.

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