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Neodymium, Erbium, and Europium Complexes with 1,6-Bis(diphenylphosphoryl)-2,5-dioxahexane (L): The Crystal Structure of $[Nd_2(NO_3)_6L_3]$

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Abstract—Solid complexes $M(NO_3)_3 \cdot 1.5L$ (M = Nd, Er, Eu; L is 1,6-bis(diphenylphosphoryl)-2,5-dioxahexane) have been synthesized. A new, convenient method of synthesis of L has been suggested. The crystal structure of $[Nd_2(NO_3)_6L_3]$ has been determined by single-crystal X-ray diffraction. The nonacoordination environments of the Nd(1) and Nd(2) atoms are composed each of six O atoms of bidentate nitracote ions and three phosphoryl O atoms of the L molecules (av. Nd–O, 2.543 and 2.374 Å, respectively). Two independent L molecules act as bridges linking the Nd atoms to form centrosymmetric tetramers $[L\text{-}Nd(NO_3)_3\text{-}L\text{-}Nd(NO_3)_3\text{-}L_2\text{-}Nd(NO_3)_3\text{-}L\text{-}Nd(NO_3)_3L]$. The third L molecule is disordered over two positions with site occupancy factors of 0.602(4) and 0.398(4) so that most of the molecules chelate the terminal Nd atoms in the tetramer, and the other molecules combine tetramers into longer associates. On the basis of elemental analysis data and IR spectra, it has been assumed that the Er and Eu complexes have the same structure as $[Nd_2(NO_3)_6L_3]$.

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As known, the most common technique for industrial isolation of such an important raw material as rare earth elements (REEs) is extraction. Polydentate neutral organophosphorus compounds have long been studied as extractants for a wide range of REEs [1]. It has been shown that an equimolar mixture of oligo(ethylene glycol) bis(diphenylphosphorylmethyl) ethers with the H-form of chlorinated cobalt(III) dicarbollide in solutions of polar diluents are efficient REE extractants [2]. The structures of the REE extraction complexes have been little studied. The extraction of REEs with 1-(methoxydiphenylphosphoryl)-2-diphenylphosphoryl-4-ethylbenzene (L^{MP}) has been studied [3]. The crystal structure of isostructural neodymium and ytterbium complexes with L^{MP} isolated from an extraction solution has been determined by X-ray crystallography, and the structures of free L^{MP} and its adduct with water and nitric acid have been determined [4]. The same structure of the complex cation has also been found in the Er compounds with L^{MP} and 1-(methoxydiphenylphosphoryl)-2-diphenylphosphorylbezene, their crystals being obtained under milder synthetic conditions—from neutral solutions [5].

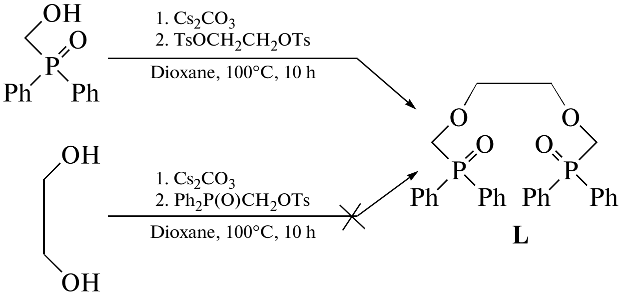
The cation exchange extraction of Eu(III) and Sr(II) from aqueous nitrate solutions with diphenyldiphosphine dioxides containing a methyl, ethyl, or poly(ethylene glycol) bridge between the phosphorus atoms has been studied [6]. The IR spectra have provided evidence that most of the formed complexes have a chelate structure and that, when taken in high concentration, the ligand with the poly(ethylene glycol) bridge can act as a monodentate ligand. Studying lanthanide complexes in solutions is a challenging task since it requires the use of several methods; it should be noted that NMR and EPR methods are of limited use because most of lanthanide cations exhibit paramagnetic properties. X-ray crystallography enables the unambiguous determination of the structure of crystalline complexes.

Here, were report the synthesis of the $M(NO_3)_3 \cdot 1.5L$ complexes (L is 1,6-bis(diphenylphosphoryl)-2,5-dioxahexane; M = Nd (**I**), Er (**II**), Eu (**III**)) and the crystal structure of complex **I** determined by single-crystal X-ray diffraction and suggest a new efficient (81%) one-stage procedure for synthesis of L.

EXPERIMENTAL

First oligo(ethylene glycol) bis(diphenylphosphorylmethyl) ethers have been synthesized almost 30 years ago [7]. Relatively recently, 1,6-bis(diphenylphosphoryl)-2,5-dioxahexane (L) have been synthesized through alkylation of lithium glycolates with diphenylchloromethylphosphine oxide. Lithium glycolates have been produced in a separate stage by treating ethylene glycol with butyllithium [8]. The synthesis of this ether with the use of a non-aqueous two-phase liquid/solid system has also been described in [8]. A mixture of KOH and K_2CO_3 powders was used as the solid phase, and the second phase was a solution of diphenylphosphinic acid and 1,2-bis(chloromethoxy)ethane in benzene. The synthesis was catalyzed by 18-crown-6 as a phase-transfer catalyst. The yield of L was only 33%.

In the present work, compound L was synthesized by alkylation of diphenyloxymethylphosphine oxide with ethylene glycol ditosylate in dry dioxane at 100°C in the presence of anhydrous Cs_2CO_3 as the base (Scheme 1). Thin-layer chromatography and ^{31}P NMR have shown that alkylation of ethyl glycol with diphenylphosphorylmethanol tosylate does not lead to the formation of L.



Scheme 1. Synthesis of 1,6-bis(diphenylphosphoryl)-2,5-dioxahexane (L).

The synthesis with the use of anhydrous cesium carbonate was carried out in a dry argon atmosphere. The course of reaction and purity of the target compound were monitored by thin-layer chromatography on Silufol plates. The chromatograms were developed with iodine vapor. For column chromatography, silica gel L (particle size, 100–160 μm) was used. Elution was accomplished with $CHCl_3$ and a $CHCl_3$–*i*-PrOH (20 : 1) mixture. The yield of the target product is given for the product with the melting point that differs from the melting point of an analytical sample by no more than 5 K. The melting temperature was measured with a short-range Anschutz-type thermometer. An emergent stem correction was not applied. ^1H and ^{31}P NMR spectra were recorded on a Bruker CXP-200 spectrometer. The chemical shifts were referenced to internal TMS and external 85% H_3PO_4, respectively.

Synthesis of L. Diphenylphosphorylmethanol (23.2 g, 100.0 mmol) [9] and ethylene glycol tosylate (18.5 g, 50.0 mmol) [10] were added to a suspension of finely ground anhydrous Cs_2CO_3 (32.6 g, 100.0 mmol) in 80 mL of dry dioxane. The mixture was stirred for 8 h at 95 ± 5°C and concentrated in a vacuum. Then, 100 mL of HCl (1 : 2) was added to the residue, and extraction with chloroform (3 × 75 mL) was carried out. The extract was washed with HCl (1 : 2) (5 × 50 mL), water (5 × 50 mL) and evaporated in a vacuum. The resulting product was purified by column chromatography on a column with silica gel. The yield of L was 19.8 g (81%), mp = 163–165°C (methyl ethyl ketone).

For $C_{30}H_{32}O_5P_2$ anal. calcd. (%): C, 68.57; H, 5.75; P, 12.63.

Found (%): C, 68.60; H, 5.73; P, 12.43.

^1H NMR ($CDCl_3$, δ, ppm): 3.71 (s, 4H, $C\underline{H}_2C\underline{H}_2O$), 4.23 (d, 4H, $^2J_{H-H}$ = 7.0 Hz, $2OC\underline{H}_2P(O)$), 7.44 (m, 12H, Ar-$\underline{H}$), 7.77 (m, 8H, Ar-$\underline{H}$).

^{31}P NMR ($CDCl_3$, δ, ppm): 27.92.

Complexes I–III as fine crystalline precipitates were obtained from a mixture of ethanol solutions of the corresponding salt and the ligand (M : L = 1 : 2) on slow evaporation of the solvent. The precipitates were filtered off, washed with ethanol, and dried in air. Only the crystals of the Nd complexes turned out to be suitable for X-ray crystallography.

For **I** anal. calcd. (%): C, 47.32; H, 3.94; N, 3.94.

Found (%): C, 47.93; H, 4.28; N, 3.98.

For **II** anal. calcd. (%): C, 46.32; H, 3.86: N, 3.86.

Found (%): C, 45.95; H, 4.26; N, 3.41.

For **III** anal. calcd. (%): C, 47.01; H, 3.92; N, 3.92.

Found (%): C, 46.95; H, 4.55; N, 3.68.

IR absorption spectra were recorded as mineral oil mulls on a Bruker Vertex 70 spectrophotometer in the range 4000–400 cm^{-1}.

X-ray crystallography. The set of diffraction reflections from a crystal of **I** was collected on an automated Bruker SMART APEX2 diffractometer at the Shared Facility Center of the Institute of General and Inorganic Chemistry, RAS. The structure was solved by direct methods. The hydrogen atoms were introduced in calculated positions. In one of the ligand molecules, the ethylene glycol moiety is disordered over two orientations (C(14B)C(15B)O(3B) and C(14D)C(15D)O(3D)) with site occupancy factors of 0.602(4) and 0.398(4). Non-hydrogen atoms were refined in the anisotropic approximation, except the C(14D) and C(15D) atoms refined isotropically. The hydrogen atoms were refined as riding on their parent atoms with $U_{iso} = 1.2U_{eq}$ of the corresponding C atom.

The set of reflections was collected and processed with the use of the APEX2, SAINT, and SADABS programs [11]. Structure solution and refinement were performed with the SHELXS-97 and SHELXL-2013 [12] program packages, respectively.

Selected crystal data and experimental and refinement details for structure **I** are presented in the table.

The crystallographic data for **I** were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1036221).

RESULTS AND DISCUSSION

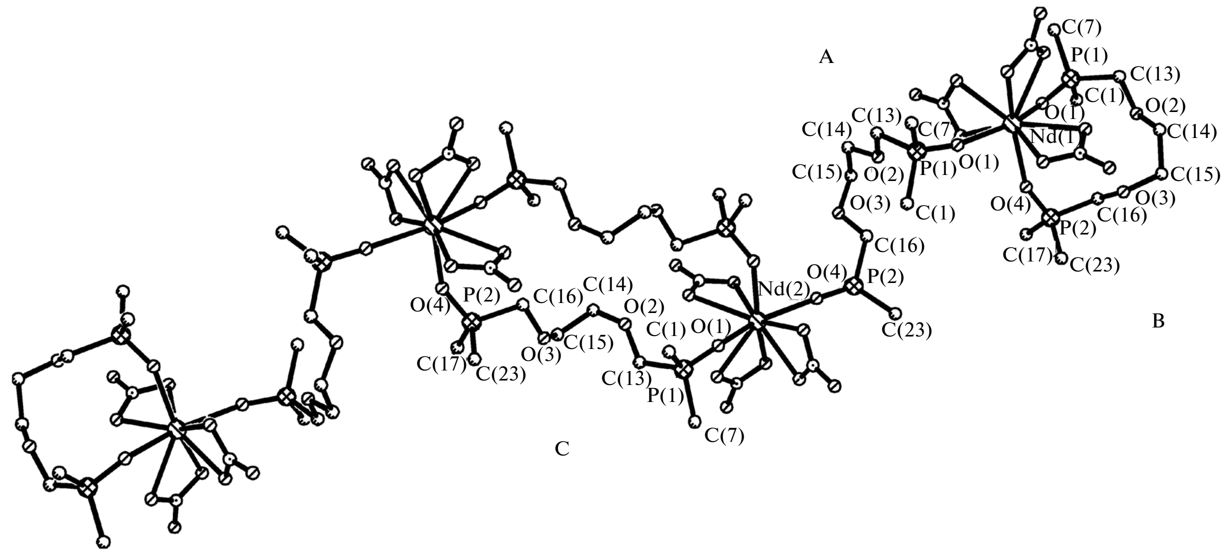
A fragment of the crystal structure of $[Nd_2(NO_3)_6L_3]$ is shown in the figure. The asymmetric unit contains two Nd atoms, six NO_3^- groups, and three L molecules (A, B, and C). The environments of the Nd(1) and Nd(2) atoms consist each of six O atoms of three bidentate nitrate ions and three O phosphoryl atoms of the L molecules. The coordination polyhedra of Nd atoms can be presented as octahedra with split vertices occupied by the oxygen atoms of the NO_3^- groups. The “octahedra” of both Nd atoms are meridional isomers. The Nd–O bond lengths are within 2.359(2)–2.585(3) Å. The Nd–O(P) bonds are shorter than Nd–O(N) (av. 2.374 and 2.543 Å, respectively).

The independent molecules of podand A, B, and C have different functions. Pairs of molecules C link the Nd(2) atoms into centrosymmetric dimers $[Nd(2)(NO_3)_3L_2]_2$. Molecule A links the Nd(1) and Nd(2) atoms, thus increasing the dimer to the tetramer. Both phosphoryl oxygen atoms of molecule B coordinate the Nd(1) atom. The C(14)–C(15)–O(3) moiety of molecule B is disordered so that the molecule either closes an 11-membered chelate ring or links two Nd(1) atoms, just like molecule C links the Nd(2) atoms. Among disordered molecules B, the number of chelating molecules is one and a half times larger than the number of bridging molecules. The crystal surely contains tetramers (figure) and, with high probability, octamers. Formation of longer oligomers with the number of Nd atoms multiple of four is theoretically possible.

Crystal data, parameters of data collection, and characteristics of structure refinement for $[Nd_2(NO_3)_6L_3]$

Parameter	Value
Empirical formula	$C_{84}H_{84}N_6Nd_2O_{30}P_6$
FW	2131.88
T, K	174(2)
Radiation, λ, Å	MoK_α, 0.71073
Space group, Z	$P\bar{1}$, 2
a, Å	15.278(3)
b, Å	16.103(4)
c, Å	18.821(4)
α, deg	93.940(30
β, deg	92.926(4)
γ, deg	96.975(3)
V, Å^3	4576.9(17)
ρ_{calcd}, g/cm^3	1.547
μ_{Mo}, mm^{-1}	1.310
T_{min}, T_{max}	0.6535, 0.7462
F(000)	2160
Crystal size, mm	0.24 × 0.10 × 0.06
θ range, deg	2.173–31.362
Number of reflections:	
measured	57378
unique (N) [R_{int}]	28792 [0.0423]
with $I > 2\sigma(I)$ (N_o)	19033
$R1$, $wR2$ for N_o	0.0505, 0.1010
$R1$, $wR2$ for N	0.0909, 0.1151
S	1.025
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	1.171/–1.450

Previously, the structure of the $[Er(NO_3)_3(Lig)(H_2O)]$ (**IV**) complex (Lig is an analogue of phosphoryl podand L with a longer $-(CH_2CH_2O)_3CH_2CH_2-$ chain between the phosphoryl groups has been studied [13]. Like in other Nd complexes, the nitrate ions in structure **IV** occupy the split vertices in the *mer* isomer of the “octahedron.” The Lig molecule chelates the Eu atom through the



Structure of the tetramer complex in the crystal of $[Nd_2(NO_3)_6L_3]$. For simplicity, the phenyl carbon atoms other than those directly bonded to the phosphorus atoms are omitted.

phosphoryl O atoms, closing a 16-membered chelate ring. As distinct from ligand L in Nd complexes, the Lig molecule in structure **IV** occupies the *trans* vertices of the Er "octahedron," which evidently creates steric hindrances to coordination of one more O atom of the diphenylphosphoryl group. The ninth coordination site is occupied by a water molecule forming intramolecular hydrogen bonds to the ether O atoms of the Lig molecule.

Since the ether O atoms of the L molecules in structure **I** are not involved in coordination of the Nd atom, the $Ph_2(O)P{-}(CH_2)_n{-}P(O)Ph_2$ molecules (L^n) in which the phosphoryl groups are linked by an alkyl chain can be treated as analogues of the L podand. The structures of lanthanide complexes with such ligands in which the number of methylene groups $n = 1$ [14], 2 [15], and 4 [16] are known. The L^1 ligand with the shortest chain forms chelate complexes with different $NO_3 : L$ ratios in the coordination sphere, in particular, $[Nd(NO_3)_2L^1_2(H_2O)]NO_3 \cdot 2H_2O$. The L^2 ligand with the ethyl spacer forms layered coordination polymers of composition $[Ln_2(NO_3)_6L^2_3]$ with Pr, Nd, Sm, and Dy. These polymers have been isolated as solvates with dichloroethane for Ln = Pr and Nd and methanol for Ln = Sm and in the unsolvated form for Ln = Nd and Dy. With the same metals, ligand L^4 forms isostructural dimeric complexes $[L^4Ln(NO_3)_3L^4Ln(NO_3)_3L^4] \cdot 1.5CH_3OH$, in which there is one bridging molecule per two chelating molecules. The Lu and Dy complexes of composition $[Ln_2(NO_3)_6L^2_3] \cdot CH_3OH$ have an analogous structure. Owing to the combination of chelating and bridging L molecules, structure **I** studied in this work is topologically closer to the dimeric structures.

Conclusions concerning the structure of complexes **II** and **III** have been drawn from elemental analysis and IR spectroscopy data.

Basic vibrational frequencies in the spectra of L and complexes **I**–**III** have been assigned using the interpretation of vibrational spectra of complexes with phosphoryl-containing podands reported in [17–19]. Inasmuch as complexation leads to the largest changes in stretching vibration frequencies of donor groups involved in formation of coordination bonds, we mainly dwell on the vibrational frequencies of P=O and COC groups.

The phosphoryl stretching vibration, whose frequency is determined by the electronegativity of the substituent at the phosphorus atom, is observed in the IR spectrum of L at ~1180 cm^{-1} as a strong and narrow band. This frequency is somewhat lower than in the spectra of $Ph_3P{=}O$, phosphoryl podands with the diphenylphosphoryl group in the *ortho*-position of the benzene ring (1195 cm^{-1}) [17–19] and in the spectrum of Lig (1185 cm^{-1}) [13].

According to [17, 18], the $\nu_{as}(COC)$ bands sensitive to the conformation of the ethylene glycol units in the podands are observed in the range 1100–1160 cm^{-1} in their IR spectra. The benzene ring vibration band is observed in the same range (1127 cm^{-1} in the IR spectrum of $Ph_3P{=}O$). The spectrum of L shows two bands of roughly the same intensity in the $\nu_{as}(COC)$ region: at 1123 and 1090 cm^{-1} with a shoulder at 1005 cm^{-1}.

In the IR spectrum of L in the range 800–1000 cm^{-1}, conformationally sensitive composite stretching–bending vibrations $\nu(CO) + \rho(CH_2) + \nu(CC)$ give rise to three moderate bands at 887, 872, and 831 cm^{-1} and to a weak band at ~943 cm^{-1}.

Complexation leads to a noticeable change in the IR spectrum of L. The spectra of complexes **I**–**III** are identical in the entire spectral range and are essentially simpler than the spectrum of L. The spectrum of the free podand shows sharp and well-resolved bands, while, in the spectra of the complexes, these bands are broad and smooth, which is typical of compounds with polymeric structure.

The coordination of the phosphoryl oxygen atoms in **I**–**III** leads to a decrease in the ν(P=O) frequency by ~20 cm^{-1}, which is evidence that these atoms are involved in coordination of the metal cation. In the spectra of complexes **I**–**III**, the phosphoryl group vibration is observed as a strong band in the range 1156–1161 cm^{-1} (depending on the cation).

In the ν_{as}(COC) range, the position of the bands in the spectra of **I**–**III** remains unaltered but their intensity ratio changes (the band at ~1093 cm^{-1} becomes stronger than the band at ~1126 cm^{-1}). In the other conformationally sensitive region of ν(CO) + ρ(CH$_2$) + ν(CC), changes are more pronounced. Instead of three well-resolved bands in the spectrum of L, the spectra of complexes **I**–**III** in this range show broad and weak bands with maxima at about 891, 877, 864, 853, and 835 cm^{-1}, and a new δ(NO$_3$) band is observed at ~817 cm^{-1}. The other absorption bands of the bidentately coordinated NO_3^- groups in the IR spectra of complexes **I**–**III** are observed at about 1458, 1310, and 1034 cm^{-1}.

It should be noted that rather noticeable changes in the IR spectra caused by conformational rearrangement of the podand are observed in the region of bending vibrations of the terminal phosphoryl-containing groups (550–500 cm^{-1}). The character of absorption in this range essentially depends on the mutual arrangement of benzene rings at the phosphorus atom [17, 18].

L:	617	569		546	515	499	487	474	438	421 cm^{-1};
I:			554	543		506	483			418 cm^{-1}.

Thus, X-ray crystallography and IR spectroscopy indicate that complexation of the podand is accompanied by its conformational rearrangement caused by the involvement of both phosphoryl groups in coordination. The Er(NO$_3$)$_3$ · 1.5L and Eu(NO$_3$)$_3$ · 1.5L complexes have the same structure as [Nd$_2$(NO$_3$)$_6$L$_3$]. The coordination polyhedra of the metal atoms are formed by nine oxygen atoms: six O atoms of three bidentate NO$_3$ groups and three O atoms of three phosphoryl groups. Owing to the combination of bridging and chelating L molecules, the structure of [Nd$_2$(NO$_3$)$_6$L$_3$] contains oligomers with the number of Nd atoms multiple of four. In the structures of Er and Eu compounds, association of complexes into oligomers with another number of metal atoms is possible.

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