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# Structures of the Compounds Preparatively Isolated in the Extraction of Rare-Earth Metals with 2-Diphenylphosphoryl-1-Diphenylphosphorylmethoxy-4-Ethylbenzene

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**Abstract**—The structures of 2-diphenylphosphoryl-1-diphenylphosphorylmethoxy-4-ethylbenzene (L), its adduct with water and nitric acid, and the complex $[(L)_2Nd(\eta^2\text{-}O_2NO)_2](NO_3) \cdot NO_3 \cdot 2C_6H_6$ were determined by X-ray diffraction. The above compounds were isolated under conditions very similar to those used for extractive separation of rare-earth metals in the system water–1,1,7-trihydrododecafluoroheptan-1-ol with L as an extractant. Assignment of the absorption bands in the IR spectra of the single crystals obtained was performed.

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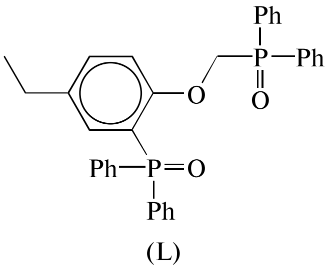
Podands, which are open-chain analogs of crown ethers, have similar complexing properties simultaneously affected by different terminal substituents [1]. Like crown ethers, podands are widely employed as extractants for separation of dissimilar metals [1, 2]. In contrast to crown ethers, the terminal fragments of podands can be regulated purposefully. For instance, introduction of a phosphoryl group into a podand molecule allows smooth variation of its electron-donating and conformational properties by altering the electronic nature of substituents at the phosphorus atom (e.g., to change its extractive properties [3–6]).

Recently, the phosphoryl-containing podand 2-diphenylphosphoryl-1-diphenylphosphorylmethoxy-4-ethylbenzene (L) has been found to be an efficient extractant as well as an impregnating agent for the preparation of solid sorbents designed to extract and concentrate some chemical (in particular, rare-earth) elements [7].



(L)

It has been demonstrated that the system water–1,1,7-trihydrododecafluoroheptan-1-ol with L as an extractant extracts the yttrium subgroup metals much better than the cerium ones, all other factors being the same. The partition coefficients of the rare-earth metals of both subgroups increase monotonically with the atomic number of the element. In addition, substantial enhancement of the extractive properties can be achieved by increasing the concentration of $HNO_3$ (at $c_{HNO_3} < 1$ mol/L, extraction does not occur at all). For a mixture of rare-earth metal nitrates, it has been found that ytterbium is extracted best, while the partition coefficient of neodymium is among the lowest ones [7].

In this work, we discuss the structures of phosphoryl-containing podand L, its adduct with water and $HNO_3$ (a possible intermediate in the extraction of rare-earth metals), and neodymium and ytterbium complexes with L, whose single crystals were obtained under conditions very similar to those used in extraction.

## EXPERIMENTAL

Podand L was prepared by alkylating 1-diphenylphosphoryl-3-ethylbenzene with diphenylphosphorylmethyl tosylate as described in [8].

**Single crystals of L** suitable for X-ray diffraction analysis were obtained by recrystallization from benzene–$CH_2Cl_2$ (1 : 1) followed by slow evaporation at room temperature.

Crystallographic parameters and the data collection and refinement statistics for structures L, **I**, and **II**

| Parameter | Value | | |
|---|---|---|---|
| | L | **I** | **II** |
| Empirical formula | $C_{33}H_{30}O_3P_2$ | $C_{45}H_{45}NO_7P_2$ | $C_{72}H_{67}N_4O_{18}P_4Nd$ |
| $M$ | 536.51 | 773.75 | 1544.42 |
| Temperature, K | 173(2) | 120(2) | 120(2) |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1/c$ | $P1$ | $P\bar{1}$ |
| Unit cell parameters: | | | |
| $a$, Å | 16.974(6) | 9.997(3) | 13.177(5) |
| $b$, Å | 11.579(4) | 10.163(3) | 17.439(6) |
| $c$, Å | 15.849(5) | 22.123(7) | 18.450(6) |
| α, deg | 90 | 77.774(5) | 101.680(5) |
| β, deg | 114.774(5) | 83.422(6) | 107.160(5) |
| γ, deg | 90 | 64.845(5) | 98.824(6) |
| $V$, Å$^3$ | 2828.2(16) | 1987.6(11) | 3863(2) |
| $Z$ | 4 | 1 | 2 |
| $\rho_{calcd}$, mg/m$^3$ | 1.260 | 1.292 | 1.328 |
| μ, mm$^{-1}$ | 0.186 | 0.162 | 0.822 |
| $F(000)$ | 1128 | 865 | 1582 |
| Crystal dimensions, mm | 0.18 × 0.14 × 0.12 | 0.14 × 0.12 × 0.10 | 0.14 × 0.12 × 0.10 |
| θ Scan range, deg | 2.26–27.00 | 2.25–25.00 | 2.12–25.00 |
| Ranges of $h$, $k$, and $l$ indices | $-21 \le h \le 21, -14 \le k \le 14, -15 \le l \le 20$ | $-11 \le h \le 11, -12 \le k \le 12, -26 \le l \le 26$ | $-15 \le h \le 15, -20 \le k \le 20, -21 \le l \le 21$ |
| Number of measured reflections | 21798 | 13914 | 31106 |
| Number of independent reflections ($R_{int}$) | 6108 (0.0702) | 12691 (0.0395) | 13480 (0.1111) |
| Number of parameters refined | 344 | 716 | 752 |
| GOOF | 1.110 | 1.151 | 0.986 |
| $R$ ($I > 2\sigma(I)$)[a] | $R_1 = 0.0587$, $wR_2 = 0.1199$ | $R_1 = 0.1302$, $wR_2 = 0.3043$ | $R_1 = 0.0805$, $wR_2 = 0.1781$ |
| $R$ (for all reflections)[a] | $R_1 = 0.1163$, $wR_2 = 0.1402$ | $R_1 = 0.1312$, $wR_2 = 0.3049$ | $R_1 = 0.1752$, $wR_2 = 0.2234$ |
| $\Delta\rho_{max}/\Delta\rho_{min}$, $e$ Å$^{-3}$ | 0.537/–0.422 | 1.205/–0.837 | 1.117/–1.121 |

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$; $wR_2 = \left\{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\right\}^{1/2}$.

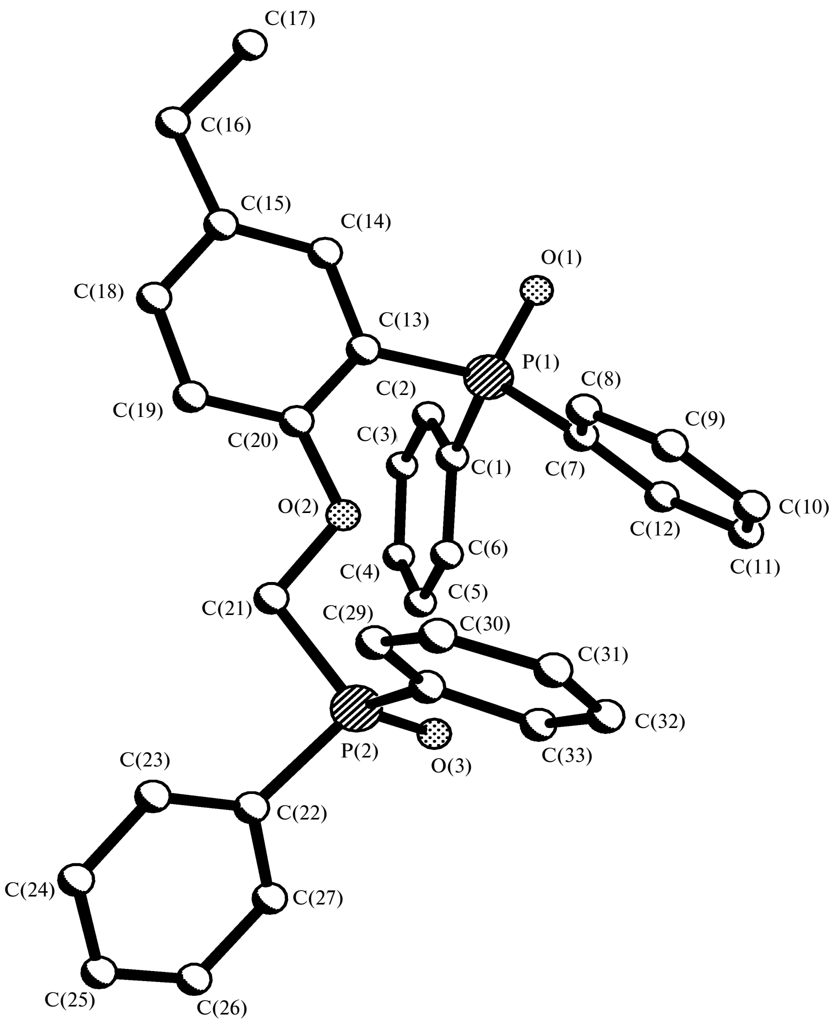


**Fig. 1.** Structure of L.

IR (frustrated total internal reflection (FTIR), ν, $cm^{-1}$): 3054 w, 2959 m, 2924 m, 2854 m, 1741 m, 1595 m, 1493 sh, 1480 m, 1436 s, 1421 w, 1401 m, 1379 w, 1290 w, 1262 w, 1244 m, 1222 m, 1193 m, 1180 sh, 1172 s, 1161 sh, 1120 s, 1103 m, 1072 s, 1028 m, 996 m, 921 w, 877 m, 836 m, 798 w, 744 m, 734 s, 717 m, 699 s, 690 s, 673 sh, 618 w, 581 m, 565 m.

**Single crystals of the adduct $L \cdot H_2O \cdot HNO_3 \cdot 2C_6H_6$ (I)** were obtained by addition of several drops of aqueous $HNO_3$ to a solution of L in benzene–$CH_2Cl_2$ (1 : 1) followed by slow evaporation of the solvents in a refrigerator at 5°C for 72 h. The single crystals of adduct **I** are very unstable, rapidly decomposing in the absence of a solvent.

IR (FTIR, ν, $cm^{-1}$): 3057 w, 3032 w, 2963 w, 2928 w, 2878 w, 2856 w, 1599 w, 1477 sbr, 1437 s, 1420 w, 1408 w, 1327 w, 1297 m, 1286 sh, 1248 m, 1212 w, 1188 w, 1145 sbr, 1122 m, 1105 m, 1080 w, 1071 w, 1032 m, 998 m, 899 w, 886 w, 868 m, 829 sh, 817 m, 811 m, 763 sh, 746 m, 733 s, 709 m, 688 s, 679 sh, 575 m.

**Single crystals of the complex $L_2Nd[(\eta^2\text{-}O_2NO)_2](NO_3) \cdot HNO_3 \cdot 2C_6H_6$ (II)** were obtained by standard extraction of neodymium nitrate from aqueous 3 M $HNO_3$ ($c_{Nd} = 2$ g/L) with a 0.05 M solution of podand L in $CHCl_3$ [7]. The solvent was removed and the resulting oil was dissolved with heating in benzene–$CH_2Cl_2$ (5 : 1, 5 mL). The solution was diluted with hexane (10 mL) and cooled to 5°C. The fine crystalline product that formed was separated from the mother liquor by decanting, dissolved in hot benzene (5 mL), and kept at 5°C for 24 h. The resulting crystals as colorless large prisms were separated by decanting, washed with hexane, and dried in an argon flow.

IR (FTIR, ν, $cm^{-1}$): 3057 w, 3034 w, 2963 w, 2930 w, 2893 w, 2873 sh, 1599 m, 1591 m, 1583 m, 1477 sbr, 1437 s, 1421 w, 1407 w, 1328 m, 1288 sh, 1280 s, 1245 m, 1212 w, 1180 w, 1136 sbr, 1122 m, 1102 sh, 1096 m, 1071 m, 1027 m, 998 m, 923 w, 898 w, 885 w, 868 m, 828 m, 819 m, 810 sh, 763 w, 753 sh, 746 m, 733 m, 723 s, 709 m, 693 sh, 688 s, 678 sh, 666 sh, 576 s.

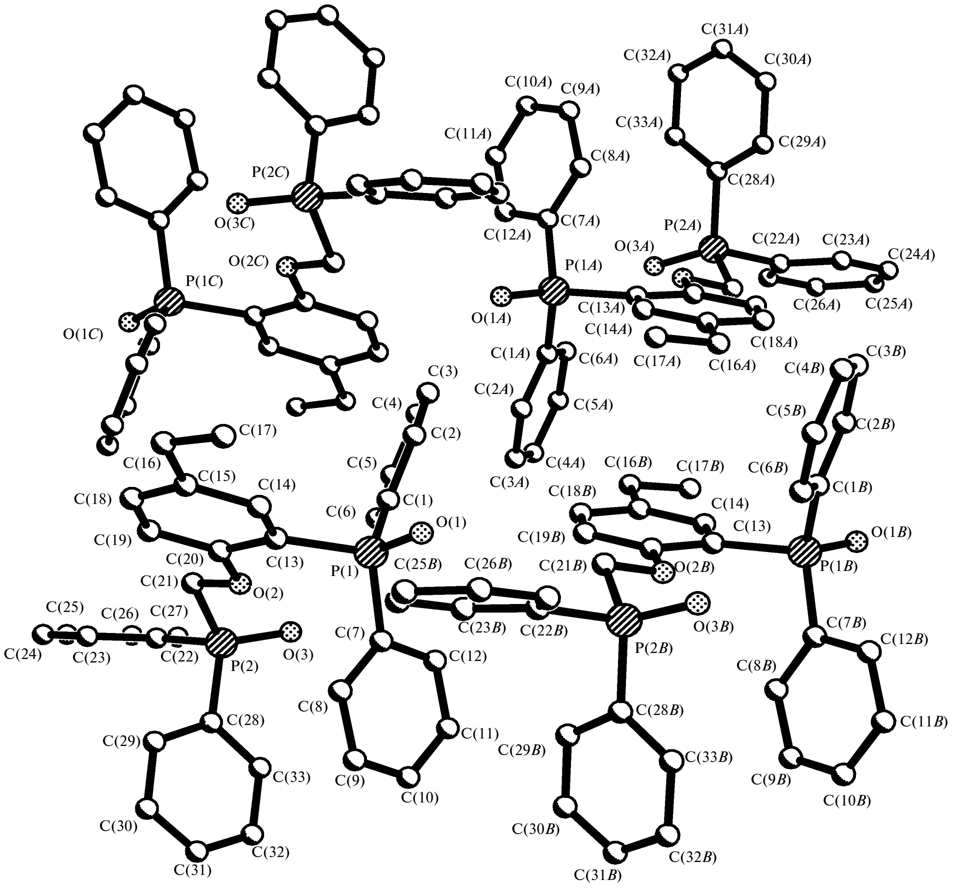


**Fig. 2.** Fragment of the molecular packing of L in the crystal.

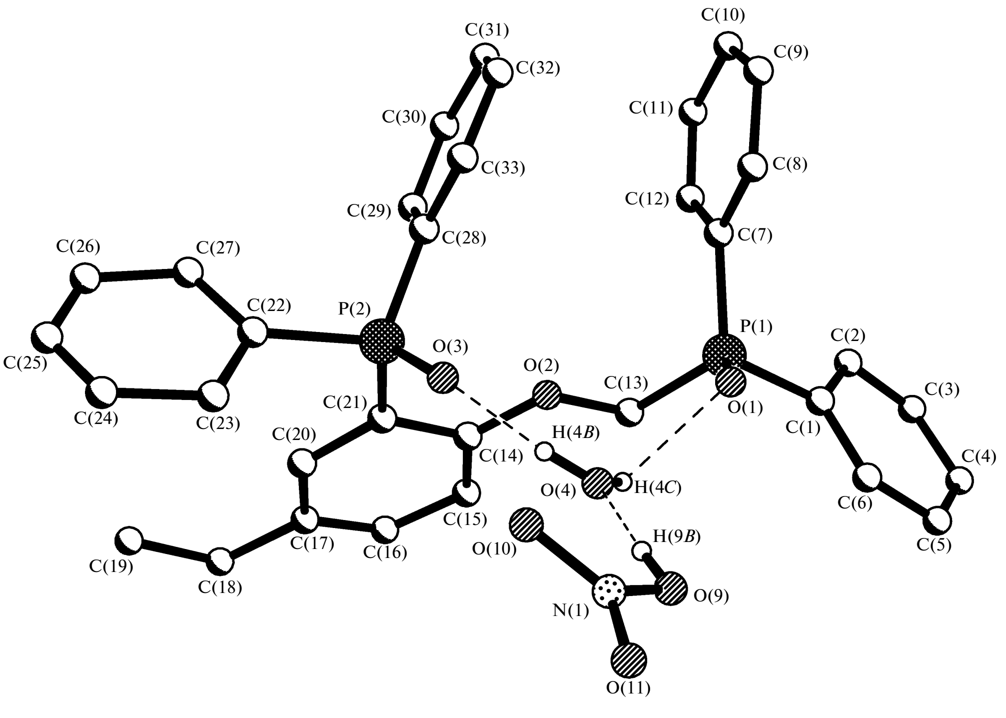


**Fig. 3.** Structure of adduct **I**.

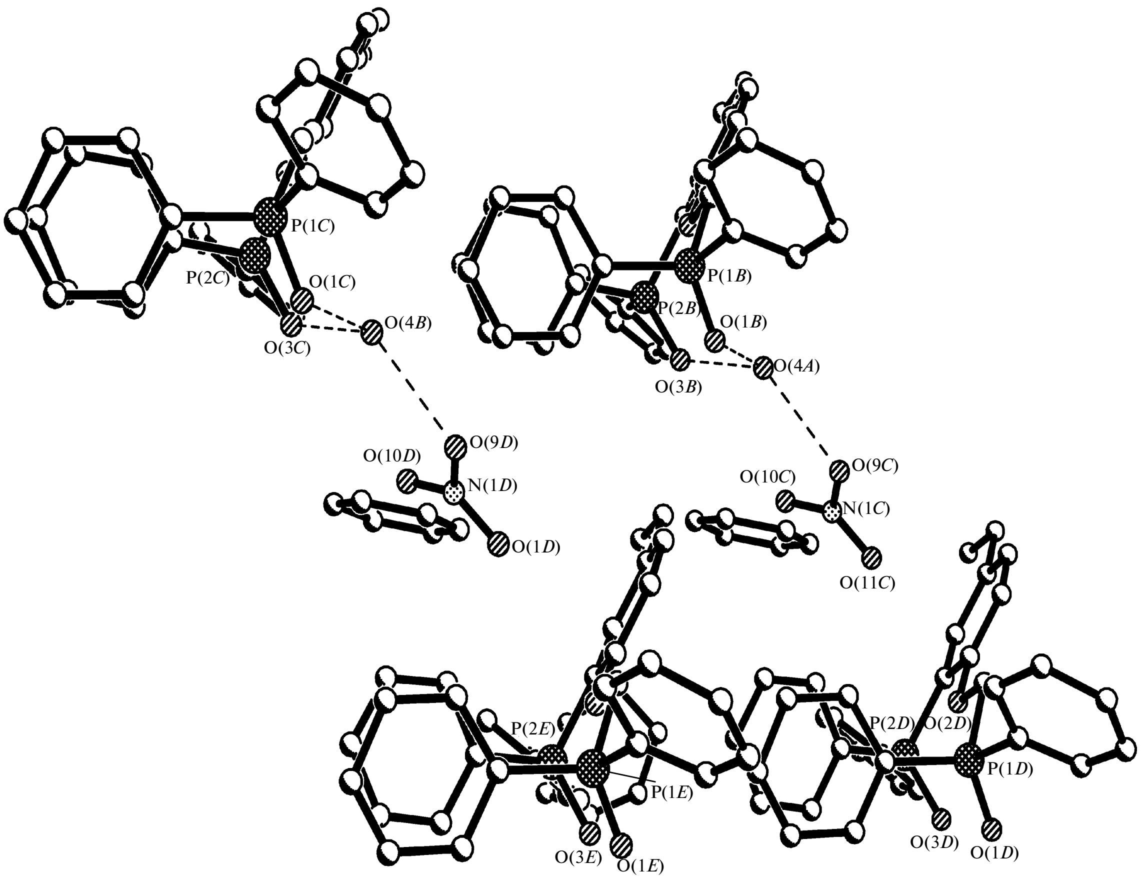


**Fig. 4.** Fragment of the molecular packing of adduct **I**.

IR spectra were recorded on a Nexus-Nicolet FTIR spectrophotometer in the 550–4000 cm$^{-1}$ range by using frustrated total internal reflection from a single crystal of a test compound.

**X-ray diffraction study** was carried out according to a standard procedure on a Bruker SMART Apex II automated diffractometer equipped with a CCD detector (Mo$K_\alpha$ radiation, graphite monochromator, ω scan mode). The structures of podand L, adduct **I**, and complex **II** were calculated with the SHELXTL PLUS program package (PC version) and refined with the SHELXTL-97 program [9, 10]. Crystallographic parameters and the data collection and refinement statistics are summarized in table. The comprehensive tables of the atomic coordinates, bond lengths, and bond angles in structures L, **I**, and **II** have been deposited with the Cambridge Crystallographic Data Centre (nos. 907137–907139; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

## RESULTS AND DISCUSSION

We found that dissolution of podand L in benzene–$CH_2Cl_2$ followed by slow evaporation of the solvent in air gives colorless single crystals. According to X-ray diffraction data, two phosphoryl groups $Ph_2P{=}O$ (P(1)–C, 1.800(3) and 1.807(3) Å; P(1)–O, 1.4829(19); P(2)–C, 1.793(4) and 1.806(3) Å; P(2)–O, 1.470(2) Å) in structure L are linked by the asymmetric organic fragment $-CH_2OPh(Et)-$(P(1)–C(13) 1.800(3) Å; P(2)–C(22), 1.806(3) Å; O(2)–C(20), 1.381(3) Å; O(2)–C(21), 1.421(3) Å) (Fig. 1). The O atoms of the phosphoryl groups are formally oriented in the opposite directions; the angle between the plane P(1)O(1)P(2) and the line P(2)–O(3) is 21.7°. The geometry of L is due to the mutual repulsion of the closely spaced substituents P=O; in addition, intramolecular π···π-contacts between the nearly parallel (16.5°) phenyl substituents C(7)–C(12) and C(28)–C(33) of the phosphoryl groups (3.797–4.023 Å) and intermolecular interactions in the crystal unit cell also affect this geometry (Fig. 2): π···π $Ph_{C(1)-C(6)}\cdots Ph_{C(1A)-C(6A)}$ 3.987–4.002 Å; CH···π C(18)/C(19)···$Ph_{C(1)-C(6)}$ 3.631–3.924 Å; C(25)···$Ph_{C(1)-C(6)}$ 3.804–4.007 Å.

The conformation of L in adduct **I** substantially differs from that of individual L because of a hydrogen-bonded solvate water molecule that enters the structure upon the recrystallization of L from benzene–$CH_2Cl_2$ in the presence of aqueous $HNO_3$ (X-ray diffraction data, Fig. 3).

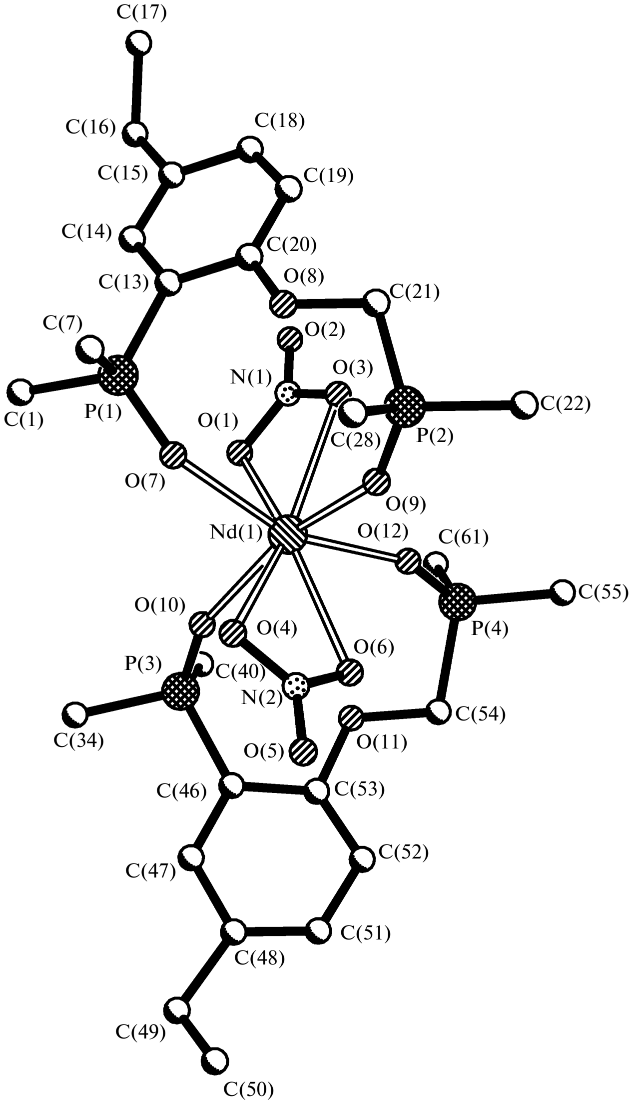


**Fig. 5.** Structure of complex **II** (the phenyl substituents at the phosphoryl groups are omitted).

In structure **I**, the phosphoryl groups undergo partial rotation because of the formation short hydrogen bonds between the H atoms of the solvate water molecule and the O atoms of two P=O groups (O···O 2.474(9)–2.527(9) Å). This results in a virtually coplanar arrangement of the O and P atoms (the angle between the plane P(1)O(1)P(2) and the line P(2)–O(3) is 3.7°). The π···π-contacts between the phenyl substituents C(7)–C(12) and C(28)–C(33) of the phosphoryl groups are retained (3.561–3.851 Å), with nearly the same angle between them (16.9°). In contrast to individual L, the crystal unit cell of adduct **I** (Fig. 4) is much more porous because of the presence of two solvate benzene molecules and a nitric acid molecule. The latter is also linked by a strong hydrogen bond to the water molecule (O···O, 2.508 and 2.561 Å). Despite the changed conformation, the geometry of adduct **I** changes only slightly (P=O 1.491(7)–1.518(7) Å, P–$C_{Ph}$ 1.788(10)–1.796(12) Å, O–C 1.346(14)–1.432(12) Å).

It is not improbable that adduct **I** is a possible key intermediate in the extraction of rare-earth metal nitrates. In [7], it has been demonstrated that the extraction process itself largely depends on the concentration of $HNO_3$ in the aqueous phase.

After the extraction of neodymium nitrate from aqueous 3 M $HNO_3$ ($c_{Nd} = 2$ g/L) with a 0.05 M solution of podand L in $CHCl_3$ [7], the solvents were completely removed and the resulting oil was dissolved in benzene–$CH_2Cl_2$ (5 : 1), diluted with hexane, and cooled. The fine crystalline precipitate that formed was recrystallized to give single crystals of a Nd(II) complex. Earlier, a similar procedure has been used to obtain single crystals of an ytterbium complex with L (**III**) [7].

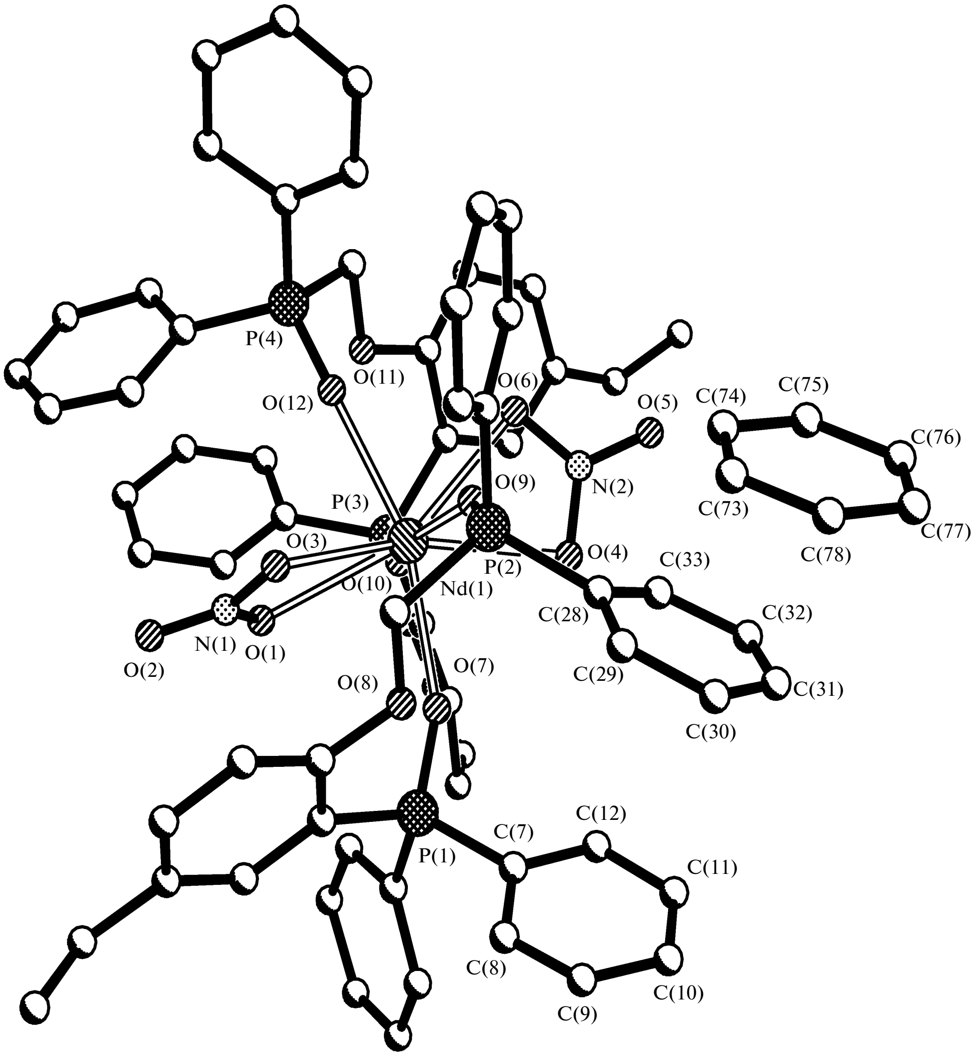


**Fig. 6.** $\pi$-$\pi$-Contacts between the solvate benzene molecule C(73)–C(78) and the phenyl substituent C(28)–C(33) in the coordinated podand L.

According to X-ray diffraction data, the central metal atom in the isostructural complexes of Nd(II) (Fig. 5) and Yb [7] is coordinated to eight O atoms. Four of them belong to two *trans*-arranged $\eta^2$-nitrate anions (Yb–O, 2.395(4)–2.438(4) Å; Nd–O, 2.516(7)–2.564(7) Å), while the other four come from the phosphoryl groups of two ligands L (Yb–O, 2.225(4)–2.245(4) Å; Nd–O, 2.344(6)–2.376(6) Å). The outer-sphere nitrate anion is linked by a short hydrogen bond to the H atom of solvate nitric acid (O···O, 2.476(5) Å; H–O, 1.62 Å in **II**; O···O, 2.457(8) Å; H–O, 1.60 Å in **III**). The longer bonds between the metal atom and the O atoms of both the coordinated anions and ligand L in the neodymium complex compared to the ytterbium one is due to the smaller size of the Nd atom. The geometry of ligand L is virtually unaffected by its coordination to the metal atom in complexes **II** and **III**. The phosphoryl fragments are coplanar. The angles between the plane P(1)O(7)P(2) and the line P(2)–O(9) are 6° and 8.1° and those between the plane P(3)O(10)P(4) and the line P(4)–O(12) are 2.3° and 3.3° in complexes **II** and **III**, respectively. The P=O bond lengths are 1.487(5)–1.501(5) Å in **II** and 1.492(7)–1.512(6) Å in **III** (P–$C_{Ph}$ 1.783(17)–1.809(9) Å, O–C 1.386(10)–1.456(13) Å).

In the coordinated ligands, two phenyl substituents are virtually parallel to each other and show a $\pi\cdots\pi$-contact (3.582–4.009 Å). One solvate benzene molecule is parallel to one of the phenyl rings of the phosphoryl group (Ph···Ph 3.667–3.960 Å) (Fig. 6).

The nonequivalence of the phosphoryl groups in podand L, which was revealed by X-ray diffraction, is manifested as two bands at 1193 and 1172 $cm^{-1}$ (P=O stretches) in the IR spectra (FTIR, 4000–550 $cm^{-1}$) of the single crystals. The former band can be assigned to the group P(1)O(1) bound to three aromatic substituents, while the latter band, to the group P(2)O(3) [11]. The band $\nu$(P=O) is very sensitive to the environment of the phosphoryl group. Upon the complexation giv-

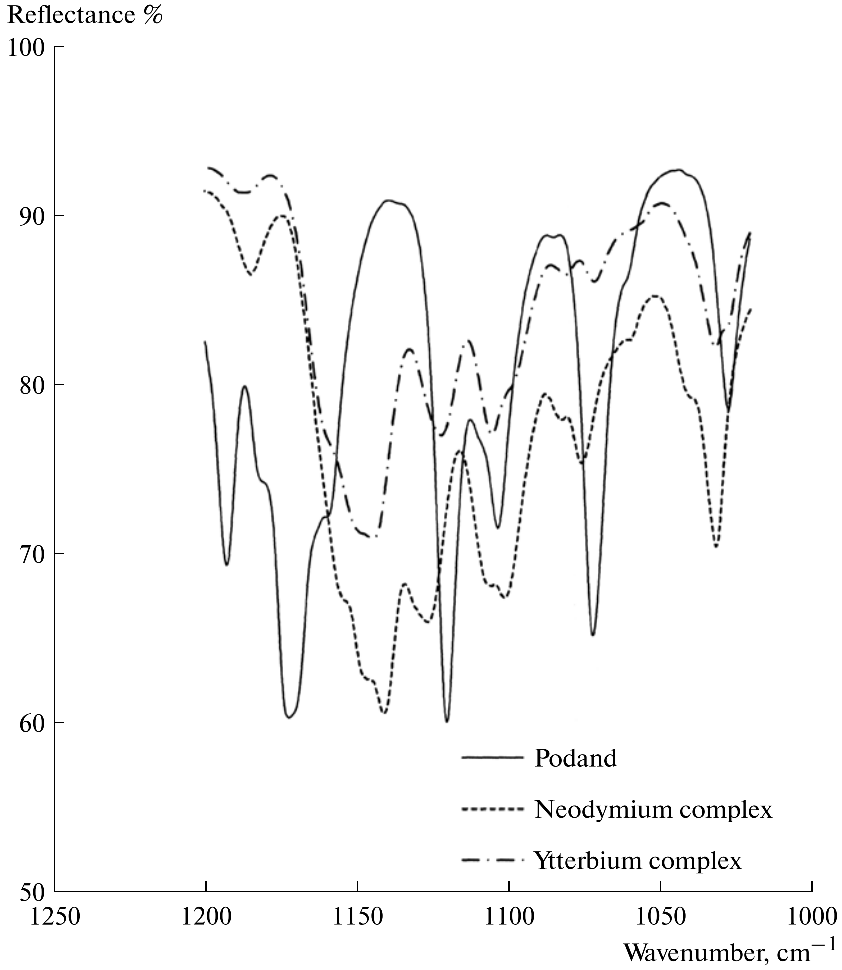


**Fig. 7.** IR spectra of podand L and its neodymium and ytterbium complexes (the range of the P–O stretching vibrations).

ing rise to the P=O → $M^{3+}$ bonds, these bands shift to the lower frequencies and coalesce into a more intense band at 1145 (for **II**) and 1136 cm$^{-1}$ (for **III**). Equalization of the P=O bond lengths in the complexes seems to be a possible reason for this.

Because the general geometry of ligand L is virtually unaffected by the complexation, the bands in the IR spectra that relate to all the other groups of atoms retain their positions. The variable portion of the IR spectra is shown in Fig. 7.

Since the adduct with $HNO_3$ is unstable in air, we failed to record its IR spectrum and carried out a model experiment. An extract of the adduct L · $HNO_3$ in chloroform was applied to a diamond crystal of a FTIR attachment. After evaporation of the solvent, an IR spectrum was immediately recorded. Two more spectra were recorded in 15-min intervals. These spectra in the range of the P=O stretching vibrations (Fig. 8) show a wide band with two subpeaks at 1190 and 1170 cm$^{-1}$ resulting from superposition of two individual bands ν(P=O) of the starting podand. A new band at 1138 cm$^{-1}$ was assigned to ν(P=O) of the adduct. The considerable shift to the lower frequencies, which is larger than the corresponding shifts for complexes **II** and **III**, is due to strong hydrogen bonds between water molecules and the podand (see X-ray diffraction data). As a result, the P=O bond length in the adduct is 1.50–1.52 Å against 1.49–1.50 Å in **II** and 1.49–1.51 Å in **III**. It can be seen in Fig. 8 that the intensity of this band gradually decreases with time and so does the intensity of the band at 3400–3500 cm$^{-1}$ (O–H stretches of water). The dynamic changes in the IR spectra suggest that the adduct L · $HNO_3$ is unstable in air, losing the water molecule as a result of the hydrogen bond cleavage.

The formation of an intermediate which, on the one hand, contains strongly lengthened P=O bonds and, on the other hand, is unstable in air is a good prerequisite for further participation of podand L in complexation with rare-earth metals during extractive processes.

To sum up, we obtained and structurally characterized the compounds that seem to play a key role in the extraction of rare-earth metal salts with the phosphoryl-containing podand 2-diphenylphosphoryl-1-diphenylphosphorylmethoxy-4-ethylbenzene (L).

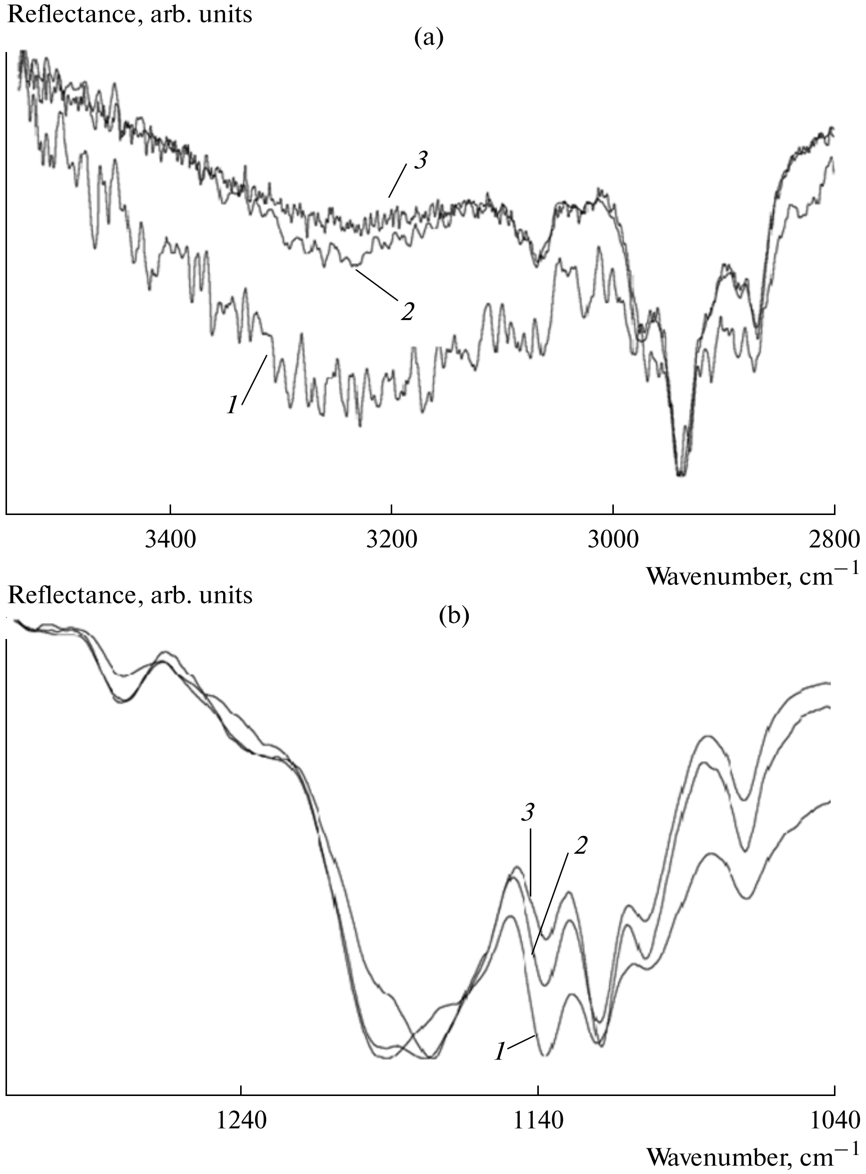


**Fig. 8.** IR spectra of the extracted adduct L · $HNO_3$ upon the removal of chloroform in the (a) 3000–3500 and (b) 1000–1300 cm$^{-1}$ ranges: (*1*) initial extract, (*2*) after 15 min, and (*3*) after 30 min.

## ACKNOWLEDGMENTS

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