

# Phosphoryl-containing acidic podands as extractants for recovery of f-elements

## 1. Synthesis and comparison of podands different in polyether chain length and structure

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The extraction efficiency of uranium(VI), thorium(IV), and lanthanum(III) from nitric acid solutions to 1,2-dichloroethane was compared for a series of phosphoryl podands of the acidic type different in polyether chain length and number of oxygen atoms: 2-[(HO)(EtO)(O)P]—C<sub>6</sub>H<sub>4</sub>—(OCH<sub>2</sub>CH<sub>2</sub>)<sub>m</sub>—OC<sub>6</sub>H<sub>4</sub>—2-[P(O)(EtO)(OH)] (1–3, where *m* = 1–3) and 2-[(HO)(EtO)(O)P]—C<sub>6</sub>H<sub>4</sub>—O(CH<sub>2</sub>)<sub>5</sub>O—C<sub>6</sub>H<sub>4</sub>—2-[P(O)(EtO)(OH)] (4). The synthesis of podands 1 and 4 obtained for the first time is described. The molecular and crystal structures of podand 1 were determined by X-ray diffraction analysis, and the formation of a strong intramolecular hydrogen bond was observed. Podand 2 is the most efficient extractant for the selective recovery of Th<sup>IV</sup> in the presence of U<sup>VI</sup> and La<sup>III</sup> among the studied podands. Micellar aggregates 3–5, 6–90, 3–70, and 7–10 nm in size were found by the dynamic light scattering data in thorium extracts of podands 1–4, respectively.

**Key words:** phosphoryl podands, diphosphonic acids, synthesis, extraction, thorium, uranium, lanthanum, micelles.

Phosphorus acids (RO)<sub>2</sub>P(O)OH, R(RO)P(O)OH, and R<sub>2</sub>P(O)OH (R are various linear and branched alkyl or aryl substituents) are widely used as extractants for the group extraction of lanthanides and actinides from highly active waste of radiochemical industry and irradiated nuclear fuel processing. Primarily they were developed for the TALSEPAK (USA) and DIDPA (Japan) processes, and their use has recently started in the DIAMEX-SAN-EX process (France).<sup>1</sup> It was found later than diphosphonic acids (HO)(RO)(O)P—(CH<sub>2</sub>)<sub>n</sub>—P(O)(OR)(OH) (R is 2-ethylhexyl; *n* = 1, 2, and 4) and related polymer sorbents have very strong affinity to cations of 5f-elements.<sup>2–4</sup> In this connection, they were patented as reagents for extraction and chromatographic separation and concentrating of tri-, tetra-, and hexavalent actinides.<sup>5</sup>

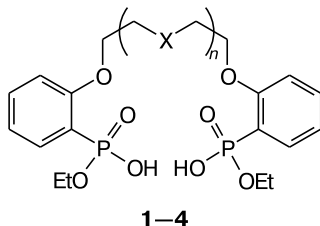
The main regularities of the influence of alkylendiphosphonic acid structure on the extraction of s-, p-, d-, and f-elements from nitric acid solutions were established. The detailed study of the extraction processes showed that both diphosphonic acids themselves and extracted metal complexes exist as aggregates in the organic phase, and the degree of aggregation depends on both the acid structure (alkylene bridge length) and nature of extracted metal (the dependence of the degree of aggregation on the experimental conditions was studied separately).<sup>3,4,6</sup> In addition, very important and practically useful property of diphosphonic acids (unlike carboxylate analogs and the most part of neutral extractants) was discovered: their unique ability to strongly bind actinides in highly acidic solutions.<sup>2</sup>

Up to presently, these results stimulate the preparation of new modified diphosphonic acids and study the extraction properties of both newly synthesized and known compounds of this class.<sup>7</sup>

The group of phosphoryl-containing podands of the acidic type in which two phosphonic  $-\text{P}(\text{O})(\text{OR})(\text{OH})$  fragments are linked by the polyether chain with *o*-phenyl substituents as terminal groups is also referred to diphosphonic acids.<sup>8</sup> Although the first phosphoryl podands of the acidic type were synthesized rather long ago,<sup>9</sup> data on their coordination properties are few<sup>10</sup> and the study of the extraction properties has started only recently. However, already the first results showed high efficiency of some of them for the selective extraction of  $\text{Th}^{\text{IV}}$  in the series of  $\text{U}^{\text{VI}}$  and  $\text{La}^{\text{III}}$  from nitric acid media.<sup>11</sup>

Continuing our studies on search for efficient and selective extractants for the extraction and separation of lanthanides and actinides, it seemed reasonable to establish the main regularities of the influence of the structures of phosphoryl podands of the acidic type on the extraction of f-elements.

The purpose of this work is to compare the properties of a series of acidic phosphoryl-containing podands **1–4** different in length and number of oxygen atoms in the polyether chain for  $\text{U}^{\text{VI}}$ ,  $\text{Th}^{\text{IV}}$ , and  $\text{La}^{\text{III}}$  recovery and to choose the most promising extraction system for thorium(IV) extraction from nitric acid solutions to dichloroethane.



1–4

**1:**  $n = 0$ ; **2:**  $n = 1$ ,  $\text{X} = \text{O}$ ; **3:**  $n = 2$ ,  $\text{X} = \text{O}$ ; **4:**  $n = 1$ ,  $\text{X} = \text{CH}_2$

The synthesis of podands **2** and **3** was described earlier.<sup>9</sup> Podands **1** and **4** were synthesized in this work for the correct evaluation of the influence of the polyether bridge structure on the properties of the extractant.

## Results and Discussion

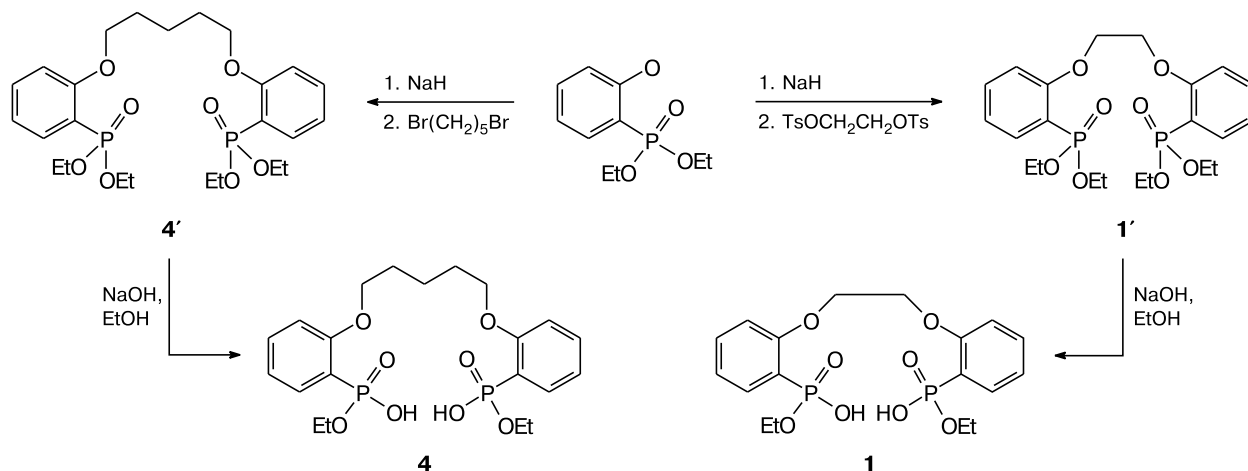
Neutral phosphorylated podands with *o*-diethoxyphosphorylphenyl terminal groups **1'** and **4'** were used as the starting substances for the synthesis of phosphoryl-containing podands of the acidic type **1** and **4**. Compounds **1'** and **4'** were synthesized by the alkylation of *o*-diethoxyphosphorylphenol with ethylene glycol ditosylate or 1,5-dibromopentane in anhydrous dioxane at 80–100 °C in the presence of sodium hydride as a base. The target diphosphonic acids were obtained by the alkaline hydrolysis of the corresponding neutral podands **1'** and **4'** in an aqueous-alcohol medium (Scheme 1).

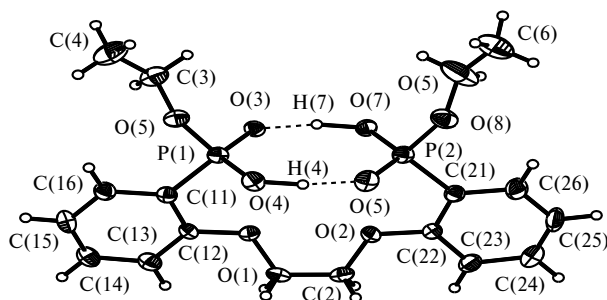
The X-ray diffraction study of podand **1** showed that its structure is built of molecules with two strong intramolecular hydrogen bonds (Fig. 1).

The geometric parameters of the molecule of podand **1** (bond lengths and bond angles, Table 1) lie in the ranges characteristic of compounds of this class<sup>12</sup> and are close to those found earlier for related phosphoryl-substituted acidic podands.<sup>13,14</sup> The  $\text{P}=\text{O}$  and  $\text{P}-\text{OH}$  bond lengths vary within 1.500(3)–1.522(3) Å. The  $\text{P}-\text{C}$  bond lengths are nearly equal: 1.781(4) and 1.786(5) Å. In the  $\text{PO}_3\text{C}$  tetrahedra, the  $\text{O}-\text{P}-\text{C}$  angles lie in the range 104.6(2)–111.2(2)°, and the  $\text{O}-\text{P}-\text{O}$  angles are 106.0(2)–115.7(2)°. The average bond lengths and bond angles of the  $\text{OCH}_2\text{CH}_2\text{O}$  unit have usual values characteristic of podands and crown ethers.<sup>14</sup>

The acidic groups of podand  $\text{P}(\text{O})\text{OH}$  form two strong intramolecular hydrogen bonds  $\text{P}-\text{OH}\cdots\text{O}=\text{P}$  (Table 2) linking two ends of the podand molecule to form three

Scheme 1





**Fig. 1.** Molecular structure of podand **1**. Thermal vibration ellipsoids are presented with 20% probability. Hydrogen atoms are shown by spheres of arbitrary radius. Hydrogen bonds are shown by dashed lines.

H-rings: eight-membered P(1)O(3)H(7)O(7)P(2)O(6)–H(4)O(4) ring and two 13-membered rings P(1)C(11)–C(12)O(1)C(1)C(2)O(2)C(22)C(21)P(2)O(6)H(4)O(4) and P(1)C(11)C(12)O(1)C(1)C(2)O(2)C(22)C(21)P(2)–O(7)H(7)O(3) (see Fig. 1). The eight-membered H-ring is planar, and the root-mean-square deviation of the atoms from the P(1)O(3)O(7)P(2)O(6)O(4) plane (ignoring H atoms) is 0.005 Å. The parameters of hydrogen bonds (distances and bond lengths) in crystal **1** (see Table 2) are close to those found for strong intermolecular hydrogen bonds in cyclic dimers of diphosphinic acids diesters Me<sub>2</sub>P(O)OH and Ph<sub>2</sub>P(O)OH (see Ref. 15) and

**Table 1.** Selected bond lengths (*d*) and bond angles ( $\omega$ ) in the structure of podand **1**

| Parameter       | Value         |
|-----------------|---------------|
| Bond            | <i>d</i> /Å   |
| P(1)–O(3)       | 1.506(3)      |
| P(1)–O(4)       | 1.507(3)      |
| P(1)–O(5)       | 1.584(3)      |
| P(1)–C(11)      | 1.781(4)      |
| P(2)–O(6)       | 1.500(3)      |
| P(2)–O(7)       | 1.522(3)      |
| P(2)–O(8)       | 1.566(4)      |
| P(2)–C(21)      | 1.786(5)      |
| Angle           | $\omega$ /deg |
| O(3)–P(1)–O(4)  | 115.7(2)      |
| O(3)–P(1)–O(5)  | 109.6(2)      |
| O(4)–P(1)–O(5)  | 106.0(2)      |
| O(3)–P(1)–C(11) | 110.2(2)      |
| O(4)–P(1)–C(11) | 110.0(2)      |
| O(5)–P(1)–C(11) | 104.8(2)      |
| O(6)–P(2)–O(7)  | 114.9(2)      |
| O(6)–P(2)–O(8)  | 106.9(2)      |
| O(7)–P(2)–O(8)  | 109.6(2)      |
| O(6)–P(2)–C(21) | 111.2(2)      |
| O(7)–P(2)–C(21) | 109.2(2)      |
| O(8)–P(2)–C(21) | 104.6(2)      |

**Table 2.** Geometric parameters of intramolecular hydrogen bonds in the structure of podand **1**

| Bond<br>D–H...A  | <i>d</i> /Å |         | Angle D–H–A<br>/deg |
|------------------|-------------|---------|---------------------|
|                  | D–H         | H...A   |                     |
| O(4)–H(4)...O(6) | 1.10(5)     | 1.43(5) | 170(5)              |
| O(7)–H(7)...O(3) | 1.11(5)     | 1.39(5) | 167(6)              |

in structures of related phosphoryl-containing acidic podands.<sup>13</sup>

In crystal, molecule **1** has a C-like conformation, where the atoms of the phenyl rings, P atoms, and O atoms of the ethoxy groups lie almost in one plane P(1)C(11)–C(16)O((1)O(2)C(21)–C(26)P(2)O(8) and the root-mean-square deviation of the atoms from this plane is 0.03 Å. The carbon atoms of the CH<sub>2</sub>CH<sub>2</sub> bridge deviate from the considered plane to one side, whereas the carbon atoms of both EtO substituents at the P atom deviate to another side. The whole molecule possesses intrinsic (non-crystallographic) symmetry C<sub>s</sub> (*m*), from which only the H(7) and H(4) atoms deviate substantially. The plane of the mirror reflection is perpendicular to the plane of Fig. 1. Note that all the three planes indicated above are almost perpendicular to each other.

**Extraction properties** of phosphoryl podands **1–4** toward f-elements were studied for the extraction of uranium(vi), thorium(iv), and lanthanum(iii) from nitric acid solutions to the organic phase at the varied concentration of nitric acid and constant concentrations of the salt in the aqueous phase and ligand in 1,2-dichloroethane.

When analyzing the data, it was taken into account that the crystal structures of podands **1** and **2** differ basically. According to the X-ray diffraction data, in crystal molecules of podand **1** form strong intramolecular bonds (this work), whereas the data of powder X-ray diffraction analysis and IR spectroscopy show that molecules **2** in crystal are bonded exclusively by intermolecular hydrogen bonds.<sup>13</sup> It can be assumed that in solutions of 1,2-dichloroethane this difference will retain to a significant extent and will appear as different degrees of self-aggregation of podands **1** and **2** and also as different complexation and extraction abilities of these compounds.

The structures of the extracted complexes of phosphoryl podands **1–4** are unknown. There are preliminary data on the structure of the solid copper complex of ligand **2** [CuL(H<sub>2</sub>O)<sub>2</sub>]<sup>0</sup> (here L is the deprotonated anion of podand **2**). The elemental analysis and IR spectral data suggest that complex [CuL(H<sub>2</sub>O)<sub>2</sub>]<sup>0</sup> is mononuclear with the chelate coordination of the dianion closing the podand to form a pseudo-macrocycle.<sup>13</sup> However, it should be mentioned that the structures of the solid complexes isolated from neutral solutions and the complexes extracted from real strongly acidic solutions do not always coincide.

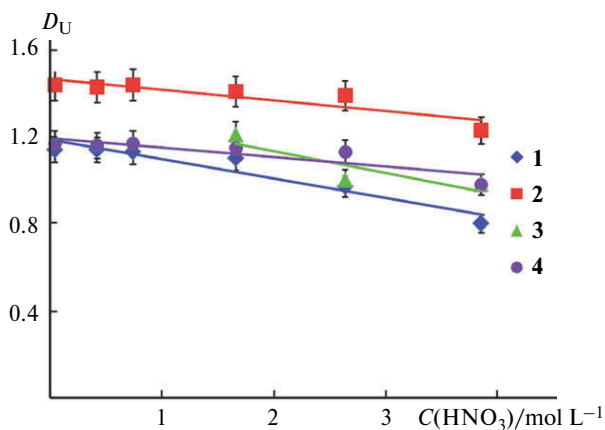
It is known that the polyether chain length exerts different effects on the complexation ability of some classes of podands.<sup>16</sup> For example, in the case of neutral phosphoryl podands, the dependence of the complexation constants on the polyether chain length is extreme for some cations (Li, Na), whereas the complexation constants for other cations (K, Rb, Cs) monotonically increase with an increase in the chain length.<sup>16</sup> The complexation ability of the podands with the  $-P(O)(OH)_2$  terminal groups toward doubly-charged cations decreases nonuniformly with the polyether chain elongation.<sup>10</sup>

In organic media, alkylendiphosphonic acids related to the studied podands form aggregates of different composition and structure, and the extracted complexes are also aggregates of different composition.<sup>3,4</sup> In the simplified form, the composition of the extracted complexes, for example, for the doubly-charged cation  $M^{2+}$ , can be presented as  $M[(HA)_2(H_2A)_n]^0$  and  $M[(A)(H_2A)_n]^0$ , where  $H_2A$  is a dibasic alkylendiphosphonic acid. The differences in the efficiency of extraction by acids with alkylene linkers are mainly determined by different degrees of aggregation of acids and their complexes, which depends, in turn, on the linker length in a complicated way.<sup>2</sup>

The results of liquid extraction of f-elements at the same concentrations of podands **1–4** in dichloroethane ( $0.01 \text{ mol L}^{-1}$ ) and salt in the aqueous phase ( $2.5 \cdot 10^{-5} \text{ mol L}^{-1}$ ) are presented in Figs 2–4.

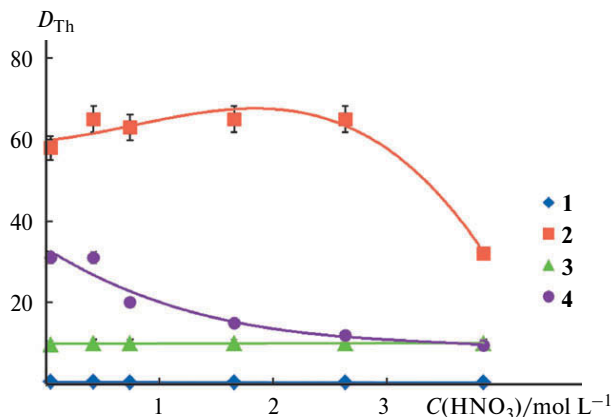
It follows from the data on uranium (see Fig. 2) that podands **1–4** demonstrate a similar dependence of the distribution ratios ( $D_U$ ) on the  $HNO_3$  concentration.

The  $D_U$  values remain almost unchanged in a range of  $HNO_3$  concentrations of  $0.04–2.64 \text{ mol L}^{-1}$  and decrease very insignificantly (on the average, by  $0.20 \pm 0.07$ ) with an increase in the  $HNO_3$  concentration to  $3.86 \text{ M}$ . The efficiency of uranium extraction for podands **1**, **3**, and **4** is



**Fig. 2.** Distribution ratios of  $U^{VI}$  vs  $HNO_3$  concentration for extraction by phosphoryl podands **1–4** ( $0.01 \text{ M}$  solution in 1,2-dichloroethane).

*Note.* Figures 2–4 are available in full color in the on-line version of the journal (<http://www.springerlink.com>).

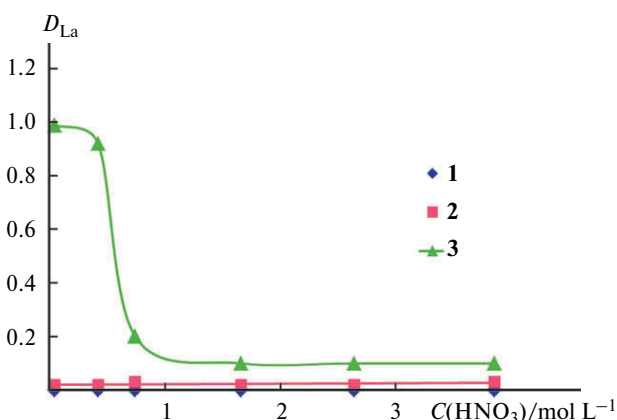


**Fig. 3.** Distribution ratios of  $Th^{IV}$  vs  $HNO_3$  concentration for extraction by phosphoryl podands **1–4** ( $0.01 \text{ M}$  solution in 1,2-dichloroethane).

almost the same and low (average  $D_U = 1.10 \pm 0.08$ ), and the extraction by podand **2** is more efficient ( $D_U = 1.43$ ).

Unlike  $U^{VI}$  extraction, the efficiency of extraction of  $Th^{IV}$  by ligands **1–4** differs substantially (see Fig. 3).

The most efficient extraction of  $Th^{IV}$  is observed for phosphoryl podand **2**, and in the concentration range of  $HNO_3$   $0.04–2.64 \text{ mol L}^{-1}$  the distribution ratios remain almost unchanged:  $D_{Th} = 63 \pm 2$ . The distribution ratio decreases to 32 only for the  $HNO_3$  concentration equal to  $3.86 \text{ mol L}^{-1}$ . Podand **1** with the shortest ethylene glycol chain extracts  $Th^{IV}$  worse than all other studied reagents, and the  $D_{Th}$  values remain almost unchanged in the whole acidity range of the aqueous phase:  $D_{Th} = 0.39 \pm 0.04$ . Podand **3** with the longest chain extracts  $Th^{IV}$  much better: the  $D_{Th}$  values are  $10 \pm 0.07$  on the average in the whole range of  $HNO_3$  concentrations. Podand **4**, whose polyether chain differs from that in podand **2** by the presence of the  $CH_2$  group instead of the  $O$  atom, exhibits rather high efficiency in the extraction of  $Th^{IV}$ , but it is twice as



**Fig. 4.** Distribution ratios of  $La^{III}$  vs  $HNO_3$  concentration for extraction by phosphoryl podands **1–3** ( $0.01 \text{ M}$  solution in 1,2-dichloroethane).

lower than that for podand **2**. Note that the distribution ratios  $D_{\text{Th}}$  decrease smoothly with an increase in the  $\text{HNO}_3$  concentration only in this case.

The efficiency of  $\text{La}^{\text{III}}$  extraction (see Fig. 4) for podands **1–3** also differs. Podands **1** and **2** nearly do not extract lanthanum in the whole range of  $\text{HNO}_3$  concentrations ( $D_{\text{La}}$  are 0 and 0.02, respectively). Unlike them, podand **3** (with the longest polyether chain) noticeably extracts lanthanum in the range of low  $\text{HNO}_3$  concentrations ( $D_{\text{La}} = 0.99–0.92$ ), but the efficiency of extraction decreases sharply ( $D_{\text{La}} = 0.2–0.1$ ) in highly acidic media (see Fig. 4).

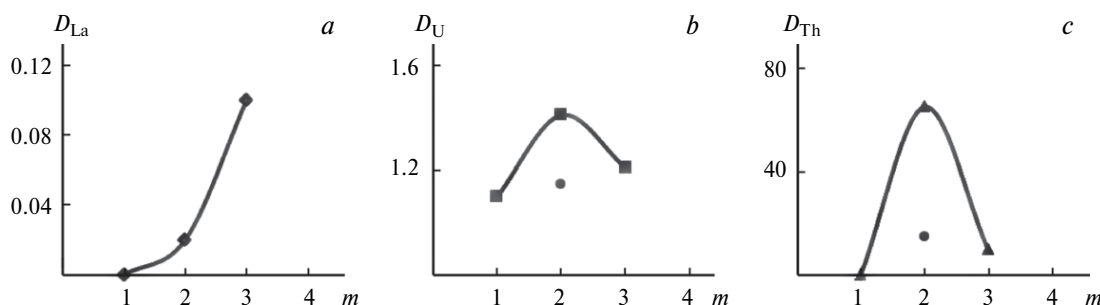
As already mentioned, the consecutive increase in the number of  $\text{OCH}_2\text{CH}_2$  units in the chain binding the terminal groups of the podands from one to three (podands **1–3**) is accompanied by the monotonic enhancement of the efficiency of  $\text{La}^{\text{III}}$  extraction (Fig. 5, *a*), although the  $D_{\text{La}}$  values themselves in the compared of  $\text{HNO}_3$  concentrations ( $>0.74 \text{ mol L}^{-1}$ ) are very low (0, 0.02, and 0.1 for podands **1**, **2**, and **3**, respectively). In the first approximation, for lanthanum extraction, this effect can be related to an increase in the lipophilicity of the extracted complexes with the polyether chain elongation.

For uranium and thorium cations, the dependence of  $D_{\text{M}}$  on the number of  $\text{OCH}_2\text{CH}_2$  units in the chain is substantially different. In both cases, some maximum at  $m = 2$  (podand **2**) is observed. However, for uranium this maximum is low: the whole range of changing  $D_{\text{U}}$  is only 0.3 (Fig. 5, *b*), whereas it is very significant for thorium: the range of changing  $D_{\text{Th}}$  is 65 (Fig. 5, *c*). Note that the  $D_{\text{U}}$  and  $D_{\text{Th}}$  values for podand **4** is lower than those for podand **2**, *i.e.*, the replacement of the  $\text{CH}_2$  group in the linker of podand **4** by the O atom (on going to the structure of podand **2**) increases the efficiency of uranium and thorium extraction. It is difficult to understand that this effect is caused by the participation of the ether oxygen atom (atoms) in coordination with the uranyl cation ( $\text{O}=\text{U}=\text{O}^{2+}$ ), whose coordination sphere assumes the coordination of the ligands on the equatorial plane only.

In fact, according to the X-ray diffraction data, the neutral phosphoryl podand having the same linker as podand **4** in a complex with uranyl manifests bidentate-bridging coordination due to the O atoms of two  $\text{P}(\text{O})$  groups, and the ether O atoms are not involved in coordination.<sup>17</sup> In principle, coordination involving the ether O atoms can be expected for the complexes of acidic podands with alkaline metal cations by analogy to the complexes of neutral phosphoryl podands.\*

However, there is very interesting example of the crystalline complex of erbium nitrate with neutral podand  $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$  (**L**), *viz.*,  $[\text{ErL}(\text{H}_2\text{O})(\text{NO}_3)_3]$ , in which the ligand is bound to the cation by the bidentate mode through the phosphoryl oxygen atoms and the coordinated  $\text{H}_2\text{O}$  molecule forms hydrogen bonds with two ether oxygen atoms of the ligand.<sup>20</sup> It can be assumed that for extraction during complex formation of the acidic phosphoryl podands ( $\text{H}_2\text{L}$ ) with the cations having large charges and radii the ether O atoms of the podand can form similar hydrogen bonds with coordinated  $\text{H}_2\text{O}$  molecules, whereas the coordination bonds with the cation are formed by the terminal  $\text{POO}^-$  groups of the podand anion ( $\text{L}^{2-}$ ). In terms of this assumption, the complexes of podand **3** should be stronger than those of podand **4**, and their lipophilicity, which depends on the number of carbon atoms in the molecule, should be nearly equal. Therefore, the extraction efficiency of the complexes of podand **3** will be higher than that for podand **4** (see Fig. 5, *b, c*).

The difference in extraction efficiency of  $\text{Th}^{\text{IV}}$  by podands **1–3** is unusually high compared to the extraction



**Fig. 5.** Distribution ratios  $D_{\text{M}}$  ( $\text{M} = \text{La}^{\text{III}}$  (*a*),  $\text{U}^{\text{VI}}$  (*b*), and  $\text{Th}^{\text{IV}}$  (*c*)) for extraction by  $2-[(\text{HO})(\text{EtO})(\text{O})\text{P}]-\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_m-\text{OC}_6\text{H}_4-2-[\text{P}(\text{O})(\text{EtO})(\text{OH})]$  (**1–3**) vs number of  $-\text{OCH}_2\text{CH}_2-$  units ( $m$ ) in the polyether chain (extraction from 1.66  $M$   $\text{HNO}_3$ , concentration of podands in 1,2-dichloroethane  $0.01 \text{ mol L}^{-1}$ , initial concentration of metal nitrates in the aqueous phase  $2.5 \cdot 10^{-5} \text{ mol L}^{-1}$ ). The values for podand **4** are put on plots *b* and *c* as particular points (circles).

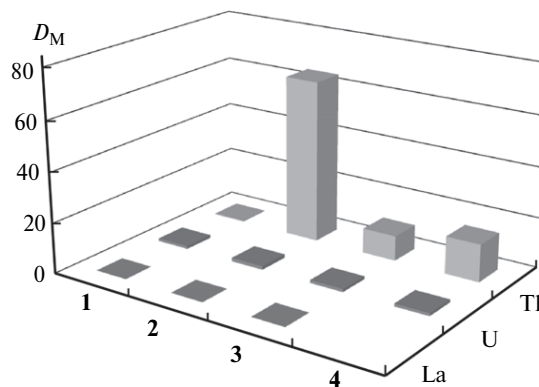
\* The cooperative interaction of all donor atoms of the podand with the central metal cation was observed in the solid complexes of the neutral phosphoryl podands with  $\text{NaI}$ ,  $\text{LiI}$ , and  $\text{Ba}(\text{NCS})_2$ ,<sup>18</sup> whereas in the complexes with  $\text{ZnI}_2$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ , and  $\text{LiI}$  the podands are bidentate-bridging coordinated only through the oxygen atoms of the  $\text{P}(\text{O})$  groups.<sup>18,19</sup> It was found that the neutral phosphoryl podands exhibit different dentate modes, depending on the metal nature.

of La<sup>III</sup> and U<sup>VI</sup>. An assumption about different compositions of the extracted complexes (considered in detail in Ref. 21) as the main reason for the difference does not seem exhausting. Evidently, the neutral intracomplex salts [ThL<sub>2</sub>]<sup>0</sup>, [UO<sub>2</sub>L]<sup>0</sup>, and [LaL(NO<sub>3</sub>)]<sup>0</sup> with chelate coordination of the dianion L<sup>2-</sup> of one acidic podand H<sub>2</sub>L should possess different lipophilicities because of the different numbers of lipophilic, chelate-coordinated anions L<sup>2-</sup> and the presence or absence of the hydrophilic nitrate ion. Then (assuming that the stability of the intracomplex salt differs insignificantly), the extraction efficiency should decrease in the series Th > U > La. However, an assumption about the same (or similar) structures of particles extracted by podands 1–4 is quite reasonably consistent with the results of extraction of La<sup>III</sup> and U<sup>VI</sup> nitrates, whereas for Th<sup>IV</sup> this assumption is explicitly insufficient: the extraction coefficients of thorium by ligands 2–4 are much higher than the values expected by prediction on the basis of  $D_{Th}$  for ligand 1. By analogy to related alkylene-diphosphonic acids, one can assume that the effect observed for Th<sup>IV</sup> extraction is mainly determined by different degrees of aggregation ( $m$ ) of both podands 1–4 ((H<sub>2</sub>L) <sub>$m$</sub> ) themselves and their complexes (in the simplified form, [ThL<sub>2</sub>(H<sub>2</sub>L) <sub>$n$</sub> ]<sup>0</sup>, [ThL(HL)<sub>2</sub>(H<sub>2</sub>L) <sub>$n$</sub> ]<sup>0</sup>, *etc.*). According to the X-ray diffraction data on the structures of molecules 1 and 2 (see above), it can be expected that in the organic phase podands 2–4 with a longer polyether chain would form larger aggregates due to intermolecular hydrogen bonds, unlike podand 1, whose molecules are stabilized by a strong intramolecular hydrogen bond. To check this assumption, we used the dynamic light scattering method to study thorium extracts by podands 1–4. In accord with expectations, they contain micellar aggregates of different sizes: 3–5, 6–90, 3–70, and 7–10 nm for extracts of podands 1, 2, 3, and 4, respectively. These data are well consistent with a change in the efficiency of Th<sup>IV</sup> extraction in the series of the studied podands: 2 > 3 > 4 > 1.

To compare the efficiency and selectivity of podands 1–4 depending on their structure, the distribution ratios of f-elements for extraction from 1.66 M solutions of HNO<sub>3</sub> were compared (Fig. 6).

All studied podands 1–4 almost do not extract La<sup>III</sup> ( $D_{La} = 0–0.1$ ) and extract U<sup>VI</sup> with moderate efficiency ( $D_U = 1.10–1.41$ ). However, podands 2–4 are of certain interest with respect to the extraction of Th<sup>IV</sup> ( $D_{Th} = 10–65$ ). Among them podand 2 is most efficient ( $D_{Th} = 65$ ) and can be recommended as an extractant for the selective extraction of Th<sup>IV</sup> from nitric acid solutions containing La<sup>III</sup>, Th<sup>IV</sup>, and U<sup>VI</sup>.

Thus, the study performed makes it possible to determine the direction of design of promising extractants for the extraction of actinides in the group of phosphoryl-containing acidic dipodands. Diethylene glycol chain –(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O– is the optimum linker for the production of extractants of this type.



**Fig. 6.** Comparison of the distribution ratios of La<sup>III</sup>, U<sup>VI</sup>, and Th<sup>IV</sup> for extraction by podands 1–4 (0.01 M solutions in 1,2-dichloroethane) from 1.66 M HNO<sub>3</sub>; initial concentration of metal nitrates in the aqueous phase  $2.5 \cdot 10^{-5}$  mol L<sup>-1</sup>.

## Experimental

<sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker-CPX-200 instrument (<sup>1</sup>H, 200 MHz; <sup>31</sup>P, 81 MHz) relative to tetramethylsilane (<sup>1</sup>H) and 85% H<sub>3</sub>PO<sub>4</sub> as an external standard (<sup>31</sup>P).

**1,2-Bis(2-diethoxyphosphorylphenoxy)ethane (1').** A 55% suspension of NaH in (1.2 g, 27.0 mmol) in Nujol was added by portions to a solution of 2-diethoxyphosphorylphenol<sup>9</sup> (6.2 g, 27.0 mmol) in anhydrous dioxane (75 mL), the mixture was stirred for 0.5 h, ethylene glycol ditosylate (5.0 g, 13.5 mmol) was added, and the mixture was heated to boiling and stirred for 15 h. After cooling, the mixture was poured to water (150 mL), acidified to pH 1 by concentrated HCl, and extracted with CHCl<sub>3</sub> (3 × 25 mL). The extract was washed with water (3 × 25 mL), and the solvent was evaporated *in vacuo*. The residue was chromatographed on a column with silica gel L (particle size 100–160 μm, CHCl<sub>3</sub> and CHCl<sub>3</sub>–Pr<sup>i</sup>OH (1 : 50) as eluents). The yield was 3.6 g (57%), m.p. 62–64 °C (benzene–pentane). Found (%): C, 54.33; H, 6.62, P, 12.75. C<sub>22</sub>H<sub>32</sub>O<sub>8</sub>P<sub>2</sub>. Calculated (%): C, 54.32; H, 6.63, P, 12.74. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 1.28 (t, 12 H, 4 CH<sub>3</sub>CH<sub>2</sub>O, <sup>3</sup>J<sub>H–H</sub> = 7.0 Hz); 5.16 (m, 8 H, 4 MeCH<sub>2</sub>O); 5.50 (s, 4 H, OCH<sub>2</sub>CH<sub>2</sub>); 8.08 (m, 4 H, ArH); 8.50 (m, 2 H, ArH); 8.82 (m, 2 H, ArH). <sup>31</sup>P NMR (CDCl<sub>3</sub>), δ: 17.8 (s).

**1,2-Bis(2-hydroxyethoxyphosphorylphenoxy)ethane (1).** Compound 1' (5.9 g, 12.2 mmol) was added to a solution of NaOH (1.5 g, 37.0 mmol) in aqueous (1 : 1) ethanol (20 mL). The mixture was refluxed for 5 h, and the solvent was removed *in vacuo*. Dilute (1 : 3) HCl (15 mL) was added to the residue, the mixture was extracted with CHCl<sub>3</sub> (2 × 15 mL), and the extract was evaporated *in vacuo*. Methyl ethyl ketone (15 mL) was added to the residue, and the precipitate formed was filtered off. The yield was 3.4 g (65%), m.p. 195–196 °C (ethanol). Found (%): C, 50.18; H, 5.64, P, 14.40. C<sub>18</sub>H<sub>24</sub>O<sub>8</sub>P<sub>2</sub>. Calculated (%): C, 50.24; H, 5.62, P, 14.40. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>), δ: 1.22 (t, 6 H, 2 CH<sub>3</sub>CH<sub>2</sub>O, <sup>3</sup>J<sub>H–H</sub> = 7.0 Hz); 4.00 (m, 4 H, 2 CH<sub>3</sub>CH<sub>2</sub>O); 4.20 (s, 4 H, OCH<sub>2</sub>CH<sub>2</sub>); 7.08 (m, 4 H, ArH); 7.48 (m, 2 H, ArH); 7.67 (m, 2 H, ArH). <sup>31</sup>P NMR (DMSO-d<sub>6</sub>), δ: 14.0 (s). The structure of podand 1 was confirmed by the X-ray diffraction method.

**1,5-Bis(2-hydroxyethoxyphosphorylphenoxy)-3-oxapentane (2) and 1,8-bis(2-hydroxyethoxyphosphorylphenoxy)-3,6-di-**



oxaotane (**3**) were synthesized using a previously described procedure.<sup>9</sup>

**1,5-Bis(2-diethoxyphosphorylphenoxy)pentane (4')**. A 55% suspension of NaH (0.4 g, 10.0 mmol) in Nujol was added to a solution of 2-diethoxyphosphorylphenol<sup>9</sup> (2.3 g, 10.0 mmol) in anhydrous dioxane (25 mL). The reaction mixture was stirred for 0.5 h, 1,5-dibromopentane (1.2 g, 5.0 mmol) was added, and the mixture was heated to boiling and stirred for 15 h. After cooling, the mixture was poured to water (75 mL), acidified with concentrated HCl to pH 1, and extracted with CHCl<sub>3</sub> (3×25 mL). The extract was washed with water (3×25 mL), and the solvent was removed *in vacuo*. The residue was chromatographed on a column with silica gel L using CHCl<sub>3</sub> and CHCl<sub>3</sub>–Pr<sup>i</sup>OH (1 : 50) as eluents. The yield was 2.1 g (79%), viscous oil. Found (%): C, 56.79; H, 6.27; P, 11.70. C<sub>25</sub>H<sub>38</sub>O<sub>8</sub>P<sub>2</sub>. Calculated (%): C, 56.81, H, 6.25; P, 11.72. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 1.12 (t, 12 H, 4 OCH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>H–H</sub> = 7.5 Hz); 1.30 (m, 8 H, 4 OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 1.54–1.79 (m, 14 H, 4 OCH<sub>2</sub>CH<sub>3</sub> + OCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>OCH<sub>2</sub>O); 7.08 (m, 4 H, ArH); 7.30 (m, 2 H, ArH); 7.37 (m, 2 H, ArH). <sup>31</sup>P NMR (CDCl<sub>3</sub>), δ: 17.4 (s).

**1,5-Bis(2-hydroxyethoxyphosphorylphenoxy)pentane (4)**. solution of NaOH (1.2 g, 30.0 mmol) in 40% aqueous ethanol (5 mL) was added to a solution of compound **4'** (2.4 g, 5.1 mmol) in EtOH (5 mL). The mixture was refluxed for 5 h and cooled, dilute (1 : 3) HCl (15 mL) was added, the mixture was stored for ~14 h, and the precipitate was filtered off. The yield was 1.6 g (69%), m.p. 109–111 °C (ethanol–water). Found (%): C, 53.29; H, 6.39; P, 13.18. C<sub>25</sub>H<sub>38</sub>O<sub>8</sub>P<sub>2</sub>. Calculated (%): C, 53.39, H, 6.40; P, 13.11. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>), δ: 1.16 (t, 6 H, 2 OCH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>H–H</sub> = 7.5 Hz); 1.73 (m, 6 H, OCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>OCH<sub>2</sub>O); 4.11 (m, 4 H, 2 OCH<sub>2</sub>CH<sub>3</sub>); 4.21 (m, 4 H, OCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>OCH<sub>2</sub>O); 7.09–7.43 (m, 8 H, ArH). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>), δ: 16.3 (s).

**X-Ray diffraction study.** Colorless crystals of podand **1** suitable for X-ray diffraction analysis were obtained by the isothermal evaporation at ~20 °C of a solution of compound **1** in 1,2-dichloroethane. The crystals of C<sub>18</sub>H<sub>24</sub>O<sub>8</sub>P<sub>2</sub> (**1**) (*M* = 430.31) are orthorhombic, at 293(2) K *a* = 7.0603(13) Å, *b* = 14.480(3) Å, *c* = 20.119(4) Å, *V* = 2056.8(7) Å<sup>3</sup>, space group *P*2<sub>1</sub>2<sub>1</sub>, *Z* = 4, *d*<sub>calc</sub> = 1.390 g cm<sup>–3</sup>. The experimental set of 13 791 reflections was obtained on a Bruker Kappa Apex II automated four-circle diffractometer with a two-dimensional detector<sup>22</sup> (Mo-*K*α radiation, graphite monochromator, φ and ω scan modes) from a single crystal 0.32×0.10×0.08 mm in size. The unit cell parameters were refined over the whole data massive.<sup>23</sup> Absorption corrections were applied using the SADABS programs.<sup>24</sup> After averaging equivalent reflections, 4698 independent reflections were obtained (*R*<sub>int</sub> = 0.0934) and used for structure decoding and refinement. The structure was solved by a direct method (SHELXS97)<sup>25</sup> and refined by the full-matrix least-squares method (SHELXL97)<sup>25</sup> against *F*<sup>2</sup> for all data in the anisotropic approximation for all non-hydrogen atoms. The H atoms of the CH, CH<sub>2</sub>, and CH<sub>3</sub> groups were placed in geometrically calculated positions and refined with isotropic temperature parameters equal to 1.2*U*<sub>eq</sub> of the C atom for the CH and CH<sub>2</sub> groups and 1.5*U*<sub>eq</sub> of the C atoms for the CH<sub>3</sub> group. The H atoms of the POOH groups were localized from the difference Fourier synthesis and refined isotropically with constraints of equality of the temperature parameters and O–H distances. The final values of *R* factors are *R*<sub>1</sub> = 0.0605 (calculated by *F*<sub>hkl</sub> for 2177 reflections with *I* > 2σ(*I*)), *wR*<sub>2</sub> = 0.1383 (calculated by *F*<sup>2</sup><sub>hkl</sub> for all reflections), GOOF = 0.962. The completeness of data collection was

99.4%, the number of refined parameters was 260, and the maximum and minimum residual electron density peaks were 0.214 and –0.291 e Å<sup>–3</sup>, respectively. The Flack parameter *x* equal to 0.15(15) shows that the absolute structure was determined correctly.<sup>26</sup>

The full tables of atomic coordinates, bond lengths, and angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1006221).

**Study of extraction.** Bidistilled water, 1,2-dichloroethane (reagent grade), arsenazo III (analytical grade), HNO<sub>3</sub> (high purity grade), UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (reagent grade), Th(NO<sub>3</sub>)<sub>4</sub>·4H<sub>2</sub>O (reagent grade), and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (reagent grade) were used to prepare solutions. Solutions were prepared by the volumetric gravimetric method. Solutions of actinide and lanthanum nitrates were prepared by the dissolution of a weighed sample of the corresponding nitrate in a 0.01 *M* solution of HNO<sub>3</sub>. The concentration of solutions of metal nitrates (0.1 mmol L<sup>–1</sup>) was refined by spectrophotometry according to an earlier described procedure<sup>27</sup> using a Cary50 Scan spectrophotometer (Varian). The concentration of solutions of HNO<sub>3</sub> was determined by potentiometric titration with 0.1 *M* NaOH using a pH/ion Analyser Radelkis-125 pH meter (model OP-300) with an accuracy of ±0.01 pH units. The electrode pair was calibrated by standard buffer solutions with pH 1.68, 4.01, and 9.22 (the values of pH at 20 °C). The concentration of a solution of NaOH was refined by potentiometric titration with 0.1 *M* HCl (fixanal).

The extraction of metal cations was studied as follows. A solution of nitric acid (1.5 mL), whose concentration was varied from 0.053 to 5.15 mol L<sup>–1</sup>, 0.5 mL of 0.1 *M* solution of metal nitrate, and 2 mL of a 0.01 *M* solution of the ligand in 1,2-dichloroethane was placed in a tube with a ground stopper. A 0.006 *M* solution of podand **2** was used because of its restricted solubility. The phases were stirred for 20 min in a Multi RS-60 BioSan multirotator (80 rpm). The time of extraction equilibration was checked by increasing the duration of phase contact to 120 min, and distribution ratios remained unchanged during this process. Phases were separated by centrifugation. After phase separation, the concentration of metals in the aqueous phase was determined by spectrophotometry.<sup>27</sup> To enhance the sensitivity of the analysis, the content of actinides in the organic and aqueous phases were monitored radiometrically using an LS-6500 Beckman Instruments liquid scintillation counter (WS-BECKLS65) (Beckman LS 6500 Liquid Scintillation Counter). For this purpose, <sup>233</sup>U<sup>VI</sup> (10<sup>4</sup> pulse s<sup>–1</sup>) and <sup>239</sup>Pu<sup>IV</sup> (10<sup>4</sup> pulse s<sup>–1</sup>) labels were introduced into solutions of uranyl and thorium nitrates during extraction. At least three independent experiments were carried out for each concentration. All experiments were conducted at 20±1 °C.

The distribution ratios (*D* = [M]<sub>org</sub>/[M]<sub>aq</sub>) were determined at constant concentrations of the extractant (0.01 mol L<sup>–1</sup> in 1,2-dichloroethane) and metal (0.025 mmol L<sup>–1</sup> in the aqueous phase).

A Malvern Zetasizer Nano analyzer of particle size (Nano-ZS) was used to establish the presence of nanosized aggregates in the organic phase. Extracts were studied after contact of a solution of the ligand (1 mmol L<sup>–1</sup> in 1,2-dichloroethane) with a 0.025 *mM* solution of thorium nitrate in 0.04 *M* HNO<sub>3</sub>. The choice of concentrations was determined by the necessity of comparison with experimental results for other podands (see Ref. 21).

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