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Synthesis, Complexing Properties, and Selectivity of Bis(diphenylphosphorylmethyl) Ethers of Oligoethylene Glycols. Crystal Structure of 1,3-Bis(diphenylphosphoryl)-2-oxapropane

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Abstract—A convenient method of synthesis of phosphoryl-substituted podands with dipehnylphosphorylmethyl end groups of the general formula $Ph_2P(O)CH_2O(CH_2CH_2O)_nCH_2P(O)Ph_2$ ($\mathbf{L}^n$, n = 0–6) is described. The stability constants of the complexes of the podands with alkali metal 2,4-dinitrophenolates were determined by conductometry. The ion-selective properties of the podands with respect to alkali and alkaline-earth metal cations were assessed by ionometry. The crystal structure of 1,3-bis(diphenylphosphoryl)-2-oxapropane was established by X-ray diffraction analysis.

Keywords: organophosphorus podands, stability constants, complex formation, alkali metals, ion-selective properties, XDR analysis

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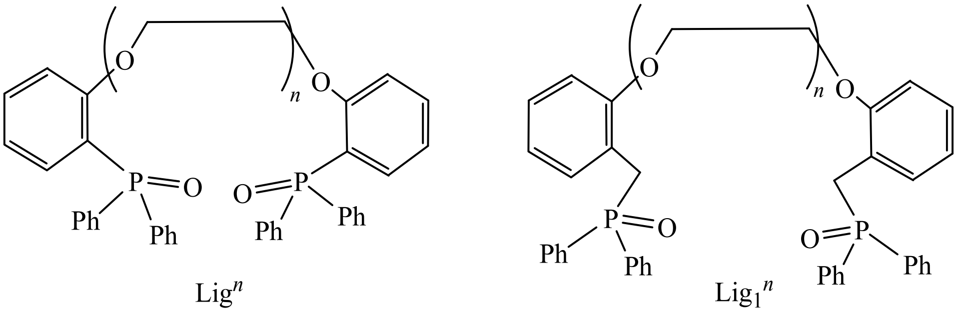
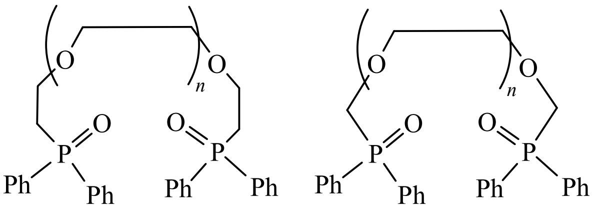
Synthetically available acyclic analogs of crown ethers (podands) are potent complexing agents for alkali and alkaline-earth metal cations. They have found application as active components of extraction systems extraction chromatographic materials, and plasticized membranes of ion-selective electrodes [1]. Of considerable interest are podands containing the phosphoryl group, which is easily polarized and possesses a high coordinating ability. The stability of complexes with phosphoryl-substituted podands and the selectivity of their formation depends on many factors, including the number and donor power of the coordinating centers and the rigidity of the ligand. We showed that phosphoryl-substituted podands with

Scheme 1.



n = 1–5.

Scheme 2.



L_1^n L^n

n = 1–5 (L_1^n), 0–6 (L^n).

ortho-phosphorylated phenol fragments (Lig^n and Lig$_1^n$) as end groups exhibit a high coordinating power with respect to alkali metal cations (Scheme 1).

The stability constants of the complexes of such podands not infrequently compare or even higher than the stability constants of similar complexes with crown ethers [2, 3]. In [4, 5] we determined the crystal structure of the complexes of Lig^n and Lig$_1^n$ with some alkali metal cations and correlated the structures and stability constants of the complexes. Earlier Baulin and co-workers [6, 7] made an attempt to correlate the structure of phosphoryl-substituted podands Lig^n, Lig$_1^n$, and L_1^n and their Li/Na selectivity, taking into account the relative fraction of the phosphoryl groups in the podand, its conformational rigidity, and ethylene glycol chain length, but the resulting data proved controversial (Scheme 2).

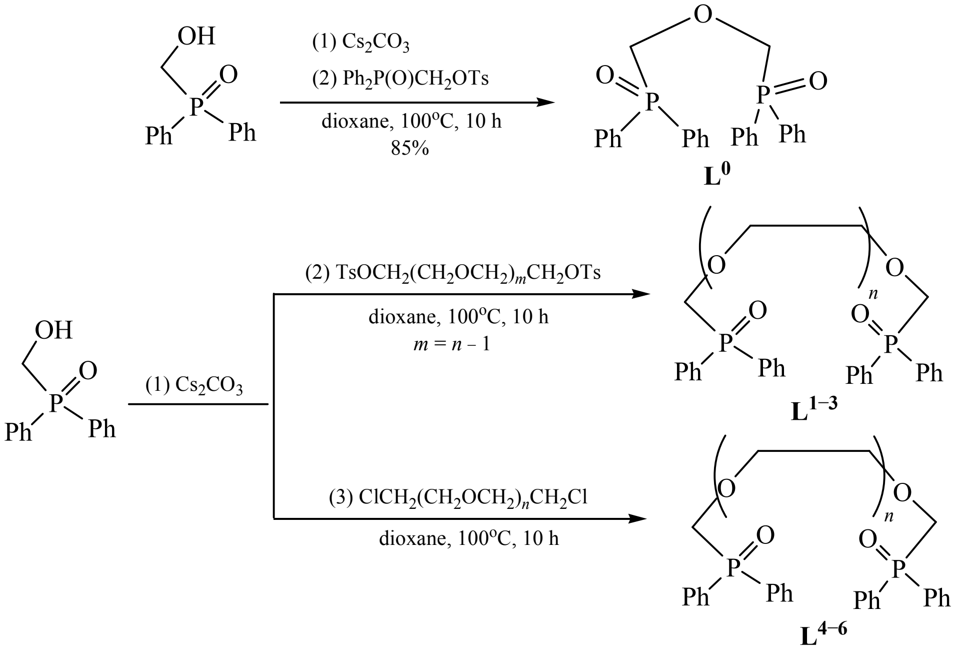
Proceeding with research into the dependence of the structure of podands and their complexing properties and selectivity, in the present work we studied phosphoryl-substituted podands $\mathbf{L}^n$ (n = 0–6) having diphenylphosphorylmethyl end groups.

Earlier some compounds of the $\mathbf{L}^n$ series were tested as extractants for europium and americium from nitric acid media [8] and for platinum from hydrochloric acid media [9]. Evidence showing that such compounds favor removal of strontium from mice was reported [10]. Podands $\mathbf{L}^n$ were also used in plasticized membranes for ion-selective electrodes for the determination of octylammonium [11] and guanidinium cations [12].

The first representatives of the $\mathbf{L}^n$ series were synthesized by the reaction of (chloromethyl)diphenylphosphine oxide with sodium mono- and (hydroxymethyl)diphenylphosphine oxide with diethylene glycol dithosylate in boiling toluene. A series of monoalkylation products were isolated and used to synthesize unsymmetrical phosphoryl-substituted podands [13]. Podand $\mathbf{L}^1$ was also synthesized in 33% yield in a nonaquoeus biphasic liquid–solid system. The solid phase was a mixture of KOH and K_2CO_3 powders, the liquid phase was a solution of diphenylphosphinous acid and 1,2-bis(chloromethoxy)ethane in benzene, and the phase-transfer catalyst was 18-crown-6. However, attempted synthesis of longer chain ethylene glycols by the reaction of diphenylphosphinous acid with bis(chloromethyl) ethers did not lead to a success [13]. The synthesis of some podands by the reaction of (chloromethyl)diphenylphosphine oxide with lithium glycolates was also reported [14, 15].

In the present work we obtained compounds $\mathbf{L}^0$–$\mathbf{L}^6$ in yields of 71–85% by the reaction of (hydroxymethyl)diphenylphosphine with corresponding glycol ditosylates or dichlorides in the biphasic Cs_2CO_3–dioxane system at 100°C (Scheme 3). Reaction progress was monitored by TLC and ^{31}P NMR. The yield of the target products was almost independent on whether the phase-transfer catalyst (18-crown-6 or tetrabutylammonium bromide) was present or absent. With solid NaOH or anhydrous K_2CO_3 as the bases, the yields of short-chain podands $\mathbf{L}^1$–$\mathbf{L}^3$ and long-chain podands $\mathbf{L}^4$–$\mathbf{L}^6$ decreased to reduced to 30–45% and 15%, respectively. The yields of compounds $\mathbf{L}^4$–$\mathbf{L}^6$ was strongly increased by the addition to the reaction mixture of equivalent quantities of CsOH or Cs_2CO_3. Therewith, by the end of the reaction, the ^{31}P NMR spectrum of the reaction mixture showed, along with the signal of the final product, a signal 0.25 ppm apart from and 15% as intense as this signal. We suggest that this signal belonged to a complex of the ligand with Cs^+, because it disappeared after the reaction mixture had been treated with dilute HCl. Apparently, here we faced template assembly of a polydentate organic ligand on the cesium cation, a phenomenon which is not infrequently observed in the synthesis of cyclic polyethers [1]. Tsvetkov et. [13] described podands $\mathbf{L}^2$ and $\mathbf{L}^3$ as oily substances. By contrast, we obtained these products in the crystalline state, and compound $\mathbf{L}^1$ had a much higher melting point. Attempted synthesis of phosphoryl-substituted podands by the reaction of *O,O*-dipentyl (hydroxymethyl)phosphonate or (2-hydroxyethyl)diphenylphosphine oxide with diethylene glycol ditosylate at varied reaction conditions failed: No other products but decomposition products of the starting reagents were detected in the reaction mixture.

Scheme 3.



The logarithms of the stability constants of phosphoryl-substituted podands $\mathbf{L}^n$ (n = 0–6) with alkali metal 2,4-dinitrophenolates, obtained by conductometry in a THF–$CHCl_3$ binary solvent (4 : 1 v/v), are listed in Table 1. As seen, the stability constants are rather low, and, therefore, podands $\mathbf{L}^n$, except for $\mathbf{L}^1$, rank below their conformationally more flexible analogs L_1^n in the efficiency of binding alkali metal cations [6, 7]. With respect to lithium and sodium cations, podands $\mathbf{L}^n$ even rank below less conformationally flexible podands Lig^n. For example, the log K_{Li^+} and log K_{Na^+} for podand Lig^3 are 7.0 and 6.1, respectively [3, 13], and the respective values for podand $\mathbf{L}^3$ are 4.8 and 4.5. In going to Cs^+ is almost leveled: log K_{Cs^+} = 3.8 and 3.7 for podands Lig^3 [3, 13] and $\mathbf{L}^3$, respectively. In general, podands $\mathbf{L}^n$ are also less efficient than isodentate crown ethers [2, 3]. Exceptions are podands $\mathbf{L}^1$ and $\mathbf{L}^2$, which more efficiently than isodentate crown ethers bind Li^+ [log K_{Li^+} = 5.7 ($\mathbf{L}^1$), 2.8 (benzo-12-crown-4), 5.2 ($\mathbf{L}^2$), 4.6 (15-crown-5)] and compare with or slightly better in binding efficiency than their analogs Lig^1 and Lig^2 (log K_{Li^+} = 5.8 and 4.6, respectively). In worth mentioning that phosphoryl-substituted podand $\mathbf{L}^1$ has a high lithium/sodium selectivity coefficient.

Table 1. Stability constants of the complexes of podands L^n (n = 0–6) with alkali metal 2,4-dinitrophenolates in a THF–$CHCl_3$ binary solvent (4 : 1 v/v)

Podand	log K					K_{Li}/K_{Na}
	Li^+	Na^+	K^+	Rb^+	Cs^+	
$\mathbf{L}^0$	4.2	3.2	2.7	2.4	2.1	10.0
$\mathbf{L}^1$	5.7	3.6	3.2	2.9	2.7	125.9
$\mathbf{L}^2$	5.2	4.2	3.8	3.5	3.2	10.0
$\mathbf{L}^3$	4.8	4.5	4.4	4.2	3.7	2.0
$\mathbf{L}^4$	4.6	5.2	5.0	4.6	4.2	–
$\mathbf{L}^5$	4.6	5.2	5.4	5.2	4.7	–
$\mathbf{L}^6$	4.6	5.1	5.1	–	–	–

The lower stability constants of the complexes of conformationally flexible podands $\mathbf{L}^n$ compared to their less flexible analogs Lig^n and $\mathrm{Lig}_1{}^n$ affect the ion selectivity of the former: none of the synthesized podands $\mathbf{L}^n$ showed potentiometric selectivity to lithium cations. Study of the membrane-active properties with respect to alkali and alkaline-earth metal cations established that podands $\mathbf{L}^n$ all, unlike Lig^n and $\mathrm{Lig}_1{}^n$, are, to a greater or lesser degree, are selective to Cs^+ (Fig. 1). Figure 2 presents the electrode characteristics of cesium-selective electrodes on the basis of podands with two ($\mathbf{L}^2$, Fig. 2a) and five (L^5, Fig. 2b) ethylene glycol units, a dibutyl phthalate plasticizer, and a potassium tetrakis(4-chlorophenyl)-borate lipophilic additive (50% with respect to the electrode-active component) in the presence of some interfering alkali and alkaline-earth metal cations.

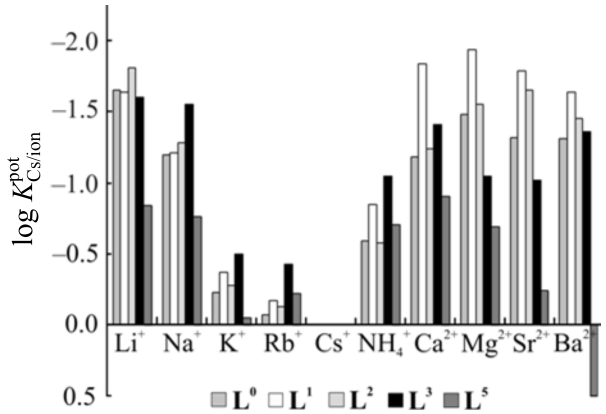


Fig. 1. Potentiometric selectivity coefficients for cesium-selective electrodes on the basis of ligands $\mathbf{L}^0$–$\mathbf{L}^3$ and $\mathbf{L}^5$ with a dibutyl phthalate plasticizer and a potassium tetrakis-(4-chlorophenyl)borate lipophilic additive (50% with respect to the electrode-active component).

Podand $\mathbf{L}^3$ showed the best electroanalytical characteristics with respect to Cs^+, even the stability constants of the corresponding complex is not the highest (Tables 1 and 2). The same correlation between stability constants and potentiometric selectivity constants was previously observed for the less flexible podands Lig^3 and $\mathrm{Lig}_1{}^3$ and Li^+ [4, 5]. The highest potentiometric selectivity with respect to alkali metal cations was displayed by podand $\mathbf{L}^3$ and with respect to alkaline-earth metal cations, its shorter-chain analog $\mathbf{L}^1$ (Fig. 1).

In our previous work [4] we analyzed the structures and stability constants of the complexes of alkali metals with podands Lig^n and $\mathrm{Lig}_1{}^n$, and isostructural crown ethers to show that the phosphoryl groups which form strong bonds with Li^+, Na^+, and K^+ contribute much to the stability of the complexes. The relative contribution of the phosphoryl groups into the stability of the complexes decreases in the order $\mathrm{Li}^+ > \mathrm{Na}^+ > \mathrm{K}^+$ due to the equalization of the cation bond lengths with the phosphoryl and ether oxygen atoms and increase of the number of ether oxygens. Unfortunately, we failed to isolate crystalline alkali metal complexes of podands $\mathbf{L}^n$. It can also be suggested that in going from Li^+ to Cs^+ the contributions of the phosphoryl and ether oxygen atoms in the stability of the complexes, too, equalize, and the stability constants gradually increase with increasing number of coordinating centers.

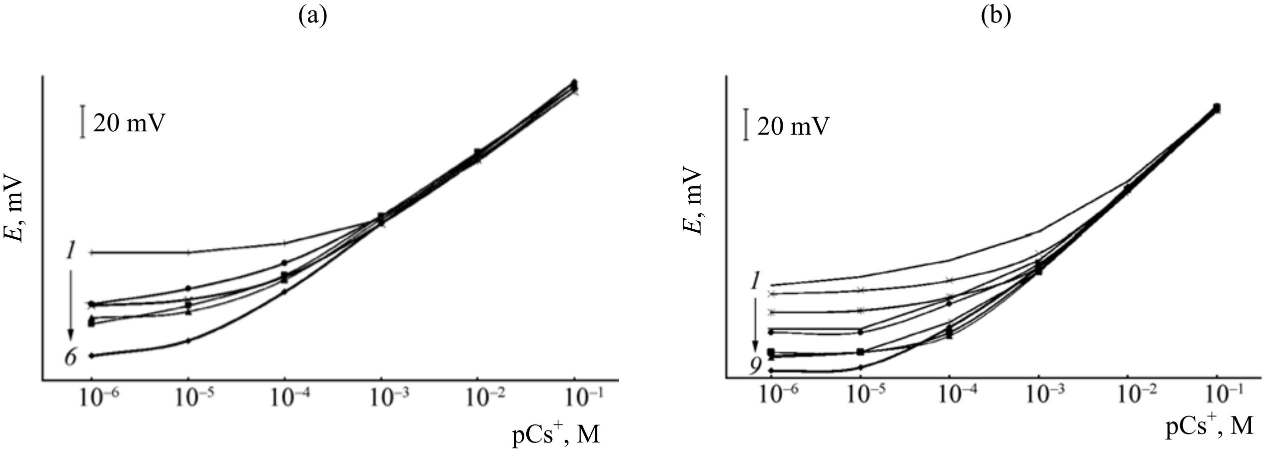


Fig. 2. Electrode characteristics of cesium-selective electrodes on the basis of podands (a) $\mathbf{L}^2$ and (b) $\mathbf{L}^5$ with a dibutyl phthalate plasticizer and a potassium tetrakis(4-chlorophenyl)borate lipophilic additive (50% with respect to the electrode-active component) in the presence of some single- and double-charged ions. a: (*1*) Rb^+, (*2*) Ca^{2+}, (*3*) Mg^{2+}, (*4*) Na^+, (*5*) Li^+, and (*6*) Cs^+; b: (*1*) Ba^{2+}, (*2*) Rb^+, (*3*) K^+, (*4*) Sr^{2+}, (*5*) Ca^{2+}, (*6*) Li^+, (*7*) Mg^{2+}, (*8*) Na^+, and (*9*) Cs^+.

Table 2. Electrode characteristics of the Cs^+-selective electrodes on the basis of podands L^n (n = 0–3, 5)

Podand	Linear range of the electrode function, M	Slope of the electrode function, mB/pCs^+	Detection limit, M
$\mathbf{L^0}$	10^{-4}–10^{-1}	54±1	6.0×10^{-4}
$\mathbf{L^1}$	10^{-4}–10^{-1}	55±1	3.4×10^{-4}
$\mathbf{L^2}$	10^{-4}–10^{-1}	51±1	7.6×10^{-5}
$\mathbf{L^3}$	10^{-4}–10^{-1}	52±1	4.0×10^{-5}
$\mathbf{L^5}$	10^{-4}–10^{-1}	50±1	5.0×10^{-5}

The crystals of 1,3-bis(diphenylphosphoryl)-2-oxapropane ($\mathbf{L^0}$) suitable of X-ray diffraction (XRD) analysis were obtained by recrystallization from a 1 : 1 benzene–hexane mixture. The general view of the molecule of podand $\mathbf{L^0}$ in crystal is shown in Fig. 3. The principal crystal data, experimental details, and structure refinement parameters are listed in Table 3. The central fragment O^1–P^1–C^{25}–O^3–C^{26}–P^2–O^2 is flattened; the rms deviation of the seven atoms from the mean plane is 0.092 Å. All bonds in the fragment have a trans configuration. The C^1–C^6 and C^{19}–C^{24} phenyl ring planes form a dihedral angle in 22.7°. The other dihedral angles between phenyl ring planes are 72.5°–81.9°.

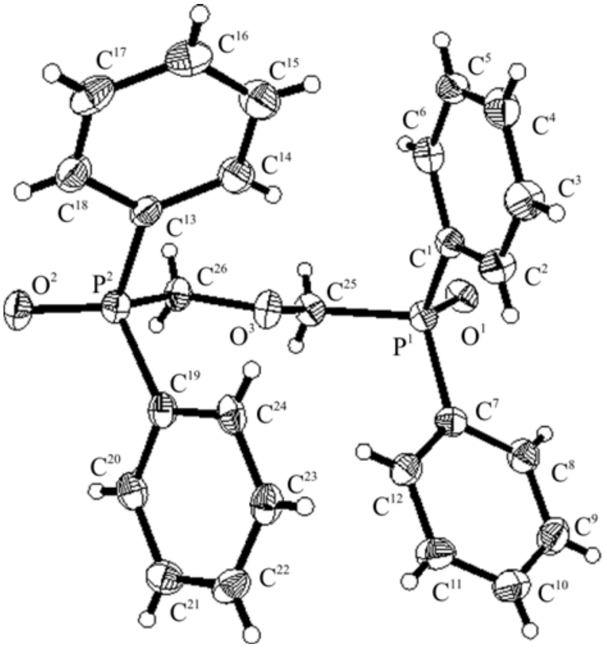


Fig. 3. General view of the molecule of 1,3-bis(diphenylphosphoryl)-2-oxapropane ($\mathbf{L^0}$) in a crystal (thermal ellipsoids are given at a 50% probability level).

The molecule of podand $\mathbf{L^0}$ in an open configuration can form a bridge between metal atoms. On the other hand, this molecule can also act as a chelating ligand similarly to podand $\mathbf{L^1}$ with a longer ethylene glycol chain in a crystal of $[Nd_2(NO_3)_6L^1_3]$, where it fulfills both bridging and chelating functions [16].

The bond lengths and bond angles in the molecule of podand $\mathbf{L^0}$ are close to standard values. The lengths of analogous bonds P^1=O^1 and P^2=O^2 [1.484(2) and 1.479(2) Å], as well as O^3–C^{25} and O^3–C^{26} [1.422(3) and 1.421(3) Å] are equal within the experimental error; the $C^{25}O^3C^{26}$ bonds is 112.6(2)°.

The ether O^3 atoms forms two weak intramolecular C–H···O hydrogen bond, and the phosphoryl O^1 atom forms two intramolecular hydrogen bonds (Table 4), one of which joins the molecules into centrosymmetric dimers, and the other joins the dimers into chains. The O^2 atom of the other phosphoryl group is involved in a weaker, directed binding with the phenyl ring of the neighboring chain.

Thus, we developed a fairly facile synthesis of phosphoryl-substituted podands $Ph_2P(O)CH_2O(CH_2CH_2O)_nCH_2P(O)Ph_2$ and thus made these compounds more accessible. The stability constants of the complexes of the synthesized podands with alkali metal 2,4-dinitrophenolates were determined. It was shown that the plasticized polymer membranes of ion-selective electrodes podands $\mathbf{L}^n$ (n = 0–4) as an active component are selective to the cesium cation. The crystal structure of 1,3-bis(diphenylphosphoryl)-2-oxapropane was established by XRD analysis.

EXPERIMENTAL

The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker CXP-200 spectrometer against TMS and 85% H_3PO_4, respectively. The melting points were measured on a Boetius PHMK 05 hot stage. Syntheses with $CsCO_3$ were performed under dry argon. Column chromatography was performed on Silica L (100–160 μm), eluent chloroform.

1,3-Bis(diphenylphosphoryl)-2-oxapropane ($\mathbf{L^0}$). (Diphenylphosphoryl)methanol, 6.0 g (26.0 mmol), and 10.0 g (26.0 mmol) of (diphenylphosphoryl)methyl *p*-toluenesulfonate were added to a suspension of 8.4 g (26.0 mmol) of finely ground anhydrous Cs_2CO_3 in 30 mL of anhydrous dioxane [17]. The mixture was stirred under reflux for 10 h and evaporated in a vacuum. The residue was mixed with

Table 3. Principal crystal data, experiment details, and structure refinement parameters for podand $\mathbf{L}^0$

Parameter	Value	Parameter	Value
Formula	$C_{26}H_{24}O_3P_2$	d_{calc}, g/cm^3	1.344
M	446.39	μ_{Mo}, mm^{-1}	0.223
T, K	150(2)	$F(000)$	936
λ, Å	0.71073	Crystal dimensions, mm	0.14×0.04×0.02
Crystal system	Monoclinic	T_{min}, T_{max}	0.6143, 0.7452
Space group	$P2_1/n$	θ range, deg	2.103–25.464
Z	4	Number of reflections: Measured unique (N) [R_{int}] with $I > 2\sigma(I)$ (N_0)	 18417 4094 [0.1077] 2531
a, Å	11.0924(12)	Number of refined parameters	352
b, Å	11.8590(13)	R_1, wR_2 at N_0	0.0482, 0.0829
c, Å	17.2761(19)	R_1, wR_2 at N	0.1004, 0.0984
β, deg	103.919(2)	S	1.003
V, Å^3	2205.8(3)	$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	0.268/–0.264

Table 4. C–H···O interactions in the crystal of podand $\mathbf{L}^0$

C–H···O	Symmetry transformations of the O atom	d, Å			CHO angle, deg
		C–H	H···O	C···O	
$C^{12}–H^{12}···O^3$	x, y, z	0.94(3)	2.59(3)	3.269(4)	130(2)
$C^{14}–H^{14}···O^3$	x, y, z	0.94(3)	2.57(3)	3.252(4)	130(2)
$C^{21}–H^{21}···O^1$	$–x, –y, –z + 1$	1.01(3)	2.41(3)	3.203(4)	135(2)
$C^{22}–H^{22}···O^1$	$x – 0.5, –y + 0.5, z – 0.5$	0.95(3)	2.50(3)	3.238(4)	135(2)
$C^5–H^5···O^2$	$–x + 1, –y, –z + 1$	0.97(3)	2.68(3)	3.366(4)	128(2)

75 mL of a double dilute HCl, and the mixture was extracted with $CHCl_3$ (5×50 mL). The extract was washed with a double dilute HCl (3×50 mL) and water (3×50 mL), and the solvent was removed in a vacuum. The residue was recrystallized from benzene–hexane (1 : 1). Yield 85%, mp 134–136°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.50 d (4H, CH_2P, $^2J_{HH}$ = 7.5 Hz), 7.33–7.75 m (20H, Ar-H). ^{31}P NMR spectrum ($CDCl_3$): δ_P 27.50 ppm. Found, %: C 69.70, 69.90; H 5.00, 4.90; P 13.40, 13.60. $C_{26}H_{24}O_3P_2$. Calculated, %: C 70.00; H 5.40; P 13.90.

Podands $\mathbf{L}^1$–$\mathbf{L}^3$ were synthesized as described in [5].

1,15-Bis(diphenylphosphoryl)-2,5,8,11,14-pentaoxapentadecane ($\mathbf{L}^4$). (Diphenylphosphoryl)methanol, 100.0 mmol, and 50.0 mmol of tetraethylene glycol dichloride were added to a suspension of 100.0 mmol of a finely ground anhydrous Cs_2CO_3 in 80 mL of anhydrous dioxane. The mixture was stirred under reflux for 8 h and evaporated in a vacuum. The residue was mixed with 100 mL of a double dilute HCl, and the mixture was extracted with $CHCl_3$ (3×75 mL). The extract was washed with a double dilute HCl (5×50 mL) and water (5×50 mL) and the solvent was evaporated in a vacuum. The residue was chromatographed on a silica column and recrystallized from ethyl methyl ketone. Yield 70%, oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.40–3.74 m (16H, CH_2CH_2O), 4.34 d (4H, CH_2P, $^2J_{HH}$ = 7.0 Hz), 7.41 m (12H, Ar-H), 7.80 m (8H, Ar-$\underline{H}$). ^{31}P NMR spectrum ($CDCl_3$): δ_P

27.97 ppm. Found, %: C 65.10, 65.40; H 6.30, 6.20; P 9.90, 9.70. $C_{34}H_{40}O_7P_2$. Calculated, %: C 65.60; H 6.50; P 10.00.

1,18-Bis(diphenylphosphoryl)-2,5,8,11,14,17-hexaoxaoctadecane (L^5) was synthesized in a similar way. Yield 71%, oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.48–3.80 m (20H, CH_2CH_2O), 4.38 d (4H, CH_2P, $^2J_{HH}$ = 7.0 Hz), 7.48 m (12H, Ar-H), 7.85 m (8H, Ar-H). ^{31}P NMR spectrum ($CDCl_3$): δ_P 27.94 ppm. Found, %: C 64.50, 64.60; H 6.50, 6.70; P 9.00, 9.80. $C_{36}H_{44}O_8P_2$. Calculated, %: C 64.90; H 6.70; P 9.30.

1,21-Bis(diphenylphosphoryl)-2,5,8,11,14,17,20-heptaoxaicosan (L^6) was synthesized in a similar way. Yield 77%, oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.47–3.75 m (24H, CH_2CH_2O), 4.35 d (4H, CH_2P, $^2J_{HH}$ = 7.5 Hz), 7.48 m (12H, Ar-H), 7.85 m (8H, Ar-H). ^{31}P NMR spectrum ($CDCl_3$): δ_P 27.93. Found, %: C 64.0; H 6.6; P 8.6. $C_{38}H_{48}O_9P_2$. Calculated, %: C 63.9; H 6.7; P 8.7.

Conductometric measurements were performed in THF–$CHCl_3$ (4 : 1, v/v) by the procedure described in [18]. Alkali metal 2,4-dinitrophenolates were used as salts. The random error (+2*s*, where *s* is the rms deviation) in the log *K* values for the complexes of the ligands with alkali metal cations was less than +0.1 log units. The concentrations of ionogenic impurities in the ligands were controlled by conductometry.

Ionometric measurements. The plasticized polymer membranes for the ion-selective electrodes containing podands $\mathbf{L}^n$ (n = 0–4) as active components were prepared as described in [19]. A solution of podand $\mathbf{L}^n$ in an organic solvent (plasticizer) was added to a solution of polyvinyl chloride in cyclohexanone. The amounts of the starting materials were chosen so that to obtain the desired polymer composition. The membranes contained the same compositions, wt %: active component 1–2%, polyvinyl chloride 30–33%, plasticizer 65–69%, and lipophilic additive [potassium tetrakis(4-chlorophenyl)borate] 0–2%. The plasticizers were dibutyl phthalate or *ortho*-nitrophenyl octyl ether. The content of the lipophilic additive was varied from 0 to 100% with respect to the electrode-active component.

The quantitative and qualitative electroanalytical parameters of the ion-selective electrode membranes were obtained using the following galvanic circuit: Ag, AgCl/KCl (1 M)/test soltion /membrane/internal filling solution/AgCl, Ag.

The emf values were measured on a Radelkis OP-300 pH ionometer. The reference electrode was a Radelkis OP-0820P silver chloride electrode. The electroanalytical parameters of the membrane were determined, according to the IUPAC recommendations, at pH 5–7 [20]. The potentiometric selectivity coefficient were determined in mixed and in individual solutions [21].

The electrode functions were measured in aqueous solutions of $CsNO_3$ with concentrations of 1×10^{-6}–1×10^{-1} M. Dibutyl phthalate or *o*-nitrophenyl octyl ether were used plasticizers and potassium tetrakis(4-chlorophenyl)borate (50% with respect to the electrode-active component) as a lipophilic additive. The detection limits of the membranes, which differed from other only by the nature of the additive, were within one order of magnitude.

X-ray diffraction study. The XRD pattern of the crystal of podand $\mathbf{L^0}$ was obtained on a Bruker APEX-II CCD automated diffractometer (MoK_α, graphite monochromator, ω scanning) at the Center for Collective Use, Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences. The structure was solved by a direct method. Absorption was included applied empirically using equivalent reflections. All hydrogen atoms were located by Fourier difference synthesis. The nonhydrogen atoms were refined by least squares on F^2_{hkl} with anisotropic thermal parameters. The coordinates of H atoms were refined independently, the isotropic thermal parameters U(H) were set at $1.2U_{\text{equiv}}$(C).

Data collection and processing were performed using APEX2, SAINT, and SADABS [22]. The structure was solved using SIR-92 [23] and refined using SHELXL-2014/7 [24]. The resulting crystal data were deposited in the Cambridge structural database (CCDC 1557290).

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