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Modified Methods to Synthesize of 1,8-Bis[2-(diphenylphosphoryl)phenoxy]-3,6-dioxaoctane (L). Crystal Structure and Vibration Spectra of [LiL]ClO₄·2C₆H₆

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Abstract—Modified methods to synthesize, 1,8-bis[2-diphenylphosphoryl)phenoxy]-3,6-dioxaoctane phosphoryl podand (L), an effective complexing agent for the lithium cation, is reported. The possibility to use the phase-transfer catalysis and microwave irradiation is shown. The crystal structure of coordination complex $[LiL]ClO_4 \cdot 2C_6H_6$ is determined by X-ray diffraction analysis.

Keywords: synthesis of phosphoryl podands, IR and NMR spectroscopy, crystallography, lithium coordination, complex formation

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Lithium compounds are used as components of compact energy sources [1]; metal lithium is used as a coolant in nuclear reactors, and isotope ⁶Li is the only industrial source of tritium which is necessary for thermonuclear energetics. Lithium salts are used in psychiatry for reductive therapy of manic states and prevention of bipolar affective (manic-depressive) disorders [2]. Organic coordination compounds which are able to effectively and selectively bind the Li⁺ cation are used for its analytical determination in technological and biological solutions and for practical recovery and purification of lithium salts from

industrial solutions. However, only few complexing organic compounds for the effective binding of lithium cation are known. As a rule, they are crown ethers with the cavity of small radius [3] and phosphoryl podands; among the latter the most interesting are oligoethylene glycol diphenyl ethers *ortho*-substituted with diphenyl-phosphoryl I [4] or diphenylphosphorylmethyl groups II [5] (Scheme 1).

The plot of stability constant logarithms of M⁺L complexes of phosphoryl podand I and II with lithium 2,4-dinitrophenolate (log $K_{\text{Li+}}$) in THF–chloroform





Fig. 1. Plot of the stability constant logarithms of complexes M^+L of phosphoryl podands **I**, **II** with lithium 2,4-dinitrophenolate in THF–chloroform (4 : 1) mixtures vs the number of ethylene glycol units *n*.

(4 : 1, vol) mixtures vs the number of the ethylene glycol units (*n*) obtained earlier by conductometry [4, 5] is given in Fig. 1.

The data of the plot show that triethylene glycol derivatives of **I** and **II** (n = 3) (L and L¹, respectively), exhibit the maximum ability to bind lithium cation. The logarithms of the stability constants measured under the same conditions for the the lithium complexes of phosphoryl podand L (log *K* 7.0) and its close structural analogue L¹ (log *K* 6.7) are higher than those for the known crown ethers (12C4, 15C5, 18C6, B18C6, and DB18C6) [4, 5].

For the first time, phosphoryl podand L was synthesized by the reaction of sodium 2-diphenylphosphoryl phenolate with triethylene glycol ditosylate in boiling dioxane [6] or DMF [7]. Podand L^1 was prepared by the analogous reaction of sodium diphenylphosphorylmethyl phenolate with triethylene glycol ditosylate in dioxane [8]. Anhydrous dioxane appeared to be the universal solvent for the synthesis of ligands L and L^1 [9]. In the exaples mentioned above the corresponding phenolates were synthesized in a separate step [8, 9].

In the present work, alkylation of 2-(diphenylphosphoryl)phenol with ditosylates and more synthetically accessible polyethylene glycol dichlorides was investigated under various reaction conditions. In order to optimize the method to synthesize of podand L, the preliminary preparation of sodium 2-(diphenylphosphoryl)phenolate was excluded; the latter was obtained *in situ* by adding NaH (as a suspension in vaseline oil) to a solution of 2-(diphenylphosphoryl)phenol in dioxane. When reactive triethylene glycol ditosylate was used, the yield of phosphoryl podand L reached 80% (Scheme 2, method a).

The possibility to prepare podand L using phasetransfer catalysis was studied. The alkylation of 2-(diphenylphosphoryl)phenol with 1,8-dichloro-3,6dioxaoctane in a two-phase system (40% aqueous solution of NaOH, toluene, 16 h, 100°C) in the presence of tetrabutyl-ammonium bromide (TBAB) afforded compound L in 51% yield; in the absence of TBAB the yield was equal to 48%. Apparently, compound L formed at the initial stage of synthesis is able to act as a phase-transfer catalyst. After the



(*a*): NaH, Ts(OCH₂CH₂)₃OTs, dioxane, 100°C, 8 h, 80%; (*b*): 40% NaOH, toluene, Ts(OCH₂CH₂)₃OTs,TBAB, 100°C, 16 h, 48–51%; (*c*): NaOH_{solid}, dioxane, Cl(CH₂CH₂O)₂CH₂CH₂Cl, 100°C, 16 h, 84%; (*d*): Cs₂CO_{3solid}, dioxane, Cl(CH₂CH₂O)₂· CH₂CH₂Cl, 100°C, 16 h, 94%.



reaction was completed, the signals of the starting 2-(diphenylphosphoryl)phenol and the target L product were registered in the ³¹P NMR spectrum of the reaction mixture. The decrease of the product yield is probably caused by the concurrent hydrolysis of 1,8dichloro-3,6-dioxaoctane. The application of an-hydrous two-phase systems appeared to be more effecttive. Thus, alkylation of 2-(diphenylphosphoryl)phenol with 1,8-dichloro-3,6-dioxaoctane in a two-phase system under anhydrous conditions (NaOH_{solid}, anhydrous dioxane, vigorous stirring, 12 h, 100°C) provided podand L in 84% yield. The use of phasetransfer system containing Cs₂CO_{3solid} and anhydrous dioxane allows one to increase the yield of the target product to 94%.

The comparison of the convection and microwave heating of the reaction mixture showed that in the procedures of 2-(diphenylphosphoryl)phenol alkylation with both triethylene glycol ditosylate and 1,8dichloro-3,6-dioxaoctane, the yield of compound L did not depend on the heating, but the microwave irradiation reduced the reaction time to 0.4–0.6 h. The microwave synthesis was performed in hermetically closed 10 mL ampoules, as well as in 75–100 mL glass flasks charged with significantly larger amounts of the reagents.

In order to find the cause of the high stability constant of phosphoryl podand L with respect to the Li^+ cation, single crystals of [LiL]ClO₄·2C₆H₆ were grown and their structure was investigated by the X-ray diffraction analysis.

According to the XRD data, the $[LiL]^+$ cation is located on the two-fold rotation axis (Fig. 2). All six oxygen atoms of ligand L are included in the Li environment. In accord with different electron donating abilities of the phosphoryl (O^1) , ether (O^3) , and anisole (O^2) oxygen atoms, the lengths of the Li–O bonds are significantly different [1.865(4), 2.115(5), and 2.639(2) Å, respectively]. The polyhedron of the Li atom has an irregular shape which can be described as a distorted flattened tetrahedron, whose O¹O^{1a}O³ and O¹O^{1a}O^{3a} faces are centered by atoms O² and O^{2a}. respectively. The dihedral angle between the Li¹O¹O^{1a} and Li¹O³O^{3a} planes which characterizes the flattening of the tetrahedron, is equal to 64.4°. The positions of the perchlorate anion are located on two crystallographically independent four-fold axes. The Cl¹ atom occupies completely a position on the axis with coordinates 1/2 1/2 z, and the general positions of the



Fig. 2. General view of complex cation $[LiL]^+$ (for the terminal phenyl rings, only the carbon atoms connected with the phosphorus atoms are shown).

 O^4 and O^5 oxygen atoms bound to it are half-occupied. The other part of ClO_4^- anion is disordered around the 00*z* axis over three closely located positions $(Cl^2O^6O^7O^8O^9, Cl^3O^{10}O^{11}O^{12}O^{13}, and Cl^4O^{14}O^{15}O^{16}O^{17})$ with the occupancy ratio 0.125 : 0.050 : 0.075.

In the structure, the complex cations recur at halftranslations along axes 2. Anions ClO₄ and benzene molecules are located in the cavities of the loose packing. Taking into account that in the structure the $Cl^{1}O_{4}^{-}$ anion can adopt two orientations, it is impossible to describe the crystal topology unambiguously. In the case that the anion retains its orientation in a layer, perpendicular to the z axis, the C–H···O hydrogen bonds between cations $[LiL]^+$ and anions $Cl^1O_4^-$ form chains running (depending on the anion orientation) along the x or y axis (Table 1). The layers of x- and y-chains can alternate arbitrarily. With the $Cl^1O_4^-$ anion disordered over the structure, only fragments of chains are formed. Some of the benzene molecules $(C^{22}-C^{27})$ form weak hydrogen bonds with the $Cl^4O_4^-$ anion.

The assignment of the main vibration frequencies in the IR spectrum of podand L and complex $[LiL]ClO_4$.

Symmetry *d*, Å DHA, D-H···A transformation deg Н…А D···A for atom A C^{11} - H^{11A} ···O⁴ y, 1-x, z2.37 3.212(7) 148 C^{12} - H^{12A} -... O^5 y, 1-x, z2.29 3.125(6) 147 $C^{25}-H^{25A}-O^{14}$ -y, x, z2.54 3.272 134 $C^{26}-H^{26A}-O^{16}$ x, -y, 0.5 + z2.36 3.155 141

 $2C_6H_6$ (Table 2) was done based on the structural and spectral investigations [10-12].

Compared to the spectrum of podand L, in the IR spectrum of $[LiL]\hat{C}IO_4 \cdot 2C_6H_6$ v(P=O) frequency (1180 cm^{-1}) is almost the same as in the spectrum of podand L (1179 cm⁻¹), and the band v(Ph–O) band is shifted to the high-frequency region by 11 cm⁻¹. A different alteration of frequencies was observed for complexes of lithium with podand L^{1} [12]: the v(P=O) was increased by $5-7 \text{ cm}^{-1}$ and the position of the v (Ph-O) band remained unchanged. The low-frequency region of the spectrum includes the vibrations that depend on the conformation of the ethylene glycol units {1090–1120 cm⁻¹ [$v_{as}(COC)$], 1000–800 cm⁻¹ $[v(CO), \rho(CH_2), v(CC)]$ or on the mutual orientation of the benzene rings $\{800-700 \text{ cm}^{-1} [\delta(\text{Ph})], \sim 500 \text{ cm}^{-1}, \}$ $[\delta(PhPO), \delta(CPO)]$ [12]. This range of the IR spectrum of podand L contains two bands: : the intense band near 1120 cm^{-1} due to vibrations of the benzene rings connected with the phosphorus atom and the medium-intensity band near 1102 cm⁻¹ due to the $v_{as}(COC)$ vibrations. In the IR spectrum of [LiL]ClO₄· $2C_6H_6$, the intense broad band of the stretching vibrations of the ClO_4^- anion appears near 1095 cm⁻¹. In the IR spectrum of $[LiL]ClO_4 \cdot 2C_6H_6$, the number of bands in the range 1000–800 cm⁻¹ is the same as in the spectrum of starting podand L, but the ratio of their intensities changes.

Relatively significant distinctions between the spectra caused by the conformational rebuilding of the podand are observed only in the region $550-500 \text{ cm}^{-1}$, where the absorption bands of bending vibrations of the terminal phosphoryl-containing groups appear. The absorption in this spectral range is significantly affected by the mutual position of the benzene rings at the phosphorus atom. Thus, in the IR spectrum of free podand L there are three strong bands (552, 526, and

1365 1350 1326 v(P-Ph)1287 1285 1272 v(PhO) 1245 1256 v(Ph=O)1179 1180 δ(Ph) 1140 1140 1120 1120 $v_{as}(COC), v(ClO_4)$ 1102 1095 δ(Ph) 1073 $v_s(COC) + v(CC)$ 1043 δ(Ph) 997 954 $v(CO) + v(CC) + \rho$ 954 (CH_2) 931 931 875 867 859 833 v(PC) 804 804 δ(Ph) 765 761 748 753 734 738 721 718 713 697 695 δ(COC), 619 $\delta(ClO_4)$ 624

L

1438

1377

 $[LiL]ClO_4 \cdot 2C_6H_6$

1446

1377

558, 533, 506, 480

517 cm⁻¹), whereas in the spectrum of [LiL]ClO₄. $2C_6H_6$ a strong band appears near 558 cm⁻¹ and three significantly weaker bands appear at 553, 506, and 480 cm^{-1} .

552, 526,

517

As noted above, the stability constant of the lithium complex with 1,8-bis[2-(diphenylphosphoryl)methylphenoxy]-3,6-dioxaoctane L^1 was somewhat lower than that of the complex with podand L. In the structure of [LiL¹]I·H₂O [10] the nearest tetrahedral environment of the lithium atom includes two phosphoryl and two ether oxygen atoms like in complex $[LiL]^+$, however, the anisole oxygen atoms were located at distances of 2.82 and 2.90 Å from Li, that is, too far to form Li-O bonds. In this complex the tetrahedron of the lithium atom is flattened to a smaller

Table 1. Geometric characteristics of theC-H-O hydrogen **Table 2.** Assignment of the main vibration frequencies (cm^{-1}) bonds in the structure of [LiL]ClO₄·2C₆H₆ in the IR spectra of podand L and complex [LiL]ClO₄·2C₆H₆

Assignment

v(P-Ph)

 $\omega(CH_2)$

δ(PhPO)

degree with respect to that in [LiL]⁺: the corresponding dihedral angle is 74.1°. Note that, the structure of [LiL¹]I·H₂O was determined with low accuracy. The Li–O bond lengths with both phosphoryl oxygen atoms are 1.8(1) Å; the bonds with ether oxygens are 2.28(7)and 2.32(7) Å. It is believed that, some weakening of the bonds between lithium and the oxygen atoms of the nearest environment and the loss of the bonds with the distant anisole oxygen atoms in complex $[LiL^1]^+$ as compared to $[LiL]^+$ results in the decrease of the stability constant. Apparently, ligand L is complementary to the Li⁺ cation to a greater degree than ligand L^1 . The ligand contour of L is shorter than that of L^1 by two CH_2 -groups. The smaller size of the pseudomacrocyclic cavity ensures the coordination of Li^+ by all six oxygen atoms. The comparison of the structure and stability of complexes $[LiL]^+$ and $[LiL^1]^+$ illustrates the principle of geometric conformity of the spatial arrangement of the coordination centers of an organic ligand and a cation and the principle of cooperativity of multiple interactions [13].

In the length of the coordination contour the phosphoryl podand L corresponds to the 18C6 crown ether. In the Cambridge database [14], the data on several lithium complexes with 18C6 are available, but only in two of them other ligands are not included in metal coordination. In compound [Li(18C6)]{Nd[(1,3- $Me_3Si_2Cp_2(SO_3CF_3)_2$ [15], the lengths of six Li–O lie within the range 2.056–2.216 Å. In [Li(18C6)]. [Li(THF)(18C6)][Fe(Pc)], where H₂Pc is phthalocyanine [16], two independent lithium atoms form five bonds each (2.039-2.108 and 2.057-2.475 Å) with oxygen atoms of 18C6 molecules. The environment of the latter atom includes additionally the oxygen atom of a THF molecule. The comparison of the length Li–O bond lengths demonstrates that the phosphoryl groups are responsible for greater stability of complex $[LiL]^+$ with respect to $[Li(18C6)]^+$.

EXPERIMENTAL

NMR spectra were registered on a Bruker-CPX-200 and a Bruker-DXP-200 (200 MHz) spectrometers with tetramethylsilane (¹H) or 85% H₃PO₄ (³¹P) as references. IR spectra were recorded on a Bruker Vertex 70 instrument in the range 4000–400 cm⁻¹ (suspensions in vaseline oil). TLC analysis was performed using Silufol plates, detecting with iodine vapor. Column chromatography was done with the use of silica gel of the L grade (100–160 µm), eluent CHCl₃ or a 20 : 1CHCl₃–*i*-PrOH mixture. Melting

Table 3. Crystallographic data and refinement parameters of the structure of $[LiL]ClO_4 \cdot 2C_6H_6$

Parameter	Value
Empirical formula	C ₅₄ H ₅₂ ClLiO ₁₀ P ₂
M	965.28
<i>Т,</i> К	150(2)
λ, Ε	Mo <i>K</i> _α , 0.71073
Space group, Z	<i>P4cc</i> , 4
<i>a</i> , Å	16.4877(6)
<i>c</i> , Å	17.9974(7)
<i>V</i> , Å ³	4892.5(4)
$d_{\rm calc}, {\rm g \ cm}^{-3}$	1.310
μ_{Mo}, mm^{-1}	0.203
T_{\min}, T_{\max}	0.6603, 0.7461
<i>F</i> (000)	2024
Crystal size, mm	$0.32 \times 0.20 \times 0.20$
θ range, deg	2.471-30.764
Reflections:	
collected	47487
independent (N) $[R_{int}]$	7599 [0.0369]
with $I > 2\sigma(I)$ (N_0)	6565
R_1 , wR_2 by N_0	0.0406, 0.1150
R_1 , wR_2 by N	0.0506, 0.1248
S	0.942
$\Delta \rho_{\rm max} / \Delta \rho_{\rm min}, e / {\rm \AA}^3$	0.315/-0.425

points were determined by means of a short Anschutz thermometer.

Focused microwave synthesis was performed on a DISCOVER type installation (CEM Corp., USA, maximal capacity 300 W, frequency 2450 MHz) equipped with temperature and pressure sensors.

1,8-Bis[2-(diphenylphosphoryl)phenoxy]-3,6-dioxaoctane (L). *a*. A suspension of 1.4 g (32.7 mmol) of NaH in vaseline oil was added to a suspension of 9.6 g (32.7 mmol) of 2-(diphenylphosphoryl)phenol [6] in 60 mL of anhydrous dioxane. The mixture was stirred for 0.5 h at 100°C. Then a solution 7.5 g (16.4 mmol) of triethylene glycol ditosylate in 100 mL of anhydrous dioxane was added, and the mixture was refluxed for 8 h. After removing the solvent 45 mL of dilute HCl (1 : 1) was added to the residue. The reaction product was extracted with CHCl₃ (3 × 35 mL). The extract was washed consecutively with 10% solution of KOH (2 × 30 mL), dilute HCl (2 × 30 mL), and water (3 × 35 mL) and evaporated in a vacuum. The residue was purified by chromatography. Yield 9.3 g (80%), mp 201–202°C (benzene–hexane, 1 : 1). ¹H NMR spectrum (CDCl₃), δ , ppm: 3.20 m (4H, CH₂CH₂O), 3.30 s (4H, CH₂CH₂O), 3.90 m (4H, CH₂CH₂O), 6.90 m (2H, ArH), 7.08 m (2H, ArH), 7.45 m (14H, ArH), 7.90 m (10H, ArH). ³¹P NMR spectrum (CDCl₃): δ_P 26.92 ppm. Found, %: C 72.20, 72.53; H 5.73, 5.79; P 8.51, 8.43. C₄₂H₄₀O₆P₂. Calculated, %: C 71.96; H 6.04; 8.63.

b. A mixture of 3.0 g (10.0 mmol) of 2-(diphenylphosphoryl)phenol, 0.02 g (0.06 mmol) of tetrabutylammonium bromide, 1.0 g (5.0 mmol) of 1,8-dichloro-3,6-dioxaoctane, 20 mL of toluene, and 10 mL of 40% solution of NaOH was stirred for 16 h at 100°C. Then the organic layer was separated, consecutively washed with 10% solution of NaOH (3×10 mL), dilute HCl (2×10 mL), and water (3×20 mL), and evaporated in a vacuum. To the residue 50 mL of water was added, and the mixture was extracted with 10% KOH solution (2×30 mL), dilute HCl (2×30 mL), and water (3×35 mL), and evaporated in a vacuum. The extract was washed with 10% KOH solution (2×30 mL), and evaporated in a vacuum. The residue spurified by column chromatography. Yield 1.8 g (51%).

c. A mixture of 3.0 g (10.0 mmol) of 2-(diphenylphosphoryl)phenol, 0.4 g (10 mmol) of crushed NaOH, and 25 mL of anhydrous dioxane was stirred for 0.5 h at 100°C. Then 0.93 g (5.0 mmol) of 1,8-dichloro-3,6dioxaoctane was added, and the mixture was stirred for 8 h for 100°C followed by evaporation in a vacuum. To the obtained residue 50 mL of CHCl₃ was added, and the resulting solution was consecutively washed with 30% NaOH solution (3 × 10 mL), dilute HCl (15 mL), and water (3 × 20 mL), and evaporated in a vacuum. To the residue 20 ml of diethyl ether was added, and the precipitate was filtered off. Yield 2.9 g (84%).

d. A mixture of 3.0 g (10.0 mmol) of 2-(diphenylphosphoryl)phenol, 3.3 g (10 mmol) of crushed Cs_2CO_3 , 0.93 g (5.0 mmol) of 1,8-dichloro-3,6dioxaoctane, and 30 mL of anhydrous dioxane was stirred for 8 h at 100°C. Then the mixture was poured into 70 mL of water, carefully acidified with conc. HCl to pH 1, and extracted with CHCl₃ (3 × 25 mL). The extract was consecutively washed with dilute HCl (2 × 20 mL), and water (3 × 20 mL), and evaporated in a vacuum. To the residue 25 mL of anhydrous diethyl ether was added and the precipitate was filtered off. The residue was purified by chromatography. Yield 3.3 g (94%).

e. A mixture of 3.2 g (10.1 mmol) of sodium 2-(diphenylphosphoryl) phenolate [10] and 0.93 g (5.0 mmol) of 1,8-dichloro-3,6-dioxaoctane in 7 mL of anhydrous dioxane was placed into the laboratory system with focused microwave heating in hermetically closed glass vial. The mixture was heated at 150°C (50 W) for 0.6 h. After cooling, the reaction mixture was poured into 50 mL of water, acidified with conc. HCl to pH 1, and extracted with CHCl₃ (3 × 30 mL). The extract was washed with dilute HCl (2 × 30 mL), and water (3 × 35 mL), and evaporated in a vacuum. To the residue 20 mL of diethyl ether was added, and the precipitate was filtered off. The filtrate was chromatographed. Yield 3.2 g (91%).

Complex [LiL]CIO₄·2C₆H₆. Preliminarity filtered solutions of lithium perchlorate in methanol and podand L in acetonitrile (M : L = 2 : 1) were mixed at room temperature and left standing in air approximately for 7 days. Crystalline precipitate was filtered off, washed with ethanol, and recrystallized from a CHCl₃-C₆H₆ (1 : 1) mixture.

Single-crystal X-ray diffraction study of [LiL] ClO₄· 2C₆H₆ was done at the Centre of Shared Equipment of the Kurnakov Institute of General and Inorganic Chemistry on a Bruker SMART APEX2 automated diffractometer. The structure was solved by the direct method followed by the calculation of the difference Fourier syntheses. The Cl^1 , O^4 , and O^5 atoms of the more regular perchlorate anion were refined in anisotropic approximation under geometric restraints. The Cl^2 , Cl^3 , and Cl^4 atoms of the perchlorate anion disordered over three positions were refined isotropically under the restraint of equal thermal parameters. Their bonds with the O atoms were accepted to be 1.41 Å. Because of the low site occupancy, atoms O⁶-O¹⁷ were refined within the riding model with thermal parameters exceeding the $U_{\rm iso}$ of the Cl atoms by a factor of 1.5. The nonhydrogen atoms of the complex cation $[LiL]^+$ and benzene molecule were refined anisotropically. The positions of the hydrogen atoms were calculated and refined within the riding model with $U_{iso} = 1.2U_{eq}$ of the corresponding C atom.

Reflections were collected and prosseced by the APEX2, SAINT, and SADABS software [16]. The structure was solved and refined by means of SIR-92 [17] and SHELXL-2013 [18] packages, respectively. The main crystallo-graphic data , parameters of data

collection, and characteristics of structure refinement are given in Table 3.

The crystallographic data have been deposited at the Cambridge Structural Database (CCDC no. 1026871).

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