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COORDINATION COMPOUNDS

Synthesis, Vibrational Spectra, and Crystal and Molecular Structure of 1,5-Bis[2-(dihydroxyphosphinyl)phenoxy]-3-oxapentane Dihydrate $[(HO)_2(O)P(C_6H_4)(OCH_2CH_2)_2O(C_6H_4)P(O)(OH)_2(H_2O)] \cdot H_2O$

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Abstract—A modified method of synthesis of a phosphoryl podand, 1,5-bis[2-(dihydroxyphosphinyl)phenoxy]-3-oxapentane (L), has been developed. The IR spectra of this podand and its dehydrate (L $[L \cdot H_2O] \cdot H_2O$ (**I**) have been studied, the structure of **I** has been determined by X-ray crystallography. The crystals are orthorhombic, $a = 9.4006(19)$ Å, $b = 25.494(5)$ Å, $c = 8.4264(17)$ Å, $V = 2019.5(7)$ Å^3, $Z = 4$, space group $Pna2_1$, $R = 0.0512$ for 3016 reflections with $I > 2\sigma(I)$. Compound **I** is a host–guest molecular complex. Phosphoryl podand L acts as a host molecule, and one of the water molecules ($H_2O(11)$) is a guest. This molecule forms one donor and one acceptor intramolecular hydrogen bond with hydroxyl groups of two phosphoryl groups (O(8)H(4) and O(3)H(2)) and combines them into an 18-membered macrocyclic ring, acting as a kind of "lock." The $H_2O(11)$ molecule forms a second donor intramolecular hydrogen bond with the O(5) ether atom. The neutral molecular complexes are linked by hydrogen bonds directly and through the second water molecule ($H_2O(10)$) into chains running along the *c* axis.

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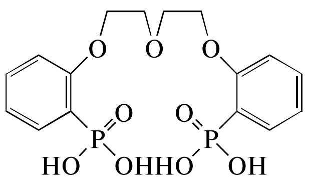
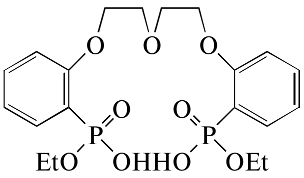
Systematic conductometric [1] and calorimetric [2, 3] studies of podands (acyclic crown ether analogues) with phosphoryl-containing terminal groups have shown that these compounds are efficient receptors for binding alkali metal cations. According to liquid extraction data, phosphoryl podands can be components of extraction systems for isolation and concentration of platinum from hydrochloric acid solutions [4], scandium from chloride solutions [5], and uranium and thorium from both chloride [6] and nitric acid solutions [7]. The can be used for extraction of gold traces [8] and lanthanide nitrates [9]. Phosphoryl podands are as good as crown ethers for binding of amine picrates. In addition, they can recognize primary amines in the presence of secondary and ternary amines. In these reactions, 3-oxapentane derivatives with three oxygen atoms in the polyether chain and rather conformationally rigid terminal groups—residues of *o*-phosphoryl-containing phenols—exhibit the best efficiency and selectivity. These molecules bind amino groups in the optimal way through two outer ether oxygen atoms and two most basic phosphoryl oxygen atoms [10].

The structures of molecular phosphoryl podands [11, 12] and their lithium [13], sodium [14], zinc and cadmium [15], and barium and mercury complexes [16] have been determined by IR spectroscopy and X-ray crystallography. In addition, penta- and hexavalent actinide complexes with phosphoryl-containing podands derived from triethylene glycol have been synthesized and structurally characterized [17]. Available data have demonstrated that the complexing ability of phosphoryl-containing podands with respect to alkali metal cations is mainly determined by the structure of the terminal moiety, which is consistent with the general terminal group concept [18]. Therefore, one of the methods of control of the efficiency and selectivity of phosphoryl-containing podands in different reactions is to change the structure of these terminal moieties. However, all above-mentioned studies have dealt with phosphine oxide derivatives, neutral phosphoryl podands, whereas acid-type podands—phosphonic acid derivatives—have been almost entirely ignored. Only some pyrocatechol derivatives [19] and 1,5-bis(dihydroxyphosphinyl)phenoxy-3-oxapentane (L) [20] have been studied.

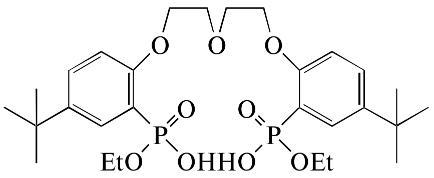


L

For the latter, the dissociation and stability constants of complexes with Ca^{2+}, Mg^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} cations [21]. It has been recently shown that 1,5-bis(hydroxyethoxyphosphinyl)phenoxy-3-oxapentane (L^1) and its 4,4'-di-*tert*-butyl analogue (L^2) are promising compounds for selective extraction of thorium(VI) in the presence of uranium(VI) and lanthanum(III) from nitric acid media and are of interest as component components of porous sorbents used for concentration, separation, and isolation of products of spent nuclear fuel treatment [22].



L^1

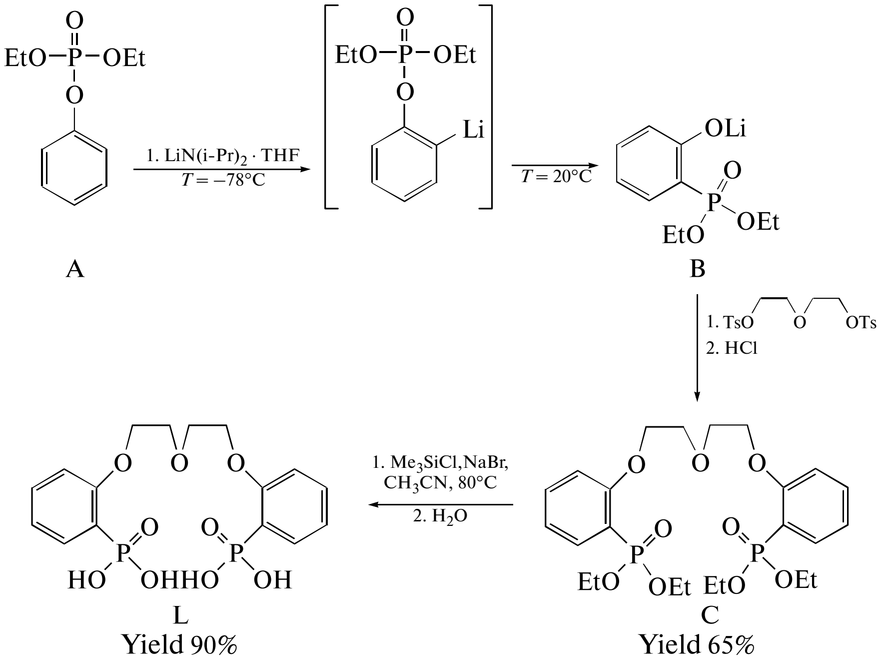


L^2

In the present paper, we describe a modified method of synthesis of compound L and preparation of its dihydrate $[L \cdot H_2O] \cdot H_2O$ (**I**) and report their IR and NMR spectra and results of X-ray crystallographic study.

EXPERIMENTAL

Synthesis of compounds L and C (Scheme 1) was carried out with the use of butyllithium in a dry argon atmosphere. For column chromatography, silica gel L (100–160 μm) and Chloroform as an eluent were used. Melting points were measured on a Boetius PHMK 05 microscope plate (uncorrected) and thermogravimetrically. Commercially available solvents were additionally purified by known methods.



Scheme 1.

1,5-Bis[2-diethoxyphosphinyl)phenoxy]-3-oxapentane (C). To a solution containing 1.11 g (0.011 mol) diisopropylamine in 25 mL of dry tetrahydrofuran (THF) cooled to –78°C (internal thermometer), 9.17 mL (0.011 mol) of 1.2 N *n*-butyllithium solution in hexane was added dropwise. The reaction mixture was stirred for 30 min at –78 ± 10°C, then a solution containing 2.30 g (0.01 mol) of phenyl diethyl phosphate (A) in 10 mL of dry THF was added, and the resulting mixture was stirred for 1 h at –78 ± 10°C. After that, the solution was heated to 20°C in 1 h and stirred for another 1 h. Then, 2.07 g (0.005 mol) of diethylene glycol ditosylate was added, the solution was heated and refluxed under stirring for 8 h, and the solvent was vacuum distilled off. Then, 50 mL of water was added to the residue, and the mixture was extracted with chloroform (3 × 30 mL). The extract was washed with water (3 × × 25 mL) and dried by sodium sulfate, and chloroform was removed under vacuum. The residue was applied to a column packed with silica gel L (100–160 μm). Chloroform and chloroform–isopropanol (20 : 1) were used for elution. The yield of compound C (viscous oil) was 1.72 g (65%).

For $C_{24}H_{36}O_9P_2$ anal. calcd. (%): C, 54.34; H, 6.84; P, 11.68.

Found (%): C, 54.22; H, 6.69; P, 11.28.

^1H NMR (δ, ppm, C_6D_6): 1.13 t, 12H, $4CH_3CH_2O$), 3.80–3.90 (m, 8H, $2OCH_2CH_2$), 4.13 (m, 8H, $4CH_3CH_2O$), 6.73–7.21 (m, 6H, Ar–H).

^{31}P NMR (δ, ppm, C_6D_6): 17.03.

1,5-Bis[2-(dihydroxyphosphinyl)phenoxy]-3-oxapentane (L). To a solution of 1.72 g (0.0032 mol) of compound *C* in 25 mL of dry acetonitrile, 2.00 g (0.019 mol) of freshly calcined sodium bromide and 2.17 g (0.020 mol) of trimethylchlorosilane were added. The resulting suspension was refluxed for 6 h, and the solvent was removed under vacuum. Then 30 mL of distilled water was added to the residue, and the mixture was allowed to stand at room temperature for 20 h. The precipitate was filtered off, washed on a filter with 50 mL of distilled water, and vacuum dried (4 h, 80°C, 10 mmHg). The yield of L was 1.34 g (90%), mp 208–213°C. The melting point of the analytical sample obtained by recrystallization from an alcohol–water (1 : 1) mixture and vacuum dried at 80°C was 212–213°C (lit.: 212–213°C [17]).

For $C_{16}H_{20}O_9P_2$ anal. calcd. (%): C, 45.94; H, 4.82; P, 14.81.

Found (%): C, 45.84; H, 4.58; P, 14.58.

^1H NMR (δ, ppm, DMSO): 3.92 (m, 4H, OCH_2CH_2), 4.18 (m, 4H, OCH_2CH_2) 7.04–7.68 (m, 8H, Ar–H), 5.96 (s, 4H, 4P–OH).

^{31}P NMR (δ, ppm): 12.30.

^{1}H and ^{31}P NMR spectra were recorded on a Bruker CXP-200 spectrometer. The ^1H and ^{31}P NMR chemical shifts were referenced to TMS (internal) and 85% H_3PO_4 (external), respectively.

Thermogravimetric studies were carried out on a TA Instruments Q-500 derivatograph in the temperature range 20–500°C in platinum crucibles at a heating rate of 5 K/min.

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

X-ray crystallography. Crystals of **I** were obtained by recrystallization for a 50% ethanol. Crystals of $C_{16}H_{24}O_{11}P_2$ (FW = 454.29) are orthorhombic, a = 9.4006(19) Å, b = 25.494(5) Å, c = 8.4264(17) Å, V = 2019.5(7) Å^3, ρ_{calc} = 1.494 g/cm^3, $\mu(MoK_\alpha)$ = 0.273 mm^{-1}, $F(000) = 952$, $Z = 4$, space group $Pna2_1$.

Experimental reflection intensities (4933 reflections, 3016 of them were unique, R(int) 0.0565) were collected at 150(2) K from a colorless crystal 0.25 × 0.20 × 0.10 mm in size on a Bruker SMART APEX II automated diffractometer (MoK_α, λ 0.71073 Å, graphite monochromator, ψ scan).Corrections for absorption were applied on the basis of measured intensities of equivalent reflections [23]. Reflections were collected in the index ranges $-9 \le h \le 10$, $-30 \le k \le 21$, $-7 \le l \le 9$ ($2.55° \le \theta \le 24.96°$; coverage on θ = 96.5%).

The structure was solved by direct methods (SHELXS-97 [24]) and refined by least-squares calculations on F^2 (SHELXL-97 [25]) in the full-matrix anisotropic approximation for all non-hydrogen atoms. The positions of the hydrogen atoms of both water molecules and two of the four hydroxyl groups at the phosphorus atoms were determined experimentally from difference electron density maps and refined isotropically. The other hydrogen atoms were introduced in geometrically calculated positions and refined as riding on their bonded carbon or oxygen atoms with isotropic temperature factors U_H equal to 1.2*U*C or 1.5*U*O.

The final residuals were $R1 = 0.0512$, $wR2 = 0.0835$, and GOOF = 0.964 for 2092 reflections with $I > 2\sigma(I)$; $R1 = 0.0846$ and $wR2 = 0.0934$ for all unique reflections. The total number of refined parameters was 287, the extinction coefficient was 0.0013(4), and the absolute structure parameter was 0.14(14). The $\Delta\rho_{max}$ and $\Delta\rho_{min}$ were 0.261 and –0.235 e A^{-3}, respectively.

The atomic coordinates and thermal parameters for structure **I** are summarized in Table 1, and bond lengths and angles are listed in Table 2.

The structural data for **I** were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 768236).

RESULTS AND DISCUSSION

An approach to the synthesis of phosphoryl podands is based on the Williamson reaction, the reaction of *ortho*-phosphorylated phenol phenolates with dihalide and ditosyl derivatives of ethylene glycols. Previously, L was obtained from *o*-diethoxyphosphinylphenol, which was converted into a sodium derivative by the reaction with sodium hydrate [20]. In the present work, we developed a scheme of synthesis of 1,5-bis(dihydroxyphosphinyl)phenoxy-3-oxapentane (L) bypassing the special stage of obtaining phenolate (Scheme 1). The initial compound was phenyl diethyl phosphate (A), which reacts with lithium diisopropylamide to give the lithium salt of *o*-diethoxyphosphinylphenol (B) [26]. The resulting salt was immediately used without isolation in the reaction with diethylene glycol ditosylate, which yields the intermediate compound tetraethyl diphosphonate (C).

It is worth noting that the use of the less "alkaline" lithium ion rather than the sodium cation and the replacement of dioxane with a boiling point of 100°C by low-boiling THF (64°C) have almost no effect on the reaction yield. The resulting ester (C), after purification by column chromatography, reacted with trimethylbromosilane (prepared in situ in the trimethylchlorsilane–sodium bromide–acetonitrile system) to give the corresponding tetrasilyl ether, which was hydrolyzed under mild conditions into tetrabasic diphospjonic acid L. The lack of separate stages of isolation of *o*-diethoxyphosphinylphenol and preparation of its phenolate as described in [20] considerably reduces the reaction time, simplifies the synthesis of L, and makes the product cheaper.

Recrystallization of L from an ethanol–water (1 : 1) mixture leads to the formation of its $[LH_2O] \cdot H_2O$ (**I**) with a melting point of 209°C.

Compound **I** is a neutral host–guest molecular complex [27], where L acts as a host and one of the water molecules is a guest (Fig. 1). The second water molecule of crystallization is involved only in hydrogen bonds between $[LH_2O]$ molecular complexes (Fig. 2).

In complex **I**, the guest molecule $H_2O(11)$ forms one donor and one acceptor intramolecular hydrogen bond with the O(8)H(4) and O(3)H(2) hydroxyl (bonds 7 and 2, Table 3) and links two ends of the podand chain to form three H rings—an 18-membered macrocyclic ring and two 11-membered (O(11)H(2)O(3)P(1)C(1)C(6)O(4)C(7)C(8)O(5)H(8) and O(11)H(7)O(8)P(2)C(16)C(11)O(6)C(10)C(9) O(5)H(8) rings—acting as a kind of "lock." The $H_2O(11)$ molecule forms a second donor intramolecular hydrogen bond with the O(5) ether atom (bond 8, Table 3).

Podand L in **I** has a C-like conformation with an approximate *m* plane passing through the central ether oxygen atom. Correspondingly, the two *gauche* O–CH_2–CH_2–O moieties of the diethylene glycol chain have opposite signs of torsion angles. The podand has a *gauche* conformation with respect to the C–C bonds and a *trans* conformation with respect to C–O (Table 4). Thus, the ethylene glycol chain is composed of two units with the same *TGT* conformation (beginning with the O(4) atom). Both phosphoryl oxygen atoms face point into the podand molecule, which favors their possible coordination to metal atoms.

Table 1. Atomic coordinates ($\times 10^4$, for H atoms, $\times 10^3$) and thermal parameters U_{eq}/U_{iso} (Å^2, $\times 10^3$) in structure **I***

Atom	x	y	z	U_{eq}/U_{iso}
P(1)	1690(1)	6185(1)	8223(2)	28(1)
P(2)	767(1)	3879(1)	8284(2)	26(1)
O(1)	658(4)	5996(1)	9422(4)	35(1)
O(2)	992(3)	6476(1)	6838(4)	37(1)
O(3)	2533(4)	5725(2)	7471(4)	33(1)
O(4)	3502(3)	6031(1)	10965(4)	38(1)
O(5)	3616(4)	5002(1)	12334(4)	36(1)
O(6)	2856(3)	3997(1)	10882(4)	35(1)
O(7)	−110(3)	4087(1)	9609(4)	31(1)
O(8)	1639(4)	4319(1)	7488(4)	31(1)
O(9)	−137(3)	3591(1)	7047(4)	35(1)
O(10)	10010(5)	4916(2)	5930(5)	43(1)
O(11)	3472(4)	5001(2)	9128(5)	33(1)
C(1)	2912(5)	6645(2)	9014(6)	28(1)
C(2)	3116(5)	7130(2)	8298(7)	33(1)
C(3)	4128(6)	7479(2)	8860(7)	41(2)
C(4)	4981(6)	7330(2)	10101(7)	41(2)
C(5)	4809(5)	6852(2)	10846(7)	37(1)
C(6)	3783(5)	6509(2)	10311(6)	31(1)
C(7)	4122(6)	5919(2)	12483(6)	41(2)
C(8)	3348(5)	5470(2)	13193(8)	39(1)
C(9)	3035(6)	4556(2)	13116(8)	42(1)
C(10)	3557(6)	4071(2)	12379(6)	45(2)
C(11)	2973(5)	3516(2)	10182(6)	29(1)
C(12)	3934(5)	3136(2)	10667(7)	38(1)
C(13)	3964(6)	2656(2)	9955(7)	40(2)
C(14)	3029(6)	2534(2)	8758(6)	39(2)
C(15)	2090(5)	2917(2)	8226(8)	33(1)
C(16)	2020(5)	3410(2)	8949(6)	25(1)
H(1)	73	626	616	55
H(2)	269(5)	546(2)	815(7)	46(16)
H(4)	114(8)	460(3)	683(8)	100(30)
H(5)	1006(8)	526(3)	539(9)	110(30)
H(6)	973(7)	466(3)	522(8)	90(30)
H(7)	275(8)	470(3)	870(8)	110(30)
H(8)	357(6)	502(2)	1011(7)	60(20)
H(3)	−22	377	625	52

* The coordinates of the hydrogen atoms involved in hydrogen bonds are given.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in structure **I**

Bond	*d*, Å	Bond	*d*, Å
P(1)–O(1)	1.481(3)	C(1)–C(2)	1.389(7)
P(1)–O(2)	1.531(3)	C(1)–C(6)	1.409(7)
P(1)–O(3)	1.549(4)	C(2)–C(3)	1.385(7)
P(1)–C(1)	1.772(5)	C(3)–C(4)	1.371(8)
P(2)–O(7)	1.486(4)	C(4)–C(5)	1.381(7)
P(2)–O(9)	1.532(3)	C(5)–C(6)	1.376(6)
P(2)–O(8)	1.543(3)	C(7)–C(8)	1.482(7)
P(2)–C(16)	1.770(5)	C(9)–C(10)	1.467(7)
O(4)–C(6)	1.364(6)	C(11)–C(12)	1.387(7)
O(4)–C(7)	1.435(6)	C(11)–C(16)	1.398(6)
O(5)–C(8)	1.419(6)	C(12)–C(13)	1.364(7)
O(5)–C(9)	1.423(6)	C(13)–C(14)	1.374(7)
O(6)–C(11)	1.366(5)	C(14)–C(15)	1.390(7)
O(6)–C(10)	1.435(6)	C(15)–C(16)	1.399(7)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)P(1)O(2)	113.4(2)	C(6)C(1)P(1)	120.4(4)
O(1)P(1)O(3)	111.7(2)	C(3)C(2)C(1)	121.2(6)
O(2)P(1)O(3)	105.9(2)	C(4)C(3)C(2)	119.0(5)
O(1)P(1)C(1)	112.5(2)	C(3)C(4)C(5)	121.5(5)
O(2)P(1)C(1)	104.1(2)	C(6)C(5)C(4)	119.6(5)
O(3)P(1)C(1)	108.8(2)	O(4)C(6)C(5)	124.8(5)
O(7)P(2)O(9)	112.03(18)	O(4)C(6)C(1)	114.8(4)
O(7)P(2)O(8)	111.18(19)	C(5)C(6)C(1)	120.4(5)
O(9)P(2)O(8)	110.40(19)	O(4)C(7)C(8)	108.3(4)
O(7)P(2)C(16)	111.9(2)	O(5)C(8)C(7)	110.9(5)
O(9)P(2)C(16)	105.1(2)	O(5)C(9)C(10)	110.3(5)
O(8)P(2)C(16)	105.9(2)	O(6)C(10)C(9)	109.3(5)
P(1)O(3)H(2)	114(3)	O(6)C(11)C(12)	123.5(5)
C(6)O(4)C(7)	117.4(4)	O(6)C(11)C(16)	116.3(4)
C(8)O(5)C(9)	111.6(4)	C(12)C(11)C(16)	120.2(5)
C(11)O(6)C(10)	117.5(4)	C(13)C(12)C(11)	120.7(5)
P(2)O(8)H(4)	120(4)	C(12)C(13)C(14)	120.8(5)
P(2)O(9)H(9C)	109.5	C(13)C(14)C(15)	119.0(5)
H(5)O(10)H(6)	110(6)	C(14)C(15)C(16)	121.4(6)
H(7)O(11)H(8)	117(5)	C(15)C(16)C(11)	117.8(5)
C(2)C(1)C(6)	118.3(5)	C(15)C(16)P(2)	120.0(4)
C(2)C(1)P(1)	121.1(4)	C(11)C(16)P(2)	122.2(4)

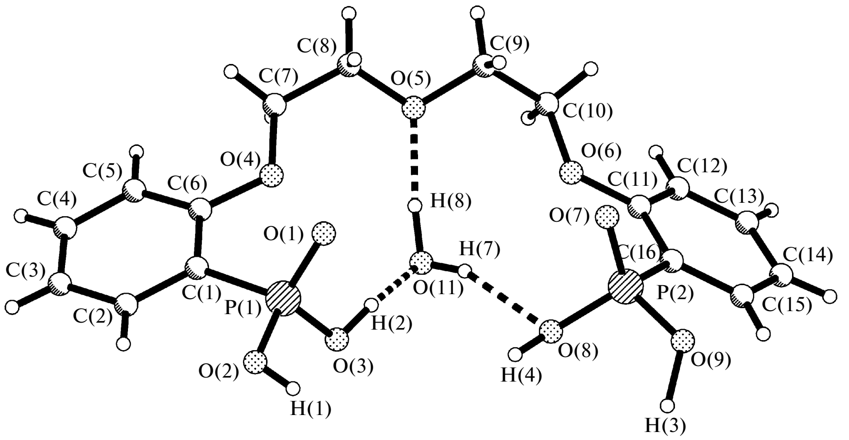


Fig. 1. Structure of the podand in structure **I**.

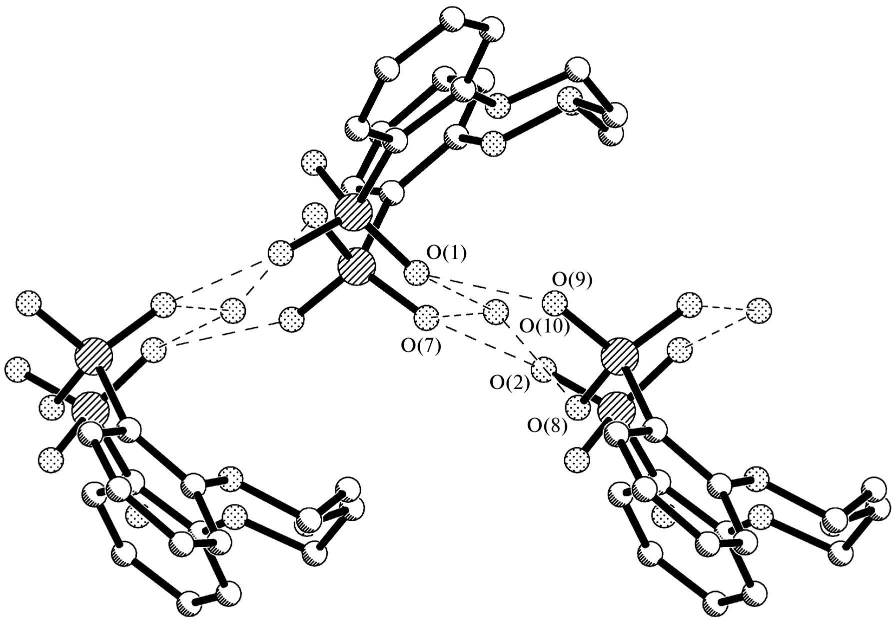


Fig. 2. A fragment of the chain of structure **I** along the *c* axis.

No information is currently available on the structures of podands or their complexes with terminal hydroxyl substituents in the phosphoryl groups. Only compounds with phenyl substituents at the phosphorus atoms have been studied. For example, the host–guest complex of 1,5-bis(diphenylphosphinyl)phenoxy-3-oxapentane (**II**) with *DL*-phenylglycine ethyl ester trifluoromethanesulfonate **II** · $H_3N^+CH(Ph)C(O)OEt$ · $F_3CSO_3^-$) (**III**) [28] has been studied [28]. The podands in **I** and **III** differ only in the substituents at the phosphorus atoms (two OH groups in **I** and two Ph rings in **III**). In **III**, the ammonium cation of *DL*-phenylglycine ethyl ester (guest) binds the phosphoryl groups of the podand through two N–H···O donor hydrogen bonds and occupies the position analogous to the water molecule position in **I**. The third donor bond of the ammonium cation also involves the ether oxygen atom of podand **II**. As in **I**, both phosphoryl oxygen atoms point into the podand molecule, which has a C-shaped conformation, pseudosymmetry plane *m*, and opposite signs of the O–CH_2–CH_2–O angles in the diethylene glycol chain.

The geometric parameters of phosphoryl podand L are close to common values. Both phosphorus atoms have a distorted tetrahedral coordination. The P=O and P–C bond lengths are equal to each other with 3σ (av. 1.483(4) and 1.771(5) Å, respectively). Their values are consistent with the corresponding distances for

Table 3. Geometries of hydrogen bonds in structure **I**

No.	D–H···A contact	Distance, Å			DHA angle, deg	Atom A coordinates
		D–H	H···A	D···A		
1	O(2)–H(1)···O(7)	0.82	1.69	2.506(4)	171	$-x, -y + 1, z - 1/2$
2	O(3)–H(2)···O(11)	0.91(5)	1.60(6)	2.477(5)	162(5)	x, y, z
3	O(8)–H(4)···O(10)	1.02(8)	1.54(8)	2.527(5)	164(7)	$x - 1, -y + 1, z$
4	O(9)–H(3)···O(1)	0.82	1.70	2.498(4)	164	$-x, -y + 1, z - 1/2$
5	O(10)–H(5)···O(7)	0.98(7)	1.80(7)	2.775(5)	174(7)	$-x + 1,-y + 1, z - 1/2$
6	O(10)–H(6)···O(1)	0.92(7)	1.84(7)	2.724(6)	159(6)	$-x + 1, -y + 1, z - 1/2$
7	O(11)–H(7)···O(8)	1.08(8)	1.76(8)	2.811(5)	163(5)	x, y, z
8	O(11)–H(8)···O(5)	0.84(6)	1.87(6)	2.704(5)	173(6)	x, y, z

the $Ph_3P=O$ modifications: 1.483(2)–1.494(2) and 1.787(2)–1.808(2) Å, respectively [29–31]. The P–OH bonds in L vary within the range 1.531(3)–1.549(4) Å (av. 1.539(3) Å). In the PO_3C tetrahedra, the OPC and OPO angles are within 104.1(2)°–112.5(2)° and 105.1(2)°–113.4(2)°, respectively.

The average bond lengths and bond angles of the OCH_2CH_2O moieties in the L molecule have common values: O–C(sp^3) 1.428(5), O–C(sp^2) 1.365(5), C(sp^3)–C(sp^3) 1.475(7) Å, C(sp^2)–O–C(sp^3) 117.4(4)°, C(sp^3)–O–C(sp^3) 111.6(4)°, O–C(sp^3)–C(sp^3) 109.7(5)°. The C(sp^3)–C(sp^3) bond lengths in **I** are considerably smaller than the common value (1.530(15) Å [32]), which is typical of podands and crown ethers [27]. The phenyl rings in the podand are at an angle of 43.5° to each other.

In the crystal of **I**, the neutral host–guest complexes are linked directly through intermolecular hydrogen bonds 1 and 4 (Table 3). Here, the acceptors are the O(1) and O(7) phosphoryl atoms, and the donors are the hydroxyl groups. The complexes are also combined by three hydrogen bonds involving the second water molecule $H_2O(10)$: two donor bonds (5 and 6) and one acceptor bond (3). Thus, the above intermolecular hydrogen bonds form a chain running along the *c* axis. Figure 2 shows a fragment of this chain, and Fig. 3 shows the projection of the structure along the *b* axis.

Table 4. Torsion angles in structure **I**

Angle	ω, deg
P(1)C(1)C(6)O(4)	−6.1
C(1)C(6)O(4)C(7)	−166.5
C(6)O(4)C(7)C(8)	162.5
O(4)(7)(8)O(5)	68.4
(7)C(8)O(5)C(9)	172.3
C(8)O(5)C(9)C(10)	−169.1
O(5)C(9)C(10)O(6)	−74.2
C(9)C(10)O(6)C(11)	−166.4
(10)O(6)C(11)C(16)	165.0
O(6)C(11)C(16)P(2)	1.9

In the course of our study, we recorded the IR spectra of L and compound **I** obtained by recrystallization of L from 50% ethanol. It turned out that, although the spectral pattern is retained and positions of some bands remain unaltered, there are rather significant differences caused by symmetry features of molecules of L and **I**. To interpret the IR spectra, we used the results of our previous works, where a comprehensive assignment of vibrational spectra and X-ray crystallographic data were reported for some neutral phosphoryl-containing podands and their complexes [12–16, 33].

The C–H and C–C stretching and bending vibrations of the benzene rings and methylene groups are in their typical frequency ranges, and the corresponding bands in the IR spectra of L and **I** have the same frequencies (Table 5). Below 1250 cm^{-1}, the vibrational spectra of L and **I** are considerably different. However, the stretching vibration frequency for the Ph–O bond adjacent to the ethylene glycol chain remains unaltered.

In the IR spectrum of L, the important analytical ν(P=O) frequency, determined by the electronegativity of the substituents at the phosphorus atom, is 1217 cm^{-1} (1195 cm^{-1} for $Ph_3P=O$, $CH_3OPhP(O)Ph_2$, and neutral phosphoryl-containing podands [12–16]).

The IR spectra of phosphoryl-containing podands below 1125 cm^{-1} show absorption bands at frequencies depending either on the conformation of ethylene glycol units (ν_{as}(COC) = 1090–1125, ρ(CH_2) = 800–1000 cm^{-1}) or, as demonstrated in [14], on the mutual orientation of the benzene rings at the phosphorus atom (δ(Ph), δ(PhPO) 400–500 cm^{-1}). The IR spectrum of **II** with a known structure [33], which is structurally very similar to L, shows two bands at 1120 and 1104 cm^{-1} in the ν_{as}(COC) region. Inasmuch as X-ray crystallography shows that the ethylene glycol chain in **II** is composed of only *TGT* units, the band at ~1104 cm^{-1} is due to ν_{as}(COC) of two *TGT*

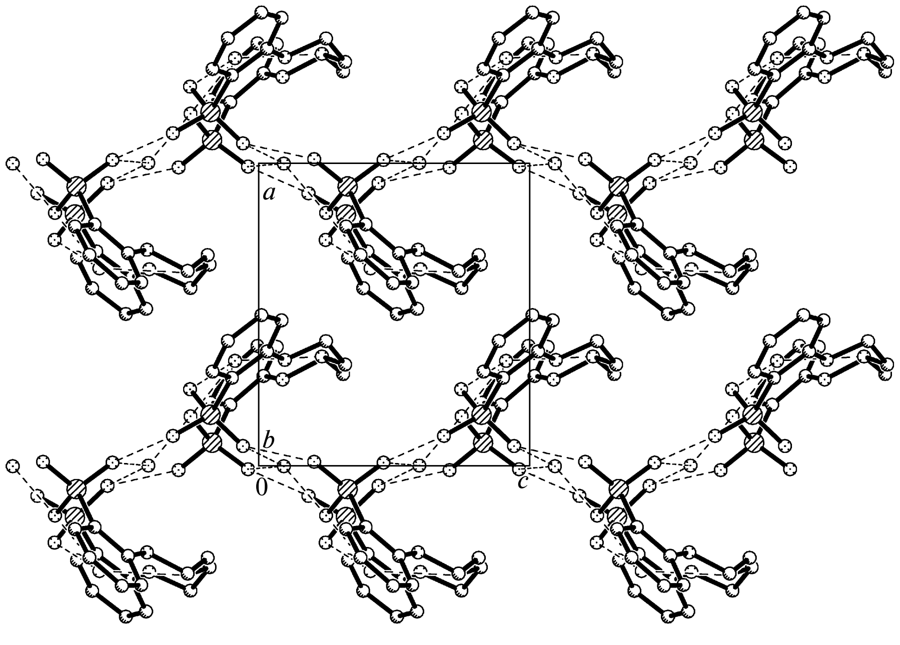


Fig. 3. Projection of structure **I** along the *b* axis.

units [33].The band at 1120 cm^{-1} is due to the δ(Ph) vibration.

The IR spectrum of L in the range of 1000–1125 cm^{-1} shows only one band of moderate intensity at ~1125 cm^{-1}, which is most likely a superposition of two bands ν_{as}(COC) and δ(Ph). According to the correlations in [13, 14], the band at 1125 cm^{-1} can be due to vibrations of ethylene glycol units with an approximate *TGG* conformation. Therefore, we can assume that the ethylene glycol chain of the L podand molecule is built of two *TGG* units.

In the range 800–1000 cm^{-1}, the IR spectrum of L shows two strong, broad bands with maxima at 986, 936, 921, and 904 cm^{-1}. According to [34], the band at ~986 cm^{-1} arises from bending vibrations δ(POH). The strong band at 904 cm^{-1} and the weak band at 830 cm^{-1} can be can be assigned to the possible presence of two *TGG* units in the L molecule.

The presence of absorption bands at 3293 and 1710 cm^{-1} in the IR spectrum of L allowed us to assume that there are strong hydrogen bonds or some number of hydration water molecules in the L molecule. Thermogravimetric study of L showed that no weight loss was observed on heating of the compound up to the melting point (209°C). Further heating led to the decomposition of the compound, which was accompanied by exothermal events at 240 and 250°C. Thus, we can state that podand L does not contain hydration water molecules, and the broad bands at 3293 and 1710 cm^{-1} are due to strong hydrogen bonds.

In the IR spectrum of **I**, P=O stretching vibrations give rise to the moderate band at 1169 cm^{-1}. This is ~48 cm lower than the ν(P=O) frequency in the spectrum of L (Table 5). This decrease in ν(P=O) is explained by the fact that, according to X-ray diffraction, both phosphoryl oxygen atoms form strong hydrogen bonds with neighboring podand molecules (Table 3).

In the range of ν_{as}(COC), the IR spectrum of **I** shows two bands of approximately equal intensity at 1122 and 1104 cm^{-1}. The former can be due to bending vibrations of the benzene rings (~1120 cm^{-1} in the spectrum of **II**), and the latter, in accord with X-ray crystallographic data, is caused by ν_{as}(COC) of the *TGT* ethylene glycol units. In another conformationally important range of 800–1000 cm^{-1}, the spectra of L and O are also different (Table 5). As mentioned above, the IR spectrum of L in this range shows two strong, broad bands of P–OH bending vibrations. In the IR spectrum of **I**, these vibrations are observed as one strong broad band with maxima at 1041, 1018, and 961 cm^{-1}, which is caused by the involvement of both the H and O atoms of the POH groups in various intra- and intermolecular hydrogen bonds.

Taking into account the fact that both OCH_2CH_2O units in the molecule of **I** have the same *TGT* conformation and using the known correlations [14], we can assign the bands at 961 and 867 cm^{-1} to composite stretching–bending vibrations of the *TGT* units.

In the range of water stretching vibrations, the spectrum of **I** shows the well-defined bands at ~3522 cm^{-1}, which, according to X-ray crystallography data, can be assigned to the presence of the outer-sphere water molecule in **I**. The broad band at 3312 cm^{-1} arises

Table 5. Assignment of basic vibrational frequencies (cm^{-1}) in the IR spectra of L and **I**

Assignment	L	**I**
$\nu(H_2O)$,		3522
$\nu(O–H\cdots O)$,	3293	3312
$\nu(H–O\cdots H)$		
$\nu(P–OH)$		2360
$\delta(O–H\cdots O)$,	1710	
$\delta(H–O\cdots H)$		
$\nu(Ph)$	1599	1593
	1575	1576
	1482	1480
$\delta(CH_2)$,	1457	1463
$\nu(P–Ph)$	1450	1443
$\omega(CH_2)$	1378	1377
	1360	
$\nu(Ph)$	1278	1286
$\nu(Ph–O)$,	1249	1249
$\tau(CH_2)$	1239	
$\nu(Ph=O)$	1217	1169
$\delta(Ph)$	1150	1151
$\delta(Ph)$, $\nu_{as}(COC)$	1125	1122
		1104
$\delta(Ph)$	1084	1089
$\nu_s(COC) + \nu(CC)$	1046	1061
		1041
$\delta(Ph)$,		1018
$\delta(POH)$	1005n	
	986	
$\nu(CO) + \nu(CC) +$		961
$\rho(CH_2)$		947
	936	
	921	
	904	
		867
		847
	830	
	807	801
$\nu(P–C)$, $\delta(Ph)$	776	
	769	765
	741	736
	726	723
	698	704
$\delta(COC)$,	614	613
$\delta(PhPO)$	556	559
	539	
	516	514
	502	
	486	482

from stretching vibrations of the coordinated H_2O molecule.

Thermogravimetric studies of **I** showed that the outer-sphere water molecule is removed at 93°C, and the inner-sphere water molecule is removed at 111°C (the temperatures correspond to the even maxima). The overall water weight loss is 7.31% (calculated, 7.92%). The melting point of compound **I** is 200°C, and the decomposition temperature is 260°C.

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