PHOSPHORUS-CONTAINING PODANDS. 9.* SYNTHESIS OF OLIGOETHYLENE GLYCOL BIS(DIPHENYLPHOSPHINYLETHYL) ESTERS AND THEIR COMPLEXING PROPERTIES WITH RESPECT TO ALKALI METAL CATIONS IN A LOW-POLARITY SOLVENT

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The complexing ability of phosphoryl-containing monopodands with the general formula $Ph_2P(O)CH_2CH_2O(CH_2CH_2O)_nCH_2CH_2P(O)Ph_2$ *(n = 0-5, 6.4, 8.7, 13.2) with respect to alkali metal cations was investigated conductometrically in tetrahydrofuran:chloroform mixed solvent (4:1, vol.) at 25°C. It was found that ligands of this type are efficient complexing agents relative to all alkali metal cations, and the monopodand with n = 0 also exhibits elevated Li/Na and Li/K selectivity. The effect of the structure, particularly the "rigidity" of the terminal fragments of the monopodands, on their complexing capacity was discussed. The method of synthesis of this type of ligand was described.*

Keywords: *phosphorus-containing monopodands, complexing ability, synthesis, conductometry.*

The complexing and selective properties of polyether podands (opened analogs of crown ethers) with respect to metal cations are determined by many factors, including the nucleophilicity and number of donor sites and the conformational rigidity of the ligand. Based on general considerations, we can hypothesize that an increase in the conformational mobility of the ligand should be accompanied by a decrease in its complexing ability because of an entropic factor due to an increase in the number of possible conformers. It was recently shown in oligotetrahydropyran compounds [2, 3] that a decrease in the conformational mobility of the polyether chain causes a significant increase in the efficiency of these podands relative to some alkali metal cations. Alteration of the conformational rigidity of the podand thus allows controlling its complexing ability and perhaps its selective properties. However, the creation of acyclic ligands with a conformationally rigid chain is usually associated with multistage synthesis. For this reason, it is much more convenient to alter the structure of the terminal fragment, which has also been done in many studies whose results are the basis for the concept of terminal groups [4]. We showed that polyether podands whose terminal groups are phosphorylated phenol fragments exhibit elevated complexing ability with respect to alkali metal cations. In many cases, they are as good as or even better than the most efficient crown ethers [5-8]. Some characteristics of the effect of the basicity of the phosphoryl oxygen and the distance between the phosphoryl group and nearest oxygen atom in the polyether chain on the complexing ability with respect to alkali metal cations were determined. However, the question of the degree of the effect of conformational rigidity of terminal groups on the efficiency of phosphoryl-containing podands is still open. The complexing properties of a new class of ligands – oligoethylene glycol bis(diphenylphosphinylethyl) esters (**1**) – were investigated in the present study. Monopodands **1** are complete structural analogs of glymes and differ from the phosphoryl-containing monopodands that we previously investigated [5-8] due to the lack of rigid *o*-phenylene fragments in the polyether chain.

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*See [1] for preceding communication.

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TABLE 1. Characteristics of Podands $Ph_2P(O)CH_2CH_2(OCH_2CH_2)_n$-$OCH_2CH_2P(O)Ph_2$ (**1a-i**) and o-$[Ph_2P(O)]C_6H_4-(OCH_2CH_2)_{13.2}-OC_6H_4[P(O)Ph_2]-o$ (**2i**)

Compound	n	Yield, %	Mp, °C (solvent)	Found/Calculated, %			Empirical formula
				C	H	P	
1a	0	57	134-136 * Benzene-hexane	70.9/70.9	6.0/5.9	13.2/13.0	$C_{28}H_{28}O_3P_2$
1b	1	70	101-102 **	–	–	–	–
1c	2	77	Oil	67.9/68.3	6.2/6.5	11.0/11.0	$C_{32}H_{36}O_5P_2$
1d	3	82	Oil	67.3/67.3	6.8/6.7	10.0/10.2	$C_{34}H_{40}O_6P_2$
1e	4	76	Oil	66.5/66.5	7.2/6.8	9.3/9.5	$C_{36}H_{44}O_7P_2$
1f	5	83	Oil	65.9/65.7	7.0/7.0	8.7/8.6	$C_{38}H_{48}O_8P_2$
1g	6.4	83	Oil	–	–	8.7/8.2	$C_{40.8}H_{54.7}O_{9.4}P_2$
1h	8.7	81	Oil	–	–	7.6/7.2	$C_{45.4}H_{62.8}O_{11.7}P_2$
1i	13.2	88	Oil	–	–	6.2/5.7	$C_{54.4}H_{80.8}O_{16.2}P_2$
2i	13.2	75	Oil	–	–	4.9/5.3	$C_{62.4}H_{80.8}O_{16.2}P_2$

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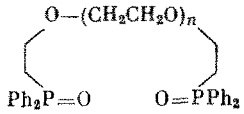
*Mp 81-82°C (monohydrate) [9].

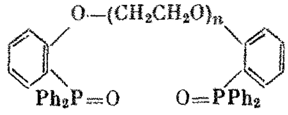
**Mp 101-102°C [5].

TABLE 2. Data from PMR and ^{31}P NMR spectra of Podands $Ph_2P(O)$-$CH_2CH_2(OCH_2CH_2)_n$ $OCH_2CH_2P(O)Ph_2$ (**1a, c-f**)

Compound	n	Solvent	PMR (δ, ppm)		^{31}P NMR (δ, ppm)
			polyether protons	aromatic protons	
1a	0	Acetone-d_6	3.54 m (4H), 3.64 m (4H)	7.54 m (12H), 7.86 m (8H)	27.28
1c	2	$CDCl_3$	2.68 m (4H), 3.44 m (8H), 3.76 m (4H)	7.44 m (12H), 7.78 m (8H)	30.50
1d	3	$CDCl_3$	2.70 m (4H), 3.50 m (12H), 3.78 m (4H)	7.50 m (12H), 7.76 m (8H)	30.35
1e	4	$CDCl_3$	2.68 m (4H), 3.54 m (16H), 3.74 m (4H)	7.46 m (12H), 7.74 m (8H)	30.80
1f	5	$CDCl_3$	2.70 m (4H), 3.50 m (20H), 3.74 m (4H)	7.46 m (12H), 7.74 m (8H)	30.34



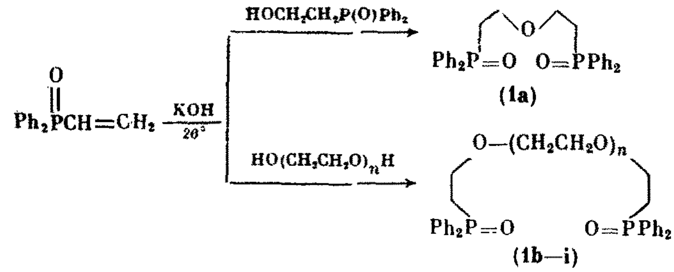
(**1a—i**)



(**2b—f,i**)

$n = 0$ (**a**), 1 (**b**), 2 (**c**), 3 (**d**), 4 (**e**), 5 (**f**), 6.4 (**g**), 8.7 (**h**), 13.2 (**i**)

The compounds investigated have not been described in the literature except for podands **1a, b**. The first one was obtained in the form of the hydrate by the reaction of lithium diphenylphosphide with diethylene glycol ditosylate with subsequent oxidation of the diphosphine formed by hydrogen peroxide [9]. We synthesized this compound by addition of 2-hydroxyethyldiphenylphosphine oxide to vinyldiphenylphosphine oxide in the presence of potassium hydroxide in dioxane. We previously [5] also prepared ligand **1b** similarly from ethylene glycol. Podands **1c-f** with a longer polyether chain were synthesized by analogous addition of different oligoethylene glycols. Not only individual oligoethylene glycols but also more available polymeric glycols with molecular weights of 300, 400, and 600, corresponding (on average) to n = 6.4, 8.7, and 13.2 (ligands **1g-i**), were used as the glycol component. It should be noted that addition of glycols to diphenylopropenylphosphine oxide does not take place in analogous conditions. The proposed method of synthesis is relatively simple, which makes these compounds more accessible in comparison to phosphorus-containing podands of other classes.



We compared the complexing and selective properties of monopodands **1a-f** and previously studied ligands **2b-f** [7], totally identical with respect to the number and with a similar type of donor sites, but with a conformationally more rigid phosphoryl-containing terminal group. The latter also includes polymeric podand **2i**, obtained by alkylation of *o*-diphenylphospinylphenol with oligoethylene glycol ditosylate with a molecular weight of 600.

The stability constants of M^+L complexes of monopodands **1** and **2i** with respect to alkali metal cations were determined conductometrically in THF:$CHCl_3$ mixed solvent (4:1, vol.) at 25°C.

EXPERIMENTAL

The ^1H and ^{31}P NMR spectra were recorded on a Bruker CXP-200 spectrometer versus TMS and 85% H_3PO_4, respectively. The melting points were measured on a Boetius PHMK 05.

1,5-Bis(diphenylphosphinyl-3-oxapentane (1a). Here 0.1 g (0.9 mmole) of finely ground KOH was added to a solution of 2.2 g (8.7 mmole) of 2-hydroxyethyldiphenylphosphine oxide [10] in 35 ml of dry dioxane. The mixture was stirred for 1 h at 20°C, then 2.0 g (8.7 mmoles) of vinyldiphenylphosphine oxide was added [10]. The reaction mixture was held for 48 h at 20°C and the solvent was eliminated in a vacuum. Then 30 ml of water was added to the residue, the mixture was acidified with conc. HCl to pH 2 and extracted with $CHCl_3$ (3 × 20 ml). The extract was washed with water (2 × 20 ml), dried with Na_2SO_4, and vacuum evaporated. The residue was chromatographed in a column with brand L silica gel (eluent: $CHCl_3$). Yield of **1a** = 2.7 g (Tables 1 and 2).

Compounds **1c-f** were prepared similar to **1b** [5] from vinyldiphenylphosphine oxide and di-, tri-, tetra-, and pentaethylene glycols (Tables 1 and 2). The products of polymerization of ethylene oxide with molecular weights of 300, 400, and 600 were used as the glycol component in synthesis of compounds **1g-i** (Table 1).

Polyethylene glycol bis(*o*-diphenylphosphinylphenyl) ester (2i) was prepared by the method in [11] from 5.0 g (17 mmoles) of *o*-diphenylphosphinylphenol and 7.7 g (8.0 mmoles) of polyethylene glycol ditosylate (mol. wt. 600), yielding 8.1 g of **2i** (Table 1).

The method of the conductometric measurements in the THF:$CHCl_3$ system (4:1, vol.) was reported previously [5]. The random error (±2*s*, where *s* is the standard deviation of the arithmetic mean) in determining the logarithms of the stability constants of complexes of ligands **1** and **2i** with alkali metal cations was less than ±0.1 log. unit. The concentration of ionogenic impurities in the ligands was monitored conductometrically. Alkali metal 2,4-dinitrophenolates were used as the salts.

DISCUSSION OF THE RESULTS

The results of determining the complexing properties of monopodands **1a-i** and **2i** are reported in Table 3. The logarithms of the stability constants of the alkali metal cation complexes M^+L as a function of the number n of CH_2CH_2O fragments in the polyether chain and the number m of ligand donor sites are presented in Fig. 1a. For comparison, the analogous curve for monopodands **2b-f** with conformationally rigid *o*-(diphenylphosphinyl)phenyl terminal groups is shown in Fig. 1b [7].

Ligands **1** were relatively efficient complexing agents with respect to all alkali metal cations. However, as anticipated, the increase in the conformational mobility of ligands **1** in comparison to **2** significantly decreases their efficiency in almost all cases. This is especially graphically seen in Li^+ and Na^+ cations. The highest values of log K attainable in the case of the lithium complex of ligand **2d** and the sodium complex of ligand **2e** are decreased by 1.4 and 0.5 log. units in going to the corresponding complexes of less rigid isodentate ligands **1d** and **1e** (see Fig. 1). However, there are examples of the opposite effect for Li^+ and

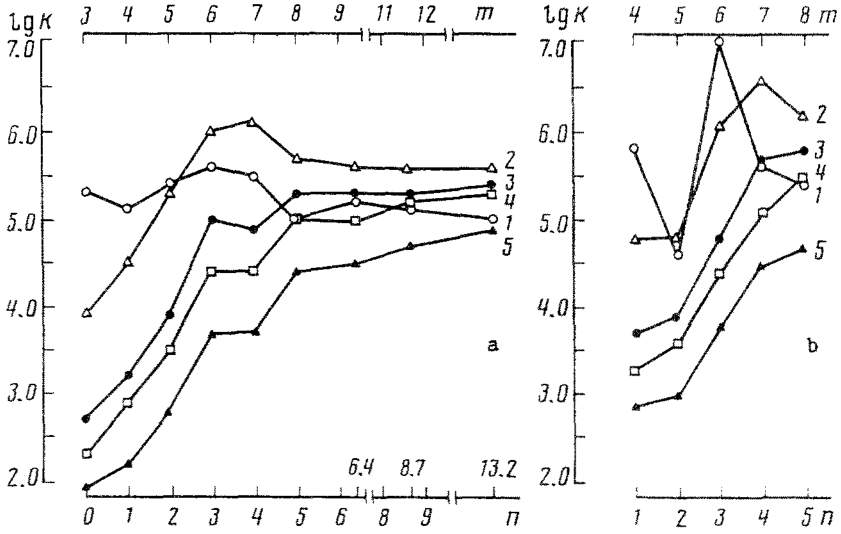


Fig. 1. Curves of the logarithms of stability constants of oligoethylene glycol bis(diphenylphopshinylethyl) (**1**) (a) and bis[2-diphenylphosphinyl)phenyl] (**2**) (b) [7] complexes with alkali metal cations vs. length of polyether chain *n* and number of donor sites *m*: 1) Li^+; 2) Na^+; 3) K^+; 4) Rb^+; 5) Cs^+.

TABLE 3. Logarithms of Stability Constants (log *K*) of M^+L Complexes of Alkali Metal Cations with Monopodands **1a-i**, **2i**, and Some Crown Ethers in THF:$CHCl_3$ Mixed Solvent (4:1, vol.) at 25°C

Ligand	*n*	Cation				
		Li^+	Na^+	K	Rb^+	Cs^+
1a	0	5.3	3.9	2.7	2.3	1.9
1b	1	5.1	4.5	3.2	2.9	2.2
1c	2	5.4	5.3	3.9	3.5	2.8
1d	3	5.6	6.0	5.0	4.4	3.7
1e	4	5.5	6.1	4.9	4.4	3.7
1f	5	5.0	5.7	5.3	5.0	4.4
1g	6.4	5.2	5.6	5.3	5.0	4.5
1h	8.7	5.1	5.6	5.3	5.2	4.7
1i	13.2	5.0	5.6	5.4	5.3	4.9
2i	13.2	5.1	5.7	5.6	5.5	5.0
15-Crown-5 [6]		4.6	4.9	4.9	4.7	4.0
18-Crown-6 [5]		5.5	6.6	5.5	4.9	4.5

Na^+ cations – in going from ligand **2c** to **1c**, log *K* of the lithium and sodium complexes increases significantly (by 0.8 and 0.5 log. units, respectively). As we previously observed in [7, 8], this anomaly is probably because the structures of monopodands, similar to the structure of ligand **2c** with $n = 2$, are conformationally least favorable for optimum cooperative interaction of ligand donor sites with cations of small radius. For this reason, the increase in the conformational possibilities of ligand **2c** which arises in going to its analog **1c** or when an additional CH_2 unit is incorporated between the phenyl ring and *o*-$Ph_2P(O)$ group [6] significantly increases log *K* of the complexes of these ligands with Li^+ and Na^+ cations. On the whole, these features cause smoothing or even the disappearance of the extremes on the log *K* vs. *n* curves for Li^+ and Na^+ cations, although the type, "strength," and number of ligand donor sites remain constant.

The complexing ability of "conformationally rigid" ligands **2** is almost always greater than or equal to the ability of their isodentate analogs **1** with a more flexible terminal group in the case of "large" cations (K^+, Rb^+, and Cs^+) (see Fig. 1). It should be noted that the efficiency of monopodands **1** with respect to the "large" cations K^+, Rb^+, and Cs^+ usually increases monotonically with an increase in *n* and *m*. These findings have been repeatedly noted in the literature [12]. This is usually correlated with an increase in the degree of cooperation of the ion–dipole interaction of the ligand donor sites in formation of a complex with a metal cation. We previously discussed these properties with respect to phosphorus-containing monopodands related to ligands **1** [6-8].

However, it should be emphasized that an increase in the length of the polyether chain binding the terminal groups of monopodands **1** from $n = 5$ to $n = 13.2$ (ligands **1f-i**) has almost no effect on their complexing ability relativve to Li^+, Na^+, K^+, and Rb^+ cations (see Fig. 1a). The increase in n to 13.2 increases the strength of cesium complexes by 0.5 log. units only in the case of the Cs^+ cation. It is noteworthy that the differences in the complexing properties of ligands **1** and their isodentate analogs **2** with a conformationally rigid terminal group almost totally disappear for higher values of n (see Table 3; ligands **1i** and **2i**).

The selective properties in the series of cations K^+, Rb^+, and Cs^+ are not a function of the type of terminal group and are almost the same for ligands **1** and **2**. However, the elevated conformational mobility of podands **1** in comparison to isodentate analogs **2** significantly affects the Li/Na and Na/Li selectivity.* For example, in going from ligand **2b** to **1b** and from ligand **2e** to **1e**, the Li/Na and Na/Li selectivity of the ligands respectively decreases from 10 to 4. It is interesting that inversion of the selective properties is observed in going from ligand **2d** to **1d**: the moderate (7.9) Li/Na selectivity of ligand **2d** changes to weak (2.5) Na/Li selectivity of isodentate analog **1d**. The "rigidity" of ligand **2d** thus very significantly increases its efficiency with respect to the Li^+ cation.

In conclusion, it is necessary to note the high values of the Li/Na and Li/K selectivity (25 and 400, respectively) of the simplest, widely available monopodand **1a**, which has no analog in the series of ligands **2**. This ligand also exhibits elevated an complexing ability relative to the Li^+ cation comparable to the most efficient 18-crown-6 in this system of solvents (see Table 3).

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*In this case, the selectivity of the ligand is determined as the ratio of the stability constants of complexes of two different M^+ cations.