## PHOSPHORUS-CONTAINING PODANDS.

4.\* EFFECT OF POLYETHER CHAIN LENGTH OF OLIGOETHYLENE GLYCOL BIS(ORTHO-DIPHENYLPHOSPHINYLMETHYL)PHENYL ETHERS ON THEIR COMPLEX-FORMING AND SELECTIVE PROPERTIES WITH RESPECT TO ALKALI METAL CATIONS

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Alkylation of o-(diphenylphosphinylmethyl)phenol by oligoethylene glycol ditosylates leads to a series of acyclic polyether complexing agents (podands) with phosphinylmethylphenyl terminal groups. A conductometric method in tetrahydrofuranchloroform (4:1 by volume) has been used to determine the stability constants of the podands with alkali metal 2,4-dinitrophenoxides. Several of the prepared ligands exhibited a high Li/Na, Na/K, and Li/K selectivity. For lithium and sodium cations, the curve of complex-forming ability against the overall number of donor centers in the structure of the podand has a maximum for the case of tetraethylene glycol bis(o-diphenylphosphinylmethyl)phenyl ether. For lithium cations, this compound surpasses the crown ethers in terms of its effectiveness and is the most powerful of the phosphoryl-containing complexing agents. For potassium, rubidium, and cesium cations, the complex-forming ability increases with increase in the number of oxygen donor centers in the polyether chain of the ligand.

Acyclic analogs of crown ethers (podands) are powerful complexing agents with respect to alkali and alkaline earth metal cations, and from the point of view of effectiveness, the main interest is directed to compounds with strong donor terminal groups, for example, quinoline, ortho-carboxyphenyl, and other groups [1]. Podands with phosphoryl-containing groups are also found in this class; their donor ability can be modified by varying the substiuents on the phosphorus atom. In previous communications, devoted to compounds with ortho-(diethoxyphosphinyl)phenyl [2] and ortho-(diethoxyphosphinylmethoxy)phenyl [3] terminal groups we reported a study of the effect of ethylene glycol chain length and the overall number of donor centers on the complexing ability of phosphoryl-containing monopodands with respect to alkali metal cations. We therefore demonstrated the principal differences in the complexforming and selective properties of monopodands of both types which are determined more than anything by differences in terminal group structure.

In the present work, we have prepared monopodands (Ia-e) with ortho-(diphenylphosphinylmethyl)phenyl terminal groups by alkylation of the ditosylates of oligoethylene glycols by the corresponding sodium phenoxides

<sup>\*</sup>For previous communications, see [2, 3].

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TABLE 1. Characteristics of Podands  $(Ia)-(Ie) \circ [Ph_2P(0) \circ CH_2]C_6H_4(OCH_2CH_2)_nC_6H_4[CH_2P(0)Ph_2]-\circ$ 

	n	Yield, %	Mp, °C (solvent)	Found, %			Calculated, %			
Com- pound				с	н	Р	Empirical formula	с	н	Р
(Ia)	1	86	145,5-147,0	74,8	5,8	9,6	$C_{40}H_{36}O_4P_2$	74,8	5,7	9,6
(Ib)	2	72	(benzene-nexane) 144-146	73,3	5,8	8,7	$C_{42}H_{40}O_5P_2$	73,5	5,9	9,0
(1¢)	3	81	(benzene-hexane) 131,5-133 (benzene-hexane)	72,3	5,7	8,4	$C_{44}H_{44}O_6P_2$	72,3	6.0	8,5
(I₫) (Ie)	45	69 83	0ii »	71,2 70,3	6,6 6,8	<b>8,0</b> <b>7,2</b>	$\begin{array}{c} C_{46}H_{48}O_7P_2\\ C_{48}H_{52}O_8P_2 \end{array}$	71,3 70,4		8,0 7,5



Of the compounds prepared, only (Ib) is known already [4]. The preparation of the phenol starting material from salicylaldehyde and diphenylphosphine [4, 5] was improved in the present work, particularly at the stage of isolating the final product.

Quantitative evaluation of the complexing ability of the podands (Ia-e) with respect to alkali metal cations was carried out in terms of the stability constant of the complex  $M^+L$  which was determined by a conductometric method in 4:1 THF-chloroform. A comparison was made of the complexing and selective properties of the podands (I) and the compounds described earlier [2] (Ia-e) but with  $R = P(0)(OEt)_2$ , (IIa-e) which are identical in terms of number and type of donor centers. The reasons for the observed differences in effectiveness and selectivity between complexes (I) and (II) are discussed.

#### EXPERIMENTAL

A Bruker CXP-200 spectrometer was used to obtain  $^1\rm H$  and  $^{31}\rm P$  NMR spectra with TMS and 85%  $\rm H_3PO_4$  as reference materials. Melting points were determined on a Boetius PHMK 05 apparatus.

<u> $\sigma$ -(Diphenylphosphinylmethyl)phenol (III)</u>. A mixture of 20.50 g (0.110 mole) diphenylphosphine and 20 ml conc. HCl was heated to 70°C and 14.00 g (0.115 mole) salicylaldehyde added dropwise, the temperature rising to 105°C. The mixture was heated at 80-90°C for 15 min and then, at 70°C, 10 ml alcohol was added followed by 20% NaOH, dropwise, until the pH rose to 6.5-7.0. The precipitate was filtered off. Yield 32.20 g (95%) (III), mp 177.0-177.5°C. After recrystallization from ethyl acetate, yield 29.30 g (86%), mp 177.5-178.5°C [4, 5].

Ethylene Glycol Bis(o-diphenylphosphinylmethyl)phenyl Ether (Ia). A solution of EtONa, prepared from 0.08 g (0.0032 mole) Na and 10 ml abs. alcohol, was added to a solution of 1.00 g (0.0032 mole) (III) in 20 ml abs. alcohol and the mixture stirred for 10 min and then evaporated in vacuum. The residue was dried for 3 h, 100°C, 10 torr. To the phenoxide so obtained was added 30 ml dry dioxan and 0.59 g (0.0016 mole) ethylene glycol ditosylate [6]. The mixture was stirred at bp for 6 h, the solvent evaporated in vacuum and 25 ml 20% NaOH added to the residue. The mixture was extracted with chloroform ( $3 \times 15$  ml) and the extract washed with 20% NaOH (20 ml), dilute HCl (1:1, 20 ml), and with water until neutral. It was then dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuum. The residue was chromatographed on a column of type L silica gel using chloroform as eluent. Yield (Ia), 0.87 g (Tables 1 and 2).

Compounds (Ib-e) were prepared in a similar way from (III) and the ditosylates of di-, tri-, and tetraethylene glycols [7] with a reaction time of 7 to 9 h (Tables 1 and 2). Commercial benzo-12-crown-4 and 15-crown-5 were used in this work, their purity being confirmed by elemental analysis and GLC. The technique for conductometric measurements in a 4:1 (vol.)

Com- pound			PMR (ô ppm, J, Hz)				
	n	Solvent	CH₂P	0CH2	aromatic protons	<sup>a1</sup> P ô, ppm	
(Ia)	1	Acetone-d <sub>6</sub>	3,83 d (4H, <sup>2</sup> J <sub>HP</sub> =15)	4,26 s (4H)	6,83 (2H), 6,95m (2H), 7,40m (16H), 7,8m (8H)	27,97	
(Ib)	2	CDCl₃	3,84d (4H, ²J <sub>HP</sub> =15)	3,70 m (4H), 3,86 m (4H)	6,68m (2H), 6,84m (2H), 7,16m (2H), 7,39m (14H), 7,82m (8H)	31,70	
(Ic)	3 .	Acetone-d <sub>6</sub>	3,80 d (4H, ²J <sub>HP</sub> ≕15)	3,78 m (8H), 3,93 m (4H)	7,80m (4H), 7,18m (2H) 7,43m (14H), 7,85m (8H)	28,51	
(Id)	4	CDCl₃	3,50-4,00	m (20H)	7,60m (2H), 6,84m (2H) 7,08 <sup>m</sup> (2H), 7,34 <sup>m</sup> (14H) 7,68 <sup>m</sup> (8H)	32,01	
(Ie)	5	Acetone	3,40-4,00 n	n (28H)	6,48 m (4H), 7,10 m (2H), 7,46 m (14H), 7,80 m (8H)	28,69	

TABLE 2. PMR and <sup>31</sup>P NMR Spectra of Podands (Ia)-(Ie)

TABLE 3. Logarithms of Stability Constants log  $\beta$  of Complexes M<sup>+</sup>L of Alkali Metal Cations with Ligands (I) in the System THF:CHCl<sub>3</sub> (4:1 by vol.) at 25°C

	Cation						
Ligand	Li+	Na+	K+	Rb+	Cs+		
$\begin{array}{c} (Ia), n=1 \\ (Ib) *, n=2 \\ (Ic), n=3 \\ (Id), n=4 \\ (Ie), n=5 \\ Ph_2P(0)CH_2P(0)Ph_2 \ [9] \\ Bu_2P(0)CH_2CH_2P(0)Bu_2 \ [10] \end{array}$	4,8 5,0 6,7 5,2 4,9 4,9 5,1	3.6 4,3 6,1 5,7 5,5 4,4	2.6 3.1 4,0 4,6 4,9 3,5 2,9	2.1 2.8 3.6 4.2 4.5 -	1,9 2,3 3,1 3,6 3,9 2,9 -		
$\begin{array}{c} 0 \\ Ph_{2}P \\ (IIc), n=3 [2] \end{array} $ [8]	5,8 6,3	4,8 5,7	3,7 4,5	3,3 4,1	2,9 3,5		
$\begin{array}{c} Ph_2(0)P \\ Ph_2(0)P \\ N \\ N \\ Ph_2(0)P \\ N \\ N \\ P(0)Ph_2 \end{array} $ [11]	5,9	6,3	5,0	_	3,6		
Benzo-12-crown-4 15-Crown-4 18-Crown-6 [8] Dibenzo-18-crown-6 [8]	2.8 4,6 5,5 4,6	3,0 4,9 6,6 6,0	2,6 4,9 5,5 5,0	2,4 4,7 4,9 4,6	2,2 4,0 4,5 4,4		

\*A conductometric study of the complexing properties of ligand (Ib) towards alkali metal cations in the same solvent system was carried out earlier [4]. The reasons for some discrepancy in the results has been discussed in [8].

THF-chloroform system has been detailed previously [8]. The random error in the determination of the logarithms of the stability constants of the complexes of ligands (Ia-e) and crown ethers with alkali metals was less than  $\pm 0.1$  logarithmic units. The concentration of ionogenic impurities in the ligands was monitored conductometrically. The salts used in the experiments were the 2,4-dinitrophenoxides of the alkali metals.



Fig. 1. Plots of the logarithm of the stability constant of complexes of bis(ortho-(diphenylphosphinyl)phenyl) ethers of oligoethylene glycols (I) (a), and (II) [3] (b) with alkali metal cations against the length of the polyether chain n and the number of donor centers m: 1)  $Li^+$ , 2) Na<sup>+</sup>, 3) K<sup>+</sup>, 4) Rb<sup>+</sup>, 5) Cs<sup>+</sup>.

### RESULTS AND DISCUSSION

The results of the determination of the complexing properties of monopodands (Ia-e) are set out in Table 3 and presented in Fig. 1a as a plot of the logarithm of the stability constants of the complexes of alkali metal cations  $M^+$  against the number n of  $CH_2CH_2O$  fragments in the polyether chain bonded to the terminal groups, and the overall number m of donor centers in the structure of the ligand. For comparison, Fig. 1b shows similar results obtained previously [2] for monopodands (IIa-e) with o-(diethoxyphosphinyl)phenyl terminal groups.

It follows from the results obtained that an increase in the number of donor centers m in the structure of ligands (I) leads, as a rule, to an increase in complexing ability towards all akali metal cations. This, in our opinion [2], is explained by an increase in the extent of cooperative ion-dipole interaction of the phosphoryl and ether oxygen coordination centers of the ligand on complex formation with a metal cation. This tendency is most clearly displayed in the case of 'larger' alkali metal cations (K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>): as the overall number of donor centers increases from four to eight there is, for these ions, a monotonic increase in the effectiveness of the ligand (I) (Fig. 1a). However, in the case of Li<sup>+</sup> and Na<sup>+</sup> cations, which have a small radius and hence a high charge density, a similar plot shows a maximum when the number of donor centers m = 6 (ligand (Ic), n = 3). The observed maximum is particularly sharp for Li<sup>+</sup>, and at this point increasing or decreasing the length of the polyether chain even by only one CH2CH2O fragment, i.e., moving from ligand (Ic) (n = 3, m = 6) to ligand (Ib) (n = 2, m = 5) or (Id) (n = 4, m = 7) leads to a sharp reduction (by a factor of 50 and 30) in the strength of the corresponding lithium complexes. For the Na<sup>+</sup> cation, which is larger in size, a similar, though less pronounced, effect is observed. Thus, for cations of small diameter (Li<sup>+</sup> and Na<sup>+</sup>) which, as the experiments of [2, 3] demonstrated, impose stringent spatial demands on a ligand in the formation of a complex, the structure of the hexadentate monopodand (Ic) (chain length, conformational mobility, number and type of coordinating centers) proves to be favorable for the achievement of optimum packing of the ligand around the metal cation. Evidence of this is provided by the high value of the logarithm of the stability constant of the corresponding lithium complex, which exceeds analogous values for the strongest of the phosphorus-containing complexing agents of [2, 8-11], including the close analog of (Ic) but with diethoxyphosphinylphenyl terminal groups [2] (Table 3). It would seem that the sodium complex of ligand (Ic) is also characterized by high stability for the same reason. It should be emphasized that in the given solvent system the complexing ability of a series of crown ethers towards the Li<sup>+</sup> cation is considerably inferior to that of ligand (Ic). In the case of the Na<sup>+</sup> cation, however, ligands (Ic), (Ie), 18-crown-6, and dibenzo-18-crown-6 prove to be comparable in efficiency (Table 3).

Ligand	$\frac{\beta_{Li}}{\beta_{Na}}$	$\frac{\beta_{Li}}{\beta_{K}}$	$\frac{\beta_{Na}}{\beta_{K}}$	β <sub>K</sub> β <sub>Rb</sub>	$\frac{\beta_{Rb}}{\beta_{Cs}}$
(Ia) (Ib) (Ic) (Id) (Ie) (IIa) (IIb) (IIc) (IId) (IIe) Benzo-12-crown-4 15-Crown-5 18-Crown-6 [8] Dibenzo-18-crown-6 [8]	$\begin{array}{c} 15,8\\ 5,0\\ 4,0\\ 0,32\\ 0,25\\ 4,0\\ 0,8\\ 4,0\\ 0,06\\ 0,06\\ 0,63\\ 0,50\\ 0,08\\ 0,04\\ \end{array}$	158795014,0635,0631,00,161,60,51,00,4	$10.0 \\ 15.8 \\ 126 \\ 4.0 \\ 15.8 \\ 6.3 \\ 15.8 \\ 2.5 \\ 2.5 \\ 1.0 \\ 12.6 \\ 10.0 \\$	$\begin{array}{c} 3.2\\ 2.0\\ 2.5\\ 2.5\\ 2.5\\ 4.0\\ 2.0\\ 2.5\\ 3.2\\ 2.0\\ 1.6\\ 1.6\\ 4.0\\ 2.5\end{array}$	1.63.23.24.02.54.04.05.06.31.65.02.51.6

TABLE 4. Selectivity of Monopodands (I) and (II), and of a Series of Crown Ethers, in 4:1 THF-CHCl<sub>3</sub> at 25°C

In comparing the complexing abilities of monopodands (I) and phosphonate monopodands (II) idential in number and type of donor centers, it has to be noted that these latter compounds have significant differences, above all the higher basicity of the phosphoryl oxygen of ligands (I). In addition, ligands (I) must differ markedly from their phosphonate analogs in their conformational properties. These compounds contain in their structure not only different substituents on the phosphorus atom but also two additional  $CH_2$  groups which give rise to an increase in the 'geometric' length of the ligand and correspondingly a change in the mutual location of the 'strong' (phosphoryl oxygen atoms) and the 'weak' (ether oxygen atoms of the polyether chain) donor centers on coordination with a metal cation. Thus the features mentioned can lead to disturbance of the cooperative interaction of the donor centers with M<sup>+</sup> and consequently to a change in the complexing and selective properties of the ligand (I) in comparison with those of the phosphonate analogs (II) towards the series of alkali metal cations.

On comparing a and b in Fig. 1, it is not difficult to see that in the case of the Li<sup>+</sup> cation the strength of the corresponding complexes of ligands (I) at all values of n and m is markedly higher than the strength of the lithium complexes of the phosphonates (II). This fact finds a natural explanation in the increased basicity of the phosphoryl oxygen atom of compounds (I) in comparison with ligands (II). We note that the increased affinity of small cations (Li<sup>+</sup> and Na<sup>+</sup>) for the more basic donor centers of a ligand has been remarked on more than once [12-14]. The effect of the conformational-geometric differences of the ligands (I) and (II) on the strength of the lithium complexes formed most probably has a secondary significance. Evidence of this is provided by the sharp maxima in the complexing ability of ligands of both types with identical length of polyether chain bonding the terminal groups and consequently with an identical number of donor centers (ligands (Ic) and (IIc); n = 3, m = 6). Bearing in mind the high value of the logarithm of the stability constant of the lithium complexes of ligands (Ic) and (IIc) and the high value of the logarithm of the stability constant of the lithium complexes of ligands (Ic) and the high value of the logarithm of the stability constant of the lithium complexes of ligands (Ic) and the high value of the logarithm of the stability constant of the lithium complexes of ligands (Ic) and the high value of the logarithm the stability constant of the lithium complexes of ligands (Ic) and the high value of the logarithm the stability constant of the lithium complexes of ligands the terminal groups and consequently with an identical number of donor centers (ligands (Ic) and the high value of the logarithm of the stability constant of the lithium complexes of ligands (Ic) and the high value of the logarithm the stability constant of the lithium complexes of the ligands (Ic) and the high value of the logarithm the stability constant of the lithium complexes that in both cas

A similar comparison in the case of the Na<sup>+</sup> cation reveals two main differences in the dependence of the strength of the sodium complexes of ligands (I) and (II) on n and m. Firstly, in spite of the higher basicity of the phosphoryl donor centers, compounds (I) are inferior to compounds (II) in terms of the strength of the corresponding sodium complexes. In particular there is in this case a marked drop on the logarithm of the stability constant of the complex (by 0.7 logarithmic units) for ligand (Ia) in comparison with (IIa) (n = 1, m = 4). Moreover, the maximum complexing ability of ligands (I) relative to the Na<sup>+</sup> cation (log  $\beta = 6.1$ ) is not, as would be expected, greater than that for the phosphonates (II) and is even somewhat lower (Table 3). Secondly, the maximum complexing ability in the case of compounds (I) is attained at a shorter length of the polyether chain and correspondingly a smaller number of donor centers (ligands (Ic); n = 3, m = 6) than in the case of the phosphonates (II). For the latter, the maximum complexing ability towards Na<sup>+</sup> cations is observed for n = 4 and m = 7 (Fig. 1b), all seven donor centers of the ligand evidently taking part (IIe).\* This

\*According to x-ray structural analysis, it is possible for eight donor centers to participate in coordination with a sodium cation [15].

shift in the maximum signifies that the introduction of two additional  $CH_2$  units, i.e., an increase in the overall length of the chain between terminal P(0) groups in comparison with the phosphonate analogs, results in optimum coordination of the six donor centers in the ligand (Ic) with an Na<sup>+</sup> cation being realized with a shorter polyether chain length than in the case of the phosphonate (IIe). Here, the virtual coincidence of the maximum complexing ability of the phosphonates (II) and the phosphine oxides (I) (log  $\beta = 6.3$  and 6.1 respectively) can be explained if one assumes that the participation of a larger number of donor centers of the ligand (IId) (m = 7) in coordination with a Na<sup>+</sup> cation is fully compensated by the higher basicity of the phosphoryl donor centers of the ligand (Ic) (m = 6). We note also that on passing from ligand (Ic) to ligands (Id) and (Ie) with a greater number of donor centers (m = 7 and 8) optimal coordination of all the donor centers with a Na<sup>+</sup> cation is not realized, apparently because conformational restrictions in the structure of the ligands come into play, a marked reduction in the strength of the sodium complexes being evidence of this.

As has been noted above, the increase in the overall number of donor centers in the ligand structure from m = 4 to 8 is accompanied by a practically linear growth in the complexing ability with respect to the 'larger' alkali metal cations (K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>) in the case of compounds (I) and of their phosphonate analogs (II) (Fig. 1). If we assume that for any values of n and m all the donor centers of ligands (I) and (II) take part in coordination with the 'larger' cations, then this fact could apparently be interpreted as a consequence of the cations K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> being coordinately unsaturated in the corresponding complexes, even where m = 8. We note that according to results in the literature, on the formation of a 1:1 complex of the cation K<sup>+</sup> with dibenzo-30-crown-10 [12] and of the cation Rb<sup>+</sup> with octaethylene glycol bis(8-hydroxyquinoline) ether [1] all ten donor centers of these ligands take part in coordination. However, for the present it remains unclear why in all cases without exception the strength of the complexes of the 'larger' cations with the phosphonates (II) is considerably higher (Fig. 1) than in the case of the ligands (I) with more basic phosphoryl donor centers. It would seem that, at any values of n and m, the geometry of compounds (II) is more favorable than that of compounds (I) for optimal coordination of the donor centers with the 'larger' alkali metal cations. If we allow that the cations K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> are not very sensitive to the basicity of the donor centers of the ligand, which has been noted more than once [12-14], then the geometric factor could, in principle, prove to be the determining effect on the absolute value of the stability constants of the corresponding complexes.

Comparative examination of the selective properties of monopodands (I) and (II) and of a series of crown ethers in THF:CHCl<sub>3</sub> shows that in the series of 'larger' alkali metal cations (K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>) the selectivity of these ligands is approximately the same and is small in absolute value (Table 4). However, in the series of cations Li+, Na+, K+ the selective properties begin to depend on the type of ligand and the strength of its donor centers. Thus, for the phosphonates (II) a small, but clearly expressed, Li/Na selectivity is characteristic together with a quite high Li/K and Na/K selectivity, exceeding that of the crown ethers. Evidently, the preferred bonding of small diameter cations (Li<sup>+</sup> and Na<sup>+</sup>) by ligands (II) results more than anything from the presence of 'strong' (phosphoryl oxygen atom) donor centers. Such a relationship has been noted previously [12-14]. In fact, the increase in the base strength of the oxygen atom of the phosphoryl group on moving from phosphonates (II) to phosphine oxides (I) leads to a considerable increase in the selectivity, especially in respect of Li<sup>+</sup> and Na<sup>+</sup> cations. Thus, in the case of ligand (Ia) the Li/Na selectivity increases by almost 4 times in comparison with phosphonates (IIa) and (IIc), and the Li/K and Na/K selectivity of ligand (Ic) is almost an order of magnitude higher than the analogous value for phosphonates (IIa) and (IIc) (Table 4). Here, the Li/Na selectivity of ligand (Ia) (15.8) proves to be not only considerably higher in absolute value than the analogous value for 12-crown-4 in acetonitrile (1.2) and 15-crown-5 in propylene carbonate (3.6), but it is also comparable to the Li/Na selectivity of cryptand-[2.1.1] in DMSO (16.2) and DMF (58) [12].\*

# CONCLUSIONS

1. Alkylation by oligoethylene glycol ditosylates has yielded a series of phosphoruscontaining monopodands with o-(diphenylphosphinylmethyl)phenyl terminal groups.

2. The complexing ability of the oligoethylene glycol bis(o-diphenylphosphinylmethyl) phenyl) ethers with respect to alkali metals cations has been determined in THF-chloroform

<sup>\*</sup>The higher values of the Li/Na selectivity among the crown ethers, which were calculated according to the results in the review by Izatt and co-workers [12] as the ratio of the stability constants of the corresponding complexes of the two cations, are quoted.

by a conductometric method. It has been shown that several representatives of the phosphoruscontaining monopodands examined display high Li/Na, Na/K, and Li/K selectivity.

3. For K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>, the complexing properties become monotonically stronger as the number of oxygen donor centers in the polyether chain of the ligand increases. For Li<sup>+</sup> and Na<sup>+</sup> the curve of the complexing properties against the overall number of donor centers in the structure of the monopodand has a maximum for the case of tetraethylene glycol bis(o-(diphenylphosphinylmethyl)phenyl) ether. This compound is markedly superior to the crown ethers in its effectiveness and is the strongest of the phosphorus-containing complexing agents with respect to Li<sup>+</sup>.

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