4. G. K. Fraenkel, J. Phys. Chem., 71, 139 (1967).
5. V. K. Cherkasov, G. A. Abakumov, I. A. Teplova, et al., Abstracts of Papers, 6th Europ. Conf. on Organometallic Chemistry, Riga (1985), p. 108.
6. J. R. Kirchoff, D. R. McMillin, W. R. Robinson, et al., Inorg. Chem., 24, No. 23, 3928 (1985).
7. G. A. Abakumov, Yu. A. Kurskii, V. I. Nevodchikov, and V. K. Cherkasov, Dokl. Akad. Nauk SSSR, 251, No. 1, 103 (1980).

PHOSPHORUS-CONTAINING PODANDS.

7.[*] COMPLEXING PROPERTIES OF ortho-DIPHENYLPHOSPHINYL-SUBSTITUTED DIPHENYL ETHERS OF OLIGOETHYLENE GLYCOLS WITH RESPECT TO ALKALI-METAL CATIONS

V. I. Evreinov, V. E. Baulin,
Z. N. Vostroknutova, Z. V. Safronova,
I. B. Krashakova, V. Kh. Syundyukova,
and E. N. Tsvetkov

UDC 542.91:541.49:547.558.1+547.26'118

Stability constants of complexes of alkali-metal cations with oligoethylene glycol diethers $RO(CH_2CH_2O)_nR$ (n = 1-5), where R = $2\text{-}Ph_2P(O)C_6H_4$ and $2\text{-}Ph_2(O)\text{-}4\text{-}t\text{-}BuC_6H_3P$, have been determined conductometrically in a tetrahydrofuran—chloroform mixture (4:1 by volume). The dependence of complexing ability on a number of monopodand donor centers for Li^+ and Na^+ has multiple extrema. For K^+, Rb^+, and Cs^+ the complexing abilities steadily increase with the length of the ligand polyether chain. Monopodands based on triethylene glycol and its pyrocatechol analog are highly effective (log K = 6.7-7.0) with respect to Li^+. The synthesis of ligands with a lipophilic tert-butyl substituent in the terminal group is described.

Open-chain analogs of crown ethers (podands) are known [3] to be less effective as complexing agents than their cyclic prototypes. One possible way to improve the complexing ability of such compounds is to increase the conformational rigidity of the polyether chain, which has recently been accomplished in the case of oligotetrahydropyran podands [4, 5]. We have undertaken a systematic study of another way to improve the effectiveness of podands by modifying the nature of their terminal residues. In previous communications on phosphoryl-containing monopodands [2, 6-8] we have studied the effect of the nature of terminal groups and the length of the oligoethylene glycol chain on the complexing ability of ligands toward alkali-metal cations using as an example diphenyl ethers of oligoethylene glycols substituted in the ortho position to the phenolic hydroxyl by various phosphorus-containing groups ($Ph_2P(O)CH_2$, $(RO)_2P(O)CH_2O$, $(RO)_2P(O)$, etc.). In certain cases phosphoryl-containing monopodands proved to be highly effective and selective with respect to Li^+, Na^+, K^+, and Rb^+ cations, being as good as or even appreciably better than the entire series of crown ethers with respect to these properties.

The present study concerns the effect of length and structure of the oligoethylene glycol chain on the complexing ability toward alkali-metal cations of neutral monopodands of the phosphine-oxide type with ortho-(diphenylphosphinyl)phenyl terminal groups (Ia-e),[†] the pyrocatechol analog of one of the members of this series (II), and also compounds (IIIa-e) containing in the para position to the phenolic oxygen tert-butyl groups which increase the lipophilic nature of the ligands.

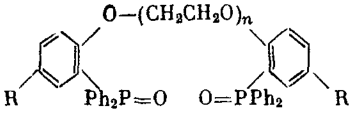
---

[*] For previous communication, see [1]. The number of the communication in [2] is 5, not 4 as printed in error.

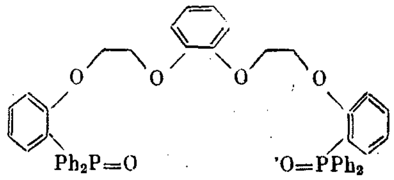
[†] Previously the complexing abilities of monopodands (Ia-e) toward $CaCl_2$ in C_2H_5OH have been studied using solution calorimetry [9].

Institute of Physiologically Active Materials, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 1992-2000, September, 1991. Original article submitted October 5, 1990.

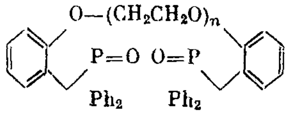
The complexing ability of monopodands (I), (II), and (III) toward alkali-metal cations was evaluated quantitatively according to the stability constants of the M^+L complexes determined conductometrically in a mixed THF—chloroform solvent (4:1 by volume) at 25°C. Comparisons were carried out on the complexing and selective properties of (Ia-e) and (IIIa-e) monopodands and (IVa-e) ligands, identical in number and type of donor centers [2].



(I), (III)



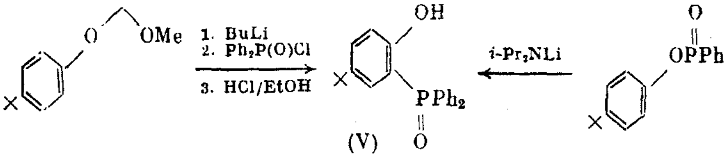
(II)



(IV)

R = H, *n* = 1 (Ia), 2 (Ib), 3 (Ic), 4 (Id), 5 (Ie).
R = *t*-Bu, *n* = 1 (IIIa), 2 (IIIb), 3 (IIIc), 4 (IIId), 5 (IIIe).
n = 1 (IVa), 2 (IVb), 3 (IVc), 4 (IVd), 5 (VIe).

The synthesis of monopodands (Ia-e) and (II) have been described previously [10]. Podands (III) were obtained by alkylation of sodium 4-tert-butyl-2-diphenylphosphinylphenolate with oligoethylene glycol ditosylates in dioxane at 100°C. The original phenol (V) was synthesized in two ways: 1) the methoxymethyl ether of 4-tert-butylphenol was converted by butyllithium into the ortho-lithium derivative, which was converted into the phenol (V) by reaction with diphenylphosphinic acid chloride and subsequent hydrolysis [11]; 2) rearrangement [12] of the 4-tert-butyl ester of diphenylphosphinic acid by the action of lithium diisopropylamide. In both cases the yield of phenol (V) is ~80%.



EXPERIMENTAL

The PMR and ^{31}P NMR spectra were recorded using a Bruker CXP-200 spectrometer with $CDCl_3$ as solvent and TMS and 85% H_3PO_4 as standards. Melting points were measured in a Boetius PHMK 05 apparatus. Yields, constants, and averaged analytical data and NMR data are given in Table 1. All operations involving organolithium compounds were carried out in an atmosphere of dry argon.

Methoxymethyl Ether of p-tert-Butylphenol. A solution of 38.2 ml (0.51 mole) monochlorodimethyl ether in 30 ml benzene was added dropwise with stirring at 25-30°C to a mixture of 47.9 g (0.32 mole) p-tert-butylphenol in 200 ml benzene, 20.6 g (0.52 mole) NaOH in 50 ml water, and 5.1 g (0.02 mole) Bu_4NBr. The mixture was boiled for 5 h, then the organic layer was separated, washed with 20% NaOH (5 × 100 ml), dried with $CaCl_2$, and evaporated under vacuum. The residue was distilled. Yield 41.6 g (67%), bp 63.5-65°C (1 mm). PMR spectrum (δ, ppm): 1.28 s (9H, CH_3), 3.42 s (3H, OCH_3), 5.10 s (2H, OCH_2), 6.94-7.32 m (4H, C_6H_4). d_4^{20} 0.9935, n_D^{20} 1.4945. Found: C 74.2; H 9.4%. Calculated for $C_{12}H_{18}O_2$: C 74.2; H 9.3%.

2-Diphenylphosphinyl-4-tert-butylphenol (V). a) To a solution of 9.8 ml (0.05 mole) of the methoxymethyl ether of p-tert-butylphenol in 80 ml anhydrous THF was added dropwise 18.8 ml 2.93 N solution of butyllithium in hexane at −15 ± 5°C. The mixture was stirred for 1 h, gradually raising the temperature to 20°C, and then stirring continued for a further 3 h. The resulting organge solution of 2-methoxymethoxy-5-tert-butyllithium was added dropwise with stirring at −60 ± 5°C to a solution of 11.8 g (0.05 mole) diphenylphosphinic acid chloride in 25 ml anhydrous THF. After raising the temperature to 20°C the reaction mixture was stirred for 3 h at 20°C and evaporated under vacuum. The residue was dissoved in 70 ml $CHCl_3$, washed with 100 ml saturated KH_2PO_4 solution and water (3 × 60 ml). The extract was dried

TABLE 1. Characteristics of Compounds Obtained

Compound	Yield, %	Mp, °C (solvent for crystallization)	Found/Calculated, %			Empirical formula	PMR spectrum (δ, ppm)			^{31}P NMR spectrum (δ, ppm)
			C	H	P		CH_3— s(18H)	—OCH_2—	aromatic protons m (26H)	
(IIIa)	84	163–164 (benzene–pentane)	76,0/76,0	7.0/6,7	8,2/8,5	$C_{46}H_{48}O_4P_2$	1,25	3,40 s (4H)	7,45–7,64	28,6
(IIIb)	65	158–159 (benzene–hexane)	74,5/74,8	6,8/6,8	8,0/8,0	$C_{48}H_{52}O_5P_2$	1,25	3,10 m (4H) 3,80 m (4H)	6,80–7,84	27,8
(IIIc)	69	186–187 (benzene–hexane)	73,4/73,7	6,9/6,9	7,2/7,6	$C_{50}H_{56}O_6P_2$	1,28	3.18 m (4H) 3,30 s (4H) 3,88 m (4H)	7,43–7,78	27.6
(IIId)	62	Oil	72,5/72,7	7.0/7.0	6.9/7,2	$C_{52}H_{60}O_7P_2$	1.30	3,24–3,92 m (16H)	7,45–7,82	27,9
(IIIe)	61	Oil	71,4/71,8	7.0/7,1	6,9/6,9	$C_{54}H_{64}O_8P_2$	1,24	2.80–3.88 m (20H)	7,44–7,75	28,1

with Na_2SO_4 and evaporated under vacuum. Then 40 ml of a saturated solution of HCl in alcohol was added to the residue. The mixture was allowed to stand for 12 h and then evaporated under vacuum. The residue was dissolved in 70 ml $CHCl_3$, washed with 100 ml 10% $NaHCO_3$ and water (2 × 50 ml), and dried with Na_2SO_4. The solvent was evaporated under vacuum and the residue chromatographed on a column of grade L silica gel; eluant $CHCl_3$. Yield of (V): 13.9 g (79%), mp 194-195°C (methyl ethyl ketone–pentane). Found: C 75.3; H 6.6; P 8.9%. Calculated for $C_{22}H_{23}O_2P$: C 75.4; H 6.6; P 8.8%. PMR spectrum (δ, ppm): 1.15 s (9H, CH_3), 6.85-7.80 m (13H, Ar). ^{31}P NMR spectrum (δ, ppm): 40.10 ppm.

b) To a solution of 7.2 g (0.02 mole) of the 4-tert-butylphenyl ester of diphenylphosphinic acid[*] in 50 ml anhydrous THF was added dropwise with stirring at −70°C a lithium diisopropylamide solution (prepared from 5.4 ml 3.35 N butyllithium solution in hexane and 2.6 ml diisopropylamine in 15 ml dry THF). The mixture was stirred for 25 min at −70°C then the temperature was raised to 20°C (1 h) and stirring continued for a further 2 h. The solvent was evaporated under vacuum; 50 ml water were added to the residue and the pH adjusted to 2 with conc. HCl. The mixture was extracted with $CHCl_3$ (3 × 30 ml). The extract was washed with 10% $NaHCO_3$ (40 ml), water (3 × 30 ml), dried with Na_2SO_4, and evaporated under vacuum. The residue was chromatographed on a column of grade L silica gel; eluant $CHCl_3$. Yield of (V): 5.7 g (80%).

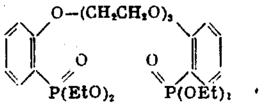
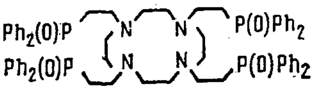
Bis-(2-diphenylphosphinyl-4-tert-butylphenyl) Ether of Ethylene Glycol (IIIa). To a solution of 4.0 g (0.011 mole) of phenol (V) in 20 ml abs. alcohol we added a solution of sodium ethylate (prepared from 0.27 g sodium in 30 ml abs. alcohol); the mixture was boiled for 10 min and then evaporated under vacuum. The residue was dried under vacuum (1 h, 100°C, 1 mm). To the resulting phenolate we added 2.2 g (0.005 mole) ethylene glycol ditosylate [14]. The reaction mixture was stirred for 11 h at 100°C and evaporated under vacuum. We added 40 ml water to the residue and extracted the mixture with $CHCl_3$ (3 × 30 ml). The extract was washed with 10% KOH (3 × 30 ml), water (3 × 40 ml), dried with Na_2SO_4, and evaporated under vacuum. The residue was chromatographed on a column of grade L silica gel; eluant $CHCl_3$. Yield of (IIIa): 3.7 g.

Compounds (IIIb)-(IIIe) were obtained similarly by alkylation of the phenol (V) with di-, tri-, tetra-, and pentaethylene glycol ditosylates [14] respectively.

---

[*] Obtained using the method from [13]. Yield 67%, mp 162-164°C. Found: C 75.7; H 6.8; P 8.7%. Calculated for $C_{22}H_{23}O_2P$: C 75.4; H 6.6; P 8.8%.

TABLE 2. Logarithms of Stability Constants (log K) of M^+L Complexes of Alkali-Metal Cations with (I), (II), and (III) Monopodands in a Mixed THF:$CHCl_3$ Solvent (4:1 by volume) at 25°C

Ligand	*n*	Li	Na+	K+	Rb+	Cs+
(Ia)	1	5,8	4,8	3,7	3,3	2.9
(IIIa)	1	5,6	4,7	3,8	3,3	2.8
(Ib)	2	4,6	4,8	3,9	3,6	3,0
(IIIb)	2	4,6	4,6	3,8	3,5	3,0
(Ic)	3	7,0	6,1	4,8	4,4	3,8
(II)	3	7,0	6,1	4,9	4,4	3,7
(IIIc)	3	6,8	5,9	4,8	4,4	3,8
(Id)	4	5,6	6,6	5,7	5,1	4,5
(IIId)	4	5,4	6,2	5,3	5,0	4.4
(Ie)	5	5,4	6,2	5,8	5,5	4,7
(IIIe)	5	5,3	6,0	5,6	5,3	4,7
(IVc)	3 [2]	6,7	6,1	4,0	3,6	3,1
	– [7]	6,3	5,7	4,5	4,1	3,5
	– [23]	5,9	6,3	5,0	–	3,6
Benzo-12-crown-4	– [2]	2,8	3,0	2,6	2,4	2,2
15-Crown-5	– [2]	4,6	4,9	4,9	4,7	4,0
Benzo-15-crown-5*	–	3,9	4,5	4,4	3,8	3,3
18-Crown-6	– [2]	5,5	6,6	5.5	4,9	4.5
Benzo-18-crown-6*		5,1	6,3	5,4	4,7	4,5
Dibenzo-18-crown-6	– [2]	4,6	6,0	5,0	4,6	4,4

*The authors are grateful to V. I. Kal'chenko for a gift of the benzo-15-crown-5 and benzo-18-crown-6 preparations.

The procedure for conductometric measurements in the THF—$CHCl_3$ system (4:1 by volume) has been described previously [6]. Random error (+2s) in determination of the logarithmic stability constants of the complexes of ligands (I), (II), and (III) with alkali-metal cations was less than ±0.1 log units. The content of ionogenic impurities in the ligands was monitored conductometrically. Alkali-metal 2,4-dinitrophenolates were used as the salts.

RESULTS AND DISCUSSION

Results from determination of the complexing properties of monopodands (I), (II), and (III) are given in Table 2. For comparison this also gives published values of log K for complexes of certain crown ethers and the most effective P(O)-containing ligands. Figure 1 (a and b) shows the logarithmic stability constants of complexes of alkali-metal cations M^+ as functions of the number (n) of CH_2CH_2O links in the polyether chain and of the total number of donor centers (m) in the structure of ligands (I) and (III). For comparison Fig. 1c shows the analogous dependence for the monopodands (IV) obtained previously [2].

These results show that the (I) and (III) monopodands are highly effective complexing agents with respect to alkali-metal cations. However their effectiveness depends substantially on the length of the oligoethylene glycol chain. Increasing the number of donor centers m in the structure of the (I) and (III) ligands leads, as a rule, to enhanced complexing ability toward all the alkali-metal cations. In our opinion [2, 7], this is due to enhanced cooperation of ion—dipole interaction of phosphoryl and ethereal oxygen donor centers of the ligand during formation of a complex with a metal cation. In that case the ligand probably forms a pseudomacrocyclic cavity around the M^+ cation. This tendency is most clearly expressed in the case of the "larger" cations K^+, Rb^+, and Cs^+, as reflected in the steady increase in log K with increase in n and m (see Fig. 1a and b).* However, for the "small" Li^+ and Na^+ cations

---

*These patterns have been noted repeatedly in the literature and we have considered them in detail previously [2, 7, 15].

the dependences of log K on n and m of the ligand are not smooth. In the case of Li^+ there are two distinctly expressed maxima at n = 1 and 3 and a minimum at n = 2, but for Na^+ there is one maximum at n = 4. As noted previously [2, 7], the extremum character of the log K dependence on the length of the ligand polyether chain is probably due to rigid steric requirements of small cations with respect to ligand structure, which does not provide optimum participation of donor centers in cooperative interaction with an M^+ cation for all values of n.* From this point of view the structures of tetra- and hexadentate monopodands (Ia), (IIIa), and (Ic), (II), and (IIIc) in the case of Li^+ and heptadentate monopodands (Id) and (IIId) in the case of Na^+ are the most favorable for producing optimum packing of all ligand donor centers around M^+; this is corroborated by the high values of log K for the corresponding complexes of these ligands, particularly with Li^+.

The pattern revealed for the effect of the length of the polyether chain on the complexing ability of podands (I) and (III) is analogous to that observed previously [7] in the case of "phosphonate" monopodands with ortho-diethoxyphosphinylphenyl terminal groups: the maxima and and minima of their complexing ability toward Li^+ and Na^+ occur for the same values of n and m as in the case of the "phosphine-oxide" monopodands (I) and (III). This fact undoubtedly points to a fundamental similarity in the formation processes of complexes with Li^+ and Na^+ for isodentate ligands of both types. However, comparison of the complexing ability of "phosphine-oxide" podands (I) with their "phosphonate" analogs also reveals interesting features in the relative effect of nucleophilic nature of terminal residues and ethereal oxygen atoms in the polyether chain on the overall coordinating ability of a ligand. For the "hard" Li^+ cation the change from monopodand (Ia) (n =1) to (Ib) (n = 2) and similarly from monopodand (IIIa) to (IIIb) is accompanied by a reduction in log K of the complexes by about an order of magnitude; this may be connected with attenuation of ion—dipole interaction of Li^+ with donor centers of the ligand due to a less advantageous stereochemical fit of the cation. The analogous change in the case of "phosphonates" lowers log K by only 0.5 log units, indicating the substantial role of the phosphoryl oxygen in ion—dipole interaction. With increase in cationic radius (Na^+, K^+) the lowering of log K on changing from (Ia) to (Ib) disappears. Moreover, for Rb^+ and Cs^+ this change is even accompanied by a certain increase in the stability constant (of 0.1 and 0.3 log units respectively), which is enhanced in the case of their "phosphonate" analogs (0.6 log units for both Rb^+ and Cs^+). Thus, reducing the basicity of terminal phosphonate groups and weakening their interaction with cations in the case of "soft" alkali metals makes it possible to reveal the "positive" role of "weak" coordination centers in the overall coordinating ability of a ligand, which as a whole is lowered compared with "phosphine-oxide" monopodands.

The masking action of strong-donor terminal groups is also revealed on comparing log K for the "pyrocatechol" podand (II) and its bisphosphonate analog [7]. Introducing a pyrocatechol moiety into the polyether chain of "phosphine-oxide" podands ((Ic) → (II)) has no effect on log K, whereas the analogous change in the "phosphonate" series reveals a reduction in log K (by 0.4 and 0.5 log units respectively) only in the case of Li^+ and Na^+, again corroborating the very well-known [16] elevated sensitivity of these cations toward decrease in the "stengths" of donor centers during complex formation. As a rule, introduction of a pyrocatechol bridge into the structure of a monopodand [17] or crown ether (see Table 2 and [16]) is accompanied by a reduction in the stability of its complexes with all the alkali-metal cations; this is usually explained by a reduction in the nucleophilic nature of the donor centers on replacing two simple ethereal oxygen atoms by pyrocatechol oxygens. The somewhat unexpected constancy of log K for alkali-metal complexes on changing from podand (Ic) to its "pyrocatechol" analog (II) suggests that in this case there is probably complete compensation for the energy losses (due to lowering of the coordinating ability of the two oxygen centers) during complex formation by the decrease in entropy resulting mainly from the more restricted conformational mobility of ligand (II). As already mentioned, for tri- and tetra(tetrahydropyrane) monopodands, which have a considerably smaller set of conformers than the acyclic ethers glyme-3 and glyme-4 respectively, there is an appreciable and probably an "entropic" increase in log K for complexes of alkali metals since these ligands are isodentrate and their donor centers are similar in their nature [4, 5].

---

*Note that a dependence with multiple extrema has been found by calculation for the enthalpy of metal—ligand bond rupture in ZnX_n complexes, where X = H_2O or NH_3 and n= 1-7, "compounds with even coordination numbers having an elevated stability" [24].

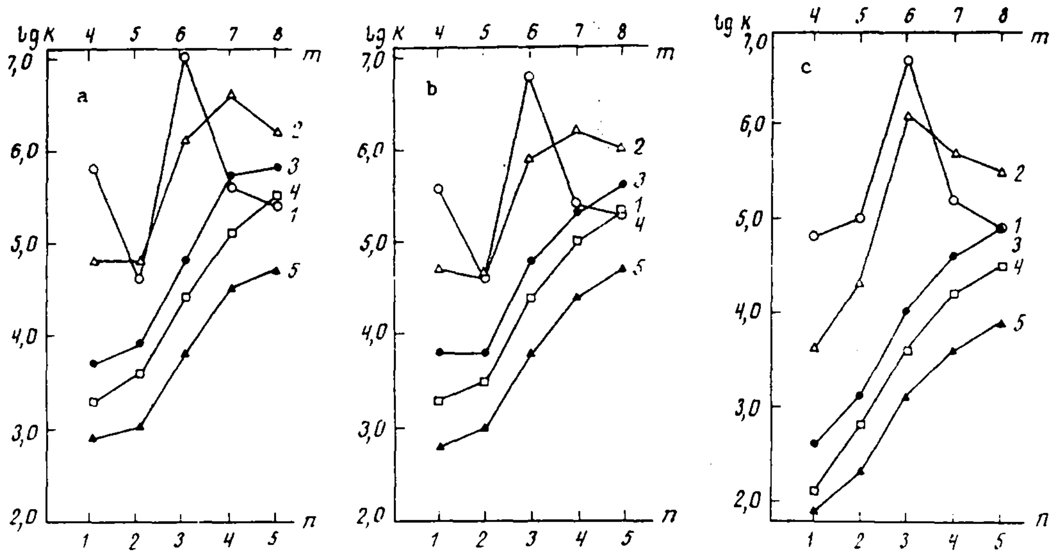


Fig. 1. Dependence of logarithms of stability constants of complexes of bis-[2-(diphenylphosphinyl)phenyl] (I) (a), bis[2-(diphenylphosphinyl) (4-tert-butylphenyl)] (III) (b), and bis[2-(diphenylphosphinylmethyl)phenyl] (IV) (c) [5] ethers of oligoethylene glycols with alkali-metal cations on length of the polyether chain (n) and number of donor centers (m): (1) Li^+, (2) Na^+, (3) K^+, (4) Rb^+, (5) Cs^+.

Comparison of complexing properties of monopodands (I) and (III) with podands (IV) (see Fig. 1) containing donor centers completely identical in number and type also indicates the important role of steric factors in the formation of complexes of these ligands with alkali-metal cations. A decrease in the "geometrical" length of podands (I) and (III) by two CH_2 groups compared with the (IV) ligands should in principle alter the mutual disposition of "strong" (phosphoryl oxygen atoms) and "weak" (ethereal oxygen atoms in the polyether chain) donor centers during coordination with M^+ and, consequently, the complexing and selective properties of these ligands should also change. In fact, comparing their curves (Fig. 1a and c) it is not difficult to see that monopodands (I) are almost always appreciably more effective than their isodentate analogs (IV). This pattern is expressed particularly clearly in the case of the "large" cations K^+, Rb^+, and Cs^+ where the differences in log K of the corresponding complexes are 0.7-1.2 log units. For sodium complexes of the isodentate ligands (I) (IV) the differences in log K are also quite large (from 0.5 to 1.2 log units), apart from the hexadentate ligands (Ic) and (IVc) which are identically effective towards Na^+. Only in the series of corresponding lithium complexes is there a single case where the effectiveness of the tetradentate monopodand (IVb) is higher (by 0.4 log unit) than that of its isodentate analog (Ib), the complexing ability of the remaining (I) ligands being 0.3-1.0 log unit higher than that of the corresponding (IV) ligands. Comparison of curves b and c in Fig. 1 shows that the relationships between log K for complexes of the alkali metals with isodentate monopodands (III) and (IV) are much the same but somewhat less pronounced.

It should be stressed that conformational-geometric differences in monopodands (I), (III), and (IV) qualitatively alter the character of the dependences of log K for their complexes with Li^+ and Na^+ on the length of the polyether chain. For lithium complexes of ligands (I) and (III) this is expressed by the occurrence of a sharp maximum (at $n = 1$) and a minimum (at $n = 2$) which do not occur on the analogous dependence of log K on n and m for the (IV) ligands. At the same time the highest maximum (which is almost identical in absolute magnitude) of complexing ability toward Li^+ occurs at the same values of n and m (3 and 6) for all three series of ligands, as well as for compound (II) (see Fig. 1 and Table 2). These facts, in our opinion, indicate that a decrease in the "geometric" length of the ligand by two CH_2 groups scarcely alters the degree of cooperative interaction of donor centers of hexadentate monopodands (Ic), (II), and (IIIc) ($n = 3$) compared with their isodentate analog (IVc) ($n = 3$). Considering the high values (6.7-7.0) of log K for their lithium complexes, it is evidently possible that in all four cases with m = 6 a state is reached which is close to coordination saturation of the Li^+ cation.* At the same time, changing to "abridged" isodentate ligands, from (IVa) to (Ia) and (IIIa) (n = 1, m = 4), and from (IVb) to (Ib) and (IIIb) (n = 2, m = 5), leads to emergence of a sharp maximum and correspondingly a minimum on the log K dependences on n and m for lithium complexes of ligands (I) and (III) with m = 4 and 5; this is probably due to enhancement and correspondingly weakening of the degree of cooperative ion—dipole interaction of the donor centers of these ligands with the Li^+ cation.

From a similar comparison for Na^+ (see Fig. 1) it is not difficult to see that the maximum for complexing ability of "abridged" monopodands (I) and (III) towards this cation occurs for n = 4 and m = 7 in contrast with monopodands (IV), where this maximum is observed for n = 3 and m = 6. The displacement of the maximum of complexing ability by +1 (from n = 3 and m = 6 to n = 4 and m = 7) on changing ligands from (IV) to (I) and (III) suggests that in the case of Na^+ the ethylene glycol moiety CH_2CH_2O, tentatively speaking, is "conformationally equivalent" to two CH_2 groups, i.e., a decrease in "geometric" length of a ligand by two CH_2 groups requires "compensation" in the form of an additional CH_2CH_2O link to achieve the maximum effectiveness of monopodands of this type towards Na^+. Participation of this additional donor center (ethereal oxygen atom) for ligands (Id) and (IIId) in coordination with Na^+* probably increases the maximum of the complexing ability in absolute magnitude by 0.5 and 0.1 log unit, respectively, compared with the most effective monopodand towards Na^+ (IVc).

As already noted, ligands (I), (II), and (III) are highly effective complexing agents towards all the alkali-metal cations. However, we should particularly note the high values of log K for lithium complexes of (Ic), (II) [20], and (IIIc), which are substantially higher than the analogous values for the strongest phosphorus-containing complexing agents and crown ethers (see Table 2 and [15]). Towards the other alkali-metal cations the complexing ability of monopodands (I), (II), and (III) is on the same level as or even exceeds that of the crown-ether series. Note that log K for ligand (III) complexes containing a tert-butyl substituent in the terminal group is always somewhat lower than the corresponding log K for ligand (I) complexes without this substituent. Similar patterns, such as the steady decrease in the effectiveness of benzo-substituted crown ethers towards alkali-metal cations on gradual elongation of alkyl substituents [21], have been noted previously and interpreted in terms of variation in solvation processes during complex formation [22].

Finally, let us note that in their selective properties towards a number of alkali-metal cations monopodands (I), (II), and (III) are appreciably inferior to the (IV) monopodands. However the Li/Na, Li/K, and in some cases even Na/K selectivity of these ligands (defined as the ratio of stability constants of pairs of identical complexes) is superior to that of crown ethers (see Table 2 and Fig. 1) in the given solvent system. We have carried out a more detailed comparative analysis of the selective properties of monopodands (IV) previously [2].

LITERATURE CITED

1. V. P. Solov'ev, L. V. Govorkova, O. A. Raevskii, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 575 (1991).
2. V. I. Evreinov, V. E. Baulin, Z. N. Vostroknutova, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 1990 (1989).
3. C. J. Pedersen, Science, 241, 536 (1988).
4. T. Iimori, W. C. Still, A. L. Rheingold, et al., J. Am. Chem. Soc., 111, No. 9, 3439 (1989)
5. T. Iimori, Sh. D. Erickson, A. L. Rheingold, et al., Tetrahedron Lett., 30, No. 50, 6947 (1989).
6. V. I. Evreinov, Z. N. Vostroknutova, V. E. Baulin, et al., Zh. Obshch. Khim., 59, No. 1, 67 (1989).
7. V. I. Evreinov, Z. N. Vostroknutova, V. E. Baulin, et al., Zh. Obshch. Khim., 59, No. 1, 73 (1989).
8. V. I. Evreinov, Z. N. Vostroknutova, A. N. Bovin, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 60 (1989).
9. V. P. Solov'ev, L. V. Govorkova, O. A. Raevskii, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 814 (1989).

---

*According to x-ray structural data, the maximum coordination numbers of Li^+ [18] and Na^+ [19] are eight.

10. E. N. Tsvetkov, V. Kh. Syundyukova, and V. E. Baulin, Zh. Obshch. Khim., 57, No. 11, 2456 (1987).
11. E. N. Tsvetkov, V. Kh. Syundyukova, and V. E. Baulin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 147 (1989).
12. K. A. Petrov, S. V. Agafonov, and V. P. Pokatun, Zh. Obshch. Khim., 57, No. 1, 98 (1987).
13. A. Williams and R. A. Naylor, J. Chem. Soc. (B), No. 10, 1967 (1971).
14. V. E. Baulin, V. Kh. Syundyukova, and E. N. Tsvetkov, Zh. Obshch. Khim., 59, No. 1, 62 (1989).
15. T. E. Kron and E. N. Tsvetkov, Usp. Khim., 59, No. 3, 483 (1990).
16. R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, et al., Chem. Revs. 85, No. 4, 319 (1985).
17. A. N. Bovin, V. I. Evreinov, Z. N. Vostroknutova, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2611 (1989).
18. P. P. Power, Acc. Chem. Res., 21, No. 1, 147 (1988).
19. S. E. V. Phillips and J. Trotter, Can. J. Chem., 54, No. 17, 2723 (1976).
20. E. N. Tsvetkov, V. Kh. Syundyukova, V. E. Baulin, et al., USSR Inventor's Certificate No. 1,300,908; Byull. Izobret. (1985).
21. N. A. Parpiev, Sh. K. Norov, B. A. Tashmukhamedov, et al., Bioorg. Khim., 9, No. 10, 1429 (1983).
22. A. A. Varnek, A. S. Glebov, Sh. K. Norov, et al., Koordinats. Khim., 15, No. 6, 740 (1989).
23. É. I. Sinyavskaya, L. V. Tsymbal, K. B. Yatsimirskii, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 176 (1986).
24. A. A. Voityuk and A. A. Bliznyuk, Koordinats. Khim., 16, No. 2, 163 (1990).