Thermodynamics and selectivity of complexation of lithium and sodium thiocyanates with phosphorus-containing podands and compounds modeling the terminal groups of these podands

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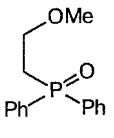
A series of model compounds and heptadentate neutral phosphorus-containing podands that differ in the conformational rigidity of the terminal groups and in the coordination properties of the phosphoryl groups were synthesized. The thermodynamic parameters of complexation and the cationic selectivity of organophosphorus compounds and podands with respect to LiNCS and NaNCS were studied by calorimetric titration in acetonitrile at 298 K. The reasons for the high selectivity of certain phosphorus-containing podands to the Li^+ cation are discussed.

Key words: phosphorus-containing neutral podands, synthesis; thermodynamics of complexation with Li^+ and Na^+ cations; selectivity of complexation; calorimetry.

It has been shown previously[1,2] that the ability of phosphorus-containing podands to form complexes is determined by the structure of their terminal moieties and the length of the polyether chain. Hence, the study of compounds that model both the terminal groups of podands and the polyether chain should probably make it possible to predict the complexation properties of ligands of this type. The complexation ability of glymes, which model the polyether chain, has been well studied,[3] but the studies of compounds that model the terminal phosphoryl-containing groups of podands are in their infancy. For example, a molecular mechanics method has been used to calculate the interaction of (2-methoxyphenyl)diphenylphosphine oxide and (β-methoxyethyl)diphenylphosphine oxide with Li^+ and Na^+ ions; the results obtained agree satisfactorily with the data obtained by calorimetry.[4] The conformations of *ortho*-diphenyl- and *ortho*-dibutylphosphinoylanisoles in



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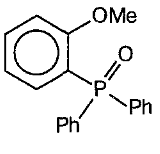

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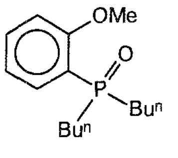

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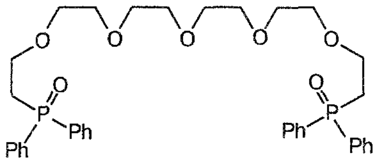

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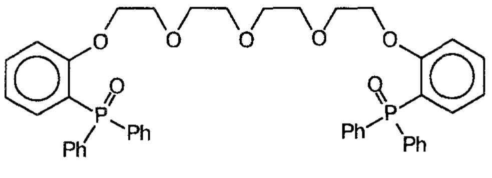

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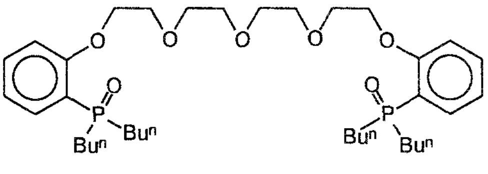

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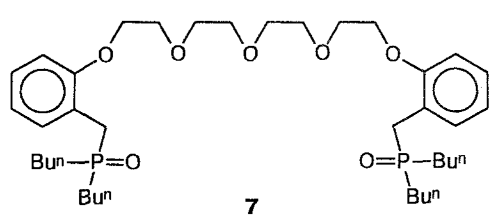

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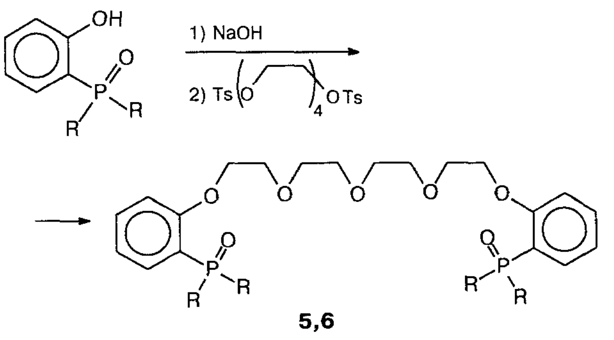
solution have been studied by IR spectroscopy and by measuring the dipole moments. It has been shown that these compounds are convenient objects for modeling the fine conformational transitions occurring in a podand molecule when it passes from the free state into a complex.[5] However, the establishment of the relationship between the structure of the phosphorus-containing moiety and the complexation properties of the corresponding podand requires the determination of the complexation ability and the selectivity with respect to metal cations for the model compound and the podand of interest under the same conditions.

Previously,[6] we have studied the ability of the heptadentate ligand, 1,17-bis(diphenylphosphinoyl)-3,6,9,12,15-pentaoxaheptadecane, to form complexes with salts of alkaline and alkaline-earth metals in acetonitrile. It has been shown that this compound is much more selective in forming complexes with the Li^+ cation than crown ethers.

With the aim of finding efficient and selective ligands for the Li^+ cation, in the present work we decided to study model compounds **1—3** and heptadentate podands **4—7**, which differ in the conformational rigidity of the terminal moiety and in the coordination ability of the phosphoryl group. Calorimetric titration in acetonitrile was used to obtain the thermodynamic characteristics of the complexation process (the stability constants, enthalpy, and entropy) and to determine the cationic selectivity of model compounds **1—3** and podands **4—7** with respect to lithium and sodium thiocyanates.

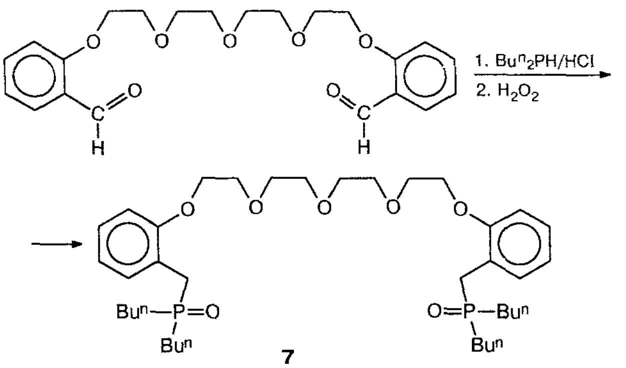
To perform a thorough study of phosphorus-containing podands, it was necessary to develop simple methods for their synthesis from the available reagents. We synthesized compounds **4—7** using improved procedures. For example, 1,17-bis(diphenylphosphinoyl)-3,6,9,12,15-pentaoxaheptadecane (**4**) was obtained using a procedure developed recently.[7] In the synthesis of ligands **5** and **6**, we managed to exclude the previously used[8] anhydrous solution of sodium ethoxide and to eliminate the step of preparation of sodium derivatives of *o*-phosphorylated phenols; instead, solid sodium hydroxide was utilized.



5,6

5: R = Ph
6: R = Bu^n

The syntheses of podands containing alkyl substituents are often complicated by difficulties associated with the purification of the target compounds from monoalkylation by-products, which are difficult to separate even by column chromatography. Therefore, we synthesized ligand **7** by a nontraditional two-step method. In the first step, alkylation of the sodium salt of salicylaldehyde with tetraethylene glycol ditosylate gave 1,11-bis(2-formylphenoxy)-3,6,9-trioxaundecane, which could be easily purified on Al_2O_3. The addition of dibutylphosphine to the resulting compound afforded podand **7**.



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Experimental

^1H and ^{31}P NMR spectra were recorded in $CDCl_3$ on a Bruker CXP-200 spectrometer relative to Me_4Si and 85 % H_3PO_4, respectively. Melting points were measured on a Boetius PHMK-05 hot stage. The heats of the reaction were measured on an LKB-2107 calorimeter at 298 K by calorimetric titration. Both titration of the ligand solution with the salt solution and titration of the salt solution with the ligand solution were carried out. The following overall concentrations of the reagents were used:

Reagent	C/mmol L^{-1}
LiNCS	0.6—45
NaNCS	0.5—38
1	1—65
2	15—20
3	1—66
4	1—43
5	18—20
6	17—25
7	20—23

The stoichiometry of the complexes that exist in equilibrium with the starting reagents, the logarithms of the equilibrium constants, and the enthalpies of complexation were calculated using the CHEM-EQU program package on PC/AT computers. The computation algorithms and the statistical criteria for selecting the model of equilibria in a solution that most precisely fits the experimental data (heats of reactions, overall concentrations of reagents, and volumes of solutions), have been reported in detail previously.[9] The acetonitrile and salts used for the preparation of solutions were preliminarily dehydrated: acetonitrile was dried with P_2O_5 followed by distillation from calcium hydride.[10] The synthesis of "pure for analysis" grade sodium thiocyanate and the monitoring of its water content were performed according to reported procedures.[11] "Pure" grade lithium thiocyanate, $LiNCS \cdot nH_2O$, was recrystallized from acetonitrile, then dry benzene (100 mL per 10 g of lithium thiocyanate) was added, and the mixture was boiled for 5 h on a water bath with a reflux condenser. The benzene was slowly distilled off (not to dryness) in a sealed system, and dry benzene was added to the product. This procedure was repeated three times. The resulting anhydrous lithium thiocyanate was additionally dried *in vacuo* (5 Pa). The absence of water in the LiNCS was monitored by IR spectra.

(β-Methoxyethyl)diphenylphosphine oxide (1) and (2-methoxyphenyl)diphenylphosphine oxide (2) were synthesized as described previously.[4] **(2-Methoxyphenyl)dibutylphosphine oxide (3)** was obtained by the recently developed procedure.[5]

1,11-Bis[2-(diphenylphosphinoyl)phenoxy]-3,6,9-trioxaundecane (5). Finely ground NaOH (0.68 g, 17 mmol) and tetraethylene glycol ditosylate (4.13 g, 8.5 mmol) were added to a suspension of *o*-diphenylphosphinoylphenol[12] (5.0 g, 17 mmol) in dry dioxane (35 mL). The reaction mixture was boiled for 10 h with stirring and concentrated *in vacuo*. Water (50 mL) was added to the residue, and the mixture was acidified with conc. HCl to pH 2 and extracted with $CHCl_3$ (3×40 mL). The extract was washed with water (3×40 mL) and concentrated *in vacuo*. The residue was chromatographed on a column with L 100/160μ silica gel using chloroform and chloroform—ethanol (10 : 1) as eluents to give 5.20 g (78 %) of compound **5**, m.p. 117—119 °C (ethyl methyl ketone). Lit. data:[8] m.p. 117—119 °C.

1,11-Bis[2-(dibutylphosphinoyl)phenoxy]-3,6,9-trioxaundecane (6) was synthesized similarly to compound **5** by alkylating *o*-dibutylphosphinoylphenol[12] with tetraethylene glycol ditosylate. The yield of compound **6** (oil) was 68 %. Found (%): C, 64.3; H, 8.8; P, 9.0. $C_{36}H_{60}O_7P_2$. Calculated (%): C, 64.8; H, 9.1; P, 9.7. ^{1}H NMR, δ: 0.96 (t, 12 H, CH_3, $^3J_{H,H}$ = 7 Hz); 1.44 (m, 16 H, CH_2); 2.06 (m, 8 H, CH_2—P); 3.68 (m, 8 H, CH_2O); 3.84 (m, 4 H, CH_2O); 4.18 (m, 4 H, CH_2O); 6.88 (m, 2 H, H arom.); 7.12 (m, 2 H, H arom.); 7.40 (m, 2 H, H arom.); 7.96 (m, 2 H). ^{31}P NMR, δ: 42.32.

1,11-Bis[2-(dibutylphosphinoylmethyl)phenoxy]-3,6,9-trioxaundecane (7). The synthesis involved two stages. First, treatment of the sodium salt of salicylaldehyde (14.6 g, 0.10 mol) with tetraethylene glycol ditosylate (25.5 g, 0.05 mol) according to the reported procedure[13] gave 13.1 g (65 %) of 1,11-bis(2-formylphenoxy)-3,6,9-trioxaundecane (oil). Found (%): C, 65.30; H, 6.55. $C_{22}H_{26}O_7$. Calculated (%): C, 65.65; H, 6.51. ^{1}H NMR ($CDCl_3$), δ: 3.84—4.30 (m, 16 H, OCH_2); 6.97 (m, 8 H, H arom.); 10.43 (s, 2 H, C(O)H). A mixture of dibutylphosphine (5.0 g, 0.034 mol) and conc. HCl (7.0 mL) was heated to 80 °C under argon, then a solution of 1,11-bis(2-formylphenoxy)-3,6,9-trioxaundecane (6.89 g, 0.017 mol) in toluene (10 mL) was added. The mixture was heated to 120 °C (in a bath) and kept for 3 h. Hydrogen peroxide (5 mL of 35 % aqueous solution) was added, and the mixture was stirred for an additional 1 h and then cooled to room temperature. $CHCl_3$ (35 mL) was added and the reaction mixture was poured into water (50 mL). The organic layer was separated, washed with 20 % NaOH (2×30 mL), HCl (1 : 1, 2×30 mL), and H_2O_2 (2×30 mL) and concentrated *in vacuo*. The residue was chromatographed on a column with L 100/160μ silica gel using chloroform and chloroform—ethanol (10 : 1) as eluents to give 8.3 g (71 %) of compound **7** (oil). Found (%): C, 65.5; H, 9.2; P, 8.7. $C_{38}H_{64}O_7P_2$. Calculated (%): C, 65.7; H, 9.3; P, 8.9. ^{1}H NMR, δ: 0.97 (t, 12 H, CH_3, $^3J_{H,H}$ = 7 Hz); 1.38—1.84 (m, 32 H, CH_2); 3.32 (d, 4 H, CH_2—P, $^2J_{H,H}$ = 16 Hz); 3.76 (m, 8 H, OCH_2); 3.94 (m, 4 H, OCH_2); 4.22 (m, 4 H, OCH_2); 6.94 (m, 2 H, H arom.); 7.28 (m, 2 H, H arom.). ^{31}P NMR, δ: 48.9.

Results and Discussion

The stoichiometry of the complexes (M : L), the logarithms of the overall constants of formation of the complexes (log β), and the enthalpies (Δ*H*), entropies (Δ*S*), and Gibbs energies (Δ*G*) of complexation of lithium and sodium thiocyanates with phosphorus-containing simple ligands **1**—**3** and with phosphorylated podands **4**—**7** are given in Table 1.

Both model compounds **1**—**3** and podands **4**—**7** can form complexes with diverse stoichiometry. Since ligands **1**—**3** have few electron-donating centers, they react with Li^+ and Na^+ cations to afford not only simple 1 : 1 complexes, but also 1 : 2 and 1 : 4 complexes containing two and four L molecules, respectively. An intermediate 1 : 3 complex of ligands **1**—**3** was not detected in either of the cases. Podands **4**—**7** possess more coordination centers and have greater conformational mobility than simple compounds **1**—**3**, which makes it possible for them to form complexes with various compositions: the Li^+ cation, whose ionic radius is small (0.060 nm), forms not only 1 : 1 complexes, but also binuclear (2 : 1) complexes with ligands **4** and **6** and polynuclear (3 : 2) complexes with ligands **5** and **7**. The Na^+ cation (whose ionic radius is 0.095 nm) reacts with the podands to give 1 : 1 complexes; a 2 : 1 complex containing two L molecules is formed only with ligand **6**. It should be noted that in the case of podand **4**, which has the highest selectivity with respect to lithium (see below), the formation of a binuclear complex (2 : 1) was additionally confirmed using lithium perchlorate.[6] The formation of a binuclear complex was also observed by us previously when we isolated a 2 : 1 crystalline complex derived from NaI; this complex was formed from a shorter pentadentate ligand[8] and the Na^+ cation, whose ionic radius is larger than that of Li^+.

The stability constants (K_1) of the 1 : 1 complexes formed by simple ligands **1**—**3** and LiNCS are approximately one order of magnitude greater than those of similar complexes formed from NaNCS. Obviously, in each of these ligands, the O atom of the phosphoryl group is the main coordinating center due to its electron-donating properties. Hence, in an acetonitrile solution the phosphoryl group preferentially binds Li^+ cations (rather than Na^+). Conversely, the values of log K_1 for the 1 : 1 complexes formed by podand ligands **4**—**7** with NaNCS are greater than those for the complexes derived from LiNCS. For sodium thiocyanate, the complex derived from podand **5** possesses the greatest log K_1 (log K_1 = 4.8), while for lithium thiocyanate the greatest log K_1 is observed with compound **4** (log K_1 = 3.5). This confirms that coordination involves not only the O atoms of the phosphoryl group, but also those of the ether group, which predominantly interact with Na^+ (*cf.* the literature data on crown ethers[9,14]).

The complexes with different stoichiometry formed by model ligands **1**—**3** with LiNCS are also more stable than those formed with NaNCS. The stability constants

Table 1. Thermodynamic characteristics of the complexation of lithium and sodium thiocyanates with ligands **1**—**7** in acetonitrile at 298 K

Salt	M : L*	logβ	ΔH /kJ mol^{-1}	ΔS /J mol^{-1} K^{-1}	ΔG /kJ mol^{-1}	$\frac{-\Delta H}{RT\ln10}$	$\frac{\Delta S}{R\ln10}$
Ligand **1**							
LiNCS	1 : 1	1.92	−8.3	8.9	−10.97	1.46	0.46
	1 : 2	3.51	−16.3	12.5	−20.06	2.86	0.65
	1 : 4	6.47	−20.2	55.9	−36.90	3.55	2.92
NaNCS	1 : 1	1.21	−10.8	−13.2	−6.91	1.90	−0.69
	1 : 2	1.81	−6.9	11.3	−10.31	1.22	0.59
	1 : 4	7.25	−9.0	108.5	−41.38	1.58	5.67
Ligand **2**							
LiNCS	1 : 1	2.03	−12.7	−3.6	−11.60	2.22	−0.19
	1 : 2	4.73	−13.9	43.8	−26.98	2.44	2.29
	1 : 4	8.99	−12.6	129.9	−51.31	2.20	6.79
NaNCS	1 : 1	1.09	−8.0	−6.0	−6.23	1.40	−0.31
	1 : 2	1.45	−4.0	14.4	−8.29	0.70	0.75
	1 : 4	6.34	−7.0	98.1	−36.19	1.22	5.12
Ligand **3**							
LiNCS	1 : 1	2.22	−13.9	−4.4	−12.65	2.44	−0.23
	1 : 2	4.42	−18.9	21.2	−25.25	3.32	1.11
	1 : 4	7.36	−27.9	47.2	−42.00	4.89	2.46
NaNCS	1 : 1	1.44	−6.7	5.2	−8.21	1.17	0.27
	1 : 2	3.66	−1.7	64.5	−20.92	0.29	3.37
	1 : 4	7.07	−7.9	108.8	−40.37	1.39	5.68
Ligand **4**							
LiNCS	1 : 1	3.5	−22.9	−9.8	−20.0	4.01	−0.51
	2 : 1	6.0	−33.0	4.2	−34.3	5.78	0.22
NaNCS	1 : 1	3.82	−27.0	−17.4	−21.8	4.73	−0.91
Ligand **5**							
LiNCS	1 : 1	2.40	−17.9	−14.0	−13.72	3.13	−0.73
	3 : 2	9.52	−28.3	87.3	−54.36	4.97	4.56
NaNCS	1 : 1	4.82	−27.0	1.7	−27.51	4.73	0.09
Ligand **6**							
LiNCS	1 : 1	2.19	−26.5	−47.0	−12.50	4.64	−2.45
	2 : 1	3.44	−15.4	14.2	−19.64	2.70	0.74
NaNCS	1 : 1	3.04	−17.0	1.2	−17.35	2.98	0.06
	1 : 2	4.43	−20.4	16.4	−25.29	3.57	0.86
Ligand **7**							
LiNCS	1 : 1	3.44	−17.1	8.5	−19.64	3.00	0.44
	3 : 2	11.81	−42.2	84.6	−67.41	7.39	4.42
NaNCS	1 : 1	3.97	−24.7	−6.8	−22.66	4.33	−0.36

Note. The mean errors in the logarithms of the stability constants are 0.15, those of the enthalpies are ~1.0 kJ mol^{-1}.

* M : L	Equilibria
1 : 1	M + L = ML
2 : 1	2 M + L = M_2L
1 : 2	M + 2 L = ML_2
3 : 2	3 M + 2 L = M_3L_2
1 : 4	M + 4 L = ML_4

of the 1 : 2 complexes are greater by 1—3 orders of magnitude, whereas those of the 1 : 4 complexes are greater, on the average, by one order of magnitude. The main feature of the interaction of neutral podands **4—7** with Li^+ is that they can form 2 : 1 and 3 : 2 polynuclear complexes having rather high stability constants (except for ligand **6**, whose 1 : 1 and 2 : 1 complexes are less stable). This fact can be explained only by the steric features of the Bu substituents at the P=O groups, which hinder the interaction of podand **6** with the Li^+ and Na^+ cations in solution.

The enthalpies of complexation ($-\Delta H_1$ and $-\Delta H_2$) for model ligands **1—3** are 1.5—2 times smaller than the $-\Delta H_1$ values for podands **4—7**. This indirectly confirms that the O atoms of both the P=O groups and the ether groups participate in the complexation of podands **4—7** with the Li^+ and Na^+ cations. This conclusion agrees with the results of X-ray studies of 1,8-bis[(2-diphenylphosphinoylmethyl)phenoxy]-3,6-dioxaoctane, in which the participation of the phosphoryl and ether O atoms in coordination with the Li^+ and Na^+ cations has been proven.[15,16]

The entropy of formation of the 1 : 1 complexes derived from model ligands **1—3** and podands **4**, **5**, and **7** with LiNCS and NaNCS (ΔS_1) varies from −17 to 10 J mol^{-1} K^{-1} without noticeable regularities. The only exception is the entropy of formation of the complex derived from podand **6** with LiNCS, where $\Delta S_1 = -47$ J mol^{-1} K^{-1}. This directly confirms the steric influence of the Bu substituents (unlike the Ph substituents in ligands **4** and **5**) at the P=O groups. However, the presence of a methylene bridge between the phosphoryl group and the benzene ring (ligand **7**) completely eliminates the difference between the ligands with Bu and Ph substituents.

We have previously suggested a generalized approach for the calculation of the selectivity of complexation in the cases when a solution contains complexes of various stoichiometries formed by various complexing agents.[17] When the solution can contain complexes of several metals with the same complexing agent, the selectivity of complexation (Sel) of the metal M_a with the ligand can be estimated using the formula

$$\mathrm{Sel}(M_a) = \frac{\sum\limits_{i=1}^{n} \nu_{ai} \cdot C_i}{\sum\limits_{k=1}^{B} \sum\limits_{b=1}^{m} \nu_{kb} \cdot C_b} = \frac{\sum\limits_{i=1}^{n} \nu_{ai} \cdot \exp(\ln\beta_i + \sum\limits_{j=1}^{N} \nu_{ij} \cdot \ln C_j)}{\sum\limits_{k=1}^{B} \sum\limits_{b=1}^{m} \nu_{kb} \cdot \exp(\ln\beta_b + \sum\limits_{j=1}^{N} \nu_{bj} \cdot \ln C_j)} \qquad (1)$$

Here C_i is the concentration of a complex containing the metal cation, M_a; ν_{ai} is the stoichiometric coefficient at M_a in the i-th complex; ν_{kb} is the stoichiometric coefficient at M_b in the k-th complex; n is the number of complexes formed by M_a with the ligand; m is the number of complexes formed by M_b with the ligand; B is the number of metals involved in complexation; C_j is the concentration of the j-th basis component; N is the number of components forming the basis; ν_{ij} is the stoichiometric coefficient at the j-th basis component in the i-th reaction; β_i is the overall constant of formation of the i-th complex from the C_j basis components (j = 1, 2, ... , N). The value of Sel(M_a) is not an absolute characteristic, but depends on the overall concentrations of the reagents; however, it varies over a limited range (from 0 to 1, or from 0 to 100 %).

Equation (1) can be used for comparing the selectivity of complexation of Li^+ and Na^+ with ligands **1—7**. Let us assume that the overall concentrations of lithium and sodium salts in solution are 0.03 mol L^{-1} (these are the maximum average concentrations that allow us to ignore the effect of the ionic strength) and the overall concentration of the ligand varies from 0 to 0.08 mol L^{-1}. Figure 1, *a—g* presents the concentration dependences of the selectivity function (see Eq. (1)) taking into account all complexes formed by Li^+ and Na^+ with each ligand. It follows from relationship (1) that the sum of the selectivities, Sel(M_a), equals 1; thus, if the overall concentrations of the Li^+ and Na^+ cations are equal, their selectivity plots should mirror each other.

Ligand **1** displays high selectivity toward Li^+ (Sel(Li) > 80 %) at an overall concentration of the ligand $C_L{}^0 < 0.01$ mol L^{-1}, because log β_1 and log β_2 are greater that the similar constants for Na^+ (Fig. 1, *a*). Ligand **2** has a high selectivity, Sel(Li) ~90 %, over a very broad range of its concentrations (Fig. 1, *b*). The selectivity, Sel(Li), of ligand **3** is also rather high (80 % at $C_L{}^0 < 0.01$ mol L^{-1}), but decreases as $C_L{}^0$ increases (Fig. 1, *c*). Hence, the phosphorus-containing compounds that model the terminal groups of the podands studied, display high selectivity to lithium compared to sodium and can serve as electron-donating centers for lithium-specific complex-forming reagents.

Podands **4—7** are characterized by more diverse dependences of the selectivity on concentration than simple ligands **1—3**. Of these podands, compound **4** displays the highest selectivity to lithium (Sel(Li) ~90 % at $C_L{}^0 <$ 0.005 mol L^{-1}). This is exclusively due to the formation of a binuclear complex, Li_2L^{2+}, because the stability constants of the simple complexes, LiL^+ and NaL^+, have similar values (Fig. 1, *d*). Podand **5** displays very high selectivity to sodium (Sel(Na) ~100 % in the range of $C_L{}^0$ from 0 to 0.02 mol L^{-1}) since the NaL^+ complex with this ligand is highly stable, whereas the LiL^+ is moderately stable (Fig. 1, *e*). Although ligand **6** forms a binuclear Li_2L^+ complex, like podand **4**, it is still more selective to sodium than to lithium (Sel(Na) ~80 % at $C_L{}^0 < 0.01$ mol L^{-1}), since log $\beta_1(NaL^+)$ is greater than log $\beta_1(LiL^+)$ (Fig. 1, *f*). Ligand **7** displays a small maximum in its selectivity to lithium (Sel(Li) ~65 % at

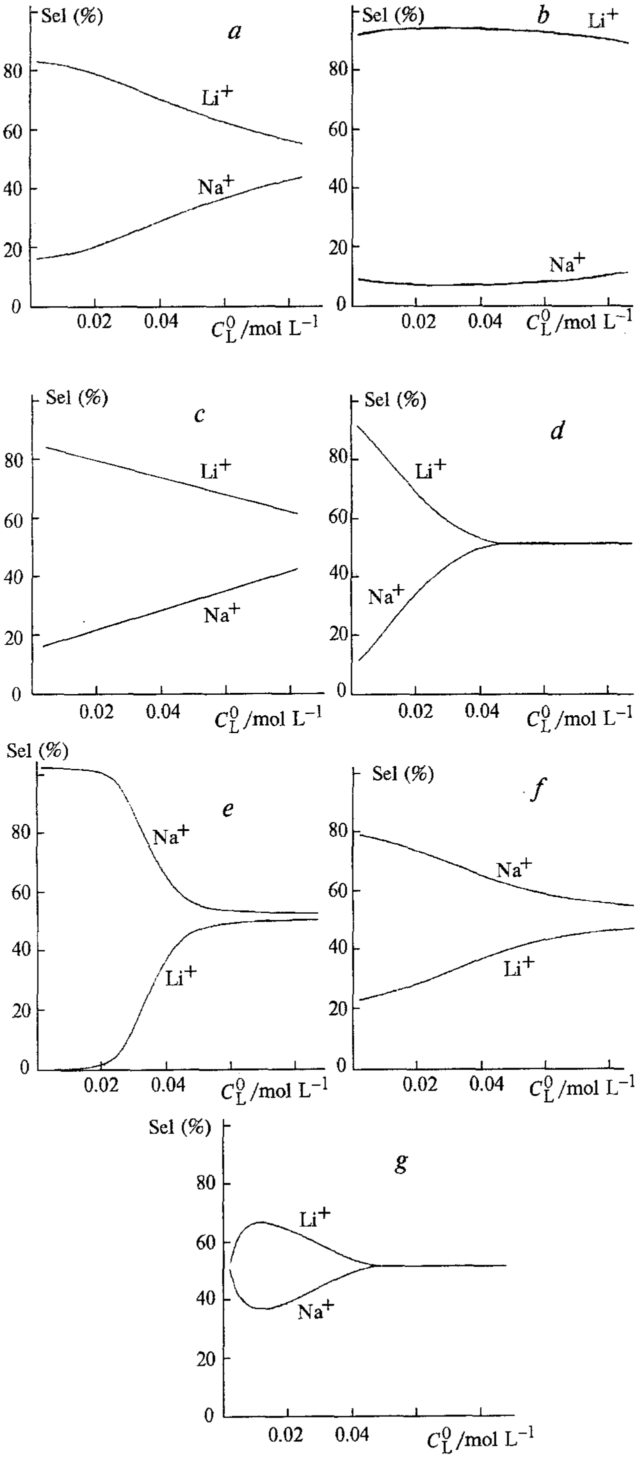

Fig. 1. Dependence of the selectivity function, Sel(M), of the Li^+ and Na^+ cations on the overall concentration of ligands: *a*, **1**; *b*, **2**; *c*, **3**; *d*, **4**; *e*, **5**; *f*, **6**; *g*, **7**.

$C_L{}^0$ = 0.01 mol L^{-1}), since it forms a polynuclear $Li_3L_2{}^{3+}$ complex along with the LiL^+ and NaL^+ complexes (Fig. 1, *g*).

Thus, the high selectivity of podands with respect to lithium is determined by the formation of polynuclear complexes, such as Li_2L^{2+} and $Li_3L_2{}^{3+}$, rather than by the high stability constants of simple LiL^+ complexes. In addition, the selectivity to lithium relative to sodium manifests itself at low concentrations of the ligands, concentrations which are significantly lower than those of the metal cations. This should also be taken into account when performing extraction and when constructing ion-selective electrodes based on podands.

The following conclusions can be drawn from a comparison of the complexing ability of model compounds **1**—**3** and podands **4**—**7**. The phosphoryl group has greater affinity for the Li^+ cation in acetonitrile than for Na^+. This effect is particularly distinct when 1 : 1 complexes are formed. A similar conclusion can also be reached for the THF—$CHCl_3$ solvent system (4 : 1, v/v) based on literature data[1,2,13] on 1 : 1 complexes. Hence, high lithium-sodium selectivity can be found for ligands, in which phosphoryl groups are the main coordinating centers. Of phosphorus-containing podands, the ligands with short polyether chains (*e.g.*, ethylene glycol derivatives) are the most interesting. The introduction of a sufficient amount of additional coordinating centers of other types, namely, O atoms of the ether groups, can significantly level off the lithium-sodium selectivity when 1 : 1 complexes are formed. However, selective bonding is also possible in this case due to the formation of polynuclear complexes (2 : 1, 3 : 2, *etc.*). Monopodands incorporating relatively long polyether chains and various polypodands with more than two phosphorus-containing terminal groups may be most promising in this case.

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