Complexation of lithium and sodium cations with β-phosphorylate ethers, modelling terminal groups of organophosphorus podands. An experimental and theoretical study

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Abstract

The organophosphorus compounds o-$Ph_2P(O)C_6H_4OCH_3$ and $Ph_2P(O)C_2H_4OCH_3$, which are analogs of podands' terminal groups, have been synthesized. The thermodynamic characteristics of their complexation with LiNCS and NaNCS in acetonitrile were obtained by calorimetry. Molecular mechanics calculations on M^+L complexes with different stoichiometries M^+:L = 1:1, 1:2 and 1:4 (M^+ = Li^+, Na^+) were performed, as well as on their solvates with a limited number of MeCN molecules. It has been shown that the experimental data could be explained by taking into account both the specific features of the complex structure and the solvent effects. The possibility of the application of additive schemes in the investigation of the complexation of polydentate molecules is discussed.

INTRODUCTION

Studies of monopodands which contain phosphoryl terminal groups have shown that these compounds are effective complexation agents with respect to alkali cations [1–6]. According to the data obtained, the stability of podates is defined by both the polyether chain length and the nature of the terminal groups. The latter seems to be especially important, because modification of the phosphorus substituent R (when the polyether chain

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length is fixed) changes the complexation selectivity of podands considerably.

It is important to study the complexation of M$^+$ with fragments of podands, as it will give a potential opportunity to predict the complexation properties of new ligands. Although the thermodynamic characteristics of the complexation of polyethers (glymes) and the structure of their metal complexes have been studied in detail [7–8], there is no corresponding information about the properties of molecules which are analogs of terminal groups of organophosphorus podands.

The aim of the present paper is the synthesis of the compounds o-Ph$_2$P(O)C$_6$H$_4$OCH$_3$ (I) and Ph$_2$P(O)C$_2$H$_4$OCH$_3$ (II), and an experimental and theoretical study of the features of their complexation with lithium and sodium cations. These compounds were chosen because of the good complexation ability of monopodands which contain corresponding terminal groups with respect to lithium and sodium. Having practically the same hydrocarbon bridge length between phosphorus and the methoxy group oxygen (O$_m$), I and II are essentially different by their conformational properties. Therefore, one can predict that the present study will shed light on the difference between the complexation properties of podands with conformationally rigid and flexible terminal groups [4,5,7].

EXPERIMENTAL AND THEORETICAL METHODS

Synthesis

2-(Methoxy)phenyl-diphenyl-phosphine oxide (I)

Product **I** was prepared by the reaction of o-methoxyphenylmagnesium bromide with diphenylphosphinic chloride (for details see ref. 9).

β-Methoxyethyl-diphenyl-phosphine oxide (II)

To a stirred solution of KOH (0.1 g, 1.7 mmoles) in methanol (30 ml), diphenylvinylphosphine oxide [10] was added. The mixture was heated at reflux for 3 h. The solvent was evaporated and the residue recrystallized from benzene/hexane to give **II**, as a white solid; yield 2.7 g (62%); m.p. 82–84°C.

(Found: C, 69.1; H, 6.6; P, 11.9. C$_{15}$H$_{17}$O$_2$P requires C, 69.2; H, 6.6; P, 11.9%). ^{1}HNMR(COCl$_3$/TMC): δ 2.64(m,2H); 3.26(s,3H); 3.70(m,2H); 7.48(m,6H); 7.76(m,4H).

Measurements of heats of reaction and determination of the thermodynamic characteristics of complexation

The calorimeter LKB-2107 was used for measurements of the heats of

reaction by means of the calorimetric titration method. Titrations were performed by adding a solution of salt to a solution of the ligand and vice versa. Concentrations of the reagents were 0.0006–0.045 M (LiNCS), 0.0005–0.038 M (NaNCS), 0.015–0.020 M (**I**) and 0.0010–0.065 M (**II**). Calculations of the stoichiometry, equilibrium constants and complexation enthalpies were carried out using the CHEM–EQU program package [11]. Details of the dehydration of the salts and the solvent can be found in ref. 5. The errors in the determined thermodynamic parameters are: ΔH, $\pm 0.5\,\mathrm{kcal\,mol^{-1}}$; ΔS, $\pm 2.5\,\mathrm{cal\,mol^{-1}\,K}$; $\lg K$, ± 0.2 (1:1 complexes); ± 0.3 (1:2 and 1:4 complexes).

The molecular mechanics force field

The conformational calculations of molecules **I** and **II**, their complexes with the cations Li^+ and Na^+ and the solvates were performed using the MM2I program package [12–13], which incorporates the Allinger force field [14] for the intramolecular interactions and the modified [12] force field by Claverie and co-workers [15,16] for the ion–molecule or the intermolecular interactions. According to refs. 15 and 16, the intermolecular interaction energy (E_i) can be written as the sum of electrostatic (E_{es}), polarization (E_{pol}) and van der Waals (E_{vdW}) terms

$$E_i = E_{es} + E_{pol} + E_{vdW}$$

The electrostatic term is calculated in the point-charge approximation; the atomic charges Q_i are determined in such a way as to reproduce the molecular electrostatic potential (MEP) distribution outside the van de Waals spheres of the atoms (PD charges [17]).

The polarization term is computed [15] using bond polarizability data [18]. The van de Waals interaction energy is calculated by the equation

$$E_{vdW} = \sum_i \sum_j k_{ij} \left[-\frac{A}{Z_{ij}^6} + \left(1 - \frac{Q_i}{N_i}\right)\left(1 - \frac{Q_j}{N_j}\right) B_0 \exp(-\alpha Z_{ij}) \right]$$

where Z_{ij} is the scaled interatomic distance, N_i is the number of valence electrons of atom i, and A, B_0 and α are fixed parameters [15]. The K_{ij} parameters were fitted to reproduce the structural and energy characteristics of model compounds. The total energy of the system under consideration is calculated as the sum of E_i and the steric energy (E_{st}). The possibility of modelling rather complicated systems including several interacting partners (ligand, cation, anion and some solvent molecules) is the specific feature of this approach, which also takes into account non-additivity effects. Computations of the geometry and energy characteristics of crown ethers and organophosphorus podands, of their complexes with alkali cations, and of ion pairs [19–20] confirmed the reliability of the employed force field combination.
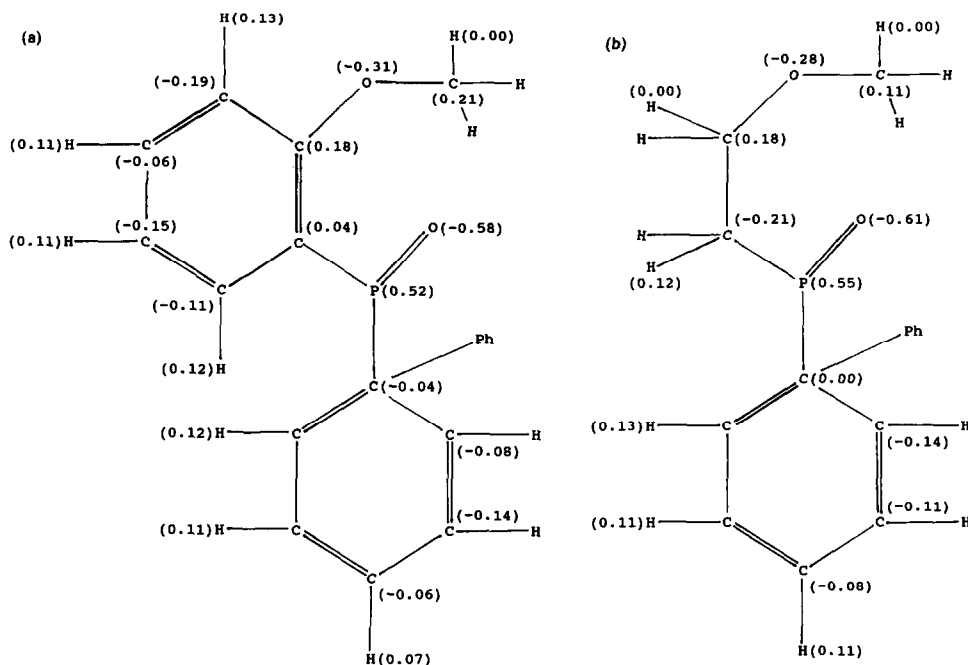
Fig. 1. PD charges of molecule (a) I and (b) II.

The PD charges of **I** and **II**, obtained by the least-squares method to reproduce the MEP on Connolly surfaces [21] and computed by the MNDO method using the MOPAC5 package [22] are presented in Fig. 1. The parameters of the applied force field, corresponding to the intramolecular interactions in molecules **I** and **II** and their intermolecular interactions with Li^+ and Na^+ were taken from ref. 20.

RESULTS AND DISCUSSION

Thermodynamics of complexation

The thermodynamic characteristics of the complexation of **I** and **II** with LiNCS and NaNCS in acetonitrile are presented in Table 1. These data show some specific features of the processes under investigation.

(i) For both **I** and **II**, complexes with different stoichiometry $M:L = 1:m$ ($m = 1,2,4$) were found. The complex stability increases with increasing m. Li^+ complexes of **I** are more stable than the corresponding complexes of **II**, whereas an opposite tendency is shown for the Na^+ complexes.

(ii) The complexation enthalpy ($|\Delta H|$) and $\lg K$ show the same trend only for complexes of **II** with LiNCS. The $|\Delta H|$ values of LiNCS with **I** are characterized in almost the same way (taking into account experimental

TABLE 1

Logarithm of the stability constant ($\lg K$), enthalpy (ΔH, $kcal\,mol^{-1}$) and entropy (ΔS, $cal\,mol^{-1}K^{-1}$) of the complexation of **I** and **II** with LiNCS and NaNCS in acetonitrile at 298.15 K

Stoichiometry of complex	**I**			**II**		
	$\lg K$	ΔH	ΔS	$\lg K$	ΔH	ΔS
LiNCS						
1:1	2.03	−3.0	−0.9	1.92	−2.0	2.1
1:2	4.73	−3.3	10.5	3.51	−3.9	3.0
1:4	8.99	−3.0	31.1	6.47	−4.8	13.4
NaNCS						
1:1	1.09	−1.9	−1.4	1.21	−2.6	−3.2
1:2	1.45	−1.0	3.4	1.81	−1.7	2.7
1:4	6.34	−1.7	23.5	7.25	−2.2	26.0

errors). In general, $|\Delta H|$ of the Na^+ complexes is lower than the $|\Delta H|$ values of the corresponding Li^+ complexes.

(iii) The complexation entropy ΔS increases upon increasing m. The complexation entropy values of the Na^+ complexes with **I** and **II** are practically the same. ΔS values of complexes of LiNCS with **I** are larger than for complexes of **II** and they increase with m.

STRUCTURE AND ENERGETICS OF THE COMPLEXES ACCORDING TO MOLECULAR MECHANICS CALCULATIONS

Molecular mechanics was used to calculate the structure and energetics of the free molecules **I** and **II**, their complexes with Li^+, Na^+ and solvents which include 1:1 or 1:2 complexes, and some solvate molecules (MeCN) of the first coordination sphere of the cation.

The complexation energies of complexes without any solvent molecules (E_c) and those including some solvent molecules (E_s) were calculated as a sum of the interaction energy (E_i) and the extra-steric energy (ΔE_{st}). The latter is defined by the difference between the steric energy of the ligand in a complex and that of the free molecule.

Complexes of molecule I

The phosphoryl oxygen atom is out of the plane which includes the atoms of the benzene ring, phosphorus, O_m and the methyl group carbon (the torsional angle $O_pPC_bC_b$ is 46°). The interaction with the cation M^+ leads to an increase in the polarity of the ligand. The cation coordinates both oxygen atoms (Fig. 2). Its interaction with O_p is more effective than that with O_m (Table 2).
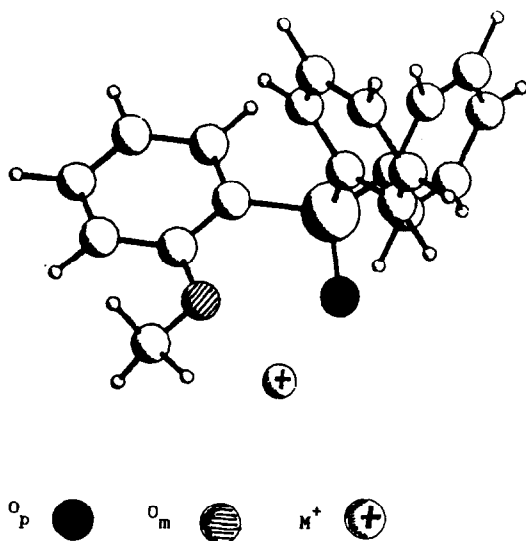
Fig. 2. 1:1 complex of Li$^+$ with molecule I.

For the 1:2 complexes, two stable conformers with planar (s) and tetra-hedral (t) coordination of the cation were found (Fig. 3). In the s-complexes, the cation is situated in the centre of the parallelogram of the ligand oxygen atoms. The lengths of the sides of the parallelogram are 2.57 and 3.42 Å in Li$^+$ complexes, and 2.70 and 3.87 Å in Na$^+$ complexes. The torsional angles $O_p(1)O_m(1)O_p(2)O_m(2)$ in the t-complexes of Li$^+$ (Na$^+$) were found to be 70° (83°), whereas in an ideal tetrahedron this angle is 71°. Interactions between ligands lead to some changes in the coordination bond lengths in comparison with 1:1 complexes. The distance $M^+ \cdots O_m$ is almost the same in the t-complexes, whereas it increased by 0.1 Å in the s-complex of Li$^+$, and

TABLE 2

Cation–oxygen distances (Å) in complexes of I and II with Li$^+$ and Na$^+$

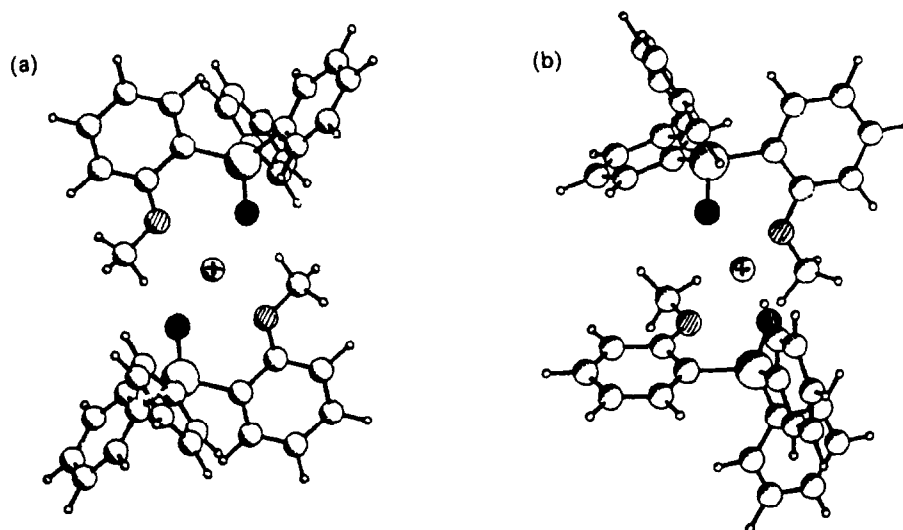| Molecule	Stoichiometry of complex	Li$^+$		Na$^+$	
		$M^+ \cdots O_p$	$M^+ \cdots O_m$	$M^+ \cdots O_p$	$M^+ \cdots O_m$
I	1:1	1.85	2.14	2.16	2.55
	1:2(s)	1.93	2.24	2.19	2.51
	1:2(t)	1.87	2.15	2.19	2.57
	1:4	2.17	3.74	2.39	3.80
II	1:1	1.90	2.11	2.16	2.47
	1:2(s)	1.92	2.34	2.19	2.51
	1:2(t)	1.90	2.22	2.18	2.50
	1:4	2.06	5.00	2.41	4.89

Fig. 3. 1:2 complexes of molecule **I** with Li$^+$ (a) s-type (b) t-type.

decreased by 0.04 Å in the corresponding Na$^+$ complex. As the distance M$^+ \cdots$ O$_p$ in the complexes of both types were found to be practically the same, the differences in the M$^+ \cdots$ O$_m$ distances must specify the difference in the s/t-complex stability in vacuum (see Table 2).

The t-coordination of Li$^+$ is 2 kcal mol^{-1} more favorable than the s-coordination, whereas the s-complex of Na$^+$ was found to be 1.6 kcal mol^{-1} more stable than the corresponding t-complex (Table 3). Increasing the number of ligands in the complexes from two to four leads to the removal of the O$_m$ atoms from the coordination sphere of the cation, the latter being

TABLE 3

ΔE_{st} and ΔE_c (kcal mol^{-1}) in the complexes of **I** and **II** with Li$^+$ and Na$^+$

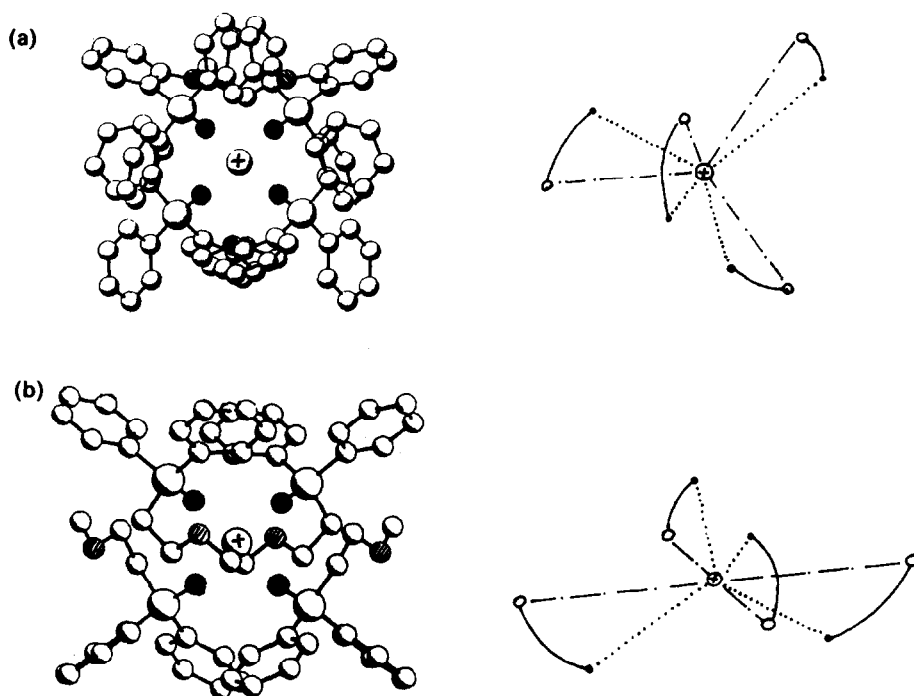| Molecule	Stoichiometry of complex	Li$^+$			Na$^+$		
		$-\Delta E_c$	$-\Delta E_c/n$	ΔE_{st}	$-\Delta E_c$	$-\Delta E_c/n$	ΔE_{st}
I	1:1	61.1		1.6	45.3		1.0
	1:2(s)	110.5	55.3	2.3	85.1	42.6	1.2
	1:2(t)	112.5	56.3	1.8	83.5	41.8	2.1
	1:4	164.0	41.0	2.7	144.1	36.0	2.5
II	1:1	64.8		3.7	50.8		0.7
	1:2(s)	115.7	57.8	2.8	92.0	47.0	1.1
	1:2(t)	111.2	55.6	7.6	90.9	45.5	1.2
	1:4	161.6	40.4	0.2	130.6	32.7	0.0

Fig. 4. 1:4 complexes of Na$^+$ with (a) molecule **I** (b) molecule **II**.

situated in a tetrahedral surrounding of O_p atoms (Fig. 4(a)). The O_m atoms are situated relatively far away from the cation; at 3.74 Å for Li$^+$ and 3.80 Å for Na$^+$. They form a second tetrahedral coordination sphere. The $M^+ \cdots O_p$ distances increase by 0.16 Å (Li$^+$) and 0.22 Å (Na$^+$) in comparison with the 1:1 complexes. The difference between the radii of the Li$^+$ and the Na$^+$ complexes, which are defined by the distance $M^+ \cdots O_p$, is 0.22 Å; this is considerably less than the difference between the ion radii of Li$^+$ and Na$^+$ (0.31 Å) [23]. The specific feature of the above complexes is the similarity of the geometry parameters of ligands in the complexes of different stoichiometry and the free molecule **I**.

Complexes of molecule II

The essential difference between molecules **I** and **II** is the possibility of free rotation around the C–C bond in the latter; hence, two conformers with different PCCO torsional angles are possible: (+)gauche (**IIa**) and (−)gauche (**IIb**). Conformer **IIa** is characterized by a relatively large distance between the oxygen atoms (3.7 Å) and therefore only one of the oxygen atoms can bind to the cation, whereas in **IIb** both oxygen atoms are able to coordinate with the cation (distance $O_p \cdots O_m = 2.7$ Å). Therefore, it

is not surprising that the ligand accepts conformation **IIb** in $1:1$ and $1:2$ (s,t)-complexes and **IIa** in $1:4$ complexes where the cation only coordinates O_p atoms.

$1:2$ s-Complexes with planar positions of donor atoms appear to be more stable than t-complexes with a tetrahedral coordination of the cation, both for Li^+ and Na^+. It should be noted that the $M^+ \cdots O$ distances were found to be smaller for the t-coordination of the cation (Table 2), which corresponds with a stronger interaction between the cation and the ligands. However, in the case of the t-complexes, the changes in steric energy of the ligands are considerably larger than for the s-complexes (Table 3). Thus, the s-complexes are more stable than the t-complexes.

Analogous to the complexes of **I**, an increase in the number of ligands in the coordination sphere of the cation in **II** leads to the increase in the $M^+ \cdots O$ distance. Thus, the coordination bond lengths $M^+ \cdots O_p$ increased by 0.02–$0.03\,\text{Å}$ (Li^+,Na^+) in $1:2$ complexes, and by $0.16\,\text{Å}$ (Li^+) and $0.25\,\text{Å}$ (Na^+) in $1:4$ complexes. The range of $M^+ \cdots O_m$ distances in $1:2$ complexes is wider: 0.11–$0.23\,\text{Å}$ (Li^+) amd 0.03–$0.04\,\text{Å}$ (Na^+). In $1:4$ complexes the cation is coordinated tetrahedrally by the phosphoryl oxygen atoms, whereas the O_m atoms lie in one plane with the cation; corresponding $M^+ \cdots O_m$ distances are $5.00\,\text{Å}$ (Li^+) and $4.89\,\text{Å}$ (Na^+) (Fig. 4(b)). The extent of removal of O_m atoms from the coordination sphere of the cation is more pronounced for the complexes of **II**, in comparison with **I**, due to the flexibility of the former.

The energy characteristics of the complexes are presented in Table 3. From these data it follows that in its $1:1$ and $1:2$ complexes, the interaction between M^+ and **II** is stronger than that between M^+ and **I**. This might be explained by the conformational flexibility of **II**, which allows a more effective interaction with the cation in comparison with the rigid molecule **I**. The effectivity of the cation–ligand interaction, which is defined by $|E_c/m|$, decreases upon increasing m. Changes in the steric energies of the ligand do not make a large contribution to E_c. The biggest ΔE_{st} value was obtained for the t-complex of Li^+, where it contributes only 6.8% to the overall complexation energy.

Solvates of the complexes of molecules I and II

To simulate the solvation shells of the $1:1$ and $1:2$ complexes, we assumed that the coordination sphere of the cation included no more than six donor atoms. Thus, the compositions of the solvate under consideration are $M^+ \cdot L \cdot 4S$ and $M^+ \cdot 2L \cdot 2S$, where $S = MeCN$.

In solvates $M^+ \cdot L \cdot 4S$ ($L = I$), the coordination polyhedron is an octahedron. Both oxygen atoms and two nitrogen atoms of the solvent lie in one plane with the cation. Two other MeCN molecules coordinate the cation

from axial positions. The solvates of the $M^+ \cdot 2L$ complexes of the s-type, where MeCN molecules are in axial positions, are also octahedral. However, the structure of the coordination spheres of Li^+ and Na^+ in the solvates of the t-complexes is quite different. The coordination polyhedron of Li^+ is a trigonal bipyramid. One of its bases includes two nitrogen atoms of the solvent and one O_p atom of the first ligand, and the other base includes two oxygen atoms of the second ligand and the O_m atom of the first. In the corresponding solvate of the Na^+ complex, only one solvent molecule coordinates with the cation; the second MeCN molecule is removed from the cation's coordination sphere. The cation's coordination polyhedron is a disturbed tetragonal pyramid, in which the atoms $O_m(1)$, N, $O_p(2)$ and $O_m(2)$ form the base; $O_p(1)$ is situated on the top of the pyramid. From Table 4, it follows that the interaction with solvent molecules leads to consider-

TABLE 4

Cation–oxygen and cation–nitrogen distances (Å) in the solvated complexes of **I** and **II** with Li^+ and Na^+

| Molecule	Stoichiometry of complex	Li^+		Na^+	
		$M^+ \cdots O_p$	$M^+ \cdots O_m$	$M^+ \cdots O_p$	$M^+ \cdots O_m$
I	1:1	1.88	2.30	2.26	2.72
	1:2(s)	1.94	2.31–2.34	2.22	2.68–2.74
	1:2(t)	1.89–1.93	2.41–2.43	2.22	2.68–2.74
II	1:1	1.89	2.25	2.27	2.82
	1:2(s)	1.94	2.34–2.39	2.20	2.54
	1:2(t)	1.89	2.16–2.22	2.21	2.55–2.67
		$M^+ \cdots N$		$M^+ \cdots N$	
I	1:1	2.29–2.53		2.37–2.45	
	1:2(s)	2.31–2.33		2.45–2.46	
	1:2(t)	2.54–2.65		2.36–3.72	
II	1:1	2.36–2.80		2.43–2.59	
	1:2(s)	2.56–2.58		2.75–2.82	
	1:2(t)	2.73–3.60		2.39–3.26	

able changes in the $M^+ \cdots O$ distances. This appears in solvates of 1:1 complexes, especially where the coordination bond lengths $M^+ \cdots O_m$ increase by 0.16 Å (Li^+) and 0.25 Å (Na^+). In solvents of 1:2 complexes (t) the corresponding changes were 0.25 Å (Li^+) and 0.13 Å (Na^+). The biggest change in $M^+ \cdots O_p$ distance was found in solvates of the t-complex of Li^+ (0.07–0.08 Å).

TABLE 5

ΔE_{st} and ΔE_s (kcal mol^{-1}) in the solvated complexes of **I** and **II** with Li$^+$ and Na$^+$

Molecule	Stoichiometry of complex	Li$^+$		Na$^+$	
		$-\Delta E_s$	ΔE_{st}	$-\Delta E_s$	ΔE_{st}
I	1:1	102.6	1.2	89.6	0.7
	1:2(s)	127.1	1.1	103.9	1.0
	1:2(t)	120.6	3.3	95.9	1.7
II	1:1	102.9	3.5	89.8	0.8
	1:2(s)	128.5	2.0	106.1	1.5
	1:2(t)	126.9	7.5	105.3	1.8

The structures of the solvates of the 1:1 Li$^+$ complex of **II**, and the Li$^+$ and Na$^+$ 1:2 complexes (s) (Fig. 5) are analogous to those of the corresponding complexes of **I**. The coordination sphere of Na$^+$ in the solvate of its 1:1 complex includes four nitrogen atoms which lie in a plane and coordinate the cation from one side; the ligand oxygen atoms coordinate Na$^+$ from the other side (Fig. 6). The coordination polyhedron of Li$^+$ in the solvate of its
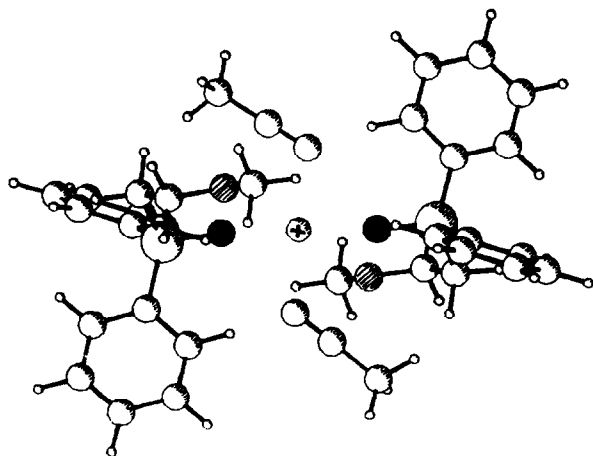
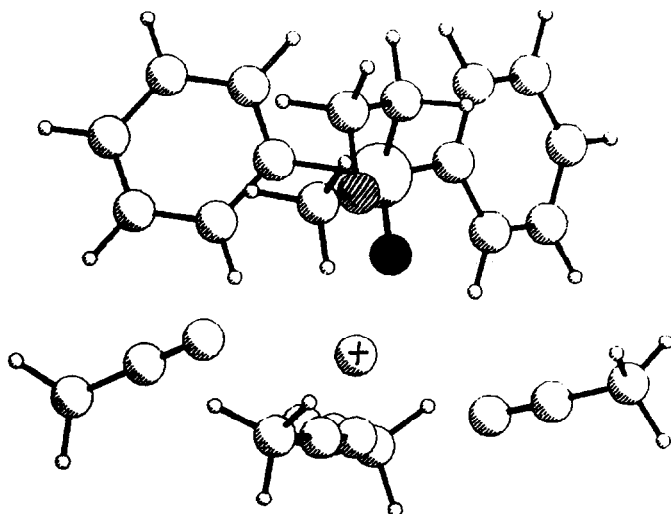Fig. 5. Solvate of the 1:2 s-type complex of Li$^+$ with molecule **II**.

Fig. 6. Solvate of the 1:1 complex of Na$^+$ with molecule II.

t-complex is similar to the coordination polyhedron of Na$^+$ in the solvate of its t-complex with I. Only one acetonitrile molecule interacts with the cation in the solvate of the Na$^+$ t-complex of II. The line Na$^+\cdots$N is perpendicular to the base of the tetrahedron, which is formed by the atoms $O_m(1)$, $O_p(1)$ and $O_m(2)$.

As a rule, interaction with the solvent leads to smaller changes in M$^+\cdots$O distances for complexes of II compared with those of I. However, the interaction between complexes of II and MeCN is less effective: the M$^+\cdots$N distances are considerably larger than in the corresponding solvates of I (Table 4). An analysis of the solvates' energy characteristics proves the greater stability of s-complexes in solution compared with t-complexes, due to the better availability of the cation for solvent molecules.

To study the solvation features of the free molecules I and II, we assumed that both of them could interact with two acetonitrile molecules directly. The structures of the solvates of I and IIb are similar (Fig. 7). One MeCN molecule forms an H-bond $O_p\cdots$H–C with length 2.46 Å. The other solvent molecule realizes its bonds both with O_p (2.76 Å (I) and 2.72 Å (II)) and O_m (2.68 Å (I) and 3.08 Å (IIb)). The interaction energies of I and IIb with solvent molecules differ insignificantly, and are equal to -8.0 kcal mol^{-1} (IIb) and -7.6 kcal mol^{-1} (I). It should be noted that the conformer IIa, with its oxygen atoms pointing in reverse directions, is less solvated than IIb (-4.2 kcal mol^{-1}).

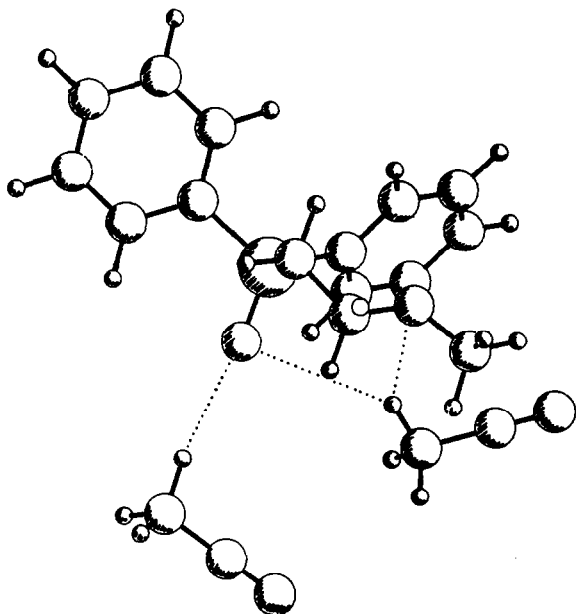The above results indicate that the cation M$^+$ interacts more effectively

Fig. 7. Solvate of molecule **II**.

with the phosphoryl oxygen than with the ether (anisole) oxygen. This is manifested in small changes in the $M^+ \cdots O_p$ distances in comparison with the $M^+ \cdots O_m$ ones in several complexes of different types. A similar tendency is found for the complexes of lithium and sodium with organo-phosphorous podands, where the lengths of the coordination bonds $M^+ \cdots O_p$ are practically independent of the lengths of the polyether chain, whereas the distances between the cation and the anisole oxygen (or terminal ether oxygen) are changed [20]. On the whole, these data correspond with well-known ideas of complexation mechanisms of podands, which contain donor centers in their terminal groups: polyether chain oxygen atoms arrange around the cation which is already strongly bound to the terminal groups' donor atoms [7].

Analysis of complexation thermodynamics

We now consider the question of whether the calculated data can reproduce the tendency of ΔH changes for the complexes of **I** and **II** with the same stoichiometry. According to the thermodynamic cycle model [19], the difference in complexation energies ($\delta E_{i,j}^{M^+}$) of the cation M^+ with ligands L_i and L_j is defined by a sum of terms. These are the difference in interaction energies of L_i and L_j in vacuum, the difference in solvation energies of the complexes $L_i M^+$ and $L_j M^+$, and the difference in desolvation energies

$\delta(E_s^0)_{i,j}$ of the free molecules L_i and L_j. In our case it is obvious that $\delta(E_s^0)_{i,j}$ should be calculated by taking into account the number of ligands m in the complex:

$$\delta(E_s^0)_{i,j} = - [(E_s^0)_I - (E_s^0)_{II}] \times m$$

The sum of the other components of $\delta E_{i,j}^{M^+}$ is equal to the difference in E_s values, corresponding with the solvates of the **I** and **II** complexes with M^+ $((E_s^{M^+})_I$ and $(E_s^{M^+})_{II})$. Hence

$$\delta E_{I,II}^{M^+} = [(E_s^{M^+})_I - (E_s^{M^+})_{II}] - [(E_s^0)_I - (E_s^0)_{II}] \times m$$

The values of $\delta E_{I,II}^{M^+}$ (kcal mol^{-1}), which were obtained using data from Tables 3 and 5 and the solvation energies of the free molecules I and II are respectively: 0.7 (Li$^+$), 0.6 (Na$^+$) in 1:1 complexes; 2.2 (Li$^+$), 3.0 (Na$^+$) in 1:2 complexes; -0.8 (Li$^+$), -11.8 (Na$^+$) in 1:4 complexes (E_c values were used here).

The comparison of these data with Table 1 shows that the calculations qualitatively reproduced the tendency of ΔH changes for the 1:2 complexes (where differences in enthalpy ($\Delta(\Delta H)_{I,II}$) are 0.6 kcal mol^{-1} (LiNCS) and 0.7 kcal mol^{-1} (NaNCS)) as well as for the Na$^+$ 1:1 complex ($\Delta(\Delta H)_{I,II} = 0.7$ kcal mol^{-1}). The reason for the discrepancy between the calculated and experimental data is probably related to a correct but insufficient procedure for the estimation of the solvation energies. Only the interaction with the solvent molecules in the closest surroundings was taken into account. However, interactions with solvent molecules that coordinate with neither the cation nor the oxygen atoms of the free molecules could be rather important. This is most obvious in the case of the 1:4 complexes. The complex Li$^+ \cdot L_4$ (L = I) has a spherical form with radius ≈ 8 Å, whereas L = II is a truncated sphere with the same radius and a distance of about 5.5 Å from Li$^+$ to the "section plane". Hence, the effective sizes of the 1:4 complexes with II are essentially less than the size of the complexes with I. This corresponds to a less effective solvation of the latter, which is probably related to its smaller $|\Delta H|$ values in comparison with complexes of II.

Another possible source of errors upon estimating $\Delta(\Delta H)_{I,II}$ is the exclusion of the anion from the present theoretical study. The point is that thiocyanates of Li$^+$ and Na$^+$ in acetonitrile can form both separated solvates and contact ion pairs [24].

The following question arises: it is possible to predict the complexation properties of podands in terms of additive schemes or correlation relationships? In fact, such an opportunity can be realized if the cation interacts in the same way both with donor atoms of the podand and with donor atoms of its fragments. The results obtained here and in ref. 20 show differences between bonds of M$^+$ with oxygen atoms of the methoxy group in its

complexes with **I** and **II**, and corresponding bonds with the oxygen atoms of the polyether chain in $M^+ \cdot [R-O-(-CH_2-CH_2-O-)_n-R]$. It proves the impossibility of the simulation of the podand complexes and the prediction of their complexation ability, on the basis of information about the structure and energetics of the complexes of a cation with selected fragments of these polydentate agents.

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