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COMPLEXING ABILITY OF PHOSPHORYL-CONTAINING PODANDS WITH RESPECT

TO ALKALI METAL 2,4-DINITROPHENOXIDES

T. E. Kron, É. I. Sinyavskaya, and E. N. Tsvetkov

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The acyclic analogs of the crown ethers, the so-called podands [1], are known to be effective complexing agents for salts of alkali and alkaline-earth metals [2]. It might be expected that the introduction of strong donor centers, such as phosphoryl groups, into the polyether chain of a podand will improve the complexing ability of these compounds. We previously synthesized mono-, di-, and tripodands of the phosphine oxide type with phosphinylmethyl terminal groups [3, 4]. The complexation constants obtained for the first representatives of the phosphoryl-containing podands turned out to be fairly high [5].

In the present work we used an electrical conductivity method to investigate the complexing properties of a series of phosphoryl-containing podands, viz., compounds I-IX with the general formula $R_m P(0)[CH_2(OA)_n OCH_2 P(0)R_2']_{3-m}$, where OA denotes an ethylene glycol fragment, a pyrocatechol fragment, or a combination of these fragments, n = 1 to 6, and m = 2 (monopodands) or 0 (tripodands) (Table 1). The complexing ability of the ligands was evaluated on the basis of the stability constants of their complexes with ions of the alkali metals of the corresponding 2,4-dinitrophenoxides in a 4:1 THF-chloroform mixture.

Compounds Ia and II-IV, as well as VI-IX were previously described in [3, 4]. For the purpose of improving the solubility of the ligands in organic solvents, we synthesized analogs of dioxide Ia containing one or two t-Bu groups in the pyrocatechol ring (ligands Ib and c) by reacting the corresponding phenoxides with Ph_P(0)CH_Cl. Dioxide V was synthesized by alkylating a salt of o-ciphenylphosphinylmethylphenol with diethylene glycol bis-(tosylate). The original phenol was obtained from diphenylphosphine and salicylaldehyde in analogy to the synthesis of diphenylbenzylphosphine oxide in [6].

EXPERIMENTAL

The synthesis of the ligands was carried out in an atmosphere of dry Ar. The NMR spectra were recorded on a Bruker WM-250 spectrometer relative to HMDS or 85% H₃PO4 in CDCl₃. The melting points were measured by shortened Anschutz thermometers.

Bis(diphenylphosphinylmethyl) Ether of 3-tert-butylpyrocatechol (Ib). A solution of MeONa obtained from 1.1 g of Na and 25 ml of anhydrous MeOH was given an addition of 3.6 g of 3-tert-butylpyrocatechol [7]. The mixture was evaporated in a vacuum. The residue ws held for 1 h, in a vacuum with a residual pressure of 1 mm at 90-110°C. The salt obtained was given an addition of 50 ml of anhydrous o-xylene and 11.0 g of $Ph_2P(0)CH_2C1$ [8] in two portions at 100°C. The mixture was boiled for 10 h and evaporated in a vacuum. The residue was dissolved in chloroform, and the solution was washed with water, 10% NaOH, and water. The extract was dried by Na₂SO₄ and evaporated in a vacuum. The substance crystallized following the addition of EA to the residue. The yield of Ib was 9.5 g (67%), and the mp was 157-159°C. Recrystallization from and EA-MeCN mixture gave 7.1 g (55%) of product IB with

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mp 162-163°C. Found: C 72.6; H 6.2; P 10.5%. Calculated for $C_{36}H_{36}O_4P_2$: C 72.7; H 6.1; P 10.4%. PMR spectrum (δ , ppm): 1.19 s (t-Bu), 4.62 d (CH_2 -P, J_{HP} = 9 Hz), 6.78 d (H_{arom} , J_{HH} = 9 Hz), 6.82 d (H_{arom} , J_{HH} = 3 Hz), 6.90 d (H_{arom} , J_{HH} = 9 Hz), 7.32-7.55 s (C_6H_5), 7.91 m (C_6H_5). ³¹P NMR spectrum (δ , ppm); 27.10.

<u>Bis(diphenylphosphinylmethyl)</u> Ether of 3,5-Di-tert-Butylpyrocatechol (Ic). A solution of MeONa prepared from 0.16 g of Na and 10 ml of anhydrous MeOH was given an addition of 0.7 g of 3,5-di-tert-butylpyrocatechol [9]. The mixture was evaporated in a vacuum. The salt obtained was given an addition of 20 ml of anhydrous o-xylene and 1.6 g of $Ph_2P(0)CH_2C1$ at 100°C. The mixture was boiled for 20 h and evaporated in a vacuum. The residue was dissolved in chloroform, and the solution was washed with water, 10% NaOH, and water. The extract was dried by Na_2SO_4 and evaporated in a vacuum. The residue (1.9 g) was chromatographed in a column with silica gel L, the eluant being EA. This gave 1.1 g (57%) of Ic. The substance crystallized after prolonged standing in a C_6H_6 -hexane mixture. Recrystallization of the residue gave 0.8 g (41.4%) of the product, mp 160-161°C (from a C_6H_6 -hexane mixture). Found: C 73.7; H 6.8; P 9.4%. Calculated for $C_{40}H_{44}O_4P_2$: C 73.8; H 6.8; P 9.5%. PMR spectrum (δ , ppm): 1.16 s (t-Bu), 1.20 s (t-Bu), 4.75 d (CH_2 -P, J_{HP} = 6 Hz), 4.87 d (CH_2 -P, J_{HP} = 8 Hz), 6.92 d (H_{arom} , J_{HH} = 3 Hz), 7.0 d (H_{arom} , J_{HH} = 3 Hz), 7.49 m (C_6H_5), 7.84 (C_6H_5). ³¹P NMR spectrum (δ , ppm): 26.37, 27.40.

<u>o-Diphenylphosphinylmethylphenol.</u> A mixture of 13.2 g of diphenylphosphine, 8.7 g of salicylaldehyde, and 285 ml of a 1:2 mixture of AcOH and conc. HCl was boiled for 13 h. After cooling, chloroform was added to the reaction mixture. The extract was washed with a solution of NaHCO₃ and water and dried by Na₂SO₄. The solvent was driven off in a vacuum. The yield of the product was 19.1 g (86%), and the mp was 170-172°C. Recrystallization from MeCOEt gave 14.8 g (68%) of o-diphenylphosphinylmethylphenol, mp 177.5-179°C (compare [10]).

<u>Bis(o-diphenylphosphinylmethylphenyl)</u> Ether of Diethyl Glycol (V). A solution of MeONa obtained from 1.0 g of Na and 40 ml of anhydrous MeOH was given an addition of 11.5 g of o-diphenylphosphinylmethylphenol. The solvent was driven off in a vacuum and 50 ml of anhydrous o-xylene and 5.9 g of diethylene glycol bis(tosylate) [11] were added to the phenoxide at 100°C. The mixture was boiled for 18 h and evaporated in a vacuum. The residue was dissolved in chloroform and washed with water, 10% NaOH, and water. The organic layer was dried by Na₂SO₄ and evaporated in a vacuum. The substance crystallized after MeCOEt was added to the residue. The yield of V was 11.5 g (89.5%), and the mp was 137.5-140°C. Recrystallization from MeCN gave 5.9 g (51%) of product V, mp 145.5-146°C. Found: C 73.3; H 5.9; P 9.3%. Calculated for $C_{4.2}H_{4.0}O_5P_2$: C 73.5; H 5.9; P 9.0%. PMR spectrum (δ , ppm): 3.73 d (CH₂-P, J_{HP} = 14.5 Hz), 3.75 m (CH₂CH₂), 6.66 d (H_{arom}, J_{HH} = 8 Hz), 6.85 t (H_{arom}, J_{HH} = 8 Hz), 7.11 m (H_{arom}), 7.25 m (C₆H₅), 7.66 m (C₆H₅).

Measurements. The alkali metal 2,4-dinitrophenoxides were dehydrated in a vacuum with heating. The solvents were purified and dehydrated by ordinary methods [12]. The electrical conductivity of the solutions was measured with the aid of an R-5010 ac bridge in a thermostated (25 \pm 0.1°C) cell with platinized platinum electrodes. The constant of the vessel was equal to 0.17. The method for the determination of the stability constants of the complexes of the alkali metals with ligands I-IX involved the measurement of the electrical conductivity of solutions with a constant concentration of the salt of the alkali metal (MX) and a variable concentration of the ligand up to the ratio $C_M:C_L = 1:10$. The error in the determination of the resistance was $\pm 3\%$. The stability constants (β) of the complexes of the type ML⁺, which may be expressed by the ratio $\beta = [ML^+]/[M^+][L]$, were evaluated on the basis of the dependence of the values of $(\lambda/\lambda_0)^2$ on the initial concentration of the ligand [13]. (Here λ_0 and are the equivalent conductivity of the free salt and of the latter in the presence of the ligand, respectively.) The slope of the plots of this linear dependence gives the values of β . The error in the determination of the values of β by this method was equal to ±10%. All the operations involved in the measurement of the electrical conductivity were carried out in air.

DISCUSSION OF RESULTS OBTAINED

The values of the logarithms of the stability constants of the complexes are presented in Table 1. This table also gives the ratios of the constants for two pairs of complexes, viz., the lithium-sodium pair (β_{Li}/β_{Na}) and the sodium-potassium pair (β_{Na}/β_K), which characterize the differences in the complexing ability of the particular ligand with respect to the cations of two neighboring elements of the same group. These values can serve as coef-

Com- pound	Formula	lg bLi	lg B _{Na}	lg βK	lg ß _{CS}	βLA/βNa	β_{Na}/β_K
(1)	R ₁ OCH ₂ P(0)Ph ₂ OCH ₂ P(0)Ph ₂						
(1a) (1b) (1c)	$ \begin{array}{c} \dot{R}^{2} \\ R^{1} = R^{2} = H \\ R^{1} = t - Bu, R^{2} = H \\ R^{1} = R^{2} = t - Bu \\ O & O \end{array} $	4.40 4.25 4.72	3.46 3.34 3.54	$2.95 \\ 2.66$	2.48 2.27	9 8 15	 2.4 7.6
(11) (ffa) (11b)	$ \begin{array}{c} \parallel \\ \text{Me}_2\text{PCH}_2\text{OCH}_2(\text{CH}_2\text{OCH}_2)_n\text{PMe}_2\\ n=0\\ n=2\\ 0 \\ \text{P}(0)\text{Ph}_2 \end{array} $	4.04 4,38	2,81 3,60	$2.26 \\ 3.15$	1.80 2.45	17 6	3.5 2.8
-(111)	0 0 P(0)Ph ₂	4.20	4.16	4.02	3.30	1	1.4
∢IV)				-			
~(IVa) ~(IVb)	$\begin{array}{c c} R^{2}P=0 & 0=PR^{2}\\ R=Me & R=Ph & 0 \\ 0 & 0 & 0 \end{array}$	4.02 3,65	3.86 4.01	3,93 4,19	3.11 3.50	1.4 0.4	0.8 0.7
-(V)	$Ph_2P=0 \qquad O=PPh_2$	4.34	3.98	4.01	2.21	2.3	0.9
(VI)		3.75	4.34	4.82	3.96	0.3	0.3
·(VIJ)		4.18	5,12	4.73	4.45	0.1	2.5
(VIII)	$\begin{array}{c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$	4.49	4.16	3.72	3.04	2.1	2.7
(IX)	(Ph ₂ PCH ₂ OCH ₂ CH ₂ OCH ₂) ₃ P Dibenzo-18 - crown-6	4.45 4.06	4.51 5.60	4,12 4.66	3.84 3.27	0.9 0.03	$2.4 \\ 24.5$

TABLE 1. Logarithms of the Stability Constants of the Complexes of Alkali Metal Cations from 2,4-dinitrophenoxides with Podands I-IX in a 4:1 Tetrahydrofuran-Chloroform Mixture and Values of the Ratios of the Constants of Two Pairs of Complexes

ficients which reflect the selective properties of the particular ligand (discrimination coefficients).

The compounds studied are polyether ligands with an open-chain structure and termination coordination center in the form of phosphoryl groups. When such compounds are reacted with alkali metal ions, the complexes probably form mainly due to the electron-donor properties of the phosphoryl oxygen atoms, which greatly surpass those for the oxygen atoms of the ether groupings. Complexation by means of the terminal functional groups can result in the closure of a macrocycle, as was shown in [14] for podands with terminal quinoline groups. The type of ligand just indicated may apparently be treated as an intermediate between cyclic and open-chain polyether complexing agents.

Monopodands I form complexes which are close in stability to the complexes with the previously studied analog of ligand Ia, in which the phenyl groups at the phosphorus atom were replaced by methyl groups [5]. The fairly large variation of the stability constants along the series of the alkali metals evinced by the values of the ratio $\beta_{\rm Li}/\beta_{\rm Na}$ which deviate significantly from unity, is probably due to the fact that the coordination with the metal ions is effected predominantly by the oxygen atoms of the phosphoryl groups with the formation of ion-dipole bonds. The strength of these bonds decreases with decreasing ionic potential of the cation.

In the series of ligands II the introduction of additional glycol fragments between the terminal phosphoryl groups causes increases in the stability constants of the complexes for all the alkali metals studied. In the case of the lithium complex of compound II with n = 1, log $\beta = 4.19$ [15]. Such variation of the values of the stability constants is probably attributable to the increase in the coordination capacity of the ligands.

It should be noted that podands Ia-c, IIa, and IIb were found to be especially effective with respect to the Li⁺ cation. This group of compounds displays a monotonic decrease in the stability constants of the complexes along the series of alkali metals, and Fig. 1 shows a typical graphical dependence of these constants on the reciprocal of the ionic radius of the cation in the example of ligand IIb.

In the case of compound II, which has an additional pyrocatechol fragment in comparison to ligand IIb, the values of the stability constants become closer: the ratios β_{Li}/β_{Na} and β_{Na}/β_K are close to unity. Increasing the number of donor atoms by introducing a second pyrocatechol fragment into the molecule (ligand IVb) had practically no effect on the complexing ability in comparison to compound III, with the exception of the interaction with Li⁺. The decrease in the stability of the complex with Li, which has the smallest ionic radius in the series of alkali metals, is possibly due to the fact that the increased rigidity of the ligand molecule and the increase in the distance between the phosphoryl groups hinder the electrostatic interaction of the latter with a cation. The replacement of the phenyl groups at the phosphorus atom by methyl groups (ligand IVa) had a slight effect on the values of the stability constants of the complexes.

Compound V, in which the phosphoryl groups are bonded to the benzene rings by means of only methylene groups has the lowest coordination capacity; nevertheless, its complexing ability with respect to Li⁺ surpasses that of ligand IVb. However, as the radius of the cation is increased, the stability of the comlexes of ligand V decreases more rapidly than does that of ligand IVb, apparently due to the decreased coordination capacity of dioxide V, which has an appreciable effect only in the case of the complex with cesium. The increase in the stability of the complex of ligand V with Li may be attributed to the increase in the nucleophilicity of the phosphoryl groups due to the increased distance of the electronegative oxygen atom from the α position of ligand IVb, whereas the pyrocatechol oxygen atoms scarcely participate in the coordination with the lithium ion.

Thus, the group of podands consisting of III-V are characterized by similar, fairly high values for the stability constants. A small decrease in the values of the constants is observed only for the cesium cation, which has the largest radius, this decrease being most pronounced in the case of the ligands with a small number of ethereal oxygen atoms. Figure 1 presents a characteristic plot of the dependence of the stability constants on the reciprocal of the ionic radius of the cation for this group of ligands in the example case of compound V.

The further increase in the number of donor centers and the increase in the length of the polyether chain in the molecules of monopodands VI and VII result in the preferential formation of complexes with Na⁺, K⁺, and Cs⁺ ions. A comparison of ligand VI with ligand VII, which has only one more potential donor center, but is conformationally more flexible as a consequence of the predominance of the glycol fragments in the molecule, shows that the latter forms more stable complexes with the entire series of metals studied. In addition, the high basicity of the phosphoryl groups and some of the ethereal oxygen atoms in compound VII, which also promote the stability of the complexes, must be taken into account. It should be noted that the value of the ratio $\beta_{\rm Li}/\beta_{\rm Na}$ for ligand VII differs significantly from unity. This attests to the fairly high selectivity of this ligand in its interaction with the sodium cation (see Fig. 1).



Fig. 1. Dependence of the logarithms of the stability constants of complexes on the reciprocal of the ionic radius of the cation.

A comparison of tripodands VIII and IX reveals a picture similar to that which was observed in the case of monopodands VI and VII. The chains of compound VIII contain rigid pyrocatechol fragments, while in ligand IX they have been replaced by flexible glycol fragments, and the basicity of the phosphoryl group in ligand IX is higher. Consequently, it forms stabler complexes with close values of the constants, except in the case of the complex with Li. It is noteworthy that the tripodands, which have four strong donor centers such as the phosphoryl groups and a high coordination capacity, were found to be only slightly more effective than the simpler monopodands. Apparently, when they form complexes with the alkali metals, the cooperative participation of the donor centers in the coordination with the metal is not realized due to the steric factors.

A comparison of the podands studied with dibenzo-18-crown-6 shows that the complexing ability of these compounds is comparable. In contrast to the macrocycle, the acyclic complexing agents form fairly stable complexes with the entire series of cations.

CONCLUSIONS

1. Phosphorus-containing monopodands with short polyether chains between the terminal phosphoryl groups are effective complexing agents with respect to the lithium cation.

2. Phosphorus-containing mono- and tripodands of high coordination capacity form fairly stable complexes with the whole series of alkali metals, the stability of the complexes in the case of the ligands with flexible glycol fragments being higher than that in the case of the ligands with rigid pyrocatechol fragments.

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DETERMINATION OF COORDINATION SITES IN POLYETHER PHOSPHORYL

LIGANDS USING MODEL COMPOUNDS

E. N. Tsvetkov, T. E. Kron, and É. I. Sinyavskaya UDC 542.91:541.49:547.1'118:546.34-128.4

The macrocyclic polyethers are well known as complexing agents for cationic alkali and alkaline earth metals [1]. Efforts to improve their complexing abilities has led to the synthesis of macrocycles containing in addition to the ether oxygen atoms most nucleophilic donor sites, including phosphoryl groups. At the present time a large number of macrocycles are known that contain one or more phosphoryl groups [2, 3]. Their complexing ability has been studied [4], and in some cases the means by which the metal is coordinated with the macrocyclic ligands in the compounds has been determined [5, 6].

The aim of this work was to synthesize a new phosphoryl-containing macrocyclic compound and to determine by the use of model compounds the coordination sites in it and in some noncyclic phosphoryl-containing ligands in the interaction between 2,4-dinitrophenol and the alkali metals. The macrocyclic oxide of phosphine (I) is the analog of a macrocycle containing a phosphonate group [2] obtained by alkylation of the disodium derivative bis-(2-(o-oxyphenoxy)diethyl)ether by the oxide of methyldi(chloromethyl)phosphine (mechanism I). By reaction of the latter with the Na-salt of o-methoxyphenol, the acyclic analog (II) of ligand (I) was synthesized.



Models of a number of acyclic complexing agents previously obtained by us [7] were prepared by reacting the corresponding phenolates of alcoholates with tosyls, halide-containing compounds (cf. Reaction 2). For example, the dioxide (III) forms as a result of the reaction of the Na-salt of o-(2-diphenylphosphinylethyl)phenol with the bistosylate of diethylene glycol. The reaction of 1,5-dibromopentane with the Na-salt of o-diphenylphosphinylmethoxyphenol yields compound (IV). As a result of the reactions depicted in Fig. 2, the dioxide (VII) is obtained from the Li alcoholate (V) and its tosylate (VII). Compounds (VIII), (IX) (Table 1), segments of the macrocycle (I), were obtained by a previously described method [8, 9].

The stability constants of the synthesized compounds with cationic alkali metals were determined by an electrical conductivity method (cf. Table 1). The constancy of the values for the stability constants of the crown-ether complexes (I) for all of the alkali metals studied, except cesium, should be noted. The macrocycle (I) proved to be more effective than its acyclic analog (II). The smallest difference in the stability constants is observed for the reaction with Li⁺, which is apparently related with the preferred coordination of the P=O group with some fractional participation in the case of the crown ether of the central ether oxygen atom. This explanation is consistent with PMR data obtained by us earlier [6].

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