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Macrocyclic Polyfunctional Lewis Bases.
VIII. Complexation Abilities of Aromatic Diaminopolyethers

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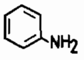
The protonation constants of o-aminophenol ethers and the stability constants of their complexes with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} were determined by a potentiometric method in dioxane–water solution. The obtained values are discussed in terms of the structure–property relationships.

Introduction

The ability of podands [1] to form complexes is usually much lower than that by structurally similar coronands. This is not, however, a general case. The macrocyclic effect [2–4] which is assumed to be responsible for the mentioned phenomenon does not occur in the interaction between some azacoronands and transition metal cations [5]. The lack of the macrocyclic effect was recently shown by comparing the complexation abilities of aliphatic diaminopolyether podands and the respective diazacoronands towards transition metal cations [6]. We present here results of investigations of complexing powers of podands, derivatives of *o*-aminophenol with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} measured by the potentiometric method. Since the investigated ligands *1–6* are poorly soluble in water and, as was shown by preliminary experiments, form very weak complexes, studies were performed in a dioxane–water (85:15 v/v) mixture [7].



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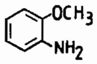

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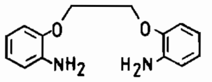

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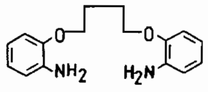

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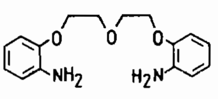

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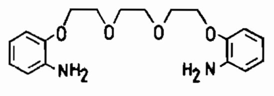

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Experimental

Chemicals

Ligands *3–6* [8, 9] (Fig. 1) were prepared according to known methods. Dioxane was purified as described [10]. The concentrations of stock solutions of cobalt, nickel and zinc perchlorates in a dioxane–water (85%) mixture were determined using standard complexometric methods. Copper(II) and tetraethylammonium hydroxide in dioxane–water stock solutions were determined spectrophotometrically [11] and by pH-metric titration respectively. The average concentrations of metal ion, ligand and the titrant were $0.5\cdot10^{-2}$, $0.5-1\cdot10^{-2}$ and $1\cdot10^{-2}$ Mdm^{-3} respectively. All the solutions, including the titrant solution, were made up to formal ionic strength $I = 0.05$ by adding the calculated amount of tetraethylammonium perchlorate.

The solution of perchloric acid in dioxane–water mixture is stable for at least 3 days.

Procedure

All measurements were performed on a N-517 (MERA-ELWRO) pH-meter equipped with a V-541 (MERATRONIC) digital voltmeter with the use of the following thermostated (±0.1°) cell [*cf.* 12]:

0020-1693/83/$3.00

Hg	Hg_2Cl_2, KCl satd. water	0.05 *M* NaCl, 85% v/v dioxane–water	0.05 NEt_4ClO_4, 85% v/v dioxane–water	test solution	glass electrode

A stream of purified argon was passed through a dioxane–water (85%) mixture before passing through the test solution. The glass electrode–calomel electrode system was calibrated in water at 20 °C using the respective buffers (pH = 1.10 and 4.00). The changes arising from the temperature changes to 25 or 30 °C were compensated. The glass electrode was conditioned for 2 hours in dioxane–water (85%) mixture before use.

In general the method used corresponds to the standard potentiometric method except that the B value indicated by the millivoltmeter does not give direct information on the hydrogen ion concentration. According to Van Uitert and Haas [10] the negative logarithm of the formal hydrogen ion concentration is

$$\mathrm{pH} = \mathrm{B} + \log \mathrm{U_H} + \mathrm{E'_j}$$

and hence

$$\mathrm{pH} - \mathrm{B} = \log \mathrm{U_H} + \mathrm{E'_j}$$

The $\log U_H$ is constant [10] and E'_j is the liquid-junction potential connected with the difference in hydrogen ion concentration in the test solution and the salt bridge. The (pH – B) value was determined using a set of dioxane–water solutions of perchloric acid and tetraethylammonium perchlorate of total concentration 0.05 *M* [*cf.* 10, 7]. We found the value to be constant for $1.8 \leqslant B \leqslant 3.0$ and equal to 1.08, 1.09 and 1.12 at 20, 25 and 30 °C, respectively. Hence, when $1.8 \leqslant B \leqslant 3.0$, the influence of the liquid-junction potential E'_j and the variability of the perchloric acid dissociation degree [13], connected with $\log U_H$, on measured pH values may be neglected.

Titrations were performed as follows. The test dioxane–water solution (volume $V + V_a$) containing the studied ligand (concentration C_L), tetraethylammonium perchlorate and a known volume V_a of 0.05 *M* perchloric acid in 85% dioxane was titrated with tetraethylammonium hydroxide. The total concentration of acid C_a in the solution is given by

$$C_a = \frac{V_a \cdot 0.05}{V + V_a}$$

The B values rounded off to 0.005 units were read 10 minutes after each addition of the titrant. They were used to calculate pH and finally the formal hydrogen ion concentration $[H^+]$. Volume changes during titration were considered in the calculations.

Calculations

The formation function may be expressed by

$$\bar{n}_p = \frac{C_a - aC_L - [H^+]}{C_L} \qquad (1)$$

where a is the titration fraction. To calculate protonation constants the following equation is used [14]:

$$\frac{\bar{n}_p}{(1-\bar{n}_p)[H^+]} = K_1 + K_1K_2\,\frac{(2-\bar{n}_p)[H^+]}{1-\bar{n}_p} \qquad (2)$$

Constants K_1 and K_2 were estimated by the least squares method.

When titration was performed in the presence of a metal perchlorate of concentration C_M, the concentration of the free ligand [L] and the average ligand number $\bar{n}$ were calculated from (3) and (4)

$$[L] = \frac{C_a - aC_L - [H^+]}{\beta_H} \qquad (3)$$

$$\bar{n} = \frac{C_L - \alpha_{L(H)}[L]}{C_M} \qquad (4)$$

where

$$\alpha_{L(H)} = 1 + K_1[H^+] + K_1K_2[H^+]^2$$

and

$$\beta_H = K_1[H^+] + 2K_1K_2[H^+]^2$$

It was found, within the accuracy of the employed method, from the dependence $\bar{n} = f([L])$ that ligands *2–6* form weak complexes of the ML^{2+} type. The stability constants

$$K_{ML} = \frac{\bar{n}}{(1-\bar{n})[L]} \qquad (5)$$

were calculated for all titration points and refined with the use of the SCOGS programme [*cf.* 6].

Results and Discussion

The protonation constants of ligands *1–6* are shown in Table I. As was expected, aniline *1* is a stronger base as compared to *o*-anisidine *2*. This easily explained by assuming the concept of steric strain involving the $-NH_3^+$ group solvating molecules and that the ortho methoxy group would reduce the extent of solvation [15]. But the protonation constants increase for ligands *3* and *4* and come very close to the K value for aniline. Moreover, a further significant increase is observed for ligands *5*

TABLE I. Protonation Constants of Ligands *1–6* in a Dioxane–Water 85:15 v/v Mixture.

Ligand	Temp. °C	$\log K_1$[a]	$\log K_2$[a]	ΔH_{298} kJ mol^{-1}	ΔS_{298} J mol^{-1} K^{-1}
1	25	3.68			
2	25	3.48			
3	20	3.73	2.95	$\Delta H_1 = -24 \pm 4$	$\Delta S_1 = -11 \pm 12$
	25	3.64	2.76	$\Delta H_2 = -55 \pm 6$	$\Delta S_2 = -132 \pm 19$
	30	3.59	2.63		
4	20	3.75	3.19	$\Delta H_1 = -32 \pm 8$	$\Delta S_1 = -38 \pm 28$
	25	3.64	3.11	$\Delta H_2 = -55 \pm 22$	$\Delta S_2 = -125 \pm 73$
	30	3.59	2.92		
5	20	3.97	3.30	$\Delta H_1 = -24 \pm 4$	$\Delta S_1 = -6 \pm 13$
	25	3.88	2.91	$\Delta H_2 = -120 \pm 12$	$\Delta S_2 = -347 \pm 41$
	30	3.83	2.60		
6	20	4.21	3.32	$\Delta H_1 = -30 \pm 4$	$\Delta S_1 = -22 \pm 14$
	25	4.13	3.20	$\Delta H_2 = -40 \pm 2$	$\Delta S_2 = -73 \pm 7$
	30	4.04	3.09		

[a] The limits of errors, corresponding to two standard deviations are lower than ±0.01.

TABLE II. Stability Constants of Co^{2+}–Zn^{2+} Complexes with Ligands *2–6* in a Dioxane–Water 85:15 v/v Mixture.

Ligand	Ion	$\log K$[a]			ΔH_{298} kJ mol^{-1}	ΔS_{298} J mol^{-1} K^{-1}
		20 °C	25 °C	30 °C		
2	Co^{2+}		<1.30			
	Ni^{2+}		<1.30			
	Cu^{2+}		1.48 ± 0.1			
	Zn^{2+}		<1.30			
3	Co^{2+}	1.30 ± 0.15	<1.30	<1.30		
	Ni^{2+}	<1.30	<1.30	<1.30		
	Cu^{2+}	1.59 ± 0.05	1.58 ± 0.05	1.58 ± 0.05		
	Zn^{2+}	<1.30	<1.30	<1.30		
4	Co^{2+}	<1.30	<1.30	<1.30		
	Ni^{2+}	1.85 ± 0.03	1.78 ± 0.05	1.60 ± 0.05	−52 ± 29	−140 ± 97
	Cu^{2+}	2.04 ± 0.03	1.60 ± 0.05	1.48 ± 0.05	−98 ± 49	−298 ± 165
	Zn^{2+}	1.90 ± 0.03				
5	Co^{2+}	2.28 ± 0.02	2.15 ± 0.03	2.11 ± 0.03	−31 ± 17	−63 ± 58
	Ni^{2+}	2.10 ± 0.05	2.02 ± 0.05	1.90 ± 0.03	−24 ± 11	−42 ± 37
	Cu^{2+}	2.66 ± 0.03	2.35 ± 0.03	2.15 ± 0.03	−92 ± 23	−264 ± 76
	Zn^{2+}	<1.30	<1.30	<1.30		
6	Co^{2+}	2.00 ± 0.03	2.00 ± 0.03	1.90 ± 0.03	−10 ± 23	+5 ± 76
	Ni^{2+}	<1.30	<1.30	<1.30		
	Cu^{2+}	2.40 ± 0.01	2.39 ± 0.01	2.36 ± 0.01	−5 ± 8	+28 ± 27
	Zn^{2+}	<1.30	<1.30	<1.30		

[a] The limits of errors correspond to two standard deviations.

and *6* containing a greater number of oxygen donor atoms. As the inductive effects in these ligands do not essentially change the electron density on nitrogen atoms, the only explanation of the increase in protonation constants may lie in the assumption that oxygen atoms take part in the binding of solvated protons attached to the amino group. This resembles the situation of solvated protons complexed inside the macrocyclic hole [16]. It is worth adding that in a series of aliphatic polyetherodiamines $H_2N-CH_2-(CH_2-O-CH_2)_x-CH_2-NH_2$ where $x = 0, 1, 2$ the chain length practically does not influence the K_1 and K_2 values [*cf.* 6]. The different behaviour between aliphatic and aromatic diaminopolyethers may be ascribed to the greater conformational flexibility of the former as compared to ligands *3–6*.

The values of protonation constants K_2 for ligands *3–6* are lower by less than one order than the respective K_1 values, implying that the protonated amino group does not significantly interact with the second free amino group.

The stability constants of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} complexes with ligands *2–6* are listed in Table II. In general, stability constants for the complexes of ligands *2*, *3* and *4* are very small. This agrees with the small basicities of these ligands. Significantly higher stability constants are found for ligands *5* and *6*, which were stated to simultaneously possess a higher proton-acceptor power. The significant rise in the stability constants for complexes in the order from *2* to *6* may be explained assuming a partial participation of oxygen atoms in the binding of the central cation. This assumption is additionally supported by the direction of the entropy changes. In the ligand series from *4* and *5* to *6* the entropy changes become more positive, and this indicates the greatest desolvation of the metal ion during complex formation with ligand *6*.

In general the differences in stability constants of Cu^{2+} complexes as compared with Co^{2+} and Ni^{2+} complexes are small. For complexes of ligand *5* and especially *6* it is easy to notice the partially reversed Irving–Williams series [*cf.* 6 and 17]. It is well reflected by the positive entropy changes of the complexation reaction of *6*. The situation is then similar to other examples of the general deviation from the Irving–Williams rule [18].

It is rather unusual that Zn^{2+}, within the accuracy of the employed method, does not form complexes with the investigated ligands. Similarly it was found that *6* does not form complexes with sodium cations.

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