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Complexes of 18-Crown-6 Macrocyclic Ethers with Sodium Monoalkyl [2-Sodium Phenoxide[[4-(Phenylazo)-Phenyl] Amino] Methyl] Phosphonate

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NOTE

COMPLEXES OF 18-CROWN-6 MACROCYCLIC ETHERS WITH SODIUM MONOALKYL [2-SODIUM PHENOXIDE[[4-(PHENYLAZO)-PHENYL]AMINO]METHYL] PHOSPHONATE

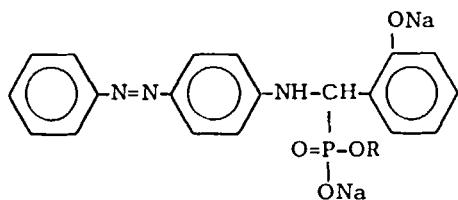
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There is currently considerable interest in crown ether complexation of alkali metal salts of organic chelating anions because of their relevance to such fundamental processes as ion-exchange¹ and ion-transport across biological membranes.² The chelating anions mostly used have been those derived from various phenols, aminobenzoic acids and aminophosphonic acids.³⁻¹¹ In continuing our investigations of crown ether complexes with alkali salts of monoalkyl esters of various α -anilinobenzylphosphonic acids,⁸⁻¹¹ this note describes the synthesis and some spectroscopic studies of new complexes of the crown ethers 18-crown-6 and dibenzo-18-crown-6 with the sodium monoethyl ester and the sodium monobutyl ester of [2-sodium phenoxide[[4-(phenylazo)phenyl]amino]methyl] phosphonic acid. The results are compared and discussed relative to the corresponding crown ether complexes obtained separately with sodium phenoxide^{6,7} and with various sodium monoalkyl benzeneazophosphonates.^{8,11}

Keywords: Sodium, crown ether, 18-crown-6, dibenzo-18-crown-6, complexes, benzeneazophosphonates



Salt	R
Na ₂ EPP	Et
Na ₂ BPP	Bu

EXPERIMENTAL

Materials

Macrocyclic polyethers 18-crown-6 (18C6) and dibenzo-18-crown-6 (DB18C6) obtained commercially were purified by repeated recrystallization from the appropriate solvents, 18C6 from acetonitrile and DB18C6 from acetone. Anhydrous sodium salts of the monoethyl ester and the monobutyl ester of [2-sodium phenoxide [[4-(phenylazo)phenyl] amino] methyl]phosphonate (Na₂EPP, Na₂BPP) were prepared according to literature procedures.¹² Analytical grade solvents were used for the preparation of the salt complexes.

Preparation of the complexes

A mixture of equimolar amounts of macrocyclic ether (18C6, DB18C6) and sodium salt (Na_2EPP , Na_2BPP) in absolute ethanol or acetonitrile was refluxed for 8 h with continuous stirring. Solvent was partly removed from the filtered solution to give, on gradual cooling, an orange-red precipitate. The crystalline complex was filtered off, washed with cold reaction solvent and dried under high vacuum at 50°C for 10 h.

Physical measurements

Microanalyses were carried out by the microanalytical laboratories of the Rudjer Bošković Institute. Melting points were determined on a hot stage and are uncorrected. Electronic spectra were run in ethanol, acetonitrile and chloroform solutions on a Cary Model 17 spectrophotometer. IR spectra were recorded on a Perkin Elmer 580B spectrophotometer in KBr disks. ^1H NMR spectra were obtained with a Jeol 90Q Fourier-transform NMR spectrometer in CDCl_3 solution. Molar conductivities were measured in methanol on a Tacussel CD 7A conductivity bridge.

RESULTS AND DISCUSSION

Investigations of the interaction of 18-crown-6 and dibenzo-18-crown-6 polyethers with benzeneazophosphonate-phenoxide salts Na_2EPP and Na_2BPP have shown that only 1:1 polyether:disodium salt complexes formed, regardless of various preparative conditions (solvent, duration of reaction, excess of reactants). It may be presumed that both sodium ions are coordinated to the crown ether oxygens, although it has been generally accepted that 18-crown-6 macrocycles with sodium salts form 1:1 polyether:metal complexes. The sodium ion (ionic diameter 1.94 Å) fits well into the hole of the 18-membered polyether ring (2.6–3.2 Å diameter)¹³ with the anion and solvent molecules having possibilities of interacting with the metal from axial directions. The structures of various salt complexes clearly show that the complex is affected not only by the size of the cation relative to the size of the crown ether cavity, but also the counterion and the reaction solvent have a marked effect. "Hard" anions such as ethyl acetoacetate,¹⁴ phenoxide^{6,7} and benzeneazophosphonate¹⁵ are closely associated with the complexed alkali metal and pull the cation out of its ideal nesting position.

The X-ray structure determination of the 1:1 complex of DB18C6 with sodium monoethyl[α -(4-benzeneazoanilino)-N-benzyl] phosphonate shows strong bonding between the crown ether complexed cation and the phosphonate anion.¹⁵ Sodium is coordinated to all six crown oxygens at distances from 2.601 to 2.769 Å in the base of a hexagonal pyramid and to one of the phosphonate oxygen atoms in the apical position at a distance of 2.183 Å. Therefore, it could be concluded that stronger interactions exist between the sodium ion and the phosphonate oxygen than with the oxygens in the crown ring. A strong cation-anion electronic interaction is observed in acetonitrile, while in more polar solvents such as alcoholic, the ion-pair complexes are almost completely dissociated.^{9,10} Furthermore, it was shown that 18-crown-6 macrocycles in ether could form complexes with sodium phenoxide of 1:2 macrocycle:salt stoichiometry, while 18C6 also gives a complex with 1:3 ratio.⁶ The crystal structure of the dicyclohexano-18-crown-6 complex consists of a tetramer of

sodium phenoxides in which two macrocyclic ether molecules each complex two sodium ions.⁷ One sodium is coordinated to the six hexaether oxygens and to one of the phenoxide oxygens, while the other sodium is coordinated to only one of the crown oxygens and to three phenoxide oxygens. The crown adopts a highly irregular conformation.

The novel sodium complexes prepared (I–IV) together with some physical properties, analytical and conductance data are presented in Table I. The most important spectroscopic data are summarized in Table II. Complexes are microcrystalline, coloured from orange to red and those derived from 18C6 are hygroscopic. After drying in vacuum they were obtained anhydrous. Free sodium salts are completely dissociated in alcoholic solution and exhibit conductivities comparable to those of 2:1 electrolytes, whereas their complexes show much lower molar conductivities due to complexation to the macrocyclic ethers. In acetonitrile, sodium salts and their complexes are only slightly soluble at room temperature and conductance measurements could not be performed. The structure of the complexes were deduced mainly from these spectral data. Attempts to grow suitable crystals for X-ray diffraction have not been successful.

Spectroscopic studies

Free sodium salts Na₂EPP and Na₂BPP have in absolute ethanol and acetonitrile an absorption maximum at about 398 and 400 nm, respectively, which corresponds to conjugation of the azo group with the aromatic rings (π – π^* transition). No significant changes in the spectra are noted after complexing with the crown ethers, suggesting essentially the same ion-pair structure for sodium salts and their complexes, although the conductance data show a much greater solubilization and a smaller association to ion-pairs in methanol than in acetonitrile solution. Spectroscopic studies in chloroform have demonstrated a pronounced red shift of the absorption maximum in the spectra of complexes relative to the free sodium salts, indicating that complexation causes a change in the ion-pair structure. While the free sodium salts, which are very slightly soluble in chloroform, may be classified as contact ion-pair salts, their more soluble crown ether complexes exist as crown separated ion-pairs. Similar behaviour was found for various other benzeneazophosphonate complexes.⁹

The IR spectra of the complexes are too complex to allow a precise assignment of the absorption bands. However, they are distinctively different from the spectra of the physical mixture of the metal salt and the free ligand, and show the absence of the uncomplexed constituents. Generally the data are very similar to those obtained for the corresponding crown ether complexes of some sodium monoalkyl benzeneazophosphonates, indicating that ether-metal-anion interactions are essentially the same in these complexes.^{8,11} In passing from the free crown ethers to their complexes, the most significant differences are related to the various deformation modes of the methylene groups in the 1000–900 cm⁻¹ region. Free polyethers have two bands associated with these vibrations, at 990 and 948 cm⁻¹ for 18-crown-6, and at 997 and 932 cm⁻¹ for DB18C6. Upon complexation, they are missing, and a rather strong band appears around 970 and 950 cm⁻¹, respectively. Some bonding between oxygens atoms of the crown ether ring and the sodium ions presumably causes less restriction on the coupling of these vibrations.

In the ¹H NMR spectra of the complexes the resonances of the methylene polyether

TABLE I
Physical and analytical data for the new complexes.

Complex	M.p. (°C)	Found (calcd) (%)						Λ_M^a
		C	H	N	P	Na		
I	70-71	55.3 (55.1)	6.2 (6.2)	5.5 (5.8)	4.2 (4.3)	6.1 (6.4)	113 (148)	
II	68-70	56.4 (56.2)	6.3 (6.5)	5.7 (5.6)	4.4 (4.1)	6.3 (6.2)	110 (145)	
III	158-159	60.5 (60.4)	5.6 (5.4)	5.3 (5.1)	3.6 (3.8)	5.5 (5.6)	108 (148)	
IV	150-152	61.4 (61.2)	5.5 (5.7)	4.8 (5.0)	3.5 (3.7)	5.6 (5.5)	106 (145)	

^aConcentration 10^{-3} M in methanol at 25°C (in $\text{cm}^2 \text{mol}^{-1} \text{ohm}^{-1}$). Data for the free sodium salts are given in parentheses for comparison.

TABLE II
Selected electronic, IR and ¹H NMR spectroscopic data for the complexes.

Complex	λ_{\max} (log ϵ)	IR data (cm ⁻¹) ^c	¹ H NMR data (δ in ppm, J in Hz) ^d
I	CH ₃ CN: 402 (4.20)	3390 m, 3450 m (ν NH); 1250 m ($\nu_{\text{as}}\text{PO}_2^-$);	1.12 (t, 3H, CH ₃ , J = 7); 3.36–3.84 (m, 2H, POCH ₂); 3.63 (s, 24H, OCH ₂ CH ₂ O); 4.80
	[400 (4.63)] CHCl ₃ : 387 ^b (373)	1136 s, 1108 vs, 1070 sh ($\nu_{\text{sym}}\text{PO}_2^-$), $\nu_{\text{as}}\text{CH}_2\text{-O-CH}_2$, $\nu\text{P-O-C}$; 980 sh, 967 s ($\omega_{\text{r}}\text{CH}_2$, $\nu_{\text{aliph}}\text{C-C}$)	(d, 1H, PCH, J = 22.3); 5.33 (s br, 1H, NH); 6.41–7.67 (m, 13H, ArH)
II	CH ₃ CN: 402 (4.51)	3390 s, 3453 s (ν NH); 1250 m ($\nu_{\text{as}}\text{PO}_2^-$);	0.64–1.67 (m, 7H, CH ₂ CH ₂ CH ₃); 3.39–3.81
	[401 (4.57)] CHCl ₃ : 382 ^b (358)	1138 s, 1108 vs, 1075 sh ($\nu_{\text{sym}}\text{PO}_2^-$), $\nu_{\text{as}}\text{CH}_2\text{-O-CH}_2$, $\nu\text{P-O-C}$; 980 sh, 967 s ($\omega_{\text{r}}\text{CH}_2$, $\nu_{\text{aliph}}\text{C-C}$)	(m, 2H, POCH ₂); 3.59 (s, 24H, OCH ₂ CH ₂ O); 4.78 (d, 1H, PCH, J = 23); 5.49 (s br, 1H, NH); 6.41–7.71 (m, 13H, ArH)
III	CH ₃ CN: 403 (4.55)	3600 m, 3352 s (ν NH); 1270 sh, 1248 m	c
	[400 (4.63)] CHCl ₃ : 380 ^b (373)	($\nu_{\text{as}}\text{Ar-O-CH}_2$, $\nu_{\text{as}}\text{PO}_2^-$); 1146 m, 1102 s 1078 s, 1052 vs ($\nu_{\text{sym}}\text{PO}_2^-$, $\nu_{\text{as}}\text{CH}_2\text{-O-CH}_2$, $\nu\text{P-O-C}$); 970 s ($\omega_{\text{r}}\text{CH}_2$, $\nu_{\text{aliph}}\text{C-C}$)	
IV	CH ₃ CN: 403 (4.45)	3600 w, 3380 m br (ν NH); 1257 s, 1238 sh	0.62–1.65 (m, 7H, CH ₂ CH ₂ CH ₃); 3.40–3.82
	[401 (4.57)] CHCl ₃ : 377 ^b (358)	($\nu_{\text{as}}\text{Ar-O-CH}_2$, $\nu_{\text{as}}\text{PO}_2^-$); 1130 vs, 1108 s, 1065 s ($\nu_{\text{sym}}\text{PO}_2^-$, CH ₂ -O-CH ₂ , $\nu\text{P-O-C}$); 974 m, 950 sh ($\omega_{\text{r}}\text{CH}_2$, $\nu_{\text{aliph}}\text{C-C}$)	(m, 2H, POCH ₂); 3.91 (s, 16H, OCH ₂ CH ₂ O); 4.59 (d, 1H, PCH, J = 23); 5.93 (s br, 1H, NH); 6.33–7.89 (m, 21H, ArH)

^aIn the 330–500 nm region. Data for the free sodium salts are given in parentheses for comparison.

^bSpectra of the saturated complex solution.

^cKBr pellet.

^dIn CDCl₃.

^eComplex too insoluble for measurements.

ring protons show an upfield shift of 7–18 Hz with respect to the free crown ethers. These differences may be explained by the proximity of the crown ether molecule to the aromatic rings of the anion in spite of the complexation with the alkali cation which in itself would induce a downfield shift due to the increased electronegativity of the oxygen atoms. Furthermore, the slight broadening of these absorptions in the complexes indicates the slow dissociation rate of the ion-pair complexes in chloroform solution. The aromatic anion and crown ether protons in complex IV are overlapped, giving an unresolved multiplet. The resonances of the other anion protons are very similar with those obtained for the sodium benzeneazophosphonate complexes with crown ethers.^{8,11}

It may be presumed that both sodium ions are involved in bonding to the crown ether oxygens, but not necessarily to the same macrocyclic molecule. It is possible that each crown molecule complexes two sodium ions, one above the approximate plane of the macrocyclic ring and one below from two different sodium salt molecules.

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