Spectroscopic Study of Azo- and Azoxycrowns Binding with Cations of Similar Ionic Radius

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Abstract. The complexation of 13- and 16-membered azo- and azoxycrowns with metal cations of similar ionic diameter (Na^+ and Ca^{2+}; and K^+, Ba^{2+}, Ag^+ and Pb^{2+}) was studied by uv/visible spectroscopic titration in acetonitrile and MeOH. In MeOH the 13-membered azo- and azoxycrowns **1** and **2** are weakly and non-selectively bound to hard cations of similar ionic diameter, but different charge (Na^+ and Ca^{2+}). At the same time the binding to the soft cation Ag^+ of larger size than the macrocycle cavity is considerably stronger. In contrast to solutions in acetonitrile no binding with the small Li^+ cation was found. The 16-membered azocrowns **3** and **4** also discriminate silver cation in MeOH with $\log K = 3.65 \pm 0.1$ for both compounds. Unexpectedly low binding with the hard barium divalent cation of similar size ($\log K = 1.55 \pm 0.4$ and 1.95 ± 0.2, respectively) was found for these compounds. Similarly to 13-membered compounds no binding with the small Li^+ cation was detected. A reverse order of selectivity was observed for these crowns in acetonitrile with binding constant for association of **3** with Ba^{2+} ($\log K \geq 5.3$) considerably higher than for other cations. The previously observed strong binding with the smaller Li^+ and Na^+ cations is confirmed.

Key words: azocrowns, complexation, metal cations, absorption spectroscopy.

1. Introduction

An introduction of photo- and electroactive —N=N— or —N(O)=N— residues into crown ether macrocycles can result in highly selective chemical sensors. Over recent years, we have been studying the family of 13- and 16-membered azo- and azoxycrowns [1–12]. We have already reported voltammetric recognition properties of some of these materials in thin films adsorbed on a mercury electrode [5] and in Langmuir–Blodgett films [5, 8, 10]. Earlier Shiga *et al.* [13] determined the stability constants of metal iodide and unsubstituted azocrown complexes by a spectroscopic method in acetonitrile. These authors were not able to determine the stability constant for the 13-membered azocrown with NaI and KI, while for the 16-membered crown and KI $\log K$ was 3.15 [13]. In drastic disagreement with the ion-cavity size match concept Li^+ forms the most stable complexes [13]. However,

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Li^+ was not extracted by the azocrowns; the 13- and 16-membered azocrowns extracted preferentially Na^+ and K^+, respectively, just according to the ion-cavity size concept [14]. Recently we have estimated the binding constants with matching size cations, Na^+ for the 13-membered and K^+ for the 16-membered azocrowns, using UV-titration [8, 10, 11] and square wave voltammetry [11]. The binding selectivity with a number of cations was obtained using the ion-selective electrode technique [3, 6, 12].

The influence of the charge density, polarizability and the size of the cations on the cation - macrocycle association is an extensively studied subject. A wide range of data on the thermodynamics of macrocycle-cation interactions can be found in an exhaustive review [15]. For dibenzo-18-crown-6, whose cavity size matches the ionic diameter of K^+, the binding constant for this cation in acetonitrile was found to be in the range of $\log K = 4.2$–5.07 [16–18]. For the Ba^{2+} cation of similar size a close value of 4.32 was determined [19]. Similar in radius Ag^+ exhibited a $\log K$ value in the range of 2.92–4.52 [20, 21]. The $\log K$ values obtained by the same technique (polarography) were 4.2–4.75 [15, 16]; 4.32 [18]; 2.92 [20] for K^+, Ba^{2+} and Ag^+, respectively. This order of selectivity with a lower value for the soft cation Ag^+ corresponds well to the tendency of the oxygen atoms in the macrocycle to have a higher affinity for hard alkali and alkali-earth cations and the sulfur atom for soft Ag^+, Hg^{2+} and Pb^{2+} cations [14]. Another example of the dependency of binding properties on the cation charge is substituted diaza-18-crown-6 [22]. For this macrocycle values of $\log K$ of 4.2 and 7.6 were determined spectroscopically in acetonitrile for K^+ and Ba^{2+}, respectively. The stronger binding with Ba^{2+} is possibly due to the higher charge of this cation. $\log K$ values in acetonitrile and MeOH for 18-crown-6 are collated in Table I. The order of selectivity in both solvents is $Ba^{2+} > K^+ > Ag^+$.

For the smaller benzo-15-crown-5, whose cavity size matches the ionic diameter of Na^+, $\log K$ for similar sized Na^+ and Ca^{2+} were determined (potentiometry in MeOH) to be 2.78 [23] and 2.33 [24], respectively. However, an opposite order of selectivity was found by potentiometry [23] for the nitro derivative of the latter compound under the same conditions.

For compounds **1–4** the order of binding with cations of similar ionic radii is unknown except for ion-selective electrode data for the 13- and 16-membered azo- and azoxycrowns [3, 12]. However, the selectivities of ion-selective membrane electrodes are very seldom comparable with stability constant values [3]. Here we report the systematic study of the association of 13- and 16-membered azo- and azoxycrowns with similar size cations by a spectroscopic technique.

2. Experimental

Compounds **1** –**4** were obtained as described in [3, 9], respectively.

Optical absorption spectra were recorded using a Specord UV-VIS spectrometer (East Germany). KPF_6, $NaPF_6$, $KClO_4$, $Ba(ClO_4)_2$ (all Aldrich), $AgNO_3$

Table I. Stability constants for complexation of 18-crown-6 with cations

Cation	Solvent	log K	Reference
K^+	Acetonitrile	5.2–6.3[a]	15
Ba^{2+}	–	>5[a]	18
Ag^+		4.79[c]	20
K^+	MeOH	>5; 6.07–6.29[b]; 5.5[c]	31
–	–	6.02[d]	32
		6.55[a]	33
		6.08–6.15[e]	30, 31, 34
Ba^{2+}		7.31–7.38[b]; > 5.5[c]	30
Ag^+		4.58–4.67[b,c,e]	30

[a] Polarography.
[b] Calorimetry.
[c] Conductometry.
[d] Ion-selective electrode.
[e] Potentiometry.

1 X=nil, n=1, R=(CH$_3$)$_3$CCH$_2$C(CH$_3$)$_2$

2 X=O, n=1, R=(CH$_3$)$_3$CCH$_2$C(CH$_3$)$_2$

3 X=nil, n=2, R=n-C$_{12}$H$_{25}$
RR=nC

4
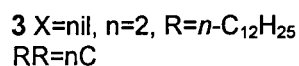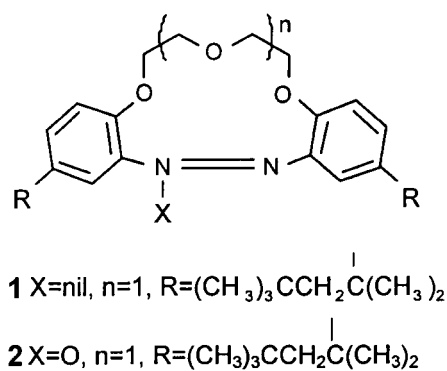
Scheme 1.
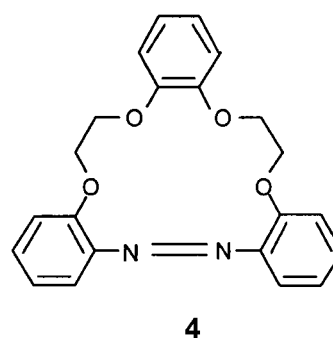
(Fluka), LiClO$_4$ (Fluka, microselect), Bu$_4$NClO$_4$ (Fluka, electrochemical grade), PbAc$_2$·3H$_2$O, KSCN, CaCl$_2$, AgNO$_3$, Et$_4$NCl (manufactured in Russia) were used for the preparation of solutions. Acetonitrile (pure, manufactured in Russia) was heated under reflux with KMnO$_4$ + Na$_2$CO$_3$, distilled, treated with H$_2$SO$_4$, and distilled again over P$_2$O$_5$. MeOH (manufactured in Russia) was distilled before use.

Generally, the solution of the azo- or azoxycrown compound in a working 1 cm length cuvette was titrated with a solution of metal salt containing the same concentration of the macrocycle. For salts, which absorb in the UV range (Ag$^+$ and

Pb^{2+}), aliquot addition of the salt solution to both working and reference cuvettes to compensate for the salt absorbance or the subtraction of salt absorption were used. In cases of low stability constant solid aliquots of metal salt were added.

3. Results and Discussion

For the 13-membered crowns **1** and **2**, whose cavity size corresponds approximately to the ionic diameter of Na^+ [26], Ca^{2+} was chosen for comparison as these cations have similar ionic radii (0.95 and 0.99, respectively [27]). It was previously found in aqueous solution [3] that the order of selectivities measured using ion-selective membrane electrodes is $Ag^+ \gg Na^+ \gg Ca^{2+}$ (the ionic diameter of the silver cation is larger than the cavity size). In contrast a high association constant was determined for small Li^+ in acetonitrile [13]. In the latter work the spectral changes in the presence of CaI_2 were significant, however the value of the association constants were scattered due to a more complex mechanism and were not reported [13]. Here we studied complexation with these cations in MeOH. Only compound **1** (and only in the presence of $NaClO_4$) exhibits clear isosbestic points at ca. 33300, 40800 and 43500 cm^{-1} (300, 245 and 230 nm), indicating that 1 : 1 complexation occurs (Figure 1). In the presence of $AgNO_3$ a random change of the spectrum in the UV range was observed due to the strong absorbance of $AgNO_3$ despite compensation. At longer wavelengths two isosbestic points at ca. 25300 and 27400 cm^{-1} (395 and 365 nm) were observed for compound **1** in the presence of $AgNO_3$ (Figure 1). Otherwise (data not shown) only a gradual increase in absorbance in the entire measured spectral range was observed in the presence of metal salts. This may indicate that not only a 1 : 1 complex is formed and/or the extinction coefficient for the complex is higher than the extinction coefficient of the free macrocycle in the studied spectral range. We have treated the experimental spectroscopic titration data using a non-linear fitting procedure according to an equation derived on the basis of the law of mass action and Beer's law (for a 1 : 1 complex neglecting metal salt absorption). This equation has been successfully used before [28] by one of us

$$\Delta D = 0.5\Delta\epsilon l\{[AC] + [M] + 1/K - (([AC] - [M])^2 + (2/K)^*([AC] + [M]) + 1/K^2)^{1/2}\}. \tag{1}$$

Here $\Delta D = D - D_0$, D is the absorbance, D_0 is the absorbance without metal salt present, $\Delta\epsilon = \epsilon_{com} - \epsilon_{AC}$, ϵ_{com} is the extinction coefficient of the complex, ϵ_{AC} is the extinction coefficient of the azocrown, l is the cuvette path length, [AC] is the azocrown concentration, and [M] is the metal salt concentration. The values of K for the complexation of 13-membered macrocycles at different wavelengths are collated in Table II. In some cases a wavelength dependence of the K value was observed. We believe that involvement of cis-trans isomerisation, complexes of other stoichiometry, complexation with anion and solvent, and experimental errors
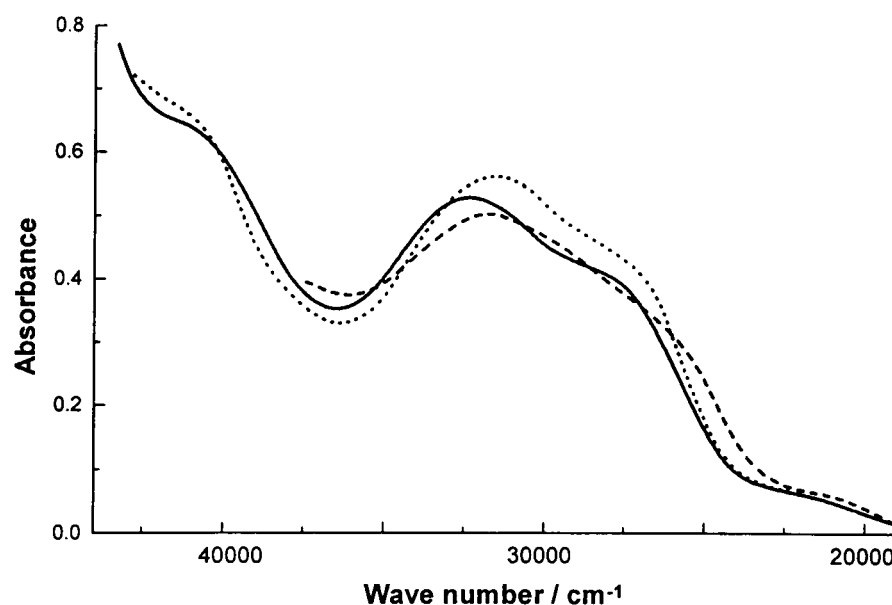
Figure 1. Absorption spectra of compound **1** (4.3×10^{-5} M) in MeOH (solid line); containing NaClO$_4$ (dotted line) at a concentration of 0.04 M, and AgNO$_3$ (dashed line) at a concentration of 0.01 M.

due to intrinsic metal salt absorption are possible reasons. The average log K value for compounds **1–4** are collated in Table III. To exclude possible complexation with anions, complexation with Na$^+$ was studied with two different anions and the stability constants for compound **1** were found to be similar (Table II). In addition the spectral changes were studied in the presence of Et$_4$NCl and Bu$_4$NClO$_4$ (large onium cations do not apparently bind to azocrowns). Even though some spectral changes were observed, these were not large enough to allow stability constant estimation (see comments in Tables II and V). Independently of how weak the association with anions (and/or solvent) is, this may result in the absence of isosbestic points. The complexation with Li$^+$ was also tested. A high constant was found for compound **1** in acetonitrile (log K = 3.28 ± 0.25). In contrast, although small spectral changes were observed in the presence of LiClO$_4$ in MeOH, we were not able to fit these data to Equation (1). The examples of absorbance changes with metal cation concentrations and non-linear fits to Equation (1) are presented in Figure 2 for compound **1**. The association of 13-membered compounds with Na$^+$ in MeOH is several times weaker than in acetonitrile [8, 11]. This corresponds to an inverse relationship of the stability of the complexes and the Gutmann donicity of the solvents [15], as according to Gutmann [29] the donor numbers of acetonitrile and MeOH are 14.1 and 19, respectively. In addition azoxycrown **2** binds weaker with all studied cations. This could be explained by the fact that in azoxycrowns a hard metal cation binds by the oxygen of the N(O)=N group as recently found
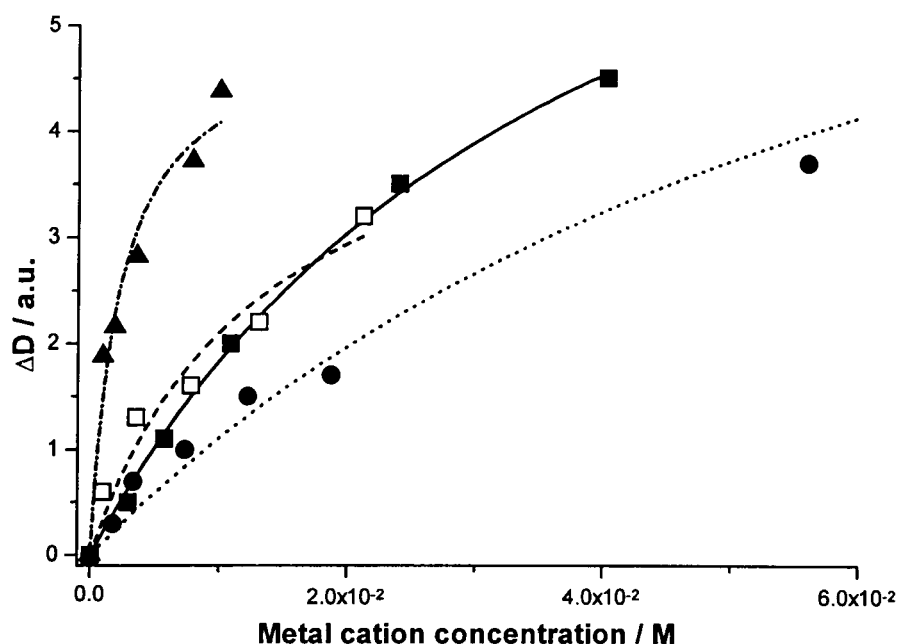
Figure 2. Non-linear fit of the experimental absorbance data in MeOH *versus* metal cation concentration to Equation (1) for compound **1**: solid squares (solid line) – $NaClO_4$ at 365 nm, open squares (dashed line) – $NaPF_6$ at 365 nm, solid circles (dotted line) – $CaCl_2$ at 365 nm, triangles (dash-dotted line) – $AgNO_3$ at 475 nm.

for the complex of Na^+ with a 16-membered azoxycrown [30]. The binding by oxygen of the azoxygroup could be weaker than binding by the entire macrocycle. Moreover, the N=O oxygen enters the cavity, thus diminishing its size. For both compounds **1** and **2** the order of selectivity is $Ag^+ > Na^+ \geq Ca^{2+}$. This deviates from the order observed by the ion-selective electrode technique [3, 29], however the selectivities of ion-selective membrane electrodes are very seldom comparable with stability constant values [30]. This also differs from data observed in acet-onitrile [8, 13]. The difference in association with Na^+ and Ca^{2+} is also smaller than previously observed for 15-crown-5 in the same solvent [22, 23]. It was sug-gested earlier [13] that azocrowns are more distorted and disordered compared to ordinary crowns and it is likely that the azo group does not contribute much to the stabilisation of the complex. This also probably leads to the relatively higher affinity of the azocrown to the small Li^+ cation in acetonitrile [13 and this paper]. 13-Membered macrocycles are weakly and non-selectively bound to hard cations and much stronger to the soft Ag^+ cation.

For the 16-membered azocrowns **3** and **4** with the cavity size matching the ionic diameter of K^+, Ba^{2+}, Ag^+ and Pb^{2+} were chosen for comparison as these cations have similar ionic radii (1.33, 1.35, 1.26 and 1.20, respectively [26]). The complexation was studied in acetonitrile and MeOH as $PbAc_2 \cdot 3H_2O$ is insoluble

Table II. Stability constants (M^{-1}) for the complexes of **1** and **2** in MeOH

Wavelength, nm/K	260	280	320	340	380	400	450
Na^{+e} compound **1/2**		(40 ± 20^{b})	35 ± 20^{a} (35 ± 7^{b})	(30 ± 8)	75 ± 40^{a} (25 ± 3^{b}) /13 $\pm$ 2		
Ca$^{2+,d}$	35 ± 3		$20 \pm 3/14 \pm 9$		15 ± 4		
Ag^{+}					/37 $\pm$ 6	1080 ± 80^{c} /150 $\pm$ 20^{c}	460 ± 130^{c}

^a NaPF$_6$.
^b NaClO$_4$.
^c With subtraction of salt absorption.
^d The spectral changes in the presence of Et$_4$NCl were not consistent.
^e The spectral changes for compound **2** in the presence of Bu$_4$NClO$_4$ were smaller than in the presence of NaClO$_4$.

Table III. Average stability constants (M^{-1}) for the complexes of compounds **1–4** with cations

Compound/ log K	K^+ acetonitrile/ MeOH	Ba^{2+}	Ag^+	Pb^{2+}	Na^+	Ca^{2+}	Li^+
1			$-/2.9 \pm 0.25$		2.2^a [8, 11]/ 1.5 ± 0.35	$-/1.35 \pm 0.2$	$3.28 \pm 0.25^b/-$
2			$-/2.0 \pm 0.4$		2.25 [11]/ 1.1 ± 0.1	$-/1.15 \pm 0.2$	
3	$3.35 \pm 0.15^c/$ 3.15 ± 0.2	$5.3 \pm 0.3/$ 1.95 ± 0.2	$2.7 \pm 0.1/$ 3.65 ± 0.1	$-/2.45 \pm 0.4$	$4.0 \pm 0.3^d/$ 2.60 ± 0.03		$4.0 \pm 0.1^e/-$
4	$2.55 \pm 0.6/$ 2.2 ± 0.1	$2.45 \pm 0.05/$ 1.55 ± 0.4	$2.1 \pm 0.45/$ 3.7 ± 0.05	$-/2.65 \pm 0.05$	$2.85 \pm 0.1/$ 2.1 ± 0.2		$3.42 \pm 0.05/-$

[a] $\log K = 2.3$ in acetone.
[b] $\log K = 4.1$ with LiI for unsubstituted analogue [13].
[c] $\log K = 3.15$ for unsubstituted analogue with KI [13].
[d] $\log K = 3.69$ with NaI for unsubstituted analogue [13].
[e] $\log K = 4.0$ with LiI for unsubstituted analogue [13].

Table IV. Stability constants for the complexes of **3**

Wavelength, nm/M^{-1}	K$^+$ acetonitrile/ MeOH	Ba^{2+}	Ag$^+$	Pb^{2+}	Na$^+$	Li$^+$
280	2900 ± 600/ 2070 ± 240				10930 ± 200/ 380 ± 20	8250 ± 600
300		/125 ± 45				
320	1950 ± 200/ 1550 ± 290	3 × 10^5 ± 3.2 × 10^{4,a}/ 56 ± 25	/4090 ± 1770[c]	/225 ± 70[b]	4800 ± 1060/ 430 ± 20	10380 ± 300
380	1580 ± 270/ 845 ± 160	1 × 10^5 ± 4 × 10^{4,a}/	/5325 ± 700[c]	/110 ± 30[b]	14400 ± 1060/ 380 ± 20	11380 ± 1130
400			620 ± 270/ 3410 ± 470[c]			
420			400 ± 100	/367 ± 145[c]		9910 ± 240
450			430 ± 80/ 5000 ± 1460	/426 ± 144[c]		

[a] Approximate minimum value, saturation of spectrum change was observed at 1 equivalent of Ba^{2+}.
[b] Metal salt addition to both cuvette.
[c] With subtraction of salt absorption.

Table V. Stability constants for the complexes of **4**.

Wavelength, nm/M^{-1}	K$^+$ acetonitrile/ MeOH	Ba^{2+}	Ag$^+$	Pb^{2+}	Na$^+$	Li$^+$
230		270 ± 45/			590 ± 70/ 45 ± 17	2340 ± 460/
260	(560 ± 120[b])/	250 ± 20/				2590 ± 200/
280	(870 ± 310[b])/ 190 ± 15	260 ± 25/			830 ± 70/ 200 ± 50	
300	(540 ± 90[c])/ 135 ± 10	/17 ± 3				2420 ± 330
320	280 ± 40[a] (70 ± 15[b])/	295 ± 40/	220 ± 80/ 4460 ± 560[f]		680 ± 30/ 85 ± 30	
350				/455 ± 175[e]	910 ± 20/ 120 ± 30	2890 ± 170
380	210 ± 15[a] (140 ± 7[b]; 440 ± 80[c])/125 ± 6	310 ± 15/ 67 ± 4	/5510 ± 1090[f]			
420			58 ± 5[f]/	/420 ± 110[e,f]		2930 ± 80
450	(100 ± 35[b])/	/27 ± 5			650 ± 25/ 130 ± 17	
490			100 ± 25[f] (145 ± 25[d])/ 4420 ± 370[f]			

[a] KClO$_4$. [b] KPF$_6$. [c] KSCN. [d] AgNO$_3$. [e] Aliquot addition of the salt solution to both working and reference. [f] With subtraction of salt absorption. [g] The spectral changes in the presence of Bu$_4$NClO$_4$ were smaller than in the presence of Ba(ClO$_4$)$_2$

in acetonitrile. The previously observed binding selectivity order by ion-selective electrode techniques was found to be $Ag^+ \gg K^+ \gg Ba^{2+}$; Pb^{2+} was not measured [6, 12]. In acetonitrile the binding order of $Li^+ > Na^+ > K^+$ was found spectroscopically [13]. In this solvent complexation of compound **4** with K^+ was studied with three different anions, the association constants were found to be similar (Table V). Clear isosbestic points were observed in the presence of K^+ and Ba^{2+}. For compound **3** the isosbestic points were at ca. 22700 and 33550 cm^{-1} (440 and 298 nm) in the presence of KPF_6 [10], and at 22200 and 32250 cm^{-1} (450 and 310 nm) in the presence of $Ba(ClO_4)_2$ (Figure 3). Just less than 1 equivalent of Ba^{2+} caused significant spectral change (data not shown), which indicates strong binding with this cation. Derivative **4** exhibits one isosbestic point in the presence of K^+ (at ca. 305 nm with KPF_6 and ca. 290 nm with $KClO_4$ or KSCN, Figure 3). Complexation of this compound with Ba^{2+} resulted in the isosbestic points at ca. 41700, 40800, 32800 and 20800 cm^{-1} (240, 245, 305 and 480 nm, Figure 4). Both 16-membered macrocycles did not show any isosbestic points in the presence of Ag^+ in acetonitrile possibly due to the intrinsic absorbance of the Ag^+ salt at lower wavelengths. Among other complications discussed above for 13-membered crowns complexation of the soft Ag^+ cation with molecules of the soft solvent acetonitrile is also possible. This may result in weaker binding with this cation in acetonitrile compared with MeOH (Table III). The binding constants are collated in Tables III–V. The examples of absorbance change with metal cation concentrations and non-linear fits to Equation (1) for compound **3** are presented in Figure 5. This picture clearly demonstrates the binding selectivity for cations of similar size $Ba^{2+} \gg K^+ > Ag^+$ for this compound (Table III). Our results confirm the previously observed [13] high affinity of compound **3** to Li^+ and Na^+ in acetonitrile (Table IV). This places these smaller cations into second place after Ba^{2+} in the selectivity order.

The stability constants with all the studied cations are lower for complexes of compound **4** in acetonitrile (Table III). Two plausible explanations can be offered. First, the electron density on the oxygens of the additional benzene residue is lower as compared with the $O—CH_2CH_2—O$ residue due to the mesomeric effect. Secondly, the catechol residue is planar and conformationally rigid as opposed to the dioxyethylene residue. The more flexible macrocycle can adopt a preferential conformation suitable for stronger binding. This results in a different selectivity order for compound **4** of $Ba^{2+} \cong K^+ > Ag^+$, which is in general agreement with the selectivity order observed previously for 18-crown-6 derivatives (see Table I and discussion in Introduction). The stronger binding of compound **3** with Ba^{2+} is possibly due to the higher charge density of this cation. However, it remains unclear why this factor does not influence an interaction with compound **4**. We believe this can be attributed to the factors discussed above responsible for the generally weaker binding of compound **4**. Similarly to compound **3** strong binding with smaller Li^+ and Na^+ cations is observed (Table V), this locates Li^+ and Na^+ into first and second places in the selectivity order, respectively.
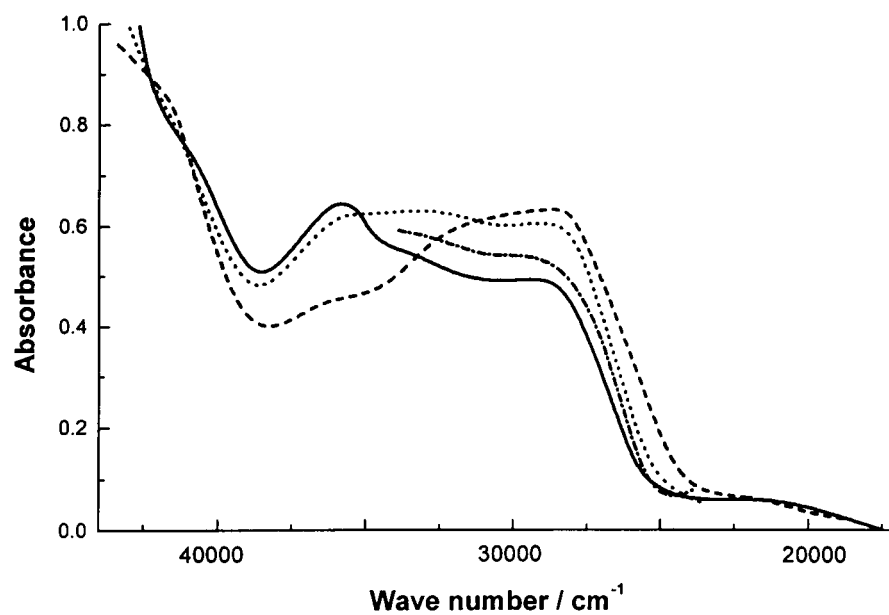
Figure 3. Absorption spectra of compound **4** (5.7×10^{-5} M) in acetonitrile (solid line); containing $KClO_4$ (dotted line) at a concentration of 8.4×10^{-3} M, $Ba(ClO_4)_2$ (dashed line) at a concentration of 8.7×10^{-3} M, and $AgNO_3$ (dot-dashed line) at a concentration of 0.01 M.
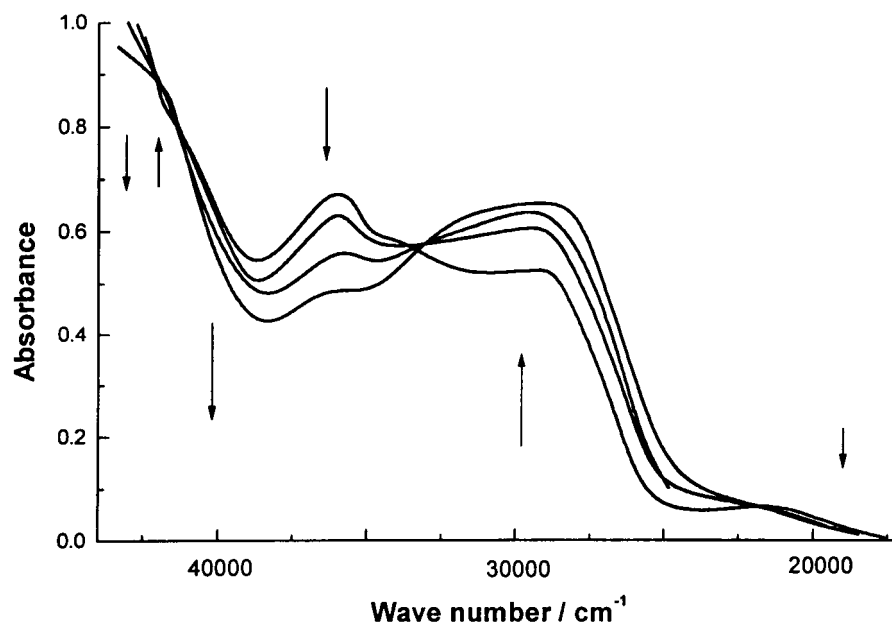

Figure 4. Absorption spectra of compound **4** (5.7×10^{-5} M) in acetonitrile containing $Ba(ClO_4)_2$ at concentrations of 0, 2.8×10^{-3}, 4.8×10^{-3} and 8.7×10^{-3} M.
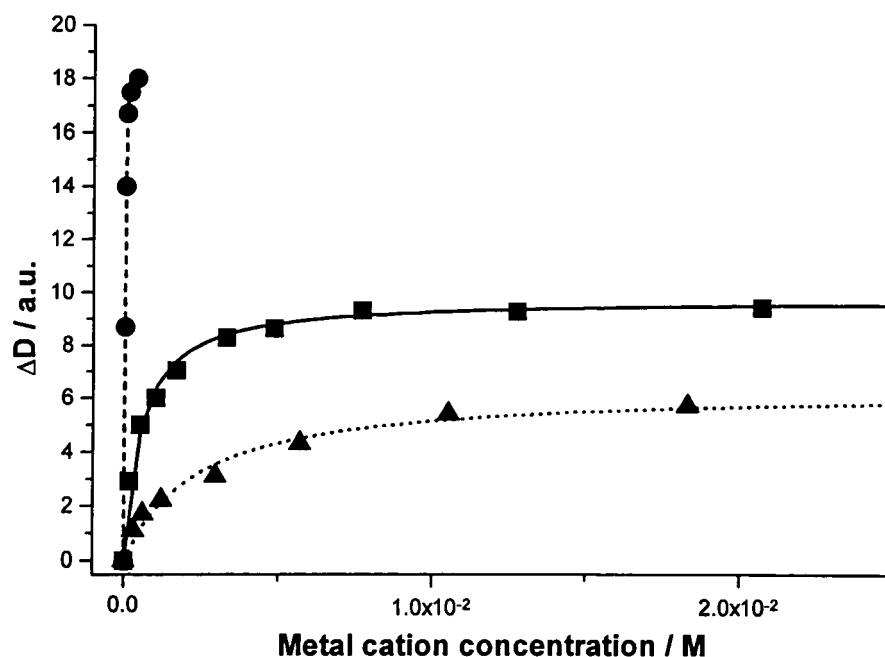
Figure 5. Non-linear fit of the experimental absorbance data in acetonitrile *versus* metal cation concentration to Equation (1) for compound **3**: squares (solid line) – KPF_6 at 315 nm (experimental data from [10]), circles (dashed line) – $Ba(ClO_4)_2$ at 330 nm, triangles (dotted line) – $AgNO_3$ at 435 nm.

Different results were obtained for 16-membered macrocycles in MeOH. Clear isosbestic points were observed in the presence of K^+. For compound **3** isosbestic points were at ca. 23500 and 32800 cm^{-1} (425 and 305 nm) while for compound **4** at 19600 and 34500 cm^{-1} (510 and 290 nm, Figure 6). Upon complexation with Ba^{2+} only compound **3** exhibits isosbestic points at 21000, 31250 and 39200 cm^{-1} (475, 320 and 255 nm, data not shown). The 16-membered azocrowns exhibit isosbestic points in the presence of Ag^+ (at ca. 380, 350, 315 nm and 365, 350, 305 nm for **3** and **4**, respectively). However, these isosbestic points changed their position upon addition of an increasing amount of Ag^+ probably due to the intrinsic absorbance of the silver salt. Both macrocycles **3** and **4** did not show isosbestic points in the presence of Pb^{2+} possibly due to the intrinsic absorbance of Pb^{2+} salt at lower wavelengths. Even though some spectral changes were observed in the presence of $LiClO_4$ we were not able to fit the data to Equation (1). At the same time Na^+ binds stronger than Ba^{2+} to both compounds **3** and **4** (Tables IV and V). The calculated stability constants are collated in Tables III–V. The examples of absorbance change with metal cation concentrations and non-linear fits to Equation (1) for compound **4** are presented in Figure 7. The binding selectivity is $Ag^+ > K^+ > Pb^{2+} > Ba^{2+}$ for compound **3** and probably $Ag^+ > Pb^{2+} > K^+ > Ba^{2+}$ for compound **4** (Table III). It is remarkable that both compounds show similar binding
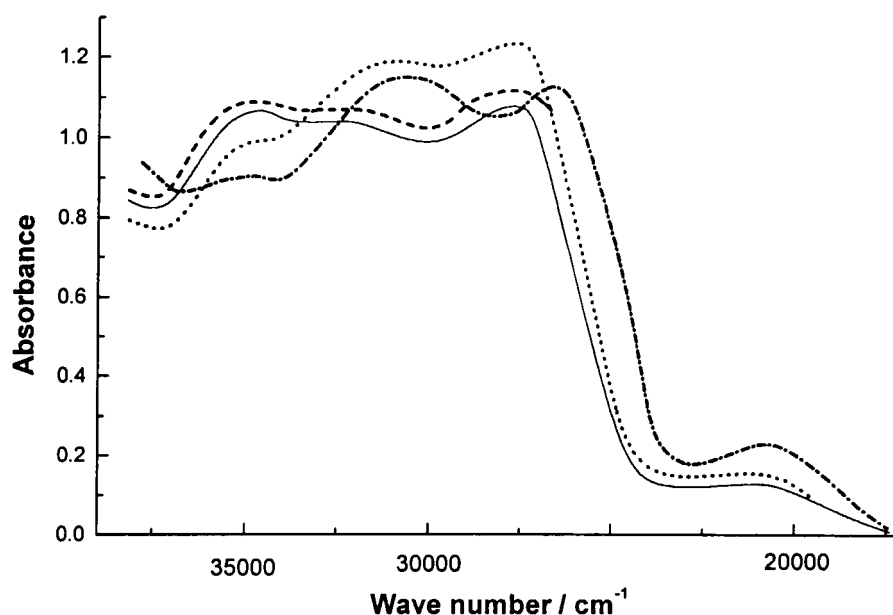
Figure 6. Absorption spectra of compound **4** (8.4×10^{-5} M) in MeOH (solid line); containing KSCN (dotted line) at a concentration of 0.03 M, $Ba(ClO_4)_2$ (dashed line) at a concentration of 0.06 M, and $AgNO_3$ (dot-dashed line) at concentration of 0.015 M.

with Ag^+ while binding to other cations differs. The observed order of selectivity is in strong disagreement with that observed previously for 18-crown-6 derivatives (see Table I and discussion in Introduction), where the selectivity order was Ba^{2+} > K^+ > Ag^+. We cannot offer any explanation for the unexpectedly low binding with Ba^{2+} in MeOH. Similarly to 13-membered macrocycles the association with hard cations corresponds to an inverse relationship between the stability of the complexes and the Gutmann donicity of the solvents. With the soft silver cation the opposite effect of considerably increased binding in MeOH (Table III) can be attributed to competition for silver association between acetonitrile and the crown.

4. Conclusions

The 13-membered azo- and azoxycrowns **1** and **2** in MeOH are weakly and non-selectively bound to hard cations of similar ionic diameter Na^+ and Ca^{2+}. At the same time binding to the soft cation Ag^+, which is larger than the size of the macrocycle cavity, is considerably stronger. In contrast to acetonitrile solutions small Li^+ is very weakly bound to compound **1**.

The 16-membered azocrowns **3** and **4** also discriminate silver in MeOH and exhibit similar values of the stability constants with this cation in MeOH. The unexpectedly low binding with the hard divalent cation of similar size Ba^{2+} was observed for these compounds in MeOH. Also Li^+ is not bound to compound **1**.
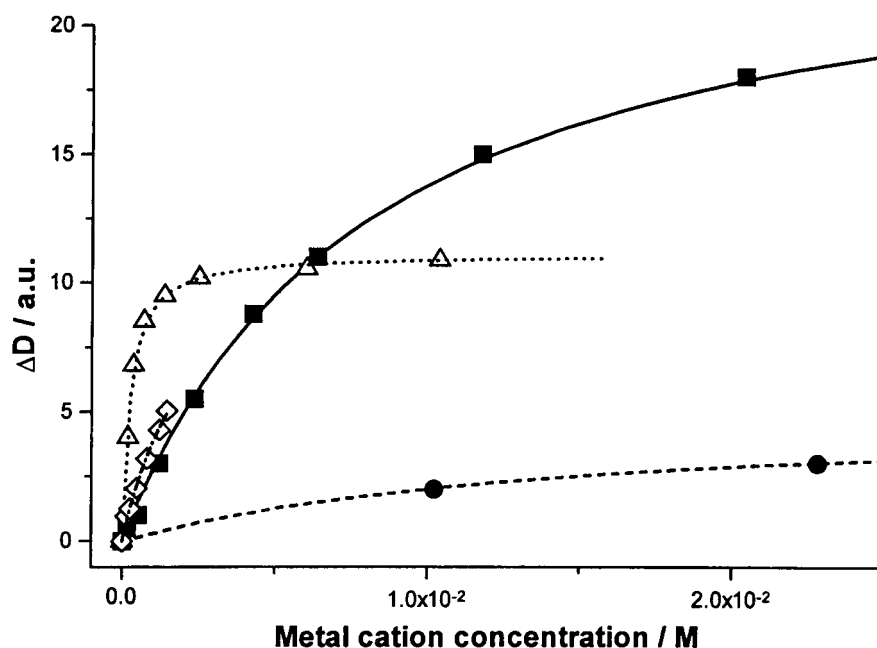
Figure 7. Non-linear fit of the experimental absorbance data in MeOH *versus* metal cation concentration to Equation (1) for compound **4**: squares (solid line) – KSCN at 360 nm, circles (dashed line) – $Ba(ClO_4)_2$ at 375 nm, open triangles (dotted line) – $AgNO_3$ at 475 nm, open diamonds – $PbAc_2 \cdot 3H_2O$ at 420 nm.

This results in a selectivity order of $Ag^+ > K^+ > Pb^{2+} > Na^+ > Ba^{2+} \gg Li^+$ for compound **3** and $Ag^+ > Pb^{2+} > K^+ > Na^+ > Ba^{2+} \gg Li^+$ for compound **4**.

A reverse order of selectivity was observed for 16-membered crowns in acetonitrile with binding constant for association of **3** with Ba^{2+} considerably higher than for other cations. The unusually strong affinity of these compounds to Li^+ and Na^+ in acetonitrile is confirmed by our data.

Acknowledgements

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