Influence of metal cations on spectral characteristics of crown ether vinylogs with different terminal polar groups

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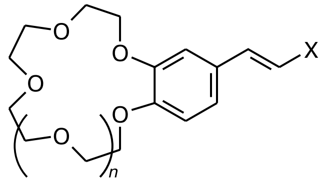
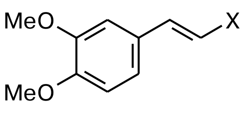
Complexation of crown ether vinylogs containing different terminal polar groups with alkali and alkali-earth metal ions in solutions was studied by spectrophotometry. The hypsochromic shift of absorption band maxima in the UV-Vis absorption spectra indicates that the ligands containing the monobenzocrown ether fragments interact with metal ions. The scheme of complexation was proposed, and the stability constants of the complexes were determined. The efficiency of complexation depends on the metal cation size and the structure of the ionophoric fragment.

Key words: crown ethers, vinylogs, complexation, UV-Vis absorption spectra.

Crown ether derivatives containing different chromophoric functional groups are used as selective chromo- and fluoroionophores[1—8] (including photocontrolled ionophores[7,8]) for the determination of different metal cations.[1—4] Among them are recently proposed[9—12] crown-containing unsaturated compounds, which can be used as analytical reagents and promising precursors for syntheses of crown-containing iono- and fluorophores or photochromes in the form of either individual molecules or supramolecular ensembles.



1—6



7—9

X = CO_2Et (**1, 4, 7**), CN (**2, 5, 8**), CHO (**3, 6, 9**)
n = 1 (**1—3**), 2 (**4—6**)

We studied the interaction of crown ether vinylogs containing different terminal polar groups (**1—6**) with alkali, alkali-earth, and rare-earth metal ions in acetonitrile solutions by spectrophotometry.

Experimental

We studied new crown-containing unsaturated compounds **1—6** with terminal polar groups, *viz.*, ester, cyano, and formyl groups, and model compounds **7—9** containing the 3,4-dimethoxyphenyl fragment instead of the crown ether ionophore. This fragment is also an electron donor but cannot form stable complexes with metal ions.

Compounds **1**, **2**, **4**, and **5** were synthesized by the Horner—Emmons olefination[13] of the corresponding 4´-formylbenzocrown ethers using the phosphonate synthons containing the ester or cyano group. Substituted cinnamic aldehydes **3** and **6** were synthesized by the reduction of nitriles **2** and **5** in the presence of $AlBu^i{}_2H$ [6,9—12] or by the reduction of the corresponding cinnamic acid chlorides in the presence of $LiAl(OBu^t)_3H$.[14] Model compounds **7—9** were synthesized similarly.[6,9—12]

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Spectrophotometric studies were carried out in solutions of acetonitrile (Aldrich (USA), water content 0.005%). Lithium, magnesium, calcium, barium, and lanthanum perchlorates (reagent grade) were used for complexation. The ratio of concentrations of metal salts and ligands (c_M/c_L) was varied from 0.1 to 10^3 at $c_L = 2 \cdot 10^{-4}$ mol L^{-1}. UV-Vis absorption spectra of the solutions under study were recorded on a Shimadzu UV-3100 spectrophotometer at ~20 °C

Results and Discussion

Spectral properties of ligands 1—9. The UV-Vis absorption spectra of solutions of all compounds studied contain two groups of bands. The first group of bands at 290—340 nm is caused by the absorption of the whole chromophore, and the bands in the short-wave spectral region (<240 nm) characterize the isolated benzocrown ether or 3,4-dimethoxyphenyl fragments (Fig. 1).

The UV-Vis absorption spectra of crown ether vinylogs **1** and **4**, **2** and **5**, and **3** and **6** with the same types of terminal groups but different sizes of the macrocycle virtually coincide with the spectra of model compounds **7—9** (Fig. 1, Table 1) but differ from them by the higher molar absorption coefficients, which increase with an increase in the strain of the macroheterocycle. The position of λ_{max} of the long-wave absorption band of the crown ether vinylogs depends on the nature of the terminal group and correlates with its electron-withdrawing properties. For example, the absorption band maxima in the spectra of cinnamic aldehydes are bathochromically shifted by ~10 nm compared to the spectra of the compounds containing the terminal CN and CO_2Et groups, *i.e.*, the more electron-withdrawing formyl group results in a greater decrease in the electron density on the oxygen atom in the *para*-position.

Spectral properties of the complexes with ligands 1—6 with metal ions. The addition of lithium, lanthanum, and alkali-earth metal perchlorates to solutions of crown ethers **1—6** induces, unlike model compounds **7—9**, considerable changes in their UV-Vis spectra. The UV-Vis spectra of compound **2** in the presence of the lithium, magnesium, calcium, and barium cations are presented in Fig. 2. The interaction of this ligand with metal ions results in the intensity redistribution and hypsochromic shift of the absorption band maxima in the long-wave spectral region due to the coordination of the crown ether fragment of the molecule with the metal ion (Scheme 1). The shift of the absorption band maximum $\Delta\lambda_{max}$ due to complexation depends on both the macrocycle size and the size and charge of the metal cation. For 15-crown-5 ethers **2** and **3**, $\Delta\lambda_{max}$ decreases in the series $Mg^{2+} > Ba^{2+} > Li^+$ (see Fig. 2 and Table 1) according to the decrease in the positive charge density on the cation.

Table 1. Spectral characteristics of solutions of crown ether vinylogs **1—6** and model compounds **7—9** in MeCN ($c_L = 2 \cdot 10^{-4}$ mol L^{-1}) in the absence and presence of metal perchlorates ($c_M/c_L = 100$)

Ligand	λ_{max}/nm ($\Delta\lambda_{max} = \lambda_{ML} - \lambda_L$)				
	Free ligand	Li^+	Mg^{2+}	Ba^{2+}	La^{3+}
1	321	—	298 (−23)	308 (−13)	307 (−14)
2	321	312 (−9)	298 (−23)	308 (−13)	317 (−4)
3	330	320 (−10)	304 (−26)	305 (−25)	315 (−15)
4	322	—	313 (−9)	312 (−10)	308 (−14)
5	323	—	320 (−3)	310 (−13)	310 (−13)
6	332	—	323 (−9)	319 (−13)	310 (−22)
7	321	—	321	321	321
8	321	—	321	321	321
9	332	—	332	332	332

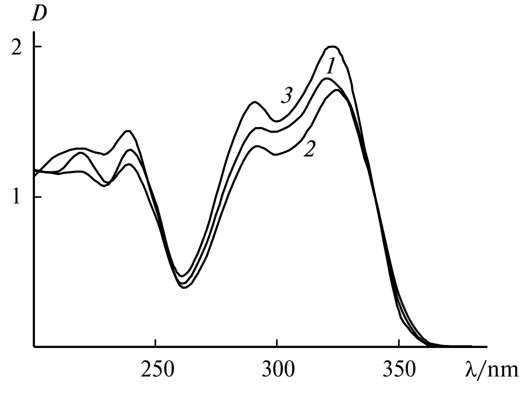
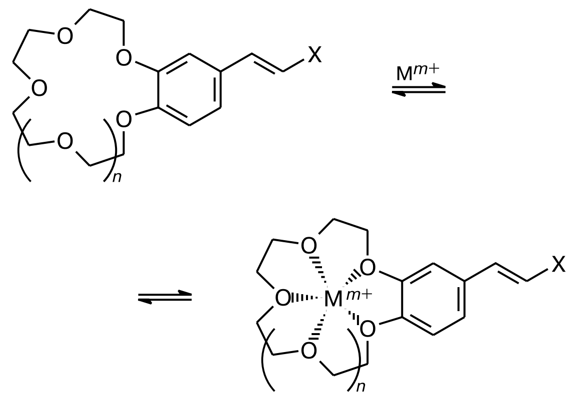


Fig. 1. Absorption spectra of solutions of nitriles **2** (*1*), **5** (*2*), and **8** (*3*) ($c_L = 2 \cdot 10^{-4}$ mol L^{-1}) in MeCN.

Scheme 1



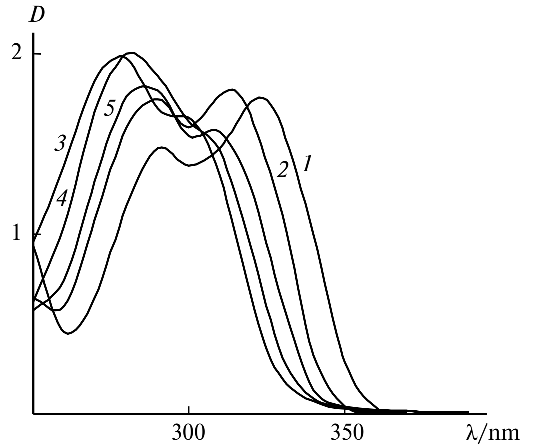


Fig. 2. Absorption spectra of solutions of compound **2** in MeCN in the absence (*1*) and presence of lithium (*2*), magnesium (*3*), calcium (*4*), and barium (*5*) perchlorates ($c_L = 2 \cdot 10^{-4}$ mol L^{-1}, $c_M/c_L = 10^3$).

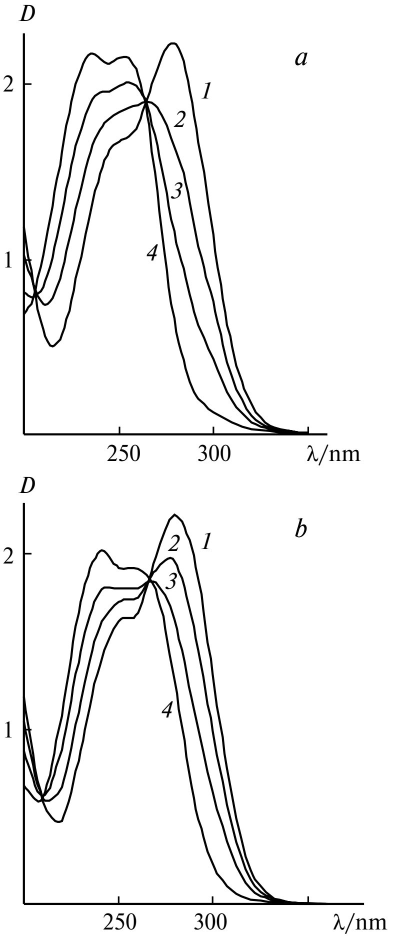


Fig. 3. Absorption spectra of solutions of ligand **3** in MeCN in the presence of magnesium (*a*) and barium (*b*) perchlorates ($c_L = 2 \cdot 10^{-4}$ mol L^{-1}); *a*: $c_M/c_L = 0$ (*1*), 1 (*2*), 2 (*3*), and 10 (*4*); *b*: $c_M/c_L = 0$ (*1*), 0.1 (*2*), 0.2 (*3*), and 1 (*4*).

The metal ions exert qualitatively the same effect on the electronic characteristics of the complexes with the benzo-15-crown-5 and benzo-18-crown-6 ether fragments, resulting in the hypsochromic shift of their absorption bands (see Table 1). The UV-Vis spectra of aldehydes **3** and **6** in the presence of magnesium and barium perchlorates are shown in Figs. 3 and 4. The values of the spectral shifts in the UV-Vis spectra of compound **3** caused by the introduction of the magnesium and barium salts into solutions are close (see Fig. 3). In the case of the barium cations, the highest spectral response is detected at lower salt concentrations. This can be related to the formation of the $L_2 \cdot Ba^{2+}$ sandwich complexes characteristic of 15-crown-5 ethers.[15]

The introduction of magnesium perchlorate results in much weaker changes in the UV-Vis spectrum of the complex of 18-crown-6-containing ligand **6** (see Fig. 4, *a*),

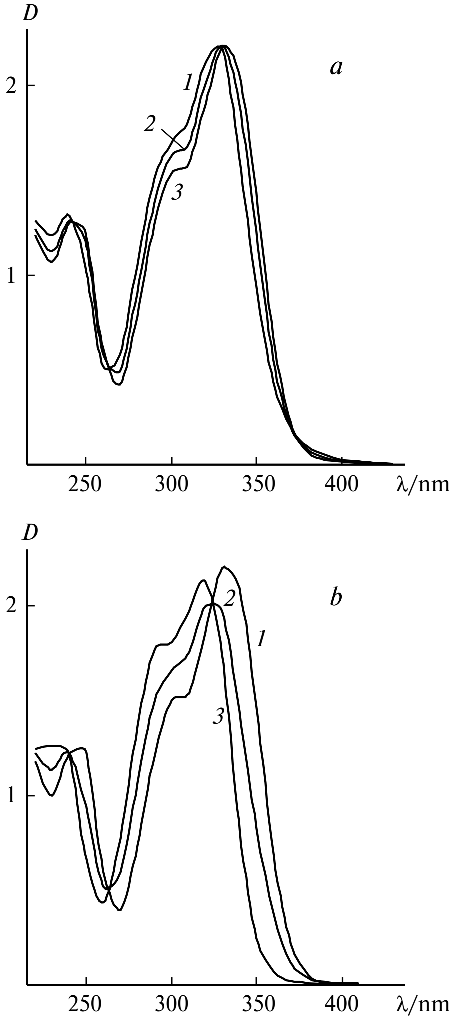


Fig. 4. Absorption spectra of solutions of ligand **6** in MeCN in the presence of magnesium (*a*) and barium (*b*) perchlorates ($c_L = 2 \cdot 10^{-4}$ mol L^{-1}); *a*: $c_M/c_L = 0$ (*1*), 50 (*2*), and 500 (*3*); *b*: $c_M/c_L = 0$ (*1*), 0.5 (*2*), and 2 (*3*).

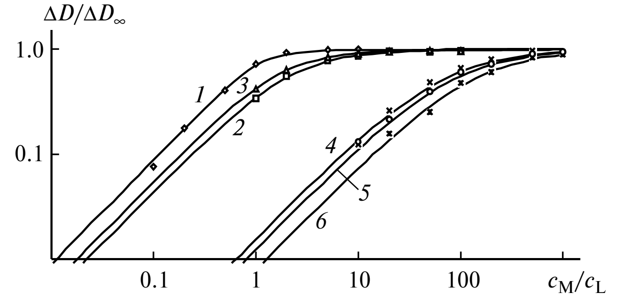


Fig. 5. Relative changes in the intensity of long-wave absorption bands of solutions of ligands **1** (*1*), **2** (*2*), **3** (*3*), **4** (*4*), **5** (*5*), and **6** (*6*) in MeCN with addition of magnesium perchlorate. The calculated relations corresponding to the 1(L) : 1(M) complexation model are shown by solid lines. Logarithmic ordinate scale.

unlike the complex of aldehyde **3** with the 15-crown-5 ether fragment. The size of the 18-crown-6 ether cavity significantly exceeds the size of the Mg^{2+} ion and, most likely, provides no efficient complexation. On the contrary, the addition of the barium cations to a solution of aldehyde **6** results in considerable spectral changes (see Fig. 4, *b*) caused by the better correspondence of the size of the crown ether cavity to the Ba^{2+} ion radius.

The hypsochromic shift of the absorption bands observed upon complexation is caused by the influence of the metal cation on the π-electron density distribution in the conjugation chain of ionophore molecules **1—6**.

Stability constants. The relations of the absorption spectra of solutions of ligands **1—6** to the concentration of the metal ions make it possible to determine the stoichiometry of the complexes formed and calculate their stability constants.

The good correspondence of the experimental curves of titration of crown ethers **1—6** with magnesium perchlorate (Fig. 5) to the complexation model

$$L + M \xrightleftharpoons{K} LM,\ K = [LM]/([L][M]),$$

indicates that the stoichiometry of the complexes formed is 1(L) : 1(M). The stability of the complexes of benzo-15-crown-5 ether vinylogs **1—3** with the magnesium cations is much higher than the stability of the complexes of ligands **4—6** containing the monobenzo-18-crown-6 ether fragments. This is demonstrated by comparison of the stability constants of the complexes of ligands **1—6** with the magnesium cations in acetonitrile presented below.

Ligand	K/mol^{-1} L	Ligand	K/mol^{-1} L
1	4.6	**4**	1.9
2	3.6	**5**	1.6
3	3.8	**6**	1.8

Therefore, the crown ether fragment of benzo-15-crown-5 ethers fits to the magnesium ion size to a greater extent than that of benzo-18-crown-6 ethers. Analysis of the spectra of compounds **7—9** containing no crown ether fragment indicates that complexation is absent up to $c_M/c_L = 1000$.

Thus, the spectral characteristics of the benzocrown ether vinylogs and their complexes with the metal ions depend on the presence of the crown ether fragment in the molecule and its size. The complexes are formed only for the crown-containing compounds and is characterized by considerable spectral changes. The stability of the complexes depends on the charge of the metal ion and correspondence of the sizes of the crown ether fragment and metal ion.

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