Crown ether styryl dyes

17.* Influence of the length of the N-substituent in betaines of chromogenic 15-crown-5-ethers on complexation with cations of alkaline-earth metals

O. B. Stanislavskii,[a] E. N. Ushakov,[a*] S. P. Gromov,[b*] O. A. Fedorova,[b] and M. V. Alfimov[b]

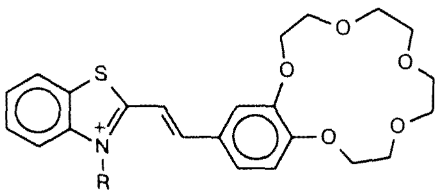
[a]Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588
[b]N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Photochemistry Department,
7a ul. Novatorov, 117421 Moscow, Russian Federation.
Fax: +7 (095) 938 2156

The stoichiometry of complexation of crown ether styryl dyes with Mg^{2+}, Ca^{2+}, and Ba^{2+} ions and the dependence of the stability constants of these complexes on the length of the N-sulfoalkyl substituent were investigated. Introduction of a terminal sulfo group into the N-ethyl substituent had but a small effect on the stability constant for the complexes with 1 : 1 stoichiometry. Increase in the length of the N-substituent by one or two methylene groups resulted in a jumpwise rise of this constant. The effect observed was attributed to the formation of the intramolecular ion pair. The dimerization constant for Mg^{2+} complexes increased dramatically when passing from the sulfopropyl N-substituent to the sulfobutyl one. The increase in the constant results from the decrease in steric strains in the dimeric complex.

Key words: crown ether styryl dyes, Mg^{2+}, Ca^{2+}, and Ba^{2+} complexes, stability constants, dimerization constant.

Limiting the conformational freedom of molecules by means of organization into supramolecular structures is an effective way of controlling the rate and selectivity of chemical reactions.[2] It is known that complexation may change the conformation of molecules, resulting in a significant reorganization of their structure. From this point of view, crown ether styryl dyes (CSD) containing N-sulfoalkyl group are rather promising compounds for the control of photochemical processes.

The CSD **1—4** previously synthesized by us[3,4] belong to the class of chromoionophores.[5]



1—4

R = C_2H_5, the counterion is ClO_4^- (**1**);
R = $(CH_2)_nSO_3^-$, n = 2 (**2**), 3 (**3**), 4 (**4**).

The crown ether cycle of the CSD **1—4** is able to bind cations of alkaline-earth metals in acetonitrile.[3,4] Complexation causes a significant hypsocromic shift of the absorption spectra of the CSD. The value of the shift does not depend on the presence of the sulfo group in the N-substituent and remains practically unchanged within the series **1—4**.

At the same time, preliminary studies[4] showed that the apparent stability constant of the complexes increases within the series **2—4** and a jumpwise increase is observed when passing from complex **2** to **3**. This effect cannot be explained by the formation of a direct intramolecular coordination bond between the sulfo group and a metal cation located in the cavity of the crown ether moiety. Simple models of *trans*-isomers of CSD **2—4** show that even the length of the sulfobutyl group is insufficient for the formation of such a bond.

The presence of the N-sulfoalkyl group in the CSD molecule effects significantly not only the stability of complexes but also the complexation mechanism. It was shown[6,7] that the *trans*-isomers **3** and **4** are able to form dimeric complexes of 2 : 2 stoichiometry with cations of alkaline-earth metals even in a dilute solution due to intermolecular coordination. At the same time, an attempt to observe the formation of such structures for CSD **2** failed.

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Pre-organization of the molecules **3** and **4** into dimeric structures during complexation changes the course of photoprocesses with the participation of these molecules.[7,8] Primarily, such pre-organization allows one to carry out the reaction of photochemical [2+2] cycloaddition with the regio- and stereoselectivity unique for solutions.[8] This photoreaction affords the sole stereoisomer of the cyclobutane derivative, a supramolecular receptor which contains four ionophore groups (two crown ether cycles and two sulfoalkyl groups). For CSD **1—4**, the photocycloaddition does not proceed in the absence of metal cations. In addition, this reaction also does not proceed for complexes of CSD **1** and **2**.

For further development of methods for photochemical synthesis of new supramolecular receptors by means of pre-organization of reactants by complexation, several problems should be solved. One of them is the influence of the nature and length of the *N*-substituent in CSD with a terminal anionic group on the complexation mechanism and stability of complexes. This problem is also interesting by itself. It is studied in detail for crown ethers with anionic groups capable of intramolecular coordination with a metal cation.[9] For crown ethers with remote anionic groups, among which are the *trans*-isomers **2—4**, there are practically no experimental data on the influence of the nature and geometry of such groups on complexation with metal cations.

This work is devoted to a detailed study of complexation of CSD **1—4** with Mg^{2+}, Ca^{2+}, and Ba^{2+} ions. This study allowed us to follow the dependence of the stability constants for complexes of different stoichiometry and structure on the length of the sulfoalkyl substituent, involving the dimer complexes that are of greatest interest in photochemistry. CSD **1**, which does not contain sulfo group in the *N*-substituent, was used in this study as a convenient starting point.

Experimental

MeCN was distilled twice over P_2O_5, then boiled over CaH_2 for 1 h and distilled. Dry solvent was kept in a hermetically sealed flask. Magnesium, calcium, and barium perchlorates were dried *in vacuo* at 230 °C. To prevent adsorption of CSD, the surface of quartz cells and all laboratory glass was modified with a solution of dimethyldichlorosilane in toluene.[10] Preparation of CSD solutions and all the experiments were carried out in a dark room in red light.

Complexation was studied by means of spectrophotometric titration (previously we carried out the detailed experimental[3,4] and theoretical[11] investigation of spectral characteristics of the CSD and their complexes). In direct experiments, to a solution of a ligand (CSD or benzo-15-crown-5 (B15C5)) with a known concentration C_L was added a solution containing the same concentration of a ligand and a known concentration of metal perchlorate. In the experiments with a competitive ligand, to a solution of CSD and metal perchlorate with C_L and C_M concentrations, respectively, was added a solution containing the same concentrations of CSD and metal salt and a known concentration of a competitor.

The degree of complexation was calculated by the formula

$$\alpha = (D_0 - D)/(D_0 - D_c),$$

where D_0, D, and D_c are the optical density of the starting solution, the current optical density, and the optical density after complete complexation, respectively. Measurements were carried out at 460 and 470 nm, where $D_c \ll D_0$. This allows one to ignore the differences in molar absorption coefficients of complexes with different stoichiometry and structure. In the case of complexes of B15C5 with Mg^{2+} and Ca^{2+} ions, the degree of complexation α was determined from the optical density of the solution at 280 nm.

Experimental dependences were approximated by theoretical ones by a nonlinear least squares method using the Nelder-Meed simplex-algorithm included in the MATLAB application software package.

For the experimental estimation of dimerization constants of complexes, solutions were irradiated with a DRSh-250 Hg lamp for 2 s at 436 nm; the light intensity was $5 \cdot 10^{15}$ cm^{-2} s^{-1}. Optical densities of solutions were measured at 400 nm.

Results and Discussion

Interaction of CSD 1 and 2 with Mg^{2+}, Ca^{2+} and Ba^{2+} ions

The simplest scheme of complexation is

$$L^+ + M^{2+} \xrightleftharpoons{K_1} (LM)^{3+}\,, \qquad (I)$$

where L is the dye molecule, M is the metal cation, and K_1 is the stability constant of a complex. The following equation corresponds to this scheme

$$\frac{C_M}{\alpha C_L} = 1 + \frac{1}{K_1 C_L}\cdot\frac{1}{1-\alpha}. \qquad (1)$$

The plot in the coordinates of the equation (1), *i.e.*, $C_M/(\alpha C_L)$ *vs* $1/(1 - \alpha)$, is a straight line with slope $(K_1 C_L)^{-1}$ and the intercept on the ordinate axis equal to unity. From here on, we present all the results on titration with a metal salt solution precisely in these coordinates since every expansion of the Scheme 1 results in a characteristic deviation of the corresponding dependence from the straight line.

The points in Fig. 1 are the experimental dependences of α on C_M in coordinates of the equation (1) for the interaction of the dye **1** with Mg^{2+}, Ca^{2+}, and Ba^{2+} ions. The nonlinear character of these dependences indicates that the simple Scheme 1 is insufficient for the description of complexation in the given system. Interaction of perchlorate ion with the triple-charged $(LM)^{3+}$ complex is the most probable additional process. Taking into account this interaction, we obtain the following scheme:

$$L^+ + M^{2+} \xrightleftharpoons{K_1} (LM)^{3+}$$

$$(LM)^{3+} + A^- \xrightleftharpoons{K_i} (LMA)^{2+}\,, \qquad (II)$$

where $A^- = ClO_4^-$.

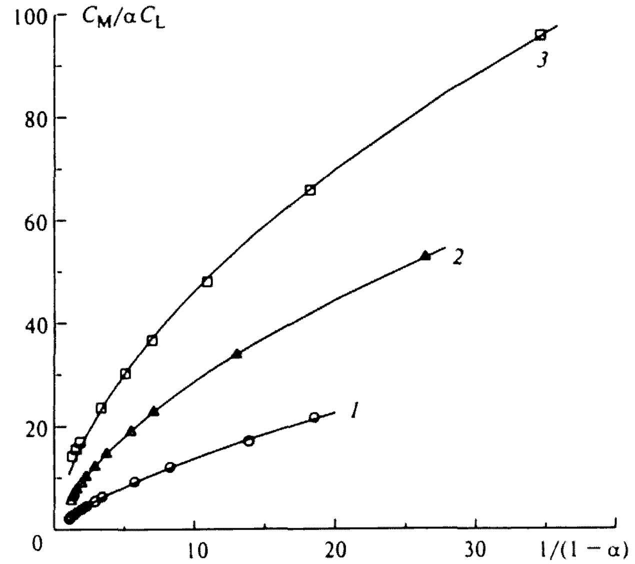

Fig. 1. Plots of the degree of complexation, α, *vs* concentration of salt added, C_M, in coordinates of equation (1) for CSD **1** and Mg^{2+} (*1*), Ca^{2+} (*2*), and Ba^{2+} (*3*). C_L/ mol L^{-1}: $2.1 \cdot 10^{-5}$ (*1*), $2.0 \cdot 10^{-5}$ (*2, 3*).

The solid lines in Fig. 1 are the theoretical dependences, which correspond to the Scheme II, with the constants presented in Table 1. A good approximation of the experimental data with the theoretical curve indicates the validity of the complexation scheme chosen. However, it should be noted that the constants determined from this scheme are averaged values since the increase in α at the experiment leads to the increase in ionic strength of the solution, and the constants of all the processes which are accompanied by a change in mutual arrangement of ions depend on the ionic strength.

To confirm the formation of $(LM)^{3+}\cdots ClO_4^-$ ionic pairs, we carried out the titration in the presence of triethylammonium perchlorate (0.02 mol L^{-1}), *i.e.*, at practically constant concentration of anions. Under these conditions, the experimental dependences of α on C_M in terms of the Scheme II in coordinates of equation (1) should be straight lines with intercept on the ordinate axis equal to unity, which is the case (Fig. 2). The apparent complexation constant determined from the slope is related to the K_1 and K_i constants by the following equation:

$$K_{app} = K_1 \cdot \frac{1 + K_i C_b}{1 + K_i^* C_b}, \qquad (2)$$

where K_i^* is the constant of formation of the $M^{2+}\cdots ClO_4^-$ ionic pair and C_b is the concentration of the buffer salt. The values of K_{app} which correspond to the lines in Fig. 2 are $3.1 \cdot 10^5$ and $3.3 \cdot 10^4$ L mol^{-1} for Mg^{2+} and Ba^{2+} ions, respectively. Substituting these values, as well as K_1 and K_i from Table 1, into equation (2), we calculated K_i^*, equal to 10 and 70 L mol^{-1} for Mg^{2+} and Ba^{2+} ions, respectively. Taking into account the poor accuracy of calculation using equation (2), we see that the first value is in good agreement with the value of 7.2 L mol^{-1} obtained earlier in the work.[12] The increase in K_i^* with increase in the diameter of the

Table 1. Stability constants of the complexes of B15C5 and CSD **1—4** with cations of alkaline-earth metals in acetonitrile at 295 K

Compound	Ion	$C_L \cdot 10^5$/mol L^{-1}	$\log K_1$	$\log K_i$	$\log K_2$	$\log K_d$[a]	Ionic strength, $I \cdot 10^5$/mol L^{-1}
B15C5	Mg^{2+}	1.0	7.2±0.3 (7.3)[b]	—	—	—	0.1—1 (3.0)[b]
	Ca^{2+}	1.0	6.6±0.2	—	≤ 4.0	—	0.3—3
CSD **1**	Mg^{2+}	2.1	4.5±0.1	2.8±0.2	—	—	1.5—90
	Ca^{2+}	2.0	4.0±0.1	2.8±0.2	—	—	5—150
	Ba^{2+}	2.0	3.7±0.1	2.8±0.2	—	—	10—250
CSD **2**	Mg^{2+}	2.2	4.7±0.1	—	—	—	1.5—60
	Ca^{2+}	2.1	4.0±0.1	2.7±0.2	—	—	5—150
	Ba^{2+}	2.0	3.7±0.1	2.9±0.2	—	—	10—250
CSD **3**	Mg^{2+}	0.4	6.7±0.2 (6.65)[b]	—	—	5.5±0.2 ≥ 5.3[c]	0.2—1.5 (3.0)[b]
	Ca^{2+}	1.9	6.0±0.2	—	3.7±0.4	—	1—8
	Ba^{2+}	2.0	5.7±0.2	—	5.0±0.2	—	0.6—8
CSD **4**	Mg^{2+}	0.4	6.6±0.5 (6.7)[b]	—	—	7.0±0.5 ≥ 6.5[b] ≥ 6.0[c]	0.15—1.3 (2.5)[b]
	Ca^{2+}	2.1	6.0±0.2	—	3.7±0.4	—	1—8
	Ba^{2+}	2.0	5.7±0.2	—	5.0±0.2	—	0.6—8

[a] For the conditions of determination of the dimerization constant, see text. [b] Measured by the method of competitive reaction. [c] Estimations obtained based on the concentration dependence of the quantum yield of photocycloaddition.

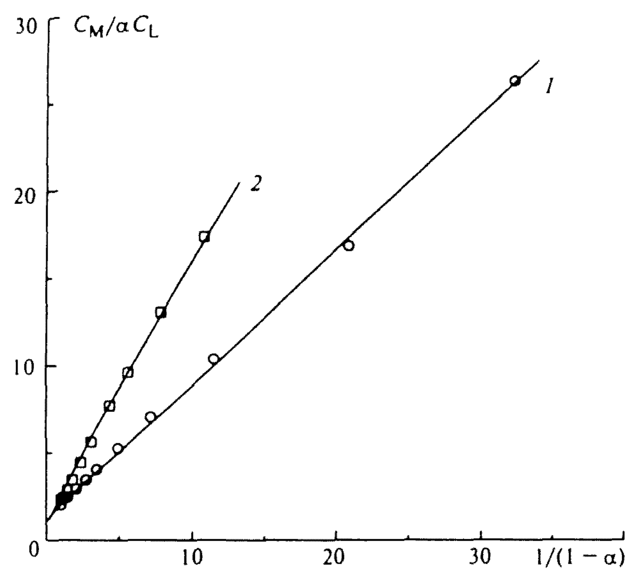

Fig. 2. Plots of the degree of complexation, α, *vs* concentration of salt added, C_M, in coordinates of equation (1) for CSD **1** and Mg^{2+} (*1*; $C_L = 4.1 \cdot 10^{-6}$ mol L^{-1}), Ba^{2+} (*2*; $C_L = 2.0 \cdot 10^{-5}$ mol L^{-1}) in the presence of tetraethylammonium perchlorate (0.02 *M*).

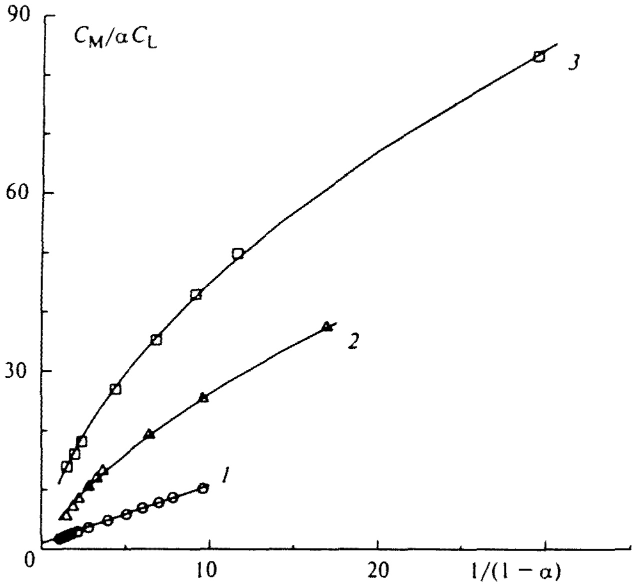

Fig. 3. Plots of the degree of complexation, α, *vs* concentration of salt added, C_M, in coordinates of equation (1) for CSD **2** and Mg^{2+} (*1*), Ca^{2+} (*2*), and Ba^{2+} (*3*). C_L/ mol L^{-1}: $2.2 \cdot 10^{-5}$ (*1*), $2.1 \cdot 10^{-5}$ (*2*), $2.0 \cdot 10^{-5}$ (*3*).

cation is in good agreement with the data for calcium perchlorate in acetonitrile, $K_i^* \approx 25$ L mol^{-1} (see Ref. 13). Though such dependence of K_i^* on the diameter of a cation does not correspond to the simplest variant of electrostatic theory, it is often observed both in polar solvents and in solvents of moderate polarity. For example, it has been shown[14] that K_i^* increases within the $Li^+ < Na^+ < K^+ < Cs^+ < Rb^+$ series for alkali metals perchlorates in 2-methoxyethanol. The effect observed has been attributed to a higher solvation ability of cations with small diameters.

Figure 3 presents the complexation curves for CSD **2** in coordinates of equation (1). It can be seen that they differ little from the corresponding curves for the dye **1** on Fig. 1. The values of the stability constants obtained are given in Table 1. Comparison with the data for the dye **1** shows that the appearance of the negatively charged sulfo group in the *N*-substituent has but little effect on the stability constants of complexes with cations of alkaline-earth metals. Only in the case of the Mg^{2+} ion is the K_1 value a little more than that obtained for CSD **1**. The complexation curve in coordinates of equation (1) is close to a straight line, and therefore we failed to determine K_i.

It is known[15] that formation of sandwich complexes with 2 : 1 stoichiometry is typical of cations with large diameter, such as Ba^{2+} and B15C5 derivatives. However, calculations show that in the experiments described above, which were carried out at low concentrations of dyes, one may completely ignore the formation of such complexes provided that the K_2 constant which corresponds to the process

$$LM + L \xrightleftharpoons{K_2} LML\ ,$$

does not exceed K_1. In addition, model calculations carried out for the hypothetical case where K_2 is significantly larger than K_1 result in complexation curves which differ substantially from the experimental ones given on Fig. 1 and 3. All confirm the validity of the Scheme II for the calculation of K_1 for the complexes of CSD **1** and **2** with Ba^{2+}.

Interaction of CSD 3 and 4 with Mg^{2+} ion

In the previous work[3] we have shown that a subsequent increase in the length of the *N*-sulfoalkyl substituent in CSD by one methylene fragment leads to an increase in the apparent stability constant of complexes with cations of alkaline-earth metals, and the jumpwise increase of the constant is observed when passing from CSD **2** to CSD **3**.

The points on Fig. 4 are the experimental dependences of α on C_M in coordinates of equation (1) for the complexes of CSD **3** and **4** with Mg^{2+}. As can be seen, the points may be well approximated by straight lines at least at $\alpha > 0.5$. However, noticeable deviations from linearity are observed when α is low. The apparent complexation constants K_{app} determined from the slope of straight line portions of the curves are $1.2 \cdot 10^7$ and

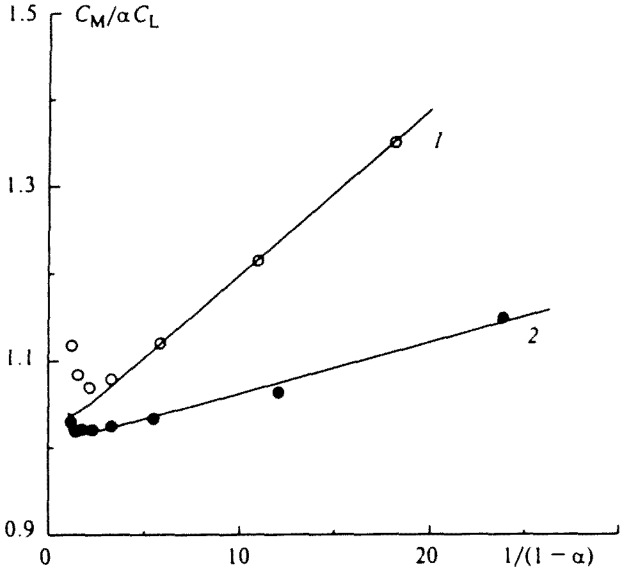

Fig. 4. Plots of the degree of complexation, α, *vs* concentration of salt added, C_M, in coordinates of equation (1) for CSD **3** (*1*) and **4** (*2*) with Mg^{2+} ($C_L = 4.2 \cdot 10^{-6}$ mol L^{-1}).

$4 \cdot 10^7$ L mol^{-1} for CSD **3** and **4**, respectively. The values obtained are more than two orders of magnitude higher than that of K_1 for CSD **1** and **2**.

Earlier[6–8] it has been shown that the complexes of CSD **3** and **4** with Mg^{2+} are able to form pseudo-cyclic dimeric structures with 2 : 2 stoichiometry even in a dilute solution. In general, this effect can make a considerable contribution to the general stability of the complexes (K_{app}). To determine the real reasons of the jumpwise dependence of K_{app} on the length of the *N*-sulfoalkyl substituent, we measured the equilibrium dimerization constants K_d for the complexes of CSD **3** and **4** with Mg^{2+}.

Taking into account the dimerization, the complexation scheme can be presented in the following way:

$$\begin{gathered} L + M^{2+} \xrightleftharpoons{K_1} (LM)^{2+} \\ (LM)^{2+} + (LM)^{2+} \xrightleftharpoons{K_d} (LM)_2^{4+} . \end{gathered} \qquad (III)$$

This scheme does not take into account interaction of the complexes with perchlorate anions. This interaction may be neglected in the case of CSD **3** and **4** since in these experiments, the concentration of the metal salt added was much lower (due to the high value of K_{app}) than in the experiments with CSD **1** and **2**.

To determine K_d, an independent photochemical experiment was conducted. The similarity of the absorption spectra of monomeric and dimeric forms of the complexes hampers determination of K_d by a direct spectrophotometric method. At the same time, for *cis*-isomers of these compounds, significant differences in the spectra of the monomeric complex and the complex incorporated into *cis*-$LMg^{2+} \cdot$ *trans*-LMg^{2+} and (*cis*-$LMg^{2+})_2$ dimeric structures are observed (see Ref. 6).

The complexes of CSD **3** and **4** with Mg^{2+} can be transformed into *cis*-forms by irradiation of the solution with visible light. The efficiency of the *trans-cis* photoisomerization is high and intermolecular coordination bonds are not destroyed.[6,7] The photoreaction affords dimeric complexes, involving *cis*-isomer molecules, which undergo very slow dissociation to form *cis*-LMg^{2+} monomers (in the case of CDS **3**, the dissociation rate constant in dry acetonitrile at room temperature is $1.8 \cdot 10^{-3}$ s^{-1} (see Ref. 6,7)). The dissociation manifests itself in a dark relaxation of the absorption spectrum of the solution. The molecules of *cis*-isomer formed from the *trans*-LMg^{2+} monomer complexes, in their turn, do not contribute to the dark relaxation of spectrum. It follows that the relaxation amplitude should be determined by the degree of dimerization of the *trans*-isomer complexes in a starting solution. This effect allows one to estimate experimentally the dimerization constant of the *trans*-isomer, K_d. If complexation is complete, K_d is related to dimerization degree β by the following equation:

$$K_d = \frac{\beta}{2(1-\beta)^2 C_L}. \qquad (3)$$

Let us propose that the quantum yields of *trans—cis*-photoisomerization are the same for the *trans*-isomer both in monomeric and in dimeric complexes (this proposal cannot be considered to be very rough since the quantum yield of the reaction is high even at a high degree of dimerization).[6–8] The fact that the differences in the absorption spectra of the monomeric and dimeric forms of the *trans*-isomer complexes are insignificant also allows us to assume that the molar extinction coefficients of these forms are equal at the irradiation wavelength. Then, within the approximation that photoisomerization percent is low and the reverse reaction may be neglected, the degree of dimerization of the *trans*-isomer complexes in a starting solution, β, is equal to the degree of aggregation of the *cis*-isomer complexes at the moment when irradiation is turned off (we take into account that the lifetime of the dimeric complexes incorporating *cis*-isomer molecules is much longer than the irradiation time). The degree of dimerization is determined by the formula

$$\frac{D_d - D_m}{D_t - D_m} \cdot \frac{\varepsilon_t - \varepsilon_m}{\varepsilon_d - \varepsilon_m} = \beta, \qquad (4)$$

where D_d, D_m, D_t are the optical densities of the solution at a fixed wavelength at the moment when irradiation is turned off, after complete dark relaxation, and before irradiation, respectively; ε_t, ε_d, ε_m are molar extinction coefficients of the *trans*-isomer complex and aggregated and monomeric forms of the *cis*-isomer complex, respectively.

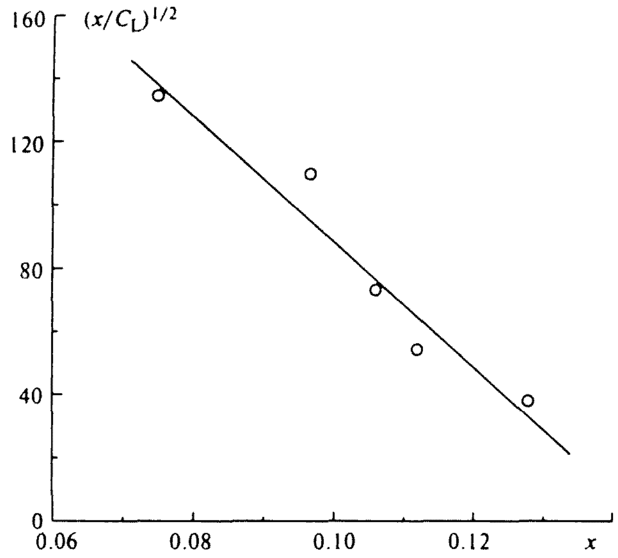

Fig. 5. Plot of the $(D_d - D_m)/(D_t - D_m) = x$ ratio *vs* concentration (C_L) in coordinates of equation (5) for the complexes of CSD **3** with Mg^{2+} at constant excess concentration of $Mg(ClO_4)_2$ ($1 \cdot 10^{-4}$ mol L^{-1}).

Let us denote the first factor on the left side of equation (4) as x and the second factor as A. Substituting equation (4) into equation (3) after algebraic transformations we obtain

$$\sqrt{x / C_L} = \sqrt{2K_d / A} - \sqrt{2K_d A} \cdot x. \qquad (5)$$

The points on Fig. 5 are the experimental dependence of $(D_d - D_m)/(D_t - D_m)$ on C_L in coordinates of equation (5) for *trans*-**3** · Mg^{2+} complex obtained at a constant excess concentration of $Mg(ClO_4)_2$ equal to $1 \cdot 10^{-4}$ mol L^{-1}.

As can be seen from the figure, the experimental dependence is satisfactorily approximated by the theoretical curve. Using the least squares method, we calculated the unknown values of equation (5) and determined the value of K_d which is presented in Table 1.

For the *trans*-**4** · Mg^{2+} complex, the value of K_d appeared to be so high that the relative change of $(D_d - D_m)/(D_t - D_m)$ within the working concentration range was, in fact, not beyond the experimental accuracy. The results obtained allowed us to make only a rough estimation of K_d. This estimation is given in Table 1.

The solid lines in Fig. 4 show the best approximation of the experimental dependences of α *vs* C_M for the complexes of CDS **3** and **4** with Mg^{2+} ion within the framework of the Scheme 3. For the approximation, we used the K_d values obtained by the photochemical method. Table 1 presents the K_1 constants which correspond to the theoretical curves.

As can be seen from Fig. 4, the deviations of the experimental data from the theoretical curve are maintained for CSD **3** at low α even in the case where dimerization is taken into account. It should be noted that these deviations were not constant for different samples of CSD **3**, whereas the slope of the straight line part reproduced better. One may assume on this basis that the reason for the deviations is the presence of an admixture in the starting dye which does not absorb in the visible region but is able to bind a metal cation.

To study the complexation of the dyes **3** and **4** with Mg^{2+} ion, we also used titration of a solution of the complex with a solution of the competitive ligand (see Experimental). The reaction scheme for this system should include three equations (Scheme IV).

$$\mathrm{L} + \mathrm{M}^{2+} \xrightleftharpoons{K_1} (\mathrm{LM})^{2+}$$

$$(\mathrm{LM})^{2+} + (\mathrm{LM})^{2+} \xrightleftharpoons{K_d} (\mathrm{LM})_2^{4+}$$

$$\mathrm{L}_1 + \mathrm{M}^{2+} \xrightleftharpoons{K_c} (\mathrm{L}_1\mathrm{M})^{2+}, \qquad \text{(IV)}$$

where L_1 is the competitive ligand.

B15C5 was used as the competitive ligand in all experiments. The stability constant of its complex with Mg^{2+} ion was measured previously by titration with a metal salt solution. The dependence of α *vs* C_M obtained for this ligand was linear in coordinates of equation (1). The K_c value calculated from the slope of the line is given in Table 1.

The points of Fig. 6 are the experimental dependences of α on the concentration of the competitor added (C_c) for **3** · Mg^{2+} and **4** · Mg^{2+} complexes. The best approximations of the experimental data by theoretical curves corresponding to the Scheme IV (K_d values in the case of CSD **3** and K_d and K_c values in the case of CDS **4** were taken from Table 1 and they were not changed) are shown as solid lines on Fig. 6. The calculated values of the constants are given in Table 1; they are in good correlation with those obtained experimentally by direct titration.

The dashed lines in Fig. 6 are the theoretical curves corresponding to the best approximation of the experimental dependences of α *vs* C_c for **3** · Mg^{2+} and **4** · Mg^{2+} complexes within the framework of a simplified complexation scheme which does not take into account the dimerization process, *i.e.*, involves only the first and third equations of the Scheme IV. In both cases, the approximation was carried out at given $\log K_c = 7.3$. As can be seen from the figure, noticeable deviations of the experimental data from theoretical curves for **3** · Mg^{2+} complex appear only at a high α, whereas in the case of the **4** · Mg^{2+} complex, which has a higher tendency for dimerization, significant deviations are observed at practically all α values. Model calculations show that a satisfactory approximation of the experimental data for **4** · Mg^{2+} complex can be obtained only at $K_d \geq 3 \cdot 10^6$ L mol^{-1}. These facts confirm additionally the estimations of the dimerization constants obtained by the photochemical method.

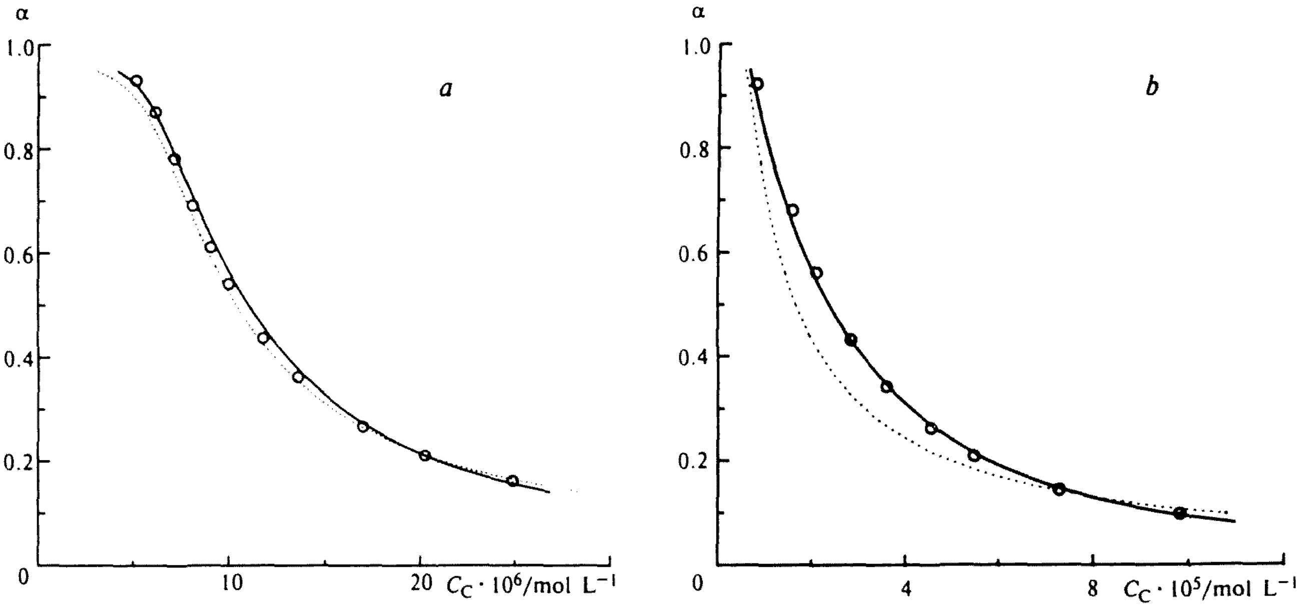

Fig. 6. Plots of the degree of complexation, α, for CSD **3** (*a*) and **4** (*b*) *vs* concentration of the B15C5 competitor (C_C) at constant concentrations of CSD **3** (C_L = 4.2·10^{-6} mol L^{-1}), **4** (C_L = 4.6·10^{-6} mol L^{-1}), and Mg^{2+} ion (C_M = 1.0·10^{-5} mol L^{-1}). The solid and dashed lines are the best approximations of the experimental dependences by Scheme 4 and the simplified scheme which includes only equations (1) and (3) of the Scheme 4, respectively.

Interaction of dyes 3 and 4 with Ca^{2+} and Ba^{2+} ions

For Ca^{2+} and Ba^{2+} ions, it is impossible to measure the dimerization constants by the above-mentioned photochemical procedure since dissociation of dimeric complexes, incorporating *cis*-isomer molecules, proceeds much faster than in the case of Mg^{2+} ion. However, the obtained concentration dependences of the quantum yield for the [2+2] autophotocycloaddition reaction, in which dimeric complexes of the *trans*-isomers of dyes **3** and **4** participate only (the results will be published later), show that the dimerization constants for the complexes with Ca^{2+} and Ba^{2+} are much lower that those for Mg^{2+} complexes. Therefore, dimerization can be ignored when describing complexation for Ca^{2+} and Ba^{2+} ions in dilute solutions. At the same time, one should take into account the formation of sandwich complexes of 2 : 1 stoichiometry, as illustrated by the dependences of α *vs* C_M. For example, in the case of Ba^{2+} ions, consumption of ligand for the complex formation at low α exceeds the concentration of the metal salt added.

Thus, complexation of CSD **3** and **4** with Ca^{2+} and Ba^{2+} ions can be represented by the following reaction scheme:

$$\begin{aligned} &L + M^{2+} \xrightleftharpoons{K_1} (LM)^{2+} \\ &(LM)^{2+} + L \xrightleftharpoons{K_2} (LML)^{2+} . \end{aligned} \qquad (V)$$

The points in Fig. 7 are the experimental dependences of α on C_M in coordinates of equation (1) for the reaction of CSD **3** with Ca^{2+} and Ba^{2+} ions (the corresponding dependences for CDS **4** are similar). The solid lines show the best approximation using the Scheme V. The K_1 and K_2 constants calculated from the best approximation are given in Table 1. Due to the low value of K_2 for the complex with Ca^{2+} ion, the formation of the complex with 2 : 1 stoichiometry cannot be established as reliably as for Ba^{2+} ion. However, there are literature data[13] on the formation of complexes of such type on interaction of B15C5 with $Ca(ClO_4)_2$ in acetonitrile.

Table 1 summarizes the stability constants of complexes of B15C5 and CSD **1—4** with cations of alkaline-earth metals. It can be seen that the stability constants of the complexes of B15C5 with Mg^{2+} and Ca^{2+} are almost three orders of magnitude higher than the corresponding constants for CDS **1**. This fact can be explained by the significant decrease in electron density at the oxygen atoms of the crown ether cycle, directly connected with benzene ring, due to the strong electron-withdrawing effect exerted by the positively charged benzothiazole residue when passing to a dye.

The obtained value of the logarithm of the stability constant for the complex of B15C5 with Ca^{2+} is two units higher than the corresponding value $\log K_1$ = 4.0 given in the literature (with ClO_4^- as a counterion).[13] In our opinion, this value is rather underestimated. Our conclusion is confirmed by a series of facts. The barium cation, which is larger in size, should form less stable

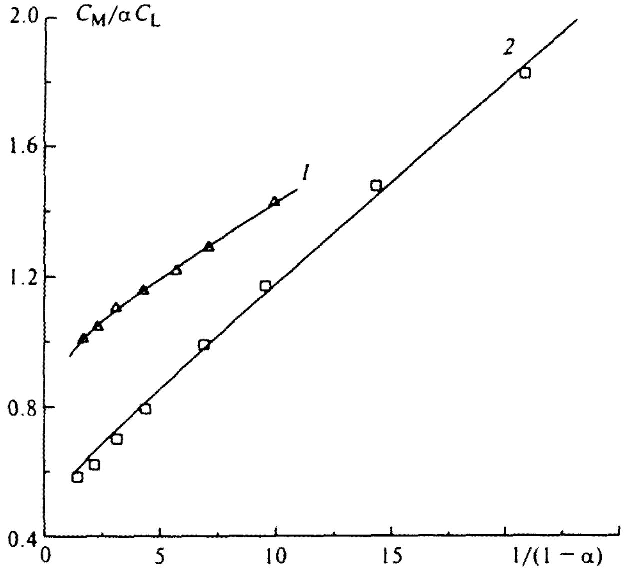

Fig. 7. Plots of the degree of complexation, α, *vs* concentration of salt added, C_M, in coordinates of equation (1) for CSD 3 and Ca^{2+} (*1*; $C_L = 1.9 \cdot 10^{-5}$ mol L^{-1}) and Ba^{2+} (*2*; $C_L = 2.0 \cdot 10^{-5}$ mol L^{-1}).

complexes with B15C5 than the calcium cation. There are literature data for barium, log$K$ > 5,[16] that correspond to our data for calcium. Among the two cations with approximately equal radii, a double-charged one forms a more stable complex in acetonitrile than the single-charged one, log$K$ = 4.17 for K^+ and log$K$ > 5 for Ba^{2+}, B15C5 (see Ref. 16), and log$K$ = 5.46 for K^+ and log$K$ = 8.88 for Ba^{2+}, 18-crown-6 (see Ref. 17). However, the literature[13] values of the constants for Na^+ (log$K$ = 4.0) and Ca^{2+} (log$K$ = 4.2) (SCN^- as a counterion) are practically the same.[18]

Note that the authors[13,18] used IR spectroscopy, which is less sensitive than UV spectroscopy. In addition, we noticed that moistening of the carefully dried acetonitrile in contact with the air or for some other reason may result in a significant decrease in the stability constants measured for complexes of crown ethers with cations of alkaline-earth metals (to a smaller extent in the case of alkaline metals).

As can be seen from Table 1, introduction of the sulfo group into the *N*-substituent (transition from CSD **1** to CSD **2**) has practically no effect on the stability constant of the complexes with 1 : 1 stoichiometry. At the same time, the increase in the length of the *N*-sulfoalkyl substituent by one methylene unit (transition from CSD **2** to CSD **3**) leads to a dramatic increase in stability of the complexes. When the length of the substituent increases by one more methylene unit (transition from CSD **3** to CSD **4**), the stability of 1 : 1 complexes remains practically unchanged.

It can be also seen that the stability constant of the sandwich complexes with Ba^{2+} ion with 2 : 1 stoichiometry also does not change when passing from CSD **3** to CSD **4**. We were not able to determine the K_2 constant in the case of CSD **1** and **2**. However, the above experimental data indicate that K_2, as well as K_1, increases dramatically when passing from CSD **2** to CSD **3**.

As was already mentioned, for CSD **2—4** direct intramolecular interaction between the sulfo group and the metal cation, located in a cavity of the crown ether moiety, is impossible. It is also evident that the jumpwise dependence of stability of the complexes with 1 : 1 and 2 : 1 stoichiometry on the length of the *N*-sulfoalkyl substituent cannot be explained by a simple gradual decrease in the distance between the sulfo group and the cation in the crown ether cavity. To explain the effect observed, one may propose that in the complexes of CDS **3** and **4** the conformation of the *N*-substituent is stabilized, which is stretched towards a cation due to the formation of an intramolecular solvent-separated ion pair, whereas such immobilization of the sulfo group is impossible in the CSD **2** complexes because of the small length of the substituent.

For all CSD, the K_1 value decreases within the Mg^{2+}, Ca^{2+}, and Ba^{2+} series with a simultaneous increase in K_2 (Table 1), indicating that the cavity size of the crown ether cycle corresponds most closely to the diameter of Mg^{2+} ion.

Table 1 also presents the constants of formation of $LM...ClO_4^-$ ion pairs for the complexes of CSD **1** and **2** with Mg^{2+}, Ca^{2+}, and Ba^{2+} cations (K_i). The K_i values are significantly higher than the corresponding constants for $M...ClO_4^-$ ion pairs (K_i^*) (see above).

The ratio of K_i and K_i^* constants has practically not been investigated for crown ethers in polar solvents. There are data for B15C5—$Ca(ClO_4)_2$—acetonitrile system only for which logK_i = 1.8 > logK_i^* = 1.4 (see Ref. 13). Although, as we have mentioned above, the constants presented by the authors[13] may be underestimated, the ratio of K_i and K_i^* corresponds with our data.

In general, many examples are known in coordination chemistry where the equilibrium constant of the process

$$L_1M + L_2 \rightleftharpoons L_1ML_2$$

exceeds the equilibrium constant of

$$L_2 + M \rightleftharpoons L_2M$$

(see Ref. 19) (in our case $L_2 = ClO_4^-$). In the system studied by us, this effect, as well as the increase in K_i^* with increase in the metal cation diameter (see above), may result from the specificity of ion solvation. In this case the effect is manifested most dramatically since the heterocyclic fragment of CSD carries a positive charge which provides an additional stabilization of $LM...ClO_4^-$ pair.

The fact that K_i is much higher than K_i^*, is in good correlation with the high values of dimerization constants for the complexes of CSD **3** and **4** with Mg^{2+} ion (Table 1) since formation of the dimers occurs also due to the interaction between the anionic group (sulfo group) and a cation located in a crown ether cavity. On the contrary, when $K_i < K_i^*$, the interaction of sulfo groups with excess metal cation is the most favorable.

Table 1 also shows that the dimerization constant of the complexes increases significantly (more than an order of magnitude) when passing from CSD **3** to CSD **4** and becomes comparable with K_1 constant. The dimeric complexes have pseudo-cyclic structure which involves two intermolecular coordination bonds.[8] When the size of the cycle increases (when passing from sulfopropyl to sulfobutyl substituent), one should expect a noticeable decrease in steric strains. In this case, the positive influence of this effect on K_d predominates over the negative effect of entropy factor.

It should be noted that the increase in the K_d constant when passing from CSD **3** to CSD **4** results in a noticeable increase in the efficiency of [2+2] autophotocycloaddition reaction where only CSD molecules, organized in dimeric complexes, take part (the data on the efficiency are given in Ref. 8). Such concordance may be explained by the fact that the rate constant of this photoreaction as well as the K_d constant, depend to some extent on the value of steric strains in the dimeric complex.

The dimeric complexes studied by us have unusual structures. The high stability of these complexes in acetonitrile is attributed not only to the $K_i > K_i^*$ correlation. Along with two coordination bonds, intramolecular interaction of chromophore groups may contribute significantly to the stability of the dimers in the system studied. The high tendency of polymethine dyes, including positively charged ones, to form dimers is well known.[20]

The reliability of the dimerization constants measured by us is confirmed by a series of independent experiments. First, the evidence for the high stability of the dimeric complexes of *trans*-**3** and *trans*-**4** with Mg^{2+} is the fact that the dissociation rate constant of similar $(cis\text{-}\mathbf{3}\cdot Mg^{2+})_2$ dimers in acetonitrile is very low.[6] Second, as was already mentioned above, the reliability of the K_d measurements is confirmed by the results of spectrophotometric titration by a competitive ligand. In the case of the complex of CSD **4** with Mg^{2+}, we were able to obtain satisfactory agreement of the theory with the experiment only when $\log K_d \geq 6.5$. Third, estimation of the lowest possible value of K_d in the case of the complex of CSD **3** with Mg^{2+} can be carried out using the previously obtained[8] concentration dependence of the quantum yield of photocycloaddition (Φ). It has been shown that Φ value does not depend on the CSD **3** concentration at $C_L \geq 5\cdot10^{-5}$ mol L^{-1}. Since only dimeric complexes of the *trans*-isomer take part in the reaction, one may conclude that these complexes are practically completely dimerized already at $C_L \approx 5\cdot10^{-5}$ mol L^{-1}, or, taking into account the accuracy of determination of Φ, which is near 20 %, the degree of dimerization $\beta \geq 0.8$. Consequently, $\log K_d \geq 5.3$, that is in full agreement with the value given in Table 1. Similar measurements for the complexes of CSD **4** with Mg^{2+} show that Φ does not depend on concentration at least at $C_L \geq 1\cdot10^{-5}$ mol L^{-1} (Φ was not measured at lower concentrations) and, consequently, $\log K_d \geq 6$.

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