Crown ether styryl dyes

23.* Synthesis and complexation of *cis*-isomers of photochromic dithia-15(18)-crown-5(6) ethers

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A novel styryl dye containing benzodithia-18-crown-6 and *N*-(4-sulfobutyl)benzothiazolium fragments was synthesized. The complex formation of the *cis*-isomers of several photochromic styryl dyes containing dithia-15(18)-crown-5(6) fragments with Hg^{2+} and Mg^{2+} ions was studied. The stability constants of the complexes with Mg^{2+} and the relative stability constants of the complexes with Hg^{2+} (with respect to benzo-1,10-dithia-18-crown-6 ether) were measured. The fact that the stability constant increases 11-fold on going from the *trans*- to the corresponding *cis*-isomer was attributed to the formation of an anion-"capped" complex.

Key words: styryl dyes; benzodithia-15(18)-crown-5(6) ethers; synthesis; photoisomerization; Hg^{2+} and Mg^{2+} ions; anion-"capped" complex; UV spectroscopy; ^1H NMR spectroscopy.

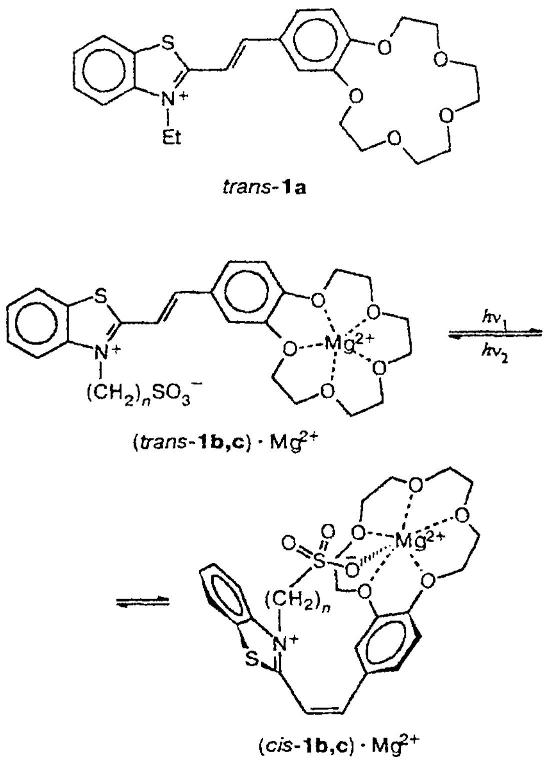
The supramolecular organic photochemistry of crown-containing styryl dyes (CSD) able to undergo photoswitching is a vigorously developing field of research.[2]

It has been found[3,4] and later confirmed by theoretical calculations[5] that of compounds obtained in our studies, the CSD similar to *trans*-**1a** but containing an ω-sulfoalkyl group rather than an alkyl group at the N atom of the benzothiazolium fragment are the most promising. Thus, we managed to synthesize for the first time photochromic CSD **1b,c** (Scheme 1) capable of "taking off" and "putting on" their anionic "cap" upon exposure to light with various wavelengths and thus to control binding of metal cations by virtue of light.[6]

Up to now, primary attention has been paid to CSD based on 15(18)-crown-5(6)-ether derivatives.[2] Styryl dyes *trans*-**2a—f** (Scheme 2) containing fragments of benzodithia-15(18)-crown-5(6) ethers[7,8] have not been studied so thoroughly, although they possess substantial advantages, because thiacrown compounds exhibit a clear-cut tendency to form complexes with heavy and transition metals.[7,9] However, the potentialities of photoswitchable CSD containing a thiacrown moiety have not yet been explored.

In this work, we studied the effect of the nature of the terminal group in the *N*-substituent, the metal cation, and the size of the dithiacrown-ether cavity of CSD on the formation of complexes by photochromic benzodithia-15(18)-crown-5(6) ethers of the benzothiazole series.

Scheme 1



trans-**1a**

(*trans*-**1b,c**) · Mg^{2+}

(*cis*-**1b,c**) · Mg^{2+}

n = 3 (**b**), 4 (**c**)

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* For Part 22, see Ref. 1.

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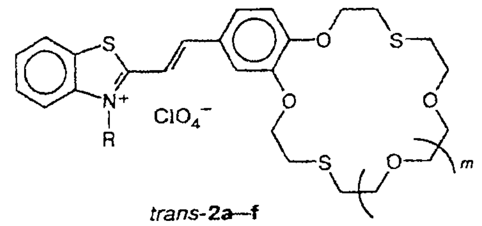
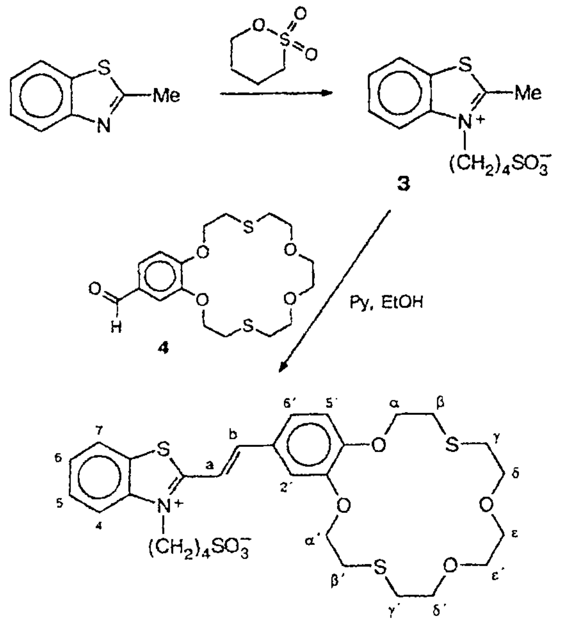
Scheme 2



m = 0 (**a**—**c**), 1 (**d**—**f**)
R = Me (**a**, **d**), $(CH_2)_3COOH$ (**b**, **e**), $(CH_2)_4COOH$ (**c**, **f**)



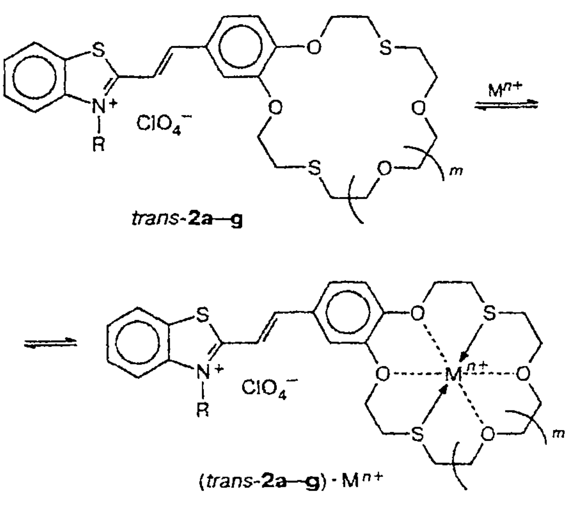
2g

The syntheses of CSD *trans*-**2a**—**f** and betaine **3** have been described in our previous publications;[7,10] CSD **2g** was prepared in 74% yield by the condensation of betaine **3** with 3′-formyl-2,3-benzodithia-18-crown-6 ether[11] (**4**) in the presence of pyridine.

The structure of CSD **2g** was proved by ^1H NMR spectroscopy (see Experimental). The results of elemental analysis corresponded to the suggested structure. Judging by the spin-spin coupling constant for the olefinic protons, $^3J_{trans}$ = 15.6 Hz (see Ref. 12), the resulting CSD **2g** had the *trans*-configuration.

The electronic absorption spectra of dyes *trans*-**2a**—**f** in MeCN are virtually identical to the corresponding spectra of *trans*-**1a**—**c** (see Ref. 3), because all these dyes incorporate identical chromogens.[7] The spectral effects caused by complexation of *trans*-**2a**—**f** with metal cations in anhydrous MeCN have been described in detail in the previous communication.[7] It was shown that in the case of complexation of *trans*-**2a**—**f** with Ag^+ and Hg^{2+}, the dependence of the absorption spectra of the dyes on the concentration of metal cation (C_M) can be described adequately taking into account only one equilibrium (Scheme 3).

Scheme 3



M^{n+} = Ag^+, Hg^{2+}

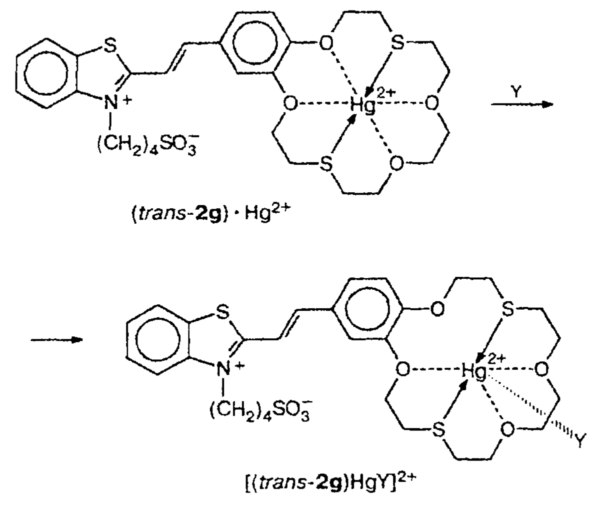
The electronic absorption spectrum of *trans*-**2g** in MeCN (λ_{max} = 432 nm) is similar to the spectra of dyes *trans*-**2a**—**f**. Dye *trans*-**2g** is much less soluble in MeCN than dyes *trans*-**2a**—**f** (the concentration of the saturated solution is ~$2.5 \cdot 10^{-6}$ mol L^{-1}). The solubility markedly increases after the addition of silver or mercuric perchlorate and almost does not change when sodium or tetrabutylammonium perchlorate is added. The increase in the solubility of *trans*-**2g** can be explained by the formation of complexes with the dithia-18-crown-6 ether (see Scheme 3). In fact, in the presence of silver (C_M = $1 \cdot 10^{-4}$ mol L^{-1}) or mercuric (C_M = $5 \cdot 10^{-5}$ mol L^{-1}) perchlorate in MeCN, the long-wavelength absorption band (LAB) of *trans*-**2g** (for the concentration of the ligand C_L = $4 \cdot 10^{-5}$ mol L^{-1}) undergoes a hypsochromic shift equal to 8 or 18 nm, respectively.

The long-wavelength electron transition in a CSD molecule is accompanied by the displacement of the electron density from the benzene ring to the heterocyclic fragment.[5] When the dithiacrown-ether fragment of *trans*-**2g** binds a Ag^+ or Hg^{2+} ion, this electron density displacement becomes energetically unfavorable, because it is directed away from the metal cation. Apparently, this accounts for the experimentally observed hypsochromic shifts of the LAB.

Previously, we have shown[5] that when complexes are formed, the interaction of the metal cation with the O atom incorporated in the conjugation chain of the chromophore exerts the greatest effect on the chromophore system of CSD. The S atoms in the dithiacrown-ether fragment of *trans*-**2a**—**f** form very strong bonds with a

Hg^{2+} ion (see Ref. 7) and cause its coordination saturation; this hampers the efficient interaction of Hg^{2+} with the O atoms linked to the benzene ring. This, apparently, accounts for the fact that the hypsochromic shift of the LAB of *trans*-**2g** resulting from the complexation with Hg^{2+} is relatively small, compared, for example, with that for the complexation of *trans*-**1a—c** with Mg^{2+} (see Ref. 2). The addition of Br^- or Cl^- ions or amines (NH_3 or pyridine) having high affinities for the Hg^{2+} ions results apparently in the cleavage of at least one Hg^{2+}- - -OAr coordination bond (Scheme 4). This follows from the fact that the influence of Hg^{2+} on the chromophore system is no longer observed, *i.e.*, the hypsochromic shift of the LAB disappears, although the complex is still more soluble than *trans*-**2g** itself.

Scheme 4



Y = Br^-, Cl^-, NH_3, Py

We suggested that ^1H NMR spectroscopy in MeCN-d_3 would provide additional information on the changes in the molecular structure of *trans*-**2g** caused by the complexation. Previously, we have shown[7] that the addition of silver or mercuric perchlorate (or nitrate) to solutions of *trans*-**2a,e** results in a downfield displacement of all the signals in the ^1H NMR spectrum.

Since *trans*-**2g** is poorly soluble in MeCN-d_3, it was impossible to compare the chemical shifts of the protons of this dye before and after its complexation with silver or mercury ions. Analysis of the results shows that in DMSO-d_6 the chemical shifts of the same type of protons in betaines *trans*-**2g** and *trans*-**1c** (see Ref. 4), which contain chromogens with similar structures, are virtually identical. In the case of cationic dyes *trans*-**2d** (see Ref. 7) and *trans*-**1a** (see Ref. 13), the chemical shifts of the aromatic and olefinic protons in MeCN-d_3 are also identical. Previously,[7] it was found that the variation of the chemical shifts of the β,β′-protons in the CH_2S groups provides an adequate estimate of the efficiency of binding of metal ions by the dithiacrown-ether moiety of *trans*-**2a—f** and that the chemical shifts of these protons themselves barely depend on the nature of the *N*-substituent. Thus, the chemical shifts of the chromogen protons in *trans*-**1c** and those of the β,β′-protons of the CH_2S groups in *trans*-**2d** can be used for comparative analysis of the changes occurring in the ^1H NMR spectra of *trans*-**2g** in MeCN-d_3 after complexation (Table 1).

In the spectra of the complexes of *trans*-**2g** with Ag^+ and Hg^{2+}, the most pronounced changes in the chemical shifts are observed for the β,β′-protons of the CH_2S groups. The Δδ values for the protons of the benzene ring, the olefinic fragment, and the benzothiazolium residue vary in the narrow range from −0.1 to 0.06 ppm, which is due to the fact that the electron-withdrawing effect of Ag^+ and Hg^{2+} on the protons is substantially attenuated along the conjugation chain of the chromophore. These changes in the chemical shifts imply that the Ag^+ and Hg^{2+} ions are bound to the dithiacrown-ether moiety of *trans*-**2g**.

The solubility of *trans*-**2g** in MeCN also markedly increases after the addition of magnesium perchlorate. Unlike the formation of (*trans*-**2g**) · Hg^{2+}, which is accompanied by a hypsochromic shift of the LAB, the formation of the complex of *trans*-**2g** with Mg^{2+} does not lead to any displacement of the LAB with respect to

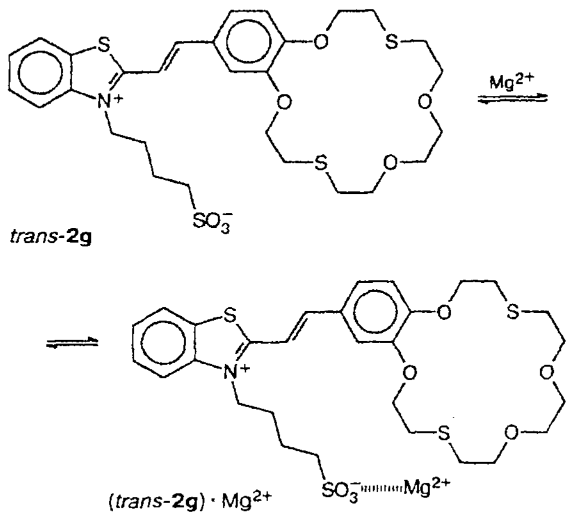
Table 1. The changes in the chemical shifts of aromatic and olefinic protons in the ^1H NMR spectra of *trans*-**2g** upon the complexation with metal perchlorates in MeCN-d_3

Compound	M^{n+}	**2g** : M^{n+} ratio	Δδ						
			β,β′ [a]	CH=CH[b]	H(C-2′)[b]	H(C-5′)[b]	H(C-6′)[b]	H(C-4), H(C-7)[b]	H(C-5), H(C-6)[b]
trans-**2g**	Ag^+	1 : 1	0.25	0	0.05	−0.03	−0.05	0.05	0.03
	Hg^{2+}	1 : 1	0.71	−0.08	0.01	−0.09	−0.1	0.05	0.06
	Mg^{2+}	1 : 1.8	−0.04	−0.41	−0.65	−0.09	0.01	0.01	−0.01
cis-**2g**	Hg^{2+}	1 : 1	—	—[c]	—	—	—	0.20	0.21

[a] $\Delta\delta = \delta_{compl} - \delta_{trans\text{-}2d}$, where δ is the average of the chemical shifts of the β,β′-protons of the methylene groups.
[b] $\Delta\delta = \delta_{compl} - \delta_{trans\text{-}1c}$, where δ, in the case of two protons, is the average of their chemical shifts. [c] The chemical shift of one of the protons is 7.63 ppm ($^3J_{cis}$ = 12.2 Hz).

its position in the spectrum of the free ligand, *i.e.*, the complexation has no effect on the chromophore system of the dye. Therefore, it appears most likely that the Mg^{2+} ion is coordinated to the sulfo-group at the *N*-substituent in *trans*-**2g** (Scheme 5), as has been observed in our previous study[3] for anion-"capped" complexes of *cis*-CSD with excessive Mg^{2+} ions.

Scheme 5



The chemical shifts of signals in the ^1H NMR spectrum of the *trans*-**2g** complex with Mg^{2+}, apparently, except for those for one of the protons at the C=C bond and for the H(C-2′) proton, do not change significantly (see Table 1). It has been found previously[2] that the sulfo group in *trans*-**1c** can form an intramolecular ion pair in which the N atom of the benzothiazolium residue is positively charged. If this ion pair does exist, the H(C-2′) and H(C-a) protons are likely to fall in the deshielding area of the sulfo group, which results in an increase in their chemical shifts. Conversely, when the ion pair completely dissociates, which can occur, for example, under the action of Mg^{2+}, the distance between the sulfo group and the above-mentioned protons increases. This should diminish or completely eliminate the deshielding effect, as has actually been observed in our experiments.

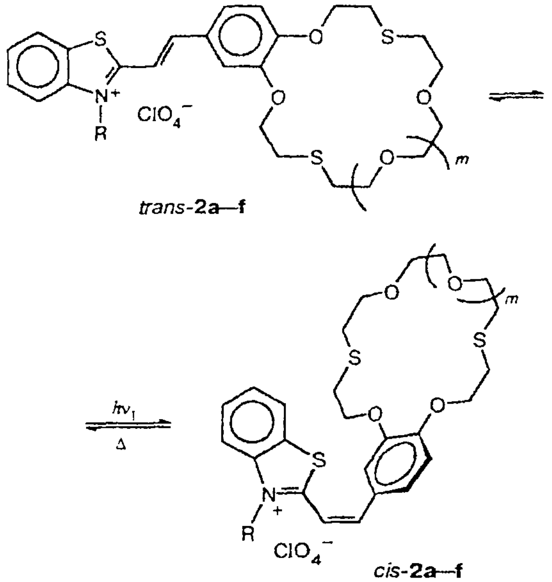
From the solubility of *trans*-**2g** in acetonitrile solutions of $Mg(ClO_4)_2$ of various concentrations (C_{Mg} = 10^{-4}—10^{-3} mol L^{-1}), we calculated the stability constant $K_1 = [(LMg)^{2+}]/([L][Mg^{2+}])$ of the (*trans*-**2g**) · Mg^{2+} complex ($\log K_1 = 4.8 \pm 0.3$). The concentration of the complex was determined by spectrophotometry, while the concentration of free *trans*-**2g** in the presence of a precipitate of the dye was taken to be equal to the concentration of a saturated solution of *trans*-**2g** in pure MeCN. The concentration of free Mg^{2+} ions was calculated from the material balance equation $[Mg^{2+}] = C_{Mg} - [(LMg)^{2+}]$. The relatively low accuracy of determination of $\log K_1$ is mostly due to the insufficient accuracy of the determination of the concentration of the saturated solution of *trans*-**2g** in MeCN.

trans—*cis*-Isomerization of 2a—g and formation of complexes by *cis*-isomers

It can be assumed that upon photoirradiation, CSD containing terminal carboxyl groups "put on" their "carboxyl cap" in the *cis*-form and "take it off" in the *trans*-form. This would enable one to control by virtue of light the formation of an additional intramolecular coordination bond (IntraCB) with Hg^{2+}.

When solutions of *trans*-**2a**—**f** and their complexes with Ag^+ or Hg^{2+} are exposed to visible light, changes typical of *trans*—*cis*-isomerization can be observed in their spectra. The *cis*-isomers formed in this reaction are unstable and in the dark, they are converted into the corresponding *trans*-isomers (Scheme 6).

Scheme 6



The absorption spectra of *cis*-**2f** containing the *N*-4-carboxybutyl substituent and of its complex with Hg^{2+} were calculated by the Fischer method[14] using the spectra of *trans*-isomers and those of the photosteady states obtained upon exposure of the initial isomer to light with λ = 365 nm and λ = 436 nm. In the case of *trans*-**2f** (see Ref. 7) and its complex with Hg^{2+} (Fig. 1), *trans*—*cis*-photoisomerization is accompanied by small hypsochromic shifts of the LAB equal to 9 and 12 nm, respectively.

At the same time, the hypsochromic shift of the LAB of anion-"capped" complexes (*cis*-**1b,c**) · Mg^{2+} (see

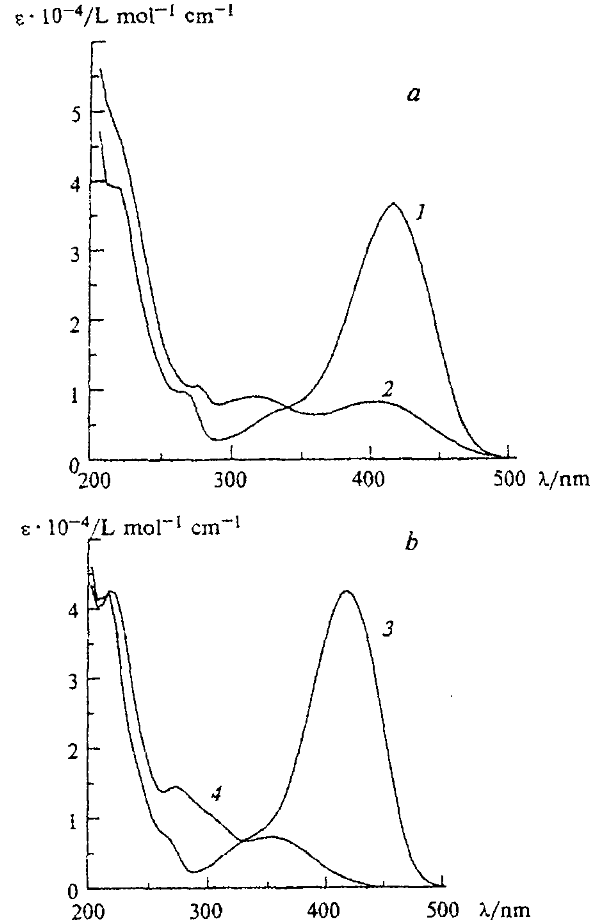


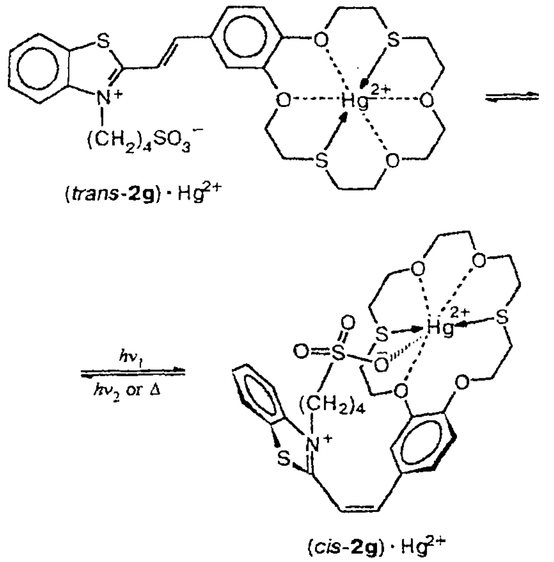
Fig. 1. Electronic absorption spectra of dye complexes in MeCN (C_L = $5 \cdot 10^{-5}$ mol L^{-1}).
a, (*trans*-**2f**) · Hg^{2+} (*1*), (*cis*-**2f**) · Hg^{2+} (*2*).
b, (*trans*-**2g**) · Hg^{2+} (*3*), (*cis*-**2g**) · Hg^{2+} (*4*).

Scheme 1) with respect to its position for (*trans*-**1b,c**) · Mg^{2+} can be as large as 72 nm; this is due to the violation of the conjugation in the chromophore caused by the transition of the molecule into a twisted conformation.[3] The results obtained make it possible to conclude that the conjugation in the chromophore of (*cis*-**2f**) · Hg^{2+} is not disturbed, and the structure of the chromophore is nearly planar. Apparently, the carboxyl group in (*cis*-**2f**) · Hg^{2+} in MeCN cannot participate in the formation of the anion-"capped" complex, because it does not dissociate in this solvent, and, hence, does not give rise to the carboxylate anion, which is known[15] to be able, being a part of a complexonate, to form a strong coordination bond with Hg^{2+}.

It may be expected that dye *trans*-**2g**, which contains a terminal anionic sulfo group, would be capable, like *trans*-**1b,c** (see Ref. 3), of forming an anion-"capped" complex upon photoisomerization.

On exposure to light with λ = 436 nm, the complexes of *trans*-**2g** with Ag^+ and Hg^{2+} undergo reversible *trans*—*cis*-photoisomerization, and their LABs shift to shorter wavelengths by 11 and 63 nm, respectively. In the case of **2g** · Hg^{2+}, a *trans*—*cis*-photosteady state is established; the equilibrium is appreciably shifted toward the *cis*-isomer (>99%). The photosteady state of **2f** · Hg^{2+} contains only 70% *cis*-isomer under the same conditions. The shift of the LAB following the photoisomerization of complex **2g** · Ag^+ differs only slightly from the corresponding value for the free ligand. Evidently, the structural changes that occur in the chromogens of *trans*-**2g** and its complex with Ag^+ during photoisomerization are similar, and they are not accompanied by the formation of an anion-"capped" complex in the case of (*cis*-**2g**) · Ag^+. On the contrary, the large shift of the LAB in the case of (*cis*-**2g**) · Hg^{2+} implies that the conjugation in the chromophore chain is violated; this can occur only upon substantial disturbance of the molecular structure, which accompanies the formation of anion-"capped" complexes[5] (Scheme 7). Previously,[16] in relation to anion-"capped" complexes (*cis*-**1b**) · M^{2+} (M = Mg, Ca, Ba), we have found that the magnitude of the spectral shift lies in a narrow range, 69—72 nm, irrespective of the size of the metal cation. This suggests that the smaller magnitude of the shift of the LAB in the case of (*cis*-**2g**) · Hg^{2+} points to weakening or cleavage of the Hg^{2+}--- OAr coordination bond, which has been observed upon the addition of Br^- or Cl^- ions to (*trans*-**2g**) · Hg^{2+}.

Scheme 7



It should be noted that the formation of IntraCB in the anion-"capped" (*cis*-**2g**) · Hg^{2+} complex results in sharp deceleration of the dark *cis*—*trans*-isomerization, and the lifetime of (*cis*-**2g**) · Hg^{2+} reaches $2 \cdot 10^7$ s.

Despite the fact that some of the signals in the ^1H NMR spectrum of (*cis*-**2g**) · Hg^{2+} are broadened and, hence, interpretation of the spectrum is complicated, analysis of this spectrum has shown that the compound in question actually does possess the *cis*-configuration and that the spin-spin coupling constant $^3J_{cis}$ for the olefinic protons is 12.2 Hz (see Refs. 10 and 12). At present, this is the only example of a complex of *cis*-CSD with a metal ion observed successfully by ^{1}H NMR spectroscopy.

It might be expected that spectrophotometric titration of solutions of **2g** with mercuric perchlorate in MeCN would make it possible to determine the stability constants of the complexes and would confirm the assumption that the anion-"capped" (*cis*-**2g**) · Hg^{2+} complex is more stable. However, in this case, direct spectrophotometric determination of the stability constants proved to be impossible, because their values are too large. In fact, logK_l for the complex of 1,10-dithia-18-crown-6 ether with Hg^{2+} in 0.5 *M* HNO$_3$ is 19.5 (see Ref. 17).

Therefore, we determined the relative stability constants of (*trans*-**2g**) · Hg^{2+} and (*cis*-**2g**) · Hg^{2+} using titration by a solution of a competing ligand (L$_c$). As the competing ligand, we used 2,3-benzo-1,10-dithia-18-crown-6 ether (BDT18C6). The reaction scheme for this system includes two equilibria:

$$\left.\begin{array}{l} \mathrm{L} + \mathrm{Hg}^{2+} \overset{K_l}{\rightleftharpoons} (\mathrm{LHg})^{2+}, \\ \mathrm{L_c} + \mathrm{Hg}^{2+} \overset{K_c}{\rightleftharpoons} (\mathrm{L_cHg})^{2+}, \end{array}\right\} \qquad (1)$$

where L is a molecule of **2g**, L$_c$ is BDT18C6; K_l = [LHg]/([Hg][L]) and K_c = [L$_c$Hg]/([Hg][L$_c$]) are the stability constants of the **2g** · Hg^{2+} and (BDT18C6) · Hg^{2+} complexes, respectively.

This scheme is described by the equation

$$C_c = [1 + K_l(1 - \alpha)/(\alpha K_c)] \cdot \{C_{Hg} - \alpha C_L - \alpha/[K_l(1 - \alpha)]\},$$

where C_c, C_{Hg}, and C_L are the total concentrations of BDT18C6, Hg(ClO$_4$)$_2$, and **2g**, respectively, and α is the degree of complexation of **2g** with Hg^{2+}, which was calculated from the formula $\alpha = (D - D_c)/(D_0 - D_c)$, where D_0, D, and D_c are the optical density of the initial solution in which **2g** is completely bound into the complex, the current optical density, and that corresponding to the complete complexation with BDT18C6, respectively.

Taking into account the fact that at C_{Hg} = 5 · 10^{-5} mol L^{-1}, $C_{Hg} >> \alpha/[K_l(1 - \alpha)]$, we obtain the following expression for the ratio of the stability constants K_l/K_c:

$$K_l/K_c = \alpha(C_c - C_{Hg} + \alpha C_L)/[(1 - \alpha)(C_{Hg} - \alpha C_L)].$$

The experimental dependences of the 1 − α values on the concentration C_c of the competing ligand for complexes (*trans*-**2g**) · Hg^{2+} and (*cis*-**2g**) · Hg^{2+} are presented by dots in Fig. 2, and the solid lines in the same figure show the best approximations of the experimental points by theoretical curves.

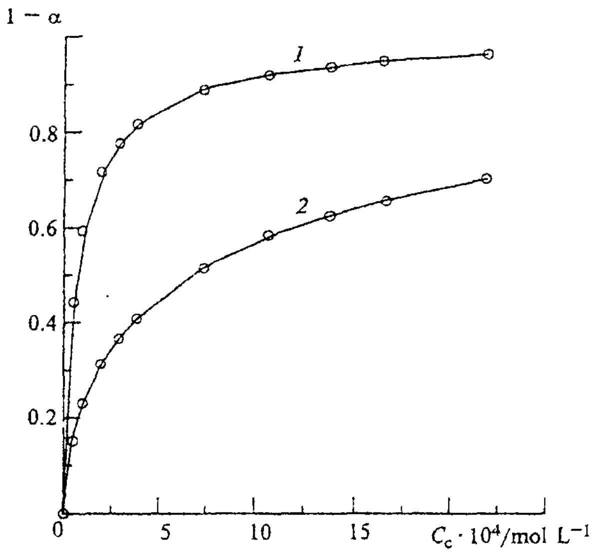


Fig. 2. Dependences of 1 − α (α is the degree of complexation of **2g**) on the concentration of the competing ligand BDT18C6 (C_c) at constant concentrations of (*trans*-**2g**) · Hg^{2+} (*1*) and (*cis*-**2g**) · Hg^{2+} (*2*). $C_L = C_{Hg} = 5 \cdot 10^{-5}$ mol L^{-1}. The solid lines show the best approximation of the experimental dependences by equilibria (1).

The K_l/K_c ratios obtained in this way for (*trans*-**2g**) · Hg^{2+} and (*cis*-**2g**) · Hg^{2+} are 1.88 and 20.1, respectively. It should be noted that the stability constant K_l of the former complex is 47 times greater than the stability constant K_l of (*trans*-**2d**) · Hg^{2+} (see Ref. 7); this difference is markedly less pronounced than the difference between the K_l constants for (*trans*-**1c**) · Mg^{2+} and (*trans*-**1a**) · Mg^{2+} (they differ 126-fold[18]). This dissimilarity of the two types of CSD is due to the fact that the formation of two coordination bonds between the S atoms and Hg^{2+} exerts a crucial effect on the stability of (*trans*-**2g**) · Hg^{2+}, whereas the electron-withdrawing effect of the positively charged benzothiazole residue is markedly less significant. The fact that K_l for betaine *trans*-**2g** is greater than that for *trans*-**2d**, as in the case of (*trans*-**1b,c**) · Mg^{2+}, is apparently due to the ability of the sulfo group in the *N*-substituent to produce an intramolecular solvent-separated ion pair with the Hg^{2+} ion located in the crown-ether cavity[18] or an intramolecular contact ion pair with the positively charged N atom of the benzothiazolium residue.[2]

It is of interest to compare the stability constants K_l of complexes of *cis*-**2g** and *trans*-**2g** with Hg^{2+}. Previously, it has been found[2] that the sulfobutyl substituent in anion-"capped" complexes is long enough to allow the formation of a strong coordination bond between the sulfo group and a metal cation located in the crown-ether cavity. In fact, the stability constant of the anion-"capped" (*cis*-**1c**) · Mg^{2+} is larger than that of the corresponding complex of the *trans*-isomer by a factor of ~4000.[18] However, in the case of anion-"capped" (*cis*-**2g**) · Hg^{2+} and (*trans*-**2g**) · Hg^{2+}, the corresponding ratio of the stability constants is only ~11. The fact that the difference between the stabilities of the complexes formed by *cis*- and *trans*-**2g** is not very large implies that the SO_3^-- - -Hg^{2+} bond is relatively weak, which can be easily explained in terms of the theory of "hard" and "soft" acids and bases.[19] Apparently, this accounts for the fact that in the concentration range covered, we have not found unambiguous evidence for the existence of dimeric complexes of **2g** with Hg^{2+} of the composition 2 : 2, which normally exist in the case of complexes of CSD **1b,c** with alkaline earth metal cations.[2]

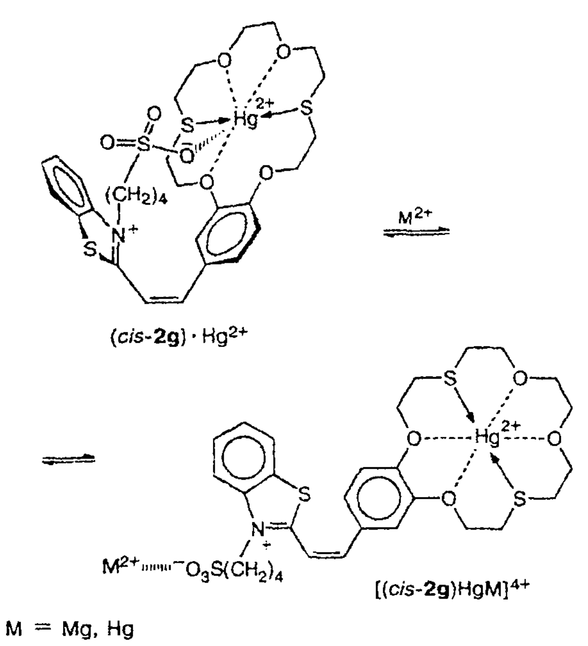
It should be expected that, since the strength of the SO_3^-- - -Hg^{2+} bond in the anion-"capped" (*cis*-**2g**) · Hg^{2+} is rather low, this bond would be cleaved relatively easily under the action of excess Hg^{2+} or other cations. A similar process has been observed previously for anion-"capped" (*cis*-**1b,c**) · Mg^{2+} complexes in the presence of Mg^{2+} ions (see Ref. 3). In fact, when the concentration of Mg^{2+} in a solution of (*cis*-**2g**) · Hg^{2+} ($C_{LHg} = 5 \cdot 10^{-5}$ mol L^{-1}) increases, absorption in the long-wavelength region of the spectrum starts to increase noticeably, and at $C_M = 10^{-1}$ mol L^{-1}, the spectral pattern completely changes. These spectral changes were attributed to the destruction of IntraCB as a result of interaction of the sulfo group with excessive Mg^{2+} ions. When the IntraCB is cleaved, the nearly planar conformation of the chromophore is restored, and, therefore, the conjugation in the chromophore is also restored (Scheme 8). The $[($*cis*-**2g**$)HgMg]^{4+}$ complex formed in this reaction is slowly converted in the dark into the corresponding *trans*-isomer. However, the lifetime of $[($*cis*-**2g**$)HgMg]^{4+}$ is sufficiently high for its stability constant $K_2 = [LHgMg]/([Mg][LHg])$ to be determined by direct spectrophotometric titration.

The degree of complexation of (*cis*-**2g**) · Hg^{2+} with Mg^{2+} ions was calculated from the formula $\alpha = (D_0 - D)/(D_0 - D_{compl})$, where D_0, D, and D_{compl} are the optical density of the initial solution, the current optical density, and the value corresponding to the complete binding of the dye into the complex, respectively. This gave $\log K_2 = 2.4 \pm 0.1$.

Apparently, when the concentration of Hg^{2+} in a solution of the anion-"capped" (*cis*-**2g**) · Hg^{2+} increases, the "open" $[($*cis*-**2g**$)Hg_2]^{4+}$ complex is also formed according to Scheme 4.

Thus, we synthesized for the first time a styryl dye incorporating benzodithia-18-crown-6 and *N*-(4-sulfobutyl)benzothiazolium fragments. The formation of complexes by the *cis*-isomers of the photochromic CSD containing dithia-15(18)-crown-5(6)-ether fragments was studied. Ion-selective formation of the anion-"capped" complex of *cis*-CSD with Hg^{2+} was discovered. A number of log*K* values and relative stability constants of complexes of CSD with Hg^{2+} and Mg^{2+} were measured.

Scheme 8



Experimental

^1H NMR spectra were recorded on a Bruker AMX-400 spectrometer (400 MHz, $MeCN-d_3$ and $DMSO-d_6$, tetramethylsilane as the internal standard). The chemical shifts were measured with an accuracy of 0.01 ppm and spin-spin coupling constants were determined with an accuracy of 0.1 Hz. The changes in the chemical shifts ^1H ($\Delta\delta$) were measured in $MeCN-d_3$ after addition of *trans*-**2g** to solutions of metal salts up to $C_L = 1 \cdot 10^{-3}$ mol L^{-1}. The quantities of metal salts that ensured the largest $\Delta\delta$ values were used.

Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer at 20±2 °C in 1-cm-thick quartz cells.

Solutions of CSD and their complexes were exposed to the light of a DRSh-100 mercury lamp. The individual lines of the spectrum of this lamp (313, 365, or 436 nm) were isolated using glass light filters.

Complex formation of **2g** with $Hg(ClO_4)_2$ was studied by spectrophotometric titration. In direct experiments, a solution with a known concentration of **2g** and a solution of $Hg(ClO_4)_2$ were added to a solution of **2g** with the same concentration. The stoichiometry of the complex was found from the titration curve. The magnitudes of the stability constants of the complexes were beyond the power of the spectrophotometric method and were not determined. In the experiments using a competing ligand, a solution containing equal amounts of **2g** and $Hg(ClO_4)_2$ ($C_L = C_M = 5 \cdot 10^{-5}$ mol L^{-1}) and BDT18C6 ($C_c = 10^{-2}$ mol L^{-1}) were added to a solution containing the same concentrations of **2g** and $Hg(ClO_4)_2$. Measurements were carried out at a wavelength of 460 nm. The ionic strength of solutions during titration was $2 \cdot 10^{-4}$ mol L^{-1}.

Complex formation of (*cis*-**2g**) · Hg^{2+} with $Mg(ClO_4)_2$ was studied by direct spectrophotometric titration. A solution of $Mg(ClO_4)_2$ with $C_M = 10^{-1}$ mol L^{-1} was added to a solution of (*cis*-**2g**) · Hg^{2+} (C_{LHg} = $5 \cdot 10^{-5}$ mol L^{-1}). The measurements were carried out at 415 nm. The ionic strength of solutions during titration varied from $2 \cdot 10^{-4}$ to $3 \cdot 10^{-3}$ mol L^{-1}.

The stability constants of the complexes were calculated by the nonlinear least-squares method using the Nelder—Mead simplex algorithm included in the MATLAB package of applied programs.

The preparation of solutions and all the experiments were carried out in red light.

Acetonitrile for spectral studies was first distilled over $KMnO_4$, then distilled twice over P_2O_5 and, finally, distilled over CaH_2. $Mg(ClO_4)_2$ was dried *in vacuo* at 240 °C. $AgClO_4 \cdot H_2O$ (Aldrich) and $Hg(ClO_4)_2 \cdot 3H_2O$ (Aldrich) were dried *in vacuo* at 40 °C.

***trans*-2-[2-(5,6,8,9,11,12,14,15,17,18-Decahydro-7,16-dithia-1,4,10,13-tetraoxa-2,3-benzocyclooctadecyn-3′-yl)vinyl]-3-(4-sulfobutyl)benzothiazolium betaine (2g).** Dry pyridine (0.3 mL) was added to a solution of betaine **3** (32 mg, 0.11 mmol) (see Ref. 10) and 3′-formylbenzodithia-18-crown-6 ether[11] (**4**) (46 mg, 0.12 mmol) in anhydrous EtOH (2 mL). The mixture was refluxed for 17 h and concentrated *in vacuo*. The residue was washed with benzene, heated with 35 mL of MeOH, and cooled to 0 °C. After 1 h, the precipitate was filtered off. Yield 53 mg (75%), m.p. 270—272 °C (decomp.). ^1H NMR (DMSO-d_6), δ: 2.02 (m, 2 H, CH_2); 2.24 (m, 2 H, CH_2); 2.77 (m, 2 H, $CH_2SO_3^-$); 2.96 (m, 2 H, CH_2S); 3.04—3.24 (m, 6 H, 3 CH_2S); 3.67 (br.s, 4 H, 2 ε-CH_2O); 3.76 and 3.81 (both m, 4 H, δ,δ′-CH_2O); 4.39 and 4.53 (both m, 4 H, α,α′-CH_2O); 5.07 (m, 2 H, CH_2N); 7.23 (d, 1 H, H(C-5′), J = 8.3 Hz); 7.69 (d, 1 H, H(C-6′), J = 8.3 Hz); 7.86 and 7.95 (both m, 2 H, H(C-5), H(C-6)); 8.00 (s, 1 H, H(C-2′)); 8.20 and 8.26 (both d, 2 H, CH=CH, J_{trans} = 15.6 Hz); 8.40 and 8.45 (both d, 2 H, H(C-7), H(C-4), J = 8.5 Hz, J = 8.1 Hz). Found (%): C, 54.29; H, 5.69; N, 2.01. $C_{29}H_{37}NO_7S_4$. Calculated (%): C, 54.45; H, 5.83; N, 2.19.

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References

1. S. P. Gromov, E. N. Ushakov, O. A. Fedorova, V. A. Soldatenkova, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1192 [*Russ. Chem. Bull.*, 1997, **46**, 1143 (Engl. Transl.)].
2. S. P. Gromov and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 641 [*Russ. Chem. Bull.*, 1997, **46**, 611 (Engl. Transl.)].
3. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, O. B. Stanislavskii, I. K. Lednev, and M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1991, **317**, 1134 [*Dokl. Chem.*, 1991 (Engl. Transl.)].
4. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, O. B. Stanislavskii, and M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1991, **321**, 104 [*Dokl. Chem.*, 1991 (Engl. Transl.)].
5. I. I. Baskin, K. Ya. Burstein, A. A. Bagatur′yants, S. P. Gromov, and M. V. Alfimov, *J. Mol. Structure*, 1992, **274**, 93.
6. A. V. Barzykin, M. A. Fox, E. N. Ushakov, O. B. Stanislavsky, S. P. Gromov, O. A. Fedorova, and M. V. Alfimov, *J. Am. Chem. Soc.*, 1992, **114**, 6381.
7. S. P. Gromov, O. A. Fedorova, A. I. Vedernikov, Yu. V. Fedorov, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 999 [*Russ. Chem. Bull.*, 1997, **46**, 959 (Engl. Transl.)].
8. M. V. Alfimov, Yu. V. Fedorov, O. A. Fedorova, S. P. Gromov, R. E. Hester, I. K. Lednev, J. N. Moore, V. P. Oleshko, and A. I. Vedernikov, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1441.
9. *Crown Compounds: Towards Future Application*, Ed. S. R. Cooper, VCH Publ., New York, 1992.
10. S. P. Gromov, E. N. Ushakov, O. A. Fedorova, A. V. Buevich, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 693 [*Russ. Chem. Bull.*, 1996, **45**, 654 (Engl. Transl.)].
11. S. P. Gromov, O. A. Fedorova, A. I. Vedernikov, V. V. Samoshin, N. S. Zefirov, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 121 [*Russ. Chem. Bull.*, 1995, **44**, 116 (Engl. Transl.)].
12. H. Günther, *NMR Spectroscopy. An Introduction*, J. Wiley and Sons, New York, 1980, Ch. 2.
13. O. A. Fedorova, S. P. Gromov, and M. V. Alfimov, *Dokl. Akad. Nauk*, 1995, **341**, 219 [*Dokl. Chem.*, 1995 (Engl. Transl.)].
14. E. Fischer, *J. Phys. Chem.*, 1967, **71**, 3704.
15. N. M. Dyatlova, V. Ya. Temkina, and K. I. Popov, *Kompleksony i kompleksonaty metallov* [*Complexones and Metal Complexonates*], Khimiya, Moscow, 1988, 544 pp. (in Russian).
16. E. N. Ushakov, Ph. D. (Chem.) Thesis, Institute of Chemical Physics in Chernogolovka of the RAS, Chernogolovka, 1995, 47 (in Russian).
17. R. M. Izatt, G. Wu, W. Jiang, and N. K. Dally, *Inorg. Chem.*, 1990, **29**, 3828.
18. O. B. Stanislavskii, E. N. Ushakov, S. P. Gromov, O. A. Fedorova, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 605 [*Russ. Chem. Bull.*, 1996, **45**, 564 (Engl. Transl.)].
19. *Benchmark Papers in Inorganic Chemistry. Hard and Soft Acids and Bases*, Ed. R. G. Pearson, J. Wiley, New York, 1973, 430 pp.

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