

Crown ether styryl dyes

21.* Synthesis, spectral properties, and complex formation of *trans*-isomers of the chromogenic dithia-15(18)-crown-5(6) ethers

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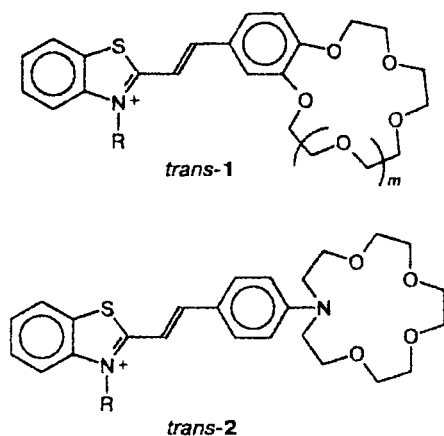
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Novel styryl dyes containing dithia-15(18)-crown-6(5)-ether moieties were synthesized. Their selective complex formation with Hg^{2+} and Ag^+ ions was studied by ^1H NMR and electronic spectroscopy; the stability constants of the Ag^+ complexes and the relative stability constants (in relation to benzodithia-18-crown-6) of the Hg^{2+} complexes were determined. The chemical shifts of the β, β' -protons in the CH_2S group change upon the complex formation in parallel with the $\log K_1$ values of the complexes.

Key words: styryl dyes; dithia-15(18)-crown-5(6) ethers, synthesis; Ag^+ and Hg^{2+} cations, complex formation; ^1H NMR spectroscopy; electronic spectroscopy.

Crown-containing dyes are able to bind selectively metal cations and also to absorb light in the visible region of the spectrum. These compounds have been used, for example, as reagents for colorimetric or luminescence determination of metal cations and as fragments of photoswitchable molecular devices.^{2,3}

Previously, we synthesized a number of crown-containing styryl dyes (CSD) incorporating 15(18)-crown-5(6)-ether (*trans*-1) and aza-15-crown-5-ether (*trans*-2) fragments, in particular, compounds *trans*-1a,b (see Ref. 4), and studied⁵⁻⁷ the formation of complexes of these dyes with Mg^{2+} , Ca^{2+} , and Ba^{2+} ions in MeCN.



1, 2: R = Et (ClO_4^- as the counterion), $m = 1$ (a);
R = $(\text{CH}_2)_3\text{SO}_3^-$, $m = 1$ (b)

* For Part 20, see Ref. 1.

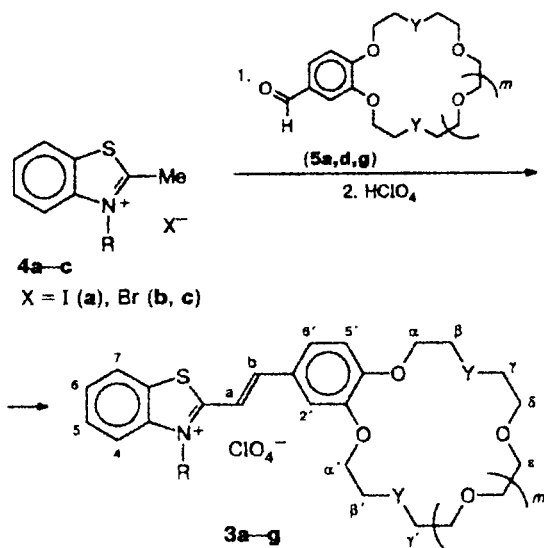
A common feature of dyes *trans*-1 and *trans*-2 is that their long-wavelength absorption bands (LAB) undergo substantial hypsochromic shifts upon the complex formation. The addition of alkali and alkaline earth metal salts to solutions of *trans*-1a results in downfield shifts of signals of all protons in their ^1H NMR spectra.

Thiacrown compounds, unlike crown and azacrown ethers, are able to form complexes with heavy and transition metals.⁸ In the present study, we synthesized styryl dyes 3a-f containing benzodithia-15(18)-crown-5(6)-ether fragments and studied the formation of their complexes with heavy metal cations.

The perchlorates of dyes 3a-f were prepared in yields of up to 72% by the condensation of quaternary salts 4a-c with 4'-formylbenzodithia-15(18)-crown-5(6) ethers (5a,d) in ethanol (containing some pyridine) followed by the addition of excess perchloric acid to the reaction mixture (Scheme 1). 4'-Formylbenzodithia-crown ethers 5a,d were synthesized by the procedures developed by us previously.⁹ Dye 3g was prepared in 83% yield from 3-(4-carboxybutyl)-2-methylbenzothiazolium bromide 4c and 4'-formylbenzo-18-crown-6 ether¹⁰ (5g) similarly to compounds 3a-f.

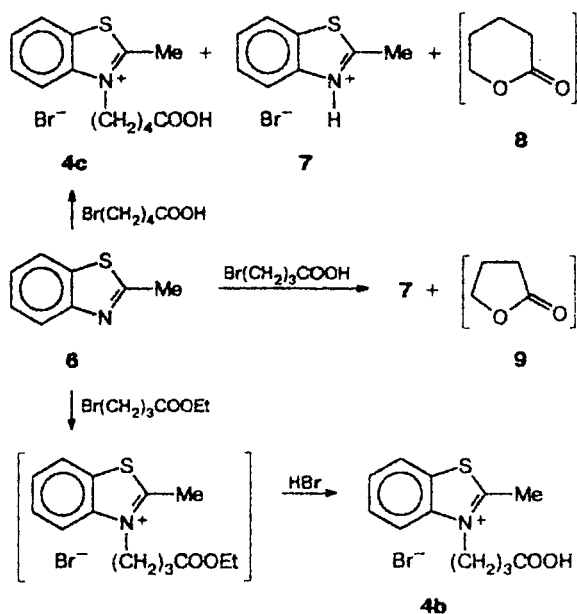
2,3-Dimethylbenzothiazolium iodide (4a) was obtained by heating 2-methylbenzothiazole (6) with methyl iodide (see Ref. 11), and the quaternary salt 4c was prepared by heating compound 6 with δ -bromovaleric acid (Scheme 2). The relatively low yield of salt 4c (38%) is due to the steric restrictions caused by the presence of the methyl group in position 2 of the heterocycle in 6, and to the possibility of the competing reaction giving δ -lactone (8) as indicated by the separation of 2-methylbenzothiazolium bromide (7) from the reaction mixture. In fact, the reaction of compound 6

Scheme 1



3, 4: $R = Me$ (a, d), $(CH_2)_3COOH$ (b, e), $(CH_2)_4COOH$ (c, f, g)
3, 5: $Y = S$ (a-f), O (g); $m = 0$ (a-c), 1 (d-g)

Scheme 2



with γ -bromobutyric acid under the same conditions yielded only bromide **7** but no quaternary salt **4b** (see Scheme 2). These results are in agreement with the known data on the transformation of ω -bromocarboxylic acids into δ - and γ -lactones under the action of bases and on the easier formation of the five-membered γ -lactone.¹² To prevent the formation of γ -lactone (**9**), we carried out quaternization of 2-methylbenzothiazole **6** with ethyl γ -bromobutyrate. Hydrolysis of the reaction product with aqueous HBr gave compound **4b**; however, its yield was relatively low (21%).

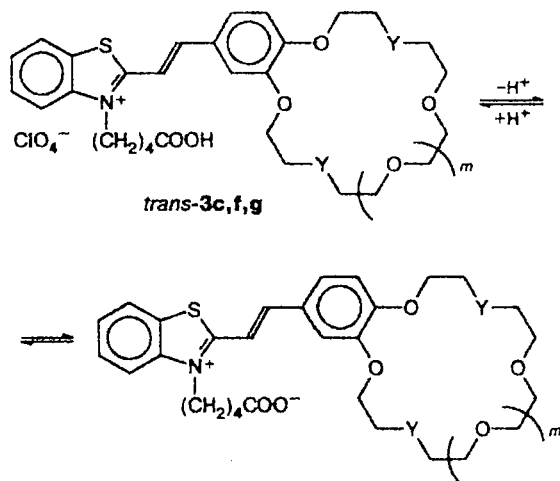
The structures of the resulting dyes **3a-g** and salts **4b,c** were confirmed by 1H NMR and IR spectroscopy (see Experimental). Judging from the spin-spin coupling constants $^3J_{trans} = 15.5$ to 16.0 Hz (see Ref. 13) for the olefinic protons, CSD **3a-g** have the *trans*-configuration.

The protons of the CH_2CO group in the 1H NMR spectra of dyes *trans*-**3c,f,g** are exhibited as two triplets with different intensities at δ 2.30 and 2.40; this probably can be explained by the presence of the deprotonated form of the dye in the $DMSO-d_6$ solutions of these CSD (Scheme 3).

The ratio of the intensities of these two lines markedly changes when dye *trans*-**3f** in $DMSO-d_6$ is treated with triethylamine; apparently, this is due to displacement of the equilibrium toward the deprotonated form. Most of the measurements were carried out using MeCN, in which the formation of the deprotonated form of the dye was not observed.

The electronic absorption spectra of CSD *trans*-**3a-g** in MeCN are almost identical to the corresponding spec-

Scheme 3

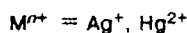
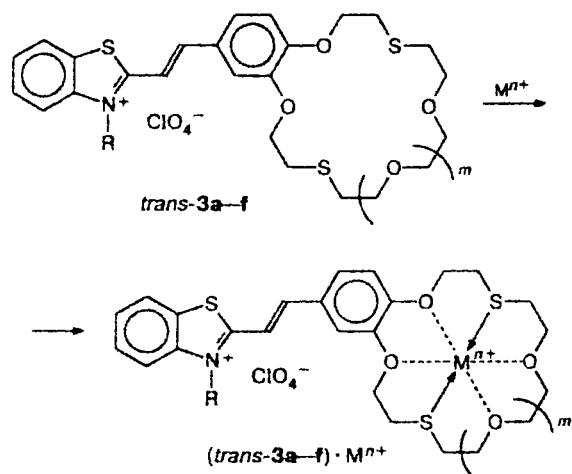


tra of *trans*-**1a,b** (see Ref. 4), because all of these dyes contain identical chromophoric fragments. The long-wavelength absorption band (LAB) of solutions of CSD *trans*-**3a-g** shifts hypsochromically as the polarity of the solvent increases. For example, the LAB of *trans*-**3f** is located at 431 nm (ϵ_{trans} 37 000) in MeCN, at 435 nm (ϵ_{trans} 39 400) in MeOH, and at 419 nm (ϵ_{trans} 34 600) in the MeOH- H_2O (1 : 4) system.

The addition of alkali and alkaline earth metal (Na, K, Mg, Ca) nitrates to solutions of *trans*-**3a-f** in MeOH causes no significant changes in the absorption spectra, because these ions possess low affinities to

sulfur-containing ligands. However, the addition of silver or mercury(II) nitrates or perchlorates as solutions of the same concentration results in hypsochromic shifts of the LAB of *trans*-3a–f (Table 1), which are evidently due to the formation of complexes (*trans*-3a–f)·Mⁿ⁺ (Scheme 4).

Scheme 4



The long-wavelength electron transition in a molecule of CSD is accompanied by the displacement of the electron density from the benzene ring to the heterocyclic moiety.¹⁴ When the dithiacrown-ether moiety binds Ag⁺ or Hg²⁺ ions, this effect becomes less pronounced, and this results in the experimentally observed hypsochromic shift of LAB.

Using silver and mercury(II) perchlorates and nitrates as examples, it was found that the nature of the counterions scarcely affects the magnitudes of the shifts of the LAB in the spectra of *trans*-3a–f. Apparently, this attests to a high degree of dissociation of the ion pairs formed by the (*trans*-3a–f)·Mⁿ⁺ cations and these anions.

Comparison of the Ag⁺ and Hg²⁺ ions having close ionic radii indicates that the latter cause larger shifts of the LAB of *trans*-3a–f, which is probably due to the higher charge density on the double-charged mercury cation.

The shifts of the LAB in the spectra of solutions of Ag⁺ and Hg²⁺ complexes with *trans*-3a–f, unlike those in the spectra of the CSD studied previously,¹⁵ are retained or even increase somewhat on going from MeCN to MeOH. This may be due to the fact that during the complex formation with the Ag⁺ and Hg²⁺ ions, MeCN molecules are able to compete with the O atom of the dithiacrown-ether moiety to a larger degree than MeOH. However, relatively large shifts of the LAB were observed in the MeOH–H₂O system, which indicates that (*trans*-3a–f)·Mⁿ⁺ complexes are formed under conditions under which alkali and alkaline metal cations do not form complexes with CSD.

When *trans*-3a–f are bound into complexes with Ag⁺ and Hg²⁺, the shifts of LAB are virtually identical for the same metal ion and the same solvent. Only in the case of Hg²⁺ in MeOH–H₂O, are the LAB shifts for *trans*-3a–c containing dithia-15-crown-5 moieties larger (by 5 nm, on the average) than those for *trans*-3d–f.

It should be noted that the hypsochromic shift of the LAB of *trans*-3g in the presence of Hg²⁺ in MeCN is not much smaller than the shifts of the corresponding bands of dyes *trans*-3d–f, whereas the constants of complex formation of mercury(II) ions with benzocrown ethers and benzodithiacrown ethers differ appreciably.¹⁶ Previously we showed¹⁴ that the interaction of the cation with the O atom incorporated in the conjugation chain of the chromophore during complexation exerts the greatest effect on the chromophoric system of the CSD. Probably, the S atoms of the dithiacrown-ether moiety of CSD *trans*-3d–f, which form very strong bonds with Hg²⁺ ion, saturate its coordination capacity, and this prevents efficient interaction of the Hg²⁺ ion with the O atoms conjugated with the benzene ring. Therefore, the hypsochromic shifts of the LAB following the complex formation are relatively small, for example, compared to those resulting from the interaction of

Table 1. Spectral properties of dyes *trans*-3a,d–g and their complexes with silver and mercury(II) nitrates in various solvents

Compound	MeCN ^a			MeOH ^b			MeOH–H ₂ O ^b (1 : 4)		
	λ_{max} /nm	$\Delta\lambda$ /nm		λ_{max} /nm	$\Delta\lambda$ /nm		λ_{max} /nm	$\Delta\lambda$ /nm	
		Ag ⁺	Hg ²⁺		Ag ⁺	Hg ²⁺		Ag ⁺	Hg ²⁺
<i>trans</i> -3a	427	8	16	429	12	18	416	6	13
<i>trans</i> -3d	429	9	16	432	12	20	417	6	9
<i>trans</i> -3e	433	7	16	436	11	19	420	4	8
<i>trans</i> -3f	431	8	17	435	12	19	419	5	8
<i>trans</i> -3g	431	0	10	—	—	—	—	—	—

^a The ratio of the ligand concentration to the salt concentration was 1 : 10; $\Delta\lambda = \lambda_{max}(\text{ligand}) - \lambda_{max}(\text{complex})$.

^b The ratio of the ligand concentration to the salt concentration was 1 : 30.

trans-1a with Mg^{2+} (see Ref. 6). On the other hand, the bonds of Hg^{2+} with the S atoms of the dithiacrown-ether fragment of CSD are so strong that the shifts of the LAB are observed even in the presence of water.

Study of the fluorescence spectra obtained on excitation with light with $\lambda = 365$ nm showed that when Hg^{2+} is added to solutions of CSD *trans-3d,f* ($\lambda_{max}^f = 538$ (3d) and 537 nm (3f)) in MeCN, fluorescence is quenched and λ_{max}^f shift to shorter wavelengths by 24 and 22 nm, respectively; the fluorescence and absorption spectra of dyes *trans-3d,f* shift in parallel upon complex formation. The quantum yields of fluorescence (ϕ_f) decrease on complex formation from 0.021 and 0.027 for *trans-3d,f* to 0.011 and 0.015 for (*trans-3d,f*) $\cdot Hg^{2+}$, respectively, which is similar to the behavior of CSD like *trans-1a* that we studied previously.¹⁷

In general, it can be stated that electronic spectroscopy provides little information on the formation of complexes of CSD *trans-3a-f* involving the S atoms, because these atoms are fairly remote from the chromophoric system of the dye and do not participate in conjugation with it.

The 1H NMR spectra (in MeCN- d_3) make it possible to obtain more detailed information on the changes in the molecular structure of dyes *trans-3* upon complex formation. Previously it was shown that the addition of alkali and alkaline earth metal salts to solutions of *trans-1a* results in downfield shifts of signals of all the protons in the 1H NMR spectrum.⁶

In the case of dyes *trans-3a,e*, the best agreement is observed between the shifts of the LAB and the changes in the chemical shifts ($\Delta\delta$) of the α,α' -protons of the methylene groups that are directly bound to the O atoms in the conjugation chain of the chromophore (see Tables 1 and 2). The chemical shifts of the protons of the methylene groups in CSD *trans-3a,e*, unlike those in *trans-1a*, are substantially different, due to the presence of two S atoms in the crown-ether fragment. For protons far removed from the dithiacrown-ether moiety, the $\Delta\delta$ values are smaller by 0.10–0.15 ppm for the benzene-ring protons and by 0.01–0.03 ppm for the

H(a) and H(b) protons. Obviously, this is due to the fact that the electron-withdrawing effect of the coordinated metal cation on the protons decreases gradually along the conjugation chain of the chromophore.

The largest $\Delta\delta$ values upon the interaction with Ag^+ , Hg^{2+} , and Cd^{2+} ions are observed for the β,β' - and γ,γ' -methylene protons of the CH_2S groups in dyes *trans-3a,e*, which implies that they form the strongest bonds with the S atoms of the dithiacrown-ether fragment. In the case of Hg^{2+} and *trans-3a,e*, the $\Delta\delta$ values for these protons are almost three times larger than those in the case of Ag^+ , which is probably due to the fact that the charge density on the single-charged silver cation is lower.

The presence of two S atoms in the crown-ether moiety results apparently in the loss of the ability of CSD *trans-3e* to form complexes with "hard" metal cations. For example, when Ca^{2+} is added to *trans-3e*, no changes in the 1H NMR chemical shifts and no displacements of the LAB in the electronic spectra are observed.

Conversely, the absence of S atoms in a crown-ether fragment, as has been shown for *trans-1a* and Mg^{2+} , is a condition for the efficient formation of complexes with "hard" metal cations,⁶ but it greatly decreases the ability of the macroheterocycle to bind "soft" metal cations. Therefore, the $\Delta\delta$ of the β,β' -protons caused by the formation of the complex between Hg^{2+} and *trans-3g* are much smaller than those in the case of, for example, *trans-3e* and Hg^{2+} (see Table 2) and are also markedly smaller than those for *trans-1a* and Mg^{2+} .

In the 1H NMR spectra of dyes *trans-3a,e*, the difference between the chemical shifts of the α -H and α' -H protons is the largest among $\Delta\delta$ for all pairs of like protons in the dithiacrown-ether fragment; this difference increases on going to the complexes of these CSD with metal ions. This attests to efficient conjugation of the chromophore with the O atom located in the *para*-position with respect to the C=C bond. In the case of the (*trans-3a*) $\cdot Hg^{2+}$ complex, this difference is 0.36 ppm, while for (*trans-3e*) $\cdot Hg^{2+}$, it is only

Table 2. Variation of the chemical shifts of the methylene groups in the 1H NMR spectra of dyes *trans-3a,e,g* and *trans-1a* upon the formation of complexes with metal salts in MeCN- d_3

Compound	$M^{n+}X_n^-$	3 : $M^{n+}X_n^-$	$\Delta\delta^a$				
			α,α' -H	β,β' -H	γ,γ' -H	δ,δ' -H	ϵ,ϵ' -H
<i>trans-3a</i>	$AgClO_4$	1.0 : 10.0	0.05	0.24	0.05	-0.06	—
<i>trans-3a</i>	$Hg(ClO_4)_2$	1.0 : 1.5	0.27	0.78	0.68	0.21	—
<i>trans-3e</i>	$AgNO_3$	1.0 : 2.0	0.16	0.28	0.21	0.04	0.06
<i>trans-3e</i>	$Hg(NO_3)_2$	1.0 : 5.0	0.28	0.74	0.69	0.25	0.21
<i>trans-3e</i>	$Cd(ClO_4)_2$	1.0 : 10.0	0.24	0.39	0.33	0.21	0.34
<i>trans-3g</i>	$Hg(ClO_4)_2$	1.0 : 1.5	0.16	0.17	0.14		0.19 ^b
<i>trans-1a</i>	$Mg(ClO_4)_2$	1.0 : 1.0	0.41	0.33		0.33 ^c	—

^a $\Delta\delta = \delta(\text{complex}) - \delta(\text{ligand})$, where δ is the average value over the chemical shifts of protons of methylene groups of the same type.

^b The chemical shifts of the δ,δ' - and ϵ,ϵ' -protons are identical.

^c The chemical shifts of the γ,γ' - and δ,δ' -protons are identical.

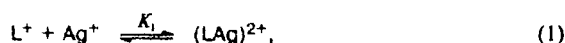
Table 3. Stability constants of complexes of *trans*-3a–f with AgNO₃ in MeCN at 295 K

Compound	logK ₁	Compound	logK ₁
<i>trans</i> -3a	4.1±0.1	<i>trans</i> -3d	4.8±0.1
<i>trans</i> -3b	4.4±0.1	<i>trans</i> -3e	4.9±0.1
<i>trans</i> -3c	4.1±0.1	<i>trans</i> -3f	5.1±0.1

0.07 ppm; this probably indicates that in *trans*-3a, the corresponding O atom participates in the interaction with Hg²⁺ to a greater degree.

It can be assumed that the magnitudes of the complex-formation constants for Ag⁺ and Hg²⁺ vary in parallel with the Δλ and Δδ values in the electronic and ¹H NMR spectra of their complexes with *trans*-3a–f, respectively.

The simplest scheme of complex formation

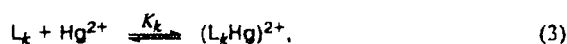
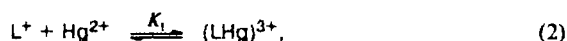


(L⁺ is the cation of *trans*-3a–f; K₁ = [LAG]/([Ag][L]) is the stability constant of the complex) is described by the equation C_{Ag} = α/[K₁(1 - α)] + αC_L, where α is the degree of complexation, C_{Ag} and C_L are the concentrations of AgNO₃ and the ligand (CSD), respectively (see Experimental). The logK₁ values for the (*trans*-3a–f)·Ag⁺ complex are listed in Table 3.

It follows from the data of Table 3 that for dyes containing a dithia-18-crown-6 moiety, the stability constants increase by 0.7 order of magnitude on going from *trans*-3a–c to *trans*-3d–f. Apparently, the size of the cavity and the position of the S atoms in this macroring corresponds to a greater degree to the diameter of the cation and to the most favorable mutual arrangement of the Ag⁺ ion and atoms in the ligand than those in the dithia-15-crown-5 moiety.

It was also found that the magnitudes of the LAB shifts following the complex formation between *trans*-3a–f and the Ag⁺ ion are insensitive to the size of the dithiacrown-ether moiety. At the same time, the Δδ values for the β,β'-protons and logK₁ vary in parallel.

Spectrophotometric titration of solutions of *trans*-3a–f with mercury(II) perchlorate in MeCN made it possible to identify the existence of only one type of complex of the composition 1 L : 1 Hg²⁺. However, in this case, direct spectrophotometric determination of the stability constants of the complexes proved to be impossible, due to their very high magnitudes. For example, according to published data,¹⁸ the logK₁ value for 1,10-dithia-18-crown-6 ether and Hg²⁺ in 0.5 M HNO₃ is equal to 19.5. Therefore, we determined the relative stability constants of (*trans*-3d,f)·Hg²⁺ by the method of titration with a solution of a competing ligand. As the competing ligand we used benzo-1,10-dithia-18-crown-6 ether (BDT18C6). The reaction scheme for this system includes two equilibria.



where L⁺ is the cation from *trans*-3d,f; L_k is BDT18C6.

This scheme corresponds to the equation

$$C_k = [1 + K_1/(K_k\alpha)(1 - \alpha)][C_{Hg} - \alpha C_L - \alpha/(1 - \alpha)/K_1],$$

where C_k, C_{Hg}, and C_L are the overall concentrations of BDT18C6, Hg(ClO₄)₂, and *trans*-3d,f, respectively; K₁ = [LHg]/([Hg][L]) and K_k = [L_kHg]/([Hg][L_k]) are the stability constants of the (*trans*-3d,f)·Hg²⁺ and (BDT18C6)·Hg²⁺ complexes, respectively; α is the degree of complexation of *trans*-3d,f with Hg²⁺, which was calculated from the formula α = (D - D_k)/(D₀ - D_k) (D₀, D, and D_k are the optical densities of the solution at complete complexation with *trans*-3d,f, the current solution, and the solution at the complete complexation with BDT18C6, respectively).

Taking into account the fact that at C_{Hg} = 5 · 10⁻⁵ mol L⁻¹, C_{Hg} ≫ α/(1 - α)/K₁, we obtain the following expression for the K₁/K_k ratio of the stability constants

$$K_1/K_k = [\alpha(C_k - C_{Hg} + \alpha C_L)]/(1 - \alpha)/(C_{Hg} - \alpha C_L).$$

The dots in Fig. 1 show the experimental dependence of (1 - α) on the concentration C_k of the competing ligand added to the (*trans*-3f)·Hg²⁺ complex, while the solid line in the same Figure shows the best

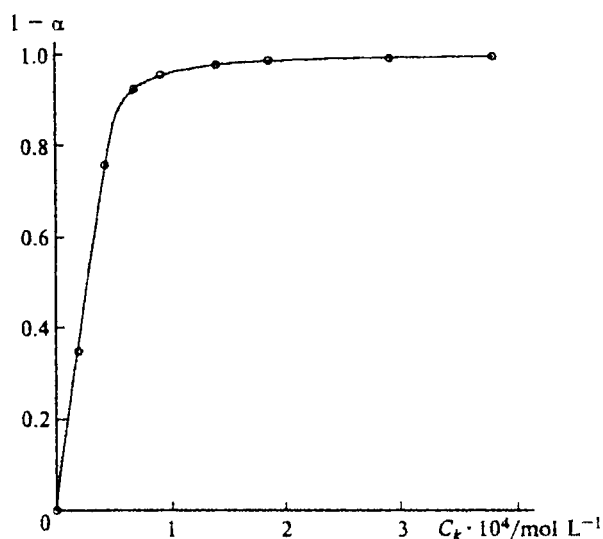


Fig. 1. Dependence of 1 - α (α is the degree of complexation of *trans*-3f) on the concentration of the competing BDT18C6 (C_k) at constant concentrations of *trans*-3f and Hg(ClO₄)₂ (C_L = C_{Hg} = 5 · 10⁻⁵ mol L⁻¹). The solid line shows the best approximation of the experimental dependence by complex formation equations (2) and (3).

approximation of the theoretical curve to the experimental points.

The resulting K_1/K_k values for $(trans-3d) \cdot Hg^{2+}$ and $(trans-3f) \cdot Hg^{2+}$ are 0.040 and 0.035, respectively, i.e., the stability constants of these complexes K_1 are 25 and 29 times smaller than the constant K_k for the complex of BDT18C6 with Hg^{2+} . This can be explained by the fact that on going to the dye, the electron density on the O atoms incorporated in the crown-ether ring and conjugated with the benzene ring substantially decreases, owing to the strong electron-withdrawing effect of the positively charged benzothiazole residue. However, the stability constant of $(trans-1a) \cdot Mg^{2+}$ is almost three orders of magnitude smaller than that for the complex of benzo-15-crown-5 ether with the Mg^{2+} ion (see Ref. 5). These distinctions between the properties of the two types of CSD are due to the fact that the formation of two coordination bonds of the S atoms with Hg^{2+} has a crucial effect on the stability of the $(trans-3d,f) \cdot Hg^{2+}$ complexes. Conversely, the stability of the coordination bonds of the O atoms with Hg^{2+} is, evidently, relatively small, and this hampers appreciably the transfer of the electron-withdrawing effect of the positively charged benzothiazole residue along the conjugation chain.

Thus, styryl dyes containing benzodithia-15(18)-crown-5(6) ether fragments were synthesized for the first time. It was shown that these CSD form the most stable complexes with Ag^+ and Hg^{2+} ions. The corresponding $\log K_1$ values and the relative stability constants were measured. It was found that the variations of the chemical shifts of the β, β' -protons of the CH_2S groups

provide a more adequate evaluation of the efficiency of binding of metal ions with CSD of this type than the hypsochromic shifts of the LAB and are in good agreement with the stability constants of the corresponding complexes.

Experimental

1H NMR spectra were recorded on Bruker AC-200p and Bruker AMX-400 spectrometers using $MeCN-d_3$ and $DMSO-d_6$ as the solvents and $SiMe_4$ as the internal standard. 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 1H chemical shifts ($\Delta\delta$) were determined in $MeCN-d_3$ after the addition of metal salts to solutions of $trans-3a,e,g$ and $trans-1a$ with $C_L = 1 \cdot 10^{-3}$ mol L^{-1} . Metal salts were added until the maximum $\Delta\delta$ values were attained.

IR spectra were recorded on a Shimadzu IR-470 spectrophotometer in KBr. The electronic absorption spectra were obtained on a Shimadzu UV-3100 spectrophotometer at 22 °C. The hypsochromic shifts of the LAB were measured in $MeCN$, $MeOH$, and the $MeOH-H_2O$ (1 : 4) system after the addition of metal salts ($C_M = 5 \cdot 10^{-4}$ mol L^{-1} in $MeCN$ and $5 \cdot 10^{-3}$ mol L^{-1} in the rest of solvents) to solutions of dyes $trans-3a-f$ with the initial concentration $C_L = 5 \cdot 10^{-5}$ mol L^{-1} . The stability constants for the complexes of CSD with $AgNO_3$ and the relative stability constants for the complexes of CSD with $Hg(ClO_4)_2$ in $MeCN$ were determined by spectrophotometric titration: a solution containing a CSD ($C_L = 5 \cdot 10^{-5}$ mol L^{-1}) and $AgNO_3$ or $Hg(ClO_4)_2$ ($C_M = 10^{-3}$ mol L^{-1}) was added to a solution containing the ligand in the same concentration. In the experiments using a competing ligand, a solution containing a CSD and $Hg(ClO_4)_2$ in equal concentrations ($C_L = C_M =$

Table 4. Characteristics of compounds 4b,c and CSD $trans-3a-g$

Compound	M.p. (decomp.) /°C (from MeOH)	Yield (%)	Found — (%)			Molecular formula
			Calculated	C	H	
4b	218—219	21	45.44	4.56	4.48	$C_{12}H_{14}BrNO_2S$
			45.72	4.48	4.45	
4c	208—209	38	47.41	4.96	4.06	$C_{13}H_{16}BrNO_2S$
			47.42	4.90	4.26	
$trans-3a$	229—230	71	50.24	4.93	2.64	$C_{24}H_{28}ClNO_7S_3$
			50.26	4.92	2.44	
$trans-3b$	209—211	37	49.96	4.96	1.73	$C_{27}H_{32}ClNO_9S_3$
			50.23	5.00	2.17	
$trans-3c$	208—210	72	50.90	5.19	1.64	$C_{28}H_{34}ClNO_9S_3$
			50.98	5.20	2.12	
$trans-3d$	232—233	65	50.48	5.27	1.96	$C_{26}H_{32}ClNO_8S_3$
			50.56	5.23	2.27	
$trans-3e$	203—205	64	50.50	5.27	1.77	$C_{29}H_{36}ClNO_{10}S_3$
			50.50	5.26	2.03	
$trans-3f$	185—187	72	50.67	5.41	1.57	$C_{30}H_{38}ClNO_{10}S_3$
			51.20	5.45	1.99	
$trans-3g$	145—147*	83	53.11	5.88	2.12	$C_{30}H_{38}ClNO_{12}S \cdot 0.5H_2O$
			52.90	5.77	2.06	

*Without decomposition.

Table 5. Spectral parameters of compounds 4b,c and *trans*-3a–g

Compound	IR (KBr), $\nu_{\max}/\text{cm}^{-1}$	^1H NMR (DMSO- d_6), δ (J/Hz)
4b	3440 (O–H); 1718 (C=O)	2.10 (m, 2 H, NCH_2CH_2); 2.55 (t, 2 H, COCH_2); 3.23 (s, 3 H, Me); 4.75 (m, 2 H, NCH_2); 7.81, 7.92 (2 m, 2 H, HC(6), HC(5)); 8.40, 8.48 (2 d, 2 H, HC(7), HC(4), $J = 8.0$, $J = 8.1$); 12.38 (br.s, 1 H, COOH)
4c	3360 (O–H); 1714 (C=O)	1.68 (m, 2 H, COCH_2CH_2); 1.90 (m, 2 H, NCH_2CH_2); 2.31 (t, 2 H, COCH_2); 3.21 (s, 3 H, Me); 4.74 (m, 2 H, NCH_2); 7.79, 7.88 (2 m, 2 H, HC(6), HC(5)); 8.32, 8.44 (2 d, 2 H, HC(7), HC(4), $J = 8.5$, $J = 8.2$); 12.20 (br.s, 1 H, COOH)
<i>trans</i> -3a	—	3.00 (m, 4 H, 2 CH_2S); 3.18 (m, 4 H, 2 CH_2S); 3.82 (m, 4 H, 2 CH_2O); 4.42 (m, 7 H, 2 CH_2O , NMe); 7.25 (d, 1 H, HC(5'), $J = 8.5$); 7.73 (d, 1 H, HC(6'), $J = 8.5$); 7.81 (s, 1 H, HC(2')); 7.87, 7.97 (2 m, 2 H, HC(5), HC(6)); 7.98 (d, 1 H, HC(a), $^3J_{\text{trans}} = 16.0$); 8.24 (d, 1 H, HC(b), $^3J_{\text{trans}} = 16.0$); 8.31, 8.49 (2 d, 2 H, HC(7), HC(4), $J = 8.7$, $J = 7.8$)
<i>trans</i> -3b	1722 (C=O)	2.10 (m, 2 H, NCH_2CH_2); 2.50 (t, 2 H, COCH_2); 2.89 (m, 4 H, 2 CH_2S); 3.07 (m, 4 H, 2 CH_2S); 3.71 (m, 4 H, 2 CH_2O); 4.32 (m, 4 H, 2 CH_2O); 4.88 (m, 2 H, NCH_2); 7.17 (d, 1 H, HC(5'), $J = 8.9$); 7.67 (m, 2 H, HC(2'), HC(6')); 7.78, 7.88 (2 m, 2 H, HC(5), HC(6)); 7.87 (d, 1 H, HC(a), $^3J_{\text{trans}} = 15.7$); 8.20 (d, 1 H, HC(b), $^3J_{\text{trans}} = 15.7$); 8.31, 8.42 (2 d, 2 H, HC(7), HC(4), $J = 7.9$, $J = 7.9$)
<i>trans</i> -3c	3440 (O–H); 1723 (C=O)	1.66 (m, 2 H, COCH_2CH_2); 1.88 (m, 2 H, NCH_2CH_2); 2.31, 2.41 (2 t, 2 H, COCH_2); 2.91 (m, 4 H, 2 CH_2S); 3.07 (m, 4 H, 2 CH_2S); 3.71 (m, 4 H, 2 CH_2O); 4.32 (m, 4 H, 2 CH_2O); 4.95 (m, 2 H, NCH_2); 7.16 (d, 1 H, HC(5'), $J = 8.9$); 7.67 (m, 2 H, HC(2'), HC(6')); 7.74–7.89 (m, 3 H, HC(5), HC(6), HC(a)); 8.18 (d, 1 H, HC(b), $^3J_{\text{trans}} = 15.5$); 8.27, 8.40 (2 d, 2 H, HC(7), HC(4), $J = 8.3$, $J = 8.0$)
<i>trans</i> -3d*	—	2.97 (m, 4 H, 2 CH_2S); 3.14 (m, 4 H, 2 CH_2S); 3.59 (s, 4 H, 2 CH_2O); 3.71 (m, 4 H, 2 CH_2O); 4.26 (s, 3 H, NMe); 4.31 (m, 4 H, 2 CH_2O); 7.08 (d, 1 H, HC(5'), $J = 8.1$); 7.46 (d, 1 H, HC(6'), $J = 8.1$); 7.49 (s, 1 H, HC(2')); 7.56 (d, 1 H, HC(a), $^3J_{\text{trans}} = 15.7$); 7.77, 7.87 (2 m, 2 H, HC(6), HC(5)); 8.02, 8.20 (2 d, 2 H, HC(7), HC(4), $J = 8.5$); 8.04 (d, 1 H, HC(b), $^3J_{\text{trans}} = 15.7$)
<i>trans</i> -3e*	3408 (O–H); 1724 (C=O)	2.34 (m, 2 H, NCH_2CH_2); 2.63 (t, 2 H, COCH_2); 2.96 (t, 4 H, 2 CH_2S); 3.14 (m, 4 H, 2 CH_2S); 3.59 (s, 4 H, 2 CH_2O); 3.71 (m, 4 H, 2 CH_2O); 4.33 (m, 4 H, 2 CH_2O); 4.76 (m, 2 H, NCH_2); 7.09 (d, 1 H, HC(5'), $J = 8.4$); 7.47 (d, 1 H, HC(6'), $J = 8.4$); 7.58 (s, 1 H, HC(2')); 7.74 (d, 1 H, HC(a), $^3J_{\text{trans}} = 15.5$); 7.77, 7.87 (2 m, 2 H, HC(5), HC(6)); 8.08 (d, 1 H, HC(b), $^3J_{\text{trans}} = 15.5$); 8.13, 8.20 (2 d, 2 H, HC(7), HC(4), $J = 7.9$, $J = 7.9$)
<i>trans</i> -3f	3424 (O–H); 1722 (C=O)	1.68 (m, 2 H, COCH_2CH_2); 1.89 (m, 2 H, NCH_2CH_2); 2.31, 2.41 (2 t, 2 H, COCH_2); 2.91 (t, 4 H, 2 CH_2S); 3.10 (m, 4 H, 2 CH_2S); 3.53 (s, 4 H, 2 CH_2O); 3.64 (t, 4 H, 2 CH_2O); 4.25 (m, 4 H, 2 CH_2O); 4.95 (m, 2 H, NCH_2); 7.16 (d, 1 H, HC(5'), $J = 8.6$); 7.64 (s, 1 H, HC(2')); 7.66 (d, 1 H, HC(6'), $J = 8.6$); 7.77, 7.86 (2 m, 2 H, HC(5), HC(6)); 7.84 (d, 1 H, HC(a), $^3J_{\text{trans}} = 15.5$); 8.20 (d, 1 H, HC(b), $^3J_{\text{trans}} = 15.5$); 8.27, 8.40 (2 d, 2 H, HC(7), HC(4), $J = 8.3$, $J = 8.1$)
<i>trans</i> -3g	3420 (O–H); 1723 (C=O)	1.72 (m, 2 H, COCH_2CH_2); 1.94 (m, 2 H, NCH_2CH_2); 2.33, 2.41 (2 t, 2 H, COCH_2); 3.60 (m, 12 H, 6 CH_2O); 3.84 (m, 4 H, 2 CH_2O); 4.26 (m, 4 H, 2 CH_2O); 4.94 (m, 2 H, NCH_2); 7.16 (d, 1 H, HC(5'), $J = 8.9$); 7.63 (d, 1 H, HC(6')); 7.65 (s, 1 H, HC(2')); 7.74–7.91 (m, 3 H, HC(a), HC(5), HC(6)); 8.15 (d, 1 H, HC(b), $^3J_{\text{trans}} = 15.6$); 8.25, 8.39 (2 d, 2 H, HC(7), HC(4), $J = 8.1$, $J = 7.7$)

* The ^1H NMR spectrum was recorded in CD_3CN .

$5 \cdot 10^{-5}$ mol L^{-1}) and BDT18C6 ($C_k = 10^{-2}$ mol L^{-1}) was added to a solution containing the CSD and $\text{Hg}(\text{ClO}_4)_2$ in the same concentrations. The ionic strength of the solution during titration was $2 \cdot 10^{-4}$ mol L^{-1} .

The degree of complexation of *trans*-3a–f with AgNO_3 was calculated from the equation $\alpha = (D_0 - D)/(D_0 - D_c)$, where D_0 , D , and D_c are the optical densities of the initial solution of the dye, of the current solution, and of the solution at the complete complexation, respectively. The measurements were carried out at $\lambda = 460$ nm at which $D_c \ll D_0$. The ionic strength of the solution varied during titration from $5 \cdot 10^{-5}$ to 10^{-3} mol L^{-1} . The solutions were prepared and all the experiments were carried out in red light in order to prevent the formation of the *cis*-isomers of the dyes and their complexes.

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

The steady-state fluorescence spectra were measured on a Shimadzu RF-5000 spectrofluorimeter. The quantum yields of fluorescence (φ_f) were determined with respect to fluorescein in 0.01 *M* aqueous KOH with excitation with light at $\lambda = 365$ nm (the inaccuracy was ~15%).

The MeCN needed for spectroscopy was first distilled over KMnO_4 , then twice distilled over P_2O_5 , and finally distilled over CaH_2 ; MeOH was used without additional purification; salts $\text{Mg}(\text{ClO}_4)_2$ and $\text{Cd}(\text{ClO}_4)_2$ were dried *in vacuo* at 230 and 120 °C, respectively; AgNO_3 (chemically pure) and $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ (Aldrich) were used as received; $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$

(chemically pure) and $\text{Hg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (Aldrich) were dried *in vacuo* at 40 °C.

3-(4-Carboxybutyl)-2-methylbenzothiazolium bromide (4c). A mixture of δ -bromovaleric acid (1.0 g, 5.53 mmol) and 2-methylbenzothiazole **6** (2.1 mL, 16.5 mmol) was heated for 6 h at 120 °C. The reaction mixture was washed with a 1 : 2 MeCN–benzene mixture, and the insoluble residue was chromatographed on a column with SiO_2 (L 40/100, Chemapol); the elution was carried out successively with MeCN and a 2 : 1 MeCN–MeOH mixture to give 2-methylbenzothiazolium bromide **7**. The ^1H NMR spectrum of compound **7** (400 MHz, DMSO- d_6) [δ : 2.91 (s, 3 H, Me); 7.49, 7.58 (2 m, 2 H, HC(6), HC(5)); 8.00, 8.14 (2 d, 2 H, HC(7), HC(4), $J = 8.0$ Hz, $J = 7.9$ Hz)] was identical to that of an authentic sample. The second fraction containing a crude product was evaporated *in vacuo*, the residue was triturated with hot MeCN, and the solid product was filtered off to give 0.69 g of compound **4c**.

The reaction of γ -bromobutyric acid with 2-methylbenzothiazole (6). A mixture of γ -bromobutyric acid (1.31 g, 7.85 mmol) and 2-methylbenzothiazole **6** (3.0 mL, 23.6 mmol) was heated for 6 h at 120 °C. The reaction mixture was washed with benzene, and the insoluble material was chromatographed on a column with SiO_2 (L 40/100, Chemapol); the elution was carried out with a 2 : 1 MeCN–EtOH mixture to give 1.013 g (56%) of 2-methylbenzothiazolium bromide **7**.

3-(3-Carboxypropyl)-2-methylbenzothiazolium bromide (4b). A mixture of ethyl γ -bromobutyrate (0.70 mL, 4.89 mmol) and 2-methylbenzothiazole **6** (1.25 mL, 9.83 mmol) was heated for 6 h at 120 °C. The reaction mixture was washed with benzene, 4 mL of 24% HBr was added, and then the mixture was heated for 6 h at 55 °C. The aqueous solution was concentrated *in vacuo*, the residue was extracted with MeCN, the extract was concentrated *in vacuo*, and the residue was chromatographed on a column with SiO_2 (L 40/100, Chemapol); the elution was successively carried out with a 20 : 1 MeCN–EtOH mixture and a 10 : 1 MeCN–EtOH mixture to give 0.33 g of compound **4b**.

Synthesis of dyes *trans*-3a–g (general procedure). A mixture of 0.11 mmol of quaternary salt **4a–c** and 0.12 mmol of 4'-formylbenzocrown ether **5a,d,g** was dissolved in 2 mL of anhydrous EtOH, 0.3 mL of dry pyridine was added, and the mixture was refluxed for 6 h. The solvent was evaporated *in vacuo*, the residue was washed with benzene and dissolved in the minimum quantity of hot MeOH, and 57% HClO_4 (0.05 mL, 0.44 mmol) was added. The precipitate that formed on cooling was filtered off to give compounds *trans*-3a–g as orange or red crystals.

The main physicochemical characteristics of these compounds and the parameters of their ^1H NMR and IR spectra are listed in Tables 4 and 5, respectively.

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