Crown-containing butadienyl dyes
8.* Structures and complexation of chromogenic dithia-15(18)-crown-5(6) ethers

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The structures of new butadienyl dyes of the benzothiazole series containing the dithia-15-crown-5 (**2a**) or dithia-18-crown-6 (**2b**) fragments were established by X-ray diffraction. Complexation of dyes **2a**,**b** with Hg^{2+}, Pb^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, and alkaline-earth cations in aqueous-acetonitrile solutions was studied by spectrophotometry. At a high percentage of water in solutions ($P_w \approx 50\%$), these dyes have a very low ability to bind Pb^{2+} cations ($\log K < 2$) and virtually do not bind Cd^{2+}, Zn^{2+}, and alkaline-earth cations. At the same time, these dyes form stable 1 : 1 complexes with Hg^{2+} and Ag^+ cations at all P_w. The stability constants of complexes with the Ag^+ cation increase with increasing P_w because the free energy of hydration of this cation is much lower than the free energy of solvation in acetonitrile. In the P_w range from 0 to 75%, the stability constants of the complexes of dyes **2a**,**b** with the Hg^{2+} cation are larger than those of the corresponding complexes with the Ag^+ cation by more than four orders of magnitude.

Key words: dithiacrown ethers, butadienyl dyes, chromoionophores, X-ray diffraction, complexation, stability constants, mercury, silver, lead.

Crown ethers were first synthesized by Pedersen.[2] These compounds have found wide use in different fields of chemistry due to their ability to selectively bind alkali and alkaline-earth cations. In particular, first selective reagents for the photometric determination of alkali cations were constructed based on crown ethers.[3,4] Most of the known chromogenic crown ethers (chromoionophores) can be divided according to the mechanism of the metallochromic effect into two main groups.[5,6] One of these groups includes systems, in which the color changes occur due to bond dissociation in the chromophoric frag-ment upon coordination of a metal cation to the macro-cycle. Another group includes crown ethers containing a chromophoric fragment, which exists as a conjugated do-nor—acceptor pair. In these systems, coordination of a metal cation to the macrocycle can cause a substantial electron density redistribution in the chromophoric frag-ment and, as a consequence, the hypsochromic or batho-chromic effect. The direction of color changes depends on which fragment of the chromophore (donor or accep-tor) is bound to the polyether macrocycle. Crown-con-taining styryl and butadienyl dyes are examples of chromo-ionophores, which show cation-induced hypsochromic shifts.[7—9]

The properties of chromogenic crown ethers as selec-tive reagents for the colorimetric determination of alkali and alkaline-earth cations are rather well studied, whereas
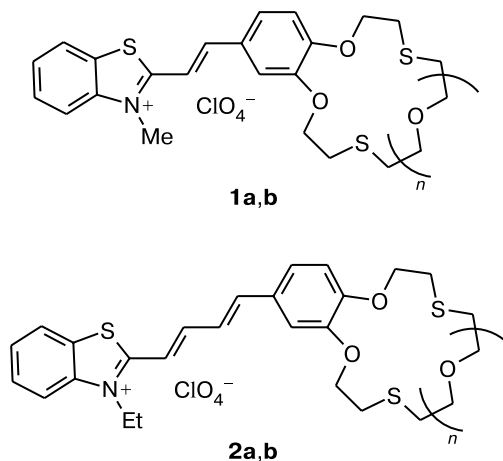
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the possibilities of the use of macrocyclic ligands for the design of optical molecular chemosensors for transition and heavy metal cations were not fully explored.

It is known[10] that the replacement of one or several oxygen atoms in crown ethers with other donor atoms can substantially change the ability of the ligand to bind metal cations. For example, 1,10-dithia-18-crown-6 ether has a very low affinity for alkali cations compared to 18-crown-6 ether but, at the same time, it forms much more stable complexes with Hg^{2+} and Ag^+ both in organic solvents and water.[10,11] Earlier,[12—14] attempts have been made to use the selective properties of thiacrown ethers for the construction of photoswitchable ligands and chromogenic reagents for heavy metal cations. It was demonstrated that styryl dyes containing the dithia-15-crown-5 (**1a**) or dithia-18-crown-6 (**1b**) fragment selectively bind Hg^{2+} ions in acetonitrile. Complexation is accompanied by the hypsochromic effect, which is, however, substantially smaller than that observed in the reactions of alkaline-earth cations with analogous systems based on crown ethers.

From the practical standpoint, it was of interest to examine the influence of the medium on the selectivity of complexation of chromoionophores of types **1a,b** and the cation-induced hypsochromic effect. For this purpose, we synthesized new chromogenic dithiacrown ethers **2a,b** based on butadienyl dyes of the benzothiazole series. Experimental data obtained earlier for chromogenic crown ethers demonstrated[9] that the replacement of the styryl chromophore with the butadienyl moiety leads not only to a substantial bathochromic shift of the S_0—S_1 absorption band of the chromoionophore but also to a substantial increase in the molar absorption coefficient.

1a,b

2a,b

$n = 1$ (**a**), 2 (**b**)

In the present study, we established the structures of chromogenic dithiacrown ethers **2a,b** by X-ray diffraction data and investigated complexation of these ligands with Hg^{2+}, Pb^{2+}, Cd^{2+}, Ag^+, Zn^{2+}, and alkaline-earth cations in aqueous-acetonitrile solutions containing different percentages of water by spectrophotometry.

X-ray diffraction study

The crystal structures of **2a** and **2b · MeCN** are shown in Figs 1 and 2, respectively. The main geometric parameters of the chromophoric fragments of **2a,b** are given in Table 1. In the structure of **2a**, the crown ether macrocycle is disordered over two positions of the C(1)—C(2)—S(1)—C(3)—C(4)—O(2)—C(5) chain be-
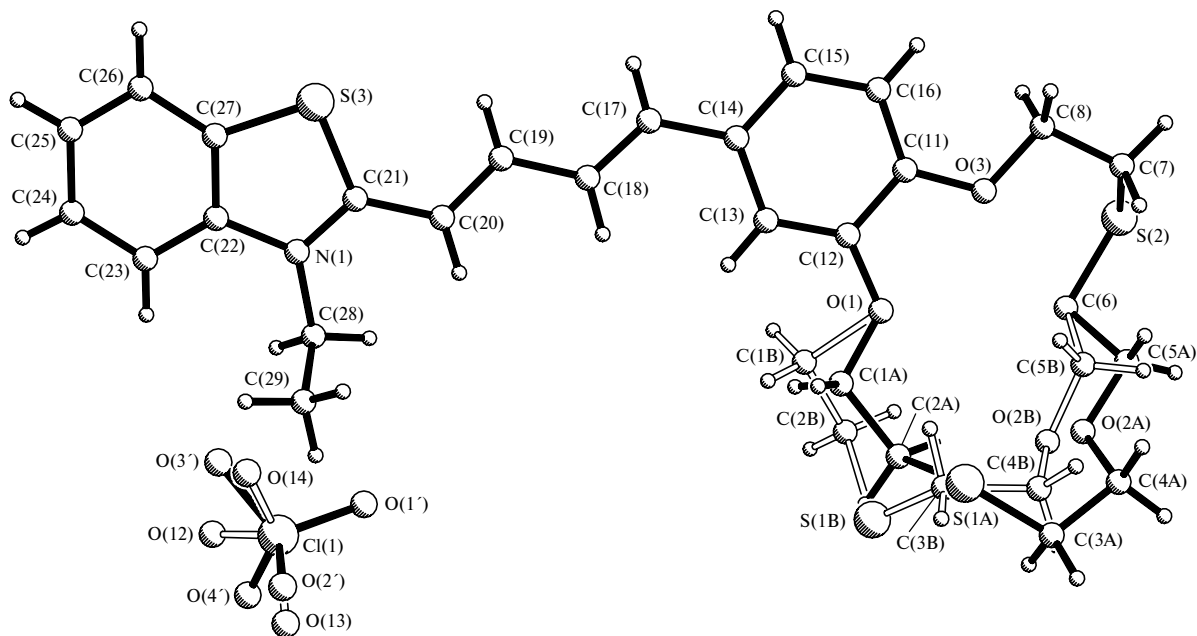

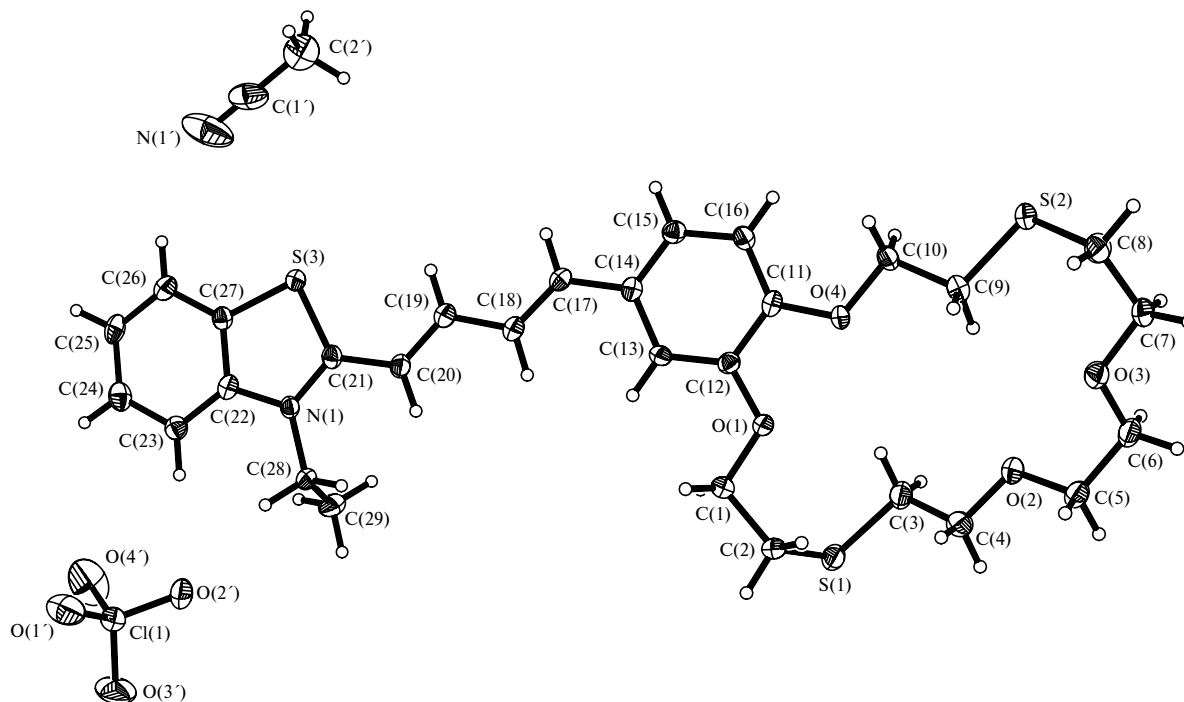**Fig. 1.** Crystal structure of **2a**.

Fig. 2. Crystal structure of **2b · MeCN**.

tween the O(1) and C(6) atoms. The perchlorate anion in this structure is also disordered over several positions. In spite of the fact that this disorder decreases the accuracy of X-ray diffraction data for **2a**, a comparison of the geometric parameters of the chromophoric fragments of molecules **2a** and **2b** made it possible to reveal the general

Table 1. Selected bond lengths (*d*) and bond angles (ω) in the chromophoric fragments of **2a** and **2b**

Parameter	2a	2b
Bond		*d*/Å
O(1)—C(12)	1.377(7)	1.365(4)
O(3)—C(11)	1.357(6)	1.358(4)
C(11)—C(12)	1.413(7)	1.411(4)
C(12)—C(13)	1.367(8)	1.369(4)
C(13)—C(14)	1.434(8)	1.416(4)
C(14)—C(15)	1.387(9)	1.383(4)
C(15)—C(16)	1.399(7)	1.393(4)
C(16)—C(11)	1.386(7)	1.383(4)
C(14)—C(17)	1.448(8)	1.454(4)
C(17)—C(18)	1.357(9)	1.348(4)
C(18)—C(19)	1.428(8)	1.426(4)
C(19)—C(20)	1.365(8)	1.352(4)
C(20)—C(21)	1.437(7)	1.429(4)
Angle		ω/deg
O(1)—C(12)—C(11)	114.5(5)	113.8(3)
O(1)—C(12)—C(13)	125.2(5)	125.7(3)
O(3)/O(4)—C(11)—C(12)	115.9(4)	115.0(3)
O(3)/O(4)—C(11)—C(16)	124.7(4)	124.4(3)

tendencies concerning the deviations of these parameters from the standard values.

In both organic cations, a pronounced alternation of the bonds in the benzene ring of the benzothiacrown moiety and a substantial localization of the double bonds in the butadiene fragment are observed. In addition, the changes observed in the exocyclic bond angles at the C(11) and C(12) atoms of the benzene ring, which are involved in two cyclic systems, are typical of benzocrown systems.[9,15] In molecules **2a,b**, the O(1)—C(12)—C(13) and O(3)/O(4)—C(11)—C(16) bond angles are larger (~125°), whereas the O(1)—C(12)—C(11) and O(3)/O(4)—C(11)—C(12) bond angles are smaller (~115°). The chromophoric fragment in both organic cations is nearly planar. The dihedral angle between the planar benzene and butadiene fragments is 2.0(4) and 3.5(2)° for **2a** and **2b**, respectively, and the dihedral angle between the planar butadiene and benzothizazole fragments is 9.6(4) and 1.6(2)° for **2a** and **2b**, respectively.

In the macrocyclic fragment of molecule **2b**, both sulfur atoms deviate from the plane of the macrocycle, which is the characteristic structural property of thiacrown ethers in single crystals.[10,13] If the macrocycle adopts this geometry, the orbitals of the lone pairs of the sulfur atoms should point away from the center of the macrocycle. Taking into account also a rather large distance between the S(1) and S(2) atoms (7.75 Å), it can be concluded that the conformation of the dithiacrown macrocycle observed in the crystals of **2b · MeCN** is unfavorable for the formation of inclusion complexes with heavy metal cat-

ions. An analogous conclusion is true for one of the conformers of the macrocyclic fragment of molecule **2a** (see Fig. 1, the S(2) and S(1B) atoms).

Below, we consider the data on efficient complexation of **2a**,**b** with heavy metal cations in solution. These data suggest that the dithiacrown systems of these dyes are rather flexible due to which they can rather easily adopt conformations favorable for the formation of inclusion complexes. This assumption agrees well with the fact that this macrocycle exists in two conformations in the crystal structure of **2a**.

Spectrophotometric study

In acetonitrile, the spectra of dyes **2a**,**b** show broad S_0—S_1 absorption bands with maxima at ~457 and 460 nm, respectively, and the extinction coefficients of ~54000 L mol^{-1} cm^{-1}. In the spectra of **2a** and **2b** measured in aqueous solutions, the S_0—S_1 band is shifted hypsochromically by 17 and 20 nm, respectively, and the extinction coefficients decrease by approximately 10%. The hypsochromic effect observed with increasing polarity of the solvent indicates that the S_0—S_1 electronic transition in cations **2a** and **2b** leads to the positive charge delocalization,[16] *i.e.*, to a shift of a part of the charge from the benzothiazole fragment to the benzodithiacrown fragment. Evidently, the charge-transfer excited state should be destabilized upon coordination of a metal cation to the dithiacrown fragment of the dye. Complexation of **2a**,**b** with metal cations would be expected to be accompanied by a hypsochromic shift of the S_0—S_1 band of the dye.

First, we studied the influence of metal perchlorates on the absorption spectra of aqueous-acetonitrile solutions of dyes **2a**,**b** (~10^{-5} mol L^{-1}) with a percentage of water $P_w = 50\%$ (v/v). The presence of Hg^{II} or Ag^I perchlorates at $C_M = 1 \cdot 10^{-3}$ mol L^{-1} causes a substantial hypsochromic shift of the S_0—S_1 absorption band of dyes **2a**,**b**. This shift remained unchanged as C_M was further increased, which is evidence that Hg^{2+} and Ag$^+$ ions form rather stable complexes involving the dithiacrown fragment. By contrast, the presence of Zn^{II}, Cd^{II}, Pb^{II}, or alkaline-earth perchlorates at $C_M = 1 \cdot 10^{-3}$ mol L^{-1} has virtually no effect on the shape and position of the S_0—S_1 absorption band of dyes **2a**,**b**. An increase in C_M in these systems to 0.1 mol L^{-1} was accompanied by only slight spectral changes. The exception is the **2b**/Pb(ClO$_4$)$_2$ system, in which a substantial hypsochromic effect was observed at $C_M > 0.01$ mol L^{-1}. This effect was attributed to the formation of a 1 : 1 complex with the stability constant $K < 100$ L mol^{-1}.

Therefore, preliminary experiments demonstrated that dyes **2a**,**b** have a low ability to bind Pb^{2+} and virtually do not bind Cd^{2+}, Zn^{2+}, and alkaline-earth cations in solutions containing a high percentage of water. At the same

Table 2. Positions of the maximum (λ_{max}) of the S_0—S_1 absorption band for dyes **2a**,**b** and the hypsochromic shifts ($\Delta\lambda_{max}$)* for the complexes **2a**,**b**·Ag$^+$, **2a**,**b**·Hg^{2+}, and **2b**·Pb^{2+} in acetonitrile, water, and an aqueous-acetonitrile solution at $P_w = 50\%$

Compound	$\Delta\lambda_{max}$ (λ_{max})/nm		
	MeCN	MeCN/H$_2$O	H$_2$O
2a	(457)	(453)	(440)
2a·Ag$^+$	10.5	8	3.5
2a·Hg^{2+}	23	17	10
2b	(460.5)	(455)	(440.5)
2b·Ag$^+$	10	6.5	1.5
2b·Hg^{2+}	20	13.5	5
2b·Pb^{2+}	20.5	—	—

* $\Delta\lambda_{max} = \lambda_{max}$(dye) — λ_{max}(complex).

time, these dyes easily form complexes with Hg^{2+} and Ag$^+$ with the participation of the dithiacrown fragment.

The influence of the percentage of water P_w on the thermodynamic stability of the complexes in the **2a**,**b**/Ag$^+$, **2a**,**b**/Hg^{2+}, and **2b**/Pb^{2+} systems was studied by spectrophotometric titration. The percentage P_w was varied from 0 to 75% or from 0 to 50% for dyes **2a** and **2b**, respectively. It was difficult to perform experiments at higher P_w because of poor solubility of the dyes and a rather weak hypsochromic effect (particularly, in the case of compound **2b**, see Table 2). The total concentration of the dye remained unchanged during spectrophotometric titration and was $1 \cdot 10^{-5}$ mol L^{-1} (1-cm cell) or $2 \cdot 10^{-6}$ mol L^{-1} (5-cm cell). The total concentration of metal perchlorate was varied from 0 to 0.01 mol L^{-1}. The solutions contained HClO$_4$ (0.01 mol L^{-1}). The presence of the acid prevents hydrolysis of the complexes with heavy metal cations in aqueous solutions. Preliminary, it has been established that perchloric acid has virtually no effect on the absorption spectra of dyes **2a**,**b**.

The spectra of solutions of **2a**,**b**, which were measured depending on the concentration of the metal salt, were analyzed by methods of matrix algebra as described in the study.[8] It was found that the complexation of **2b** with Pb^{2+} and of **2a**,**b** with Ag$^+$ and Hg^{2+} under these experimental conditions can be described by the equilibrium

$$L + M \xrightleftharpoons{K} LM,$$

where L is the dye molecule, M is the metal cation, and K is the stability constant of the complex.

The absorption spectra of dye **2a** and the complexes **2a**·Ag$^+$ and **2a**·Hg^{2+} in acetonitrile are shown in Fig. 3. The values of λ_{max} for the S_0—S_1 absorption band of dyes **2a**,**b** and the hypsochromic effects, $\Delta\lambda_{max} = \lambda_{max}$(dye) — λ_{max}(complex), for the complexes **2a**,**b**·Ag$^+$ and **2a**,**b**·Hg^{2+} in water, acetonitrile, and an aqueous-aceto-nitrile solution with $P_w = 50\%$ are given in Table 2. The
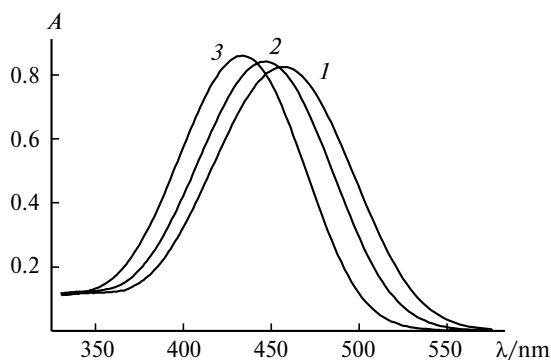
Fig. 3. Electronic absorption spectra of dye **2a** (*1*) and the complexes **2a·Ag⁺** (*2*) and **2a·Hg²⁺** (*3*) in acetonitrile at a concentration of $3 \cdot 10^{-6}$ mol L^{-1} ($l = 5$ cm).

Table 3. Stability constants (log$K$) of the complexes **2a·Ag⁺**, **2b·Ag⁺**, and **2b·Pb²⁺** in aqueous-acetonitrile solutions containing different percentages of water

P_w (vol.%)	log$K$*		
	2a·Ag⁺	**2b·Ag⁺**	**2b·Pb²⁺**
0	4.77	5.35	6.43
10	4.94	5.51	2.1
50	5.68	6.33	<2
75	6.46	—	—

* In the presence of HClO$_4$ (0.01 mol L^{-1}) at 22±2 °C; the total measurement error of the stability constants was ~20%.

stability constants of the complexes **2a·Ag⁺**, **2b·Ag⁺**, and **2b·Pb²⁺** in aqueous-acetonitrile solutions with different P_w are presented in Table 3. The stability constants of the complexes **2a·Hg²⁺** and **2b·Hg²⁺** were found to be higher than 10^7 L mol^{-1} at all P_w.

The hypsochromic effects for the complexes of dyes **2a,b** in acetonitrile appeared to be slightly larger than those observed for the corresponding complexes of styryl dyes **1a,b**. For the latter, $\Delta\lambda_{max}$ are 8—9 and 16 nm in the case of Ag⁺ and Hg²⁺, respectively. The hypsochromic effect decreases with increasing P_w to an extent that dyes **2a,b** in water do no act as chromoionophores.

The stability constants of the complexes **2a·Ag⁺**, **2b·Ag⁺**, and **2b·Pb²⁺** in acetonitrile are several times larger than those of the corresponding complexes of styryl dyes **1a,b** (log$K$ = 5.6 (**1b·Pb²⁺**),[14] 4.1 (**1a·Ag⁺**), and 4.8 (**1b·Ag⁺**)[12]). An analogous effect, *viz.*, an increase in the thermodynamic stability of complexes after the replacement of the styryl chromophore with the butadienyl moiety has been observed earlier[9] for complexes of chromogenic 15-crown-5 ethers with alkaline-earth metal cations. This effect is attributed to the fact that an elongation of the polymethine chain in the positively charged chromophoric fragment of crown ethers leads to an increase in the degree of charge delocalization and, consequently, to a weakening of the Coulomb repulsion between the chromophore fragment and the metal cation.

The thermodynamic stability of the complexes of dyes **2a,b** with Ag⁺ noticeably increases with increasing percentage of water in solution. By contrast, the stability constant of the complex **2b·Pb²⁺** decreases by more than four orders of magnitude as P_w increases from 0 to 10%. Due to the contrast character of the plots of log$K$ *vs.* P_w for the complexes **2b·Ag⁺** and **2b·Pb²⁺**, the selectivity of ligand **2b** changes with a change in the nature of the medium. At P_w = 50%, this dithiacrown ether has a high selectivity with respect to Ag⁺ compared to Pb²⁺, whereas this ether binds predominantly Pb²⁺ ions in anhydrous acetonitrile.

It is known that solvation of metal cations has a substantial effect on both the thermodynamic stability of the complexes with crown ethers and the selectivity of complexation.[17] Presumably, the observed dependence of the selectivity of ligand **2b** on the nature of the medium is attributed primarily to the difference in the solvation characteristics of the Ag⁺ and Pb²⁺ ions.

Experimental data on the thermodynamics of the transfer of Ag⁺, Pb²⁺, and Hg²⁺ ions from acetonitrile into water were published in the literature. For Pb²⁺, the Gibbs free energy of the transfer from acetonitrile into water, $\Delta_t G$(AN→W), is negative (~−42 kJ mol^{-1}),[18] *i.e.*, this cation is much better hydrated than solvated with acetonitrile. To the contrary, the Ag⁺ ion is predominantly solvated with acetonitrile because $\Delta_t G$(AN→W) for Ag⁺ is positive (according to different estimates, it is 22—25 kJ mol^{-1}, see Refs 18 and 19). Therefore, the direction and magnitude of the change in log$K$ with increasing P_w for the complexes **2b·Ag⁺** and **2b·Pb²⁺** correlate, respectively, with the sign and value of $\Delta_t G$(AN→W) for the Ag⁺ and Pb²⁺ ions.

It is known that complexes of dithiacrown ethers with Hg²⁺ in acetonitrile are characterized by very high thermodynamic stability. For example, the values of log$K$ for the complexes **1a·Hg²⁺** and **1b·Hg²⁺** determined by the polarographic method are 15.9 and 18.2, respectively.[14] Even larger values of log$K$ are possible for Hg²⁺ complexes with butadienyl dyes **2a,b**. However, the thermodynamic stability of these complexes in aqueous solutions should decrease because of the preferential hydration of Hg²⁺ ions (see Refs 18 and 20) and, correspondingly, the selectivity of ligands **2a,b** with respect to Hg²⁺ compared to Ag⁺ should decrease. However, it is impossibe to predict the extent of these changes because the published data on $\Delta_t G$(AN→W) for Hg²⁺ are substantially different (vary from −3 to −48 kJ mol^{-1} depending on the method of measurements[18,20]).

We attempted to estimate the ratio of the stability constants of the complexes with Hg²⁺ and Ag⁺, K_{Hg}/K_{Ag}, for **2a,b** in solutions containing a high percentage of water (50—75%) by spectrophotometric titration. In the course

of spectrophotometric titration, the total concentrations of the dye and $AgClO_4$ were maintained at $1 \cdot 10^{-5}$ and 0.01 mol L^{-1}, respectively. The $Hg(ClO_4)_2$ concentration was varied from 0 to $1 \cdot 10^{-4}$ mol L^{-1}. All solutions contained $HClO_4$ (0.01 mol L^{-1}). Analysis of the results of spectrophotometric titration demonstrated that K_{Hg}/K_{Ag} for both dyes are larger than the measurement limit ($\sim 10^4$) even at $P_w = 75\%$.

In conclusion, the conformations of the dithiacrown macrocycles in the crystals of **2a** and **2b** · MeCN are unfavorable for the formation of inclusion complexes with heavy metal cations. However, this fact does not hinder the formation of stable complexes of dyes **2a,b** with Hg^{2+} and Ag^+ ions in solutions, which is attributed to a rather high conformational flexibility of the dithiacrown macrocycles. The complexation is accompanied by a substantial hypsochromic effect. In aqueous-acetonitrile solutions containing a high percentage of water ($P_w \sim 50\%$), dyes **2a,b** exhibit a very high selectivity with respect to Hg^{2+} or Ag^+ compared to Pb^{2+}, Cd^{2+}, Zn^{2+}, and alkaline-earth cations. The thermodynamic stability of the complexes of **2a,b** with Ag^+ increases with increasing P_w. This is associated with the fact that the free energy of hydration of the Ag^+ ion is much lower than the free energy of solvation in acetonitrile. In the P_w range from 0 to 75%, the stability constants of the complexes of **2a,b** with Hg^{2+} are larger than those of the corresponding complexes with Ag^+ by more than four orders of magnitude. These results show that dyes **2a,b** can be used as optical molecular chemosensors for Hg^{2+} and Ag^+ ions in aqueous-organic media.

Experimental

3-Ethyl-2-[(1*E*,3*E*)-4-(2,3,5,6,8,9,11,12-octahydro-1,7,13,4,10-benzotrioxadithiacyclopentadecyn-15-yl)-1,3-butadienyl]-1,3-benzothiazolium perchlorate (**2a**) and 3-ethyl-2-[(1*E*,3*E*)-4-(2,3,5,6,8,9,11,12,14,15-decahydro-1,7,10,16,4,13-benzotetraoxadithiacyclooctadecyn-18-yl)-1,3-butadienyl]-1,3-benzothiazolium perchlorate (**2b**) were prepared by condensation of the corresponding dithiacrown-containing cinnamaldehydes[21] with 3-ethyl-2-methylbenzothiazolium perchlorate in ethanol. The synthesis will be described in detail elsewhere. Perchloric acid and the salts $AgClO_4 \cdot H_2O$, $Hg(ClO_4)_2 \cdot 4H_2O$, $Pb(ClO_4)_2 \cdot 3H_2O$, $Cd(ClO_4)_2 \cdot 6H_2O$, and $Zn(ClO_4)_2 \cdot 6H_2O$ (Sigma-Aldrich) were used without additional purification. Solutions were prepared with the use of bidistilled water and acetonitrile of special purity grade-0 (Kriokhrom).

X-ray diffraction study. Crystals of **2a** and **2b** · MeCN were grown by slow saturation of acetonitrile solutions of the dyes with benzene vapor at room temperature. Single crystals of the dyes were coated with a perfluorinated oil and mounted on a Bruker SMART-CCD diffractometer under a stream of cold nitrogen. The experimental X-ray intensity data sets were collected from single crystals (Mo-Kα radiation) using the ω-scanning technique. The X-ray intensity data were processed using the Bruker SAINT software.[22] The structures of **2a** and **2b** · MeCN were solved by direct methods and refined by the full-matrix

Table 4. Crystallographic data and characteristics of X-ray diffraction study for compounds **2a** and **2b** · MeCN

Compound	**2a**	**2b** · MeCN
Molecular formula	$C_{27}H_{32}ClNO_7S_3$	$C_{31}H_{39}ClN_2O_8S_3$
Molar weight/g mol^{-1}	614.17	699.27
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$C2/c$
a/Å	14.6336(8)	45.6357(16)
b/Å	10.6202(6)	8.3550(3)
c/Å	18.5711(10)	18.1476(6)
β/deg	94.284(3)	103.630(3)
V/Å^3	2878.1(3)	6724.6(4)
Z	4	8
ρ_{calc}/g cm^{-3}	1.417	1.381
$F(000)$	1288	2944
μ(Mo-Kα)/mm^{-1}	0.396	0.351
Crystal dimensions/mm	0.30×0.20×0.10	0.28×0.22×0.06
T/K	120.0(2)	120.0(2)
Radiation/Å	Mo-Kα	
λ/nm	0.71073	
Scan mode	ω	ω
Scan range, θ/deg	2.20—28.00	0.92—28.00
Ranges of indices	$-19 \le h \le 18$	$-54 \le h \le 60$
of measured reflections	$-13 \le k \le 14$	$-11 \le k \le 11$
	$-24 \le l \le 20$	$-19 \le l \le 23$
Number of measured reflections	20206	25644
Number of independent reflections	6927	8096
R_{int}	0.0938	0.0710
Number of reflections with $I > 2\sigma(I)$	5196	8096
Number of parameters in refinement	444	410
R factors based on reflections with $I > 2\sigma(I)$: $\quad R_1$	0.1160	0.0558
$\quad wR_2$	0.2515	0.1425
based on all reflections: $\quad R_1$	0.1428	0.1100
$\quad wR_2$	0.2617	0.1601
Goodness-of-fit on F^2	1.130	1.041
Residual electron density (min/max)/e Å^{-3}	−0.402/0.665	−0.365/0.464

least-squares method against F^2 with anisotropic displacement parameters for all nonhydrogen atoms. The positions of the hydrogen atoms were calculated geometrically and refined using a riding model. All calculations were carried out with the use of the SHELXTL-Plus program package.[23] The crystallographic parameters and characteristics of X-ray diffraction study are given in Table 4. The atomic coordinates and other experimental data for the structures of **2a** and **2b** · MeCN were deposited with the Cambridge Crystallographic Data Center.*

Spectrophotometry. The absorption spectra were recorded on a Specord-M40 spectrophotometer in the 330—500 nm re-

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gion with a step of 80 cm^{-1} at room temperature. Solutions of dyes **2a**,**b** were prepared in a dark room under red light because the dyes underwent *trans-cis* photoisomerization under sunlight.

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