

Synthesis, complexation, and *E–Z* photoisomerization of azadithiacrown-containing styryl dyes as new optical sensors for mercury cations

E. V. Tulyakova,^{a*} O. A. Fedorova,^b Yu. V. Fedorov,^b G. Jonusauskas,^c
L. G. Kuz'mina,^d J. A. K. Howard,^e and A. V. Anisimov^d

^aDepartment of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie Gory, 119992 Moscow, Russian Federation.

Fax: +7 (495) 932 8568. E-mail: tulyakova@petrol.chem.msu.ru

^bPhotochemistry Center, Russian Academy of Sciences,

7A ul. Novatorov, 119421 Moscow, Russian Federation.

Fax: +7 (495) 936 1255. E-mail: fedorova@photonics.ru

^cCenter for Molecular, Optical, and Hertzian Physics, University of Bordeaux I,
351 Cours de la Libération, 33405 Talence, France.*

Fax: (33) 540 00 6970. E-mail: g.jonusauskas@cpmoh.u-bordeaux1.fr

^dN. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 119991 Moscow, Russian Federation.

E-mail: kuzmina@igic.ras.ru

^eDepartment of Chemistry, University of Durham,

South Road, Durham DH1 3LE, UK.

E-mail: j.a.k.howard@durham.ac.uk

New styryl dyes containing azadithia-15-crown-5 fragments were synthesized. The complexation of these compounds with Ag⁺, Pb²⁺, Cu²⁺, Hg²⁺, and H⁺ cations was studied by ¹H NMR spectroscopy, steady-state, and time-resolved spectroscopy. The stability constants of the complexes were calculated from the spectrophotometric titration data. The photophysical properties and *E–Z* photoisomerization of styryl dyes and their complexes with mercury and copper(II) cations in acetonitrile were examined.

Key words: styryl dyes, phenylazadithia-15-crown-5 ether, complexation, photochemistry, *E–Z* photoisomerization.

A considerable progress in chemistry of macrocyclic compounds is associated not only with their fundamental importance but also with their practical applications in organic synthesis, biology, medicine, and industry.^{1–5} Macroheterocyclic sulfur-containing compounds (crown compounds, cryptands, catenanes, rotaxanes, and cyclophanes) have attracted great interest^{6–11} because of their ability to selectively form stable complexes with transition and heavy metal cations. These compounds are of considerable interest as by-products in the synthesis of polymers containing thiacycrown groups, selective chromogenic and photochromic reagents for metal cations, and extractants for metal salts.

The aim of the present study was to synthesize derivatives of azathiacrown ethers having affinity for heavy and transition metal cations, investigate the complexation of metal cations with different heteroatoms of the macrocycle, and reveal the influence of complexation on the optical and photochemical characteristics of these compounds. Studies of azacrown-containing styryl dyes demonstrated^{12,13} that complexation with rare-earth metal cations leads to shifts in absorption spectra as large as 50–70 nm. On the one hand, the compounds synthesized and investigated in the present study contain the ionophoric fragment of the phenylazacrown macrocycle, which gives promise that the complexation with metal cations will result in a large optical response. On the other hand, the introduction of sulfur atoms into the macrocycle makes it possible to achieve selective binding with metal salts, which is of

* Centre de Physique Moléculaire Optique et Hertzienne — UMR CNRS 5798, Bordeaux University I, 351 Cours de la Libération, 33405 Talence, France.

importance for the development of the industrial cation analysis.

Results and Discussion

Synthesis and structure determination. The synthesis pathway of styryl dyes containing the azadithia-15-crown-5 fragment is presented in Scheme 1. Earlier, it has been reported that compound **3** can be synthesized by Vilsmeier formylation of unsubstituted phenylazadithia-15-crown-5 ether. In the present study, we developed an alternative procedure based on condensation of linear precursors, one of which already contains the formyl group. This procedure makes it possible to circumvent the partial opening of the macrocycle and the formation of a podand, which is generated as a by-product in direct formylation of phenylazadithia-15-crown-5 ether. The starting compound, *viz.*, *p*-di(2-chloroethyl)aminobenzaldehyde (**2**), involved in the synthesis of the crown ether, was prepared by the reaction of *N,N*-di(2-hydroxyethyl)aniline with POCl₃ followed by Vilsmeier formylation of the resulting *N,N*-di(2-chloroethyl)aniline (**1**).¹⁴ Condensation of aldehyde **2** with the corresponding dithiol in the presence of cesium carbonate in an EtOH–H₂O medium afforded the formyl derivative of phenylazathiocrown compound **3**.¹⁵ The reaction of the latter with quaternary benzothiazolium salts¹⁶ in anhydrous ethanol in the presence of pyridine as a catalyst produced crown-containing styryl dyes *E*-**4** and *E*-**5** (see Scheme 1).

The fact that compounds **4** and **5** exist as *E* isomers is evidenced by the ¹H NMR spectroscopic data (the spin-spin coupling constants of the protons of the vinylene fragment ³*J*_E = 15.2 and 15.6 Hz, respectively).

The structure of compound **3** was established by X-ray diffraction. The structures of two crystallographically in-

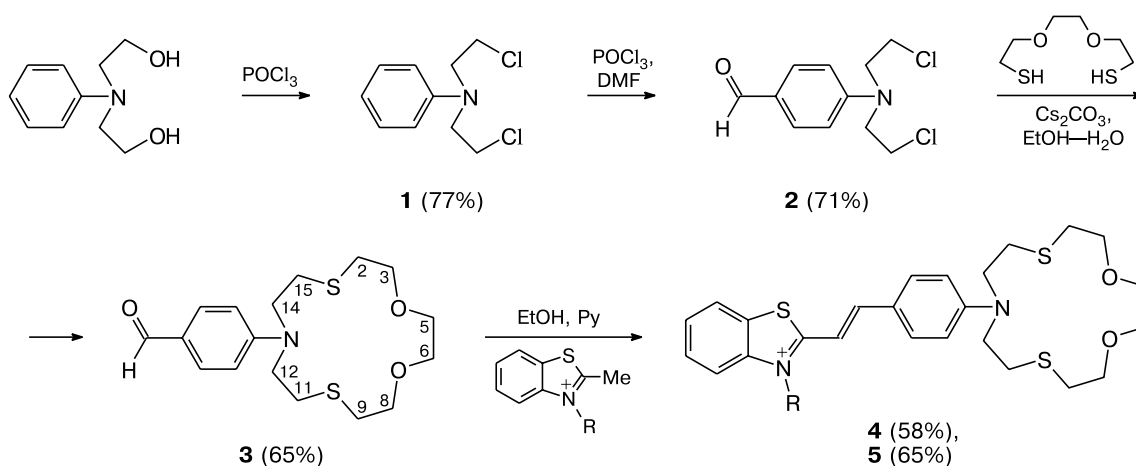
dependent molecules *A* and *B* and the atomic numbering scheme are presented in Fig. 1. Selected bond lengths and bond angles are given in Table 1.

Slight random differences in the bond lengths involving the S atoms are, apparently, attributed to thermal motion of these atoms and are associated with a high flexibility of the macrocycle, particularly, in the vicinity of the S atoms. In addition to higher anisotropic temperature factors of the S atoms compared to those of most of C atoms, this is also evidenced by the presence of two crystallographically independent molecules containing the macrocycles in different conformations. The existence of two crystallographically independent molecules has been observed earlier¹⁰ for the tricyanovinyl derivative of phenylazadithia-15-crown-5 ether.

The bonds at the N atom have a planar-trigonal configuration (the sums of the bond angles at this atom in two independent molecules are 359.7 and 359.8°). The plane passing through these bonds is almost coplanar to the plane of the benzene ring (the dihedral angles are 9.3 and 4.7°). This is indicative of the presence of conjugation between the lone electron pair of the N atom and the benzene ring. This conjugation is evidenced by a noticeable perturbation of the bond lengths in the benzene ring. Actually, the C(12)–C(13) (in both molecules, 1.382(5) Å) and C(15)–C(16) (1.375(5) and 1.374(5) Å) bonds are substantially shorter than the other bonds in the benzene ring (1.393(6)–1.416(5) Å), which corresponds to the contribution of the *para*-quinoid structure. It should be noted that the analogous distortion of the geometry of the benzene ring is observed in all benzoazacrown ethers.

Complexation. To estimate the complexation ability of the resulting compounds, we analyzed the ¹H NMR spectra of the formyl derivative of phenylazadithiacrown compound **3** in the presence of heavy and transition metal

Scheme 1



R = Et(ClO₄)⁻ (**4**), (CH₂)₄SO₃⁻ (**5**)

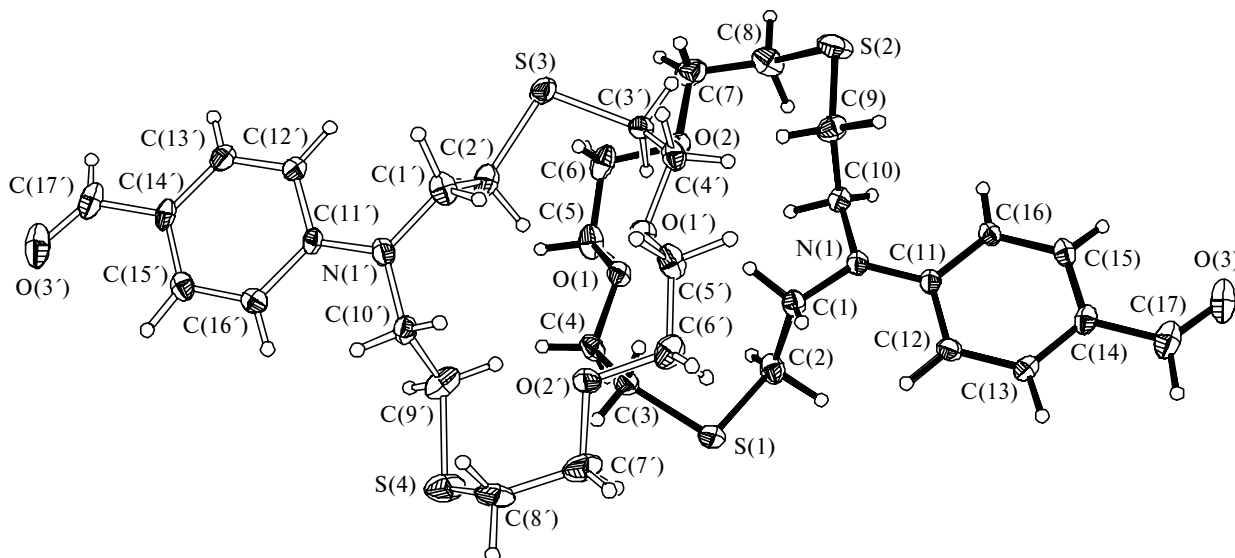


Fig. 1. Structures of two crystallographically independent molecules of compound **3**. The corresponding atoms, except for the S atoms, in molecules *A* and *B* are numbered in the same way, but the atoms in molecules *B* are primed.

perchlorates (Table 2). The addition of Zn^{2+} ions has no effect on the positions of the proton signals in the spectrum of compound **3**; the addition of Cd^{2+} ions leads only to slight changes in the spectrum, which is indicative of low stability of the resulting complexes. The addition of Ag^+ or Hg^{2+} perchlorates to an acetonitrile solution of compound **3** causes substantial changes in the positions of the signals for all protons in the ^1H NMR spectrum. The largest changes are observed for the chemical shifts of the methylene protons of the macrocyclic fragment bound to the S atoms. For the complexes with Pb^{2+} perchlorate, the changes in the chemical shifts of the protons ($\Delta\delta$) of the methylene groups bound to the S atoms are similar to

those for the methylene groups bound to the O atoms. The observed effects can be attributed to the fact that Ag^+ cations have a high affinity for S atoms, whereas Pb^{2+} cations are equally well coordinated by S and O atoms. For all the metal cations under consideration, the smallest $\Delta\delta$ were observed for the α, α' - CH_2N protons. In this case, the metal cations are most weakly coordinated by the N atom, which may be a consequence of the involvement of the free electron pair of the N atom in conjugation with the benzene ring. The changes in $\Delta\delta$ for the methylene protons were also studied in the presence of HClO_4 . The addition of HClO_4 leads to protonation of the N atom, which is manifested primarily in the

Table 1. Selected bond lengths (*d*) and bond angles (ω) in molecules *A* and *B* of compound **3**

Bond	<i>d</i> /Å		Bond	<i>d</i> /Å	
	<i>A</i>	<i>B</i>		<i>A</i>	<i>B</i>
S(1)[S(3)]—C(2)	1.814(4)	1.841(5)	N(1)—C(10)	1.461(5)	1.452(5)
S(1)[S(3)]—C(3)	1.815(4)	1.807(4)	N(1)—C(11)	1.364(4)	1.380(5)
S(2)[S(3)]—C(8)	1.809(4)	1.811(4)	C(11)—C(12)	1.415(5)	1.415(5)
S(2)[S(3)]—C(9)	1.803(4)	1.805(4)	C(11)—C(16)	1.423(5)	1.416(5)
O(1)—C(4)	1.429(5)	1.425(5)	C(12)—C(13)	1.382(5)	1.382(5)
O(1)—C(5)	1.427(4)	1.418(4)	C(13)—C(14)	1.400(5)	1.398(6)
O(2)—C(6)	1.420(5)	1.422(5)	C(14)—C(15)	1.397(6)	1.393(6)
O(2)—C(7)	1.420(6)	1.418(5)	C(15)—C(16)	1.375(5)	1.374(5)
N(1)—C(1)	1.469(5)	1.466(5)	C(14)—C(17)	1.459(5)	1.460(5)
Angle	ω /deg		Angle	ω /deg	
C(2)—S(1)[S(3)]—C(3)	103.6(2)	101.9(2)	C(1)—N(1)—C(11)	120.9(3)	121.3(3)
C(8)—S(2)[S(3)]—C(9)	105.6(2)	104.5(2)	C(10)—N(1)—C(11)	121.8(3)	120.9(3)
C(4)—O(1)—C(5)	110.7(3)	110.4(3)	C(12)—C(11)—C(16)	117.9(3)	117.3(3)
C(6)—O(2)—C(7)	112.3(3)	111.9(3)	C(13)—C(14)—C(15)	118.0(3)	117.6(3)
C(1)—N(1)—C(10)	117.0(3)	117.6(3)			

Table 2. Changes in the proton chemical shifts ($\Delta\delta = \delta_{\text{compl}} - \delta_{\text{L}}$) for the phenylazadithiacrown group of compound **3** upon complexation*

Cation M^{n+}	$\Delta\delta$				
	12,14-CH ₂ N	11,15-CH ₂ S	2,9-CH ₂ S	3,8-CH ₂ O	5,6-CH ₂ O
Cd ²⁺	0.02	0.03	0.04	0.02	0.03
Pb ²⁺	0.01	0.31	0.28	0.17	0.14
Ag ⁺	-0.02	0.20	0.19	0.05	0.05
Hg ²⁺	0.04	0.37	0.44	0.02	0.07
H ⁺	0.31	-0.08	0.18	0.00	0.13

* The conditions: CD₃CN at 20 °C, $C_{\text{L}} = 4.68 \cdot 10^{-2} \text{ mol L}^{-1}$, and $C_{M^{n+}} = 4.68 \cdot 10^{-2} \text{ mol L}^{-1}$.

changes in the positions of the signals for the α, α' -CH₂N protons.

The electronic absorption spectrum of dye *E-4* in MeCN shows an intense long-wavelength absorption band with a maximum at 523 nm (19120 cm⁻¹); the extinction coefficient $\epsilon_{\text{max}} = 7.00 \cdot 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Fig. 2, curve *I*). The maximum of the long-wavelength absorption band of betaine dye *E-5* is characterized by $\lambda = 521 \text{ nm}$ (19010 cm⁻¹) and $\epsilon_{\text{max}} = 6.41 \cdot 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Fig. 3, curve *I*). In compound *E-5*, there is an electrostatic interaction between the negatively charged sulfonate group and the positively charged N atom of the heterocyclic moiety of the molecule, resulting in partial disruption of conjugation, which is responsible for a decrease in the extinction coefficient compared to that of dye *E-4* and a small shift in the maximum of the long-wavelength absorption band to higher energies. In the presence of Mg²⁺ cations, which interact with the sulfonate group of the dye and eliminate the above-mentioned electrostatic interaction, the spectrum of compound *E-5* shows a small

bathochromic shift of the long-wavelength absorption band (by 5 nm) and a slight increase in the absorbance ($\epsilon_{\text{max}} = 6.46 \cdot 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$).

The position of the maximum of the long-wavelength absorption band in the spectra of compounds *E-4* and *E-5* depends on the nature of the solvent (Table 3). An increase in the polarity of the solvent in the series PrⁿOH, EtOH, MeOH, and H₂O is accompanied by a small hypsochromic shift of the long-wavelength absorption band of *E-4* and *E-5* (the negative solvatochromic effect). However, by contrast to less polar ethyl acetate, the solvatochromic effect is not observed in more polar ethanol, which is apparently indicative of the influence of the specific effects of the solvents (in particular, possible hydrogen bonding in protic solvents) on the absorption spectra of *E-4* and *E-5*.

The addition of Pb²⁺, Hg²⁺, Ag⁺, or Cu²⁺ perchlorates to solutions of *E-4* and *E-5* causes hypsochromic shifts of the long-wavelength absorption band due to complexation at the crown fragment of the molecules (Figs 2 and 3, Table 4). It is known^{12,18} that the introduction of a metal cation into the cavity of the crown fragment of

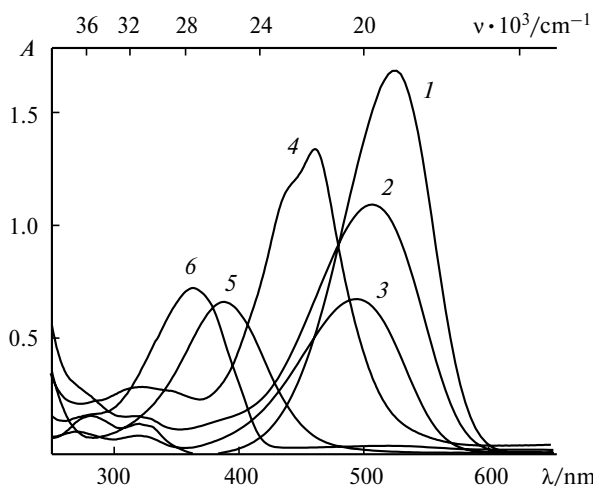


Fig. 2. Absorption spectra of *E-4* at a concentration of $2.5 \cdot 10^{-5} \text{ mol L}^{-1}$ (*I*) and in the presence of Pb(ClO₄)₂ ($4.06 \cdot 10^{-2} \text{ mol L}^{-1}$) (2), AgClO₄ ($2.58 \cdot 10^{-2} \text{ mol L}^{-1}$) (3), Cu(ClO₄)₂ ($1.90 \cdot 10^{-4} \text{ mol L}^{-1}$) (4), Hg(ClO₄)₂ ($2.75 \cdot 10^{-5} \text{ mol L}^{-1}$) (5), or HClO₄ ($2.78 \cdot 10^{-3} \text{ mol L}^{-1}$) (6) in MeCN at 293 K.

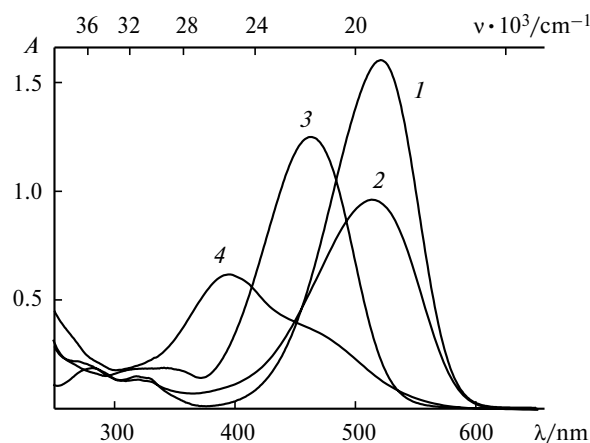


Fig. 3. Absorption spectra of *E-5* at a concentration of $2.5 \cdot 10^{-5} \text{ mol L}^{-1}$ (*I*) and in the presence of Pb(ClO₄)₂ ($2.20 \cdot 10^{-2} \text{ mol L}^{-1}$) (2), Cu(ClO₄)₂ ($1.16 \cdot 10^{-4} \text{ mol L}^{-1}$) (3), or Hg(ClO₄)₂ ($2.75 \cdot 10^{-5} \text{ mol L}^{-1}$) (4) in MeCN at 293 K.

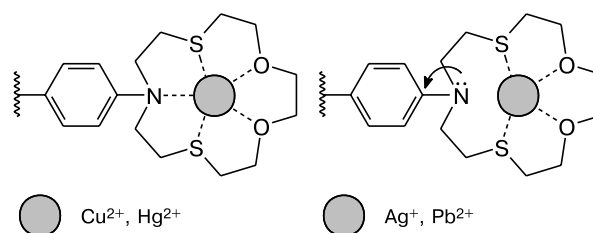
Table 3. Influence of the nature of the solvent on the absorption spectra of *E-4* and *E-5*

Solvent	λ_{\max}/nm ($\epsilon_{\max} \cdot 10^4/\text{L mol}^{-1} \text{cm}^{-1}$)	
	<i>E-4</i>	<i>E-5</i>
EtOAc	529 (6.61)	530 (6.32)
(CH ₂) ₂ (OMe) ₂	534 (6.82)	534 (5.50)
CH ₂ Cl ₂	546 (9.25)	543 (8.30)
Me ₂ CO	524 (8.15)	525 (6.24)
MeCN	523 (7.00)	521 (6.41)
DMSO	526 (6.44)	526 (4.72)
(CH ₂) ₃ CO	526 (6.10)	525 (6.07)
H ₂ O	505 (4.86)	510 (5.68)
MeOH	525 (6.31)	526 (7.27)
EtOH	529 (5.57)	530 (7.15)
(CH ₂) ₂ (OH) ₂	528 (5.08)	529 (5.27)
Pr ⁿ OH	533 (6.33)	531 (6.76)
<i>n</i> -C ₅ H ₁₁ OH	535 (5.92)	533 (7.00)
<i>n</i> -C ₁₀ H ₂₁ OH	538 (5.78)	535 (7.36)

crown-containing styryl dyes hinders the charge transfer from the crown ether to the heterocyclic moiety, which leads to hypsochromic shifts of the long-wavelength absorption band.

The hypsochromic shifts of the long-wavelength absorption band for *E-4* and *E-5* upon complexation in MeCN are given in Table 4. The metal cations under study can be divided into two groups. In the presence of Pb²⁺ or Ag⁺, small changes in the position of the maximum of the long-wavelength absorption band (by 6–26 nm) were observed. The addition of Cu²⁺ or Hg²⁺ cations leads to a shift of the maximum of the long-wavelength absorption band by 92–140 nm. Small shifts of the long-wavelength absorption band upon complex-

ation with Ag⁺ or Pb²⁺ may be a consequence of the fact that Ag⁺ cations are predominantly coordinated by S atoms, whereas Pb²⁺ cations are coordinated by the O atoms of the azadithiacrown group, resulting in slight spectral shifts due to small conformational rearrangements of the dye molecules. This was demonstrated above by NMR experiments. In this case, the involvement of the N atom in complexation is, apparently, insignificant. On the contrary, large hypsochromic shifts of the long-wavelength absorption band upon complexation of Cu²⁺ and Hg²⁺ are indicative of the involvement of the N atom of the crown fragment in coordination to these cations (Scheme 2).

Scheme 2

The stability constants of the complexes of *E-4* and *E-5* with metal cations were evaluated with the use of spectrophotometric titration and the HYPERQUAD calculation program.¹⁹ In the calculations, different pathways of the formation of the complexes were taken into account (Scheme 3).

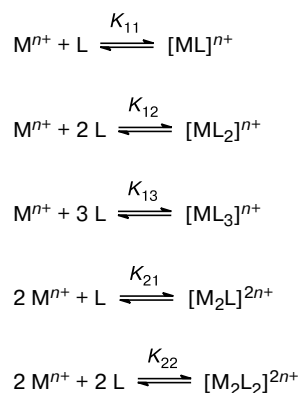
The calculated stability constants are given in Table 4. The direct spectrophotometric determination of the stability constants of the complexes of dyes *E-4* and *E-5* with Hg²⁺ cations appeared to be impossible because of

Table 4. UV–Vis data and the stability constants of dyes *E-4* and *E-5* and their complexes with lead, silver, mercury, and copper perchlorate and perchloric acid at 293 K

Complex	Cation radius (according to Shannon ¹⁷)/Å	Ionic strength /mol L ⁻¹	λ_{\max}/nm ($\Delta\lambda^*/\text{nm}$)	Stability constant of the complex
<i>E-4</i> + Pb ²⁺	1.33	0–8.29 · 10 ⁻²	507 (16)	log <i>K</i> ₁₁ = 1.78 ± 0.01
<i>E-4</i> + Ag ⁺	1.29	0–4.46 · 10 ⁻²	495 (28)	log <i>K</i> ₁₁ = 2.63 ± 0.01
<i>E-4</i> + Cu ²⁺	0.87	0–1.24 · 10 ⁻³	438 (sh), 461 (62)	log <i>K</i> ₁₁ = 5.50 ± 0.10
<i>E-4</i> + H ⁺	—	0–4.95 · 10 ⁻³	363 (160)	log <i>K</i> ₁₁ = 4.26 ± 0.02
<i>E-4</i> + Hg ²⁺	1.16	0–1.58 · 10 ⁻⁴	388 (135)	log <i>K</i> ₁₁ = 14.8 ± 0.10
<i>E-5</i> + Pb ²⁺	1.33	0–4.87 · 10 ⁻²	515 (6)	log <i>K</i> ₁₂ = 11.82 ± 0.17 log <i>K</i> ₁₃ = 18.16 ± 0.26 log <i>K</i> ₁₁ = 5.81 ± 0.12 log <i>K</i> ₂₁ = 7.49 ± 0.12
<i>E-5</i> + Cu ²⁺	0.87	0–3.67 · 10 ⁻⁴	463 (58)	log <i>K</i> > 7
<i>E-5</i> + Hg ²⁺	1.16	0–1.32 · 10 ⁻⁴	391, 470 (sh) (130)	log <i>K</i> ₁₁ = 19.3 ± 0.2

* $\Delta\lambda = (\lambda_{\max})_{\text{L}} - (\lambda_{\max})_{\text{compl}}$.

Scheme 3



their very high values. Hence, the corresponding stability constants were determined by titration with a solution of a competitive ligand, for which the stability constant of the complex with the Hg^{2+} cation is known from the literature data.²⁰ The complex of dye *E-4* with Hg^{2+} was titrated with a styryl dye containing the benzodithia-15-crown-5 group; the complex of *E-5* with Hg^{2+} , with benzodithia-18-crown-6 ether.

Complexation with copper(II) cations. The addition of Cu^{2+} cations to *E-4* (Fig. 4) results in the disappearance of the long-wavelength absorption band with a maximum at 521 nm (19190 cm^{-1}) and the appearance of the absorption band with a maximum at 461 nm (21690 cm^{-1} , $\epsilon \approx 4.66 \cdot 10^4\text{ L mol}^{-1}\text{ cm}^{-1}$), a shoulder at 438 nm (22830 cm^{-1} , $\epsilon \approx 4.00 \cdot 10^4\text{ L mol}^{-1}\text{ cm}^{-1}$), and two new absorption bands with maxima at 777 (12870 cm^{-1} , $\epsilon \approx 8.57 \cdot 10^2\text{ L mol}^{-1}\text{ cm}^{-1}$) and 862 nm (11600 cm^{-1} , $\epsilon \approx 1.08 \cdot 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$). An analogous situation was observed for *E-5* (Fig. 5). According to the published data on the electronic absorption spectra of Cu^{II} complexes

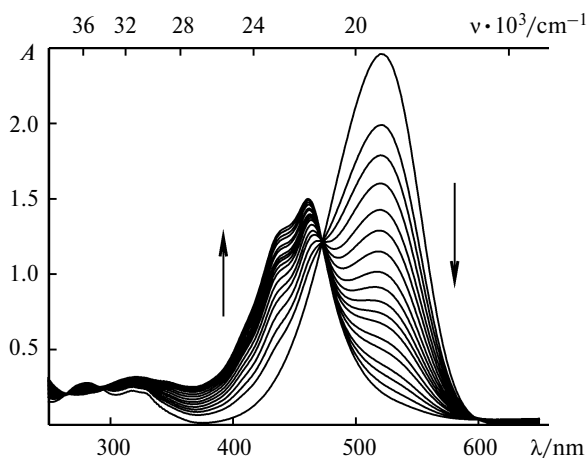


Fig. 4. Spectrophotometric titration of *E-4* by copper(II) perchlorate in MeCN ($C_L = 3.5 \cdot 10^{-5}\text{ mol L}^{-1}$); the additives of copper(II) $0 \leq x_{M/L} \leq 5.4$.

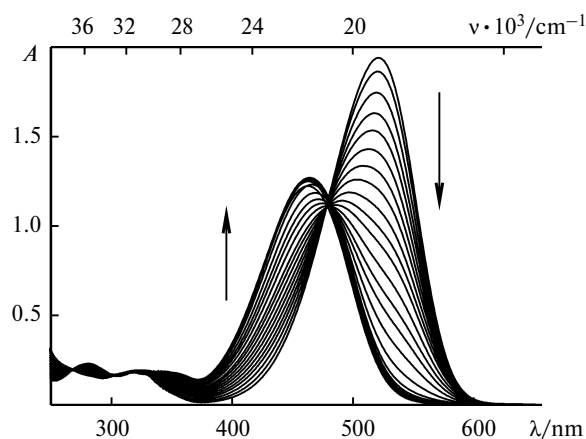


Fig. 5. Spectrophotometric titration of *E-5* by copper(II) perchlorate in MeCN ($C_L = 3.0 \cdot 10^{-5}\text{ mol L}^{-1}$); the additives of copper(II) $0 \leq x_{M/L} \leq 3.8$.

with thio esters,^{21–23} the two lowest-energy bands can be assigned to $d-d^*$ transitions of Cu^{II} .

Complexation with lead(II) cations. The complexation of compound *E-4* with Pb^{2+} cations is characterized by a low stability constant and is accompanied by small spectral changes. The dependence of the absorption spectrum of *E-5* on the concentration of Pb^{2+} cations is presented in Fig. 6, *a*. As opposed to compound *E-4*, substantial changes in the spectrum of *E-5* are observed already in the presence of Pb^{2+} cations at low concentrations and are different in character. At $C_{Pb^{2+}}/C_{E-5} = 0.5$, the maximum is hypsochromically shifted, which is accompanied by an increase in the absorbance at the long-wavelength edge of the spectrum. At high Pb^{2+} concentrations, the absorption spectral pattern of the $[(E-5)(Pb^{2+})]$ complex is similar to that of the $[(E-4)(Pb^{2+})]$ complex. However, the shift of the long-wavelength absorption band is only 6 nm, whereas the shift of the long-wavelength absorption band for $[(E-4)(Pb^{2+})]$ is 16 nm.

As can be seen from the dependence of the fluorescence spectra of *E-5* on the Pb^{2+} concentration (Fig. 6, *b*), an increase in the cation concentration initially causes a decrease in the intensity of the fluorescence band, the position of the maximum remaining unchanged, and then the intensity increases, which is accompanied by a slight shift of the maximum to shorter wavelengths. Earlier,¹² a similar behavior has been observed for betaine dyes containing the phenylaza-15-crown-5 group in the presence of a small amount of Ca^{2+} cations, which was attributed to aggregation of the dye molecules. In this case, a decrease in the intensity of the fluorescence band and a sharp decrease in the quantum yield of *E-5* in the presence of small amounts of Pb^{2+} cations (Table 5) are also characteristic of aggregation of *E-5* in solution.

Actually, betaine dye molecules contain two possible coordination sites of Pb^{2+} cations, *viz.*, the crown frag-

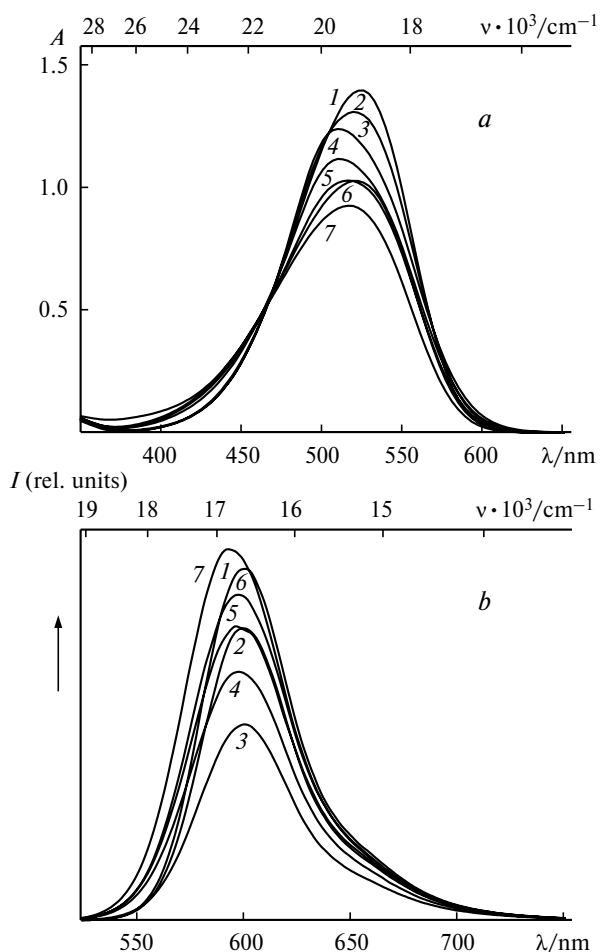


Fig. 6. Dependence of the absorption spectra (*a*) and fluorescence spectra (*b*) of *E-5* on the concentration of Pb^{2+} ions: $C_{\text{Pb}^{2+}}/C_{E-5} = 0$ (1), 0.12 (2), 0.25 (3), 0.94 (4), 2.62 (5), 41 (6), and 387 (7); MeCN, 293 K, $\lambda_{\text{exc}} = 460$ nm.

ment and the sulfonate group. The spectrophotometric titration data for cationic dye *E-4* demonstrated that the stability constant of the complex with Pb^{2+} cations for the

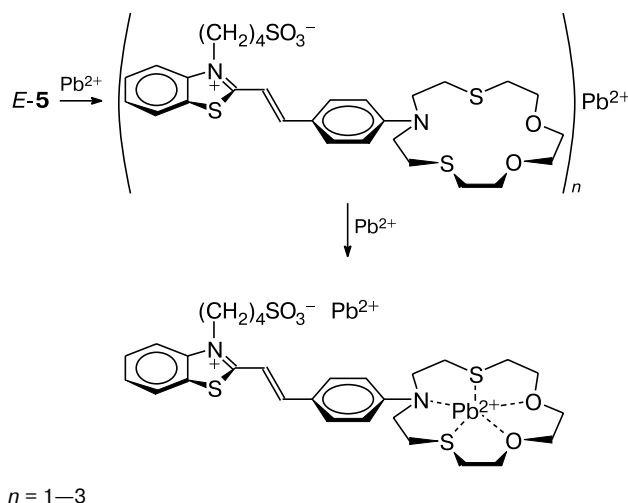
Table 5. Influence of the concentration of lead(II) perchlorate on the fluorescence quantum yields (ϕ^{fl}) of *E-5* ($C = 2.27 \cdot 10^{-5}$ mol L^{-1}) in MeCN at 293 K

$C_{\text{Pb}^{2+}}$ /mol L^{-1}	$\lambda_{\text{max}}^{\text{fl}}$ /nm ($\Delta\lambda^{\text{fl}}$ /nm)*	ϕ^{fl}
$2.80 \cdot 10^{-6}$	602 (–1)	0.054
$5.96 \cdot 10^{-6}$	602 (–1)	0.036
$1.19 \cdot 10^{-5}$	597 (4)	0.037
$2.15 \cdot 10^{-5}$	596 (5)	0.048
$5.95 \cdot 10^{-5}$	596 (5)	0.057
$1.88 \cdot 10^{-4}$	598 (3)	0.062
$0.93 \cdot 10^{-3}$	598 (3)	0.063
$0.88 \cdot 10^{-2}$	593 (8)	0.071

* $\Delta\lambda^{\text{fl}} = (\lambda_{\text{max}}^{\text{fl}})_{\text{L}} - (\lambda_{\text{max}}^{\text{fl}})_{\text{compl}}$.

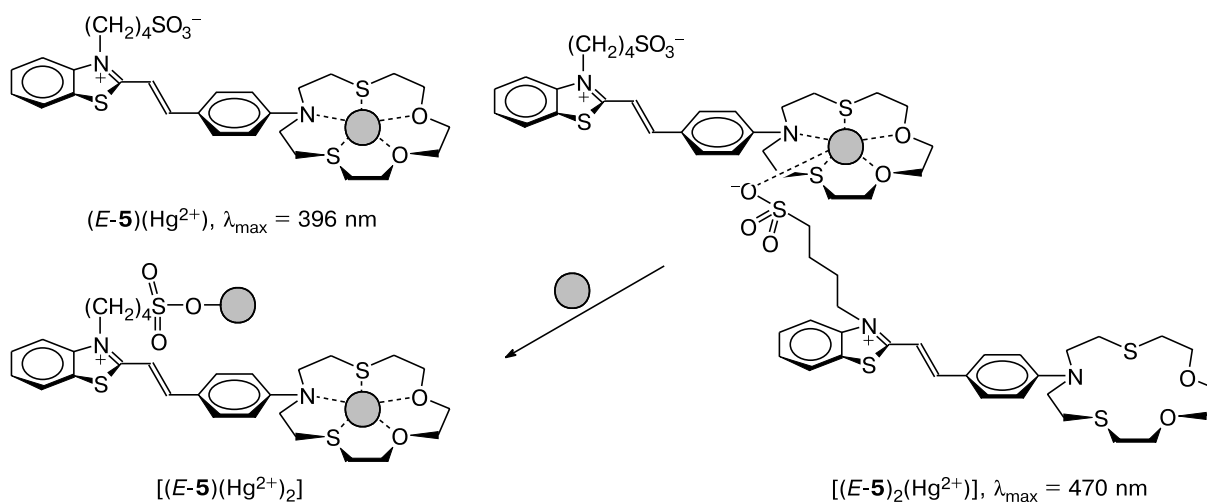
crown fragment is low. Hence, the sulfonate group can serve as a preferred binding site of Pb^{2+} cations compared to the crown fragment. According to the calculations of the complexation constants from the spectrophotometric titration data (see Table 4), the formation of aggregates, in which two or three betaine dye molecules are coordinated to the Pb^{2+} cation apparently with the involvement of the sulfonate group, is possible at low Pb^{2+} concentrations. An increase in the Pb^{2+} concentration leads to a shift of the equilibrium toward complexes containing one dye molecule. The interaction between the Pb^{2+} cation and the sulfonate group in the complex of compound *E-5* is confirmed by the fact that the position of the maximum of the fluorescence band remains unchanged in the presence of small amounts of Pb^{2+} . A further increase in the Pb^{2+} concentration in solution leads to the formation of complexes, in which the Pb^{2+} ion is bound to the azathiocrown fragment of molecule *E-5*, and the position of the maximum of the fluorescence band is shifted to shorter wavelengths by 8 nm (Scheme 4).

Scheme 4



Complexation with mercury(II) cations. As opposed to compound *E-4*, the formation of the complex of *E-5* with Hg^{2+} cations is accompanied by the appearance of the absorption band with a maximum at 396 nm, and a long-wavelength shoulder is observed at 470 nm. The latter cannot be assigned to residual absorption of the free ligand. Apparently, two types of complexes, *viz.*, monomeric [*E-5*](Hg^{2+}) and dimeric [*E-5*]₂(Hg^{2+}), exist in equilibrium in solution (Scheme 5). In the dimeric complex, there is an additional coordination bond between the metal cation located in the crown ether cavity of one of the dye molecules and the sulfonate group of another molecule, resulting in an increase in stability of the complex (see Table 4). This additional binding leads to disruption of

Scheme 5



the coordination bond between the N atom of the macrocycle and the Hg^{2+} cation. The spectrum of the complex, in which the involvement of the N atom is insignificant, is observed at longer wavelengths ($\lambda_1 = 470 \text{ nm}$) compared to the spectrum of the complex, in which the lone electron pair of the N atom is involved in the coordination bond with the Hg^{2+} cation ($\lambda_2 = 396 \text{ nm}$). Earlier, we have found dimeric complexes with Hg^{2+} cations²⁰ when studying styryl dyes containing the benzothiacrown group.

The formation of dimeric complexes is confirmed by electrospray mass spectra. Under the same analysis conditions, we found that an acetonitrile solution of *E-4* in the presence of Hg^{2+} contains primarily the $[(E-4)(Hg^{2+})]$ complex, whereas a solution of *E-5* in the presence of Hg^{2+} consists of a mixture of the monomeric and dimeric complexes (Table 6).

All data obtained by analyzing the dimeric complex by NMR methods suggest the structure of the resulting dimer (see Scheme 5). For example, the addition of mercury perchlorate to both dyes *E-4* and *E-5* led to identical spectral changes, *viz.*, to downfield shifts of the signals of all protons (Figs 7 and 8). The signals for the protons of the aliphatic moiety of the molecules are rather difficult to interpret because of a considerable broadening. The

largest changes in the aromatic region are observed for the signals of the H(17), H(21) and H(18), H(20) protons ($\Delta\delta$ 0.74 and 0.28 ppm, respectively) belonging to the benzene ring in the phenylazadithiacrown group and the signals for the H(22) and H(23) olefinic protons with the spin-spin coupling constant $^3J_{trans} = 15.9 \text{ Hz}$ ($\Delta\delta$ 0.43 and 0.15 ppm, respectively).

Presumably, the dimeric complex $[(E-5)_2(Hg^{2+})]$ has a linear structure (Scheme 6). If the dye molecules are arranged one above another (dimer stacks), the anisotropic effect is observed, resulting in substantial upfield shifts of the proton signals in the 1H NMR spectra.²⁰ In the linear dimer, the effect of the metal cation is analogous to that observed in the complex of the cationic dye $[(E-4)(Hg^{2+})]$.

The existence of the dimeric complex is additionally confirmed by the results of an experiment, in which an excess of Hg^{2+} cations was added to a solution of this complex. In this case, a shoulder of the long-wavelength absorption band at 470 nm disappeared. The presence of excess mercury leads to decomposition of the dimeric complex to form the $[(E-5)(Hg^{2+})_2]$ complex, in which the second Hg atom is coordinated by the sulfonate group of the *N*-sulfoalkyl substituent (see Scheme 5).

Fluorescence. The fluorescence quantum yields and the lifetimes of the excited state of dyes *E-4* and *E-5* and their complexes in acetonitrile are given in Table 7.

The introduction of the *N*-sulfonatobutyl group into the benzothiazolium moiety of the ligand molecule is accompanied by an increase in the lifetime of the excited state.

The addition of Hg^{2+} or Cu^{2+} to solutions of *E-4* and *E-5* in MeCN causes shifts of the steady-state fluorescence spectra of the corresponding ligands to shorter wavelengths (see Table 7). The hypsochromic shifts in the absorption spectra of the complexes of *E-4* and *E-5* with

Table 6. ESI-MS data for the complexes of dyes *E-4* and *E-5* with mercury perchlorate in acetonitrile

Complex	<i>m/z</i>
<i>E-4</i> + Hg^{2+}	407.8 $[(4)(Hg^{2+})]$
<i>E-5</i> + Hg^{2+}	923.0 $[(5)(Hg^{2+})(ClO_4^-)]$,
	753.0 $[(5)_2(Hg^{2+})(MeCN)(H_2O)]$,
	723.0 $[(5)_2(Hg^{2+})]$,
	441.9 $[(5)(Hg^{2+})(MeCN)(H_2O)]$,
	411.8 $[(5)(Hg^{2+})]$

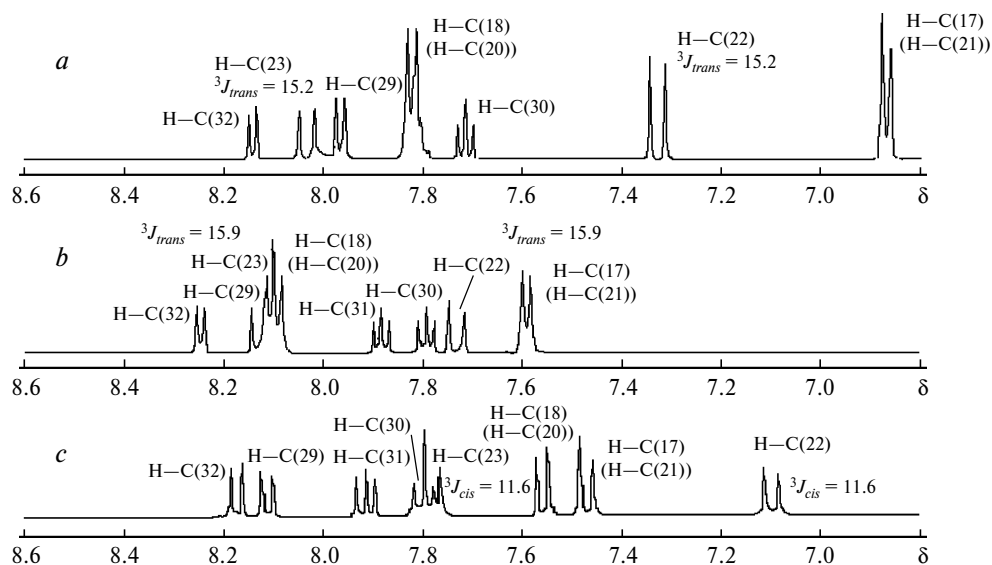


Fig. 7. ^1H NMR spectra (the aromatic region) of *E-4* (a), [*E-4*](Hg^{2+}) (b), and [(*Z-4*)](Hg^{2+}) (c) in CD_3CN at 303 K; the spin-spin coupling constants (Hz) are given.

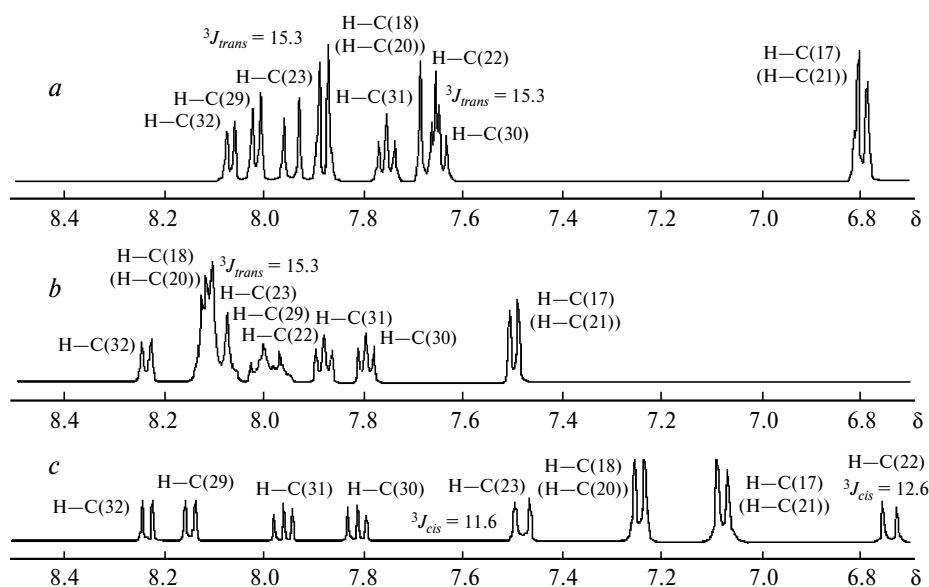
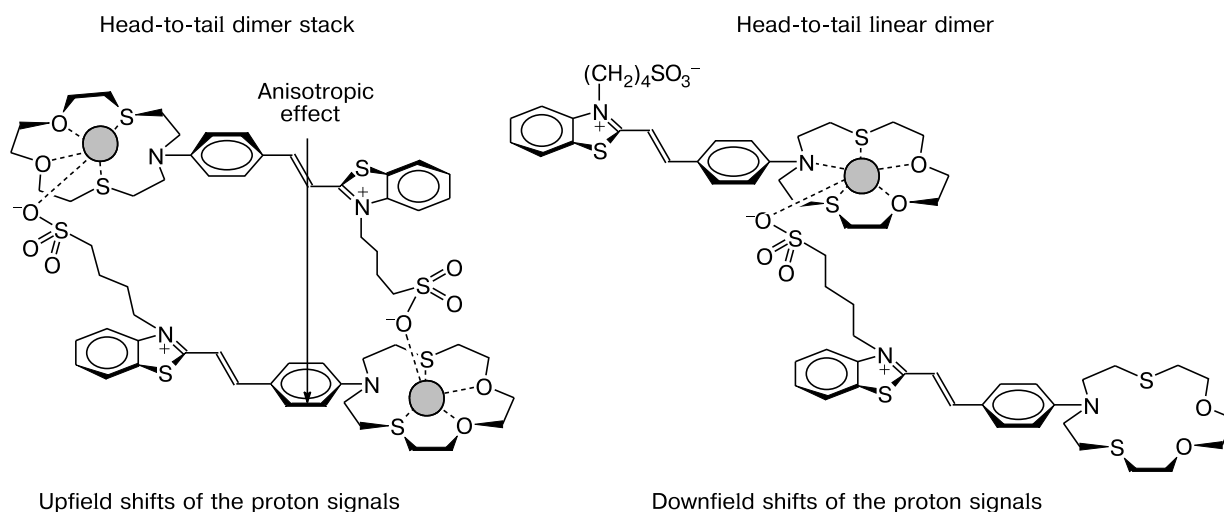


Fig. 8. ^1H NMR spectra (the aromatic region) of *E-5* (a), [*E-5*](Hg^{2+}) (b), and [(*Z-5*)](Hg^{2+}) (c) in CD_3CN at 303 K; the spin-spin coupling constants (Hz) are given.

Hg^{2+} and Cu^{2+} (see Table 4) were found to be substantially larger than those in the emission spectra. These phenomena were described in sufficient detail in the literature^{18,24} and are associated with decoordination of metal cations from the N atom of the crown fragment in the excited state. For the [(*E-4*)](Cu^{2+}), [(*E-5*)](Cu^{2+}), [(*E-4*)](Hg^{2+}), [(*E-5*)](Hg^{2+}), and [(*E-5*)₂](Hg^{2+}) complexes, fluorescence quenching relative to the starting ligand was observed, which may be due to the heavy atom effect²¹ in the case of Hg^{2+} cations.

The fluorescence lifetimes of *E-4* and *E-5* are substantially changed upon complexation. The fluorescence quenching curves can be described by monoexponential kinetic equations, except for the complex of *E-5* with Hg^{2+} cations. The fluorescence quenching curve for the latter complex can be described only by a biexponential kinetic equation with the lifetimes of 94 and 310 ps for the fast and slow components, respectively. The appearance of two lifetimes may be associated with the simultaneous excitation of two different complexes in the ground state.

Scheme 6

**Table 7.** Fluorescence characteristics of dyes *E-4* and *E-5* and their complexes in MeCN at 295 K

Compound	$\lambda_{\text{max}}^{\text{fl}}/\text{nm}$ ($\Delta\lambda^{\text{fl}}/\text{nm}$) ^a	ϕ^{fl}	Lifetime $\tau_{\text{fl}}/\text{ps}$
<i>E-4</i>	601	0.026	72
[(<i>E-4</i>)(Cu ²⁺)]	569 (32)	0.013	96
[(<i>E-4</i>)(Hg ²⁺)]	568 (33)	0.012	65
<i>E-5</i>	601	0.063	160
[(<i>E-5</i>)(Cu ²⁺)]	568 (33)	0.057	220
[(<i>E-5</i>)(Hg ²⁺)]	574 (27) ^b	0.029	94
[(<i>E-5</i>) ₂ (Hg ²⁺)]	582 (19) ^c	0.069	310

^a See the note to Table 5.^b $\lambda_{\text{exc}} = 390$ nm.^c $\lambda_{\text{exc}} = 470$ nm.

However, the emission spectrum of the complexes of dye *E-5* with Hg²⁺ cations substantially depends on the excitation wavelength. An analysis of the fluorescence quenching curves for the complexes of *E-5* with Hg²⁺ cations for the excitation wavelength changing from 390 to 470 nm showed that the relative amplitude of the fast component decreases with changing λ from 390 to 470 nm, whereas the relative amplitude of the slow component increases. The appearance of the long-lived component may be associated with the formation of the dimeric complex. An increase in the lifetime is also typical of the complex of *E-5* with Cu²⁺ cations. Earlier, we have noted²⁵ that dimeric complexes of styryl dye bases with metal cations have longer lifetimes of the excited state compared to the monomeric complexes. In addition, the fluorescence quantum yield changes only slightly upon the formation of the [(*E-5*)₂(Hg²⁺)] complex (unlike the [(*E-4*)(Hg²⁺)] complex). This can be attributed to the fact that the N atom of the crown fragment is not involved in the

formation of the [(*E-5*)₂(Hg²⁺)] complex, and the complexation has no substantial effect on the chromophoric system.

Photochemistry. Earlier,¹³ we have demonstrated that irradiation of acetonitrile solutions of styryl dyes causes the reversible photochemical *E*–*Z* isomerization reaction. Upon irradiation of *E-4* and *E-5* with light at $\lambda = 546$ nm, the *Z* isomer was not detected by spectroscopic methods. This is, apparently, associated with the fact that relaxation of the excited state of these ligands occurs primarily due to rotation about the C–Ph bond accompanied by the transformation into the twisted state, which can be stabilized in a polar aprotic solvent (MeCN). The metal cation prevents deactivation of the excited state of the dye in the [(*E-4*)(Hg²⁺)], [(*E-5*)(Hg²⁺)], and [(*E-5*)₂(Hg²⁺)] complexes through the twisted state, and the *E*–*Z* photoisomerization makes a large contribution to radiationless deactivation of excitation.^{18,21} For example, irradiation of acetonitrile solutions of the [(*E-4*)(Hg²⁺)] and [(*E-5*)(Hg²⁺)] complexes at $\lambda = 436, 365,$ and 546 nm (Figs 9 and 10) causes fast changes in the absorption spectra due to reversible *E*–*Z* photoisomerization (Scheme 7).

The absorption spectrum of the *Z* isomer of the [(*Z-4*)(Hg²⁺)] complex was calculated from the corresponding spectra of [(*E-4*)(Hg²⁺)] and the photostationary states obtained by irradiation with light at wavelengths of 405 and 313 nm (see Fig. 9).²⁶

The possibility of coordination of Hg²⁺ cations at the crown and benzothiazolium moieties of the ligand molecule *E-5* leads to the formation of a complex having a more rigid structure with a smaller number of rotational degrees of freedom, resulting in an increase of the nonradiative time for the photostationary state of the [(*Z-5*)₂(Hg²⁺)₂] complex into the *E* form by ten times

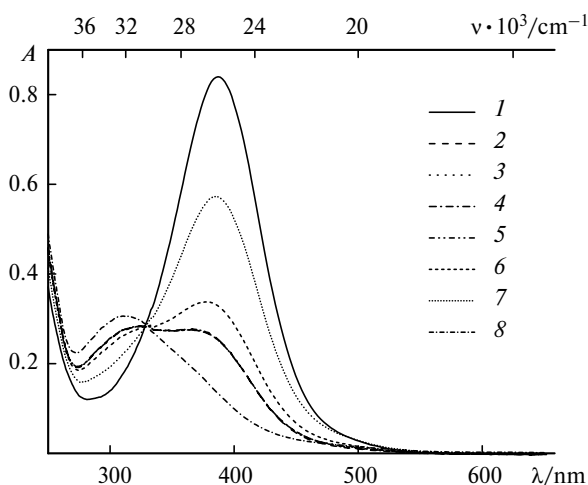


Fig. 9. Absorption spectra of $[(E-4)(Hg^{2+})]$ ($C = 2.5 \cdot 10^{-5}$ mol L^{-1}) before (1) and after irradiation with light at $\lambda = 436$ (2, 3), 405 (4, 5), 365 (6), and 313 nm (7) for 2 (2, 4, 6, 7), 4 (3), and 10 min (5), and the spectrum of $[(Z-4)(Hg^{2+})]$ calculated by Fischer's method (8).

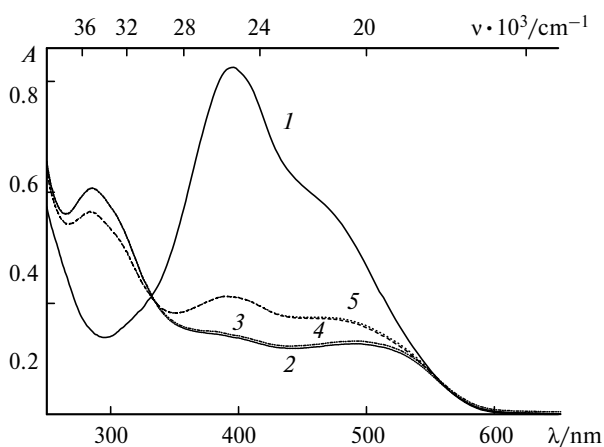
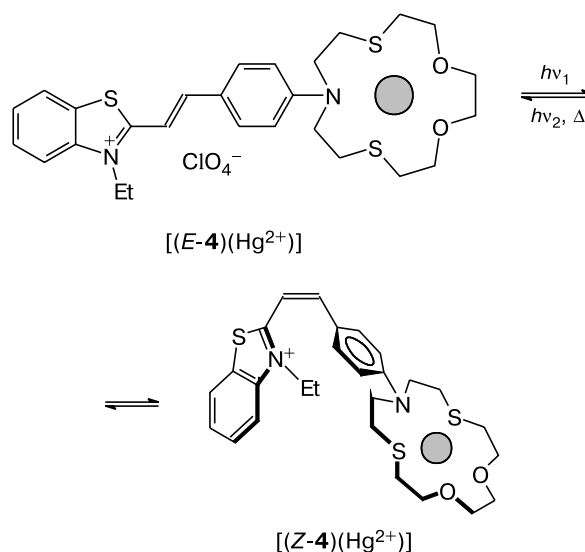


Fig. 10. Absorption spectra of $[(E-5)(Hg^{2+})]$ ($C = 2.5 \cdot 10^{-5}$ mol L^{-1}) before (1) and after irradiation with light at $\lambda = 436$ (2, 3) and 365 nm (4, 5) for 2 (2, 4) and 4 min (3, 5).

compared to the $[(Z-4)(Hg^{2+})]$ complex. We failed to calculate the absorption spectrum of the *Z* isomers of the $[(Z-5)(Hg^{2+})]$ and $[(Z-5)_2(Hg^{2+})]$ complexes because Fischer's method,²⁶ which is used for calculations of absorption spectra of *Z* isomers, has been developed only for two-component systems.

The light irradiation of solutions of the complexes of dyes *E-4* and *E-5* with Hg^{2+} cations causes substantial changes in the positions of the proton signals in the 1H NMR spectra. The signals for the olefinic protons H(22) and H(23) at δ 7.10 and 7.79 ($[(Z-4)(Hg^{2+})]$) and at δ 6.74 and 7.47 ($[(Z-5)(Hg^{2+})]$) appear as doublets with the spin-spin coupling constants characteristics of *Z* isomers of olefins (11.6 and 12.6 Hz, respectively; see Figs 7 and 8).

Scheme 7



To summarize, we developed a new procedure for the synthesis of the formyl derivative of phenylazathiocrown ether. Condensation of the latter with quaternary benzo-thiazolium salts afforded azathiocrown-containing styryl dyes *E-4* and *E-5*. The complexation ability of the starting formyl derivative of the phenylazathiocrown compound toward heavy and transition metal ions (Zn^{2+} , Cd^{2+} , Pb^{2+} , Ag^+ , and Hg^{2+}) was evaluated by the 1H NMR method.

It was found that in acetonitrile, photochromic ligands *E-4* and *E-5* form complexes with heavy and transition metal cations, which is accompanied by a hypsochromic shift of the long-wavelength absorption band. In addition, these ligands exhibit high selectivity and a large optical response to Hg^{2+} cations. Due to the involvement of the sulfonate group of the *N* substituent (a spacer) in coordination, ligand *E-5* was demonstrated to be able to form both monomeric and dimeric complexes with Hg^{2+} cations, which differ in the optical characteristics and stability. The above-described features can be useful for the development of new and the improvement of the already available optical sensors for heavy and transition metal cations.

Experimental

The TLC monitoring was carried out on DC-Alufolien Kieselgel 60 F_{254} plates. Column chromatography was performed on silica gel Kieselgel, 200–600 nm. The melting points (uncorrected) were measured on a Mel-temp II instrument. The 1H NMR spectra were recorded on Bruker DRX-500 (500.13 MHz) and Bruker DRX-400 (400.13 MHz) spectrometers. The chemical shifts and the spin-spin coupling constants were measured with an accuracy of 0.01 ppm and 0.1 Hz, respectively. The mass spectra were obtained on a Varian

MAT 311A instrument using a direct inlet system; the ionization energy was 70 eV. The electrospray ionization mass spectra (ESI-MS, 2 kW) were measured on a JEOL AccuTOF JMS-T100LC mass spectrometer.

The molar concentrations of the solutions of Hg, Pb, Ag, and Cu perchlorates were determined by direct titration of the corresponding EDTA solutions in the presence of murexide or Xylenol orange as the indicator. Acetonitrile of spectral grade with a water content of <0.005% (Aldrich) was used without additional purification. Solutions of ligands *E-4* and *E-5* were prepared and studied under red light. The electronic absorption spectra were recorded on a Varian-Cary spectrophotometer and a Specord M-40 instrument connected with a computer. The fluorescence spectra were measured on a FluoroLog (Jobin Yvon) spectrofluorimeter at 20 ± 1 °C. The fluorescence quantum yields of the ligands and the complexes were determined for air-saturated acetonitrile solutions at 20 ± 1 °C with the use of 9,10-diphenylanthracene in cyclohexane as the standard ($\phi_F = 0.9$). The excitation wavelength was 370 nm. The quantum yields were calculated from the corrected fluorescence spectra. The complexation of compounds *E-4* and *E-5* with Hg, Cu, Ag, and Pb perchlorates and perchloric acid was studied by spectrophotometric titration at 20 ± 1 °C by varying the concentration of the corresponding perchlorate at a constant concentration of the ligand. The complexation constants and the absorption spectra of the complexes were calculated from the electronic absorption spectra of solutions using the HYPERQUAD program.¹⁹ The time-resolved fluorescence spectra were measured on a system consisting of a Chromex 250 spectrograph connected with a Hamamatsu 5680 streak camera equipped with an M5676 fast sweep unit (the time resolution was 2 ps). The pulses for fluorescence excitation were generated using a home-made optical parametric generator with a further frequency doubling; the generator was pumped by the second harmonic of a Ti-sapphire femtosecond laser system (Femtopower Compact Pro). All lifetimes of the excited states were determined using depolarized excitation light. The maximum energy of the fluorescence excitation pulse was ≤ 100 nJ, the average power was 0.1 mW, and the pulse repetition frequency was 1 kHz. The excitation beam was focussed onto a quartz cell ($l = 10$ mm) at a spot of a diameter of 0.1 mm. The convolution of the streak camera slit at the time scale of 250 ps with a jitter of the electronic startup of scanning gave a Gaussian (by more than four orders of magnitude) apparatus function with a full width at half maximum (FWHM) of 20 ps. The fluorescence kinetics was analyzed by fitting the curves with the use of the Levenberg–Marquardt least-squares method and the solution of differential equations, which describe the time behavior of one excited state without consideration of changes in the occupancy of the ground state by the equation

$$dI(t)/dt = \text{Gauss}(t_0, \Delta t, A) - I(t)/\tau,$$

where $I(t)$ is the fluorescence intensity, τ is the lifetime of the excited state, Gauss is the Gaussian excitation pulse, t_0 is the time position of the maximum, Δt is the pulse width, and A is the pulse amplitude. The initial conditions: $I(-\infty) = 0$. All chosen solutions were characterized by χ^2 larger than 10^{-4} , and the correlation coefficient $R > 0.999$. The error of calculations of the lifetime was ≤ 0.1 ps. The fluorescence integration time was ≤ 90 s.

***N,N*-Bis(2-chloroethyl)aniline (1).** *N*-Phenyldiethanolamine (20 g, 0.11 mol) was added portionwise to phosphorus oxychloride (46 g, 0.3 mol) at 5 °C. The reaction mixture was kept at 100 °C for 1 h, cooled, and poured into benzene (60 mL). The benzene solution was poured onto ice (100 g). Then the benzene solution was separated, and the aqueous solution was extracted with benzene (3×50 mL). The benzene solutions were combined and dried with sodium sulfate. The solvent was removed on a rotary evaporator. After recrystallization from hot MeOH, the yield of compound **1** was 18.6 g (77%), m.p. 44 °C.

4-[Bis(2-chloroethyl)amino]benzaldehyde (2). A solution of *N,N*-bis(2-chloroethyl)aniline (**1**) (18.6 g, 0.085 mol) in DMF (65.7 mL) was added to a solution of phosphorus oxychloride (13.2 g, 0.086 mol) in DMF (65.7 mL) cooled to 0 °C. The reaction mixture was stored at 15 °C for 15 min, heated at 40 °C for 2 h, and poured into a mixture of water and ice. Unconsumed *N,N*-bis(2-chloroethyl)aniline (**1**) was rapidly filtered off. The filtrate was kept at 0 °C for 0.5 h. The precipitate was filtered off and recrystallized from EtOH. Compound **2** was obtained in a yield of 14.9 g (71%), m.p. 88 °C (*cf. lit. data*¹⁴: m.p. 85–88 °C). ¹H NMR (CDCl₃, 30 °C), δ : 3.66 (t, 4 H, H(9), H(14), ³J = 6.4 Hz); 3.82 (t, 4 H, H(8), H(13), ³J = 6.4 Hz); 6.73 (d, 2 H, H(2), H(6), ³J = 8.3 Hz); 7.75 (d, 2 H, H(3), H(5), ³J = 8.3 Hz); 9.76 (s, 1 H, H(11)).

4-(1,4-Dioxo-7,13-dithia-10-azacyclopentadec-10-yl)benzaldehyde (3). Solutions of 1,2-bis(2-mercaptoethoxy)ethane (1.14 g, 0.006 mol) and 4-[bis(2-chloroethyl)amino]benzaldehyde (1.4 g, 0.006 mol) each in EtOH (75 mL) were simultaneously added to a refluxing solution containing cesium carbonate (9.3 g, 0.028 mol), EtOH (300 mL), and water (300 mL) for 1 h. The reaction mixture was stirred at 60 °C for 20 h and then the solvent was evaporated under vacuum. The residue was extracted with benzene from water. The extracts were washed with water and concentrated under vacuum. The residue was chromatographed on a silica gel column using a 1 : 2 hexane–ethyl acetate mixture as the eluent, m.p. 86 °C. The yield was 1.4 g (65%). ¹H NMR (CDCl₃, 30 °C), δ : 2.74 (s, 4 H, H(11), H(15)); 2.88 (t, 4 H, H(2), H(9), ³J = 7.5 Hz); 3.62 (s, 4 H, H(5), H(6)); 3.70 (t, 4 H, H(3), H(8), ³J = 7.5 Hz); 3.78 (t, 4 H, H(12), H(14), ³J = 4.6 Hz); 6.65 (d, 2 H, H(17), H(21), ³J = 8.3 Hz); 7.69 (d, 2 H, H(18), H(20), ³J = 8.3 Hz); 9.70 (s, 1 H, H(22)). ¹³C NMR (100 MHz, CDCl₃), δ : 29.34 (C(11), C(15)); 31.43 (C(2), C(9)); 51.96 (C(12), C(14)); 70.67 (C(3), C(8)); 74.26 (C(5), C(6)); 111.09 (C(17), C(21)); 125.48 (C(16)); 132.18 (C(18), C(20)); 151.69 (C(19)); 189.88 (C(22)). MS (EI), m/z (I_{rel} (%)): 355 [M⁺] (100), 282 (9), 269 (4), 220 (8), 204 (24), 192 (22), 160 (32), 147 (34), 134 (23), 118 (12), 104 (8), 87 (12), 74 (13), 60 (11), 45 (11).

2-{(E)-2-[4-(1,4-Dioxo-7,13-dithia-10-azacyclopentadec-10-yl)phenyl]vinyl}-3-ethyl-1,3-benzothiazolium-3 perchlorate (4) and 2-{(E)-2-[4-(1,4-dioxo-7,13-dithia-10-azacyclopentadec-10-yl)phenyl]vinyl}-3-(4-sulfonatobutyl)-1,3-benzothiazolium-3 perchlorate (5). A mixture of 3-ethyl-2-methyl-1,3-benzothiazolium (3-sulfonatobutyl-1,3-benzothiazolium) perchlorate (0.41 mmol) and compound **3** (0.42 mmol) in pyridine (0.15 mL) and anhydrous EtOH (5 mL) was refluxed on an oil bath for 30 h. Then the reaction mixture was concentrated. The residue was washed with hot benzene and MeOH, dried, and recrystallized from MeOH.

Compound E-4. The yield was 0.150 g (58%), m.p. 255–257 °C. Found (%): C, 52.90; H, 5.99; N, 4.41.

$C_{27}H_{35}ClN_2O_6S_3$. Calculated (%): C, 52.71; H, 5.73; N, 4.55. 1H NMR (CD_3CN , 30 °C), δ : 1.63 (t, 3 H, H(34), $^3J = 7.3$ Hz); 2.81 (t, 4 H, H(11), H(15), $^3J = 4.9$ Hz); 2.97 (t, 4 H, H(2), H(9), $^3J = 7.9$ Hz); 3.65 (s, 4 H, H(5), H(6)); 3.80 (t, 4 H, H(3), H(8), $^3J = 4.9$ Hz); 3.84 (t, 4 H, H(12), H(14), $^3J = 7.9$ Hz); 4.72 (q, 2 H, H(33), $^3J = 7.3$ Hz); 6.88 (d, 2 H, H(17), H(21), $^3J = 9.2$ Hz); 7.32 (d, 1 H, H(22), $^3J_{trans} = 15.2$ Hz); 7.71 (t, 1 H, H(31), $^3J = 7.9$ Hz); 7.82 (t, 1 H, H(2), H(31), $^3J = 8.5$ Hz); 7.83 (d, 2 H, H(18), H(20), $^3J = 9.2$ Hz); 7.97 (d, 1 H, H(29), $^3J = 8.5$ Hz); 8.03 (d, 1 H, H(23), $^3J_{trans} = 15.2$ Hz); 8.15 (d, 1 H, H(32), $^3J = 7.9$ Hz). ^{13}C NMR (100 MHz, $DMSO-d_6$), δ : 13.47 (C(34)); 28.85 (C(2), C(9)); 30.63 (C(11), C(15)); 43.2 (C(33)); 51.10 (C(12), C(14)); 69.67 (C(3), C(4)); 72.50 (C(5), C(6)); 105.58 (C(22)); 111.6 (C(17), C(19)); 115.34 (C(29)); 123.59 (C(23)); 127.16 (C(30)); 128.68 (C(31)); 132.76 (C(18), C(20)); 149.96 (C(32)). ESI-MS of ligand *E-4* in MeCN, m/z : 515.0 [*E-4*] $^+$.

Compound E-5. The yield was 0.165 g (63%), m.p. 234–236 °C. Found (%): C, 55.74; H, 6.45; N, 4.48. $C_{29}H_{38}N_2O_5S_4$. Calculated (%): C, 55.92; H, 6.15; N, 4.50. 1H NMR (CD_3CN), δ : 1.25 (t, 2 H, H(35), $^3J = 7.3$ Hz); 2.76 (t, 4 H, H(11), H(15), $^3J = 4.9$ Hz); 2.80 (t, 2 H, H(34), $^3J = 6.7$ Hz); 2.91 (t, 4 H, H(2), H(9), $^3J = 7.3$ Hz); 3.12 (m, 2 H, H(36)); 3.66 (s, 4 H, H(5), H(6)); 3.77 (t, 4 H, H(12), H(14), $J = 4.9$ Hz); 4.74 (t, 2 H, H(33), $^3J = 7.9$ Hz); 6.77 (d, 2 H, H(17), H(21), $^3J = 8.5$ Hz); 7.64 (t, 1 H, H(29), $^3J = 7.3$ Hz); 7.66 (d, 1 H, H(22), $^3J_{trans} = 15.2$ Hz); 7.74 (t, 1 H, H(30), $^3J = 7.9$ Hz); 7.87 (d, 2 H, H(18), H(20), $^3J = 8.5$ Hz); 7.94 (d, 1 H, H(23), $^3J_{trans} = 15.2$ Hz); 8.00 (d, 1 H, H(28), $^3J = 7.9$ Hz); 8.05 (d, 1 H, H(31), $J = 7.9$ Hz). ESI-MS of ligand *E-5* in MeCN, m/z : 661.0 [(*E-5*)(K^+)], 645.0 [(*E-5*)(Na^+)], 623.1 [(*E-5*)(Na^+)].

Synthesis and analysis of complexes of ligand E-4 with Hg^{2+} perchlorate in MeCN. A solution of $Hg(ClO_4)_2$ ($1.25 \cdot 10^{-3}$ mol L^{-1}) in MeCN (66 μL) was added to a solution of *E-4* ($2.5 \cdot 10^{-5}$ mol L^{-1}) in MeCN (2.934 mL) prepared by dilution of the stock solution ($1.99 \cdot 10^{-3}$ mol L^{-1}). A complex predominantly of the 1 : 1 composition (ligand : cation) was obtained. **Complex [(E-4)(Hg^{2+})].** 1H NMR (CD_3CN), δ : 1.59 (t, 3 H, H(34), $^3J = 7.3$ Hz); 3.41–3.51 (m, 8 H, H(2), H(9), H(11), H(15)); 3.73 (br.s, 6 H, H(5), H(6), H(8)); 3.99 (s, 4 H, H(12), H(14)); 4.90 (q, 2 H, H(33), $^3J = 7.3$ Hz); 7.62 (d, 2 H, H(17), H(21), $^3J = 8.5$ Hz); 7.73 (d, 1 H, H(22), $^3J_{trans} = 15.9$ Hz); 7.86 (t, 1 H, H(31), $^3J = 7.9$ Hz); 7.95 (t, 1 H, H(2), H(31), $^3J = 7.9$ Hz); 8.11 (d, 2 H, H(18), H(20), $^3J = 8.5$ Hz); 8.16 (d, 1 H, H(29), $^3J = 8.5$ Hz); 8.18 (d, 1 H, H(23), $^3J_{trans} = 15.9$ Hz); 8.30 (d, 1 H, H(32), $^3J = 7.9$ Hz). ESI-MS of ligand *E-4* in MeCN in the presence of Hg^{2+} cations, m/z : 407.8 [(*E-4*)(Hg^{2+})], 339.7 [(Hg^{2+}) $_2$ (ClO_4^-) $_2$ (MeCN) $_2$]. **Complex [(Z-4)(Hg^{2+})].** 1H NMR (CD_3CN), δ : 1.59 (t, 3 H, H(34), $^3J = 7.3$ Hz); 3.23–3.67 (m, 8 H, H(2), H(9), H(11), H(15)); 4.81 (q, 2 H, H(33), $^3J = 7.3$ Hz); 5.55–6.13 (m, 12 H, H(5), H(6), H(8), H(12), H(14), H(15)); 7.10 (d, 1 H, H(22), $^3J_{cis} = 11.6$ Hz); 7.47 (d, 2 H, H(17), H(21), $^3J = 8.1$ Hz); 7.56 (d, 2 H, H(18), H(20), $^3J = 8.1$ Hz); 7.79 (d, 1 H, H(23), $^3J_{cis} = 11.6$ Hz); 7.80 (t, 1 H, H(31), $^3J = 7.8$ Hz); 7.91 (t, 1 H, H(30), $^3J = 7.8$ Hz); 8.11 (d, 1 H, H(29), $^3J = 8.3$ Hz); 8.17 (d, 1 H, H(32), $^3J = 8.3$ Hz).

Synthesis and analysis of complexes of ligand E-5 with Hg^{2+} perchlorate in MeCN. A solution of $Hg(ClO_4)_2$ ($1.25 \cdot 10^{-3}$ mol L^{-1}) in MeCN (66 μL) was added to a solution of *E-5* ($2.5 \cdot 10^{-5}$ mol L^{-1}) in MeCN (2.934 mL) prepared by dilution of the concentrated solution ($3.21 \cdot 10^{-4}$ mol L^{-1}). A complex

predominantly of the 1 : 1 composition (ligand : cation) was obtained. **Complex [(E-5)(Hg^{2+})].** 1H NMR (CD_3CN), δ : 1.27 (s); 2.95 (t, 2 H, $^3J = 6.7$ Hz); 3.28–3.95 (m, H(2), H(5), H(6), H(8), H(9), H(11), H(12), H(14), H(15), H(34)); 4.91 (t, 2 H, H(33), $^3J = 7.9$ Hz); 7.51 (d, 2 H, H(17), H(21), $^3J = 7.3$ Hz); 7.70 (t, 1 H, H(29), $^3J = 7.9$ Hz); 7.88 (t, 1 H, H(30), $^3J = 7.9$ Hz); 7.97 (d, 1 H, H(22), $^3J_{trans} = 15.2$ Hz); 8.01 (d, 1 H, H(28), $^3J = 9.7$ Hz); 8.08 (d, 1 H, H(23), $^3J_{trans} = 15.2$ Hz); 8.15 (d, 2 H, H(18), H(20), $^3J = 7.3$ Hz); 8.22 (d, 1 H, H(31), $^3J = 7.9$ Hz). **Complex [(Z-5)(Hg^{2+})].** 1H NMR (CD_3CN), δ : 1.27 (s); 3.39–3.94 (m, H(2), H(5), H(6), H(8), H(9), H(11), H(12), H(14), H(15), H(34)); 6.74 (d, 1 H, H(22), $^3J_{cis} = 12.6$ Hz); 7.06 (d, 2 H, H(17), H(21), $^3J = 6.1$ Hz); 7.23 (d, 2 H, H(18), H(20), $^3J = 6.1$ Hz); 7.47 (d, 1 H, H(23), $^3J_{cis} = 11.6$ Hz); 7.81 (t, 1 H, H(29), $^3J = 6.8$ Hz); 7.97 (t, 1 H, H(30), $^3J = 6.8$ Hz); 8.15 (d, 1 H, H(28), $^3J = 7.9$ Hz); 8.23 (d, 1 H, H(31), $^3J = 7.9$ Hz). ESI-MS of a solution of ligand *E-5* in MeCN in the presence of Hg^{2+} cations, m/z : 923.0 [(*E-5*)(Hg^{2+})(ClO_4^-)], 753.0 [(*E-5*) $_2$ (Hg^{2+})(MeCN)(H_2O)], 723.0 [(*E-5*) $_2$ (Hg^{2+})], 661.0 [(*E-5*)(K^+)], 645.0 [(*E-5*)(Na^+)], 441.9 [(*E-5*)(Hg^{2+})(MeCN)(H_2O)], 411.8 [(*E-5*)(Hg^{2+})].

Photochemical transformations were performed by irradiating acetonitrile solutions of *E-4*, *E-5*, [(*E-4*)(Hg^{2+})], and [(*E-5*)(Hg^{2+})] with a light of a mercury lamp (DRK-120, 120 W). The lines of the mercury lamp spectrum were separated with the use of glass light filters from a standard kit of colored glass light filters (UFS-2 + ZhS-3, UFS-6 + BS-7, PS-13 + ZhS-10, and PS-7 + SZS-21 + ZhS-18 for separation of lines at $\lambda = 313, 365, 405,$ and 546 nm, respectively). The photoprocesses were studied with stirring in a 1-cm quartz cell equipped with a fluoroplast stopper; the radiation intensity was $5.233 \cdot 10^{-6}$ Einstein $s^{-1} L^{-1}$. To calculate the spectrum of *Z-4* by Fischer's method, a solution of *E-4* was irradiated with light at $\lambda = 365$ and 436 nm until the corresponding photostationary states were established; to calculate the spectrum of *Z-5*, at $\lambda = 313, 365, 405,$ and 436 nm.

X-ray diffraction study. Single crystals of **3** suitable for X-ray diffraction study were grown by crystallization from a hexane solution. A single crystal coated with perfluorinated oil was mounted on a Bruker SMART CCD diffractometer. The experimental X-ray data were collected at low temperature. The crystal parameters and the X-ray diffraction data collection and refinement statistics for compound **3** are given in Table 8. The structure was solved by direct methods and refined by the full-matrix least-squares method against F^2 with anisotropic displacement parameters for all nonhydrogen atoms. The H atoms were located in difference Fourier maps and refined isotropically. The unusually high residual electron density maxima are, apparently, attributed to an additional disorder of the macrocycles over a number of closely spaced positions of the S atoms. All highest electron density peaks are located near these atoms. This conclusion is consistent with high flexibility of the macrocycle. All calculations were carried out using the SHELXTL-Plus program package.²⁷ The results were deposited with the Cambridge Structural Database (CSD-632898).*

* These data can be obtained, free of charge, on application to the Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 12 2333 6033; e-mail: deposit@ccdc.cam.ac.uk).

Table 8. Crystal parameters and the X-ray diffraction data collection and refinement statistics for compound **3**

Parameter	Characteristic
Molecular formula	C ₁₇ H ₂₅ NO ₃ S ₂
Molecular weight (kg kmol ⁻¹)	355.50
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> /Å	8.248(5)
<i>b</i> /Å	14.618(8)
α /deg	102.024(3)
γ /deg	104.931(2)
<i>V</i> /Å ³	1799.2(2)
<i>Z</i>	4
ρ_{calc} /g cm ⁻³	1.312
<i>F</i> (000)	760
μ (Mo-K α)/mm ⁻¹	0.310
Crystal dimensions/mm	0.42×0.38×0.32
<i>T</i> /K	123.0(2)
Radiation (λ /Å)	Mo-K α (0.71073)
Scan mode	ω
θ -Scanning range/deg	1.32–27.00
Ranges of reflection indices	$-9 \leq h \leq 10, -18 \leq k \leq 18, -21 \leq l \leq 20$
Number of measured reflections	8979
Number of independent reflections	7020 ($R_{\text{int}} = 0.0247$)
Number of reflections with $I > 2\sigma(I)$	5358
Number of refinement variables	607
<i>R</i> Factors based on reflections with $I > 2\sigma(I)$	$R_1 = 0.0895,$ $wR_2 = 0.233$
<i>R</i> Factors based on all reflections	$R_1 = 0.112,$ $wR_2 = 0.249$
Goodness-of-fit on F^2	1.073
Residual electron density/e Å ⁻³ (min/max)	-0.912/2.903

This study was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-33201), the INTAS (Grant 03-51-4696), and the US Civilian Research and Development Foundation (CRDF, Grant RUC2-2656-MO-05).

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Received September 19, 2006;
in revised form January 26, 2007