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New dithiacrown–ether butadienyl dyes: synthesis, structure, and complex formation with heavy metal cations

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Benzothiazole type butadienyl dyes containing a dithia-15-crown-5 (2a) or dithia-18-crown-6 ether (2b) moieties were synthesized. The structures of dyes 2a,b and their complexes with Ag^+ and Pb^{2+} were studied by an X-ray crystallography. It was found that the conformations of dithiacrown–ether moieties of dyes 2a,b are unfavorable for complex formation and change significantly upon binding of Ag^+ or Pb^{2+}. The complexation of 2a,b with Ag^+, Cd^{2+}, Pb^{2+}, and Hg^{2+} in water–acetonitrile mixtures with different contents of water ($P_W = 0$–75%, v/v) was studied by ^1H NMR, UV–Vis spectroscopy, and polarography. In anhydrous acetonitrile, the stability constants of 1:1 complexes change in the sequence $Cd^{2+} < Pb^{2+} \leq Ag^+ << Hg^{2+}$ in the case of 2a and in the sequence $Cd^{2+} < Ag^+ < Pb^{2+} << Hg^{2+}$ in the case of 2b. As P_W increases, the thermodynamic stability of Ag^+ complexes increases. The opposite effect is observed for the complexes with Cd^{2+}, Pb^{2+}, and Hg^{2+}. When $P_W \sim 50\%$, the stability constants of complexes with Cd^{2+} and Pb^{2+} become too small to be measured. The selectivity of ligands 2a,b toward Hg^{2+} *versus* Ag^+ is very high at any P_W values (selectivity coefficients $> 10^4$). The complexation of 2a,b with Hg^{2+} at $P_W \leq 50\%$ is accompanied by a substantial hypsochromic effect. This allows dithiacrown-containing butadienyl dyes to be used as selective optical molecular sensors for heavy metal ions, in particular, in aqueous solutions. Copyright © 2009 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: butadienyl dyes; dithiacrown–ethers; heavy metals; optical molecular sensors

INTRODUCTION

Crown ethers have found wide use in various fields of chemistry owing to their ability to selectively bind alkali and alkaline-earth metal cations. Specifically, the first selective reagents for colorimetric determination of alkali metal cations were based on crown ethers.[1,2] In the case of chromogenic crown-compounds with donor–acceptor type chromophores, the formation of a cation–macrocycle complex can be accompanied by a substantial change in the energy of the long-wavelength absorption band, provided that the crowned cation forms a coordination bond with at least one of the heteroatoms of the chromophore.[2–5] The coordination of the cation to a heteroatom of the electron-donor moiety leads to hypsochromic changes in the absorption spectrum. In contrast, the electronic interaction of the cation with a heteroatom of the electron-acceptor fragment results in a bathochromic effect. Crown-containing styryl and butadienyl dyes are examples of donor–acceptor chromoionophores possessing negative ionochromism.[6–8]

The properties of chromogenic crown ethers as selective reagents for the colorimetric determination of alkali and alkaline-earth metal cations have been adequately studied. However, the advantages of macrocyclic ligands for the development of optical molecular sensors for transition, noble, and heavy metal cations remain largely unutilized.

It is known that replacement of one or several oxygen atoms in crown ethers by other donor atoms may considerably change their ability to bind metal cations. For example, 1,10-dithia-18-crown-6 ether exhibits a very low affinity for alkali metal cations compared to that of 18-crown-6 ether, but it forms much more stable complexes with Hg^{2+} and Ag^+ both in organic

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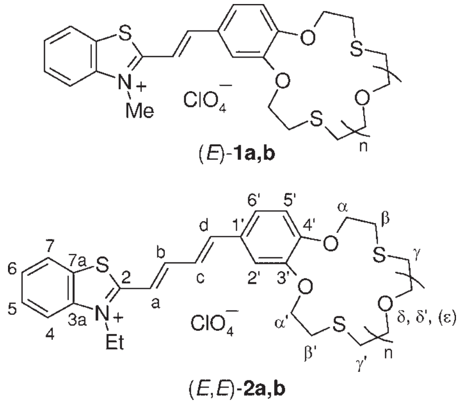


Scheme 1. Dyes **1** and **2**: $n = 1$ (**a**), 2 (**b**)

solvents and in water.[9,10] Previously, we made attempts to use the ion-selective properties of thiacrown ethers for the design of photoswitchable ligands and chromogenic reagents for heavy metal cations.[11–14] It was shown that styryl dyes containing a dithia-15(18)-crown-5(6)-ether moiety (**1a,b**, Scheme 1) effectively bind Hg^{2+} ions in MeCN; the complexation is accompanied by hypsochromic effect, which is, however, much less pronounced than that in reactions of alkaline-earth metal cations with similar crown ether-based structures.

The experimental data obtained previously for crown-containing polymethine dyes demonstrate[8] that the replacement of vinyl fragment by butadienyl is advantageous; in particular, this replacement induces a bathochromic shift and an increase in intensity of the long-wavelength absorption band. Therefore, we synthesized new chromogenic dithiacrown ethers **2a,b** based on benzothiazole butadienyl dyes (Scheme 1). From a practical point of view, it is of interest to study the effect of the medium on the selectivity of complexation of chromoionophores **2a,b** and on the magnitude of cation-induced hypsochromic effect. In our opinion, compounds with dithiacrown ether and butadienyl dye fragments could find use as optical molecular sensors for heavy metal cations.[15]

This paper presents the synthesis of dyes **2a,b**, X-ray diffraction data for **2a,b,** and complexes **2a**·Ag^+ and **2b**·Pb^{2+}. The complexation of dyes **2a,b** with Hg^{2+}, Ag^+, Pb^{2+}, and Cd^{2+} in acetonitrile and water–acetonitrile mixtures was studied by ^1H NMR, UV–Vis spectroscopy, and differential pulse polarography.

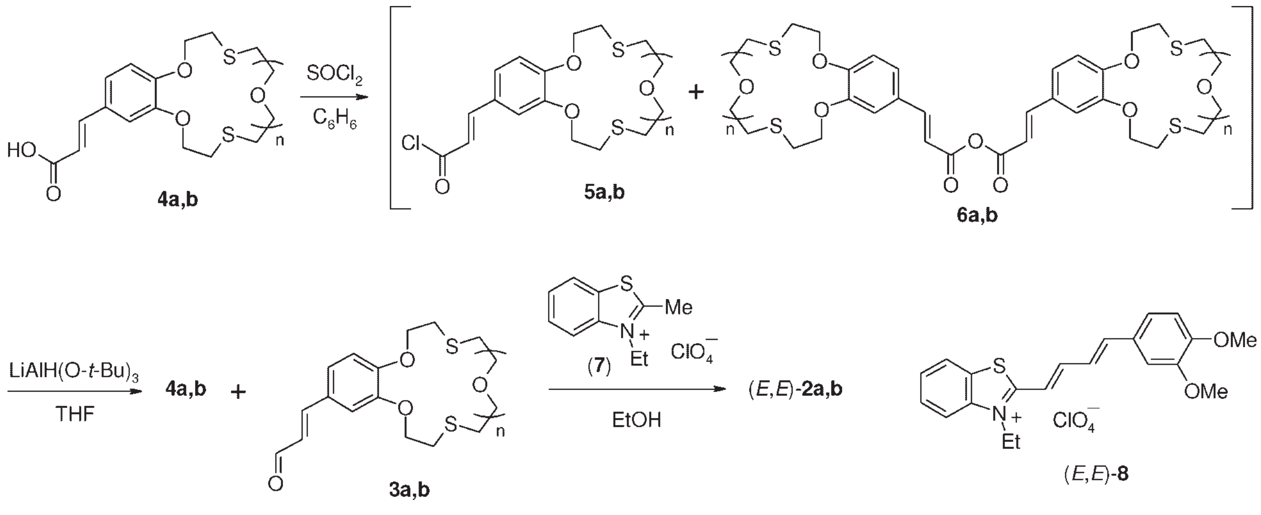
RESULTS AND DISCUSSION

Synthesis

Dithiacrown-containing butadienyl dyes **2a,b** were synthesized as depicted in Scheme 2. The key intermediates, *viz.*, dithiacrown-ether cinnamaldehydes (*E*)-**3a,b**, were prepared by a published procedure.[16] For this purpose, cinnamic acids (*E*)-**4a,b** were heated in benzene with a threefold excess of $SOCl_2$ in order to prepare acyl chlorides **5a,b**, which were then treated with $LiAlH(O\text{-}t\text{-}Bu)_3$. In the study cited, the compounds **5a,b** were used without isolation and the yields of aldehydes **3a,b** did not exceed 65%. ^1H NMR study showed that treatment of acids **4a,b** with $SOCl_2$ (3 equiv.) gives not only acyl chlorides **5a,b** but also cinnamic acid anhydrides **6a,b** (**5**:**6** molar ratio is about 2:1). An attempt to increase the relative content of chloride **5a** in the mixture by increasing the excess of $SOCl_2$ (to 20 equiv.) was not a success. Mixtures of **5** and **6** were treated with $LiAlH(O\text{-}t\text{-}Bu)_3$ in anhydrous THF and, after hydrolysis of the reaction mixture, the initial cinnamic acids **4a,b** (recovery 20–53%) and target cinnamaldehydes **3a,b** (yields 66–73% based on converted **4a,b**) were isolated. Judging by the yields of **3a,b**, anhydride **6**, like acyl chloride **5**, can be reduced by $LiAlH(O\text{-}t\text{-}Bu)_3$ to give **3**; however, in this case, cinnamic acid **4** is formed as a by-product of reduction.

Dyes **2a,b** were prepared by condensation of dithiacrown-ether cinnamaldehydes **3a,b** with 2-methyl-3-ethylbenzothiazolium perchlorate **7**[17] on long-term heating in anhydrous EtOH (yields 55% (**2a**) and 58% (**2b**)). According to spin–spin coupling constants $J_{H(a),H(b)} = 14.8$, $J_{H(c),H(d)} = 15.3$, and $J_{H(b),H(c)} = 10.3$ Hz (the atom numbering differing from that dictated by the IUPAC rules is shown in Scheme 1), dyes **2a,b** have *E,E* configuration and s-trans conformation of the butadiene fragment.

The reference butadienyl dye **8** (Scheme 2) was synthesized as described previously.[8] This dye contains two methoxy groups in place of the dithiacrown–ether moiety and, therefore, it cannot form complexes with metal cations.



Scheme 2. Synthesis of dyes **2a,b** (**2**–**6**: $n = 1$ (**a**), 2 (**b**)); structure of dye **8**

X-ray diffraction studies

X-ray diffraction studies of butadienyl dyes **2a,b**, **8**, and two complexes with heavy metal perchlorates were performed to elucidate the features of bond length distribution in the chromophore fragments and the macrocycle conformations. The cations of dyes from structures **2a**, **2b**·MeCN, and **8**·$C_4H_8O_2$ are shown in Fig. 1. Selected components of structures **2a**·$AgClO_4$·3MeCN and **2b**·$Pb(ClO_4)_2$·0.5C_6H_6 are represented in Fig. 2. Identical atom numbering schemes in the chromophore fragments are used for all structures.

The chromophore fragments in **2a**, **2b**·MeCN, and **8**·$C_4H_8O_2$ are virtually planar. The dihedral angles between the benzene ring C(14), . . ., C(19) and planar butadiene system C(9), . . ., C(14) and those between the latter system and the benzothiazole residue are 2.0 and 9.3° for **2a**, 3.5 and 1.7° for **2b**, and 2.8 and 3.5° for **8**, respectively. Selected geometric parameters are listed in Table 1S of Supporting Information. Comparison of the

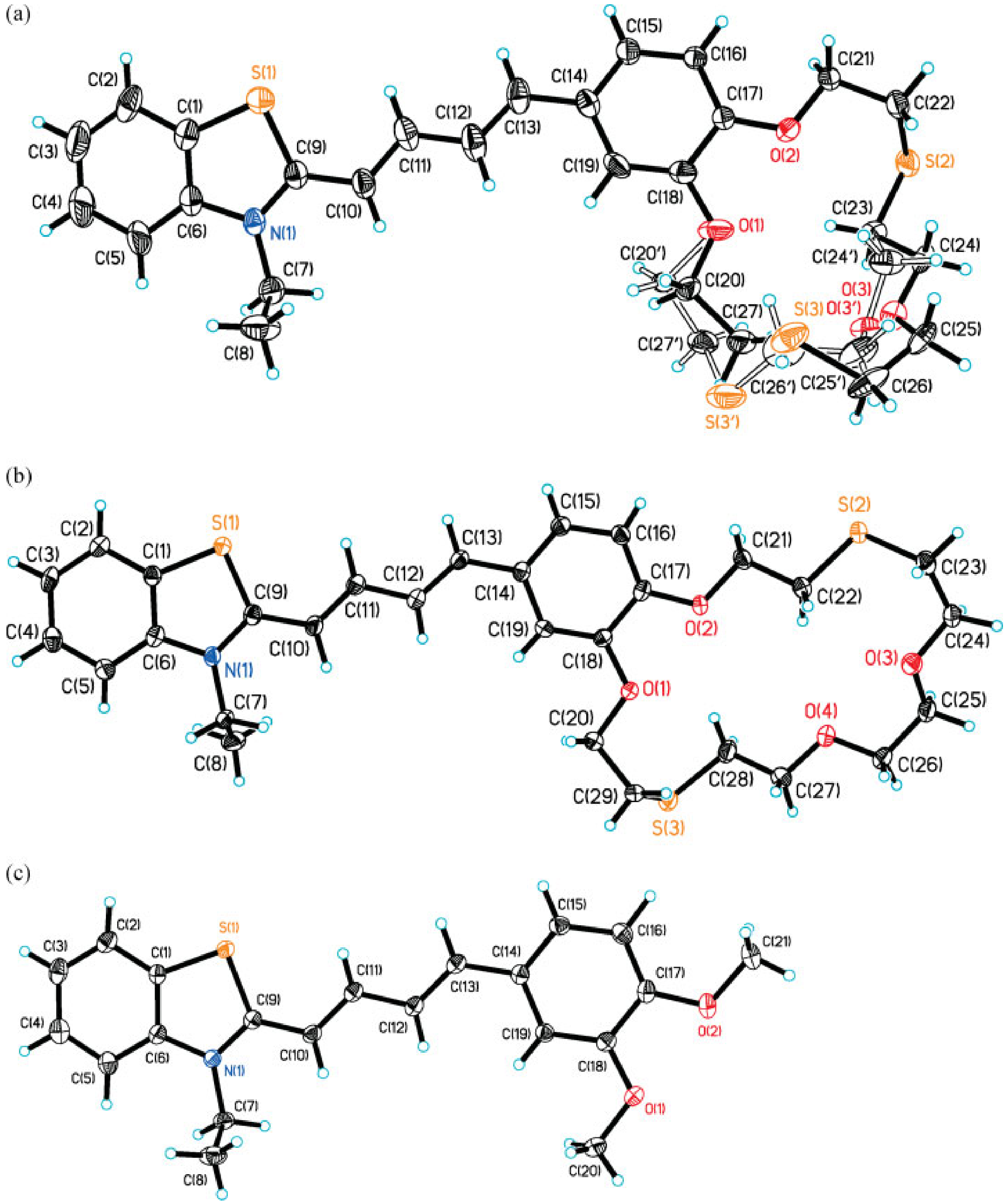


Figure 1. Cations of dyes from structures **2a** (a), **2b**·MeCN (b), and **8**·$C_4H_8O_2$ (c). The crown–ether fragment is disordered over two positions in **2a**. All non-hydrogen atoms are shown with 40% (a) and 50% (b,c) probability of thermal anisotropic atom displacement parameters

corresponding geometric parameters of **2a**, **2b**, and **8** reveals similar trends in bond length distribution in the chromophore fragments. This means that geometric parameters of the chromophore are little affected by the macrocyclic fragment. Pronounced tendency to bond length alternation in the benzene ring of the benzocrown–ether system and significant localization of the double bonds in the butadiene bridge are evident. In all structures, the C(17)—C(18) bond common to the benzene and crown–ether systems [av. 1.416(5) Å] is markedly elongated, whereas two adjacent bonds [C(16)—C(17) and C(18)—C(19), av. 1.384(5) and 1.371(5) Å], are shortened. The C(14)—C(19) bond [av. 1.422(5) Å] is nearly as much elongated as the C(17)—C(18) bond, and the other two bonds, C(14)—C(15) and C(15)—C(16), are more similar in the length [av. 1.389(5) and 1.395(5) Å] than any other two adjacent bonds in the ring. This fact may be a consequence of some influence of the butadiene system located in the s-trans position to C(14)—C(15) bond (it is well known that conjugation of two double bonds is more efficient in systems with s-trans position of the bonds).

Exocyclic (with respect to the benzene ring) bond angles at the C(17) and C(18) atoms undergo a deformation previously observed for all benzocrown–ether systems.[8,9,18] Actually, the bond angles O(1)—C(18)—C(19) and O(2)—C(17)—C(16) are opened to $\sim 125.3(3)^\circ$, whereas the bond angles O(1)—C(18)—C(17) and O(2)—C(17)—C(18) are reduced to $\sim 114.9(3)^\circ$ in compounds **2a,b** and **8**. This type of deformation results in the O(1) and O(2) oxygen atoms approaching each other to a distance of 2.54–2.58 Å, which is shorter than the sum of the van der Waals radii (~2.8 Å). This is usually interpreted in terms of conjugation between the lone electron pairs (LEPs) in the p orbitals of O(1) and O(2) atoms and the benzene ring π-system. The conjugation is favored by the conformation of the C(20)—O(1)—C(18)—C(19) and C(21)—O(2)—C(17)—C(16) fragments where these torsion angles are fairly small (-16.6–20.8°).

In the dithia-18-crown-6-ether moiety of **2b**, both the sulfur atoms are oriented outside the macrocycle, i.e. the observed conformation of macrocycle is imperfect with regard to the polydentate coordination of a heavy metal cation. It is clear that this coordination requires significant reorientation of the macrocycle chain. In structure **2a**, the dithia-15-crown-5-ether fragment is disordered over two positions corresponding to two orientations of the chain between the C(23) and O(1) atoms (Fig. 1a). In both conformers of **2a**, the sulfur atoms are oriented outside the macrocycle similar to **2b**·MeCN. So, the formation of dithia-15-crown-5-ether metal complexes should also be accompanied by a significant reorientation of atoms of the macrocycle chain.

The conformations of the benzodithia-15(18)-crown-5(6)-ether moieties favorable for their coordination with a heavy metal cation can be derived from structure determination of complexes **2b**·$Pb(ClO_4)_2 \cdot 0.5C_6H_6$ and **2a**·$AgClO_4 \cdot 3MeCN$. Selected geometric parameters for these complexes are listed in Tables 2S and 3S of Supporting Information, respectively. The too low accuracy of these X-ray structures prevents definite conclusions about bond length redistribution in the whole chromophore fragment. However, the bond length alternation in the butadiene fragments is quite evident and bond length distribution in the benzene rings analogous to that found in free dyes **2a,b** and **8** may also be traced.

In complex **2b**·$Pb(ClO_4)_2 \cdot 0.5C_6H_6$ (Fig. 2b), the Pb(1) atom is coordinated by all heteroatoms of the macrocycle and two pairs of oxygen atoms from two perchlorate anions situated above and below the macrocycle. The coordination polyhedron of Pb(1) is irregular which is typical of this metal. The Pb(1) ion forms equatorial coordination bonds with two sulfur and four oxygen atoms of the macrocycle and is displaced from the mean plane of the equatorial heteroatoms by 0.07 Å. Two oxygens, O(3) and O(4), which are sp^3 hybridized, interact closer with the metal than two other oxygens, O(1) and O(2), whose LEPs occupying the corresponding p orbitals are involved in conjugation with the benzene ring and LEPs occupying the sp^2-hybrid orbitals participate in interactions with Pb(1) [the Pb(1)—O(1)/O(2) distances are 2.731(8) and 2.857(7) Å, the bond angles Pb(1)—O(1)—C and Pb(1)—O(2)—C vary within 113.8(6)–122.2(6)°]. Since the van der Waals radius of sulfur is ~0.4 Å longer than that of oxygen, the Pb(1)—S(2)/S(3) distances [3.065(3) and 2.979(3) Å] and the Pb(1)—O(3)/O(4) distances [2.698(8) and 2.633(7) Å] correspond to similar interactions.

The fact that the conformation of the macrocycle changes dramatically upon its coordination with the Pb^{2+} ion is evident from Fig. 3, which shows superposition of fragments over the benzene rings in **2b**·MeCN and **2b**·$Pb(ClO_4)_2 \cdot 0.5C_6H_6$. The macrocycle adopts a crown-like conformation in the complex, whereas the conformation of the free crown–ether moiety in **2b**·MeCN is flattened. So we may conclude that the benzodithia-18-crown-6 ether is flexible enough to fit its conformation to coordination requirements of a metal cation.

The crystal unit cell of **2a**·$AgClO_4 \cdot 3MeCN$ contains the cation of dye **2a** coordinated to Ag(1) (Fig. 2a), two perchlorate anions, one of which is disordered over two positions, and three acetonitrile solvate molecules. The 15-membered macrocycle adopts a crown-like conformation in this complex, similar to the structure **2b**·$Pb(ClO_4)_2 \cdot 0.5C_6H_6$. The coordination polyhedron of Ag(1) is irregular, which is typical of a single-charged silver cation. The Ag(1) ion is situated under a center of the macrocyclic cavity at a distance of 0.95 Å from the mean plane of the macrocyclic heteroatoms. The Ag(1) atom forms three strong bonds with two sulfur atoms and nitrogen atom N(1S) of the acetonitrile molecule. The Ag(1)—S(2)/S(3) distances [2.5199(19) and 2.4954(19) Å] are even shorter than the Ag(1)—O distances [2.709(4)–2.866(5) Å], which demonstrates a higher affinity of silver(I) to sulfur as compared to that of lead(II).

Angular deformations of C(17) and C(18) atoms, similar to those in structure **2a**, are also found in structure **2a**·$AgClO_4 \cdot 3MeCN$. This means that the O(1) and O(2) atoms have sp^2 hybridization favorable for conjugation with the whole chromophore, which is also evident from the bond angles at these atoms [115.8(5) and 118.2(5)°] and torsion angles C(20)—O(1)—C(18)—C(19) and C(21)—O(2)—C(17)—C(16) (15.3 and -3.7°, respectively). The Ag(1)—O(1)—C and Ag(1)—O(2)—C angles vary within 108.9(4)–114.2(4)°, which is not ideal for interaction of the sp^2-hybridized orbitals of the oxygen LEPs with the metal and distinguishes the coordination of this metal from that of Pb(1) in **2b**·$Pb(ClO_4)_2 \cdot 0.5C_6H_6$. With this geometry, the LEPs of O(1) and O(2) in **2a**·$AgClO_4 \cdot 3MeCN$ occupying their p orbitals are partly oriented toward the metal ion and can interact with it. This effect should result in lower involvement of these LEPs in conjugation with the chromophore, giving rise to a hypsochromic shift in the absorption spectra upon complex formation (discussed below). This conclusion agrees with the fact that the bonds of Ag(1) with oxygen atoms O(1) and O(2) closest to the benzene ring are shorter [2.736(4) and 2.709(4) Å] than the bond with the oxygen atom O(3) more distant from the benzene ring [2.866(5) Å], whereas, in **2b**·$Pb(ClO_4)_2 \cdot 0.5C_6H_6$, the opposite correlation is observed.

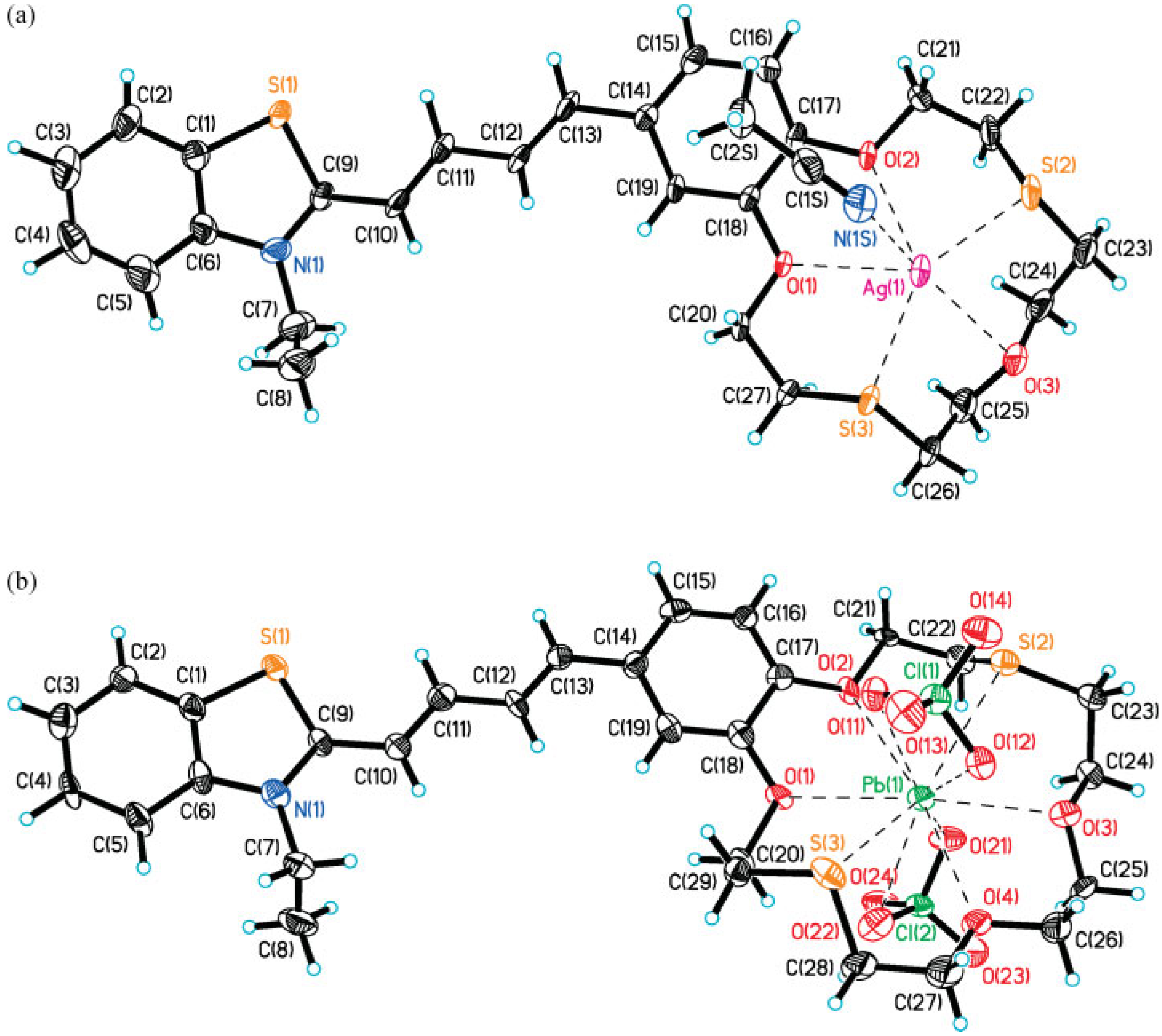


Figure 2. Selected components of structures **2a**·AgClO$_4$·3MeCN (a) and **2b**·Pb(ClO$_4$)$_2$·0.5C$_6$H$_6$ (b). The components that do not coordinate with the metal cation are not shown. All non-hydrogen atoms are shown with 50% probability of thermal anisotropic atom displacement parameters

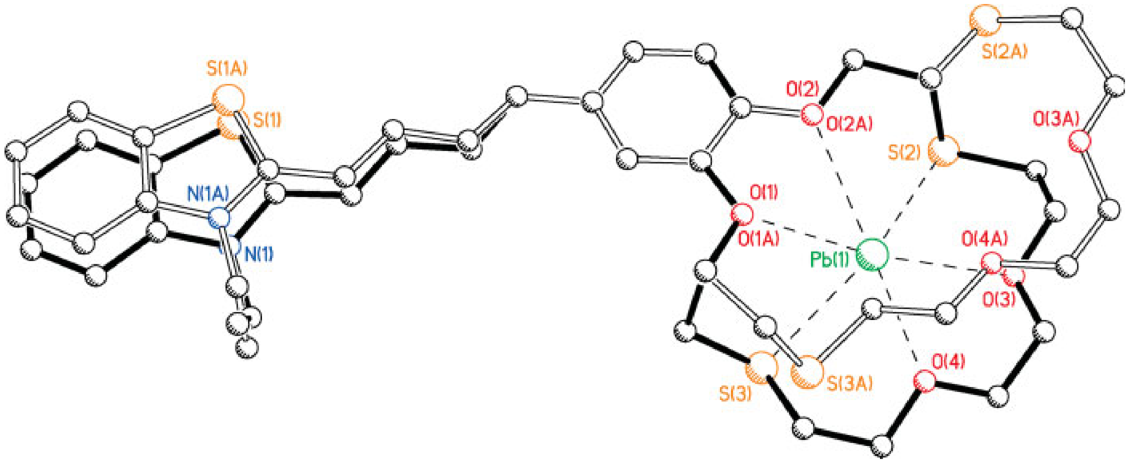


Figure 3. Superposition of cations from structures **2b**·Pb(ClO$_4$)$_2$·0.5C$_6$H$_6$ (solid lines) and **2b**·MeCN (hollow lines) over benzene rings

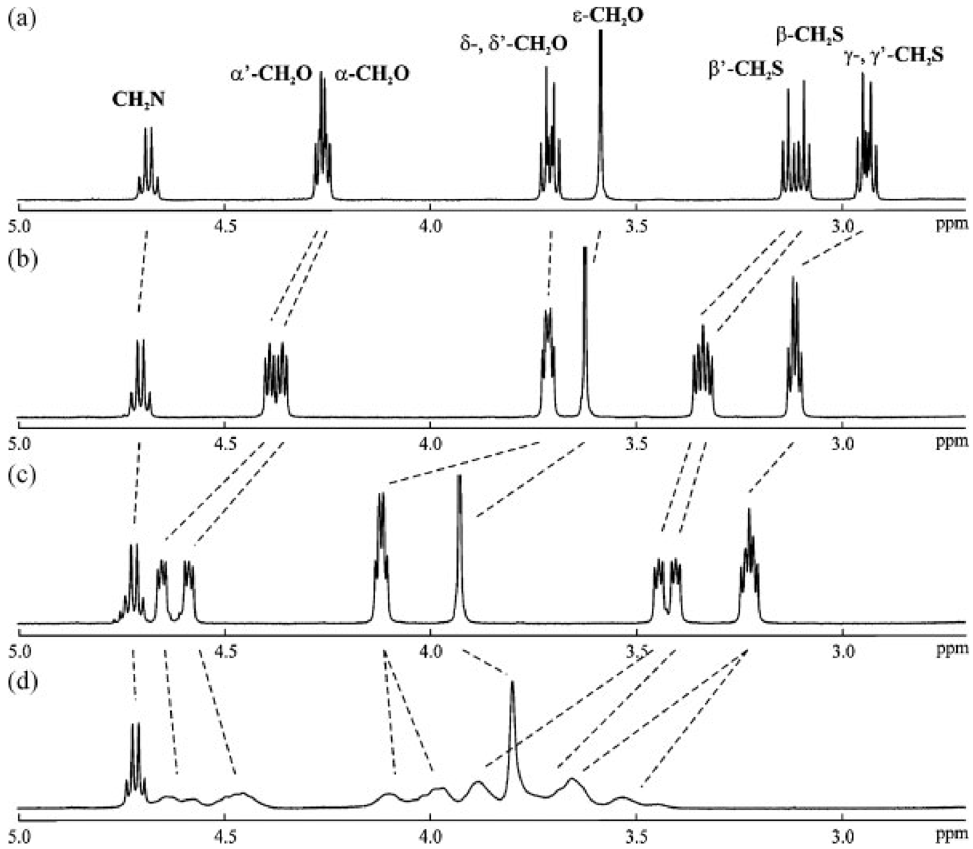


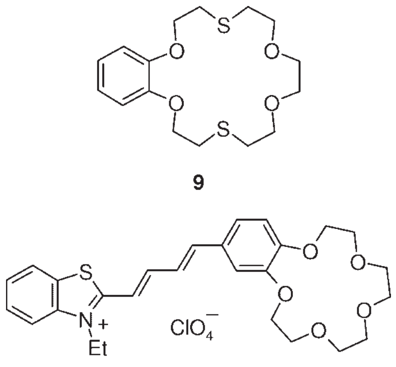
Figure 4. ^{1}H NMR spectra (region of aliphatic protons) of dye **2b** ($C = 5 \times 10^{-3}$ M) (a) and its mixtures with $AgClO_4$ (b), $Pb(ClO_4)_2$ (c), and $Hg(ClO_4)_2$ (d) ($C_M = 6 \times 10^{-3}$ M) in MeCN-d_3 at 30 °C

NMR spectroscopy studies

The complexation of dyes **2a,b** with heavy metal perchlorates in MeCN-d_3 was studied by ^{1}H NMR spectroscopy. All ^{1}H NMR signals of the dyes were found to shift downfield after the addition of Ag(I), Cd(II), Pb(II), or Hg(II) perchlorate (Fig. 4 for **2b**). The most pronounced shifts ($\Delta\delta_H$ up to 0.6 ppm) were found for the signals of methylene protons of the dithiacrown–ether moiety, which is indicative of complex formation between the metal cation and the macroheterocycle. The degrees of involvement of macro-ring heteroatoms in the binding of metal cation are different depending on the nature of the cation. In systems **2a,b**/Ag^+ and **2a,b**/Hg^{2+}, the ring methylene groups linked directly to sulfur atoms show the largest $\Delta\delta_H$. This is a consequence of the high affinity of 'soft' Ag^+ and Hg^{2+} ions to the 'soft' sulfur(II) atoms (the X-ray data for the complex **2a**·$AgClO_4$·3MeCN also attest to relatively high affinity of Ag^+ for sulfur atoms). In the systems **2a,b**/Cd^{2+} and **2a,b**/Pb^{2+}, the $\Delta\delta_H$ values for the methylene protons of the dithiacrown–ether moiety differ insignificantly, which implies an almost equivalent involvement of all macrocycle heteroatoms in the binding of Cd^{2+} and Pb^{2+} (the same conclusion was drawn for the crystalline complex **2b**·$Pb(ClO_4)_2$·$0.5C_6H_6$).

The addition of heavy metal perchlorates to a solution of model dye **8** barely affected the ^{1}H NMR spectrum, which is due to the absence of a crown–ether moiety in **8**.

Using ^{1}H NMR titration, we determined the composition and thermodynamic stability of complexes **2a,b** and model benzo-4,13-dithia-18-crown-6 ether (**9**)[19] (Scheme 3) with Ag^+, Cd^{2+}, and Pb^{2+} ions in MeCN-d_3. The direct titration procedure was used in the case of relatively low stability constants ($K < 10^5$ M^{-1}); in those cases where the stability constants were slightly above the upper limit of applicability of direct NMR titration ($10^5 < K < 10^6$ M^{-1}), competitive titration was used. The experimental conditions and data processing method are given in the Experimental section. The plots of $\Delta\delta_H$ *versus* the metal-to-ligand ratio for some protons in the systems **2a**/Ag^+ and **2a**/Pb^{2+} are shown in Figs 1S and 2S of Supporting Information, respectively. According to ^{1}H NMR titration data, in



9

(*E,E*)-**10**

Scheme 3. Compound **9** and dye **10**

all systems except for **2a**/Pb^{2+}, only 1:1 complexes were formed (Eqn (1)):

$$L + M^{m+} \overset{K_{1:1}}{\rightleftharpoons} L \cdot M^{m+} \qquad (1)$$

where L is the dithiacrown compound, $K_{1:1}$ (M^{-1}) is the stability constant of complex 1(L):1(M^{m+}) ($m = 1, 2$).

The system **2a**/Pb^{2+} was found to contain 1:1 and 2:1 complexes in the concentration range studied. The latter may be sandwich type complexes formed according the following equation:

$$L \cdot M^{m+} + L \overset{K_{2:1}}{\rightleftharpoons} L_2 \cdot M^{m+} \qquad (2)$$

where $K_{2:1}$ (M^{-1}) is the stability constant of complex 2(L):1(M^{m+}). The stability constants of the complexes are summarized in Table 1.

The stability constants for complexes **9**·Ag^{+} and **9**·Cd^{2+} are somewhat higher than those for the corresponding complexes of dyes **2a,b**. This undoubtedly reflects the electron-withdrawing effect of the positively charged benzothiazolium residue in **2a,b**, which decreases the capacity of the oxygen atom located in the *para* position to the butadiene bridge to donate its LEP for coordination with the metal cation. Owing to the large number of heteroatoms in the macrocycle, the dithia-18-crown-6-containing dye **2b** binds metal cations more efficiently than dithia-15-crown-5-containing dye **2a**. It is noteworthy that no 2:1 complexes are formed in the system **2a**/Ag^{+}, unlike **2a**/Pb^{2+}, despite the fact that Ag^{+} and Pb^{2+} ions have comparable effective radii (1.17 and 1.11 Å, respectively). This fact may be indicative of filling of the first coordination sphere of Ag^{+} in **2a**·Ag^{+}.

UV–Vis spectroscopy and differential pulse polarography

Of interest are macroheterocyclic compounds that can operate as optical molecular sensors for metal cations not only in organic but also in aqueous media. The complexation of dithiacrown-ether butadienyl dyes **2a,b** with heavy metal cations in water–acetonitrile mixtures with different water contents (P_W, v/v) was studied by UV–Vis spectroscopy and differential pulse polarography.

Table 1. Stability constants for complexes of dyes **2a,b** and **9** with heavy metal cations[a]

	lg$K_{1:1}$ (lg$K_{2:1}$)[b]		
M^{m+}(ClO$_4^-$)$_m$ M^{m+}	**2a**	**2b**	**9**
Ag^{+}	4.9	>5	>5
		5.1 [c]	5.7 [d]
Cd^{2+}	1.6	2.8	3.2
Pb^{2+}	4.6 (3.3)	> 6 [e]	> 6 [e]

[a] MeCN-d$_3$, 30 °C.

[b] $K_{1:1} = [L \cdot M]/([L] \cdot [M])$ (M^{-1}), $K_{2:1} = [L_2 \cdot M]/([L \cdot M] \cdot [L])$ (M^{-1}). The total measurement errors of the stability constants were ~20% and ~30% for the direct and competitive titrations, respectively.

[c,d] From competitive ^{1}H NMR titration with **9**[c] or **2a**[d].

[e] NMR titration is inapplicable due to very high value of the stability constant.

The absorption spectra of **2a,b** in MeCN exhibit a broad and strong S$_0$–S$_1$ band with a peak at about 457 nm in the case of **2a** and about 460 nm for **2b** (the ε_{max} value is about 54 000 M^{-1} cm^{-1} in both cases). On changing to aqueous solutions, the S$_0$–S$_1$ band shifts hypsochromically by 17 nm in the case of **2a** and by 20 nm for **2b** (the ε_{max} value decreases in both cases by about 10%). The negative solvatochromic effect indicates that the S$_0$–S$_1$ electronic transition in the cations of dyes **2a**,**b** results in positive charge delocalization[20] caused by electron density shift away from the electron-donating benzodithiacrown–ether moiety toward the electron-withdrawing benzothiazole residue. Obviously, the charge-transfer excited state should be destabilized upon binding of the metal cation by the dithiacrown–ether moiety of the dye. In other words, it can be predicted that complexation of **2a,b** with metal cations would be accompanied by a hypsochromic shift of the long-wavelength absorption band.

The addition of Hg(II) or Ag(I) perchlorates into water–acetonitrile solutions of **2a,b** ($C_L \sim 10^{-5}$ M, $P_W = 50\%$) actually induced substantial hypsochromic shifts (Fig. 5 for **2b**/Hg(ClO$_4$)$_2$), indicative of binding of Hg^{2+} and Ag^{+} ions by dithiacrown–ether fragments. However, the presence of Zn(II), Cd(II), or alkaline-earth metal perchlorates at a concentration of 0.1 M had almost no influence on the absorption spectra of **2a,b**. This means that in solutions with high water contents, dyes **2a,b** cannot bind Cd^{2+}, Zn^{2+}, or alkaline-earth metal cations. In addition, with $P_W = 50\%$, dye **2a** also proved to be unable to bind Pb^{2+}. This can be explained by two factors. First, the dithiacrown–ether moieties of **2a,b** have relatively low affinity to Cd^{2+}, Zn^{2+}, and alkaline-earth metal cations, and the dithia-15-crown-5-ether fragment of **2a** has a relatively low affinity to Pb^{2+} ions (Table 1). Secondly, these metal cations probably have relatively high energies of hydration. It is well known that the preferential hydration of cations in water-containing solutions can dramatically decrease the thermodynamic stability of crown–ether complexes.

In the system **2b**/Pb^{2+} ($P_W = 50\%$), an increase in the concentration of metal cation (C_M) in the region $C_M > 0.01$ M was accompanied by hypsochromic shifts of the long-wavelength absorption band, which were attributed to the formation of the 1:1 complex with the stability constant $K_{1:1} < 100$ M^{-1}.

Analysis of the spectrophotometric titration data showed that in systems **2a,b**/Ag^{+}, **2a,b**/Hg^{2+}, and **2b**/Pb^{2+} ($C_L \sim 10^{-5}$ M), only

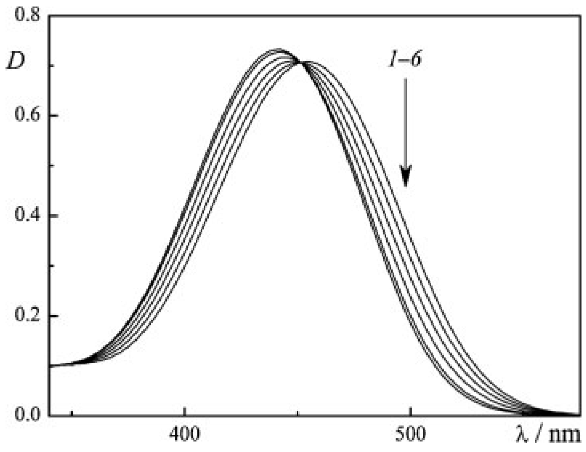


Figure 5. Absorption spectra of **2b** (1.4×10^{-5} M, 1 cm cell) in a water–acetonitrile solution ($P_W = 50\%$) containing Hg(II) perchlorate at: (1) 0, (2) 3.3×10^{-6}, (3) 6.6×10^{-6}, (4) 9.7×10^{-6}, (5) 1.3×10^{-5}, and (6) 1.9×10^{-5} M

Table 2. Hypsochromic shifts, $\Delta\lambda_{max} = \lambda_{max}$(free dye) $- \lambda_{max}$(complex), for complexes **2a,b**·Ag$^+$, **2a,b**·Hg^{2+}, and **2b**·Pb^{2+} in MeCN, water and water–acetonitrile mixtures with $P_W = 50\%$ (v/v)

	$\Delta\lambda_{max}$ (nm)		
Complex	MeCN	MeCN/H$_2$O (1:1)	H$_2$O
2a·Ag$^+$	10.5	8	3.5
2a·Hg^{2+}	23	17	10
2b·Ag$^+$	10	6.5	1.5
2b·Hg^{2+}	20	13.5	5
2b·Pb^{2+}	20.5		

1:1 complexes are formed according to Eqn (1) at any P_W value. The hypsochromic shifts $\Delta\lambda_{max}$ for complexes **2a,b**·Ag$^+$, **2a,b**·Hg^{2+}, and **2b**·Pb^{2+} in water, MeCN, and water–acetonitrile mixture with $P_W = 50\%$ are presented in Table 2. The stability constants of the Ag$^+$ and Pb^{2+} complexes were determined from spectrophotometric titration data, as described in the Experimental section. In the case of Hg^{2+}, the stability constants were estimated from half-wave potentials of mercury oxidation in the presence of ligands **2a,b**. The half-wave potentials were measured by differential pulse polarography (refer to the Experimental section). The lg$K_{1:1}$ values for complexes **2a**,**b**·Ag$^+$, **2a**,**b**·Hg^{2+}, and **2b**·Pb^{2+} at different P_W values are presented in Table 3.

In MeCN, the complexes of butadienyl dyes **2a,b** show more pronounced hypsochromic shifts than the complexes formed by styryl dyes **1a,b**.[11,12,14] As P_W increases, the $\Delta\lambda_{max}$ values for complexes **2a**,**b** decrease, which is related to their negative solvatochromism. It is pertinent to compare the $\Delta\lambda_{max}$ values for **2a**·Hg^{2+} and for the 1:1 complex formed by 15-crown-5 butadienyl dye **10** [8] (Scheme 3) with Ca^{2+}. The Hg^{2+} and Ca^{2+} ions have comparable effective radii (0.94 and 1.01 Å, respectively). However, the $\Delta\lambda_{max}$ value for **2a**·Hg^{2+} (23 nm) is appreciably lower than that for complex **10**·Ca^{2+} (37 nm). This is due to the fact that the metal cation in complex **2a**·Hg^{2+} forms very strong coordination bonds with the sulfur atoms of the dithiacrown–ether moiety, which markedly reduce the effective charge on the metal cation and, hence, weaken the interaction between the metal ion and the macrocycle oxygen atoms.

The stability constants of complexes **2a**·Ag$^+$, **2b**·Ag$^+$, and **2b**·Pb^{2+} in MeCN are several times higher than the stability constants of the corresponding complexes of styryl dyes **1a,b** (for **1b**·Pb^{2+} lg$K_{1:1} = 5.6$,[14] for **1a**·Ag$^+$ and **1b**·Ag$^+$ lg$K_{1:1} = 4.1$ and 4.8, respectively[11]). The increase in the thermodynamic stability is caused by the fact that an elongation of the polymethine chain in the dye mitigates the electron-withdrawing effect of the heterocyclic residue on the benzocrown–ether moiety.

The thermodynamic stability of complexes **2a,b** with Ag$^+$ considerably increases with an increase in the water content in the solution. Meanwhile, the $K_{1:1}$ value for complex **2b**·Pb^{2+} decreases by more than four orders of magnitude as P_W increases from 0 to 10%. Due to the contrasting patterns of dependence of $K_{1:1}$ on P_W for **2b**·Ag$^+$ and **2b**·Pb^{2+} (Fig. 6), a change in the medium results in a change in the selectivity of ligand **2b**. When $P_W = 50\%$, this ligand exhibits high selectivity toward Ag$^+$ *versus* Pb^{2+}, while in anhydrous MeCN, the Pb^{2+} ions are bound preferentially.

The solvation of metal cations is known to have an enormous effect on both the thermodynamic stability of complexes with

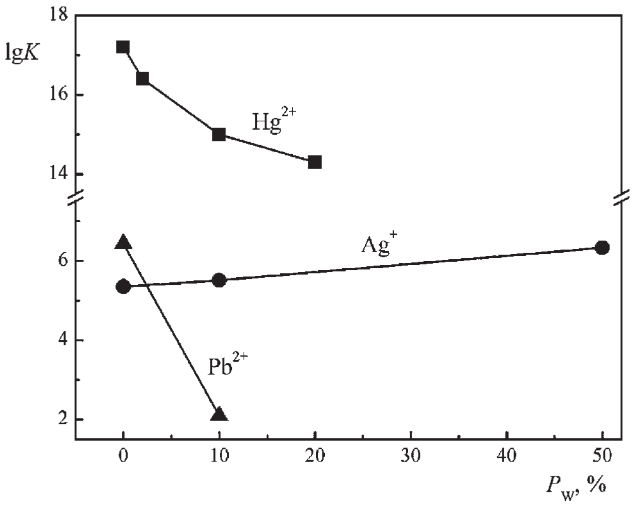


Figure 6. Plots of lg$K_{1:1}$ *versus* P_W for complexes **2b**·Ag$^+$, **2b**·Hg^{2+}, and **2b**·Pb^{2+}

Table 3. Stability constants of complexes **2a,b**·Ag$^+$, **2a,b**·Hg^{2+}, and **2b**·Pb^{2+} in MeCN and water–acetonitrile mixtures with different water contents

	lg$K_{1:1}$ ^{a}				
P_W (%, v/v)	**2a**·Ag$^{+\,b}$	**2b**·Ag$^{+\,b}$	**2a**·Hg$^{2+\,c}$	**2b**·Hg$^{2+\,c}$	**2b**·Pb$^{2+\,b}$
0	4.77	5.35	14.8	17.2	6.43
2				16.4	
10	4.94	5.51	12.8	15.0	2.1
20				14.3	
50	5.68	6.33			<2
75	6.46				

[a] The total measurement errors of the stability constants are ~20%.
[b] Spectrophotometric titration in the presence of HClO$_4$ (0.01 M).
[c] Differential pulse polarography in the presence of Bu$_4$NClO$_4$ (0.02 M).

crown ethers and the selectivity of complexation.[21] Evidently, the main reason for the inversion of selectivity of ligand **2b** upon the change in the medium is the difference in the solvation properties of Ag^+ and Pb^{2+}. Experimental data on the thermodynamics of Ag^+ and Pb^{2+} transfer from MeCN into water have been reported in the literature. For Pb^{2+}, the Gibbs free energy for transfer from MeCN into water, $\Delta_tG(\text{MeCN} \rightarrow \text{W})$, is negative being about $-42\,\text{kJ mol}^{-1}$,[22] i.e., this cation is much better hydrated than solvated by MeCN. Conversely, the Ag^+ ion is preferably solvated by MeCN, as $\Delta_tG(\text{MeCN} \rightarrow \text{W})$ for Ag^+ is positive ranging from 22 to $25\,\text{kJ mol}^{-1}$ according to different data.[22,23] Thus, the direction and the magnitude of the change in $\lg K_{1:1}$ following an increase in P_W for complexes **2b**$\cdot Ag^+$ and **2b**$\cdot Pb^{2+}$ correlate, respectively, with the sign and magnitude of $\Delta_tG(\text{MeCN} \rightarrow \text{W})$ for Ag^+ and Pb^{2+} ions.

The stability constants of complexes **2a,b** with Hg^{2+} decrease by approximately two orders of magnitude as P_W increases from 0 to 20%, which is due to preferential hydration of Hg^{2+}.[22,24]

Using spectrophotometry, we attempted to estimate the selectivity coefficients of ligands **2a,b** toward Hg^{2+} *versus* Ag^+ at higher P_W (50–75%). In solutions containing the dye ($C_L = 1 \times 10^{-5}$ M), $AgClO_4$ (0.01 M), and $HClO_4$ (0.01 M), the $Hg(ClO_4)_2$ concentration was varied from 0 to 1×10^{-4} M and the **2a,b**$\cdot Ag^+ \rightarrow$ **2a,b**$\cdot Hg^{2+}$ transition was observed by monitoring the changes in the absorption spectra. Analysis of these data has shown that the ratio of the stability constants of the Hg^{2+} and Ag^+ complexes exceed the measurement limit, equal to $\sim 10^4$, for both dyes even for $P_W = 75\%$.

CONCLUSION

New dithia-15(18)-crown-5(6)-ether butadienyl dyes were synthesized. The conformations of dithiacrown–ether fragments observed in the crystals of these dyes are unfavorable for complex formation with heavy metal cations as the sulfur atoms are oriented outside the macroheterocycle. This, however, does not prevent these macrocyclic ligands from forming Hg^{2+}, Pb^{2+}, and Ag^+ complexes in the crystals and solutions, which is attributable to rather high conformational flexibility of dithiacrown–ether moieties and high affinity of 'soft' sulfur atoms for 'soft' heavy metal cations. In water–acetonitrile solutions with water content $P_W \geq 20\%$, ligands **2a,b** show very high selectivity toward Hg^{2+} or Ag^+ *versus* Pb^{2+}, Cd^{2+}, Zn^{2+}, or alkaline-earth metal cations. The complexation with Hg^{2+} and Ag^+ at $P_W \leq 50\%$ induces considerable hypsochromic shifts. The dependences of the stability constants on P_W for complexes of **2a,b** with Hg^{2+} and Ag^+ are contrasting, as the Hg^{2+} ion is preferably hydrated, while the Ag^+ ion is preferably solvated by MeCN. Nevertheless, selectivity of ligands **2a,b** toward Hg^{2+} *versus* Ag^+ is very high both in MeCN and in aqueous acetonitrile with high water contents ($P_W \leq 75\%$). These results demonstrate the possibility of using dyes **2a,b** as optical molecular sensors for Hg^{2+} and Ag^+ ions in organic and water–organic media.

EXPERIMENTAL

General information

The melting points measured with an MEL–Temp II apparatus in a capillary are uncorrected. The ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX500 instrument in MeCN-d_3 and DMSO-d_6 solutions using the solvent as an internal reference (δ_H 1.96 and 2.50 ppm, respectively; δ_C 39.43 ppm for DMSO-d_6). The chemical shifts and spin–spin coupling constants were measured with an accuracy of 0.01 ppm and 0.1 Hz, respectively. $^1H-^1H$ and $^1H-^{13}C$ COSY (HSQC and HMBC) and ROESY spectra were used to assign the proton and carbon signals. Elemental analyses were performed at the microanalytical laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds (Moscow, Russian Federation). Compounds **3a,b–6a,b**[16] and **7**[17] were prepared as described previously. Perchloric acid (70%, aq), $AgClO_4\cdot H_2O$, $Cd(ClO_4)_2\cdot 6H_2O$, $Pb(ClO_4)_2\cdot 3H_2O$, $Hg(ClO_4)_2\cdot 4H_2O$, Bu_4NClO_4, and MeCN-d_3 (water < 0.05%) were used as received (Sigma–Aldrich or Merck). Water–acetonitrile mixtures were prepared using doubly distilled water and extra pure grade MeCN (Cryochrom, Russian Federation).

Synthesis procedures

2-[(1*E*,3*E*)-4-(3,4-Dimethoxyphenyl)-1,3-butadienyl]-3-ethyl-1,3-benzothiazol-3-ium perchlorate (8) was prepared according to the published procedure,[8] mp 252–253 °C (decomp.) (EtOH–MeCN), mp 234–237 °C.[8] ^1H NMR (DMSO-d_6, 30 °C) δ: 1.47 (t, $J = 7.2$, 3H, Me), 3.82 (s, 3H, 4′-OMe), 3.85 (s, 3H, 3′-OMe), 4.78 (q, $J = 7.2$, 2H, CH_2N), 7.05 (d, $J = 8.4$, 1H, H(5′)), 7.22 (dd, $J = 8.4$, $J = 1.6$, 1H, H(6′)), 7.28 (d, $J = 1.6$, 1H, H(2′)), 7.36 (dd, $J = 15.3$, $J = 10.4$, 1H, H(c)), 7.44 (d, $J = 15.3$, 1H, H(d)), 7.49 (d, $J = 14.8$, 1H, H(a)), 7.75 (m, 1H, H(6)), 7.84 (m, 1H, H(5)), 8.02 (dd, $J = 14.8$, $J = 10.4$, 1H, H(b)), 8.24 (d, $J = 8.5$, 1H, H(4)), 8.38 (d, $J = 8.1$, 1H, H(7)). ^{13}C NMR (DMSO-d_6, 30 °C) δ: 13.78 (Me), 44.09 (CH_2N), 55.42 (3′-OMe), 55.60 (4′-OMe), 109.46 (C(2′)), 111.77 (C(5′)), 114.46 (C(a)), 116.20 (C(4)), 123.21 (C(6′)), 124.26 (C(7)), 125.38 (C(c)), 127.98 (C(7a)), 128.09 (C(6)), 128.27 (C(1′)), 129.37 (C(5)), 140.73 (C(3a)), 146.05 (C(d)), 149.06 (C(3′)), 150.27 (C(b)), 151.29 (C(4′)), 170.50 (C(2)).

3-Ethyl-2-[(1*E*,3*E*)-4-(2,3,5,6,8,9,11,12-octahydro-1,7,13,4,10-benzotrioxadithiacyclopentadecin-15-yl)-1,3-butadienyl]-1,3-benzothiazol-3-ium perchlorate (2a). A mixture of 3-ethyl-2-methyl-1,3-benzothiazol-3-ium perchlorate (**7**) (82 mg, 0.30 mmol) and (*E*)-3-(2,3,5,6,8,9,11,12-octahydro-1,7,13,4,10-benzotrioxadithiacyclopentadecin-15-yl)-2-propenal (**3a**) (115 mg, 0.33 mmol) in anhydrous EtOH (10 mL) was refluxed for 100 h (oil bath). After cooling to 5 °C, the precipitate formed was filtered off and washed with cold anhydrous EtOH (2 × 3 mL) and benzene (3 mL) to get 100 mg of **2a** (55% yield) as reddish-brown crystals; mp 201–203 °C. ^1H NMR (DMSO-d_6, 30 °C) δ: 1.47 (t, $J = 7.2$, 3H, Me), 2.89 (t, $J = 6.6$, 4H, γ- and γ'-CH_2S), 3.05 (t, $J = 5.2$, 2H, β-CH_2S), 3.07 (t, $J = 5.1$, 2H, β'-CH_2S), 3.71 and 3.72 (2 t, $J = 6.6$, $J = 6.6$, 4H, δ- and δ'-CH_2O), 4.27 (t, $J = 5.1$, 2H, α-CH_2O), 4.28 (t, $J = 5.2$, 2H, α'-CH_2O), 4.79 (q, $J = 7.2$, 2H, CH_2N), 7.08 (d, $J = 8.4$, 1H, H(5′)), 7.24 (dd, $J = 8.4$, $J = 1.7$, 1H, H(6′)), 7.32 (d, $J = 1.7$, 1H, H(2′)), 7.37 (dd, $J = 15.3$, $J = 10.3$, 1H, H(c)), 7.45 (d, $J = 15.3$, 1H, H(d)), 7.49 (d, $J = 14.8$, 1H, H(a)), 7.77 (m, 1H, H(6)), 7.86 (m, 1H, H(5)), 8.04 (dd, $J = 14.8$, $J = 10.3$, 1H, H(b)), 8.27 (d, $J = 8.5$, 1H, H(4)), 8.40 (d, $J = 7.9$, 1H, H(7)). ^{13}C NMR (DMSO-d_6, 23 °C) δ: 13.79 (Me), 30.23 (β-CH_2S), 30.29 (β'-CH_2S), 30.68 and 30.73 (γ- and γ'-CH_2S), 44.10 (CH_2N), 70.42 and 70.60 (δ- and δ'-CH_2O), 70.70 (α'-CH_2O), 70.75 (α-CH_2O), 111.08 (C(2′)), 112.96 (C(5′)), 114.56 (C(a)), 116.20 (C(4)), 123.36 (C(6′)), 124.27 (C(7)), 125.64 (C(c)), 127.99 (C(7a)), 128.10 (C(6)), 128.58 (C(1′)), 129.38 (C(5)), 140.71 (C(3a)), 145.79 (C(d)), 148.31 (C(3′)), 150.18 (C(b)), 150.55 (C(4′)), 170.45 (C(2)). UV–Vis (1×10^{-5} M, MeCN) nm: 457 ($\varepsilon = 54\,000\ \text{M}^{-1}\,\text{cm}^{-1}$). Anal. calcd for $C_{27}H_{32}ClNO_7S_3$: C, 52.80; H, 5.25; N, 2.28; found: C, 52.68; H, 5.31; N, 2.34%.

2[(1*E*,3*E*)-4-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,7,10,16,4,13-benzotetraoxadithiacyclooctadecin-18-yl)-1,3-butadienyl]-3-ethyl-1,3-benzothiazol-3-ium perchlorate (**2b**) was obtained similarly to dye **2a** from **7** (50 mg, 0.18 mmol) and (*E*)-3-(2,3,5,6,8,9,11,12,14,15-decahydro-1,7,10,16,4,13-benzotetraoxadithiacyclooctadecin-18-yl)-2-propenal (**3b**) (79 mg, 0.20 mmol). Yield 68 mg (58%), reddish-brown crystals; mp 202–204 °C. ^{1}H NMR (DMSO-d$_6$, 30 °C) δ: 1.47 (t, $J = 7.2$, 3H, Me), 2.90 and 2.92 (2 t, $J = 6.3$, $J = 6.6$, 4H, γ- and γ'-CH$_2$S), 3.05 (t, $J = 6.3$, 2H, β-CH$_2$S), 3.10 (t, $J = 6.7$, 2H, β'-CH$_2$S), 3.54 (s, 4H, 2 ε-CH$_2$O), 3.63 and 3.66 (2 t, $J = 6.6$, $J = 6.3$, 4H, δ- and δ'-CH$_2$O), 4.21 (br.t, $J = 6.5$, 4H, α- and α'-CH$_2$O), 4.79 (q, $J = 7.2$, 2H, CH$_2$N), 7.06 (d, $J = 8.4$, 1H, H(5′)), 7.21 (dd, $J = 8.4$, $J = 1.5$, 1H, H(6′)), 7.30 (d, $J = 1.5$, 1H, H(2′)), 7.37 (dd, $J = 15.3$, $J = 10.3$, 1H, H(c)), 7.45 (d, $J = 15.3$, 1H, H(d)), 7.51 (d, $J = 14.8$, 1H, H(a)), 7.76 (m, 1H, H(6)), 7.85 (m, 1H, H(5)), 8.04 (dd, $J = 14.8$, $J = 10.3$, 1H, H(b)), 8.26 (d, $J = 8.5$, 1H, H(4)), 8.39 (d, $J = 7.9$, 1H, H(7)). ^{13}C NMR (DMSO-d$_6$, 21 °C) δ: 13.81 (Me), 29.96 (β-CH$_2$S), 30.02 (β'-CH$_2$S), 30.65 and 30.76 (γ- and γ'-CH$_2$S), 44.09 (CH$_2$N), 69.05 (α'-CH$_2$O), 69.50 (α- and ε-CH$_2$O), 69.64 (ε-CH$_2$O), 71.43 and 71.80 (δ- and δ'-CH$_2$O), 109.81 (C(2′)), 112.21 (C(5′)), 114.48 (C(a)), 116.20 (C(4)), 123.43 (C(6′)), 124.28 (C(7)), 125.48 (C(c)), 127.99 (C(7a)), 128.10 (C(6)), 128.34 (C(1′)), 129.38 (C(5)), 140.72 (C(3a)), 146.00 (C(d)), 148.02 (C(3′)), 150.23 (C(4′)), 150.27 (C(b)), 170.46 (C(2)). UV–Vis (1×10^{-5} M, MeCN) nm: 460 ($\varepsilon = 54\,000$ M^{-1} cm^{-1}). Anal. calcd for $C_{29}H_{36}ClNO_8S_3$: C, 52.91; H, 5.51; N, 2.13; found: C, 52.99; H, 5.61; N, 2.14%.

X-ray crystallography

Crystals of dyes **2a**, **2b**, **8**, and their metal complexes were obtained by slow saturation of acetonitrile solutions with benzene (or with dioxane for **8**) by vapour diffusion methods. Single crystals of all compounds were coated with perfluorinated oil and mounted on a Bruker SMART–CCD diffractometer under a stream of cold nitrogen [$T = 120.0(2)$ K]. The experimental X-ray intensity data sets were collected from single crystals (graphite monochromatized Mo–K$_\alpha$ radiation, $\lambda = 0.71073$ Å) using ω-scanning technique.

All of the structures were solved by the direct method and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for non-hydrogen atoms. The positions of hydrogen atoms were calculated geometrically. Hydrogen atoms were refined with an isotropic approximation (structure **2b**·MeCN) or using the riding model [structures **2a** and **2b**·Pb(ClO$_4$)$_2$·0.5C$_6$H$_6$], or their combination (structures **2a**·AgClO$_4$·3MeCN and **8**·C$_4$H$_8$O$_2$).

In structure **2a**, the crown–ether moiety was found to be disordered over two positions with the ratio of occupancies of 0.52:0.48. The perchlorate anion is also disordered over two positions corresponding to rotation about the Cl(1)–O(11) bond with 0.59:0.41 ratio of occupancies. The disorder in the crown–ether moiety and the perchlorate anion introduces additional errors in the X-ray structure of **2a** to lower its accuracy.

Crystallographic data for **2a**: $C_{27}H_{32}ClNO_7S_3$, monoclinic, space group $P2_1/c$ (no. 14), $a = 18.5711(10)$, $b = 10.6202(6)$, $c = 14.6336(8)$ Å, $\beta = 94.284(3)^\circ$, $V = 2878.1(3)$ Å^3, $Z = 4$, $d = 1.417$ g cm^{-3}, 21469 reflections measured, 7594 unique reflections [R(int) = 0.0954], $R_1 = 0.1211$, $wR_2 = 0.2176$ for 5492 reflections with $I > 2\sigma(I)$, $R_1 = 0.1531$, $wR_2 = 0.2278$ for all reflections.

Crystallographic data for **2b**·MeCN: $C_{31}H_{39}ClN_2O_8S_3$, monoclinic, space group $C2/c$ (no. 15), $a = 45.6357(16)$, $b = 8.3550(3)$, $c = 18.1476(6)$ Å, $\beta = 103.630(3)^\circ$, $V = 6724.6(4)$ Å^3, $Z = 8$, $d = 1.381$ g cm^{-3}, 27706 reflections measured, 8946 unique reflections [R(int) = 0.0762], $R_1 = 0.0568$, $wR_2 = 0.1327$ for 5221 reflections with $I > 2\sigma(I)$, $R_1 = 0.1191$, $wR_2 = 0.1467$ for all reflections.

In structure **8**·C$_4$H$_8$O$_2$, the dioxane solvate molecule is disordered over two positions with the ratio of occupancies of 0.66:0.34.

Crystallographic data for **8**·C$_4$H$_8$O$_2$: $C_{25}H_{30}ClNO_8S$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.4432(3)$, $b = 12.2096(5)$, $c = 15.3156(7)$ Å, $\alpha = 69.272(2)$, $\beta = 77.037(2)$, $\gamma = 80.226(2)^\circ$, $V = 1262.34(9)$ Å^3, $Z = 2$, $d = 1.421$ g cm^{-3}, 9987 reflections measured, 6475 unique reflections [R(int) = 0.0249], $R_1 = 0.0531$, $wR_2 = 0.1491$ for 5058 reflections with $I > 2\sigma(I)$, $R_1 = 0.0764$, $wR_2 = 0.1587$ for all reflections.

SADABS absorption correction was applied to **2a**·AgClO$_4$·3MeCN and **2b**·Pb(ClO$_4$)$_2$·0.5C$_6$H$_6$. The low accuracy of these structures caused by their fast destruction in air, resulting from the solvate molecules' release, and by difficulties in measuring the true value for the smallest dimension of the single crystals having a plate-like shape gave rise to high residuals. However, all residual electron density peaks were located in the vicinity of heavy atoms.

One of the two perchlorate anions in the structure of **2a**·AgClO$_4$·3MeCN is disordered over two positions corresponding to rotation about the Cl(2)–O(21) bond, the ratio of occupancies being 0.63:0.37.

Crystallographic data for **2a**·AgClO$_4$·3MeCN: $C_{33}H_{41}AgCl_2N_4O_{11}S_3$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.262(2)$, $b = 12.058(2)$, $c = 16.121(3)$ Å, $\alpha = 108.051(6)$, $\beta = 92.219(5)$, $\gamma = 105.320(5)^\circ$, $V = 1990.1(6)$ Å^3, $Z = 2$, $d = 1.576$ g cm^{-3}, 11796 reflections measured, 8923 unique reflections [R(int) = 0.0534], $R_1 = 0.0851$, $wR_2 = 0.1847$ for 5403 reflections with $I > 2\sigma(I)$, $R_1 = 0.1411$, $wR_2 = 0.2078$ for all reflections.

Crystallographic data for **2b**·Pb(ClO$_4$)$_2$·0.5C$_6$H$_6$: $C_{32}H_{39}Cl_3NO_{16}PbS_3$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.8944(7)$, $b = 9.1982(6)$, $c = 24.2992(17)$ Å, $\alpha = 100.254(3)$, $\beta = 95.480(3)$, $\gamma = 92.254(4)^\circ$, $V = 1944.1(2)$ Å^3, $Z = 2$, $d = 1.885$ g cm^{-3}, 13566 reflections measured, 8375 unique reflections [R(int) = 0.0845], $R_1 = 0.0728$, $wR_2 = 0.1581$ for 5511 reflections with $I > 2\sigma(I)$, $R_1 = 0.1212$, $wR_2 = 0.1758$ for all reflections.

All crystallographic data, data collection details, solution and refinement parameters for **2a**, **2b**·MeCN, **8**·C$_4$H$_8$O$_2$, **2a**·AgClO$_4$·3MeCN, and **2b**·Pb(ClO$_4$)$_2$·0.5C$_6$H$_6$ are listed in Tables 4S and 5S of Supporting Information. Selected bond lengths and angles are given in Tables 1S–3S of Supporting Information.

All the calculations were performed using the SHELXTL-Plus software.[25] CCDC reference numbers 724885 (**2a**), 625393 (**2b**·MeCN), 724886 (**8**·C$_4$H$_8$O$_2$), 724887 (**2a**·AgClO$_4$·3MeCN), and 724888 (**2b**·Pb(ClO$_4$)$_2$·0.5C$_6$H$_6$).

^{1}H NMR titrations

The titration experiments were performed in MeCN-d$_3$ solutions at 30 ± 1 °C. The concentration of **2a,b** or **9** was maintained at 5×10^{-3} M, and the concentration of metal perchlorate was gradually increased, starting from zero. The highest metal perchlorate/ligand ratio was about 3. In the case of competitive ^{1}H NMR titration, the concentrations of ligand and metal perchlorate were maintained at 5×10^{-3} and 6×10^{-3} M, respectively, and the concentration of the competing ligand was varied from 0 to 0.015 M. The proton chemical shifts were measured as a function of the metal perchlorate/(competing) ligand ratio, and the complex formation constants were then calculated using HYPNMR program.[26]

Spectrophotometric titration

Water–acetonitrile solutions of dyes **2a,b** were prepared in a dark room under red light, because the dyes are *E-Z*-photoisomerized under natural light. The absorption spectra were measured on a Specord-M40 spectrophotometer at 22 ± 2 °C. The total dye concentration in solutions was maintained at 1×10^{-5} M (1 cm cell) or 2×10^{-6} M (5 cm cell). The total metal perchlorate concentration was normally varied from 0 to 0.001 M. All solutions contained $HClO_4$ (0.01 M). It was shown preliminarily that perchloric acid has almost no influence on the absorption spectra of dyes **2a,b**. The compositions and stability constants of the complexes were determined by global analysis of the spectrophotometric data using the parameterized self-modeling method.[7]

Polarography

Polarography was employed to measure the stability constants of complexes **2a,b** with Hg^{2+} in MeCN and water–acetonitrile mixtures with different water contents (P_W). The electrochemical oxidation of mercury in the presence of ligand can be described by the equation

$$Hg + xL = (HgLx)^{2+} + 2e \tag{3}$$

where L is the ligand, x is the stoichiometric coefficient. The relationship between the half-wave potential of this process and the stability constant $K = [(HgL_x)^{2+}]/([Hg^{2+}]\ [L]^x)$ is expressed as

$$E_{1/2} = E^0 - \frac{RT}{2F}\ln K + \frac{RT}{2F}\ln\frac{2^{x-1}D_L{}^{1/2}}{x[L]^{x-1}D_C{}^{1/2}} \tag{4}$$

where E^0 is the formal potential of the Hg/Hg^{2+} pair *versus* the reference electrode, D_L and D_C are the diffusion coefficients of the free ligand and the complex, respectively.

The half-wave potentials of mercury oxidation in the presence of ligands **2a,b** were measured by differential pulse polarography under argon at 22 ± 2 °C. A Model 303A dropping mercury electrode (DME) (EG&G Princeton Applied Research) was used as the working electrode. The reference electrode Ag|AgCl|KCl (aq., sat.) was separated from the solution under study by a bridge containing an acetonitrile solution of Bu_4NClO_4 (0.1 M). A platinum wire served as the auxiliary electrode. The instrumental parameters were as follows: pulse amplitude $\Delta E = 50$ mV, potential scanning rate 4 mVs^{-1}, DME drop time 0.5 s. The half-wave potential was determined from the relation $E_{1/2} = E_p - \Delta E/2$, where E_p is the peak potential in the differential polarogram. All solutions contained 0.02 M Bu_4NClO_4. Figure 7 shows the differential pulse polarograms of mercury oxidation in the presence of ligand **2a** (5×10^{-4} M) in MeCN and in water–acetonitrile mixture with $P_W = 10\%$.

The E^0 value in MeCN was determined using the ferrocene/ferrocenium (Fc/Fc^+) redox pair as the internal reference. The standard potentials of the Fc/Fc^+ and Hg/Hg^{2+} pairs in MeCN *versus* normal hydrogen electrode in water are 0.63[27] and 1.12 V,[12] respectively. Using the value $E_{1/2} = 0.40$ V measured for the Fc/Fc^+ pair in MeCN, the formal potential is calculated to be $E^0 = 0.89$ V for Hg/Hg^{2+} in MeCN *versus* the Ag|AgCl|KCl (aq., sat.)/Bu_4NClO_4 (0.1 M in MeCN) reference electrode. The E^0 values in water–acetonitrile mixtures with different P_W values were estimated from the intersection of the anodic pulse polarograms of the corresponding 0.02 M Bu_4NClO_4 solutions in the absence of any ligand with their base lines.

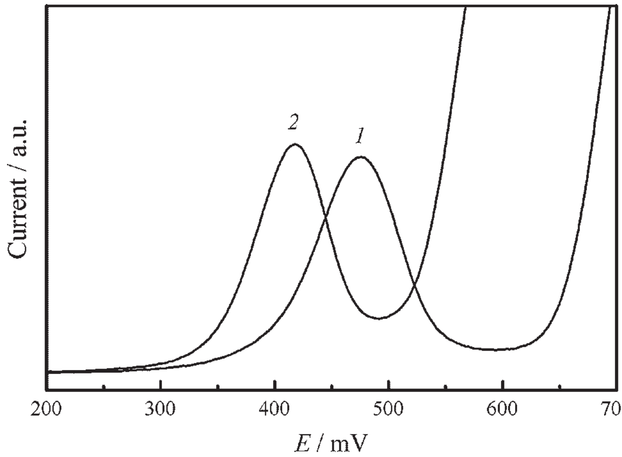


Figure 7. Differential pulse polarograms of mercury oxidation in the presence of ligand 2a in MeCN (1) and water–acetonitrile mixture with $P_W = 10\%$ (2); supporting electrolyte Bu_4NClO_4 (0.02 M), reference electrode Ag|AgCl|KCl (aq., sat.)/Bu_4NClO_4 (0.1 M in MeCN)

The formal potentials E^0 of the Hg/Hg^{2+} pair and the half-wave potentials $E_{1/2}$ of mercury oxidation in the presence of ligands **2a,b** in MeCN and water–acetonitrile mixtures with different P_W values are presented in Table 6S of Supporting Information. $E_{1/2}$ values were found to be independent of C_L in all cases, establishing the stoichiometric coefficient $x = 1$. The stability constants of complexes **2a,b**·Hg^{2+} were calculated from Eqn (4), taking $D_L = D_C$ and using the E^0 and $E_{1/2}$ values from Table 6S.

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