Synthesis, Structure, and Ion Selective Complexation of Trans and Cis Isomers of Photochromic Dithia-18-crown-6 Ethers

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Abstract: Photochromic styryl dyes containing benzodithia-18-crown-6 and *N*-substituted benzothiazolium moieties are synthesized and characterized spectroscopically and, for a specific case, by X-ray crystallography. The effects of the N-substituent and of sulfur atom substitution in the crown ether cavity on metal cation complex formation and on photochromism due to reversible trans−cis photoisomerization are evaluated. High selectivities for heavy metal ions, such as Ag^+ and Hg^{2+}, are observed, in contrast to the benzo-18-crown-6 dyes which selectively bind alkali and alkali earth cations. Relative complex formation stability constants, determined spectrophotometrically, are converted to absolute values by polarographic measurements. The stability constant for Hg^{2+} complex formation by the trans dye is enhanced 47-fold upon substitution of the 4-butylsulfonate group for methyl at the nitrogen of the benzothiazolium moiety. Photoisomerization to the cis dye is accompanied by a further 11-fold stability constant increase and by spectral changes that are consistent with formation of an ion-"capped" complex, involving intramolecular coordination of the sulfonate anion to Hg^{2+}. Addition of a large excess of Mg^{2+} ions disrupts this intramolecular coordination bond without displacing the Hg^{2+} ion from the dithiacrown ether cavity.

Introduction

Crown ether substituted dyes absorb light in the visible region of the spectrum and bind metal cations selectively.[1−5] Such compounds have been used, for example, as reagents for calorimetric or fluorimetric determination of metal cations and as components of photoswitchable molecular devices.[6−9] The supramolecular organic photochemistry of crown-containing styryl dyes (CSDs) that can undergo photoswitching is a vigorously developing field of research.[1−10] Experimental observations[11,12] and theoretical calculations[13] indicate that, of the compounds that we have investigated, the most promising CSDs differ from *trans*-**1a** by substitution of *ω*-alkylsulfonate groups for the ethyl group at the N atom of the benzothiazolium moiety. For instance, the photochromic CSDs **1b,c** (Scheme 1) allow control of the binding of metal cations by virtue of light because they are capable of "taking off" and "putting on" their anionic "cap" upon exposure to light of various wavelengths.[14] A modest photoresponsive anionic "capping" effect was reported earlier by Shinkai and co-workers for a related system that used the trans → cis photoisomerization of the azobenzene moiety and a phenoxide anionic cap.[15]

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(1) Löhr H.-G.; Vögtle, F. *Acc. Chem. Res.* **1985**, *18*, 65.
(2) Takagi, M. In *Cation Binding by Macrocycles. Complexation of Cationic Species by Crown Ethers*; Inoue, Y., Gokel, G. W., Eds.; Marcel Dekker: New York, 1990; Chapter 11, pp 465−495.
(3) Pietraszkiewicz, M. In *Comprehensive Supramolecular Chemistry*; Reinhoudt, D. N., Ed.; Pergamon: Oxford, U.K., 1996; Vol. 10, Chapter 10, pp 225−265.
(4) De Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515.
(5) Alfimov, M. V.; Gromov, S. P. In *Applied Fluorescence in Chemistry, Biology, and Medicine*; Rettig, W., Strehmel, B., Schrader, S., Eds.; Springer-Verlag: Berlin, 1998, in press.
(6) Shinkai, S. In *Cation Binding by Macrocycles. Complexation of Cationic Species by Crown Ethers*; Inoue, Y., Gokel, G. W., Eds.; Marcel Dekker: New York, 1990; Chapter 9, pp 397−428.
(7) Lehn, J.-M. *Supramolecular Chemistry. Concepts and Perspectives*; VCH: Weinheim, Germany, 1995.
(8) Balzani, V.; Scandola, F. In *Comprehensive Supramolecular Chemistry*; Reinhoudt, D. N., Ed.; Pergamon: Oxford, U.K., 1996; Vol. 10, Chapter 23, pp 687−746.

(9) Kimura, K. *Coord. Chem. Rev.* **1996**, *148*, 41.
(10) Gromov, S. P.; Alf'imov, M. V. *Izv. Akad. Nauk, Ser. Khim.* **1997**, 641; *Russ. Chem. Bull.* **1997**, *46*, 611 (Engl. Transl.).
(11) Gromov, S. P.; Fedorova, O. A.; Ushakov, E. N.; Stanislavskii, O. B.; Lednev, I. K.; Alfimov, M. V. *Dokl. Akad. Nauk SSSR* **1991**, *317*, 1134; *Dokl. Chem.* **1991** (Engl. Transl.).
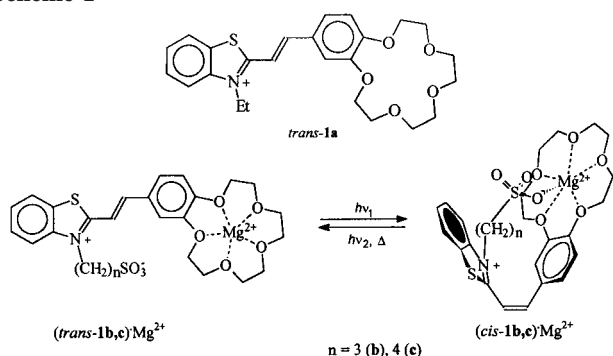(12) Gromov, S. P.; Fedorova, O. A.; Ushakov, E. N.; Stanislavskii, O. B.; Alfimov, M. V. *Dokl. Akad. Nauk SSSR* **1991**, *321*, 104; *Dokl. Chem.* **1991** (Engl. Transl.).
(13) Baskin, I. I.; Burstein, K. Ya.; Bagatur'yants, A. A.; Gromov, S. P.; Alfimov, M. V. *J. Mol. Struct.* **1992**, *274*, 93.
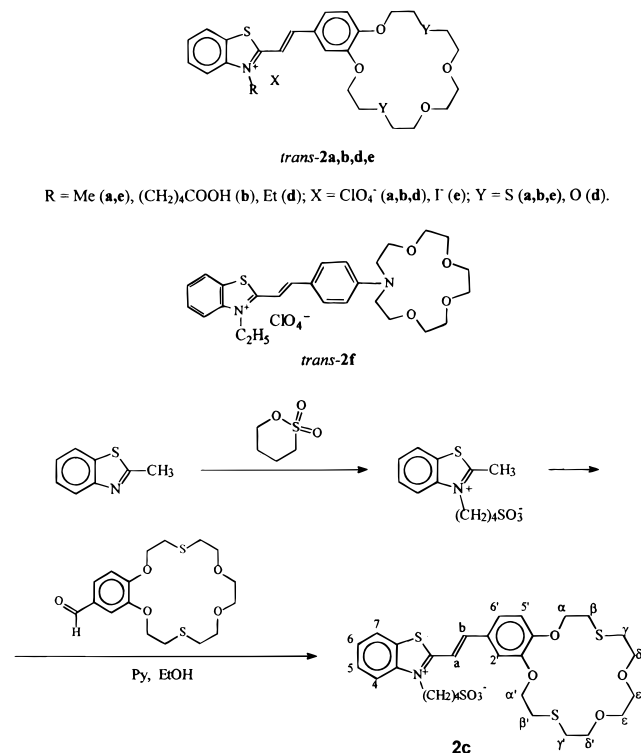(14) Barzykin, A. V.; Fox, M. A.; Ushakov, E. N.; Stanislavsky, O. B.; Gromov, S. P.; Fedorova, O. A.; Alfimov, M. V. *J. Am. Chem. Soc.* **1992**, *114*, 6381.
(15) Shinkai, S.; Minami, T.; Kusano, Y.; Manabe, O. *J. Am. Chem. Soc.* **1982**, *104*, 1967−1972.

Scheme 1

trans-**1a**

(*trans*-**1b,c**)·Mg²⁺   (*cis*-**1b,c**)·Mg²⁺

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

Scheme 2

trans-**2a,b,d,e**

R = Me (**a,e**), (CH₂)₄COOH (**b**), Et (**d**); X = ClO₄⁻ (**a,b,d**), I⁻ (**e**); Y = S (**a,b,e**), O (**d**).

trans-**2f**

2c

Primary attention has been focused on CSDs based on 15-(18)-crown-5(6) ether derivatives.[10] Styryl dyes *trans*-**2a,b** (Scheme 2) incorporating the benzodithia-18-crown-6 ether moiety[16,17] have not been studied as thoroughly, although they possess potential advantages, because thiacrown compounds exhibit a clear-cut preference for formation of complexes with heavy metal ions and with transition metal ions.[16,18]

This work concerns the effects of the nature of the terminal group of the N-substituent, the identity of the metal cation, and the size of the dithiacrown ether cavity of the CSD on the formation of complexes by photochromic benzodithia-18-crown-6 ethers of the benzothiazolium series (Scheme 2).

Results and Discussion

Synthesis. The syntheses of CSDs *trans*-**2a,b** and of betaine **3** are described in our previous publications.[16,19] CSD **2c** was

(16) Gromov, S. P.; Fedorova, O. A.; Vedernikov, A. I.; Fedorov, Yu. V.; Alfimov, M. V. *Izv. Akad. Nauk, Ser. Khim.* **1997**, 999; *Russ. Chem. Bull.* **1997**, *46*, 959 (Engl. Transl.).

(17) Alfimov, M. V.; Fedorov, Yu. V.; Fedorova, O. A.; Gromov, S. P.; Hester, R. E.; Lednev, I. K; Moore, J. N.; Oleshko, V. P.; Vedernikov, A. I. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1441.

(18) Cooper, S. R., Ed. *Crown Compounds: Towards Future Application*; VCH Publ.: New York, 1992.
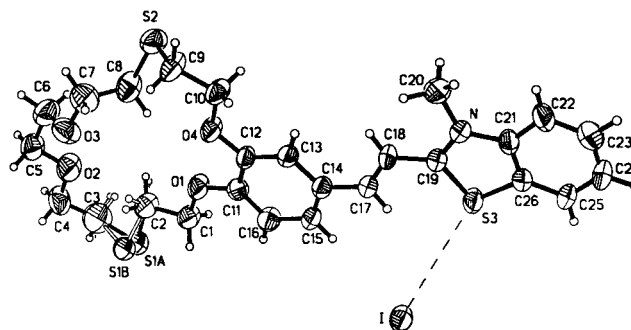
prepared in 74% yield by condensation of betaine **3** with 3′-formyl-2,3-benzodithia-18-crown-6 ether[20] in the presence of pyridine (Scheme 2). The structure of CSD **2c** was determined by ¹H NMR spectroscopy (see below and the Experimental Section). The results of elemental analysis are consistent with the structural assignment. The **2c** product was assigned the trans configuration on the basis of the spin−spin coupling constant for the olefinic protons, $J_{trans} = 15.6$ Hz.[21]

X-ray Study. The X-ray crystal structure of **2e** is shown in Scheme 3. The bonds of the benzene ring of the benzo-crown moiety alternate slightly in length. This is in contrast to the *p*-quinone pattern that was observed in the corresponding benzene ring of the dye **2f** which has an aza-crown moiety and the ethyl substituent at the benzothiazolium nitrogen atom.[22] Conjugation with the π-system of the benzene ring imposes nearly sp² hybridization at oxygen atoms O(1) and O(4) as reflected in wider bond angles [117.7(5) and 118.2(5)°, respectively] at these atoms. Lacking such conjugation, the bond angles at O(2) and O(3) [112.8(6) and 111.35(7)°, respectively] approach the value expected for sp³ hybridization. Torsional angles of −178.5 and −175.4° for C(1)O(1)C(11)C(12) and C(10)O(4)C(12)C(11), respectively, are consistent with conjugation of the lone electron pair at the p orbital of each oxygen with the π-system of the benzene ring. The bond lengths in the ethylene moiety C−C=C−C are 1.44, 1.35, and 1.44 Å, consistent with 1.339 ± 0.011 and 1.46 ± 0.011 Å, the characteristic values of double and essential single bonds, respectively, in C=C−C(Ar) systems.[23]

The three parts of the molecule (benzothiazolium−ethylene−benzene) are almost coplanar. Dihedral angles of 2.1° and 2.8° at the connections of these three components demonstrate an extensive system of π-conjugation in the molecule. Within the benzothiazolium−ethylene moieties, most bond lengths are similar to those in **2f**. Slight differences of the S(3)−C(19) and S(3)−C(26) bond lengths [1.712(6) and 1.753(7) Å] from corresponding bonds in **2f** [1.733(2) and 1.736(2) Å, respectively] may reflect a weak interaction of the anion I⁻ with S(3) in **2e**. Since the S...I distance, 3.973(4) Å, is definitely shorter than the sum of the van der Waals radii (∼4.2 Å), the mutual arrangement of these atoms may not be optimum for such an

Scheme 3

(19) Gromov, S. P.; Ushakov, E. N.; Fedorova, O. A.; Buevich, A. V.; Alfimov, M. V. *Izv. Akad. Nauk, Ser. Khim.* **1996**, 693; *Russ. Chem. Bull.* **1996**, *45*, 654 (Engl. Transl.).

(20) Gromov, S. P.; Fedorova, O. A.; Vedernikov, A. I.; Samoshin, V. V.; Zefirov, N. S.; Alfimov, N. S. *Izv. Akad. Nauk, Ser. Khim.* **1995**, *121*; *Russ. Chem. Bull.* **1995**, *44*, 116 (Engl. Transl.).

(21) Günther, H.; *NMR Spectroscopy. An Introduction*; J. Wiley and Sons: New York, 1980; Chapter 2.

(22) Alfimov, M. V.; Churakov, A. V.; Fedorov, Y. V.; Fedorova, O. A.; Gromov, S. P.; Hester, R. E.; Howard, J. A. K.; Kuz'mina, L. G.; Lednev, I. K.; Moore, J. N. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2249.

(23) Allen, F. H., Kennerd, O., Warson, D. G., Brammer, L., Orpen, G., Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

Table 1. Spectral Properties of Dyes *trans*-**2a,b,d** and Their Complexes with Silver and Mercury(II) Nitrates in Various Solvents

compd	MeCN[a]			MeOH[b]			MeOH−H$_2$O[b] (1:4)		
	λ_{max}, nm	$\Delta\lambda$, nm		λ_{max}, nm	$\Delta\lambda$, nm		λ_{max}, nm	$\Delta\lambda$, nm	
		Ag$^+$	Hg^{2+}		Ag$^+$	Hg^{2+}		Ag$^+$	Hg^{2+}
trans-**2a**	429	9	16	432	12	20	417	6	9
trans-**2b**	431	8	17	435	12	19	419	5	8
trans-**2d**	431	0	10						

[a] The ratio of the ligand concentration to the salt concentration was 1:10; $\Delta\lambda = \lambda_{max}(\text{ligand}) - \lambda_{max}(\text{complex})$. [b] The ratio of the ligand concentration to the salt concentration was 1:30.

interaction. Ideally, the directionality of secondary interactions of this type requires the counterion to be situated on a line which represents a continuation of a bond to the sulfur atom. In the structure of **2e**, the I...S(3)−C(26) angle is equal to 135.4°, the anion being significantly displaced from the mean plane of the benzothiazolium moiety. Nonetheless, the secondary I...S bond may be responsible for the small differences between the primary C−S bonds in **2e,f**.

One of the sulfur atoms of the crown ether moiety is disordered over two positions with equal occupation. Interestingly, both sulfur atoms are situated toward the exterior of the crown ether macrocycle, whereas the four oxygen atoms form a quadrangle in the interior with two long (4.820 and 4.912 Å) and two short (2.56 and 2.78 Å) sides. The shortest contact is between O(1) and O(4), the atoms bonded to the benzene ring, and the second short contact is between O(2) and O(3). Occurrence of the short contacts in the flexible system of the crown ether reflects the small size of the oxygen atoms.

Electronic Spectroscopy Studies. As expected, the electronic absorption spectra of CSDs *trans*-**2a,b** in MeCN are nearly identical to the spectra of *trans*-**1a,b**[11] because these dyes contain the same chromophoric components. The long-wavelength absorption bands (LABs) of solutions of CSDs *trans*-**2a,b** shift hypo- and hypsochromically as the polarity of the solvent is increased. For example, the LAB of *trans*-**2b** is located at 435 nm (ϵ_{trans} 39 400) in MeOH, at 431 nm (ϵ_{trans} 37 000) in MeCN, and at 419 nm (ϵ_{trans} 34 600) in the MeOH−H$_2$O (1:4) system (Table 1).

Additions of alkali or alkaline earth metal (Na, K, Mg, Ca) nitrates to solutions of *trans*-**2a,b** in MeCN (5×10^{-5} M) cause no significant changes in the absorption spectra because of the low affinities of these ions for sulfur-containing ligands. However, additions of solutions of the same concentration of silver or mercury(II) nitrates or perchlorates result in hypsochromic shifts of the LAB of *trans*-**2a,b,d** (Table 1, Figure 1), which are evidently due to formation of complexes (*trans*-**2a,b,d**)·M^{n+} (Scheme 4). The long wavelength electronic transition in these CSD molecules involves displacement of electron density from the benzene ring to the heterocyclic moiety. This effect is diminished when the dithiacrown ether moiety binds Ag$^+$ or Hg^{2+} ions, resulting in the hypsochromic shifts of the LABs.[24]

The counterion effect on the absorption spectra of the complexed dyes was investigated for (*trans*-**2a,b**)·Ag$^+$ and (*trans*-**2a,b**)·Hg^{2+}. The position and appearance of the spectral bands are essentially unaffected on changing the counterion from perchlorate to nitrate, consistent with a high degree of dissociation of (*trans*-**2a,b**)·M^{n+}/X$_n^-$ ion pairs. The larger LAB shift obtained upon complexation of *trans*-**2a,b** with Hg^{2+} reflects
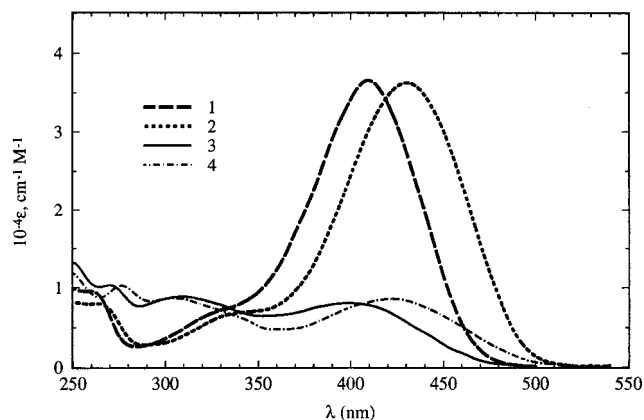
Figure 1. Electronic absorption spectra of dyes **2b** and the complexes of **2b** with Hg(ClO$_4$)$_2$ in MeCN: *trans*-**2b** (1), (*trans*-**2b**)·Hg^{2+} (2), *cis*-**2b** (3), (*cis*-**2b**)·Hg^{2+} (4).

Scheme 4
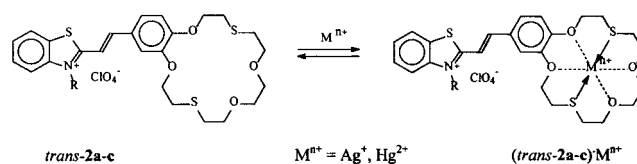
the higher charge density on this metal ion, as the ionic radii of Ag$^+$ and Hg^{2+} are nearly identical.

The hypsochromic shift of the LAB of *trans*-**2d** in the presence of Hg^{2+} in MeCN (10 nm) is not much smaller than the shifts of the corresponding bands of dyes *trans*-**2a,b** (16−17 nm), whereas the equilibrium constants for complex formation of Hg^{2+} ions with benzocrown ethers differ appreciably from those of benzodithiacrown ethers.[25] Upon complexation, the interaction of the cation with the O atom which is part of the conjugation chain of the chromophore exerts the greatest effect on the CSD chromophoric system.[24] Formation of very strong Hg^{2+}...S bonds in the dithiacrown cavity of CSDs *trans*-**2a,b** tends to saturate the coordination capacity of Hg^{2+}, thereby attenuating its interaction with the O atoms that are directly conjugated with the chromophone. Indeed, the bonds of Hg^{2+} with the S atoms of the dithiacrown ether moieties of the CSDs are so strong that the LAB shifts are observed even in the presence of water. Therefore, the hypsochromic shifts of the LABs that accompany complexation of *trans*-**2a,b** with Ag$^+$ or Hg^2 are small when compared, for example, to those resulting from the interaction of *trans*-**1a** with Mg^{2+} (34 nm),[26] because the S atoms are fairly remote from the chromophoric system of the dye and are not conjugated with it.

Trans−Cis Isomerization and Complexation of Trans and Cis Isomers of 2a−c. The dependencies of the absorption spectra of the dyes *trans*-**2a,b** on the concentration of Ag$^+$ or Hg^{2+} metal cation (C_M) are described adequately on the basis of the equilibrium shown in Scheme 4.
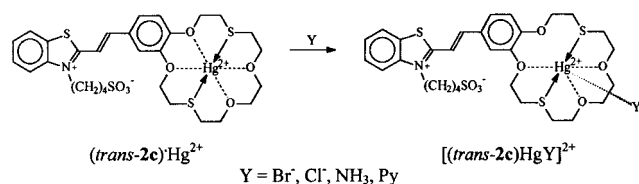
Dye *trans*-**2c** is much less soluble in MeCN than dyes *trans*-**2a,b** (a saturated solution of *trans*-**2c** is ∼2.5×10^{-6} M), but as expected, the electronic absorption spectrum of *trans*-**2c** in MeCN ($\lambda_{max} = 432$ nm) is similar to the spectra of dyes *trans*-**2a,b**. The solubility of *trans*-**2c** is not affected by the addition of sodium or tetrabutylammonium perchlorate to the solution

(24) Baskin, I. I.; Burshtein, K. Ya.; Bagatur'yants, A. A.; Gromov, S. P.; Alfimov, M. V. *Dokl. Akad. Nauk* **1992**, *325*, 306; *Dokl. Chem.* **1992** (Engl. Transl.).

(25) Izatt, R. M.; Terry, R. E.; Hansen, L. D.; Avondet, A. G.; Bradshaw, J. S.; Dally, N. K.; Jensen, T. E.; Christensen, J. J. *J. Inorg. Chim. Acta* **1978**, *30*, 1.
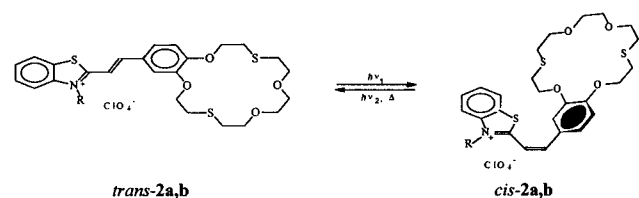
(26) Fedorova, O. A.; Gromov, S. P.; Alfimov, M. V. Dokl. *Akad. Nauk* **1995**, *341*, 219; *Dokl. Chem.* **1995** (Engl. Transl.).

Scheme 5

(*trans*-**2c**)·Hg²⁺   [(*trans*-**2c**)HgY]²⁺

Y = Br⁻, Cl⁻, NH₃, Py

Scheme 6

trans-**2a,b**   *cis*-**2a,b**

but increases 100-fold upon addition of silver or mercuric perchlorate. The increase in the solubility of *trans*-**2c** is attributed to formation of complexes with the dithia-18-crown-6 ether moiety (Scheme 4). Accordingly, in the presence of silver ($C_M = 1 \times 10^{-4}$ M) or mercuric ($C_M = 5 \times 10^{-5}$ M) perchlorate in MeCN, the LAB of *trans*-**2c** ($C_L = 4 \times 10^{-5}$ M) undergoes hypsochromic shifts of 8 and 18 nm, respectively. These shifts are reversed by addition of Br⁻ or Cl⁻ ions or amines (NH₃ or pyridine) to the solutions, without there being an effect on the solubility of the complexes. A possible explanation is given in Scheme 5, where the new ligands with their high affinities for the Hg²⁺ ion displace the para O from its coordination sphere and allow it to participate fully in the electronic transition.

Changes typical of trans−cis isomerization are observed in the spectra when solutions of *trans*-**2a,b** or their complexes with Ag⁺ or Hg²⁺ are exposed to visible light. The cis isomers thermally revert to the corresponding trans isomers in the dark (Scheme 6). Since the cis isomers and their metal ion complexes cannot be obtained in pure form, their absorption spectra must be calculated from spectra of photostationary trans−cis mixtures. We employed Fischer's method[27] to accomplish this task. The method utilizes the photostationary state relationship

$$\left(\frac{[c]}{[t]}\right)_s = \left(\frac{\epsilon_t}{\epsilon_c}\right)\left(\frac{\phi_{tc}}{\phi_{ct}}\right) \qquad (1)$$

where ϵ_t and ϵ_c are molar absorptivities for the trans and cis isomers, respectively, at the excitation wavelength and ϕ_{tc} and ϕ_{ct} are photoisomerization quantum yields in trans → cis and cis → trans directions, respectively. The unknown spectrum of one of the isomers can be calculated from a minimum of two photostationary mixture spectra obtained for different excitation wavelengths, provided that the spectrum of the other isomer is known and that the quantum yield ratio (ϕ_{tc}/ϕ_{ct}) is independent of λ_{exc}. In our systems the first condition is fulfilled because spectra for the pure trans isomers are available. However, the second condition is not secure because neither substituent on the double bond is symmetric with respect to rotation about the vinyl−aryl essential single bond and, in principle, each ground-state isomer may exist as a mixture of four conformers each having distinct absorption spectra and photoisomerization quantum yields.[28] In other diarylethylenes the efficiency and mode of photoisomerization have been shown to be highly

conformer-specific.[29,30] Up to now, a single dominant conformer has been assumed for each CSD isomer on the basis of X-ray structures for the trans isomers. Optimum proximity between the metal ion and the anionic substituent has guided the assignment of structure to anion-"capped" cis isomers.

The absorption spectrum of *cis*-**2b**, derived by applying Fischer's method on photostationary mixture spectra for $\lambda_{exc} =$ 365 and 436 nm is shown in Figure 1, together with the spectrum of *trans*-**2b** and the spectra of the Hg²⁺ complexes of the two isomers. The spectra of the complexed isomers are remarkably similar to those of the uncomplexed isomers, the major differences, upon complexation, being small hypsochromic shifts of 9 and 12 nm at the LABs of the trans and cis isomers, respectively. The small shift of the spectrum of (*cis*-**2b**)·Hg²⁺ reveals that complexation does not disturb the interaction of the conjugated moieties in this chromophore and that, consequently, its near planarity is maintained. It follows that the carboxyl group in (*cis*-**2b**)·Hg²⁺ remains undissociated and does not participate in the formation of an anion-"capped" complex in MeCN. The carboxylate anion is known to coordinate strongly with Hg²⁺.[31]

Formation of anion-"capped" complexes of *cis*-CSDs enforces a twisted conformation on the chromophore as reflected in much more pronounced hypsochromic shifts. For instance, the shifts of the spectra of (*cis*-**1b,c**)·Mg²⁺, which are anion-"capped", relative to the uncomplexed *cis*-**1b,c** are as large as 72 nm in MeCN.[11] In this work, the strategy of using an *N*-alkylsulfonate substituent to stabilize the metal ion complexes of the cis isomers was pursued in **2c**. It proved effective for Hg²⁺ but not for Ag⁺. Excitation at 436 nm of the complexes (*trans*-**2c**)· Ag⁺ and (*trans*-**2c**)·Hg²⁺ in MeCN gives trans−cis photoisomerization in both cases, but with pronounced differences in the spectra of the cis isomers. The spectrum of (*cis*-**2c**)·Ag⁺ is very similar to that of (*cis*-**2b**)·Ag⁺, displaying only an 11 nm hypsochromic shift relative to the spectrum of the free ligand *cis*-**2c**. It follows that, as in (*cis*-**2b**)·Ag⁺, (*cis*-**2c**)·Ag⁺ fails to form an ion-"capped" complex. On the other hand, the spectrum of (*cis*-**2c**)·Hg²⁺ differs dramatically from that of (*cis*-**2b**)·Hg²⁺, displaying a much larger 63 nm hypsochromic shift relative to the spectrum of *cis*-**2c**. The derivation of the spectrum of (*cis*-**2c**)·Hg²⁺ is described in the next paragraph.

The assumption that the quantum yield ratio in eq 1 is independent of λ_{exc} was tested for the Hg²⁺ complexes of *trans*- and *cis*-**2c** containing the 4-alkylsulfonate substituent. Photostationary state mixture spectra obtained in MeCN for $C_{LHg} =$ 5.0×10^{-5} M for $\lambda_{exc} =$ 313, 365, 405, and 436 nm together with the initial (*trans*-**2c**)·Hg²⁺ spectrum were subjected to singular value decomposition with self-modeling (SVD-SM).[32] The spectral matrix behaves as a robust two-component system with the two significant SVD spectral vectors accounting for 99.998% of the total variance. The SM procedure was performed on the stoichiometric line defined by the combination coefficients of the five spectra. The search for the pure (*cis*-**2c**)· Hg²⁺ absorption spectrum was guided by the premise that the Fischer condition is valid for all the mixture spectra. Moving

(27) Fischer, E. *J. Phys. Chem.* **1967**, *71*, 3704.
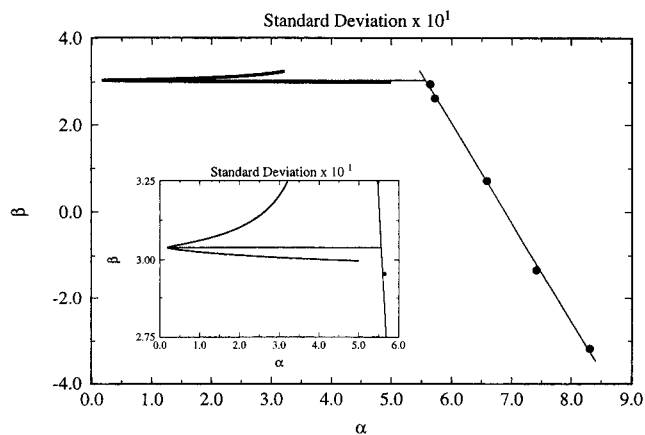(28) For a review, see: Mazzucato, U.; Momicchioli, F. *Chem Rev.* **1991**, *91*, 1679−1719.

(29) Saltiel, J.; Tarkalanov, N.; Sears, D. F., Jr. *J. Am. Chem. Soc.* **1995**, *117*, 5586−5587.
(30) Saltiel, J.; Zhang, Y.; Sears, D. F., Jr. *J. Am. Chem. Soc.* **1997**, *119*, 11202−11210.
(31) Dyatlova, N. M.; Temkina, V. Ya.; Popov, K. I. *Kompleksony i kompleksonary metallov [Complexones and Metal Complexonates]*; Khimiya, Moscow, 1988, 544 pp. (in Russian).
(32) The method is mathematically similar to principal component analysis with self-modeling[33] except that the input spectra are not normalized. It was developed recently for the treatment of matrices of difference spectra for the bacteriorhodopsin photocycle.[34]

Figure 2. Stoichiometric line in SVD eigenvector combination coefficient space for (*trans*-2c)·Hg^{2+}/(*cis*-2c)·Hg^{2+} mixture spectra; the curve (given also in the inset) is the standard deviation from the mean (ϕ_{tc}/ϕ_{ct}) value on stepping along the stoichiometric line.
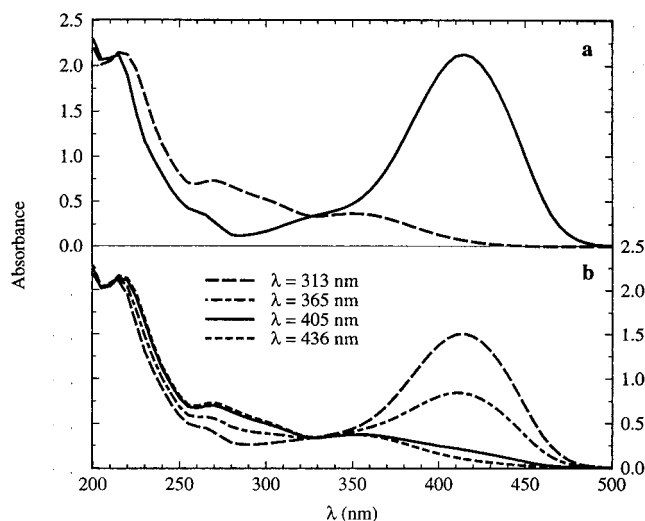

Figure 3. (a) Electronic absorption spectrum of (*trans*-**2c**)·Hg^{2+} and SVD-SM derived spectrum of (*cis*-**2c**)·Hg^{2+}. (b) Absorption spectra of photostationary mixtures at the indicated excitation wavelengths.

Table 2. SVD-SM Derived Photostationary State and Quantum Yield Ratios for **2c**·Hg^{2+} in MeCN

λ_{exc}, nm	([cis]/[trans])$_s$	ϕ_{tc}/ϕ_{ct}
313	0.42$_0$	0.42
365	1.67	0.43
405	13.8	0.44
436	72.0	0.46

stepwise along the stoichiometric line, away from the 436 nm spectral point gives trial cis isomer spectra from which trial (ϵ_t/ϵ_c) and ([c]/[t])$_s$ ratios can be obtained. Values for the (ϕ_{tc}/ϕ_{ct}) ratio were obtained from each mixture spectrum, and standard deviations from the mean of these values were calculated (Figure 2). The point on the stoichiometric line that corresponds to the minimum standard deviation for ϕ_{tc}/ϕ_{ct} defines the pure (*cis*-**2c**)·Hg^{2+} spectrum (Figure 3). The resulting photostationary states and the quantum yield ratios are listed in Table 2. It can be seen that, despite the wide range in photostationary state ratios, the quantum yield ratio is remarkably constant at 0.44 ± 0.02. This demonstration of the validity of the Fischer condition over the entire λ_{exc} range indicates that either each isomer exists as a single ground state conformer or that, if two or more conformers are present in equilibrium, their photoisomerizations fortuitously conform to the same quantum

Scheme 7
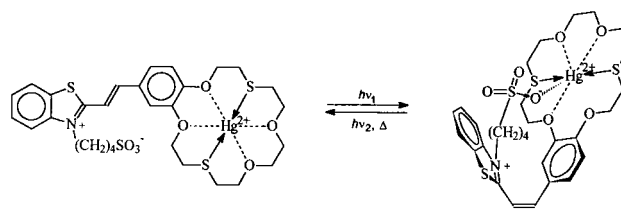
yield ratio. The single dominant conformer alternative seems more probable.

Only 1.4% trans isomer is present in the photostationary state of **2c**·Hg^{2+} at 436 nm (Table 2), whereas under the same excitation conditions, the photostationary state of **2b**·Hg^{2+} contains 30% (*trans*-**2b**)·Hg^{2+}. The behavior of **2c**·Hg^{2+} is reminiscent of the behaviors of complexes **1b,c**,[11] whose cis isomers have been assigned anion-"capped" structures.[13] Analogously, an anion-"capped" structure is assigned here to (*cis*-**2c**)·Hg^{2+} (Scheme 7). The 63 nm shift of the LAB of (*cis*-**2c**)·Hg^{2+} is due to diminished conjugation between the three moieties comprising the chromophore, consistent with the pronounced departure from planarity that accompanies formation of anion-"capped" complexes. This shift is somewhat smaller than the spectral shifts of the anion-"capped" complexes of (*cis*-**1b**)·M^{2+} (M = Mg, Ca, Ba), which lie in the narrow range of 69−72 nm, independent of the size of the metal cation.[35] Weakening or cleavage of the Hg^{2+}...OAr coordination bond, upon intramolecular coordination to the sulfonate group, could account for this difference. This explanation is supported by the spectral shifts observed upon addition of competing nucleophilic ligands to (*trans*-**2c**)·Hg^{2+} (Scheme 5). Intramolecular coordination in the anion-"capped" (*cis*-**2c**)·Hg^{2+} enhances its stability, causing a sharp deceleration of its dark cis−trans isomerization that is reflected in a much slower cis → trans rate constant of 5 × 10^{-8} s^{-1} at ambient temperature.

Equilibrium Constant Determinations. Equilibrium constants, K, for complex formation provide a quantitative measure

$$L + M^{n+} \overset{K}{\rightleftharpoons} (L \cdot M)^{n+} \qquad (2)$$
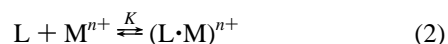
of the stability of the complexes. Anion-"capping" in (*cis*-**2c**)·Hg^{2+} should lead to an increase in K for M^{n+} = Hg^{2+} on changing L from *trans*-**2c** to *cis*-**2c**. Significant differences between the absorption spectra of the ligands and the corresponding complexes often permit direct determination of K values by spectrophotometric titration of ligand solutions with metal ion solutions. This approach is not applicable for our ligands because the K values are too large, as illustrated by the known log $K = 19.5$ value for the complex of 1,10-dithia-18-crown-6 ether with Hg^{2+} in 0.5 M HNO$_3$.[36] Relative K values can be determined in such cases by spectrophotometric titration with a solution of a competing reference ligand, L$_r$. In this work, 2,3-benzo-1,10-dithia-18-crown-6 ether (BDT18C6) was employed as L$_r$. Specifically, the competition for Hg^{2+} ions in a solution containing L$_r$ and *trans*- or *cis*-**2c** (L$_c$ or L$_t$, respectively), in the concentration range where only 1:1 complexes need be considered, is described by two equilibria, given below for *trans*-**2c**, where $K_t = [(L_t \cdot H_g)^{2+}]/([Hg^{2+}][L_t])$ and $K_r =$

(33) See, e.g.: Saltiel, J.; Sears, D. F., Jr.; Choi, J.-O.; Sun, Y.-P.; Eaker, D. W. *J. Phys. Chem.* **1994**, *98*, 35−46.

(34) Zimányi, L.; Kulsár, Á.; Lanyi, J. K.; Sears, D. F., Jr.; Saltiel, J. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 4408−4413.

(35) Ushakov, E. N. Ph.D. (Chem.) Thesis, Institute of Chemical Physics in Chernogolovka of the RAS, Chernogolovka, 1995, p 47 (in Russian).

(36) Izatt, M.; Wu, G.; Jiang, W.; Dally, N. K. *Inorg. Chem.* **1990**, *29*, 3828.
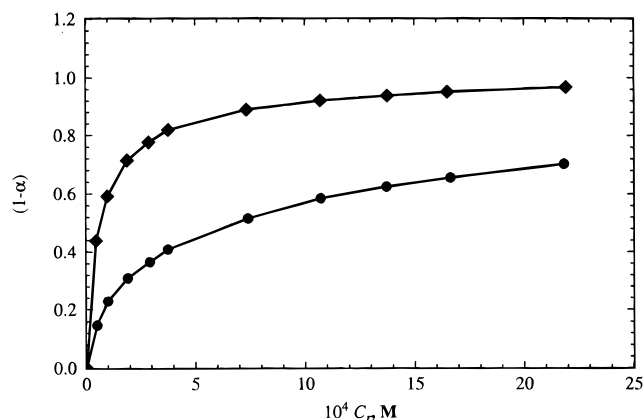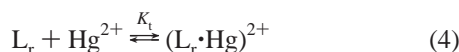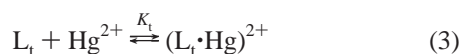
Figure 4. Dependencies of $(1 - \alpha)$ on the concentration of the competing reference ligand BDT18C6 (C_r) at constant concentrations of (*trans*-**2c**)·Hg^{2+} (◆) and (*cis*-**2c**)·Hg^{2+} (●) ($C_t = C_c = C_{Hg} = 5 \times 10^{-5}$ M). The points are experimental, and the curves are best fit lines on the basis of eq 7.

$[(L_r·Hg)^{2+}]/([Hg^{2+}][L_r])$.

$$L_t + Hg^{2+} \overset{K_t}{\rightleftharpoons} (L_t·Hg)^{2+} \qquad (3)$$

$$L_r + Hg^{2+} \overset{K_t}{\rightleftharpoons} (L_r·Hg)^{2+} \qquad (4)$$

The stoichiometry of the system requires that

$$C_r = [1 + K_t(1 - \alpha)/(\alpha K_r)]\{C_{Hg} - \alpha C_t - \alpha/[K_t(1-\alpha)]\} \quad (5)$$

where C_r, C_t, and C_{Hg} are the total concentrations of BDT18C6, *trans*-**2c**, and Hg(ClO$_4$)$_2$, respectively, and α is the fraction of *trans*-**2c** present as a complex with Hg^{2+}. The degree of complexation of L$_t$, α, is determined experimentally from

$$\alpha = (D_e - D_r)/(D_t - D_r) \qquad (6)$$

where D_t is the optical density of the initial solution in which *trans*-**2c** is completely bound into the complex, D_r is the optical density corresponding to complete complexation of BDT18C6, and D_e is the optical density attained upon complete equilibration of the competing ligands for Hg^{2+}. For large K_t and $C_t = C_{Hg} = 5 \times 10^{-5}$ M, nearly all Hg^{2+} is present as the complex and $C_{Hg} \gg \alpha/[K_t(1 - \alpha)]$. Using this inequality, eq 5 can be rearranged to

$$K_t/K_r = \alpha(C_r - C_{Hg} + \alpha C_t)/[(1 - \alpha)(C_{Hg} - \alpha C_t)] \quad (7)$$

and an analogous equation applies for *cis*-**2b**. Values of $1 - \alpha$ obtained for solutions of *cis*- or *trans*-**2c** in the presence of Hg^{2+} are plotted against the total concentration of the competing reference ligand in Figure 4. The points are experimental, and the curves are based on eq 7 by use of the best fit K_t/K_r and K_c/K_r values, 1.88 and 20.1, respectively. Accordingly, the K_c/K_t ratio for the **2c**/Hg^{2+} system is 11. The expected enhanced stability due to the intramolecular coordination bond in (*cis*-**2c**)·Hg^{2+} is observed, but the effect is much smaller than in the **1c**/Mg^{2+} system for which $K_c/K_t \sim 4000$ was determined earlier.[37]

Since the geometric requirements for the formation of anion-"capped" complexes in (*cis*-**1c**)·M$_g^{2+}$ and in (*cis*-**2c**)·Hg^{2+} are

(37) Stanislavskii, O. B.; Ushakov, E. N.; Gromov, S. P.; Fedorova, O. A.; Alfimov, M. V. *Izv. Akd. Nauk, Ser. Khim.* 1996, 605; *Russ. Chem. Bull.* **1996**, *45*, 564 (Engl. Transl.).

Scheme 8

$(cis$-**2c**$)$·Hg^{2+} $[(cis$-**2c**$)$·HgM$]^{4+}$

M = Mg, Hg
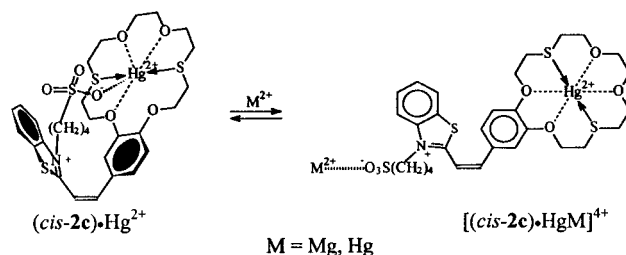
nearly identical, the reactivity leveling evident in **2c** must be sought in the O to S substitutions in the crown ether moieties of the CSDs and the attendant differences in bonding environments for the metal cations. The effect of introducing the ω-alkylsulfonate substituent in the trans isomers of the two types of CSDs is informative. The K_t ratio of (*trans*-**1c**)·M$_g^{2+}$ to (*trans*-**1a**)·M$_g^{2+}$ is 126,[37] substantially larger than 47, the K_t ratio of (*trans*-**2c**)·Hg^{2+} to (*trans*-**2a**)·Hg^{2+}.[15] In both types of CSDs, the presence of the sulfonate group as part of the N-substituent of the benzothiazolium moiety exerts a stabilizing influence on the complexes of the trans isomers. Two possible sources for this effect are (a) stabilization via an intramolecular sovent-separated ion pair interaction of the sulfonate with the M^{2+} ion located in the crown ether cavity and (b) formation of an intramolecular contact ion pair between the sulfonate and the positively charged N atom of the benzothiazolium moiety.[10] In the first instance, stabilization of the complex would occur via a more subtle direct interaction with the metal cation, and in the second instance, the electronic demand of the positive nitrogen on the rest of the chromophore would be diminished. Without wishing to express a clear preference for one of these alternatives, we note that the similarity of the absorption spectra of the free *trans*-CSD ligands and those of their metal complexes (Figures 1 and 3) suggests that, if a direct intramolecular interaction between the complexed metal ion and the sulfonate group is involved, it must function without disturbing the overall planarity of the CSDs.

The origin of the reactivity leveling effect for **c** vs **b** in CSD **1** and dithia-CSD **2** ligand families must be common to both the cis and trans isomers. Preferential S...Hg^{2+} bonding in the CSD **2** complexes reduces the electron demand of the metal cation on the OAr oxygens. Consequently, the ability of these oxygens to release electron density in response to the electron demand of the benzothiazolium moiety, while severely attenuated in **1**·M^{n+} complexes, is substantially retained in **2**·M^{n+} complexes. Furthermore, in the case of the cis isomers, the bond strength of the SO$_3^-$...Hg^{2+} bond in the anion-"capped" (*cis*-**2c**)·Hg^{2+} should be smaller than that of the SO$_3^-$...Mg^{2+} bond in (*cis*-**1c**)·Mg^{2+}, consistent with expectations based on the theory of "hard" and "soft" acids and bases that render Hg^{2+} less oxophilic than Mg^{2+}.[38] The anion-"capped" (*cis*-**1b,c**)·Mg^{2+} complexes have been shown to give a 2:1 open form in the presence of excess Mg^{2+} ions.[11] In view of the relatively weak SO$_3^-$...Hg^{2+} bond, the reaction was expected to be more facile in the case of anion-"capped" (*cis*-**2c**)·Hg^{2+}. Indeed, upon addition of Mg^{2+}, $C_M = 10^{-1}$ M, to a solution of (*cis*-**2c**)·Hg^{2+}, $C_{LHg} = 5 \times 10^{-5}$ M in MeCN, spectral changes occur that reveal the destruction of the intramolecular coordination bond due to association of the sulfonate ion with the excess cations (Scheme 8). Analogous spectral changes are observed upon addition of excess Hg^{2+} to a solution of (*cis*-**2c**)·Hg^{2+}. Formation of the open cis complexes restores the more planar chromophore

(38) Pearson, R. G., Ed. *Benchmark Papers in Inorganic Chemistry. Hard and Soft Acids and Bases*; J. Wiley: New York, 1973; p 430.

geometry, accounting for increased absorbance at longer wavelengths in both cases. The open structure is reflected in a faster dark cis → trans reaction. This was investigated in the case of [(*cis*-**2c**)·Hg Mg]$^{4+}$, the lifetime of which is sufficiently long to allow determination of its stability constant, $K_2 = $ [LHgMg]/([Mg][LHg]), by direct spectrophotometric titration. The degree of complexation of (*cis*-**2c**)·Hg^{2+} with Mg^{2+} was calculated from the optical density of the solution as a function of [Mg^{2+}], with the use of $\alpha = (D_c - D_e)/(D_c - D_{cm})$, where D_c is the optical density of pure (*cis*-**2c**)·Hg^{2+}, D_{cm} is the optical density of pure [(*cis*-**2c**)·HgMg]$^{4+}$, and D_e is the optical density of an equilibrium mixture of the two complexes. The value of $\log K_2 = 2.4 \pm 0.1$ M^{-1} was obtained by means of nonlinear least-squares fitting of the experimental measurements to $C_{Mg} = \alpha C_L + \alpha/[K_2(1 - \alpha)]$, where C_{Mg} and C_L are the total concentrations of Mg^{2+} and (*cis*-**2c**)·Hg)$^{2+}$, respectively.

Polarographic Determination of *Ks*. Conversion of the equilibrium constant ratios from the spectrophotometric studies to absolute values requires knowledge of K_r, the equilibrium constant for complex formation between Hg^{2+} and the reference compound BDT18C6. K_r and the K values for *trans*-**2a,b** were determined polarographically. Subjected to polarography at a dropping mercury electrode, acetonitrile solutions of BDT18C6 or dyes **2a,b**, in the presence of 0.1 M Et$_4$NClO$_4$ as supporting electrolyte, give well-defined mercury anodic waves. In polarogram measurements, the concentration of BDT18C6 was varied from 2×10^{-4} to 4×10^{-3} M and those of dyes **2a,b** were varied from 2.5×10^{-4} to 1×10^{-3} M. The two-electron reversible oxidation of mercury was confirmed by the 30 ± 4 mV half-width of the observed differential anodic wave. The oxidation of Hg to Hg^{2+} in the presence of BDT18C6 or dyes **2a,b** is described as

$$x\mathrm{L} + \mathrm{Hg} \rightleftharpoons (x\mathrm{L}\cdot\mathrm{Hg})^{2+} + 2\mathrm{e} \qquad (8)$$
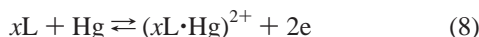
where the symbols are as previously defined and x gives the stoichiometry of the reaction. The desired equilibrium constant, $K = [(x\mathrm{L}\cdot\mathrm{Hg})^{2+}]/[\mathrm{Hg}]^{2+}[\mathrm{L}]^x$, for each ligand is related to the half-wave potential, $E_{1/2}$, of the solutions according to

$$E_{1/2} = E° - 0.0291\{\log K + \log [\mathrm{L}/2]^{x-1} - \log [k_f/k_c]\} \quad (9)$$

where $E°$ is the formal potential of the Hg/Hg^{2+} half-cell vs the Ag/(0.01 M AgNO$_3$) electrode and k_f and k_c, the diffusion rate constants of free and complexed ligand, respectively, are assumed to be identical. The difference between 1.120 V, the standard potential of the Hg/Hg^{2+} half-cell in acetonirile vs the normal hydrogen electrode (NHE, in water), and 0.548 V, the value for the Ag/(0.01 M AgNO$_3$) half-cell in acetonitrile vs NHE, gives $E_0 = 0.572$ V.[39,40] The $E_{1/2}$ values were found to be independent of [L] in all three cases, establishing $x = 1$ (see eq 9), consistent with the spectrophotometric observations. The polarographically determined log K values are shown in Table 3. The value for BDT18C6, the reference ligand in the competitive spectrophotometric studies, is identical, within experimental uncertainty, to the previously determined value for 1,10-dithia-18-crown-6 ether.[36] It was used to convert the equilibrium constant ratios to the absolute values included in Table 3. The agreement between independent determination of the log K value of the same ligand is very satisfactory.

Structural Insights from NMR Spectra. Confirmation of the above structural assignments is provided by the ^{1}H NMR

(39) Coetzee, J. F.; Campion, J. J.; Liberman, D. R. *Anal. Chem.* **1973**, *45*, 343.

(40) Coetzee, J. F.; Simon, J. M.; Bertozzi R. J. *Anal. Chem.* **1969**, *41*, 766.

Table 3. Equilibrium Constants for Hg^{2+} Complex Formation

ligand	log K^a	ligand	log K
BDT18C6	19.5(1)	*trans*-**2b**	18.0(1)^b
trans-**2a**	18.4(1)	*trans*-**2c**	20.1(1)^c
trans-**2b**	18.2(1)	*trans*-**2c**	19.8(1)^b
cis-**2c**	20.8(1)^b		

^{a} These values were determined polarographically for 0.01 M solution of Et$_4$NClO$_4$ in MeCN at 20 °C; values in parentheses are uncertainties in the last significant figure shown. ^{b} On the basis of the value for BDT18C6 and the K ratios obtained in this work. ^{c} On the basis of the value for *trans*-**2a** and the K ratio in ref 16.

Table 4. ^{1}H NMR Chemical Shift Changes in the Crown Ether Moiety upon Complexation in MeCN-d_3

L	salt	L:M^{n+}	$\delta\Delta,^a$ Hz				
			α,α'	β,β'	γ,γ'	δ,δ'	ϵ,ϵ'
trans-**2b**	AgNO$_3$	1.0:2.0	0.16	0.28	0.21	0.04	0.06
trans-**2b**	Hg(NO$_3$)$_2$	1.0:5.0	0.28	0.74	0.69	0.25	0.21
trans-**2b**	Cd(ClO$_4$)$_2$	1.0:10.0	0.24	0.39	0.33	0.21	0.34
trans-**2d**	Hg(ClO$_4$)$_2$	1.0:1.5	0.16	0.17	0.14	0.19	0.19
trans-**1a**	Mg(ClO$_4$)$_2$	1:0:1.0	0.41	0.33	0.33	0.33	

^{a} $\Delta\delta = \delta(\mathrm{L}\cdot\mathrm{M}^{n+})$, where δ is the average value for methylene hydrogens of the same type.

spectra of the CSDs studied in this work and of their complexes with metal cations. As was described earlier for *trans*-**1a**,[16] the entire spectrum shifts downfield upon association of M^{n+} with the CSD and the chemical shift changes, $\Delta\delta$, are most pronounced for the methylene hydrogens of the crown ether moiety. The comparison of $\Delta\delta$ values in MeCN-d_3 for these hydrogens upon *trans*-**1a** complex formation with Mg^{2+} and corresponding $\Delta\delta$ values for *trans*-**2b,d** complex formation with Ag$^+$, Hg^{2+}, and Cd^{2+} is instructive (Table 4). The relatively uniform contribution of all the oxygen atoms in the crown ether moieties of *trans*-**1a** and *trans*-**2d** upon coordination to Mg^{2+} is reflected in rather similar $\Delta\delta$ values for all the hydrogens of the methylenes bonded to the oxygen atoms.[16] By the same token, preferential coordination of the metal cations by the two S atoms in *trans*-**2b** is reflected in relatively large $\Delta\delta$ values for hydrogens of methylenes bonded to S. The difference in electron demand between the singly charged silver cation and the doubly charged cations leads to smaller $\Delta\delta$ values on Ag$^+$ complex formation; however, the $\Delta\delta$ values remain differentially larger for the CH$_2$S hydrogen atoms. The preference of the dithiacrown ether moiety for the "softer" metal cations is seen in the generally larger $\Delta\delta$ values for Hg^{2+} relative to Cd^{2+} complex formation. As an extreme case, addition of Ca^{2+} leads to no change in the ^{1}H NMR spectrum of *trans*-**2b**. The inability of *trans*-**2b** to form a complex with the "hard" Ca^{2+} ions is also evident in the electronic spectra which show no LAB displacement. Conversely, although the sizes of the crown ether cavities differ, the more effective solvation of "hard" metal cations by *trans*-**1a** and *trans*-**2d** probably accounts for the larger $\Delta\delta$ values upon *trans*-**1a**/Mg^{2+} complex formation than upon *trans*-**2d**/Hg^{2+} complex formation.

Direct determination of $\Delta\delta$s upon complex formation of Ag$^+$ or Hg^{2+} with *trans*-**2c** in MeCN-d_3 is not feasible because the free ligand is not sufficiently soluble in this solvent. Reliable estimates of $\Delta\delta$s were obtained by the use of *trans*-**2a** as the reference ligand (Table 5). This procedure is justified by (a) virtually identical chemical shifts for corresponding hydrogen atoms in the spectra of *trans*-**1c**[12] and *trans*-**2c** in deuterated dimethyl sulfoxide (DMSO-d_6) and (b) nearly identical chemical shifts for the aromatic and olefinic protons of *trans*-**1a**[26] and *trans*-**2a**[16] in MeCN-d_3. Taken together, these observations show that, for the free CSD ligands employed in our study, the

Table 5. ^{1}H NMR Chemical Shift Changes upon Metal Cation Complexation with *trans*- and *cis*-**2c** in MeCN-d_3

L	M^{n+} ^{a}	$\Delta\delta$,^{b} Hz						
		β,β'	a,b^d	2'^{d}	5'^{d}	6'^{d}	4,7^d	5,6^d
trans-**2c**	Ag$^+$	0.25	0	0.05	−0.03	−0.05	0.05	0.03
trans-**2c**	Hg^{2+}	0.71	−0.08	0.01	−0.09	−0.10	0.05	0.06
cis-**2c**	Hg^{2+}		e				0.20	0.21

^{a} Perchlorate salts were employed and L:M^{n+} ratios were 1:1, throughout. ^{b} See Scheme 2 for position designations. ^{c} $\Delta\delta$ as in Table 4, except that *trans*-**2a** was used as the reference free ligand. ^{d} *trans*-**1c** was used as the reference free ligand. ^{e} Only one of the vinylic protons is clearly discerned at 7.63 ppm, $J = 12.2$ Hz.

chemical shifts of the methylenes in the crown ether moiety are insensitive to the nature of the N-substituent of the benzothiazolium group and that, similarly, the chemical shifts of aromatic and olefinic hydrogens are insensitive to changes in the crown ether moiety.

The strong coordination of the metal cations to the S atoms of the crown ether moiety of *trans*-**2c** is revealed by pronounced changes in the chemical shifts of the β,β' hydrogens as in the case of *trans*-**2b**. Generally, the electron-withdrawing effect of the metal cation in the crown ether cavity is substantially attenuated along the conjugation chain of the chromophore. For the systems in Table 4, $\Delta\delta$ values for the benzene-ring protons are in the 0.10−0.15 Hz range and those for the olefinic protons, 0.01−0.03 Hz, are still smaller. Small $\Delta\delta$ values are also observed for *trans*-**2c**, and counterintuitively, some of these changes are upfield (Table 5). The ^{1}H NMR spectrum of (*cis*-**2c**)·Hg^{2+} in MeCN-d_3 is difficult to interpret because of substantially broadened signals. However, it is possible to assign a doublet at δ 7.63 to one of the olefinic protons and the magnitude of the coupling constant, $J = 12.2$ Hz, is consistent with the cis H$_a$,H$_b$ relationship.[19,28] This spectrum is the first recorded for a metal cation complex of a *cis*-CSD.

Summary

Numerous macrocyclic systems incorporating oxygen, sulfur, and nitrogen heteroatoms have been described that exhibit high cationic selectivities.[41,42] Those containing sulfur or mixed oxygen−sulfur or nitrogen−sulfur as the heteroatoms show a remarkable preference for heavy metal ions and transition metal ions. In this paper, it is shown that in combination with the proper chromophore this latter selectivity can be enhanced or modulated by the absorption of light. Specifically, the benzodithia-18-crown-6 styryl dye **2c** is rendered 11 times more selective for Hg^{2+} upon trans → cis photoisomerization. The effect is attributed to anion-"capping" by the alkylsulfonate substituent (Scheme 7). More pronounced photoresponse would be expected with the use of softer anionic-"caps", and the design and synthesis of such molecules are in progress.

Experimental Section

Materials. Unless stated otherwise, reagents and solvents were obtained from commercial sources and used as received. Acetonitrile used in spectral studies was distilled twice over P$_2$O$_5$ and then over CaH$_2$. Mg(ClO$_4$)$_2$ was dried under vacuum at 240 °C. AgClO$_4$·3H$_2$O (Aldrich) was dried under vacuum at 40 °C. The syntheses of the CSDs used were as previously described.[16,19] The procedure is given below for *trans*-**2c**.

***trans*-2-[2-(5,6,8,9,11,12,14,15,17,18-Decahydro-7,16-dithia-1,4,-10,13-tetraoxa-2,3-benzocyclooctadecyn-3-yl)]vinyl-3-(4-butylsulfonate)benzothiazolium betaine (2c).** Dry pyridine (0.3 mL) was added to a solution of betaine **3**[10] (32l mg, 0.11 mmol) and 3′-formylben-

(41) Yordanov, A. T.; Roundhill, D. M. *Coord. Chem. Rev.* **1998**, *170*, 93−124.

(42) Lindoy, L. F. *Coord. Chem. Rev.* **1998**, *174*, 327−342.

zodithia-18-crown-6 ether[21] (**4**) (46 mg, 0.12 mmol) in anhydrous ethanol (2 mL). The mixture was refluxed for 17 h and concentrated in vacuo. The residue was washed with benzene and extracted by heating with 35 mL of methanol, and the methanol solution was cooled to 0 °C. The precipitate, *trans*-**2c**, formed after 1 h and was isolated by filtration: yield 53 mg (75%); mp 270−272 °C (dec.); ^{1}H NMR (DMSO-d_6) δ 2.02 (m, 2 H, CH$_2$), 2.24 (m, 2 H, CH$_2$), 2.77 (m, 2 H, CH$_2$SO$_3^-$), 2.96 (m, 2 H, CH$_2$S), 3.04−3.24 (m, 6 H, 3 CH$_2$S), 3.67 (br. s, 4 H, 2 ε-CH$_2$O), 3.76 and 3.81 (both m, 4 H, δ,δ′-CH$_2$O), 4.39 and 4.53 (both m, 4 H, α,α′-CH$_2$O), 5.07 (m, 2 H, CH$_2$N), 7.23 (d, 1 H, H−C$_5'$, $J = 8.3$ Hz), 7.69 (d, 1 H, H−C$_6'$, $J = 8.3$ Hz), 7.86 and 7.95 (both m, 2 H, H−C$_5$, H−C$_6$), 8.00 (s, 1 H, H−C$_{2'}$), 8.20 and 8.26 (both d, 2 H, CH=CH, $J = 15.6$ Hz), 8.40 and 8.45 (both d, 2 H, H−C$_7$, H−C$_4$, $J = 8.5$ and 8.1 Hz). Anal. Calcd (%) for C$_{29}$H$_{37}$NO$_7$S$_4$: C, 54.45; H, 5.83; N, 2.19. Found (%): C, 54.29; H, 5.69; N, 2.01.

Complex of *trans*-2-[2-(5,6,8,9,11,12,14,15,17,18-decahydro-7,16-dithia-1,4,10,13-tetraoxa-2,3-benzocyclooctadecin-3-yl)]vinyl-3-(4-butylsulfonate)benzothiazolium betaine with Hg(ClO$_4$)$_2$ [(*trans*-2c)·Hg(ClO$_4$)$_2$]. Hg(ClO$_4$)$_2$·3H$_2$O (0.25 mg, 0.00055 mmol) and *trans*-**2c** (0.32 mg, 0.0005 mmol) were dissolved in 1 mL of CD$_3$CN in red light. The resulting (*trans*-**2c**)·Hg(ClO$_4$)$_2$ solution was used for NMR investigation and preparation of (*cis*-**2c**)·Hg(ClO$_4$)$_2$): ^{1}H NMR (CD$_3$-CN, 25 °C) δ 3.18 (t, 2 H, CH$_2$SO$_3$), 3.46−4.18 (br. m, 12 H, 2 CH$_2$O and 4 CH$_2$S), 4.30 and 4.46 (both br. m, 4 H, 2 CH$_2$O), 4.69 and 4.96 (both br. m, 4 H, 2 CH$_2$O), 4.89 (t, 2 H, NCH$_2$), 6.91 and 7.00 [both br. m, 1 H, H(C-5′)], 7.35 and 7.41 [both br. m, 1 H, H(C-6′)], 7.88 and 7.97 [both t, 2 H, H(C-5), H(C-6)], 7.99 [br. s, 1 H, H(C-2′)], 8.03 and 8.10 (both d, 2 H, CH=CH, J_{trans} = 15.7 Hz), 8.20 and 8.33 [both d, 2 H, H(C-4), H(C-7), $J = 8.5$ Hz, $J = 8.4$ Hz].

Complex of *cis*-2-[2-(5,6,8,9,11,12,14,15,17,18-decahydro-7,16-dithia-1,4,10,13-tetraoxa-2,3-benzocyclooctadecyn-3-yl)]vinyl-3-(4-butylsulfonate)benzothiazolium betaine with Hg(ClO$_4$)$_2$ [(*cis*-2c)·Hg(ClO$_4$)$_2$]. A solution of (*trans*-**2c**)·Hg(ClO$_4$)$_2$) in CD$_3$CN (0.5 mL, 5×10^{-4} M) was irradiated at 436 nm. An isomer mixture containing more then 98% of (*cis*-**2c**)·Hg(ClO$_4$)$_2$ was obtained for NMR investigation: ^{1}H NMR (CD$_3$CN, 25 °C) δ 3.20−4.75 (br. m, 24 H, CH$_2$SO$_3$, 6 CH$_2$O, 4 CH$_2$S, NCH$_2$), 6.80−7.18 [br. m, 4 H, H(C-2′), H(C-5′), H(C-6′), H(C−a) or H(C−b)], 7.63 [d, 1 H, H(C−b) or H(C−a), J_{cis} = 12.2 Hz], 7.94 and 8.00 [both t, 2 H, H(C-5), H(C-6)], 8.23 and 8.37 [both d, 2 H, H(C-4), H(C-7), $J = 8.5$ Hz, $J = 8.4$ Hz].

Analytical Methods. ^{1}H NMR spectra were recorded on a Bruker AMH-400 spectrometer (400 MHz, MeCN-d_3 and DMSO-d_6, tetramethylsilane internal standard). Chemical shifts and spin−spin coupling constants were measured to ± 0.01 and ± 0.1 ppm, respectively. Changes in ^{1}H chemical shifts, $\Delta\delta$, were measured in MeCN-d_3 for addition of *trans*-**2c** (up to $C_L = 1 \times 10^{-3}$ M) to solutions of metal salts. Concentrations of metal salts that ensured the largest $\Delta\delta$ values were selected for use.

Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer at 20 ± 2 °C in 1-cm quartz cells. Complex formation of **2c** with Hg(ClO$_4$)$_2$ was studied by spectrophotometric titration. In direct experiments, aliquots of a solution containing known concentrations of **2c** and of Hg(ClO$_4$)$_2$ were added to a solution of **2c** alone of the same concentration. The absorption spectrum of each solution was recorded and the stoichiometry of the complex was found from the titration curve. The magnitude of the stability constant was too large to be determined by the direct spectrophotometric method. In experiments with the competing ligand, aliquots of a solution containing equal amounts of **2c**, Hg(ClO$_4$)$_2$ ($C_L = C_M = 5 \times 10^{-5}$ M), and BDT18C6 ($C_r = 10^{-2}$ M) were added to a solution containing only the same concentrations of **2c** and Hg(ClO$_4$)$_2$. Absorption measurements were recorded at 460 nm. The ionic strengths of these titration solutions were 2×10^{-4} M. Complex formation of (*cis*-**2c**)·Hg^{2+} with Mg(ClO$_4$)$_2$ was studied by direct spectrophotometric titration. Aliquots of a solution of Mg(ClO$_4$)$_2$ ($C_M = 10^{-1}$ M) were added to a solution of (*cis*-**2c**)·Hg^{2+} ($C_{LHg} = 5 \times 10^{-5}$ M). Absorption measurements were recorded at 415 nm. During these titrations ionic strengths varied from 2×10^{-3} to 3×10^{-3} M.

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

Table 6. Crystal Data, Data Collection, Structure Solution, and Refinement Parameters for **2e**

identification code	1
empirical formula	$C_{26}H_{32}O_4S_3$
formula weight	645.61
color, habit	red, prism
crystal size, mm	$0.5 \times 0.2 \times 0.2$
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimens	9.71(1)
a, Å	12.304(9)
b, Å	13.715(9)
c, Å	64.01(6)
α, deg	85.28(9)
β, deg	71.29(9)
γ, deg	1392(2)
V, Å^3	2
Z	1.540
density (calcd), g/cm^3	1.407
absorption coeff, mm^{-1}	656
$F(000)$	Enraf-Nonius CAD-4
diffractometer	293
temp, K	graphite monochromatized Mo Kα (0.71073)
radiation, $(\lambda,$ Å$)$	$\omega/2\theta$
scan mode	$0.8 + 0.35\tan\theta$
scan width, deg	
min/max scan rate, deg/min	2/8
θ range, deg	2.22–25.97
index ranges	$-11 \le h \le 8, -14 \le k \le 15,$ $-3 \le l \le 16$
no. of reflns collected	5015
no. of ind reflns	4613 [R(int) = 0.0311]
absorption correction	empirical (ψ scan)
min and max transmn	0.78643 and 0.78643
decay correction	none
solution method	direct methods (SHELX-86)
refinement method	full-matrix least-squares on F^2 (SHELXL-93)
hydrogen treatment	all H atoms were placed in calcd positions
data/restraints/params	d(C–H) = 0.93 Å for aromatic H; d(C–H) = 0.97
goodness-of-fit on F^2	Å for others) and refined using riding model
final R indices [$I > 2\sigma(I)$]	4612/0/312
R indices (all data)	1.075
extension coefficient	$R_1 = 0.0560$, wR_2 =0.1779 $R_1 = 0.0787$, wR_2 = 1986 0.000(2)
largest diff peak and hole, e/Å^{-3}	1.745 and −0.857

Preparation of solutions and all experiments were carried out in red light.

Photochemical experiments were carried out by exposing CSD solutions and their metal complexes to filtered light of a DRSh-100 mercury lamp. Individual mercury lines of the spectrum of this lamp (313, 365, 405, and 436 nm) were isolated with the use of glass filters.

Polarographic Procedures. Polarographic experiments were carried out in acetonitrile with a Model 263a potentiostat/galvanostat (EG&G Princeton Applied Research) and a Model 303A dropping-mercury electrode (DME) (EG&G Princeton Applied Research). Potential measurements were made vs an Ag/(0.010 M AgNO$_3$ in acetonitrile) electrode, and the salt bridge solution was 0.1 M Et$_4$NClO$_4$ in acetonitrile. This reference electrode was kept in contact with the testing solution via a Vycor frit supplied by EG&G Princeton Applied Research. The method of differential-pulse polarography was used for all experiments. The potential scanning rate was 2 mV/s, and the dropping time of the DME was 1 s. The supporting electrolyte was 0.1 M Et$_4$NClO$_4$. Values of the half-wave potentials of Hg anodic waves were found from the individual polarograms. All experiments were performed at 20 °C under an argon atmosphere.

Crystal Structure Determination. Crystals of *trans*-**2e** were grown from acetonitrile solution. A crystal was mounted on an Enraf-Nonius

Table 7. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2, $\times 10^3$)

atom	x	y	z	U(eq)^a
I	2632(1)	2527(1)	750(1)	57(1)
S(1A)	9469(5)	4146(5)	3591(4)	64(1)
S(1B)	9879(5)	3602(4)	3942(4)	57(1)
S(2)	3570(3)	1525(3)	6743(2)	80(1)
S(3)	3104(2)	8341(2)	9588(2)	55(1)
O(1)	6810(6)	3985(5)	5963(4)	60(1)
O(2)	8409(7)	1868(6)	3561(5)	81(2)
O(3)	7455(6)	459(6)	5539(5)	75(2)
O(4)	5101(6)	3071(5)	7366(4)	60(1)
N	1694(6)	6799(5)	10586(4)	45(1)
C(1)	7809(9)	4417(8)	5178(6)	60(2)
C(2)	8207(10)	3539(9)	4641(7)	68(2)
C(3)	9443(14)	3419(12)	2723(10)	102(3)
C(4)	9569(10)	2146(8)	2955(8)	75(2)
C(5)	8424(10)	619(8)	3868(7)	70(2)
C(6)	7206(11)	405(10)	4574(8)	79(2)
C(7)	6277(11)	350(9)	6242(8)	79(2)
C(8)	5174(11)	1591(9)	5970(7)	74(2)
C(9)	4135(11)	1353(8)	8012(6)	67(2)
C(10)	4064(10)	2565(7)	8072(6)	61(2)
C(11)	6257(7)	4622(7)	6580(5)	48(2)
C(12)	5302(7)	4113(6)	7355(5)	45(1)
C(13)	4651(7)	4708(6)	7998(6)	46(1)
C(14)	4946(7)	5802(6)	7904(6)	42(1)
C(15)	5902(8)	6257(6)	7167(6)	51(2)
C(16)	6565(9)	5672(7)	6493(6)	56(2)
C(17)	4254(7)	6479(6)	8536(6)	49(2)
C(18)	3258(7)	6226(6)	9278(5)	48(2)
C(19)	2654(7)	7011(5)	9834(5)	42(1)
C(20)	1097(9)	5742(7)	10934(7)	60(2)
C(21)	1290(7)	7669(6)	11011(5)	46(1)
C(22)	325(8)	7659(7)	11845(6)	59(2)
C(23)	115(9)	8614(9)	12173(8)	75(2)
C(24)	796(10)	9557(8)	11701(8)	73(2)
C(25)	1719(9)	9554(7)	10896(8)	66(2)
C(26)	1960(7)	8594(6)	10578(6)	49(2)

^{a} U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

CAD-4 diffractometer at room temperature. Crystallographic data and structure solution and refinement parameters are given in Table 6. The unit cell parameters were determined using 25 accurately centered reflections. Three reflections were measured every 2 h for decay control, and two reflections, for orientation control. The structure amplitudes for the measured reflections were obtained after the usual Lorentz and polarization corrections. The structure was solved by direct methods and refined by full-matrix least squares. In the final cycles of refinement, all non-hydrogen atoms were refined with anisotropic temperature parameters. All of the hydrogen atoms were placed on calculated positions and refined using the riding model. One of the crown ether sulfur atom, S(1), is disordered over two positions—S(1A) and S(1B)— with equal occupations. The location and magnitude of the residual electron density peaks in the vicinity of the crown either fragment, apparently, correspond to another, minor, component of disordering. Table 7 gives atomic coordinates for all non-hydrogen atoms and their isotropic equivalent thermal parameters. All calculations were performed with the use of SHELXS-86[43] and SHELXL-93[44] software.

(43) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(44) Sheldrick, G. M. SHELXL-93. Program for Refinement of Crystal Structures, University of Göttingen, Germany, 1993.