Crown-ether styryl dyes
16.* Betaines of photochromic 15-crown-5 ethers and their complexes with Mg^{2+}: a surface enhanced Raman scattering spectroscopy study

A. V. Feofanov,[a]* *A. I. Ianoul,*[a] *V. A. Oleinikov,*[a] *I. R. Nabiev,*[a] *S. P. Gromov,*[b] *O. A. Fedorova,*[b] *and M. V. Alfimov*[b]

[a]*M. M. Shemyakin and Yu. A. Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences,*
16/10 ul. Miklukho-Maklaya, 117871 Moscow, Russian Federation.
Fax: +7 (095) 336 1766
[b]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
7A ul. Novatorov, 117421 Moscow, Russian Federation.
Fax: +7 (095) 938 2156

The surface enhanced Raman scattering (SERS) spectra of styryl dyes containing a crown-ether group and a heteroaromatic residue with sulfoalkyl (**1a**) or alkyl (**1b**) *N*-substituent and of their complexes with Mg^{2+} cations were recorded in the 10^{-4}—10^{-8} mol L^{-1} concentration range. A model for the interaction of compounds **1a**,**b** with a silver surface during their adsorption on an electrochemically treated electrode was suggested. Fast *cis—trans* relaxation of the adsorbed molecules **1a**,**b** and complexes (**1a**,**b**)Mg^{2+} was found. It was shown that at [**1a**] = 10^{-5} mol L^{-1} and moderate molar ratios (C_{Mg}/[**1a**] = 3/1 to 9/1) in acetonitrile solutions, (*trans*-**1a**)Mg^{2+} complexes are joined into head-to-tail type dimers. An excess of Mg^{2+} cations (C_{Mg}/[**1a**] > 100) leads to dissociation of the dimers yielding (*trans*-**1a**)$(Mg^{2+})_2$ complexes. The formation of dimers from complexes (*trans*-**1a**)Mg^{2+} is accompanied by a substantial distortion of the planar structure of *trans*-**1a**. This may be an important factor influencing the efficiency of photocycloaddition involving dimers of (*trans*-**1a**)Mg^{2+}.

Key words: surface enhanced Raman scattering (SERS), crown-ether styryl dyes, complexes with Mg^{2+}.

Variation of conformations of reacting molecules is an efficient way to control the rates and selectivities of chemical reactions. In this connection, compounds whose structures can be changed in a specified direction through the action of light or a chemical reagent are of great interest. Chromoionophores containing a crown-ether group and a heteroaromatic fragment with a sulfoalkyl (**1a**) or alkyl (**1b**) substituent have been synthesized.[2,3] These compounds change their photochromic properties on forming complexes with alkaline earth metal cations.[4] The constants of complex formation for isomers of these dyes are substantially different.[3]

A number of facts (the concentration-dependent variations of the absorption spectra of the (*cis*-**1a**)Mg^{2+} adduct, the dynamics of variation of the absorption spectrum after brief irradiation of a solution of the isomeric (*trans*-**1a**)Mg^{2+} with light,[5] the dependence of the time of the fluorescence decay on the concentration of cations,[4] the stereo- and regioselectivities of photochemical cycloaddition[1]) indicate that the complexes are self-organized in dimers. The dyes were studied by spectrophotometry,[1,3—5] Raman spectroscopy,[6—8] and X-ray diffraction analysis.[9] However, data on the structure and conditions of the formation of aggregates from these molecules in acetonitrile solutions are scarce, and for dilute solutions ($\leq 10^{-6}$ mol L^{-1}), they are completely lacking. Additional information can be gained from surface enhanced Raman scattering (SERS), which is used efficiently to study chromophores[10,11] and formation of ligand—metal complexes.[12—16]

In the present work, crown-containing styryl dyes **1a**,**b** were investigated by SERS spectroscopy for the first time. We studied characteristic features of the formation of complexes of **1a**,**b** or benzo-15-crown-5 (**2**) with Mg^{2+} and formation of dimers from (*trans*-**1a**)Mg^{2+} complexes as well as the adsorption of these compounds on the surface of a silver electrode.

Experimental

2-[2-(Benzo-1,4,7,10,13-pentaoxacyclopentadec-15-yl)vinyl]-3-(3-sulfopropyl)benzothiazolium (1a), **2-[2-(benzo-1,4,7,10,13-pentaoxacyclopentadec-15-yl)vinyl]-3-ethylbenzothiazolium perchlorate (1b)**, and **2-methyl-3-ethylbenzothiazolium perchlorate (3)** were synthesized as described previ-

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* For part 15, see Ref. 1.

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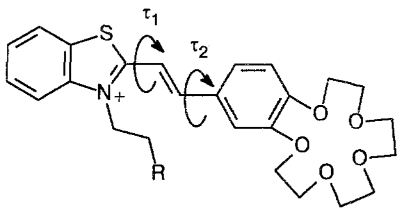
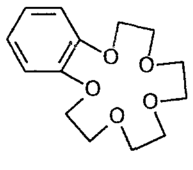
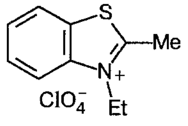


1a,b





2 **3**

R = $CH_2SO_3^-$ (**1a**); H [ClO_4^-] (**1b**)

ously.[3] Benzo-15-crown-5 (**2**) (Merck, Germany) was used without additional purification. "Specially pure" grade acetonitrile was distilled twice over P_2O_5 and CaH_2 to remove water. "Specially pure" grade $Mg(ClO_4)_2$ was dried *in vacuo* at 180 °C. All the measurements were carried out at room temperature.

Raman and SERS spectra were recorded on a Ramanor HG-2S single-beam spectrometer (Jobin Yvon, France) (with a scanning step of 1 cm^{-1} and an integration time of 1 s); excitation was accomplished by Ar^+ (164-03, Spectra-Physics) and Kr^+ (ILK-120, Karl Zeiss) lasers. The power of the laser radiation was 50, 25, 15, and 5 mWt, λ_{excit} = 647.1, 514.5, 488.0, and 457.9 nm, respectively. The SERS effect was induced using an electrochemically roughened silver electrode.

When a standard oxidation-reduction cycle in an aqueous electrolyte solution was carried out,[10] the electrode was washed with tridistilled water, dried, and washed with acetonitrile. The electrode thus liberated from the electrolyte and water was placed in a quartz cell containing a solution of the substance under study. The SERS signal arising due to the adsorption of the compound studied on the electrode surface was reproducible and stable over a period sufficient for several measurements. The spectra were recorded at least three times, a new sample being prepared for each spectrum.

Note that other SERS-active systems (silver island films[17] and colloidal silver[18]) are unstable in acetonitrile in the presence of Mg^{2+}. It was found that gold island films can be used for recording the SERS spectra of *trans*-**1a,b** molecules; however, the SERS signal is rather weak.

The concentrations and conformations of the compounds under study and the formation of their complexes (at $C \geq 2 \cdot 10^{-6}$ mol L^{-1}) were monitored using their absorption spectra, which were recorded on a Cary-209 spectrophotometer (Varian, USA) prior to and after the SERS spectra were measured. The concentrations were determined based on known extinction coefficients.[7]

Table 1. Interpretation of the Raman spectrum of compound **2** in the solid state

Compound **2**		Raman spectra of related compounds, ν/cm^{-1}
ν/cm^{-1}	Assignment	
1592 vs	ν_{8b}	1600^a
1504 m	ν_{19b}	1494^a
1461 s	δ(H—C—H)	$1446—1473^b$
1444 s	ν_{19a}	1468^a
1336 vs	w(CH_2) + δ(C—C—H)	$1174—1411^b$, 1323^c
1273 m	ν_3	1290^a
1159 m	ν_{9a}	1155^a
1139 w	ν_{as}(C—O—C) + ν_{18a}	$1102—1205^d$, 1118^a
1060 w	ν(C—C)	$885—1132^b$
1043 vs	ν_{as}(C—C—O)	$1050—1070^d$
849 m	$\nu_{12} + \nu_{17a}$	826^a, 862^a
814 m	ν_s(C—O—C)	$700—924^b$
781 vs	ν_{11}	741^a
609 m	ν_{6a}	582^a
515 w	ν_{6b}	506^a
469 m	δ_s(C—O—C)	$428—499^b$
283 m	ν_{15}	255^a
210 m	ν_{10b}	180^a

Note. For vibrational modes of benzene derivatives, the Wilson classification was used. [a] *o*-Xylene.[19,20] [b] Hydrocarbons.[20] [c] Compound **1a**.[6] [d] Aliphatic alcohols and ethers.[20]

Table 2. Interpretation of the Raman spectrum of compound **3** in the solid state

Compound **3**		Raman spectra of related compounds, ν/cm^{-1}
ν/cm^{-1}	Assignment	
1579 s	ν_{8a}	1581^a
1514 vs	$\nu(N^+=C)$	1513^b
1477 m	δ(H—C—H)	$1446—1473^c$
1442 s	ν_{19a}	1447^a
1381 s	$\delta_s(CH_3)$	$1368—1385^c$
1332 s	w(CH_2) + δ(C—C—H)	$1174—1411^c$, 1323^b
1273 m	ν_3	1261^a
1204 w	ν_{13}	1210^d
1170 m	ν_{9a}	1155^a
1131 m	ν_{18a}	1139^a
1100 m	ν(C—N)	1042^e
1023 w	ν_{18b}	1023^a
989 w	ν_5	968^a
779 m	ν_{11}	800^d
671 m	ν_1	678^a
545 w	ν_{6b}	550^d
512 s	δ(C—S—C)	513^b
482 m	ν_{16b}	479^a
422 m	«Extensions» of the CCC chain	$150—425^c$
299 w	ν_{10a}	264^a
161 w	ν_{10b}	172^a

[a] *o*-Aminothiophenol.[19] [b] Compound **1a**.[6] [c] Hydrocarbons.[20] [d] *o*-Chlorotoluene.[20] [e] Glycine.[20]

The Raman bands in the spectrum of molecule **2** (Table 1) were assigned similarly to Raman spectra of benzene derivatives of the *o*-di-"light" type,[19,20] namely, veratrole, catechol, and *o*-xylene. The bands in the Raman spectrum of compound **3** (Table 2) were assigned using similar assignment made for benzene derivatives of the *o*-di-"light"-"heavy" type,[19,20] namely, *o*-aminothiophenol and *o*-chlorotoluene. Since the differences between the vibration frequencies of disubstituted *o*-di-"light" and trisubstituted 1,2,4-tri-"light" benzene derivatives are small (the ν_{7b}, ν_{9a}, and ν_{17a} modes provide an exception[19]), the

Table 3. Interpretation of the Raman spectrum of compound **1(a,b)** in the solid state

Compound **1**		Raman spectra of related compounds, ν/cm^{-1}
ν/cm^{-1}	Assignment	
1608 m	ν(C=C)	1613^a
1592 vs	ν_{8b}	1592^b
1576 sh	ν_{8a}	1579^c
1514 m	ν(N$^+$=C)	1514^c, 1513^a
1499 w	ν_{19b}	1504^b
1487 m	δ(H—C—H)	1477^c
1464 w	δ(H—C—H)	1461^b
1444 m	ν_{19a}	1444^b, 1442^c
1362 m	ν_{14} + δ(CH$_3$)	1362^a, 1381^c
1324 vs	w(CH$_2$) + δ(C—C—H)	1336^b, 1332^c, 1323^a
1267 s	ν_3	1273^b, 1273^c
1229 s	ν_{7a}	1218^d
1214 sh	ν_{13}	1204^c
1179 m	ν_{9a}	1159^b, 1170^c
1148 m	ν_{as}(C—O—C) + ν_{18a}	1139^b, 1131^c
1078 m	ν(C—C) + ν(C—N)	1060^b, 1100^c
1043 vw	ν_{as}(C—C—O)	1043^b
1032 m	ν_s(C—C—O)	884—1033^e
1023 m	ν_{18b}	1023^c
854 w	ν_s(C—S—C)	854^a
834 w	ν_{12} + ν_{17a}	849^b
814 vw	ν_s(C—O—C)	814^b
795 w	ν_{11}	781^b, 779^c
665 w	ν_1	671^c
641 m	ν_4	612^a
609 m	ν_{6a}	609^b
520 sh	ν_{6b}	515^b, 545^c
511 m	δ(C—S—C)	512^c, 513^a
465 vw	δ_s(C—O—C)	469^b
402 m	"Extensions" of the CCC chain	422^c
260 w	ν_{15} + ν_{10a}	283^b, 299^c
197 w	ν_{10b}	210^b, 161^c

[a] Compound **1a**.[6] [b] Compound **2** (see Table 1). [c] Compound **3** (see Table 2). [d] 3-(3,4-Dimethoxyphenyl)propionic acid.[19] [e] Aliphatic alcohols and ethers.[20]

Table 4. Interpretation of the SERS spectra of compounds **1a**, **2**, and **3**

1a	**2**	Assignment	**3**,	Assignment
ν/cm^{-1}			ν/cm^{-1}	
1608	1608	ν_{8b}	1608	ν_{8b}
1592	1589	ν_{8a}	1589	ν_{8a}
1507(+4)	1508(+4)	ν_{19b}	1509	ν(N$^+$=C)
1488	1488	δ(H—C—H)		
1461	1461	δ(H—C—H)	1463	δ(H—C—H)
1439	1439	ν_{19a}	1439	ν_{19a}
1361	1361	ν_{14}	1361	ν_{14}
1321(+4)	1319(+6)	δ(C—C—H) + + w(CH$_2$)	1314	δ(C—C—H) + + w(CH$_2$)
1264	1264	ν_3	1260	ν_3
1225(−4)	1225(−4)	ν_{7a}	1231	ν_{7a}
1177(−8)	1176(−3)	ν_{9a}		
1142	1140	ν_{as}(C—O—C)	1134	ν_{18a}
1075	1075	ν(C—C)	1092	ν(C—N)
1036	1036	ν_s(C—C—O)		
1023	1023	ν_{18b}	1023	ν_{18b}
851	851	ν_{12} + ν_{17a}	846	ν_s(C—S—C) + ν_{12}
792	796	ν_{11}	783	ν_{11}
662	662	ν_1		
635(+2)	633(+4)	ν_4	626	ν_4
613(+5)	611(+7)	ν_{6a}	613	ν_{6a}
510	510	ν_{6b}	509	δ(C—S—C)
454	454	δ_s(C—O—C)		

Note. The frequency shifts due to the formation of complexes with Mg^{2+} are given in parentheses.

assignment made for the spectrum of compound **2** was used to determine the contribution of vibrations of the benzo-15-crown-5 fragment to the Raman spectra of compounds **1a**,**b** (Table 3).

The positions of bands in the Raman spectra of compounds under study in the solid state (Fig. 1) and in an acetonitrile solution are close to each other (*cf.* the results of the present and previously published studies[6]). This made it possible to use the data of Tables 1—3 for the assignment of SERS-active modes of compounds **1a**,**b**, **2**, and **3** (Table 4).

Results and Discussion

Main characteristic features of the SERS spectra of 1a,b molecules and (1a,b)Mg^{2+} complexes. The SERS spectra of **1a**,**b** compounds and their complexes with Mg^{2+} in acetonitrile solutions can be obtained in a broad range of concentrations (10^{-4}—10^{-8} mol L^{-1}).

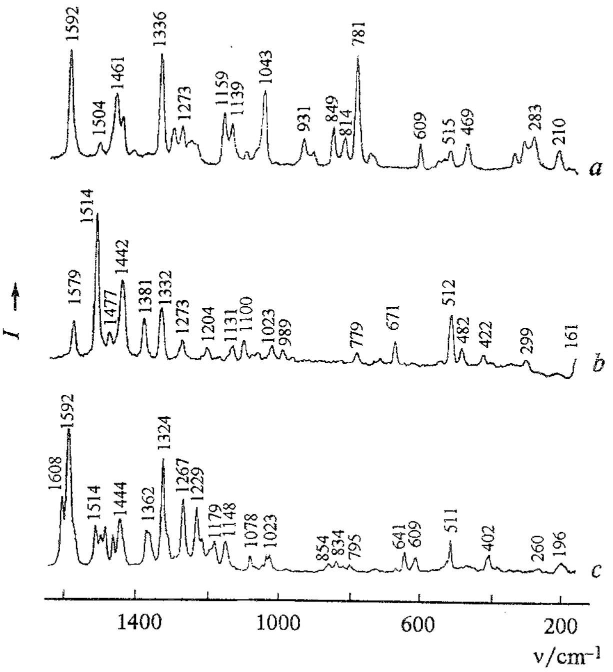


Fig. 1. Raman spectra of compounds **2** (*a*), **3** (*b*), and **1a** (*c*) in the solid state (λ_{excit} = 647.1 nm). The Raman spectra of compounds **1a** and **1b** coincide.

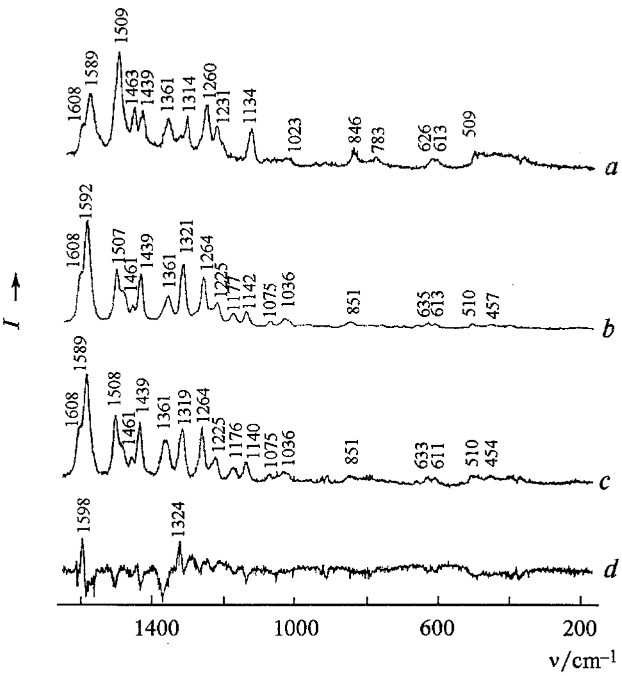


Fig. 2. SERS spectra of compounds **3** (*a*) and **2** (*c*), SERRS spectrum of the *trans*-isomer of compound **1a** (*b*) in acetonitrile (λ_{excit} = 457.9 nm, the contribution of the solvent signal was subtracted), and difference spectrum of (*trans*-**1a** minus **2**) (*d*). [**1a**] = 10^{-5} mol L^{-1}, [**2**] = 0.5 mmol L^{-1}, [**3**] = 0.5 mmol L^{-1}. SERRS spectra of the *trans*-isomers of **1b** and **1a** coincide.

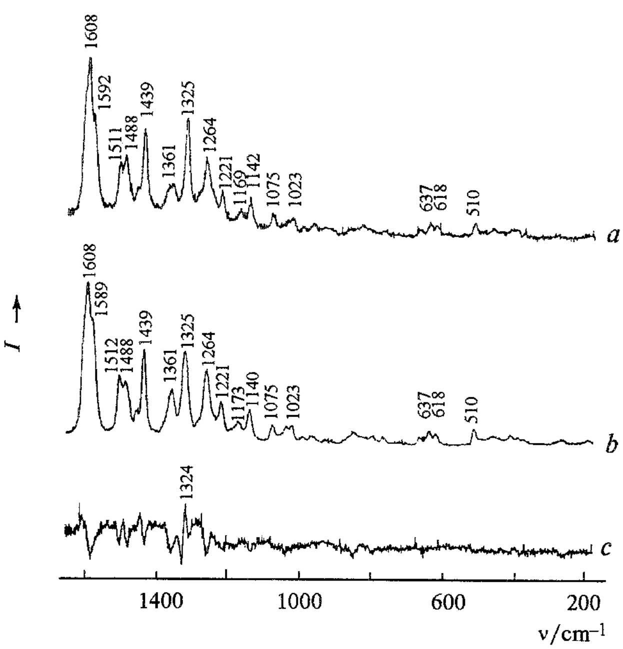


Fig. 3. SERRS spectrum of (*trans*-**1a**)Mg^{2+} ([**1a**] = 10^{-5} mol L^{-1}, C_{Mg} = 10^{-3} mol L^{-1}) (*a*), SERS spectrum of (**2**)Mg^{2+} ([**2**] = 0.5 mmol L^{-1}, C_{Mg} = 0.5 mmol L^{-1}) (*b*), and difference spectrum of ((*trans*-**1a**)Mg^{2+} minus (**2**)Mg^{2+}) (*c*). SERRS spectra of (*trans*-**1b**)Mg^{2+} and (*trans*-**1a**)Mg^{2+} coincide. λ_{excit} = 457.9 nm, the contribution of the solvent signal was subtracted.

At $C > 10^{-4}$ mol L^{-1}, **1a**,**b** samples cannot be studied by SERS due to the intense inherent fluorescence, and at $C < 10^{-8}$ mol L^{-1}, adsorption of the dyes on the cell walls introduces a considerable error in the measurements. Thus, SERS spectroscopy extends appreciably the range of concentrations at which crown-containing styryl dyes can be studied, with respect to NMR ($C > 10^{-3}$ mol L^{-1}), spectrophotometry[4] ($C > 10^{-6}$ mol L^{-1}), and resonance Raman spectroscopy[6] ($C > 10^{-4}$ mol L^{-1}). The lower limit of detection of the SERS signals of compounds **2**, (**2**)Mg^{2+}, and **3** in solution in acetonitrile is 10^{-6} mol L^{-1} (Figs. 2 and 3), which is typical of SERS spectroscopy of compounds that do not absorb in the visible region.

An additional increase in the intensity of SERS signals of **1a**,**b** compared to the intensities of their resonance Raman signals[6] or SERS signals of colorless compounds **2** and **3** is ~10^4, *i.e.*, the effect of surface enhanced resonance Raman scattering (SERRS) is observed. It has been expected that a large contribution to the SERRS spectra of **1a**,**b** would be made by the isomers and their complexes with Mg^{2+} that absorb intensely in the visible region, *viz.*, *trans*-**1a**,**b** (λ_{max} = 435 nm, ε = 39000 L cm^{-1} mol^{-1}), *cis*-**1a**,**b** (λ_{max} = 421 nm, ε = 8500 L cm^{-1} mol^{-1}), and (*trans*-**1a**,**b**)Mg^{2+} complexes (λ_{max} = 393 nm, ε = 36000 L cm^{-1} mol^{-1}).[4]

In order to distinguish the signals of the *cis*- and *trans*-isomers of **1a**,**b** in the SERRS spectra, the solutions were preliminarily irradiated with light at various wavelengths (457.9, 488.0, or 514.5 nm) and then the SERRS spectra were induced by the same light. When the relative concentration of *cis*-**1a**,**b** in the photo-steady-state mixture of isomers was varied in this way from 85 to 60 %, we did not detect any variations in the SERRS spectra at λ_{excit} = 457.9, 488.0, or 514.5 nm that could be attributed to the contribution of the *cis*-isomer.

The (*cis*-**1a**,**b**)Mg^{2+} complexes (λ_{max} = 321 nm, ε = 9000 L cm^{-1} mol^{-1})[4] virtually do not absorb in the visible region, therefore the SERS sections of the molecules of these isomers are several orders of magnitude smaller than the SERS sections of the (*trans*-**1a**,**b**)Mg^{2+} adducts. Correspondingly, the SERS signals of the (*cis*-**1a**,**b**)Mg^{2+} complexes can be manifested only if the concentration of the *cis*-form in the photo-steady-state mixture of the isomers is more than 10^{-4} mol L^{-1}, and the proportion of the *trans*-isomer is no more than 0.01 %. These conditions cannot be fulfilled during recording of the SERS spectra. Therefore, in the spectra of the (**1a**,**b**)Mg^{2+} complexes (see Fig. 3), the signals of (*trans*-**1a**,**b**)Mg^{2+} are recorded selectively.

A number of facts found by us suggest the existence of fast *cis*—*trans*-isomerization of molecules **1a**,**b** and their complexes with Mg^{2+} adsorbed on a silver electrode: (1) we were not able to detect the signal of the *cis*-isomer in the SERRS spectra of **1a,b**; (2) the intensities of the SERRS signals of the (**1a,b**)Mg^{2+} complexes do not depend on the initial state of the sample, do not change with time, and are identical for solutions kept in the dark (more than 99 % *trans*-isomers) and for those preliminarily exposed to light (more than 99 % *cis*-isomers[4]); (3) even when the concentration of the (**1a,b**)Mg^{2+} complexes is ~10^{-8} mol L^{-1}, the photoinduced transition of a solution containing initially more than 99 % *trans*-isomers into a state in which the proportion of the *trans*-isomers is less than 1 % does not result in a decrease in the intensity of the SERRS signal.

Only the molecules adsorbed on the silver electrode surface contribute to the intensity of the SERRS spectra. If we assume that fast *cis—trans*-isomerization is typical of adsorbed molecules, then the SERRS signal should not depend on the dynamics of the *cis—trans*-equilibrium in the bulk of the solution, which is really the case.

Adsorption of *trans*-1a,b molecules and (*trans*-1a,b)Mg^{2+} complexes on the silver electrode. The *trans*-**1a,b** molecules and (*trans*-**1a,b**)Mg^{2+} complexes are adsorbed on the silver electrode through their crown-ether moiety, which follows unambiguously from the similarity of the spectra of compounds **2** and *trans*-**1a,b** (see Fig. 2, *b*, *c*) as well as (**2**)Mg^{2+} and (*trans*-**1a,b**)Mg^{2+} aggregates (see Fig. 3, *a*, *b*). The absence of the set of bands typical of compound **3** (see Fig. 2, *a*) or the characteristic band of the C=C group vibrations (1610 cm^{-1} in the resonance Raman spectrum[6]) in the difference spectra (*trans*-**1** minus **2** and (*trans*-**1a,b**)Mg^{2+} minus (**2**)Mg^{2+}) (see Figs. 2, *d* and 3, *c*, respectively) makes it possible to conclude that the benzothiazole chromophore and the ethylene group in molecules **1a,b** are rather far removed from the electrode surface and do no contribute to the SERRS spectra. There are virtually no distinctions between the spectra of *trans*-**1a** and *trans*-**1b** as well as between the spectra of (*trans*-**1a**)Mg^{2+} and (*trans*-**1b**)Mg^{2+}, which implies that the sulfo group does not participate in the adsorption of molecules **1a** on the electrode.

Thus, molecules **1a,b** are adsorbed on the silver electrode through their crown-ether moieties. The C=C bond and the benzothiazole group of the molecule are located rather far from the metal surface. No effect of the sulfo group on the adsorption of compound **1a** (compared to that of compound **1b**) was detected. This type of interaction of molecules **1a,b** with the electrode is governed by the high affinity of crown ethers to metal cations. The remoteness of the benzothiazole group from the silver surface is due to some features of the electronic structure of this chromophore. Crown-containing molecules in which the benzothiazole chromophore is replaced by another dye are adsorbed in a different manner, which is indicated by the appearance of additional bands specific to this chromophore in the SERS spectra.

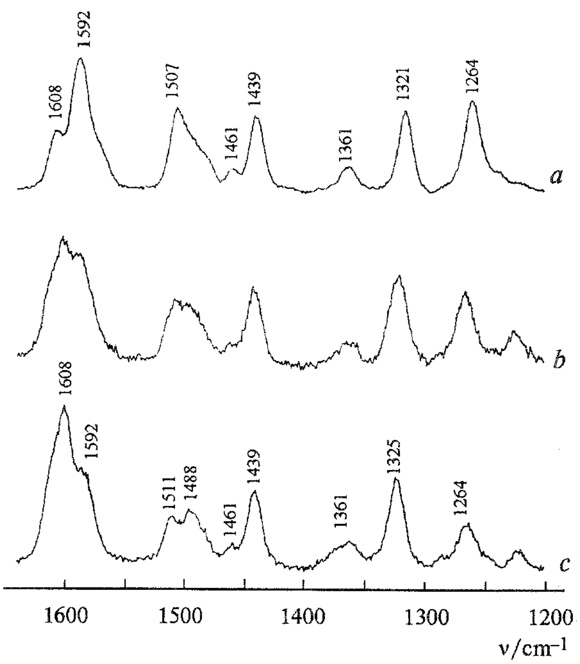


Fig. 4. SERRS spectra of *trans*-**1a** (*a*) and (*trans*-**1a**)Mg^{2+} with the ratios between molar concentrations C_{Mg}/[**1a**] = 5/1 (*b*) and C_{Mg}/[**1a**] = 100/1 (*c*). [**1a**] = 10^{-5} mol L^{-1}, λ_{excit} = 457.9 nm; the contribution of the solvent signal was subtracted.

Formation of complexes of *trans*-1a,b with Mg^{2+}. Formation of dimers of (*trans*-1a)Mg^{2+} complexes. Note that the interaction of the crown-ether fragments of molecules **1a,b** and **2** with the surface of the silver electrode does not hamper the formation of their complexes with Mg^{2+}. This is confirmed by the typical variations in the SERS spectra of **1a,b** and **2** (see Figs. 2 and 3) that generally correlate with the Mg^{2+} concentration in the solution and the magnitude of the hypsochromic shift in their absorption spectra. Apart from the shifts of the SERS bands presented in Table 4, the formation of complexes with Mg^{2+} is manifested as the variations of relative intensities of some bands (Fig. 4). The ratios between the intensities of the bands at 1608 and 1592 cm^{-1} [$I(\nu_{8b})/I(\nu_{8a})$] and the bands at 1507 and 1488 cm^{-1} [$I(\nu_{19b})/I(\delta(H-C-H))$] were found to be the most characteristic.

Characteristic features of the formation of (*trans*-**1a,b**)Mg^{2+} complexes were studied by the SERRS method at a concentration of 10^{-5} mol L^{-1}, which enabled simultaneous monitoring of the complex-formation processes in solution by their absorption spectra. The $I(\nu_{8b})/I(\nu_{8a})$ ratio was found to be 0.54 for the free **1b** and **2** and increases to 1.5 proportionally to the addition of Mg^{2+} to the solution. When the concentration of Mg^{2+} becomes sufficient (taking into account the corresponding complex-formation constants[2]) for ~95 % of the (*trans*-**1b**)Mg^{2+} and (**2**)Mg^{2+} complexes to be formed, the $I(\nu_{8b})/I(\nu_{8a})$ value flattens out. The formation of more than 95 % of the (*trans*-**1b**)Mg^{2+} complexes is also confirmed by analysis of their absorption spectra.

The SERRS study of the (*trans*-**1a**)Mg^{2+} complexes showed the presence of an intermediate plateau in the region of molar concentrations of $C_{Mg}/[\mathbf{1a}] = 3/1$ to 9/1, where $I(\nu_{8b})/I(\nu_{8a}) \approx 1.0$. A substantial excess of Mg^{2+} ($C_{Mg}/[\mathbf{1}] > 100/1$) results in the second plateau, where the ratio $I(\nu_{8b})/I(\nu_{8a}) = 1.5$, and the SERRS spectrum of (*trans*-**1a**)Mg^{2+} almost does not differ from the spectra of the (**2**)Mg^{2+} and (*trans*-**1b**)Mg^{2+} complexes. At $C_{Mg}/[\mathbf{1a}] > 3/1$, the hypsochromic shift in the absorption spectra indicates that the formation of (*trans*-**1**)Mg^{2+} complexes is virtually completed (more than 98 %). As the $C_{Mg}/[\mathbf{1a}]$ ratio increases, no further variations in the absorption spectra occur.

The presence of the intermediate plateau for (*trans*-**1a**)Mg^{2+} was interpreted as an indication of the formation of dimers of the "head-to-tail" type (**4**, **5**) in the solution. The existence of these dimers is evidenced by a number of experimental data obtained previously[1,4,5] (Scheme 1). This plateau cannot be explained by the stacking-interactions of the crown-ether groups of neighboring molecules on the electrode nor by the formation of "head-to-head" type dimers, since for (**2**)Mg^{2+} and (*trans*-**1b**)Mg^{2+}, capable of giving these structures, no plateau at $I(\nu_{8b})/I(\nu_{8a}) \approx 1.0$ was found. At the same time, the main distinction of molecule **1b** from **1a** is the presence of the sulfo group, which enables the formation of dimers **4** and **5**.

The peculiarities of the SERRS spectra of dimers of (*trans*-**1a**)Mg^{2+} complexes are explained by the weakening of the interaction of Mg^{2+} with the crown-ether ring due to the binding of the second molecule to the sulfo group, which results in the $I(\nu_{8b})/I(\nu_{8a})$ ratio decreasing to 1.0. The appreciable excess of Mg^{2+} probably causes dissociation of the dimers, giving (*trans*-**1a**)$(Mg^{2+})_2$ complexes. As this takes place, the "normal" interaction of the Mg^{2+} cation with the crown-ether ring is restored, and the $I(\nu_{8b})/I(\nu_{8a})$ ratio increases to the value typical of the monomeric (*trans*-**1b**)Mg^{2+} and (**2**)Mg^{2+} complexes. Note that with an excess of Mg^{2+}, the time of fluorescence attenuation of the (*trans*-**1a**)Mg^{2+} adduct changes, which has also been attributed to the dissociation of dimers.[6]

Structure of the dimers of the (*trans*-1a)Mg^{2+} complexes from the data of SERRS spectroscopy. Apart from those presented above, a number of experimental facts[1,4,6] providing evidence in support of the formation of dimers of the (*trans*-**1a**)Mg^{2+} complexes in acetonitrile solutions have been found, and two possible "head-to-tail" structures of the dimer, *viz.*, **4** and **5**, were suggested (see Scheme 1). Molecular mechanics simulation showed that dimers **4** and **5** are located in deep potential energy minima, which suggests that both forms coexist in solution.[21] At the same time, the structure of dimers **5** corresponds to the regio- and stereoselectivity of photocycloaddition to the greatest extent.[1]

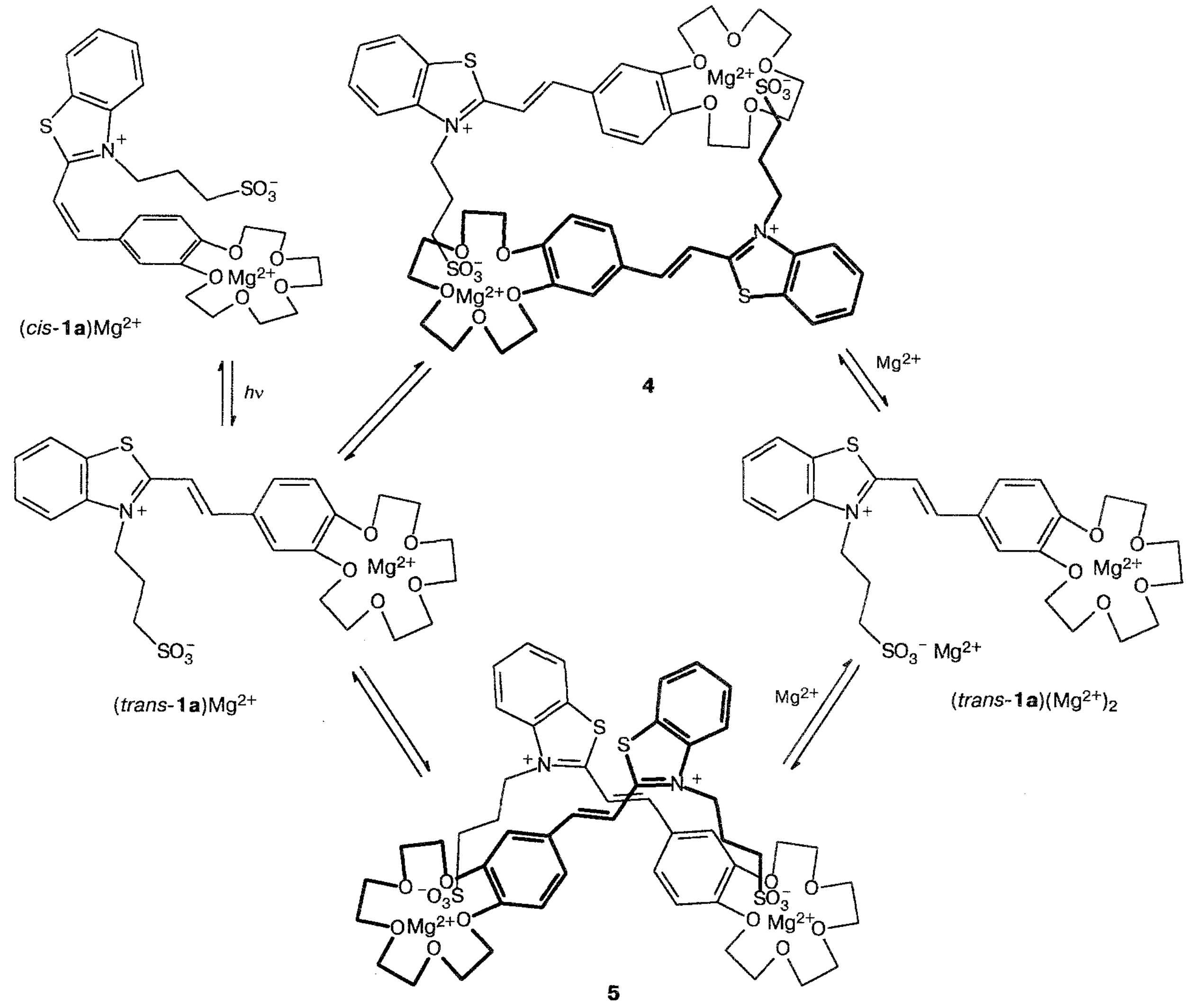
An evaluation of the contributions of the two possible dimer forms to the SERRS signal makes it possible to conclude that the adsorption of dimers **5** on the electrode alone should not lead to the appearance of new spectral bands (Fig. 4, *b*). When aggregate **4** is adsorbed, the benzothiazole fragments of the molecules are brought into close proximity to the electrode surface. This should result in the enhancement of the SERRS signal, which is characteristic of the benzothiazole chromophore, because its π-electrons participate in the formation of the $Ph-N^+=C-C=C-Ph$ conjugated π-electron system determining the resonance properties of the entire molecule.[22] In the case of adsorption of dimer **5** through both crown-ether groups, which is much favored by the high affinity of crown ethers to metals, the benzothiazole chromophores of their molecules become far removed from the electrode. This accounts for the similarity of the spectra of the monomeric and dimeric (*trans*-**1a**)Mg^{2+}. We believe that dimers **5** are selectively adsorbed on the silver electrode and are detected by SERRS, though we do not rule out the possibility that dimers **4** occur in acetonitrile solutions too.

The molecular simulation of the conformations and the electronic absorption spectra of compound **1a** showed that the *trans*-isomer of **1a** has a planar geometry ($\tau_1 = \tau_2 = 0°$), which is distorted only slightly on the formation of the complex with Mg^{2+}.[22] The hypsochromic shift of the band corresponding to the long-wavelength electron transition in *trans*-**1a** is only due to the effect of the electric field of the cation on the electronic structure of the molecule. Therefore, the weakening of the interaction between Mg^{2+} cations and the crown-ether moiety of molecule **1a** in dimer **5** that follows from the analysis of the SERRS spectra should lead to a bathochromic shift of the band corresponding to the electron transition in the (*trans*-**1a**)Mg^{2+} complex. However, the formation and dissociation of dimers of the (*trans*-**1a**)Mg^{2+} adduct do not alter its absorption spectrum, as has been noted above.

It is known[22] that with the τ_1 and τ_2 angles differing from zero, the hypsochromic shift of the band corresponding to the electron transition in complex *trans*-**1a** is rather large. The weakening of the effect of the cation on the electronic structure of compound **1a** in the dimer is likely to be counterbalanced by the distortion of the planar geometry of the (*trans*-**1a**)Mg^{2+} complex. When the τ_1 and τ_2 angles differ from zero, the steric strain inherent to planar forms of styryl dyes decreases.[22] The disturbance in the planarity of the structure is favorable for a specific mutual arrangement of the (*trans*-**1a**)Mg^{2+} adducts in dimers **5**, and it may be one of the factors affecting the efficiency of photocycloaddition.[1]

Now we are conducting a detailed study of the peculiarities of the complex formation between dye **1a** and Mg^{2+} at low concentrations of the dye (10^{-6}—10^{-8} mol L^{-1}). The possibility of using the quick *cis*—*trans*-isomerization of compound **1a** on a

Scheme 1



SERS-active silver electrode in order to increase the quantum yield of photocycloaddition is being studied.[1]

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