141612-33-1; **5**, 141612-34-2; **6**, 141612-35-3; **7**, 141612-36-4; **8**, 141612-37-5; **9**, 141612-38-6; **10**, 141612-39-7; **11**, 141612-40-0; **12**, 141612-41-1; **13**, 141612-42-2; **14**, 141612-43-3; **15**, 141723-94-6; **16**, 141612-44-4; **17**, 141723-95-7; **18**, 141612-45-5; **19**, 141612-46-6; **20**, 141612-47-7; **21**, 141612-48-8; **22**, 141612-49-9; **23**, 141612-50-2; **26**, 141612-51-3; **27**, 141612-52-4; *cis*-**28**, 141612-53-5; *trans*-**28**, 141612-54-6; *cis*-**29**, 141612-55-7; *trans*-**29**, 141612-56-8; *cis*-**30**, 141612-57-9; *trans*-**30**, 141612-58-0; **31**, 141612-59-1; *cis*-**32**, 141612-60-4; *trans*-**32**, 141612-61-5; *cis*-**33**, 141612-62-6; *trans*-**33**, 141612-63-7; **34**, 141612-64-8; **35**, 141612-65-9; **36**, 141612-66-0; **37**, 141612-67-1; **38**, 141612-68-2; **39**, 141612-69-3; dimethyl malonate, 108-59-8; palladium acetate, 3375-31-3.

Dependence of Metal Ion Complexation and Intermolecular Aggregation on Photoinduced Geometric Isomerism in a Crown Ether Styryl Dye

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Abstract: Photoisomerization and complexation with alkaline-earth metal cations of a 2-[2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-(3-sulfopropyl)benzothiazolium betaine has been studied by steady-state and time-resolved electronic spectroscopy. The dye is highly sensitive to complexed metal cations, showing characteristic hypsochromic shifts of the long wavelength absorption and fluorescence bands, as well as a decrease in the fluorescence quantum yield upon complexation. The stabilities of the complexes are drastically changed by photoisomerization, with enhanced stability of the cis ligand complex being attributed to the intramolecular interaction of the complexed cation with a tethered sulfonate anion. This intramolecular capping also induces a strong hypsochromic shift of up to 70 nm from the absorption maximum of the uncapped trans ligand complex. Unlike this capped cis complex, the uncapped trans complex is partially aggregated, even at low concentration, as a result of the association of the sulfonate anion of one dye with the "crowned" cation of a second molecule. At high metal ion concentrations, the aggregates dissociate as the sulfonate group becomes associated with a free metal cation. Similar interactions are also responsible for the relaxation of the anion-capped cis complex to its "uncapped" form at high cation concentrations.

Introduction

Chromoionophoric macrocycles are interesting primarily because of their utility in the identification and quantitative determination of metal cations.[1-3] Since cation binding is sensitive to the ligand environment, the binding equilibrium constant can be effectively controlled by employing a switch-functionalized system where a crown ether is bound intramolecularly to an antenna moiety which is responsive to an external stimulus.[4] Various responsive crown ethers have been synthesized for dynamic control of cation binding induced by changes in pH, redox potential, temperature, magnetic field, light, etc.[4,5] Photoresponsive systems are often most useful, especially if the photoexcitation causes a structural change in the antenna, e.g., photoisomerization.[4-6]

An additional method to control cation binding occurs in crown ethers bearing a tethered photoresponsive anionic cap.[4] The anionic group acts cooperatively with the crown ring: thus, the cation binding ability is altered by changing the proximity of this group, e.g., by photoisomerization. The different stabilities of capped and uncapped metal-crown ether complexes can be used for photoresponsive ion extraction and light-driven ion transport across membranes.[6]

Thus far, most studies of photoresponsive crown ethers have involved azobenzene derivatives,[3,4,7] although several reports on stilbene derivatives have also appeared.[8,9] Recently, the syntheses of styryl dyes containing heteroaromatic residues and of various crown-ether groups bearing O,N,S heteroatoms in different combinations have been reported.[10-14] These dyes are intensively colored and show significant hypsochromic shifts upon complexation with alkali- or alkaline-earth metal cations. High quantum yields for trans-to-cis and cis-to-trans photoisomerization are observed for each species investigated. Zwitterionic crown ether styryl dyes bearing a photoresponsive anionic cap have also been prepared.[11]

In this paper, we report a study of the photoisomerization and complexation of alkaline-earth metal cations with a 2-[2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-(3-sulfopropyl)benzothiazolium betaine (L, Figure 1) by steady-state and time-resolved electronic spectroscopy. Our results indicate high sensitivity of the dye to

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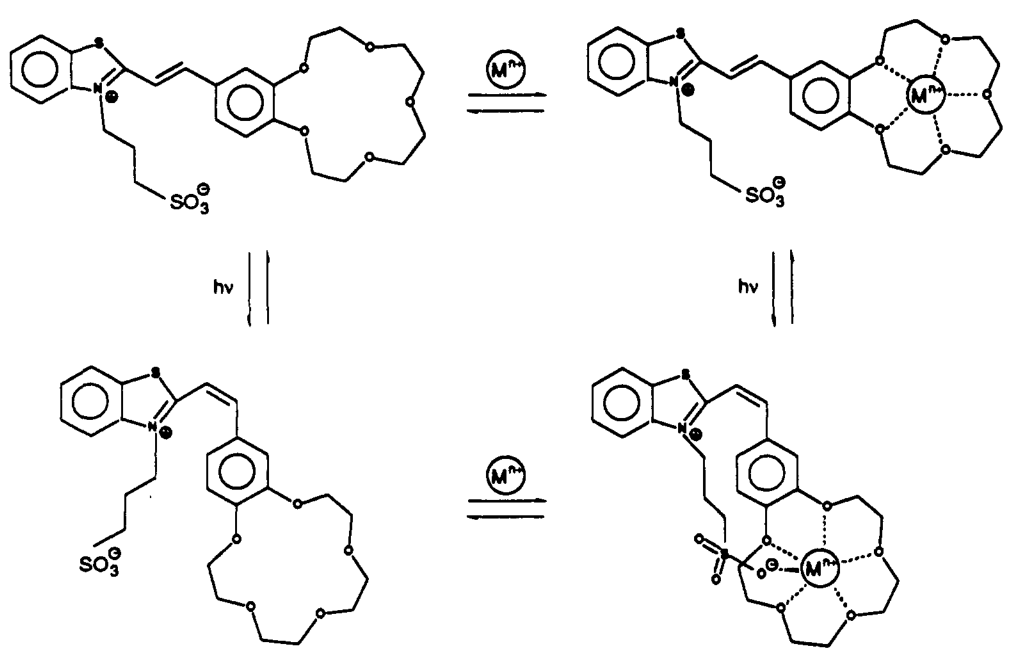

Figure 1. Photoisomerization and complexation of the crown ether styryl dye L.

complexation with metal cations as well as enhanced stability of *cis*-L complexes deriving from the additional interaction of the cation with the anionic sulfonate group, leading to a strong hypsochromic shift of the long wavelength absorption (up to 70 nm from the *trans*-L complex). For small metal cations (e.g., Mg^{2+}), a 1:1 complex is formed, while for larger cations (e.g., Ca^{2+} or Ba^{2+}) a 2:1 (two ligands:one metal cation) complex is also formed. Dimeric aggregation of the *trans*-L complexes via interaction of the metal cation in one complex with the sulfonate group in a second complex is also observed.

Experimental Section

Benzothiazolium betaine dye L was synthesized by the previously described procedure.[11] Acetonitrile was doubly distilled, first from P_2O_5 and then from CaH_2 to remove traces of water and other impurities accelerating dark cis–trans isomerization. Magnesium, calcium, and barium perchlorates were dried under vacuum at 180 °C. Dye solutions were prepared, and all experiments were performed under red light. All experiments were carried out in acetonitrile at room temperature.

Absorption spectra were measured on a Hewlett-Packard 8451A single beam spectrophotometer. Steady-state fluorescence spectra were recorded on a SLM Aminco 500C spectrofluorometer. The fluorescence quantum yields for geometric isomerization of *trans*-L in acetonitrile were determined relative to rhodamine B in ethanol, with excitation at 450 nm. The fluorescence quantum yields of the alkaline-earth metal perchlorate complexes of *trans*-L (relative to free *trans*-L) were determined at matching optical densities and calculated from integrated (albeit uncorrected) fluorescence spectra. All spectroscopic measurements were carried out in a quartz cuvette modified by treatment of the inner surfaces with trimethylchlorosilane to minimize dye adsorption on the cuvette walls. Only negligible effects on the spectral properties of these complexes were observed upon altering the identity of the counterion.

A glass-filtered 200W high pressure Hg lamp was used for photoisomerization. Quantum yields of trans–cis and cis–trans isomerization for L–M complexes were determined upon irradiation at 313 nm of the trans and cis isomers, respectively, by monitoring changes in the optical density of the trans isomer at its absorbance maximum (where the extinction coefficient of the cis complex is negligibly small). In the free ligand, the hypsochromic shift is only 15 nm, so that *trans*-L, whose absorption overlaps partially with *cis*-L, cannot be completely converted to *cis*-L by photoisomerization alone. This is consistent with only small geometry differences in the cis and trans isomers, which become much more significant in the nonplanar metal complexes. The absorption spectrum of *cis*-L was calculated by differences between the spectra of *trans*-L and of the photostationary states obtained by irradiating the solution at two different wavelength (365 and 436 nm).[15] Quantum yields of isomerization of the free ligand were determined by irradiation of *trans*-L at 313 nm while monitoring changes in the optical density at 435 nm (i.e., the *trans*-L absorption maximum). By using ϵ_{cis}(435 nm) and the ratio of ϕ_{tc}/ϕ_{ct} determined, the absorption spectra and quantum yields were obtained by Fischer's method.[15] Light intensity was measured by a PP-1 cavity receiver, giving an absolute error in the isomerization quantum yield measurements of about 20%. The dark thermal cis–trans isomerization was followed spectrophotometrically by monitoring the growth of the absorption maximum of the trans isomer.

The equilibrium constants for complexation with *trans*-LM were calculated from the dependence of complex formation on the added metal salt concentration determined spectrophotometrically as $\alpha = (D_0 - D)/(D_0 - D_c)$, where D_0 is the free ligand absorbance, D_c is the complex absorbance (at complete ligand complexation), and D is the absorbance at a given cation concentration, all at 460 nm. The experimental dependences of α on the total metal concentration, $[M^{2+}]$, were fit to eq 1:

$$\frac{[M^{2+}]}{\alpha} = \frac{1 + K_1(1-\alpha)[L] + K_1K_2(1-\alpha)^2[L]^2}{K_1(1-\alpha)\{1 + 2K_2(1-\alpha)[L]\}} \tag{1}$$

where [L] is the total ligand concentration, K_1 and K_2 are the equilibrium constants for $1L{:}1M^{2+}$ and $2L{:}1M^{2+}$ complex formation, respectively, in accordance with the equilibria in eq 2.

$$\begin{gathered} L + M^{2+} \overset{K_1}{\rightleftharpoons} LM^{2+} \\ L + LM^{2+} \overset{K_2}{\rightleftharpoons} L_2M^{2+} \end{gathered} \tag{2}$$

Inclusion of the second process in eq 2 was necessary to describe experimental data for Ca^{2+} and Ba^{2+}, while for Mg^{2+} a linear dependence of $[M^{2+}]/[L]\alpha$ vs $1/(1-\alpha)$ was established, thus establishing only 1:1 complexation.

A displacement method was employed to estimate the equilibrium complexation constant for *cis*-LMg^{2+} with benzo-15-crown-5 ether as an indicator, with the spectral changes induced by indicator addition being ascribed to the production of free ligand. This spectral change, recorded at the maximum of *cis*-L absorption (421 nm), was used to calculate the degree of ligand complexation α. The displacement equilibrium constant K_d was estimated from eq 3

$$\frac{[I]}{[M^{2+}] - \alpha[L] - \alpha/(K_L(1-\alpha))} = \frac{1-\alpha}{K_d\alpha} + 1 \tag{3}$$

where [I] is the added indicator concentration, corresponding to the equilibrium, eq 4.

$$I + LM^{2+} \overset{K_e}{\rightleftharpoons} L + IM^{2+} \tag{4}$$

Thus, K_d equals K_I/K_L where K_I and K_L are, respectively, the stability constants for the indicator and the ligand, respectively. The stability constant for the $Mg(ClO_4)_2$ complex of benzo-15-crown-5 ether in acetonitrile was measured by spectrophotometric titration and estimated to be $\gtrsim 10^7$ M^{-1}.

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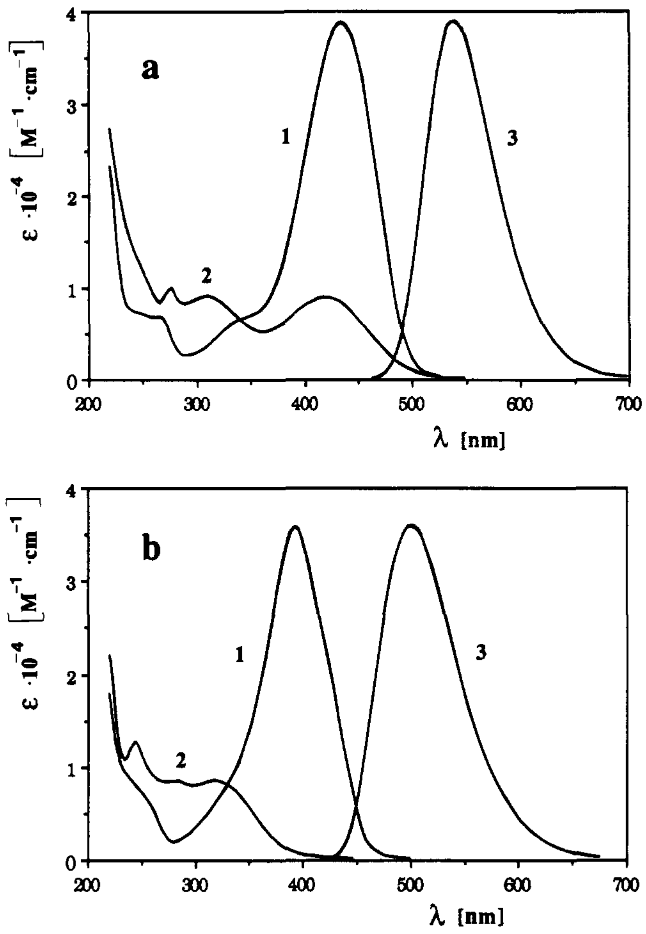

Figure 2. Absorption and fluorescence spectra of *trans*- and *cis*-L as (a) free ligand and (b) as complexes with Mg^{2+}: (1) *trans*-L absorption; (2) *cis*-L absorption; (3) *trans*-L fluorescence (excitation at 400 nm). Cis isomers are nonfluorescent at room temperature. All spectra were recorded in acetonitrile at [L] = 2×10^{-5} M, [Mg^{2+}] = 10^{-4} M.

Time-resolved emission measurements were performed with a single-photon counting apparatus of standard configuration[16] with a mode-locked frequency-doubled Nd:YAG laser (Coherent Antares) synchronously pumping a cavity-dumped dye laser (Spectra Physics 375B; pyridine-1) as excitation source. The dye laser output was frequency doubled to produce 355 nm, ca. 8 ps (fwhm) pulses. The total instrument response time was ca. 70 ps (fwhm). Cut-off filters were used to select the emission wavelength region.

Results and Discussion

In Figure 2 are shown absorption and fluorescence spectra of *trans*-L, *cis*-L, and their complexes with Mg^{2+} in acetonitrile. The absorbance spectrum of *cis*-L was calculated as described above. For the Mg^{2+} complex, the photostationary state with more than 99% *cis*-LMg^{2+} is easily attained by irradiation at 436 nm. Spectra of the Ca^{2+} and Ba^{2+} complexes possess similar structures, differing only in the positions of their absorption maxima. In Table I are reported the positions of the long wavelength absorption maxima and the corresponding molar extinction coefficients for *trans*-L, *cis*-L, and their complexes with Mg^{2+}, Ca^{2+}, and Ba^{2+} in acetonitrile, the positions of the fluorescence maxima, and the fluorescence quantum yields for trans isomers and the quantum yields of trans–cis and cis–trans isomerization. (The cis isomers are nonfluorescent at room temperature.) No excitation wavelength dependence of the fluorescence spectra of the trans isomers could be observed. Both absorption and fluorescence spectra proved to be sensitive to the metal cation, the hypsochromic shift being stronger with the smaller cation.

A very strong hypsochromic shift (about 70 nm) of the long wavelength absorption band of the cis isomer from that of the trans isomer can be attributed to intramolecular coordination between the anionic sulfonate group to the metal cation coordinated within the crown cavity, an association which is permitted spatially only in the cis isomer (Figure 1). Formation of this bond distorts the complex's structure, which in turn perturbs conjugation of the π-system, producing a strong hypsochromic shift.

Table I. Steady-State Absorption and Fluorescence Data[a] and Quantum Yields of Photoisomerization for *trans*-L, *cis*-L,[b] and Their Complexes with Mg^{2+}, Ca^{2+}, and Ba^{2+} in Acetonitrile[c]

	L	LMg^{2+}	LCa^{2+}	LBa^{2+}
λ_{trans}^{abs}, nm	435	393	397	406
$\epsilon_{trans} \times 10^{-4}$, $M^{-1}\cdot cm^{-1}$	3.9	3.6	3.6	3.7
λ_{cis}^{abs}, nm	421	321	325	338
$\epsilon_{cis} \times 10^{3}$, $M^{-1}\cdot cm^{-1}$	8.5	9.0	9.5	8.0
λ_{trans}^{fl}, nm	540	501	516	518
ϕ_{trans}^{fl}	0.06	0.02	0.02	0.03
ϕ_{tc}	0.40	0.46	0.43	0.40
ϕ_{ct}	0.49	0.58	0.60	0.58

[a] All spectra were recorded at [L] = 2×10^{-5} M, [M^{2+}] = 10^{-4} M. Fluorescence measurements were performed at λ_{ex} = 400 nm. [b] Absorption spectrum of *cis*-L was calculated by Fischer's method[15] from the spectrum of *trans*-L and that of the photostationary state obtained upon irradiating the solution with λ_1 = 365 nm and λ_2 = 436 nm light. The cis isomers are nonfluorescent at room temperature. [c] All quantum yield measurements were carried out at [L] = 1.6×10^{-5} M, [M^{2+}] = 1.2×10^{-4} M. Solutions were irradiated with λ = 313 nm light. Absolute error ≈ 20%.

Thermal cis–trans isomerization of the free ligand from the photostationary state obtained upon irradiation at 436 nm was followed by monitoring *trans*-L absorption recovery at 435 nm. Assuming this process to be monomolecular, eq 5 applies at short times

$$\Delta D(t) = \Delta D(\infty) k_{ct}^{T} t \tag{5}$$

where $\Delta D(t)$ is the time-dependent variation of the optical density of the solution with respect to the photostationary state at 435 nm and k_{ct}^{T} is the first order rate constant for the dark cis–trans isomerization.

The observed dependence of $\Delta D(t)$ was linear, with good precision for times shorter than about 10 min. However, the value of k_{ct}^{T} obtained by fitting to eq 5 depended drastically on solvent purity. The lowest value obtained for $k_{ct}^{T} \approx 2 \times 10^{-5}$ s^{-1} corresponds to an activation energy barrier of about 20 kcal. The values of k_{ct}^{T} obtained from eq 5 for the metal complexes were more than two orders of magnitude lower, indicating stabilization of the cis isomer by metal complexation. The quantum yields of trans–cis photoisomerization, ϕ_{tc}, were found to be almost the same for the free ligand and complexes, ca. 0.4. The ϕ_{ct} appear to be higher and are increased considerably upon complexation, Table I.

The equilibrium constants for complexation with *trans*-L were determined from the absorption spectra of solutions at constant ligand concentration and varying metal perchlorate concentrations. For *trans*-LMg^{2+}, a distinct isosbestic point upon titration was observed, indicating only one kind of complex formation, presumably 1:1. (The mathematical analysis of the binding curve indicates an integral relationship between metal and ligand. Although in principle, this would permit a 2:2 complex, it would be highly unusual to encounter exclusively a 2:2 complex at such low concentrations. In any case, there is a clear distinction between the integrally bound complexes and the 2:1 complex.) For Ca^{2+}, an isosbestic point was observed only at low ligand concentrations (below 5×10^{-6} M), while at higher concentrations the spectral changes indicated competing 2L:1M^{2+} complex formation. For Ba^{2+}, the 2:1 complex was formed even at very low concentrations. In Figure 3 are shown plots of $[M]/([L]\cdot\alpha)$ as a function of $1/(1 - \alpha)$ for complex formation with Mg^{2+}, Ca^{2+}, and Ba^{2+}. The results of a nonlinear least squares fit of the data to eq 1 are presented in Table II. For the small Mg^{2+} cation, 1L:1M^{2+} complex formation suffices to describe the data, while for larger cations (Ca^{2+} and, especially, Ba^{2+}) a 2L:1M^{2+} complex must also be included in the complexation scheme, eq 2. The decrease of K_1 in the series (from Mg^{2+} to Ba^{2+}) correlates with a shift in

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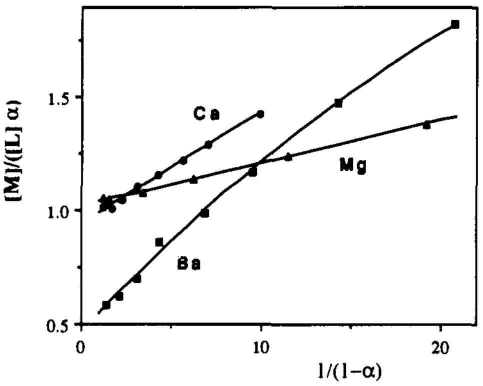

Figure 3. Plot of $[M^{2+}]$\S\dol(/)$([L]\cdot\alpha)$ vs $1/(1-\alpha)$ for the complexes of *trans*-L with Mg^{2+}, Ca^{2+}, and Ba^{2+}, where α is the degree of complex formation, $\alpha = (D_0 - D)/(D_0 - D_c)$, where D_0 is the free ligand absorbance, D_c the complex absorbance, and D the absorbance at a given cation concentration at 460 nm.

Table II. Apparent Equilibrium Constants for Complexation of *trans*-L[a] with Mg^{2+}, Ca^{2+}, and Ba^{2+} and of *cis*-L[b] with Mg^{2+}

M^{2+}	$[L] \times 10^5$, M	K_1,[a,b] M^{-1}	K_2, M^{-1}	K_{cis},[a,c] M^{-1}
Mg	0.424	10^7	0	$\gtrsim 1.4 \times 10^9$
Ca	1.94	10^6	$\lesssim 10^4$	
Ba	1.99	7×10^5	2×10^5	

[a] Determined by spectrophotometric titration via nonlinear least squares fit of the exponential dependences of eq 1. [b] K_1 apparently corresponds to a 1:1 complex (see text), and K_2 to a 2:1 complex (two ligand molecules). [c] K_{cis} was determined at $[Mg^{2+}] = 1.01 \times 10^{-5}$ M by titration with benzo-15-crown-5 ether.

the long wavelength band of the absorption spectra of these complexes. An increase of K_2 correlates with an increase of the cation size, with larger cations favoring formation of the 2L:1M^{2+} and 1L:1M^{2+} complexes.

The stability constant for *cis*-LMg^{2+}, as estimated via displacement by titration with benzo-15-crown-5 ether, is more than two orders of magnitude higher than for *trans*-LMg^{2+}. This enhanced stability of the *cis*-L complex is ascribed to the interaction of the "crowned" cation with the sulfonate group, which also leads to a strong hypsochromic shift of the long wavelength absorption. The stability constants for the Ca^{2+} and Ba^{2+} complexes of *cis*-L could not be easily determined (since another indicator would be required), but we can assume they would be considerably higher than those for *trans*-L complexes. Thus, this crown ether styryl dye presents a dramatic example of a supramolecular system which is highly sensitive to metal cations and capable of drastically changing the complexation stability by absorbing a photon of suitable energy.

Upon increasing the concentrations of $Mg(ClO_4)_2$ (above 10^{-2} M) at a fixed ligand concentration (below 10^{-4} M in all experiments), the absorption spectrum of *cis*-LMg^{2+} shifts progressively to the red, so that at $[M^{2+}] > 0.1$ M the long wavelength absorption maximum is observed at ca. 380 nm, showing almost the same hypsochromic shift from the trans isomer as the free ligand. This effect can be attributed to perturbation of the level of intramolecular coordinative association of the sulfonate group with an additional metal cation.

The anion-capped *cis*-L complex was transformed into the "uncapped" form at a complex concentration of ca. 10^{-2} M, presumably by aggregation caused by the interaction between the sulfonate group of one molecule with the crowned cation of another. The aggregation is signaled by almost the same red shift as is observed upon addition of metal perchlorate at high concentrations.

When this aggregated *cis*-L complex is diluted, relaxation to the monomeric anion-capped form takes place within several minutes, Figure 4. This relaxation time is clearly the cis aggregate lifetime. Irradiation of the trans complex does not lead instantaneously to an anion-capped cis form. First, the uncapped cis isomer is formed, which slowly relaxes to the capped form within several minutes. Since the absorption spectrum of the uncapped form overlaps considerably with that of *trans*-L complex, the pure capped *cis*-L complex was obtained by a stepwise procedure: irradiation until a photostationary state is achieved, followed by dark relaxation, a second irradiation sequence, etc.

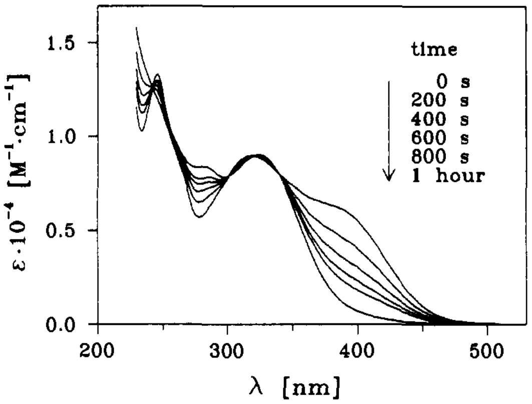

Figure 4. Temporal dependence of the absorption spectrum of *cis*-LMg^{2+} after dilution from $[L] = 2.2 \times 10^{-2}$ M to $[L] = 5.9 \times 10^{-5}$ M at excess $[Mg^{2+}] = 10^{-4}$ M.

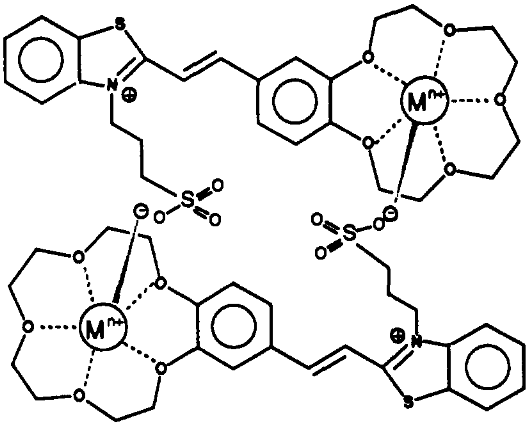

Figure 5. Proposed aggregation of *trans*-LM^{2+} complexes.

Table III. Time-Resolved Fluorescence Data for *trans*-L and Its Complexes with Mg^{2+}, Ca^{2+}, and Ba^{2+}[a]

M^{2+}	$[L] \times 10^5$, M	$[M^{2+}] \times 10^4$, M	τ_1, ps	A_1, %	τ_2, ps	A_2, %
	1.75		137	100		
Mg	1.75	1.0	24	94	380	6
Ca	2.37	0.65	20	98	490	2
Ba	1.96	0.82	35	99	550	1

[a] Excitation at 355 nm by a 8-ps laser pulse. Instrument response function is ca. 70 ps.

Thus, the *trans*-L complex aggregates even at low concentrations (ca. 10^{-6} M), with photoisomerization proceeding without aggregate decomposition, Figure 5. Then, the observed relaxation time is the mean lifetime of the cis–cis and cis–trans aggregates. When metal perchlorate was added to a free ligand cis isomer solution, anion-capped cis complex was formed instantaneously without relaxation, as the free ligand is not aggregated. Thus, we have a system in which a dye has changed its state from aggregated to monomeric upon photoisomerization, a phenomenon similar to that occurring in several previously reported photochromic molecules.[17,18]

The stability constants for this zwitterionic dye (*trans*-L) are appreciably higher than those obtained for the analogous cationic dye lacking the appended sulfonate group.[19] One reason for this

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Table IV. Concentration Dependence of the Fluorescence Decay Parameters for the Complex of *trans*-L with Mg^{2+}

[L] × 10^5, M	$[Mg^{2+}]$ × 10^3, M	τ_1, ps ±10%	A_1, %	τ_2, ps ±10%	A_2, %
4.2		138	100		
0.05	0.6	34	97	410	3
0.22	0.6	36	93	375	7
0.55	0.6	38	91	354	9
1.0	0.6	35	90	365	10
2.2	0.6	34	89	360	11
3.2	0.6	38	88	360	12
4.2	0.6	49	85	365	15
1.6	3.8	45	93	460	7
1.6	38	25	100		
1.6	270	21	100		

effect could be that trans complex aggregation occurs only for the zwitterionic dye. Thus, the reported stability constants are apparent constants.

The hypothesis of trans complex aggregation finds additional support in the time-resolved fluorescence experiments. In Table III are presented fluorescence decay parameters for *trans*-L and its complexes with Mg^{2+}, Ca^{2+}, and Ba^{2+}. Upon excitation at 355 nm by a 8-ps laser pulse, emission was detected at wavelengths above 480 nm. The decay of the free ligand is purely monoexponential with a lifetime of 137 ps, in good agreement with the value of 150 ps calculated from the fluorescence quantum yield and the radiative lifetime estimated from the absorption spectrum. The fluorescence decays of the trans complexes, however, are biexponential with a fast component lifetime τ_1 of about 25 ps and the slower component lifetime τ_2 in the subnanosecond region. The variation of τ_1 upon changing the complexed metal from Mg^{2+} through Ba^{2+} is within experimental error. (Note that the total instrument response function is ca. 70 ps fwhm). However, τ_1 for the Ba^{2+} complex was reproducibly larger than that for Mg^{2+} complex, in agreement with the relationship between the corresponding fluorescence quantum yields. The contribution of the slower component is decreased, and τ_2 increased in the series from Mg^{2+} to Ba^{2+}, correlating again with increased cation size. The faster component can thus be attributed to monomer ligand complex fluorescence, and the slower component to aggregate fluorescence.

At high metal cation concentrations (above 10^{-2} M), only the faster component is observed (Table IV). This is readily ascribed to aggregate decomposition deriving from association of the sulfonate group with an additional metal cation. With increasing ligand concentration at a fixed cation concentration (an intermediate value of 6 × 10^{-4} M was taken in order to provide complete ligand complexation, but not to cause aggregate decomposition), the contribution of the slower component is also increased, Table IV. The lifetimes of both components remain unchanged upon varying the complex concentration, within experimental error. An attempt to fit these data to a simple scheme including only the equilibrium between the monomers and dimers depicted in Figure 5 failed, thus indicating that more complex equilibria are involved. Nonetheless, aggregation influences the π-system only weakly. In fact, the observed absorption spectra of the free trans complexes were almost independent of concentration.

Summary

The complexation of a zwitterionic crown ether styryl dye with divalent alkaline-earth cations is dramatically shifted by geometric photoisomerization. The enhanced stability of the cis ligand complex is attributed to the interaction of the crowned cation with an anionic sulfonate group. Aggregation in dilute solutions of the trans complex derives from a strong interaction between the sulfonate group in one complex and the crowned cation in another.

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C-H Activation in Aqueous Medium. The Diverse Roles of Platinum(II) and Metallic Platinum in the Catalytic and Stoichiometric Oxidative Functionalization of Organic Substrates Including Alkanes

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Abstract: The oxidation of ethers, alcohols, esters, and light alkanes (ethane, propane) by K_2PtCl_4 and Pt/O_2 in aqueous medium has been studied. Results appear to indicate that unactivated C-H bonds were attacked and oxidized by Pt(II) whereas C-H bonds α to an oxygen were activated and catalytically oxidized by metallic Pt in the presence of O_2. For example, Pt(II) was found to oxidize ethane selectively to the alcohols, ethanol, and ethylene glycol. In the presence of metallic Pt and O_2, further oxidation of the alcohol functionality occurred to generate the corresponding carboxylic acids. Thus, with proper choice of the C-H activating system, it was possible to oxidize substrates with a fairly high degree of selectivity with respect to the oxidation level, as well as the particular C-H bond that was functionalized. With respect to the latter, because of the "chelate effect", the selective activation and oxidation by Pt(II) of C-H bonds suitably distant from a coordinating oxygen was achieved. For ethers, the order of reactivity was α-C-H < β-C-H < γ-C-H.

The selective, oxidative functionalization (preferably catalytic) of hydrocarbons, especially alkanes, through a C-H activation step is one of the most challenging chemical problems, in addition to being of great practical importance. There are *three* critical issues that need to be addressed in the design of a successful procedure. The first, of course, is the requirement of a facile C-H cleavage step. The other two equally important factors that need to be considered involve selectivity: selectivity with respect to the