

Spectrophotometric Investigation of the Complex Formation of Aza-15-Crown-5 Containing Styryl Dyes with Ba^{2+} and Ca^{2+} Cations*

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ABSTRACT

The complex formation of two styryl dyes, viz. 1-ethyl-2-[4-(1,4,7,10-tetraoxa-13-aza-cyclopentadecyl)styryl]-benz[cd]indolium perchlorate 1 and 1,3,3-trimethyl-2-[4-(1,4,7,10-tetraoxa-13-aza-cyclopentadecyl)styryl] indolium perchlorate 2 with $\text{Ca}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$ was investigated spectrophotometrically in acetonitrile. The estimated $\log K_{st}$ values were found to be: $1 + \text{Ca}(\text{ClO}_4)_2$, $1.78 + 0.05$; $1 + \text{Ba}(\text{ClO}_4)_2$, $1.25 + 0.02$; $2 + \text{Ca}(\text{ClO}_4)_2$, $1.72 + 0.02$; $2 + \text{Ba}(\text{ClO}_4)_2$, $1.25 + 0.03$; pK_a values for 1 and 2 were also determined.

INTRODUCTION

During recent years the synthesis of a large number of chromogenic crown ethers has been reported. For example, the synthesis of several neutral uncharged crown ether dyes has been described,¹⁻⁴ the design principle of which incorporated crown ethers with different selectivity into the conjugated system of a chromophore, so that the photophysical properties of the reagent would be directly affected by complex formation.

The chromogenic reagents described by¹⁻⁴ consist of a donor and acceptor part, which results in the presence of a long wavelength charge transfer (CT) band in the absorption spectra. The interaction with the metal ion could either destabilize the donor part or stabilize the acceptor part of the molecule, leading to a hypsochromic or bathochromic shift of

* Dedicated to Professor Dr Karl-Heinz Drexhage on the occasion of his 60th birthday.

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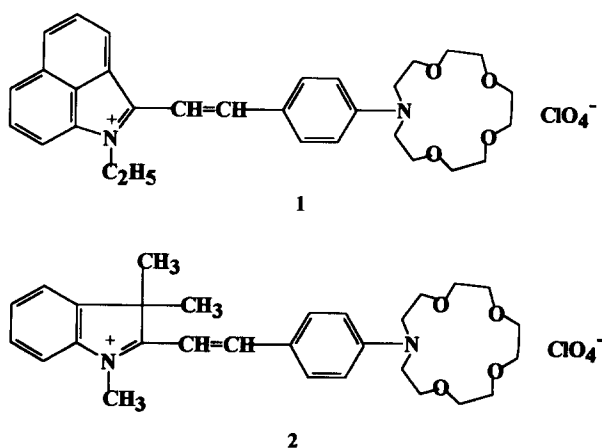


Fig. 1. Structural formulae of the ligands used.

the CT band, respectively. The degree of influence depends on the structure of the reagent, the fit between the cation diameter and the cavity dimension, the charge density of the ion, and on the reaction medium.

Recently, several interesting styryl dyes containing an aza-15-crown-5 moiety and different heterocycles have been synthesized, and their complexation ability and photophysical properties investigated.⁵⁻¹⁰

In previous work, we described the synthesis of seven styryl dyes containing an aza-15-crown-5 moiety, as well as of a new chromofluoro-ionophore with the same macrocycle.¹¹⁻¹³ We have shown that the absorption spectra of these compounds undergo a hypsochromic shift in acetonitrile solution in the presence of alkali and alkaline earth metal ions. This was not unexpected, because it is known that the aza-15-crown-5 cavity dimension is appropriate for complexing ions with diameters 1.7–2.2 Å.^{14,15} The divalent alkali earth ions cause a more significant λ_{\max} shift, because of the electrostatic nature of the interaction; Ba^{2+} and Ca^{2+} cations show the most interesting behavior.

The present paper deals with the spectrophotometric investigation of the complex formation between the ligands 1 and 2 (Fig. 1) with Ba^{2+} and Ca^{2+} cations in dry acetonitrile. The protonation of the compounds was also studied and pK_a values were determined.

RESULTS AND DISCUSSION

The presence of donor (macrocyclic nitrogen atom) and acceptor (the quaternized nitrogen atoms in the heterocyclic part) moieties in the molecules of the compounds investigated leads to a structureless long

TABLE 1
Absorption Maxima of Compounds **1** and **2** in Solvents of Different Polarity

Solvent (ϵ_d)	λ_{max} (nm)	
	1	2
C_2H_5OH (24.3)	662	547
CH_3CN (36.2)	652	540
H_2O (78.5)	603	523

wavelength absorption band ascribed to the delocalized CT transition. It appears at 652 nm and 540 nm (in acetonitrile) for **1** and **2** respectively. Hypsochromic shift of the CT absorption band was observed with increasing solvent polarity (Table 1). The interaction with cations affects the free electron pair of the macrocyclic nitrogen atom, thus inhibiting its donor ability. As a result, a hypsochromic shift of λ_{max} was observed, combined with a hypochromic effect.

By spectrophotometric titration of both ligands with solutions of Ca^{2+} and Ba^{2+} ions, a well-defined isobestic point was observed in all cases (Fig. 2). In order to obtain the spectra of the complexes, we had to use high

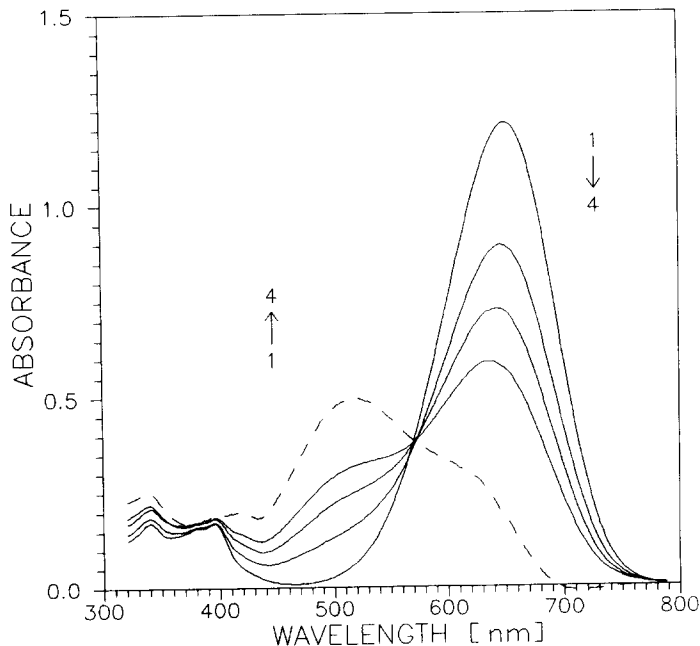


Fig. 2. Absorption spectra of ligand **1** in acetonitrile (1.4×10^{-5} M, solid line) in the presence of different amounts of $Ca(ClO_4)_2$ (10^{-4} – 10^{-2} M) and the calculated spectrum of the complex (dashed line).

salt concentrations, which cause unusual side effects. The composition of the mixture was calculated using the standard procedure for two-component system analysis.^{14,15} The calculations were made in the free absorption area of the ligand. The data were treated with the MATHCAD 3.0 program product (WINDOWS version) and the following relationships were used:



$$K_{ST} = \frac{c_K}{c_L c_M} \quad (2)$$

$$c_K + c_L = c_L^0 \quad (3)$$

$$x_L + x_K = 1 \quad (4)$$

$$K_{ST} = \frac{1 - x_L^i}{x_L^i} \frac{1}{c_M} \quad (5)$$

$$A^i = x_L^i A_L \quad (6)$$

$$x_L^i = \frac{A^i}{A_L} \quad (7)$$

where c_K and c_L are the molar concentrations of the complex and the ligand, x_L and x_K are their molar parts and A^i is the absorption at a given wavelength.

The spectrum of the complex was calculated according to the equations:

$$A = x_L A_L + x_K A_K \quad (8)$$

$$A^i = x_L^i (A_L - A_K) + A_K \quad (9)$$

As a rule, there is no direct correlation between the shift of the absorption band and the stability of the complexes. Both ligands studied form more stable complexes with Ca^{2+} cations, which also causes a larger λ_{max} shift (Table 2); this could be expected, because Ca^{2+} cations have ionic diameters closer to the crown ether cavity and a higher charge density. This observation is in agreement with the investigations on the complex stability of related compounds reported previously.^{5-8,12,13} The stabilities of the complexes are of the same order for both ligands, despite the differences in the heterocyclic moieties.

In acid solutions, both ligands undergo color changes from blue, respectively, red to yellow (Figs 3 and 4). Protonation of the macrocyclic nitrogen atom inhibits its donor ability, so that the CT band disappears and a new band is observed, which could be ascribed to localized $\pi-\pi^*$ transition. $\text{p}K_a$ values were obtained according to the relationship:

$$\text{pH} = \text{p}K_a + \lg \left(\frac{x_L}{1 - x_L} \right) \quad (10)$$

Neither ligands **1** and **2** nor their protonated forms are fluorescent.

TABLE 2
Absorption Maxima and Molar Absorptions of Compounds **1** and **2** and their Complexes, Stability Constants of the Complexes and pK_a Values

Compound	λ_{max} (nm) (ϵ)	$\log K_{st}$	pK_a
1 ^a	652 (86 640)		
1 + Ca^{2+}	522 (42 640)	1.78 ± 0.05	
1 + Ba^{2+}	548 (35 500)	1.25 ± 0.02	
1 + HCl ^b	414		0.99
2 ^a	540 (79 000)		
2 + Ca^{2+}	434 (28 630)	1.72 ± 0.02	
2 + Ba^{2+}	457 (40 420)	1.25 ± 0.03	
2 + HCl ^b	371		0.89

^a In acetonitrile.

^b In water.

Comparing the results with data reported for related compounds we can conclude that the structure of the chromophore part is very important with respect to the complex stability. More stable complexes are formed if the chromophore bears additional ligating groups able to participate in the complexation. In some cases it leads to lower selectivity, so that all these factors need to be considered when designing a new reagent.

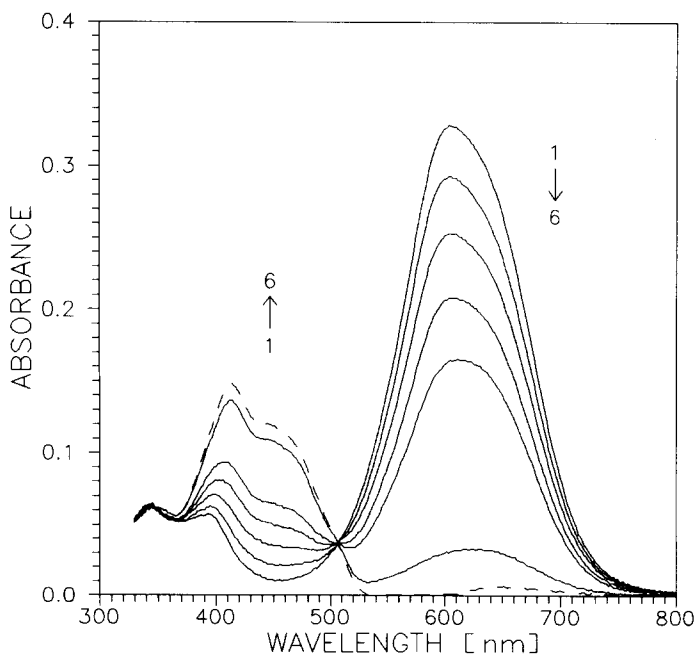


Fig. 3. Absorption spectra of ligand **1** in water at different pH values (pH 4–1, solid line) and the spectrum of the protonated form (dashed line).

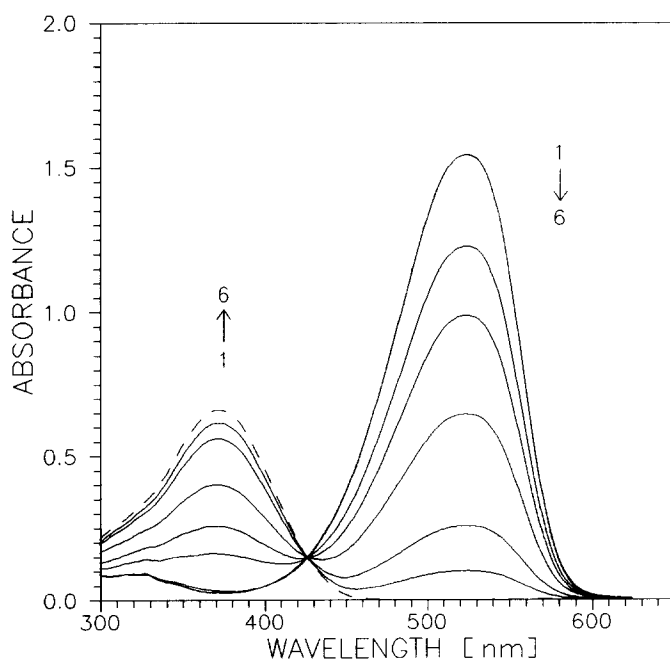


Fig. 4. Absorption spectra of ligand **2** in water at different pH values (pH 4–1, solid line) and the spectrum of the protonated form (dashed line).

EXPERIMENTAL

The absorption spectra were recorded on a Perkin–Elmer Lambda 17 spectrophotometer. pH was measured on a Radelkis OP-208 pH-meter.

The styryl dyes **1** and **2** were synthesized as previously described.¹¹

Acetonitrile (Uvasol) was dried by boiling with CaH_2 and distilled before use. $\text{Ca}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$ were synthesized from CaO and BaO , respectively, and HClO_4 , all purchased from Merck. The purity of the salts was confirmed by gravimetric determination of Ba^{2+} and Ca^{2+} (>99%). The salts were dried overnight in a vacuum drier at 200°C . For the $\text{p}K_a$ determination, HCl (Merck) was used.

The absorption spectra were recorded immediately after preparation of the solutions. The absorption measurements were from a series of acetonitrile solutions isomolar with respect to the ligand. The ligand concentration was 1.4×10^{-5} M for **1** and 1.9×10^{-5} M for **2**. To the ligand solutions were added different amounts of 0.08 M stock solutions of the salts. In order to avoid salt side effects, the same amount of salt solution was added to the reference cell. No changes were observed after exposure of the solutions to daylight at room temperature.

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