

Complexation Properties of Schiff Bases Containing the *N*-Phenylaza-15-crown-5 Moiety

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Abstract

The complexation of a series of new Schiff bases containing the *N*-phenylaza-15-crown-5 (Ph-A15C5) moiety with alkali and alkaline-earth metal ions (incl. Be²⁺ and Mg²⁺), is studied by means of UV-Vis spectroscopy. The corresponding stability constant values are determined and discussed from two aspects: the position of the Ph-A15C5 moiety in the ligand molecule and the nature of the metal ion.

Introduction

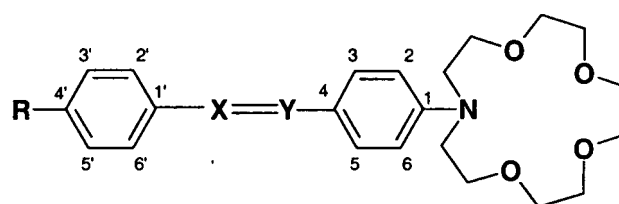
Chromo- and fluoroionophores incorporating both chromophoric and macrocyclic moieties are currently of great interest due to changes of absorption and emission properties of the ligand upon complexation [1–3]. During the last decade a series of new styryl dyes containing the Ph-A15C5 moiety were synthesized and their spectral and complexation properties studied in detail [4–9]. Complexation and photochemical properties of similar dyes containing the same moiety have also been reported [10–17] and a possible mechanism of the complexation process suggested [18, 19].

Continuing our previous investigations on the “structure – spectral and analytical properties” relation of dye systems containing Ph-A15C5, in the present paper we report some initial results concerning the spectral and complexation properties of a series of chromophores containing Schiff bases with alkali and alkaline-earth metal ions in dry acetonitrile (An) (Scheme 1).

Experimental

Materials

AR grade LiClO₄·3H₂O, NaClO₄, KClO₄, Mg(ClO₄)₂ and BeSO₄·2H₂O (Merck) were dried in a vacuum evaporator up to constant weight for ca. 72 h. Sr(ClO₄)₂, Ba(ClO₄)₂ and Ca(ClO₄)₂ were obtained from SrO, BaO and CaO (Merck)



- | | | | | | |
|----|--------|---|--------|---|--------------------------------------|
| 1 | X = N | ; | Y = CH | ; | R = H |
| 2 | X = N | ; | Y = CH | ; | R = N(CH ₃) ₂ |
| 1' | X = CH | ; | Y = N | ; | R = H |
| 2' | X = CH | ; | Y = N | ; | R = N(CH ₃) ₂ |
| 3' | X = CH | ; | Y = N | ; | R = NO ₂ |

Scheme 1.

by treating with 70% HClO₄ (Merck, p.a.) and then dried in vacuum for 20 h. Later all metal salts were vacuum dried at 150 °C for 5 days. Acetonitrile (Merck, Uvasol) was dried with CaH₂ (4 h reflux at 79 °C) and distilled over CaH₂ prior to use.

Synthesis

The synthesis of the Schiff bases and *N*-phenylaza-15-crown-5 and their characterization by elemental analysis, m.p., IR and ¹H-NMR spectral data are described elsewhere [20].

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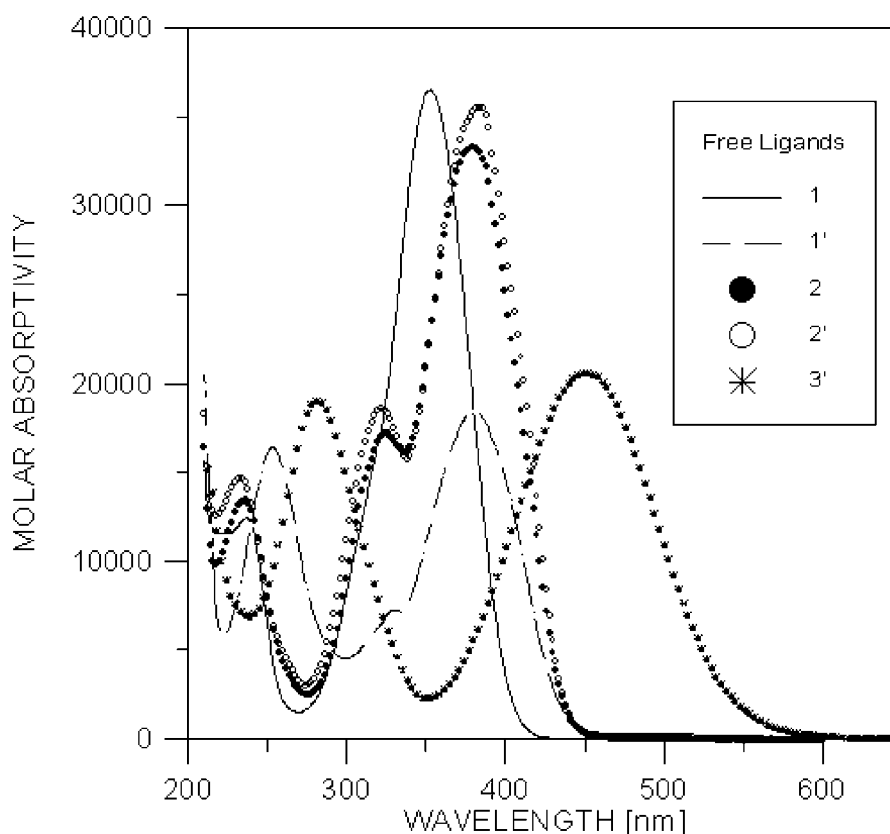
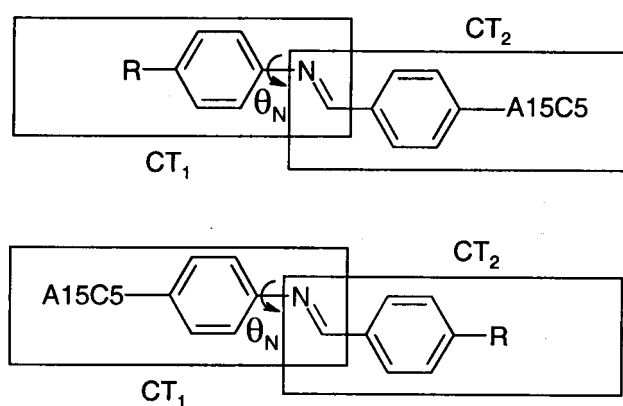


Figure 1. Absorption spectra of the studied compounds in dry An.



Scheme 2.

Spectrophotometric measurements and calculations

The spectrophotometric titrations were performed in dry An keeping the concentration of the ligand constant and step-wise addition of the metal ion salt. In order to minimize the errors possibly caused by additional interactions at relative high salt concentrations and to obtain sharp isosbestic points the titration procedure was stopped before full ligand complexation. The series of resulting spectral curves were recorded on a Perkin-Elmer Lambda 5 UV-Vis spectrophotometer immediately after preparation of the solutions. The spectral curves were then processed by a first derivative spectroscopy approach, where the rise of the baseline as a result of high salt concentration at low stability constant

ligands were avoided [21, 22], and the individual spectral curves of the corresponding complexes were estimated. Where possible (in the cases of high stability constants, for example with Ca^{2+}) the calculated spectra were confirmed experimentally with excess of the metal ion salt.

The resolution of overlapping bands was performed for individual bands over the whole interval of measurements, taking into account the requirements stated in [22, 23].

The torsion angles θ_N ($\angle(\text{C}'_2-\text{C}'_1-\text{X}-\text{Y})$ for **1** and **2**, $\angle(\text{C}_3-\text{C}_4-\text{Y}-\text{X})$ for **1'**-**3'**; see Scheme 1 for atom numbering) were estimated using the oscillator strength approach as described in [24].

In addition quantum chemical calculations were performed. All *ab initio* (HF/6-31G*) calculations were done by the Gaussian 98 program suite [25]. All stationary points were characterized as minima by frequency calculations. Zero point energies are unscaled. For the semiempirical calculations the AMPAC program package [26] with the AM1 [27] and PM3 [28] Hamiltonians was used.

Results and discussion

The absorption spectra of the free ligands are shown in Figure 1. Since it is already proven that Ca^{2+} fits best the A15C5 cavity [9] the complexation of the ligands was studied with this metal ion in order to determine the best complexation agent in the series. The spectra of the complexes obtained are collected in Figure 2 and compared with those of the free ligands in Table 1. Band shape analysis has

Table 1. Spectral and complexation properties of compounds **1–2** and **1'–3'** towards Ca²⁺.

Comp.	Ligand			Complex			
	λ_{\max} (nm)	ϵ_{\max} (1 mol ⁻¹ cm ⁻¹)	θ_N^{***} (degrees)	λ_{\max} (nm)	ϵ_{\max} (1 mol ⁻¹ cm ⁻¹)	θ_N^{***} (degrees)	log β
1	352	36480	44	337 sh	14730	59	3.90 ± 0.02
	316 sh	15170		294	17470		
	305 sh	10530					
2	380*	33280	36			****	400 ± 0.19
	325	17240		380	20020		
	310 sh	13890					
1'	381	18430	58			58	4.71 ± 0.07
	330	7220		322	10090		
	315 sh	5820					
2'	385**	35500	36	359	37750	44	4.69 ± 0.21
	323	18550		305 sh	9800		
	307 sh	14800					
3'	450	20570	–	359	12700	–	4.49 ± 0.18

* Vibrational structure: sub-bands at 370, 386 and 413 nm determined by derivative spectroscopy [23].

** Vibrational structure: sub-bands at 369, 387 and 414 nm determined by derivative spectroscopy [23].

*** Calculated using the oscillator strengths for the band at ~320 nm collected in Table 2.

**** Impossible to be determined due to strong overlapping.

been performed in order to facilitate the spectral interpretation and the results for the individual bands are given in Table 2.

The spectral data can be interpreted taking into account the following assumptions:

1. It is well known that the parent compound of the ligands studied, namely *N*-benzylidene aniline is a non-planar compound, the *N*-phenyl ring being twisted about 40–60° around the Ph—N= bond [24]. Such a geometry might also be expected for the ligands studied. The presence of a low intensity band in the interval 320–330 nm (Table 2) can be taken to support this expectation. However, irrespective of the non-planarity, the N atom contained in the macrocyclic ring is always included in the expanded conjugated system as proven by NMR investigation on the structure of the compounds [29].
2. The studied Schiff bases are donor-acceptor (D-A) systems, where the main acceptor is the central —N=CH— group and a donor group exists as the N atom of the macrocycle. A charge transfer (CT) in the frame of the ligand molecule is realized resulting in the appearance of intense CT bands in their absorption spectra (Table 1). However the studied dyes are not simple A-D systems, due to the substituent R, which could substantially affect the CT.

Taking into account these above mentioned assumptions a scheme containing two linked A-D systems with a common acceptor can be suggested (Scheme 2).

In the light of this scheme compounds **1** and **1'** exhibit simple, but different D-A features. In compound **1** the planar system is limited to the N atom from the N=CH group resulting in an efficient and therefore high intensity CT₂ band at 357 nm partially overlapped with a band at 323 nm ori-

ginating from *N*-benzylidene aniline (Table 2). This latter is used for estimation of twisting around the N—Ph bond. In these cases the N atom of the macrocycle is engaged in the CT with concomitant lower complexation abilities (lower stability constant in comparison with *N*-phenylaza-15-crown-5, see Table 3). In the case of **1'**, although θ_N is the same as in *N*-benzylidene aniline, only a slight D-A interaction occurs involving the whole molecule and a bathochromically shifted, but comparatively low intensity CT₁ band with complicated structure appears. Here the N atom of the macrocycle is slightly engaged in CT and the stability constant is near to that of *N*-phenylaza-15-crown-5. It is evident that the complexation through the macrocycle in both molecules leads to a significant decrease of the electron density of its N atom and, thus, a “switching off” of the CT. Thus, spectral properties similar to *N*-benzylidene aniline (Figure 2), where the torsion angle is estimated to be 59° [24] are found.

Evidently, therefore, compounds **1** and **1'** clearly show spectral characteristics being typical for the CT₁ and CT₂ transitions, respectively.

Compounds **2** and **2'** are particularly interesting since they contain both fragments (planar and non-planar) and should exhibit both CT₁ and CT₂. Moreover after complexation of compound **2**, CT₂ is “switched off” and the spectral behavior of the complex obtained is very similar to that of **1'**. The same is true for **2'**-Ca and **1** (see Figures 1 and 2 and Table 2). The overlapping band analysis confirms the hypothesis for two fragmental systems and two CT transitions, of course being mutually influenced (Table 2). As evident from Tables 1 and 2 the spectral curves of **2** and **2'** are practically the same and their long wavelength band consists of four sub-bands. As discussed above, the band at 323 nm can be assigned to structures describing the molecule non-planarity.

Table 2. Individual spectral characteristics of compounds **1–2** and **1'–2'** after band shape analysis.

Comp.	Ligand			Complex		
	λ_{\max} (nm)	ϵ_{\max} ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	f^*	λ_{\max} (nm)	ϵ_{\max} ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	f^*
1	<u>357</u>	<u>30611</u>	<u>0.50</u>	334	9716	0.18
	323	13870	0.35	289	17370	
2	<u>412</u>	<u>10540</u>	<u>0.08</u>	<u>407</u>	<u>6870</u>	<u>0.07</u>
	<u>391</u>	<u>16960</u>	<u>0.15</u>	<u>377</u>	<u>16780</u>	<u>0.24</u>
	<u>368</u>	<u>24660</u>	<u>0.31</u>			
	323	16700	0.44	334	**	~0.1**
1'	<u>406</u>	<u>4990</u>	<u>0.08</u>			
	<u>379</u>	<u>15180</u>	<u>0.22</u>			
	333	6750	0.19	329	8500	0.19
2'				265	14960	
	<u>412</u>	<u>13880</u>	<u>0.11</u>			
	<u>391</u>	<u>21490</u>	<u>0.19</u>			
	<u>368</u>	<u>25370</u>	<u>0.30</u>	<u>362</u>	<u>33020</u>	<u>0.55</u>
	321	18160	0.44	323	12790	0.35

* Oscillator strength.

** Estimated with substantial error.

Table 3. Stability constants and spectral characteristics of metal complexes of **1'** and *N*-phenylaza-15-crown-5 (**4**).

M^{n+}	Ion radius (\AA) [31]	Ligand 1'				Ligand 4 log β
		log β	λ_{\max} (nm)	ϵ_{\max} ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	$\Delta\nu^*$ (cm^{-1})	
Be ²⁺	0.27	2.70 ± 0.11	336	13500	3.5	2.70 ± 0.08
Li ⁺	0.59	2.77 ± 0.07	350	12040	2.3	–
Mg ²⁺	0.59	2.64 ± 0.30	319	11310	5.1	2.51 ± 0.34
Na ⁺	0.99	2.60 ± 0.01	344	11540	2.8	–
Ca ²⁺	0.99	4.71 ± 0.07	322	10090	4.8	4.84 ± 0.03
Sr ²⁺	1.13	3.64 ± 0.02	327	12580	4.3	3.89 ± 0.05
Ba ²⁺	1.34	3.86 ± 0.01	332	14010	3.9	3.70 ± 0.05
K ⁺	1.33	2.40 ± 0.04	366	17470	1.1	–

* $\Delta\lambda_{\max}$ is the cation-induced shift ($\times 10^{-3}$).

Table 4. Basic results* from the quantum chemical calculations of the dimethylamino models of the studied compounds.

comp.	AM1					HF/6-31G* (+ZPE)				
	ΔH_f (kcal/mol)	Q_{DMA} $\times 10^4$	Q_{N}	$Q_{\text{DMA}} - Q_{\text{N}}$	θ_{N} (degrees)	E (au)	Q_{DMA}	Q_{N}	$Q_{\text{DMA}} - Q_{\text{N}}$	θ_{N} (degrees)
1	81.9	–2.18	–0.362	0.362	35.4	–685.921	–0.215	–0.682	0.467	44.9
2	90.8	–38.8	–0.360	0.356	30.0	–818.919	–0.218	–0.679	0.461	39.7
1'	82.4	–51.8	–0.352	0.347	28.6	–685.918	–0.230	–0.667	0.437	38.0
2'	90.8	–91.0	–0.350	0.341	30.0	–818.919	–0.234	–0.664	0.430	39.7
3'	86.0	–64.8	–0.361	0.368	22.7	–889.386	–0.221	–0.673	0.452	33.5

* Heats of formation (AM1), total energies (HF/6-31G*), Mulliken charges of the total dimethylamino group (Q_{DMA}) and its nitrogen atom (Q_{N}) and torsional angle θ_{N} ($\angle(\text{C}2'-\text{C}1'-\text{X}-\text{Y})$ for **1** and **2**, $\angle(\text{C}3-\text{C}4-\text{Y}-\text{X})$ for **1'–3'**; see Scheme 1 for atom numbering).

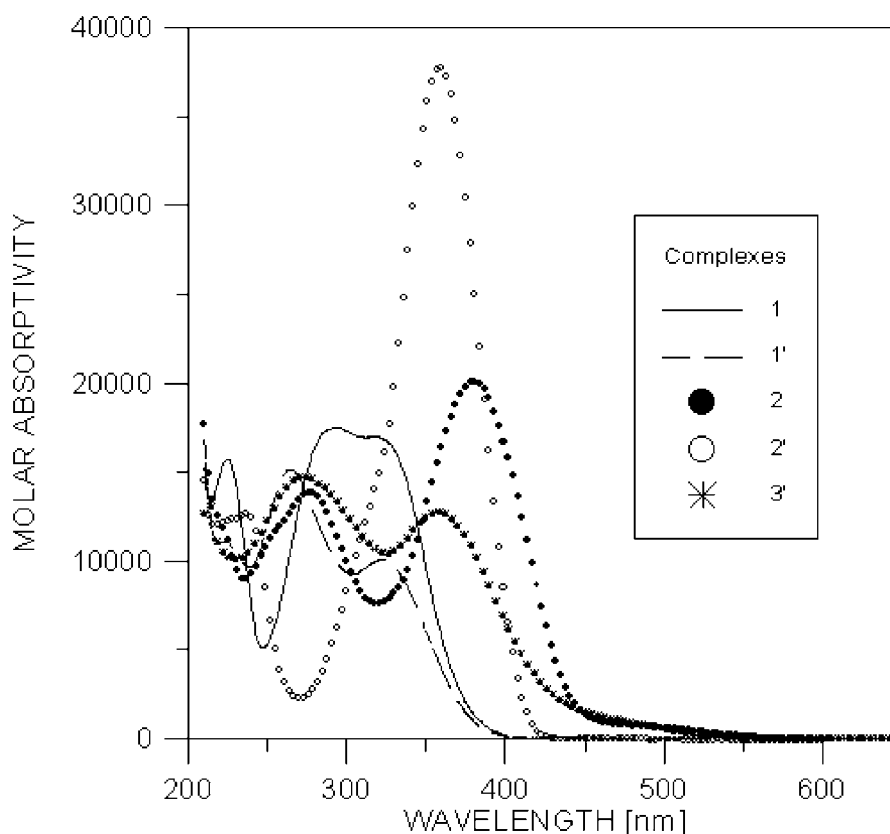


Figure 2. Absorption spectra of the corresponding complexes with Ca^{2+} in dry An.

However, the sub-band at 368 nm is very similar to CT_2 in **1**, at the same time the sub-bands at 391 and 412 nm can be assigned to the complicated band of **1'** and CT_1 . Consequently in **2'**-Ca the CT_1 is “switched off”, the corresponding sub-bands at 391 and 413 nm disappear and the spectrum of the complex is similar in shape and intensity to that of **1**, where only CT_2 exists. Analogous interpretations can be made for **2** and **2**-Ca, where CT_2 is switched off.

It is interesting in the light of this hypothesis to evaluate the spectral characteristics for various substituents in **1** given in [20]. In the case of OMe, OEt, F, Cl and Br the torsion angle is estimated to be 41, 40, 51, 45 and 42° respectively, while the CT band position is in the limits 360–363 nm with oscillator strengths lower in the case of the donor and higher in the case of acceptor substituents in comparison with **1**. These data show that due to non-planarity the substituents in the N—Ph ring cannot substantially affect the complexation abilities of **1**.

Compound **3'** is however unlikely to be described by the suggested scheme due to the strong acceptor, namely the NO_2 group. Here the system $A_{\text{strong}}(A_{\text{N}=\text{CH}} + A_{\text{NO}_2}) - D$ leads to greater extent of planarity of the whole molecule, as proved by X-ray diffraction [30], and to a strong bathochromic shift in comparison with **1'**. This increased A-D interaction leads to decreased electron density at the N of the macrocycle and a lower stability constant.

A relation between the electronic density at the N of the macrocycle and the stability constant is expected and can be confirmed by the quantum chemical results shown

in Table 4. Since the quantum chemical calculation of the A15C5 moiety is a difficult task it was replaced by the *N,N*-dimethylamino (DMA) group as a simplified model [15]. In general there is no relation between the results from the AM1 method and the experimental findings, but it can be seen that there is a reasonable relation between the calculated stability constants and the electronic density of the dimethylamino group (Q_{DMA}) predicted by the *ab initio* calculations. However the data set is too small to find a reliable correlation as in [15, 17]. At the same time there is an acceptable agreement between the θ_{N} values estimated by spectral analysis and *ab initio* calculations.

In the light of the facts discussed above the complexation properties of **1'** with different metal ions were studied and compared with these of the *N*-phenylaza-15-crown-5 estimated by the same method. The stability constants together with the corresponding spectroscopic data are presented in Table 3. As seen the stability constant with Ca^{2+} is the largest, due to the best fit of the crown cavity (1.7–1.8 Å in diameter). However, the data set is small, the discussion about relationships between complex stability, cation induced shift and the properties of the metal ions has to be careful about any overinterpretation since the correlation could not be straightforward. It could be noted that the size of the complexation induced shift decreases in the order $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} > \text{Be}^{2+} > \text{Li}^+ \approx \text{Na}^+ > \text{K}^+$ whereas for the stability constants the order is $\text{Ca}^{2+} \gg \text{Sr}^{2+} \approx \text{Ba}^{2+} \gg \text{Be}^{2+}, \text{Li}^+, \text{Mg}^{2+}, \text{Na}^+ > \text{K}^+$. A trend between both parameters and the so-called ionic index (ratio

of charge and ion radius as measure for the electrostatic attraction) is observed confirming the general conclusions of Rurack et al. [16], but with the exception of both Mg^{2+} and Be^{2+} .

Conclusions

A series of Schiff bases containing the A15C5 receptor has been studied by means of UV-Vis spectroscopy and quantum chemistry and their complexation towards alkali and alkaline-earth metal ions has been investigated in dry acetonitrile. Although their applicational aspects are limited a systematic study of different substitutional patterns within this series has been performed.

The newly synthesized ligands form complexes with relatively high stability constants with the alkali and alkaline-earth metal ions. For Be^{2+} the stability constant is equal to and for Ba^{2+} and for Mg^{2+} are even higher than the corresponding constants with the parent compound *N*-phenylaza-15-crown-5. Recently Boila-Göckel and Junek [13] also reported the synthesis of new “spacer – chromoionophores” showing higher coordination abilities towards Na^+ and K^+ ($\log \beta$ in the range 4.0–4.5 for Na^+ and $\log \beta$ in the range 3.0–4.8 for K^+), but in these cases no UV-Vis spectral changes were observed upon complexation and thus no spectrophotometric detection was possible.

It should be underlined too that both parent compounds *N*-phenylaza-15-crown-5 and its derivative **1'** are capable to coordinate to the smallest metal ion Be^{2+} [31].

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