



Spectroscopic Study of Molecular Recognition of Ions by Chromogenic Calix[4]arene Derivatives

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Abstract. The complexation properties of three new chromogenic calix[4]arenes (**1a–c**) with aliphatic amines and alkali/alkali earth metal ions have been studied by UV/Vis spectroscopy. **1c** shows the greatest complex forming ability and it is selective for Li⁺, Ca²⁺ and certain amines in polar solvents.

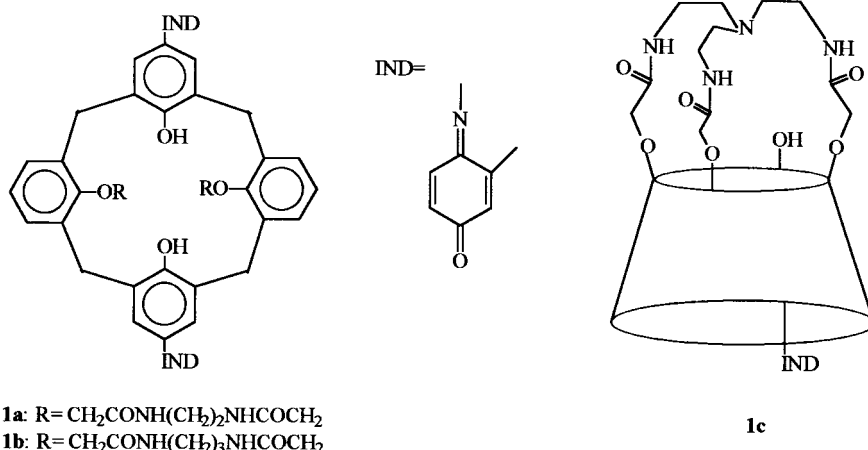
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1. Introduction

A great number of chromogenic calix[4]arenes with different coordination spheres have been synthesized in recent years. Some of them may be used in optical sensors (optrodes) since they are capable of binding aliphatic amines [1] and alkali/alkali earth metal ions [2–4] selectively. Thus, calix[4]arenes may play an important role in the selective determination of substrates in physiological fluids [5].

In our laboratory various sets of chromogenic calix[4]arenes have been synthesized and their complexation with metal ions and some primary aliphatic amines have been studied by UV/Vis spectroscopy [6–8]. In the present work the complex forming properties of three new calix[4]arene derivatives of cone conformation (**1a–c**) supplied with indophenol indicator groups have been studied by UV/Vis spectroscopy in different solvents in the presence of alkali/alkali earth metal ions and aliphatic amines. In these compounds the dicarboxamide bridges with one (**1c**) or two (in **1a, b**) adjacent chromogenic indophenol units form the binding site for cations and significant changes of their UV/Vis spectra are expected upon complexation.

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2. Experimental

The preparation of the calix[4]arene was performed by the oxidative treatment of the respective bridged derivatives [9] with 4-amino-3-cresol according to literature procedures [5].

For the spectroscopic experiment 5×10^{-5} mol dm^{-3} solutions of ligands **1** were prepared with different solvents. An aliquot ($50 \mu\text{l}$) of amine (about 5×10^3 -fold excess) was added into 3 mL solutions of the ligand. In the study of the metal ion selectivity the samples were saturated with the bromide salt of the alkali, or alkali earth metal.

3. Results and Discussion

The UV/Vis spectra of **1a**, **1b** and **1c** were recorded in ethanol, acetonitrile, acetone, dichloromethane, 1,4-dioxane and carbon tetrachloride. In general it was found that in the UV region there were two maxima from the ligands around 270–278 nm and 234–244 nm and one maximum from the amines between 229 and 279 nm (depending on the amine and the solvent), which overlap. In the visible region the ligands have a strong absorption band around 520 nm. After mixing the reactants the appearance of a new band between 600 and 700 nm is a clear indication of complex formation. In some cases the fading of the solution and/or precipitation of the complex was observed.

Table I summarizes the absorption maxima of ligands **1a**, **1b** and **1c** in three polar solvents in the absence and in the presence of aliphatic amines in the visible region. (In apolar solvents the complex formation was not observed except in carbon tetrachloride where **1a** complexed 1,3-diaminopropane and **1b** bound 3-aminopropanol, 1,3-diaminopropane and diethylenetriamine.) The selectivity of **1a** in all solvents and those of **1b** and **1c** in ethanol are poor. Calixarene **1c** can distin-

Table I. Absorption maxima (nm) of ligands **1a–c** in the presence of different amines

	1a			1b			1c		
	Acetone	MeCN	EtOH	Acetone	MeCN	EtOH	Acetone	MeCN	EtOH
–	517	515	528	517	516	527	516	517	527
Propyl- amine	682	678	663	672	677	666		672	655
3-amino- propanol	524	524	532	521	528	535	522	530	535
1,3-diamino propane	684	677	663	677	674	664		671	652
	524	535	533	521	526	534	520	528	533
<i>n</i> -butyl- amine	677	676	664	681	674	667	658	670	656
	526	563	533	530	530	539	529		535
<i>t</i> -butyl- amine	678	676	663		673	667		663	665
	523	525	529	520	524	532	526	531	534
Diethylene triamine	674	676	664		668	667			655
	523	523	528	521	524	532	525	528	535
Triethyl- amine	680	676	663	708	673	667			655
	527	519	534	526	523	532	527	525	532
	680	677			674	666			
	518	517	529	517	519	528	516	521	528

Table II. Absorption maxima (nm) of ligands **1a–c** in the presence of different salts

	1a			1b			1c		
	Acetone	MeCN	EtOH	Acetone	MeCN	EtOH	Acetone	MeCN	EtOH
LiBr							653 ◇	670	
	520	516	529	528	518	527			528
LiBr +	658	673	660	651	667	663	652	◇	649
Et ₃ N		◇	534			534		fading	
NaBr	518	516	527	516	521	528	516	516	527
NaBr +	682	680			675	663		666	654
Et ₃ N	516	515	529	513	518	529	519	529	533
KBr	517	515	528	518	517	527	515	516	526
KBr +	681	676	652		674	660		674	
Et ₃ N		521	528	519	519	528	516		528
CaBr ₂				639	640		722	◇ fading	725
	511	516	527			527	weak		
CaBr ₂ +	637	673	612	◇	◇	620	◇ fading	687	weak
Et ₃ N	◇	519							593
MgBr ₂	515	516	524	516	512	523	514	514	526
MgBr ₂ +		697			616				
Et ₃ N	519	517	530	517		585	518	518	531

◇ = precipitation.

guish amines very efficiently. In acetone only 1,3-diaminopropane was complexed while in acetonitrile the smaller substrates with normal chains were also bound.

Table II shows the absorption maxima of ligands **1a**, **1b** and **1c** and different alkali/alkali earth metal bromides in the absence and in the presence of triethylamine in the visible region. The triethylamine as a weak base is capable of facilitating the deprotonation of the —OH group of the ligands. (But as the last row of Table I shows, triethylamine itself forms complexes with **1a** and **1b** in some solvents.) In apolar solvents no complex formation was observed in the case of **1a** and **1b** but the spectra of calixarene **1c** were different; in the presence of both lithium ion and base plateaus occurred over a wide visible region providing evidence of weak complex formation. Li^+ was complexed efficiently without base only by ligand **1c** in acetonitrile, while Ca^{2+} was bound under similar conditions by calixarene **1b** in acetone and acetonitrile and by **1c** in acetone and ethanol.

In conclusion, **1c** has been found to have strong and selective complex forming ability and after quantitative measurements it may be of value in optical sensors.

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