

COMPARATIVE STUDY OF AZOBENZENE AND CROWN ETHER BRIDGED CALIX[4]ARENE BIS CROWN

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Abstract

In this study the binding abilities of 1,3-di(2,2'-azobenzene)-calix[4]bis-crown-6 toward K^+ and Na^+ cations have been established in methanol by spectrophotometric measurements at 25 ± 0.1 °C and 0.01 M ionic strength, and with using Specfit computer program; stability constants for 2:1, metal : ligand complexes has been estimated.

Comparing the results with 1,3-alternate calix[4]-bis-crown-6 showed, the complex stoichiometry of 2:1 (metal : ligand), only for the azobenzene derivative .

The results reveal that although the stability constants of the complexes formed by azobenzene derivative is larger than that formed by BC6, but only BC6 shows selectivity for Potassium.

Keywords: calix[4]crown, azobenzene, complexation, alkali cation, stability constant.

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Introduction

The first synthesis of crown compounds incorporating an azobenzene unit building block in a macrocycle was reported by Shiga et al. [1,2] 2,20-Dihydroxyazobenzene was alkylated with the appropriate dichloride or ditosylate. The complexation properties of these azobenzocrown ethers with alkali and alkaline earth metal salts were investigated spectrophotometrically in acetonitrile.[2,3]

We are interested in finding molecular system which can selectively bind Na^+ or K^+ mimicking the biological Na^+/K^+ pump.[2] According to a report by Swager and co-workers, it was found that bithiophene calix[4]arenes containing six ethereal oxygen donors were able to bind Na^+ and K^+ to different extents.[3]. In the same manner, we anticipated that an azobenzene crown calix[4]arene would also form complexes with both Na^+ and K^+ . We therefore studied the complexation properties of 1,3-di(2,2'-azobenzene)-calix[4]bis-crown-6 (L) and compare it with 1,3- calix[4]-bis-crown-6 (BC6) [4] (figure 1).

Experimental

Materials: 1,3-di(2,2'-azobenzene)-calix[4]bis-crown-6 were synthesized according to the procedure reported by Z.Asfari and co-workers. Methanol was used without further purification. The metallic salts were NaCl (Merck, p.a.) and KCl (Merck, p.a.). The supporting electrolyte used, Me_4NCl (Fluka, purum), was dried under vacuum for 24 hr at room temperature.

Stability constant measurements: The stability constants of the complexes were determined by UV/Vis spectrophotometry [5] as the stepwise addition of an alkali

cation solution in methanol to the calixarene solution in the same solvent. In all solutions, the ionic strength was maintained at 0.01 M by use of Me₄NCl. Upon addition of metal the UV/Vis spectrum of the ligand undergoes small changes in the 260-380 nm. The changes were sufficient to allow a multiwavelength treatment of the data by the Specfit program.

Results and Discussion

Assuming a 1 : 2 stoichiometry for the complexes formed between alkali ions (M⁺ = Na⁺ and K⁺) and the ligand (L), the equation describing the complexation equilibrium of

the cations is as follow: $2M^+ + L \rightleftharpoons M_2L^{2+}$

The corresponding stability constant β is then defined as:

$$\beta = \frac{[M_2L^{2+}]}{[M^+]^2[L]}$$

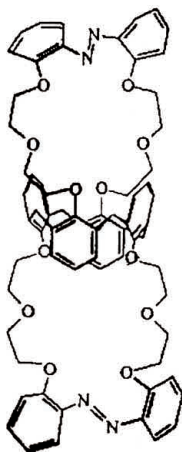
The spectra of the solution of L (1.5x10⁻⁴ M) containing increasing amounts of metal ion have been recorded between 260-380 nm. The addition of metal ion induces a increase of the absorption bands of the ligand in all cases. Figure 2 shows as an example the change in the spectrum of the ligand upon addition of KCl. The treatment of the data based on the formation of 1 : 2 complexes using the Specfit program [6] allows to measure the stability constants of the complex formed (Figure. 3 and 4). Table 1 contains the measured stability constants together with those obtained for the 1,3-calix[4]-bis-crown-6 in pure methanol .

The results reveal that L is capable to complex sodium and potassium ions with a 2:1 metal to ligand ratio. Taking into account a 1:1 complex alone or together with the binuclear one doesn't improve the fit and even leads to the rejection of the model.

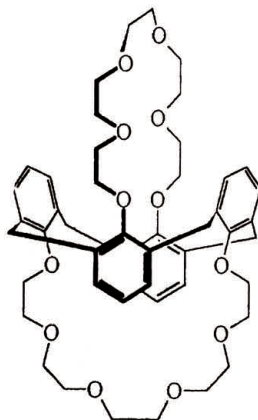
Although the stability constants of the complexes formed by L is larger than BC6 but only BC6 shows selectivity for Potassium.

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L



BC6

Figure 1: Structure of 1,3-di(2,2'-azobenzene)-calix[4]bis-crown-6 (L) and 1,3-calix[4]-bis-crown-6 (BC6).

Table 1. Logarithm of stability constants ($\log \beta$) in CH_3OH for the Complexation of Sodium and Potassium ions by 1,3-di(2,2'-azobenzene)-calix[4]bis-crown-6 and 1,3- calix[4]-bis-crown-6 in CH_3OH at 25°C ($I = 0.01\text{M}$)

Cation	Radius, Å	1,3-di(2,2'-azobenzene)- calix[4]bis-crown-6		1,3- calix[4]-bis-crown-6 ^(a)	
Na^+	1.00	$\text{M}_2 : \text{L}$	6.6 ± 0.26	$\text{M} : \text{L}$	1.52 ± 0.07
K^+	1.35	$\text{M}_2 : \text{L}$	6.7 ± 0.34	$\text{M} : \text{L}$	4.1 ± 0.1
Selectivity		$\text{M}_2 : \text{L}$	≈ 1	$\text{M} : \text{L}$	270
Na^+/K^+					

a) Data are taken from reference 4.

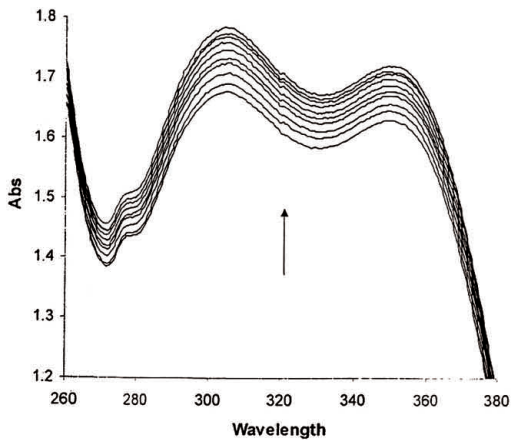


Fig. 2. Change in UV absorption spectrum of L^+ (lower curve) upon addition of KCl in CH_3OH . (after correction for dilution effects)

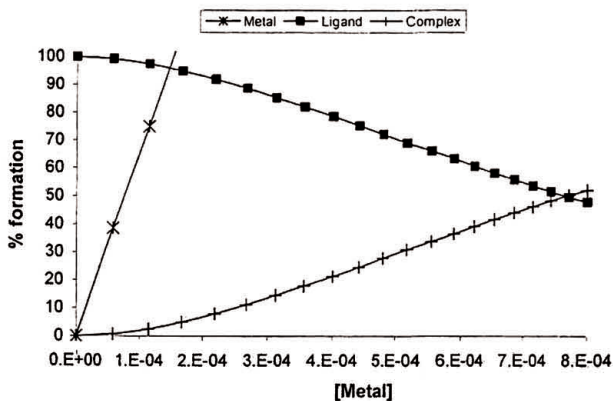


Fig. 3. Formation percent of different species of a 1.5×10^{-4} M solution of L in CH_3OH upon addition of KCl at 25°C ($I = 0.01\text{M}$, Me_4NCl), calculated by specfit.

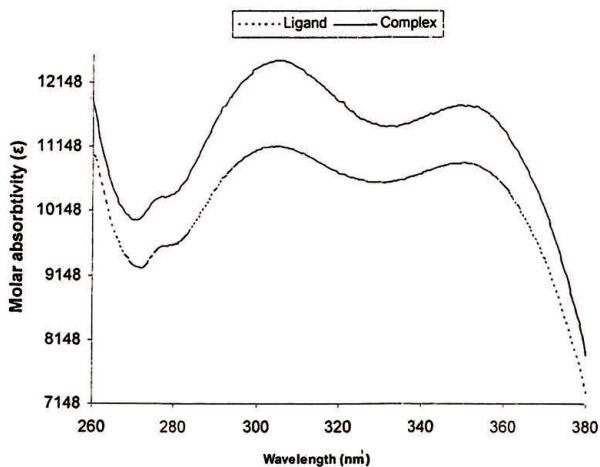


Fig. 4. Formation Molar absorbtivity (ϵ) of a L and it't M2L complex with KCl in methanol at 25°C ($I = 0.01M$, Me_4NCl) calculated by specifit.