

ALKALI CATION COMPLEXATION BY 1,3-ALTERNATE CALIX[4]-BIS-CROWN-6 IN ACETONITRILE/WATER MIXTURE SOLVENT

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Abstract

The complexive abilities of 1,3-alternate calix[4]-bis-crown-6 (L) towards alkali metal ions in the acetonitrile/water (90/10) mixture have been evaluated by UV/Vis spectroscopy. The results reveal that the ligand is capable to complex sodium, potassium, rubidium and cesium ions with a 1:1 metal to ligand ratio. The selectivity presented by L (Cs > K > Rb > Na) in the studied mixed solvent differs from those observed in pure acetonitrile and methanol. ¹H-NMR experiments provide some information that leads to conclude the probability of the formation of the 2:1 (metal/ligand) complexes. The latter complex was not detected by UV/Vis spectroscopy.

Introduction

Calixarenes [1], in particular their tetramers, are a class of synthetic macrocyclic building blocks for the construction of a variety of selective cation receptors [2]. An approach to this goal is the combination of their skeleton with different macrocyclic moieties of well known complexing abilities. Among these combined structures [3_{a,b,c}] calixcrowns, introduced by Alferi *et al.* [4], have been shown to exhibit interesting complexive, extractive and transport properties towards alkali metal ions. Following to the first report on the synthesis of *p*-*tert*-butylcalix[4]crown-5 [4], many publications concerning to the synthesis and ionophoric properties of these compounds have been appeared [5]. Doubly calix[4]crowns in 1,3-alternate conformation are a group of these compounds containing very rigid cavities with interesting complexing abilities towards metallic ions [6-8].

Recently, a series of calix[4]-bis-crowns (crown-5, crown-6 and crown-7) have been synthesized and their application in the transport of ¹³⁷Cs ions from nitric acid media through a supported liquid membrane was investigated [7]. Molecules with crown-6 moieties present to be much more efficient and selective ligands for cesium. Binding properties of some calix[4]-bis-crowns-6 towards alkali ions in acetonitrile and methanol have been reported by Arnaud-Neu *et al.* using the extraction experiments of the alkali picrates and the measurements of complex stability constants by UV/Vis spectroscopy [8]. These calixcrowns show a preference toward cesium ions as the results obtained in the transport experiments [7].

1,3-Alternate calix[4]-bis-crown-6 (L) is one of the ligands which shows their abilities towards alkali cations in transport, extraction and complexation experiments [7, 8]. Its efficacy order for these ions is reported as Cs > Rb > K > Na in both acetonitrile and methanol [8]. The mechanism of the cesium ion complexation with L was studied by proton and cesium NMR spectroscopy in chloroform upon stepwise addition of cesium picrate to a solution of ligand consists of a slow rate complexation/decomplexation of 1:1 (metal/ligand) complex on the NMR timescale, but a fast cation/ligand exchange between mono and binuclear complexes at metal/calix ratio equal about to 1. This is described by considering the reduced coordinative ability of the second cavity of the mononuclear complex with respect to that of the free ligand. However at higher metal/ligand ratio both cavities of the calixcrown can be filled and a binuclear complex is formed [9].

In this paper we describe the complexive properties of L towards alkali cations in a mixture of acetonitrile/water (90/10). The results will be compared with those reported previously in pure acetonitrile and methanol solvents [8]. Proton NMR spectra recorded at 25°C were run in order to obtain insight into the stoichiometry of the complex formed.

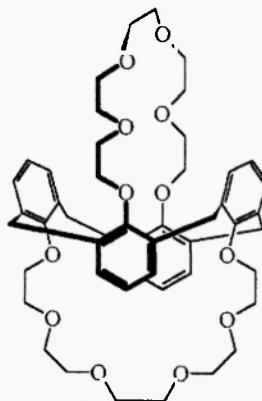


Figure 1. Structure of calix[4]-bis-crown-6 (L).

Experimental

Materials

1,3-Alternate calix[4]-bis-crown-6 (L) were synthesized according to a procedure reported previously [7]. Acetonitrile (SDS) was used without further purification. The metallic salts were LiCl (Fluka, purum), NaCl (Merck, p.a.), KCl (Merck, p.a.), RbCl₄ (Fluka, puriss.) and CsCl (Merck, p.a.). The supporting electrolyte used, Me₄NCl (Fluka, purum), was first recrystallised from methanol and acetone and dried under vacuum for 24 h at room temperature.

Stability constant measurements

The stability constants of the complexes were determined by UV/Vis spectrophotometry [10] as the stepwise addition of an alkali cation solution in acetonitrile/water (90/10) 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 250-300 nm. The changes were sufficient to allow a multiwavelength treatment of the data by the Sirko [11] program.

¹H-NMR Experiments

In an NMR tube containing a solution of the ligand (0.01 M) in CD₃CN/D₂O (90/10) was added variable amounts of CsSCN and the ¹H-NMR spectra were recorded by using a FT Bruker WP-200 SY instrument. The data were referenced to residual protonated acetonitrile.

Results and Discussion

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



The corresponding stability constant β is then defined as:

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

The spectra of the solution of L (3×10^{-4} M) containing increasing amounts of metal ion have been recorded between 250-300 nm. The addition of metal ion induces a decrease 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 CsCl. The treatment of the data based on the formation of 1 : 1 complexes using the Sirko program allows to measure the stability constants of the complex formed. Table 1 contains the measured stability constants together with those obtained for the same ligand in pure acetonitrile and methanol [8] for comparison.

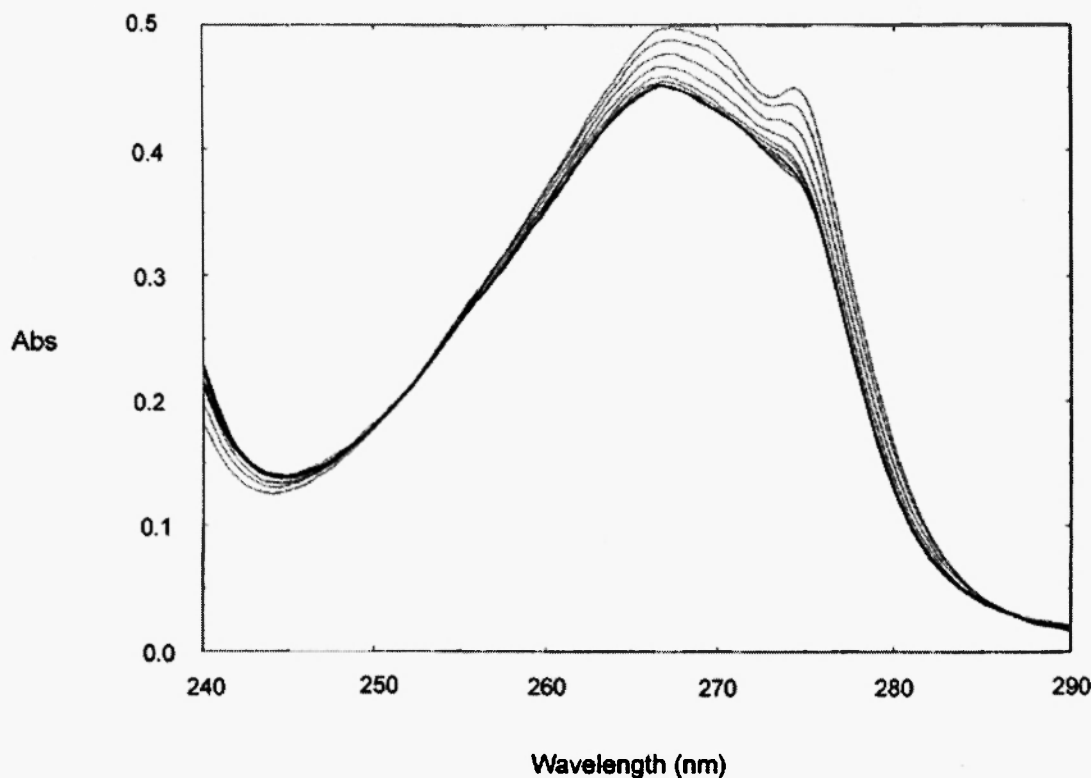


Figure 2. Change in UV absorption spectrum of L (upper curve) upon addition of CsCl in CH₃CN/H₂O (90/10).

Table 1. Logarithms of the stability constants (β) of alkali cation complexes by L.

Cation	CH ₃ CN/H ₂ O (90/10)	CH ₃ CN ^a	CH ₃ OH ^a
Na ⁺	2.4 \pm 0.1	1.97 \pm 0.08	1.52 \pm 0.07
K ⁺	4.47 \pm 0.09	4.12 \pm 0.08	4.01 \pm 0.1
Rb ⁺	4.08 \pm 0.01	4.41 \pm 0.04	4.3 \pm 0.1
Cs ⁺	4.79 \pm 0.08	4.9 \pm 0.1	4.8 \pm 0.3

^a) Data are taken from reference 8.

The results show that the selectivity of the ligand towards cesium is not modified in the acetonitrile/water mixture. However, in the case of sodium and potassium there is a significant increase in the stability of the complexes formed. A significant larger solvent effect is observed in the case of potassium. These observations could be explained considering the results on the structure of the sodium complex by the ligand [12]. The structure of the sodium ion / L complex in the presence of water shows the existence of the ion and a molecule of water in the same cavity of the ligand. These conditions force the sodium ion to be closer to the three etheral oxygen atoms of the cavity than in the complex free water structure.

The results in the case of the potassium ion can be also interpreted by the same description and a better size fitting of the ion in the presence of a molecule of water. In contrast a molecule of water forces the rubidium ion to be out of the ionophoric cavity of the ligand. In the case of the cesium ion the matching between cavity and ion size is responsible for the fact that the water molecule could not penetrate into the cavity.

The ¹H-NMR spectra of the *para* and *meta* protons of the studied calixarene plotted upon addition of CsSCN in acetonitrile/water. The corresponding chemical shifts as a function of metal/ligand ratio are presented in figure 3. As it is seen, two inflection point in the curve are consistent with the formation of 1:1 and 2:1 (metal/ligand) complexes. However, the complexation experiments performed could be satisfactory interpreted by assuming the presence of only 1:1 complexes as it was observed in pure acetonitrile and

methanol [8]. Taking into account a binuclear complex alone or together with the mononuclear one does not improve the fit the model used. In addition molecular dynamic calculations performed in methanol involving a dication showed that the decomplexation of the cation occurred after less than 5 ps [8]. In another molecular dynamic simulation for the complexation of the cesium ion in water it is shown that the repulsion between two cations in the same ligand molecule prevents to form a dication complex [9].

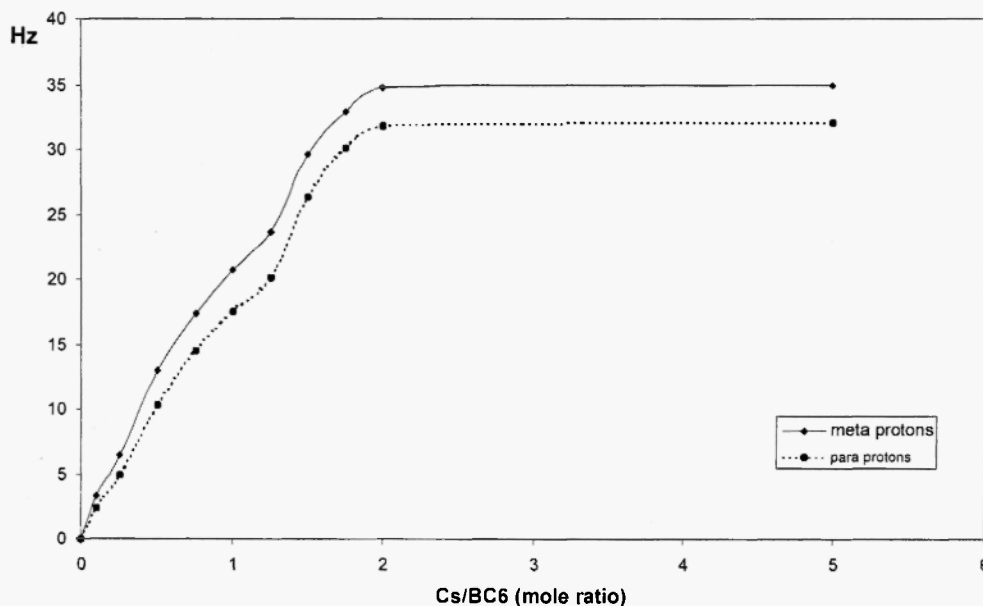


Figure 3. The corresponding chemical shifts as a function of metal/ligand ratio.

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