

## COORDINATION COMPOUNDS

# Spectrophotometric Studies of Alkali Metal Ion Complexes of *p*-Tetrabutyl-Calix[4]arenes\*

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**Abstract**—A spectrophotometric technique is used to evaluate the alkali metal ion binding selectivities of two calix[4]arenes in acetonitrile solution. On the basis of the formation constant values calculated, complexation of Cs<sup>+</sup> and Li<sup>+</sup> are favored towards 25,27-dipropoxy-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl calix[4]arene, L1, and 25,26,27-tripropoxy-28-hydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene, L2. Both ligands have been shown to form exclusively 1 : 1 (metal ion to ligand) complexes with alkali cations under our experimental conditions.

## INTRODUCTION

Calixarenes are synthetic macrocycles obtained by the condensation of *p*-substituted phenol and formaldehyde in alkaline medium. Lower and upper rim functionalization of parent calixarenes led to a large variety of derivatives. Their bowl-like structure allows them to form complexes with a variety of species [1]. Fine control of the size of calix[*n*]arenes, by changing the value of *n* and the introduction of various functional groups, makes it possible to prepare a variety of molecules with various applications. Calixarenes are of interest for chromatography, slow release of drugs, transport across membranes, ion channels, and many other applications [2–5].

It has been shown recently, using rigidified calix[4]arenes, that the complexation properties depend not only on the nature of the donor groups but also on their stereochemical arrangement, which is determined by the conformation of the calixarenes [6, 7].

Depending upon the relative orientation of the *para* and phenolic sites, the tetramer can adopt four different conformations: cone, partial cone, 1,2-alternate, and 1,3-alternate. These conformers display selective properties of complexation of alkali metal cations. The cone conformer of calix[4]arenes usually shows the highest affinity for Na<sup>+</sup>, whereas the partial cone and 1,3-alternate conformers show the best selectivity for K<sup>+</sup> and Cs<sup>+</sup> [8]. While several calixarene-metal cation complexes have been reported, most of them require that the hydroxyl groups of the calixarene be derivatized to esters or ethers [9], because of the poor solubility of the *p*-*tert*-butyl-calixarenes. The Cs<sup>+</sup>-*p*-*tert*-butyl-calixarene complex is used for the recovery of cesium from

nuclear waste solutions [10] and as a lanthanide complexing agent under basic conditions [11]. Derivatives other than ethers and esters have been examined: calixcrowns show a high Na<sup>+</sup>/Cs<sup>+</sup> selectivity and are used as carriers through supported liquid membranes [10]. The conformation of the calixarene in these complexes is normally a cone, except when derivatization forces other conformations, as in the case of 1,3-calix[4]bis-crown, which shows an alternate 1,3 conformation [10]. There is evidence of some conformational freedom for the metal complexes in solution [12]. Alkyl ketone residues have been introduced in the lower rim of calix[5]arene and calix[6]arene [13], which show affinity for complexation of alkali metal cations. Phosphoryl and amide ligands, both at the lower and upper rim, facilitate extraction of lanthanides and actinides [14–15].

We have chosen 25,27-dipropoxy-26,28-dihydroxy-5,11,17,23-tetra-*tert*-butyl calix[4]arene, L1, and 25,26,27-tripropoxy-28-hydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene, L2 for ligand framework study due to its easy synthesis and the existence of very few reports on its chelating abilities towards metal ions [16]. The four functionality ligating groups in the lower rim of the ligand can be independently modified to increase its binding ability and make it more specific for chelating by alkali cations.

In this work, the stability constants of alkali metal cations and two calix[4]arenes complexes are determined in acetonitrile at 25°C using a spectrophotometric technique. The structure of the studied calixarenes is shown in Fig. 1. The calixarenes in this study all consist of four benzene rings, which are arranged conically, so that the hydroxyl and the propoxy groups form a coordination sphere where metal cations can be bound. The different substituents in the lower rim of the ligands change the ability of these molecules to tailor them-

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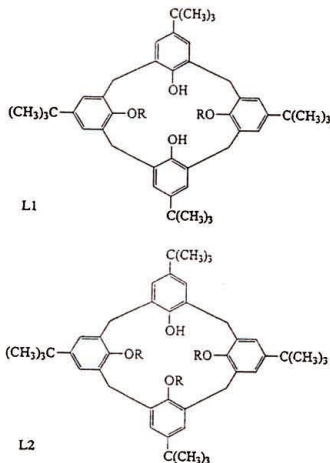


Fig. 1. Structure of L1 and L2 in their cone conformation.  
R = C<sub>3</sub>H<sub>9</sub>.

selves to different cavity sizes and rigidities, which enables them to have various preferences towards alkali cation complexation.

## EXPERIMENTAL SECTION

**Chemicals.** Parent calixarene was obtained from Aldrich and used without further purification. Two different calix[4]arenes, Fig. 1, L1 and L2, were synthesized following the procedures of Iwamoto *et al.* [16]. The solvent, acetonitrile (from Merck, p.a.), was used

without further purification. LiCl (Merck, p.a.), NaCl (Merck, p.a.), KCl (Merck, p.a.), RbCl (Fluka, purum), and CsCl (Merck, p.a.), as well as the alkali cation sources, were dried under vacuum at room temperature for at least 48 hours before use.

**Measurements.** The absorption spectra (280–290 nm) were measured on a Uvikon 992 UV-vis scanning spectrophotometer with a Pentium IV computer using 10 mm quartz cells. The system was thermostated at 25°C by circulating water from an isothermal bath. In all cases, the procedure was repeated at least three times and the resulting average values and corresponding standard deviations are shown in the text and Tables.

**Procedure.** A 2.5 cm<sup>3</sup> solution of each ligand (7.74 × 10<sup>-4</sup> and 4.07 × 10<sup>-4</sup> mol dm<sup>-3</sup> for L1 and L2, respectively) was titrated with stepwise addition of an alkali cation solution (1.51 × 10<sup>-3</sup>, 1.37 × 10<sup>-3</sup>, 9.92 × 10<sup>-4</sup>, 1.82 × 10<sup>-4</sup>, and 3.80 × 10<sup>-4</sup> mol dm<sup>-3</sup> for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>, respectively) both in acetonitrile solution.

## RESULTS AND DISCUSSION

Assuming that the absorbance of the ligand would change upon complexation with an alkali cation, we performed spectrophotometric measurements. The complex M<sub>p</sub>L<sub>q</sub> formed is characterized by its stoichiometry, *p* and *q*, where M and L represent each metal ion and each ligand, respectively. To determine the formation constant of complexation, *K<sub>s</sub>*, Eq. 1 is defined,

$$pM + qL \rightleftharpoons M_pL_q \quad K_s = [M_pL_q] / [M]^p [L]^q. \quad (1)$$

The method of determination of the formation constant has been described before [17]. The absorbance *A* was measured for the solutions as described in the experimental section. For calculating the formation constants, the spectrophotometric titration data were analyzed at a wavelength in the UV range that is given by

$$A = \varepsilon_M[\text{metal ion}] + \varepsilon_L[L] + \varepsilon_C[\text{complex}], \quad (2)$$

where  $\varepsilon_M$ ,  $\varepsilon_L$ , and  $\varepsilon_C$  are the molar absorptivities of each metal ion, each ligand, and the formed complex, respectively. For the mass balance

$$[\text{metal ion}] = c_M - [\text{complex}], \quad (3)$$

$$[L] = c_L - [\text{complex}], \quad (4)$$

where  $c_M$  and  $c_L$  are the total concentration of each metal ion and each ligand, respectively. Substituting Eqs. 1 and 3–4 into Eq. 2 and rearranging and canceling the like terms in the wavelength that the metal ion actually has no absorbance in gives

$$A = c_L \varepsilon_L - c_M \varepsilon_L - c_L \varepsilon_M + c_M \varepsilon_M + c_L \varepsilon_C + c_M \varepsilon_C - \varepsilon_L / K_s - \varepsilon_M / K_s + \varepsilon_C / K_s \pm \varepsilon_L B \pm \varepsilon_M B \pm \varepsilon_C B / 2, \quad (5)$$

Average values of log *K<sub>s</sub>* in different wavelengths for various calixarenes and alkali metal ions at 25°C

Metal ion	log <i>K<sub>s</sub></i> (L1)	log <i>K<sub>s</sub></i> (L2)
Li <sup>+</sup>	5.08 ± 0.05	4.65 ± 0.04
Na <sup>+</sup>	4.41 ± 0.04	4.05 ± 0.04
K <sup>+</sup>	3.83 ± 0.02	3.85 ± 0.01
Rb <sup>+</sup>	4.07 ± 0.03	4.18 ± 0.04
Cs <sup>+</sup>	5.09 ± 0.04	5.05 ± 0.03

where  $B$  is equal to  $(1 + 2c_L K_S + 2c_M K_S + c_L^2 K_S^2 - 2c_L c_M K_S + c_M^2 K_S^2)/K_S$ . Using a suitable computer program [18], the data were fitted to Eq. 5 for estimating the formation constant of Eq. 1. We used the Gauss-Newton nonlinear least-squares method in the computer program to refine the absorbance by minimizing the error squares sum from Eq. 6

$$S = \sum (a_i - b_i)^2 \quad (i = 1, 2, 3, \dots), \quad (6)$$

where  $a_i$  is a quasi-experimental quantity and  $b_i$  is a calculated one. The computer program consisted of two different kinds of fitting, graphical and numerical. The final selection of the species was based on both graphical and numerical methods, considering, in addition the various statistical criteria, i.e., the sums of the squared residuals, the differences of  $c_M$  (experimental) and  $c_L$  (experimental) from those of the calculated ones. Figure 2 is shown as a typical example of a graphical fitting for the observed and calculated absorbances (from the computer program).

It was checked for other proposed species existing in significant concentration over a reasonable range of data. As expected, polynuclear complexes were systematically rejected by the computer program. Taking into account a binuclear complex alone or together with the mononuclear one does not improve the goodness of the fit and even leads to the rejection of the model. The model finally chosen, formed by ML, resulted in a satisfactory numerical and graphical fitting. The average values of the formation constants for the 1 : 1 complexes of L1 and L2 + for each metal ion for various wavelengths are listed in the table.

The interesting curve resulting from the spectrophotometric titration of L1 by  $\text{Cs}^+$  and  $\text{Li}^+$ , Fig. 3, shows a sharp break point when the concentrations of metal ions to the ligand ratios reaches unity, indicating the formation of stable complexes for  $\text{Cs}^+$  and  $\text{Li}^+$ . However, the spectrophotometric titration curve of the ligand with other ions displays a more continuous variation in the absorbances with the concentration ratios. In this case, the extrapolating of the slopes at high and low metal to ligand ratios correspond to 1 : 1 complex stoichiometry at the point of the intersections. This behavior indicates a typical less stable complex than those found for  $\text{Cs}^+$  and  $\text{Li}^+$ .

The two calix[4]arenes form complexes with alkali metal cations, but show different affinities for small cations ( $\text{Li}^+$  and  $\text{Na}^+$ ) and large cations ( $\text{Rb}^+$  and  $\text{Cs}^+$ ). Between the two calixarenes, L1 appears to be more efficient for chelating alkali metal ions. The stability constants of L1 and L2 with alkali metal cations versus their ionic radius are shown in Fig. 4. The most stable complexes of L1 and L2 are formed with  $\text{Cs}^+$ . The introduction of an hydroxyl group in the ligands, from 1 to 2, leads to an increase in the stability of the complexes formed by the smaller cations,  $\text{Li}^+$  and  $\text{Na}^+$ , and

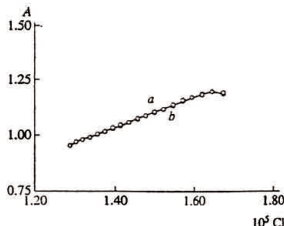


Fig. 2. A typical graphical fitting for the  $\text{Cs}^+ + \text{L2}$  system at 25°C and 281 nm: (a) experimental absorbance, (b) calculated absorbance from the computer program.

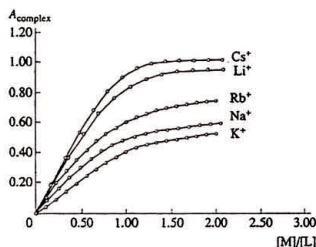


Fig. 3. Spectrophotometric titration plots of L1 by metal ions,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  at 25°C and 281 nm.

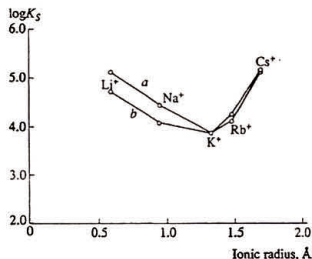


Fig. 4. The plots of  $\log K_S$  versus the ionic radii of the cations at 25°C: (a) L1, (b) L2.

practically no change in the stability of the  $K^+$ ,  $Rb^+$ , and  $Cs^+$  complexes. This result suggests that the electron donating tendency of the hydroxyl group is effective, especially on the smaller cations. The binding selectivity of L1 and L2 towards alkali cations on the stability constant values of the formed complexes (see the Table) is in the order of  $Cs^+ > Li^+ > Na^+ > Rb^+ > K^+$  and  $Cs^+ > Li^+ > Rb^+ > Na^+ > K^+$ , respectively. The results suggest that  $K^+$  could possibly be located near the cavity of L1 and, hence, be more shielded than the other ions, which better fit the cavity size of the ligand. The fact of a more continuous variation of absorbance with concentration of  $K^+$  (Fig. 3), should be due to the low complexation level of this cation. A similar discussion can be stated for L2. The binding selectivity of L1 and L2 towards  $Li^+$  could possibly be due to the cavity sizes of the ligands, and the stability constant values obtained in this work confirm that  $Li^+$  should well encaged and protect the ligands L1 and L2 and result in a higher formation constant and more stable complexes. However, in both cases,  $Cs^+$  appears to have a good tendency to chelate with the ligands. The results obtained in this work suggest that  $Cs^+$  possibly binds with the ligands and forms endo complexes due to the participation of phenyl  $\pi$  electrons with soft dispersion and induction interaction with a large soft cation.

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