

Complexation of Di and Tetra-Benzyloxy Ether Derivatives of Calix[4]Arene With Alkali Metal Cations

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Abstract

The synthesis and complexive abilities of 26, 28-bis-benzyloxy-25, 27-dihydroxy-5, 11, 17, 23-tetra-tert-butyl-calix[4]arene and 25, 26, 27, 28-tetra-benzyloxy-5, 11, 17, 23-tetra-tert-butyl-calix[4]arene towards alkali metal ions Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ in methanol-chloroform mixture have been evaluated at 25 °C, using UV-Vis spectrophotometric techniques. The results showed that the ligands are capable to complex with all of the alkali cations by 1:1 metal to ligand ratios. The selectivity presented considering the calculated stability constants are in the order $\text{Cs}^+ > \text{Li}^+ > \text{Rb}^+ > \text{Na}^+ > \text{K}^+$ and $\text{Na}^+ \cong \text{Li}^+ \cong \text{Rb}^+ \cong \text{K}^+ > \text{Cs}^+$ for the first and second ligand, respectively.

Keywords: complexation, calixarene, alkali cations, stability constant, synthesis

1. Introduction

Calixarenes have been chemically transformed into a large variety of derivatives designed for the selective binding of various metal cations. ¹⁻² The chemistry of calixarenes has been recently developed, and many papers have been published to investigate the attractive characteristics of them. ¹ The focus has been made on the introduction of donor groups onto the calixarene framework for controlling their complexation phenomena. The calixarene structure itself can behave as a soft donor group through its phenyl group π electrons, and this has been demonstrated by the inclusion of silver and thallium(I) ions. ³

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^+ , whereas the partial cone and 1,3-alternate conformers show the best selectivity for K^+ and Cs^+ . ⁴ While several calixarene-metal cation complexes have been reported, most of them require that the hydroxy groups of the calixarene be derivatized to esters or ethers ⁵ due to the poor solubility of the p-tertbutyl-calixarenes. The Cs^+ -p-tertbutyl-calixarene complex is used for the recovery of cesium from nuclear waste solutions, ⁶ and as a lanthanide complexing agent

under basic conditions. ⁷ Derivatives other than ethers and esters have been examined: calixcrowns show a high Na^+/Cs^+ selectivity, and are used as carriers through supported liquid membranes. ⁶ 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. ⁶ There is evidence of some conformational freedom for the metal complexes in solution. ⁸ Alkyl ketone residues have been introduced in the lower rim of calix[5]arene and calix[6]arene, ⁹ 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. ¹⁰⁻¹¹

We have recently synthesized two new calix[4]arenes, 26, 28-bis-benzyloxy-25, 27-dihydroxy-5, 11, 17, 23-tetra-tert-butyl-calix[4]arene, L1, and 25, 26, 27, 28-tetra-benzyloxy-5, 11, 17, 23-tetra-tert-butyl-calix[4]arene, L2, Fig. 1, for ligand framework study due to their easy synthesis. 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 constant of alkali metal cation complexes with the ligands, L1 and L2, are determined in methanol-chloroform mixture (50/50 and 30/70 by volume for L1 and L2, respectively) at 25 °C using spectrophotometric technique. The synthesized

ligands in this work consist of four benzene rings, which are arranged conically, so that the hydroxy and the two or four benzyloxy groups form a coordination sphere where metal cations can be bound.

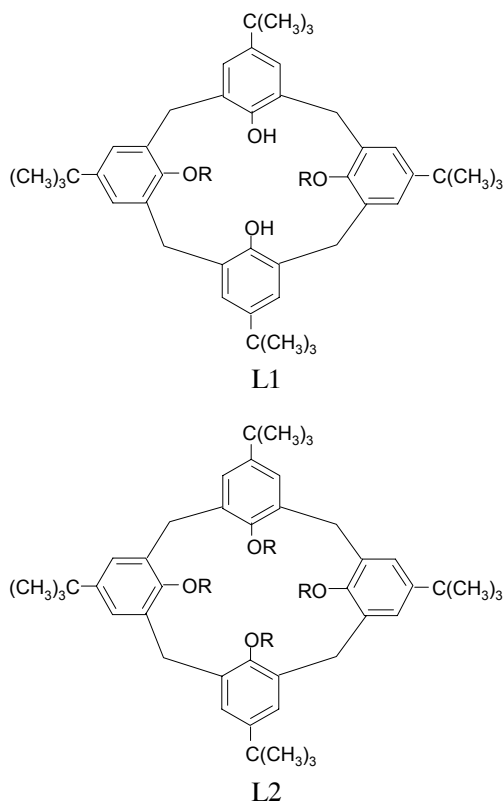


Figure 1. Structure of 26, 28-bis-benzyloxy-25, 27-dihydroxy-5, 11, 17, 23-tetra-tert-butyl-calix[4]arene, L1, and 25, 26, 27, 28-tetra-benzyloxy-5, 11, 17, 23-tetra-tert-butyl-calix[4]arene, L2, R = CH₂C₆H₅

2. 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_pL_q 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_s, Eq. 1 is defined,

$$pM + qL \rightleftharpoons M_pL_q$$

$$K_s = [M_pL_q] / [M]^p[L]^q \quad (1)$$

The method of determination of formation constant has been described before.¹²⁻¹³ The absorbance, A, was measured for the solutions, as described in experimental section. For calculating the formation constants, the spectrophotometric titration data were analyzed at a wavelength in UV range that is given by

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

where ε_M , ε_L , and ε_C are the molar absorbance coefficient of each metal ion, ligand, and the formed complex species, 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 like terms in a wavelength that the metal ion has actually no absorbance, gives;

$$A = C_L\varepsilon_L - C_M\varepsilon_L - C_L\varepsilon_M + C_M\varepsilon_M + C_L\varepsilon_C + C_M\varepsilon_C - \varepsilon_L / (K_s - \varepsilon_M / K_s + \varepsilon_C / K_s \pm \varepsilon_L B \pm \varepsilon_M B \pm \varepsilon_C B) / 2 \quad (5)$$

where B is equal to $(1 + 2C_LK_s + 2C_MK_s + C_L^2K_s^2 - 2C_LC_MK_s^2 + C_M^2K_s^2) / K_s$. Using a suitable computer program¹⁴ 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 an experimental absorbance and b_i is a calculated one. The computer program consists 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. sums of squared residuals, differences of C_M (experimental) and C_L (experimental) from those of calculated ones.

It was checked for other proposed species existed 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 for both complexes. The average values of the formation constants for the 1:1 complex species of L1 and L2 with alkali cations in various wavelengths are listed in Table 1.

The interesting curves resulting from the spectrophotometric titration of L1 and L2 with alkali cations are shown in Fig. 2. Fig. 2a shows a sharp break point when the concentrations of metal ions to the ligand ratios reaches unity, indicating the formation of stable complexes for Cs⁺, Li⁺, and Rb⁺. The same

titration for K^+ shows the absorbance increase within a very small and no significant break in complexation curve, indicating very low stability constant of formation. However, the spectrophotometric titration curve of the ligand by Na^+ displays a more continuous variation in the absorbance with concentration ratios. In this case the extrapolating of the slopes at high and low metal to ligand ratios correspond to 1:1 complex stoichiometry in the point of intersections. This behaviour indicates a typical of less stable complex than those found for Cs^+ and Li^+ . In Fig. 2b, a sharp break point is observed when the concentrations of all metal ions to the ligand ratios reach unity, indicating the formation of stable complexes for alkali cations with L2.

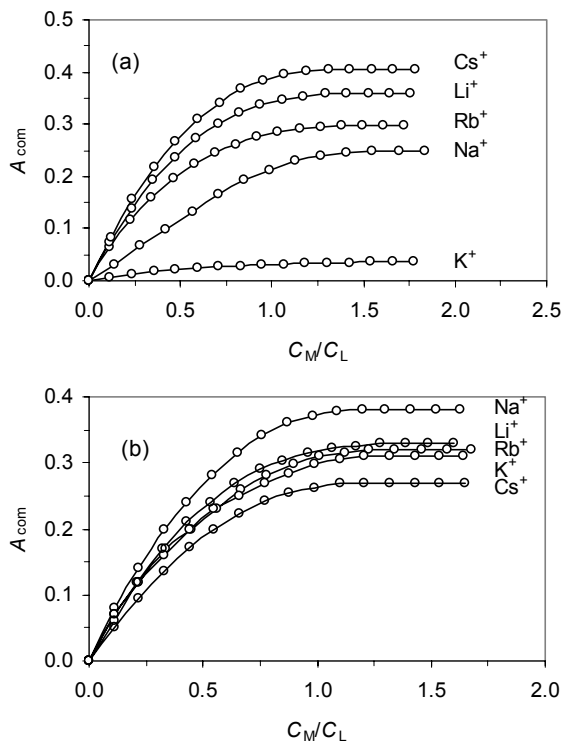


Figure 2. Spectrophotometric titration plots of the ligands L1, (a), and L2, (b), by the metal ions, Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ at 25 °C and 280 nm.

The two calix[4]arenes, L1 and L2, form complexes with alkali metal ions, but show different affinities for small cations (Li^+ and Na^+) and large cations (Rb^+ and Cs^+). L1 appears to be more efficient for chelating with Li^+ , Rb^+ , and Cs^+ . The stability constants of L1 with the metal ions versus their ionic radius are shown in Fig. 3.

The most stable of the complex species of L1 is formed by Cs^+ . However, the introduction of two extra benzyloxy groups to L1 leads to a decrease in stability of the complexes formed by Li^+ , Rb^+ , and Cs^+ , but this is not true for K^+ . This result suggests that the electron donating tendency of the hydroxy group is effective,

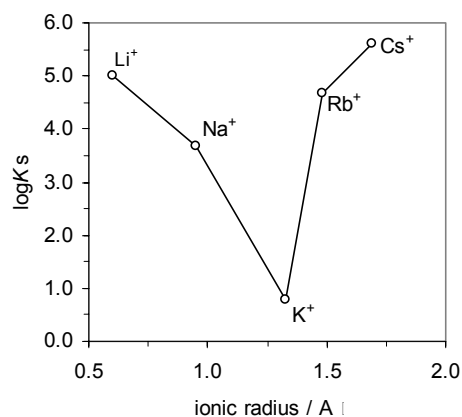


Figure 3. The plot of $\log K_s$, L1, versus the ionic radii of the alkali cations at 25 °C

especially on Li^+ , Rb^+ , and Cs^+ . The binding selectivity of L1 and L2 towards alkali cations on the stability constant values of the formed complexes, Table 1, is in the order of $Cs^+ > Li^+ > Rb^+ > Na^+ > K^+$ and $Na^+ \cong Li^+ \cong Rb^+ \cong K^+ > Cs^+$, respectively.

Table 1. Average values of $\log K_s$ at different wavelengths for the alkali cations and the ligands at 25 °C

metal ion	$\log K_s$ (L1)	$\log K_s$ (L2)
Li^+	4.99 ± 0.05	4.46 ± 0.08
Na^+	3.68 ± 0.04	4.47 ± 0.09
K^+	0.79 ± 0.06	4.41 ± 0.08
Rb^+	4.68 ± 0.03	4.45 ± 0.10
Cs^+	5.61 ± 0.04	4.38 ± 0.09

The results suggest that K^+ is possibly located near the cavity of L1 and hence, is 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. 2a), should be due to the very low complexation level of this cation. However, the complexation affinity of L2 towards alkali cations are almost the same, this is possibly due to the steric hindrance caused by the four benzyloxy groups located in the molecule.

3. Experimental

Chemicals: Parent calixarene was obtained from Aldrich and used without further purification. The ligands were synthesized following the procedure described below. The solvents, methanol and chloroform (from Merck, p.a.), were 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 the alkali cations sources were dried under vacuum at room temperature for at least 48 hours before use.

Synthesis of L1: L1 was synthesized with tetra-tert-butyl calix[4]arene (5.0 g, 7.7 mmol) and benzyl chloride (13.5 mL, 122.0 mmol) which were dissolved in acetonitrile (100.0 mmol). The solution was refluxed for 6 h in the presence of potassium carbonate (9.0 g, 65.0 mmol). The reaction mixture was diluted with water (1000.0 mL) and extracted with dichloromethane. The organic layer was then separated, dried over magnesium sulfate, filtered and evaporated to yield a white solid, which crystallized from dichloromethane-methanol, to give L1 in 63% yield: Mp: 191–194 °C, ¹HNMR: (CDCl₃, 500MHz); δ (ppm): 7.63 (4H, m, OCH₂Ph), 7.37 (2H, s, OH), 7.36 (6H, m, OCH₂Ph), 7.03 (4H, s, ArH), 6.82 (4H, s, ArH), 5.05 (4H, s, OCH₂Ph), 3.26, 4.27 (8H, 2d, J = 15Hz, ArCH₂Ar), 1.28 (18H, s, C(CH₃)₃), 0.97 (18H, s, C(CH₃)₃), ¹³CNMR: (CDCl₃, 125MHz); δ (ppm): 31.0, 32.6, 34.7, 34.9, 47.1, 79.0, 125.9, 126.4, 128.4, 128.6, 128.8, 129.5, 138.0, 142.5, 148.1, 150.7, 151.5. IR: (KBr, cm⁻¹), 3348, 2959, 1485, 1206, 696.

Synthesis of L2: Na₂CO₃ (0.07 g, 0.70 mmol) was added to a solution of calix[4]arene (0.50 g, 0.65 mmol) in 15.0 mL acetone and the reaction mixture was stirred at 60 °C for 1 h until transparent solution was obtained then 1.35 mL (12.20 mmol) benzyl chloride was added and the mixture was refluxed for 24 h. After evaporation of the solvent the residue was recrystallized from dichloromethane-methanol, to give 72% yield: Mp: 220–222 °C, ¹HNMR: (CDCl₃, 500 MHz); δ (ppm), 7.49 (20H, m, Bz) 7.01 (8H, s, ArH), 4.21, 3.49 (8H, 2d, J = 2.1 Hz, ArCH₂Ar) 4.48 (8H, s, OCH₂Ph), 1.18 [36H, s, C(CH₃)₃]

Measurements: Absorption spectra, 260–290 nm, were measured on 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 Table 1.

Procedure: 2 mL solution of the ligands (8.45×10⁻⁵ and 9.13×10⁻⁵ mol L⁻¹ for L1 and L2, respectively) were titrated with stepwise addition of an alkali cation solution (1.99×10⁻⁴, 2.04×10⁻⁴, 2.00×10⁻⁴, 1.95×10⁻⁴,

and 2.01×10⁻⁴ mol L⁻¹ for Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺, respectively) all in the same solvent. The UV-Vis spectra of the mixtures undergo small changes at 260–290 nm, but the measured absorbances were sufficient to allow the treatment of the data by the computer program.

4. Acknowledgements

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5. References

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Povzetek

Pripravili smo 26, 28-bis-benziloksi-25,27-dihidroksi-5, 11, 17, 23-tetra-tert-butil-kaliks[4]aren in 25, 26, 27, 28-tetra-benziloksi-5, 11, 17, 23-tetra-tert-butil-kaliks[4]aren in jih uporabili kot liganda za kompleksiranje Li⁺, Na⁺, K⁺, Rb⁺ in Cs⁺ v metanol-kloroform raztopini. UV-Vis spektroskopijo smo ugotovili, da oba liganda kompleksirata vse alkalijske katione v 1:1 razmerju ligand:kation. Stabilnostne konstante so Cs⁺ > Li⁺ > Rb⁺ > Na⁺ > K⁺ in Na⁺ ≅ Li⁺ ≅ Rb⁺ ≅ K⁺ > Cs⁺ za prvi oziroma drugi ligand..