

ФИЗИЧЕСКИЕ  
МЕТОДЫ ИССЛЕДОВАНИЯ

УДК

SPECTROPHOTOMETRIC STUDIES OF ALKALI AND ALKALI EARTH METAL  
IONS COMPLEXES OF MONO AMINO DERIVATIVE OF CALIX[4]ARENE

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The synthesis and complexive abilities of 5,11,17-tris(tert-butyl)-23 amino-25,26,27,28-tetrapropoxy-calix[4]arene towards alkali cations  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  and alkali earth cations  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  in methanol-chloroform mixture have been evaluated at 25°C, using UV-Vis spectrophotometric techniques. The results showed that the ligand is capable to complex with all the cations by 1 : 1 metal to ligand ratios. The selectivity presented considering the calculated formation constants are in the order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$  and  $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$  with the ligand.

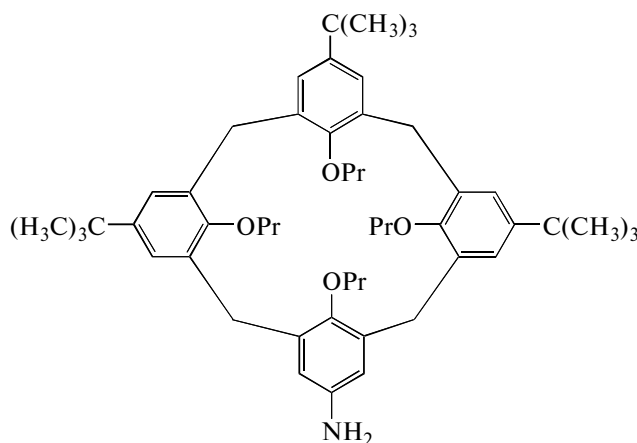
Calix[n]arenes are cyclic oligomers obtained by condensation of formaldehyde with *p*-alkyl-phenols in the basic environments [1-3]. These compounds are a very fascinating class of container molecules and their abilities towards ion or molecule recognition were studied extensively among the past decade. Calix[n]arenes are basket-shaped compounds with potential interest for host-guest complexation [4]. Fine control of the size of calix[n]arenes, by changing the value of *n* and the introduction of various functional groups on the lower or upper rims, makes it possible to prepare a variety of molecules with various applications. The focus has been on the introduction of donors groups onto the calix[n]arene framework for controlling their complexation abilities. The ability of calix[n]arene systems to interact with alkali metal ions has long been recognized and has led to several ionophores increasingly selective for a specific cation.

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 stereo-chemical arrangement, which is determined by the conformation of the calixarenes [5, 6]. 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 shows usually the highest affinity for  $\text{Na}^+$ , whereas the partial cone and 1,3-alternate conformers show the best selectivity for  $\text{K}^+$  and  $\text{Cs}^+$  [7]. 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 [8] because of the poor solubility of the *p*-tert-butyl-calixarenes. The  $\text{Cs}^+$ -*p*-tert-butyl-calixarene complex is used for the recovery of cesium from nuclear waste solu-

tions [9], and as a lanthanide complexing agent under basic conditions [10]. Derivatives other than ethers and esters have been examined: calixcrowns show a high  $\text{Na}^+/\text{Cs}^+$  selectivity, and are used as carriers through supported liquid membranes [9]. 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 [9]. There is evidence of some conformational freedom for the metal complexes in solution [11]. Alkyl ketone residues have been introduced in the lower rim of calix[5]arene and calix[6]arene [12], 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 [13, 14].

A variety of optical methods for the detection of cations in solution is well established and has been extensively reviewed [15–20]. One of the successful approaches is using spectrophotometric properties of calix[n]arenes. These compounds show UV absorption bands around 280 nm due to the electronic transitions in the phenol groups. The control of cation-binding ability of calixarenes has been the subject of more recent investigations. The focus has been on the introduction of donor groups onto the calixarenes framework for controlling their complexation phenomena. The calixarenes structure itself can behave as a soft donor group through its phenyl group  $\pi$  electrons, and this has been demonstrated by the inclusion of silver and thallium(I) cations to some calix[4]arene derivatives [21, 22].

We have recently synthesized a new calix[4]arene, 5,11,17-tris(tert-butyl)-23 amino-25,26,27,28-tetrapropoxycalix[4]arene (L) for complexation framework study with alkali and alkali earth cations, Fig. 1. The four functionality ligating groups in the lower rim as well as in



**Fig. 1.** The structure of 5,11,17-tris(tert-butyl)-23-amino-25,26,27,28-tetrapropoxycalix[4]arene.

the upper rim of the ligands are independently modified to increase their binding abilities and make them more specific for chelating by the metal ions. In this work, synthesis of the amino calix[4]arene is reported and its formation constant by the alkali and alkali earth cation complexes is determined in methanol-chloroform mixture (30/70 by volume) at 25°C, using spectrophotometric technique. The selectivity of the alkali and alkali earth cations towards the ligands is specified and discussed.

## EXPERIMENTAL SECTION

### Chemicals

Parent calix[4]arene was obtained from Aldrich and used without further purification. The ligand was synthesized following the procedure described below. The solvents, methanol and chloroform (from Merck, p.a.), were used without further purification. LiCl, NaCl, KCl, MgCl<sub>2</sub>, CaCl<sub>2</sub> and BaCl<sub>2</sub> from Merck, p.a., RbCl and SrCl<sub>2</sub> from Fluka, Purum. The alkali and alkali earth cation sources were dried under vacuum at room temperature at least 72 hours before use.

**Synthesis of the ligand:** 1.5 g (1.86 mmol) of 5,11,17-tris-tert-butyl-23-nitro-25,26,27,28-tetrapropoxycalix[4]arene was suspended in 50 mL methanol and then catalytic amount of rany nickel was added drop wise in 1.5 minutes. The mixture was heated under reflux condition for 1 hour, and then the solvent was removed by filtration. The crude was crystallized in methanol-dichloro methane to yield a 92% product: mp. 185–187°C,  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3424, 3364, 1511, 1445, 1218;  $\delta$ H (400 MHz; Cycle 3) 0.79 [9H, s, C(CH<sub>3</sub>)<sub>3</sub>], 0.90 [6H, t, CH<sub>3</sub>], 1.04 [3H, t, CH<sub>3</sub>], 1.09 [3H, t, CH<sub>3</sub>], 1.33 [18H, s, C(CH<sub>3</sub>)<sub>3</sub>], 1.93 [4H, m, CH<sub>2</sub>], 2.2 [2H, m, CH<sub>2</sub>], 3.19, 4.34 [4H, d, of d, j 12.6 Hz, ArCH<sub>2</sub>Ar], 3.75 [2H, t, OCH<sub>2</sub>], 3.81 [4H, t, OCH<sub>2</sub>], 3.39, 4.31 [4H, d, of d, j

13.9, ArCH<sub>2</sub>Ar], 6.45 [2H, d, j 2.3 Hz, ArH], 6.60 [2H, d, j 2.3 Hz, ArH], 7.16 [2H, s, ArH], 7.22 [1H, s, OH], 8.06 [2H, s, ArH];  $\delta$ C (100 MHz) 9.91, 10.79, 10.85, 23.07, 23.44, 23.60, 31.03, 31.17, 31.29, 31.78, 33.53, 34.05, 76.53, 77.09, 77.38, 114.85, 124.56, 125.28, 125.76, 132.35, 133.93, 135.38, 135.94, 136.17, 139.87, 144.35, 148.77, 153.11, 155.07; M/Z (FD) 776 (m<sup>+</sup>, 100 %).

### Measurements

Absorption spectra, 270–310 nm, were measured on Shimadzu 1201 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 deviations from the average are shown in the text and Tables.

**Table 1.** Average values of log *K* at different wavelengths for the alkali cations at 25°C

Metal ion	log <i>K</i>
Li <sup>+</sup>	3.95 ± 0.04
Na <sup>+</sup>	3.54 ± 0.05
K <sup>+</sup>	3.52 ± 0.02
Rb <sup>+</sup>	3.49 ± 0.03
Cs <sup>+</sup>	3.46 ± 0.05

**Table 2.** Average values of  $\log K$  at different wavelengths for the alkali earth cations at 25°C

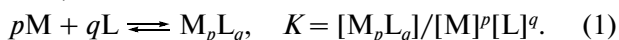
Metal ion	$\log K$
Mg <sup>2+</sup>	4.96 ± 0.04
Ca <sup>2+</sup>	4.49 ± 0.03
Sr <sup>2+</sup>	3.71 ± 0.05
Ba <sup>2+</sup>	3.19 ± 0.04

### Procedure

2 mL solution of the ligand ( $2.0 \times 10^{-4}$ – $2.5 \times 10^{-4}$  mol dm<sup>-3</sup>) were titrated with stepwise addition of an alkali or alkali earth cation solution ( $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>), all in the same solvent (methanol-chloroform 30 : 70 by volume). The UV-Vis spectra of the mixtures undergo small changes at 270–310 nm, but the measured absorbances were sufficient to allow the treatment of the data with the computer program.

## RESULTS AND DISCUSSION

Assuming that the absorbance of each ligand would change upon complexation with an alkali or an alkali earth 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,  $K$ , Eq. 1 is defined,



Determination of the formation constant was employed using the method mentioned before [23–25]. Absorbance,  $A$ , was measured by successive addition of an alkali or alkali earth metal ion solution to the ligand solution, see experimental section. The absorption bands of the ligand decrease upon addition of the metal ion solution in all cases. Treatment of the spectrophotometric data (270–310 nm with an interval of 1 nm) obtained during the titrations were conducted with the computer program Squad [26, 27].

The stoichiometric formation constants were computed from the data using the computer program. The number of experimental points were more than 30 (maximum 40) for each titration. In the computer program, if we designate  $m$  absorption spectra that will be measured at  $n$  wavelengths, the individual absorbance readings thus can be arranged in a  $m \times n$  matrix  $\mathbf{R}$ ; the  $m$  spectra form the rows of  $\mathbf{R}$  and the columns consist of the  $n$  response curves gathered at the different wavelengths. According to Beer's law, for a system with  $N$  absorbing components,  $\mathbf{R}$  can be decomposed into the product of a concentra-

tion matrix  $\mathbf{C}$  ( $m \times N$ ) and a matrix of the molar absorptivities  $\mathbf{S}$  ( $N \times n$ ). However, because of the inherent noise in the measured data, the decomposition does not represent  $\mathbf{R}$  exactly. The matrix  $\mathbf{T}$  of the residuals is given by the difference between  $\mathbf{CS}$  and  $\mathbf{R}$

$$\mathbf{T} = \mathbf{CS} - \mathbf{R}. \quad (2)$$

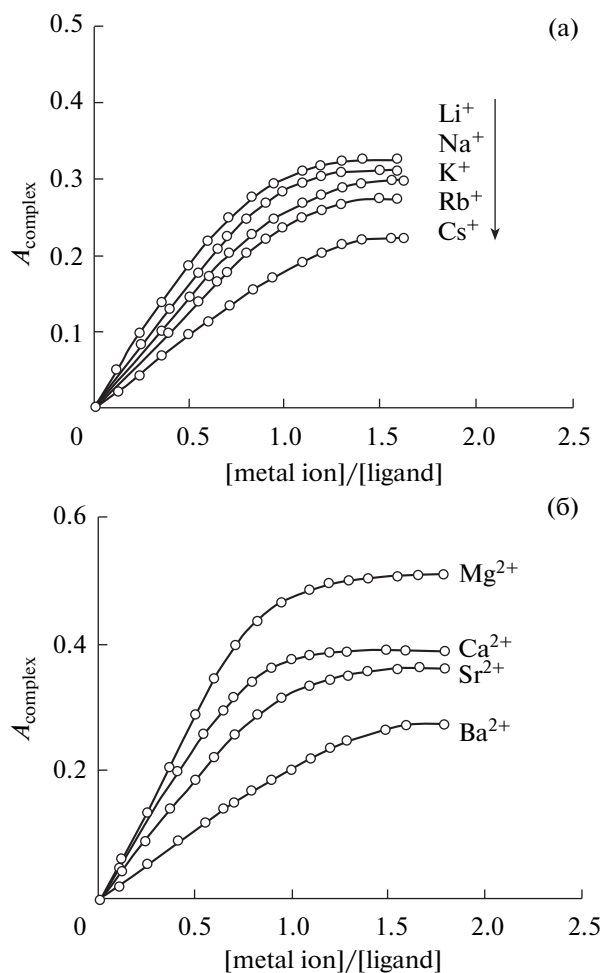
In the fitting procedure, those matrices  $\mathbf{C}$  and  $\mathbf{S}$  are determined which best represent the original matrix  $\mathbf{R}$ . The task of the fitting procedure is to optimize the matrix  $\mathbf{T}$  of the residuals, Eq. 2, according to the least-squares criterion. In Eq. 3,  $U$  is the sum of the squares of all elements of  $\mathbf{T}$ . It is the task of the nonlinear least-squares fitting to find the set of parameters that result in a minimum of  $U$ .

$$U = \sum_{i=1}^m \sum_{j=1}^n \mathbf{T}(i, j)^2 = \text{minimize}. \quad (3)$$

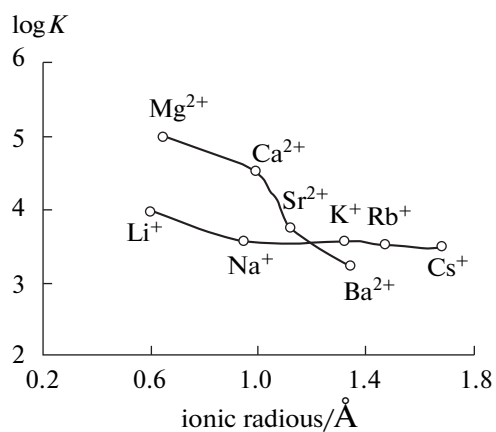
All proposed species existed in significant concentration were checked over a reasonable range of data. As expected, polynuclear complexes were systematically rejected by the computer program. Taking into account a binuclear complex alone or together with the mononuclear one does not improve the goodness 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 all systems. The average formation constant values of the 1 : 1 complex species of the ligand with alkali and alkali earth cations in the specified wavelengths are listed in Table 1 and 2.

The interesting curves resulting from the spectrophotometric titration of  $L$  with alkali and alkali earth cations are shown in Fig. 2. Figure 2 shows a break point when the concentration of metal ion to the ligand ratios reaches unity, indicating the formation of 1 : 1 complexes of the ligand with all alkali and alkali earth cations. Fig. 2a shows the spectrophotometric titration curves for the alkali cations that are in a continuous variation of the absorbance increment with the concentration ratios. This behavior indicates a relatively stable complex for Li<sup>+</sup> and less stable species for the other alkali cations. In this case the extrapolating of the slopes at high and low metal ion to the ligand ratios correspond to 1 : 1 complex stoichiometry in the point of intersections. This behavior is more evident in Cs<sup>+</sup>-L system. In Fig. 2b a sharp break point can be observed for Mg<sup>2+</sup> and Ca<sup>2+</sup> when the concentration of the metal ion to the ligand ratios reaches unity, indicating stable complex species. However, this behavior has not seen for Sr<sup>2+</sup> and Ba<sup>2+</sup>, due to their less stable complexes with ligand.

The ligand forms complexes with alkali and alkali earth metal ions, but show different affinities for the small and the large cations. Figure 3 gives the formation of alkali and alkali earth complexes with the ligand as a function of the radius of the cations. It appears that the formation constant values of the complexes increase with decreasing the ionic radius of the cations. The binding selectivity of the ligands towards the alkali cations based on the formation constant values of the complexes is in



**Fig. 2.** Spectrophotometric titration plots of the ligand L by the metal ions  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  (a) and by the metal ions  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  (b) at  $25^\circ\text{C}$  and 270 nm.



**Fig. 3.** The plots of  $\log K$  versus the ionic radii of the alkali and alkali earth cations at  $25^\circ\text{C}$ .

the order of  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$  and for the alkali earth cations is in the order of  $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ .

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