

Complexation of Calcium and Barium Cations by Calix[4]arene-bis-crown-6

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ABSTRACT

In this study the binding abilities of 1,3-calix[4]biscrown-6 (L) toward Ba²⁺ and Ca²⁺ 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.

Keywords: calix[4]crown; complexation; alkaline-earth cation; stability constant

INTRODUCTION

Calixarene-based molecules [1–4] have received intense attention in the last few years. One of the most important features of these compounds is their diversity. Calixarenes find applications as selective binders and carriers, as analytical sensors, as catalysts and as model structures for biomimetic studies.

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 [5]. 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 using the extraction experiments of the alkali picrates and the measurements of complex stability constants by UV/Vis spectroscopy [6]. These calixcrowns show a preference toward cesium ions as the results obtained in the transport experiments [5].

In this paper we describe the complexive properties of 1,3-alternate calix[4]-bis-crown-6 (Figure 1) towards Ba²⁺ and Ca²⁺ ions in methanol.

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EXPERIMENTAL

Materials: 1,3-Alternate calix[4]-bis-crown-6 were synthesized according to a procedure reported previously [5]. Methanol was used without further purification. The metallic salts were $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck, p.a.) and $\text{Ba}(\text{ClO}_4)_2$ (Ridel-dehean, 98%). 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 [7] as the stepwise addition of an alkaline-earth 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 Me_4NCl . Upon addition of metal the UV/Vis spectrum of the ligand undergoes small changes in the 240-290 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 ($\text{M}^{2+} = \text{Ca}^{2+}$ and Ba^{2+}) and the ligand (L), the equation describing the complexation equilibrium of the cations is as



$$\beta = \frac{[\text{M}_2\text{L}^{4+}]}{[\text{M}^{2+}]^2[\text{L}]}$$

The corresponding stability constant β is then defined as:

The spectra of the solution of L (3×10^{-4} M) containing increasing amounts of metal ion have been recorded between 240-290 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 CaCl_2 . The treatment of the data based on the formation of 1 : 2 complexes using the Specfit program allows to measure the stability constants and molar absorbance of the complex formed (Figures 3 and 4). 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. Table 1 contains the measured stability constants

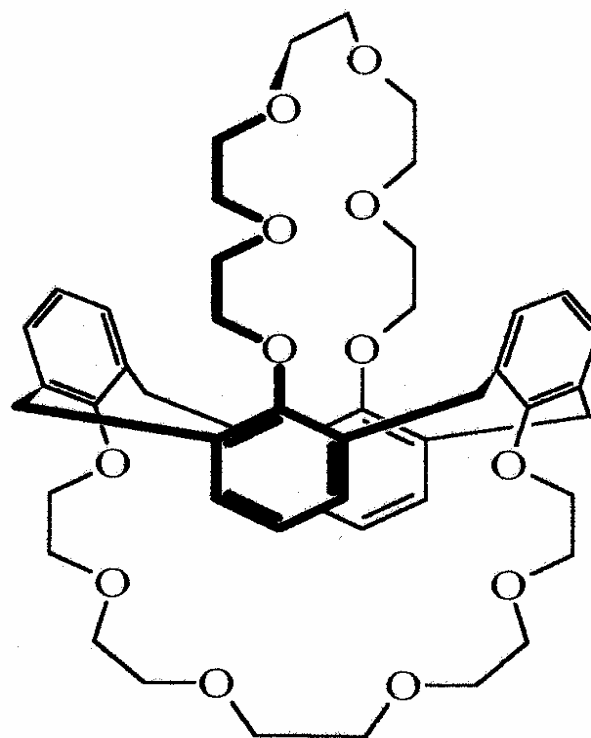


Fig. 1. Structure of 1,3-Alternate calix[4]-bis-crown-6 (L).

Table 1. Logarithm of stability constants ($\log \beta$) in CH_3OH . for the complexation of Calcium and Barium ions by L

Cation	Radii, Å	complex	$\log \beta$
Ca^{2+}	1.00	M_2L	6.1 ± 0.1
Ba^{2+}	1.35	M_2L	5.0 ± 0.4

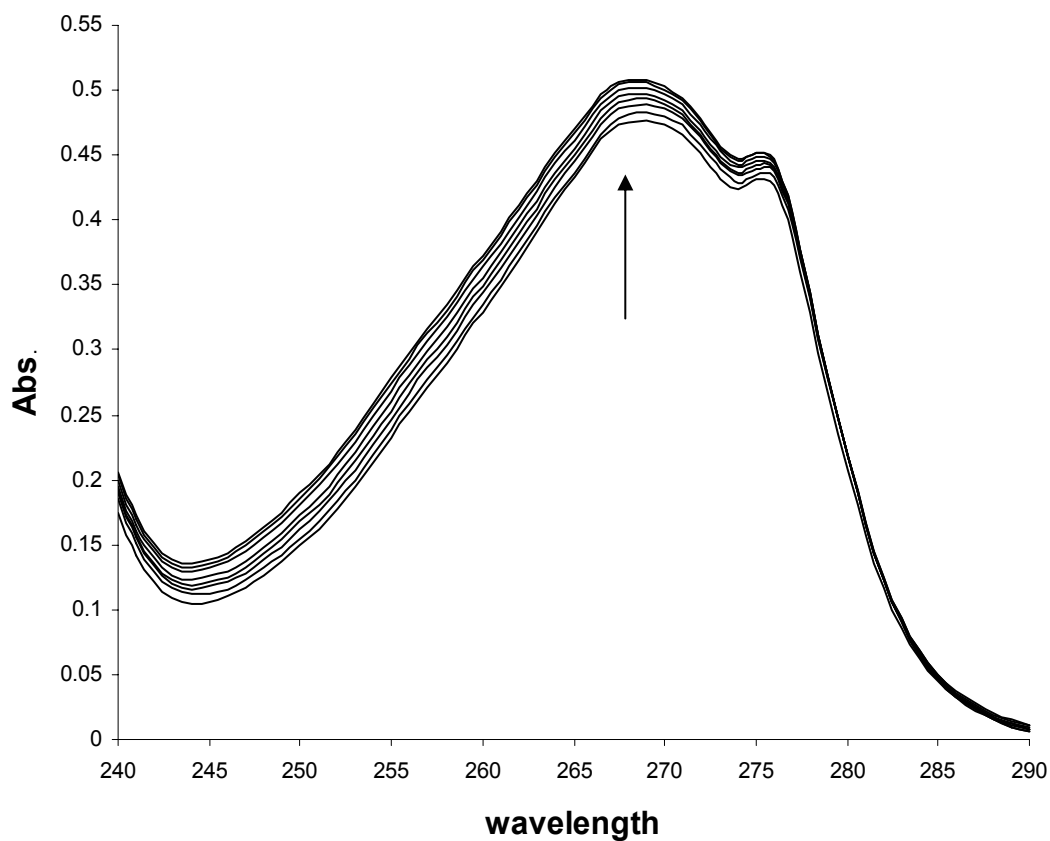


Fig. 2. Change in UV absorption spectrum of a 3×10^{-4} M solution of L in CH_3OH upon addition of CaCl_2 5×10^{-3} at 25°C ($I = 0.01\text{M}$, Me_4NCl), after correction for dilution effects.

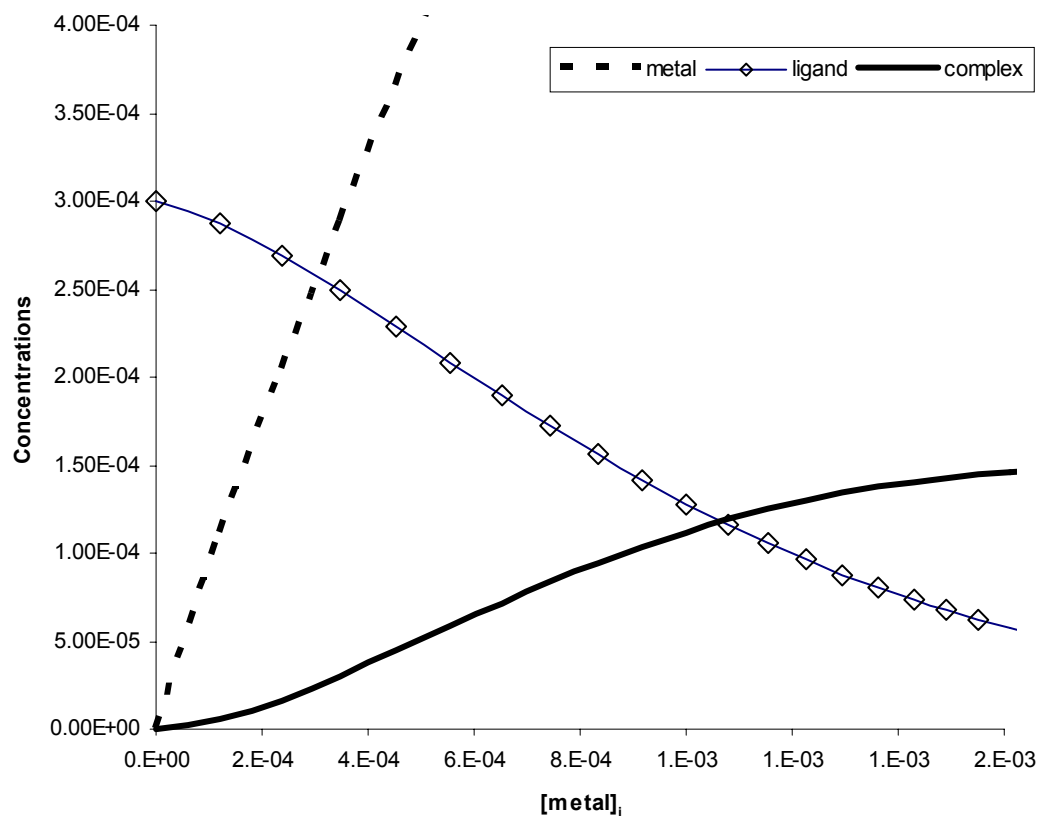


Fig. 3. Concentrations of different species of a 3×10^{-4} M solution of L in CH_3OH upon addition of CaCl_2 5×10^{-3} (at 25°C ($I = 0.01\text{M}$, Me_4NCl)).

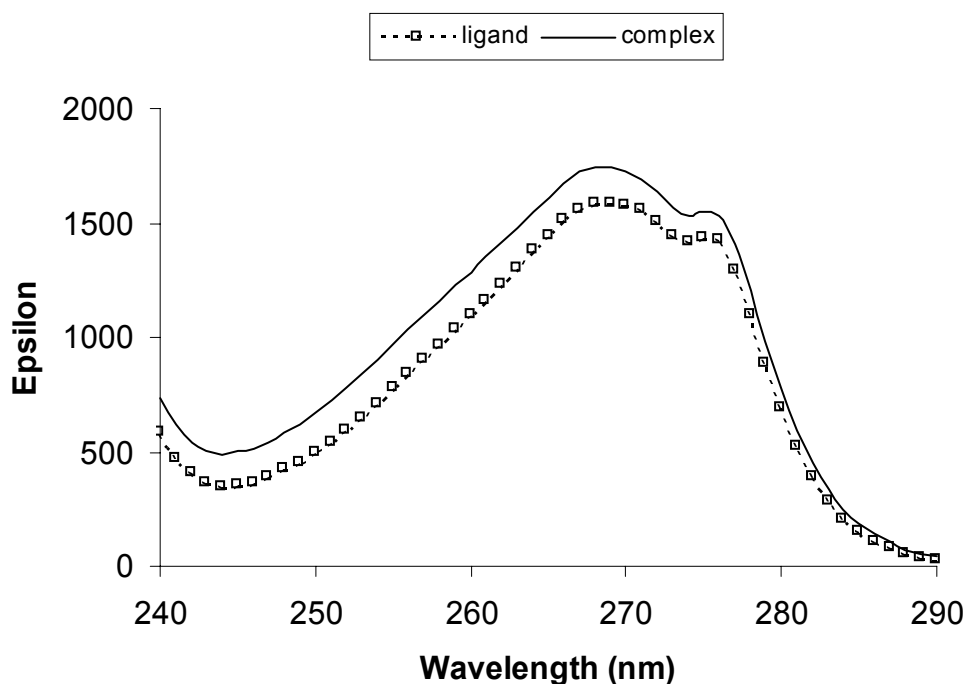


Fig. 4. Molar absorptance of L and formed complex (M_2L) calculated by specifit.

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