Journal of Inclusion Phenomena and Macrocyclic Chemistry **47:** 129–132, 2003.

Alkali Metal Complexation. Binding Properties of *cone* and *partial-cone* Calix[4]arenes Bearing a Mixed (O_2, O'_2) Donor Set (O = Phosphine Oxide; O' = Amide or Ester)

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(Received: 28 January 2003; in final form: 3 October 2003)

Key words: alkali cations, amide, calix[4]arene conformers, phosphine oxide, stability constant

Abstract

The stability constants of alkali metal complexes obtained from the following *O*-substituted calix[4]arenes were determined by UV/Vis spectroscopy in methanol at 20 °C: 5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinoylmethoxy)calix[4]arene (*cone*-**1**), 25,27-*syn*-26,28-*anti*-5,11,17,23-tetra-*tert*-butyl- 25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinoylmethoxy)calix[4]arene (*paco*-**1**), 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxy-26,28-bis(diphenylphosphinoylmethoxy)calix[4]arene (*cone*-**2**) and 25,27-*syn*-26,28-*anti*-5,11,17,23-tetra-*tert*-butyl-25,27- diethoxycarbonylmethoxy-26,28-bis(diphenylphosphinoylmethoxy)calix[4]arene (*paco*-**2**). All ligands form 1:1 complexes with alkali metal cations. The amide-containing calixarenes were found to be more efficient for alkali metal complexation than those bearing ester substituents. While sodium ions are selectively complexed by the two mixed amide-(phosphine oxide) calixarenes, the two ester-containing isomers *cone*-**2** and *paco*-**2** turned out to be selective towards potassium and rubidium ions, respectively. With all four ligands the lowest stability constants were found for the lithium and cesium ions.

Introduction

Chemical modification of the calix[4]arene platform gives access to a wide variety of multifunctional ligands suitable for selective metal ion complexation. In such systems, usually three or four convergent binding sites may act in a synergistic way and thus produce highly selective complexing agents. Many investigations have illustrated that the efficiency of functionalized calix[4]arenes not only depends on the nature of the substitutents anchored onto the macrocyclic platform but also on the calixarene conformation. These studies rely on various experimental techniques such as solvent extraction [1, 2], transport through liquid membranes [3–5], X-ray structural analyses [6–9], UV/Vis and NMR spectroscopy [10–12] as well as also on theoretical molecular dynamic methods [13].

Among the calixarenes that were shown to be particularly effective in metal ion complexation are those in which the substituents contain oxygen donor functions, such as amides [14, 15], esters [16-18] and phosphorylated groups [2, 4, 5, 13]. The high selectivity achieved by such ligands most often arises from the presence of pendant groups that delineate a pseudo-cavity constituted by a large number of oxygen atoms and which perfectly fit the size of a particular ion. This is notably the case for functionalized cone conformers where four pendant groups are oriented in the same direction. Interestingly, most extraction studies dealing with calixarenes have focussed on homo-functionalized ones. We recently investigated the binding properties of calixarenes substituted by a mixed donor set, an amide and a phosphine oxide moiety, and found that hetero-functionalization may markedly alter the binding properties with respect to related homo-functionalized systems [19, 20].

Following our previous studies on mixed ligand systems based on calixarenes [4, 13, 20], we now report on the binding properties of four calixarenes *cone*-**1**, *cone*-**2**, *paco*-**1** and *paco*-**2** (Figure 1) towards alkali ions. For this study stability constants were determined in homogeneous medium (methanol) using UV/Vis spectroscopy.

Experimental

Materials

5, 11, 17, 23-Tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinoylmethoxy)calix[4]-arene (*cone*-**1**), 25,27-*syn*-26,28-*anti*-5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphosphinoylmethoxy)calix[4]arene (*paco*-**1**), 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxy-26,28-bis(diphenylphosphinoylmethoxy)calix[4]arene

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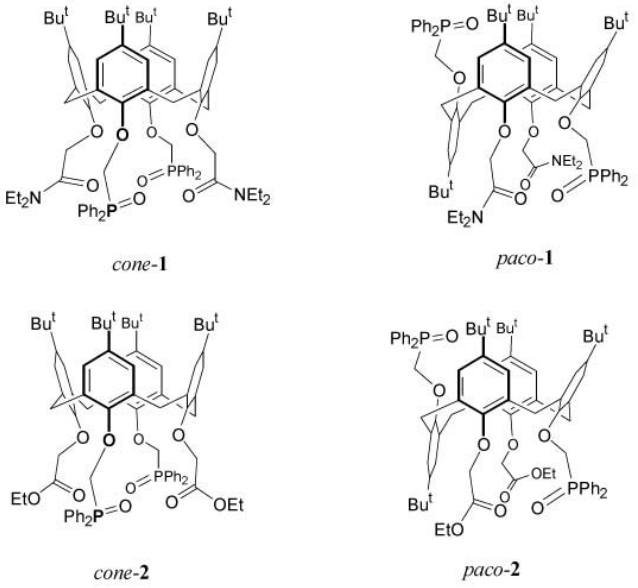

Figure 1. Functionalized calix[4]arenes used in this study.

(*cone*-**2**) and 25,27-*syn*-26,28-*anti*-5,11,17,23-tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxy-26,28-bis(diphenylphosphinoylmethoxy)calix[4]arene (*paco*-**2**) were synthesized according to the procedures reported previously [21, 22]. The metal salts used for this study were $LiBF_4$, $NaClO_4$, $KClO_4$, RbBr and CsCl (Fluka). Methanol (Merck) was used without further purification. The ionic strength was kept constant using Et_4NBr (Fluka). The latter was recrystallized twice from acetone and dried under vacuum before use.

Stability constant measurement

The stability constants were determined by UV/Vis spectroscopy [12]. For each experiment a solution of the appropriate alkali metal cation in methanol (6×10^{-3} M) was added stepwise (using a microsyringe) to a solution of the calixarene in methanol (2×10^{-4} M) until a threefold metal/ligand ratio was reached. The spectra were recorded on a Pharmacia double beam spectrophotometer using a 1 cm quartz cell. The temperature of the titration cell was kept constant at 20.00 ($\pm$0.01)°C by means of thermostated water circulating through a jacket which holds the cell. In all solutions the ionic strength was maintained at 0.01 M using tetraethylammonium bromide. Upon addition of the metal ion containing solution the UV/Vis spectrum of the ligands underwent changes in the range 250–300 nm. These changes were sufficient to allow processing of the data by a curve fitting procedure using the Kinfit program which is based on the Powel algorithm [23].

Results and discussion

The UV/Vis studies were carried out for M = Li^+, Na^+, K^+, Rb^+ and Cs^+. For the present study methanol was used as solvent. For each ligand (L) we found that the absorbance

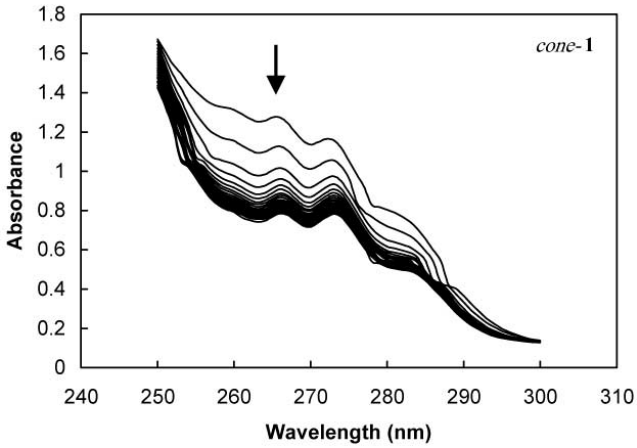

Figure 2. Absorbance variation of a *cone*-**1** solution in methanol (2×10^4 M) upon addition of methanol solution of $NaClO_4$ (6×10^{-3} M) in the presence of Et_4NBr (0.01 M) at 20 °C.

decreases upon addition of a solution containing the metal cation. As a typical example Figure 2 displays the spectral changes in the range 250–300 nm induced by addition of sodium perchlorate solution (6×10^{-3} M in methanol) to the diamide-di(phosphine oxide) *cone*-**1** (2×10^{-4} M).

Assuming a 1:1 stoichiometry for the alkali metal ion complexes formed, the following equation describes the complexation equilibrium:

$$M^+ + L \rightleftharpoons ML^+.$$

The corresponding stability constant is then defined as:

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

Processing of the experimental data using a data fitting computer program (Kinfit) allowed determination of the stability constants of the complexes formed (Table 1). For each ligand the experimental data are consistent with the formation of 1:1 complex. The variation of logarithm of the measured stability constants ($\log \beta$) is presented graphically as a function of the cation radius in Figures 3 and 4.

As can be inferred from the determined stability constants (Table 1), the amide containing calixarenes *cone*-**1** and *paco*-**1** are better alkali ion binders than the ester bearing ligands. The superiority towards alkali metal extraction of amide functions with respect to ester groups has already been demonstrated for other functionalized calixarenes [14].

The present study reveals that the amide containing ligands *cone*-**1** and *paco*-**1** display higher binding properties towards sodium than towards the other alkali metal ions. A similar selectivity had already been observed for conical calix[4]arenes bearing four carbonyl containing substituents of $-CH_2C(O)R$ type (R = NEt_2, OEt, Ph) [14, 15, 17, 18]. On the other hand, with related calixarenes bearing four $-CH_2P(O)R_2$ substituents, no selectivity was found towards Na^+ [4, 24]. Clearly, a good size fit between the sodium ion and the space delineated by the pendant arms involved in binding cannot be the sole reason for the observed binding behaviour of *cone*-**1** and *paco*-**1**. Our results with *cone*-**2**

Table 1. Logarithms of the stability constants (log β) of alkali cation complexes in methanol, ionic strength 0.01 M using Et_4NBr at 20 °C*

	Li^+	Na^+	K^+	Rb^+	Cs^+
cone-**1**	2.88 ± 0.04	4.90 ± 0.20	3.69 ± 0.05	3.02 ± 0.01	2.66 ± 0.03
	(2.6 ± 0.1)	(4.5 ± 0.1)	(3.3 ± 0.1)	(2.8 ± 0.1)	(≤ 1)
paco-**1**	2.64 ± 0.06	4.96 ± 0.33	4.21 ± 0.06	3.71 ± 0.03	2.61 ± 0.07
cone-**2**	2.58 ± 0.03	3.14 ± 0.19	4.21 ± 0.07	2.56 ± 0.05	2.50 ± 0.04
paco-**2**	2.59 ± 0.05	3.04 ± 0.02	3.22 ± 0.01	3.31 ± 0.04	2.56 ± 0.04

*Data in parentheses are given from reference 12.

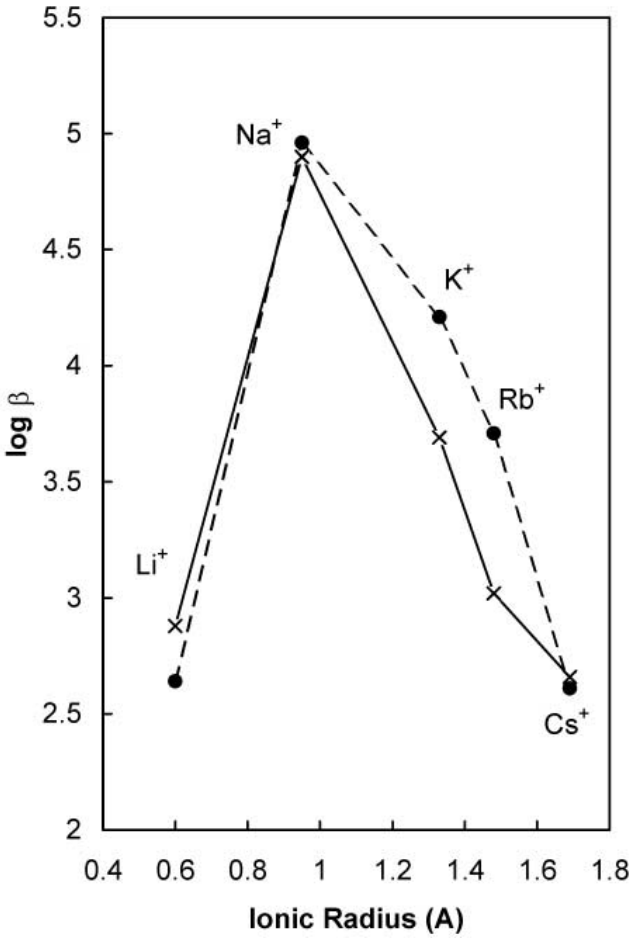

Figure 3. Stability constant variation of the alkali ion complexes obtained from *cone*-**1** (×)and *paco*-**1** (●) as a function of the ionic radius.

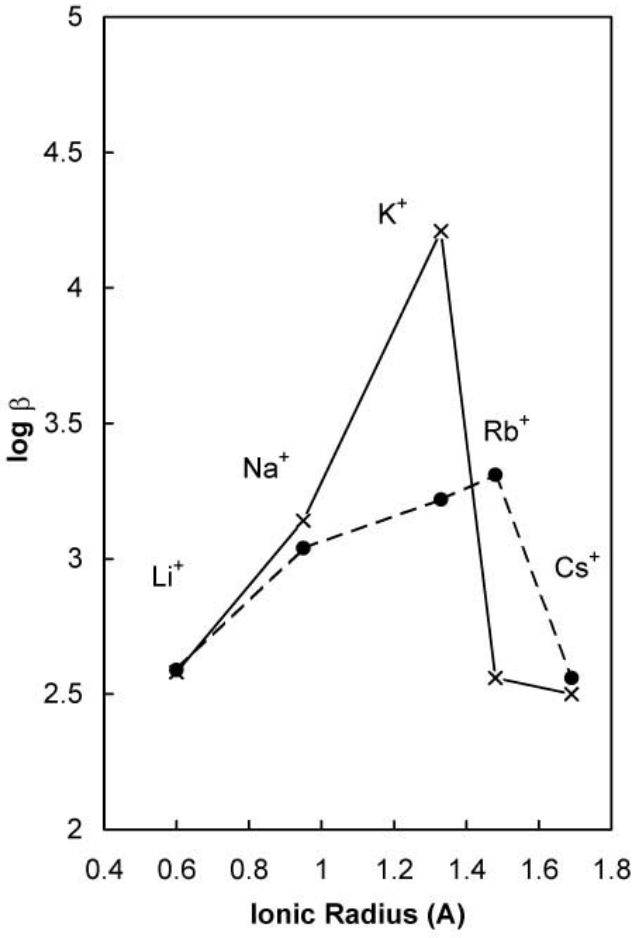

Figure 4. Stability constant variation of the alkali ion complexes obtained from *cone*-**2** (×)and *paco*-**2** (●) as a function of the ionic radius.

and *paco*-**2** confirm this assumption (*vide infra*). It should be mentioned here that Arnaud-Neu *et al.* [12] have recently reported the stability constants of the alkali ion complexes formed with *cone*-**1** in methanol, and of course our findings are in accord with these results (the values reported by these authors are also given for comparison in Table 1). For this ligand, as reported earlier, the lithium selectivity is strongly solvent dependent. Thus for example, when the experiments carried out with *cone*-**1** were performed in tetrahydrofuran instead of methanol, the selectivity was the highest for this ion and decreased regularly on going from lithium to cesium ion [4].

The intra-group selectivity is the same for both ligands, *cone*-**1** and *paco*-**1**, i.e., $Na^+ > K^+ > Rb^+ > Li^+ \approx Cs^+$. Interestingly, for the potassium and rubidium ions the stability constants were found higher with *paco*-**1**. Possibly, through "inversion" of one of the phosphorylated rings the receptor size changes, facilitating complexation of these two specific ions. It must be noted here that phosphoryl groups do not display a high affinity for the larger alkali ions, so that the loss of one P=O donor in the coordination sphere is probably not determining for complex formation. π-Bonding of the anti-oriented aryl ring seems unlikely, but could also be involved.

Replacement of the amide by ester groups induces significant selectivity changes. Thus, *cone*-**2** does no longer display a peak selectivity towards sodium. This ligand shows a marked preference for potassium ions, while *paco*-**2** binds rubidium ions preferentially.

For all four ligands the lowest complex stability was observed with the alkali metal ions at both ends of the series, namely Li^+ and Cs^+. Obviously, the former is too small, the latter too large to fit the size of the complexation domain. Similar observations were already made with other multiply homo-substituted calixarenes [15–18].

Conclusion

The drastic selectivity changes that were observed in this study on modifying the nature of one type of functional substituent and/or the conformation of the calix[4]arene backbone is a further illustration that ion selectivity results from a subtle interplay between geometrical factors (cavity size, steric encumbrance) and the donor properties of the converging binding functions. As inferred from the results obtained with the lithium ion, selectivity may also markedly been affected by changing the solvent. Overall prediction in this area remains a difficult task.

Acknowledgement

The authors thank the Research Council of Zanjan University for financial support.

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