

Complexation of metal ions by ethylester derivative of *p*-tetraphenyl tetrahomodioxacalix[4]arene

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Abstract The binding properties of ethylester derivative of *p*-tetraphenyl tetrahomodioxacalix[4]arenes (**1**) towards alkali, alkaline-earth, transition and heavy metal cations using UV-absorption spectrophotometry and ¹H-NMR spectroscopy are reported.

Keywords Tetrahomodioxacalix[4]arene · C-1,2-alternate · Alkali · Alkaline-earth metals · Transition and heavy metals

Introduction

Due to the variety of properties that calixarenes can assume by appropriate functionalization at the upper or at the lower rim, these compounds are currently a subject of great interest [1–3]. Their inclusion properties towards metal cations, in particular, have been widely explored in the last decade, especially the calix[4]arene derivatives [2–9].

The substituent group, the conformation adopted and the size of the cavity of the derivative are very important factors in the efficiency of the calix[4]arene derivative as host or carrier for a certain guest [4, 10].

As one of the calix[4]arene homologue, homooxacalix[4]arene bearing extra oxygen atoms in the macrocyclic ring has been also interesting to organic chemists because of their conformational flexibility [11–13]. Recently, No

and co-workers [14, 15] described a facile two-step synthesis of *p*-phenyl tetrahomodioxacalix[4]arene by refluxing bishydroxymethylated *p*-phenylphenol in xylene and the solid-state structure of its tetraester derivative (**1**).

As a continuation of our ongoing research on homooxacalix[4]arenes [15–18], we report here our recent results concerning the binding of alkali, alkaline-earth, transition and heavy metal ions by *p*-tetraphenyl tetrahomodioxacalix[4]arene tetraethylester (**1**), blocked in C-1,2-alternate conformation.

The present studies of the binding properties of (**1**) have been established by determination of stability constants in acetonitrile followed by UV-spectrophotometry. The solid-liquid extraction has been followed by ¹H NMR spectroscopy. Comparisons will be pointed out with already known related ligands on the complexation behaviour.

Figure 1 shows the structure of ligand (**1**), its homologue *p*-*tert*-butyltetrahomodioxacalix[4]arene (**2**) [9] in the same conformation, and the tetraethylester *p*-*tert*-butylcalix[4]arene (**3**) [19–21] in the cone conformation.

Experimental: materials and methods

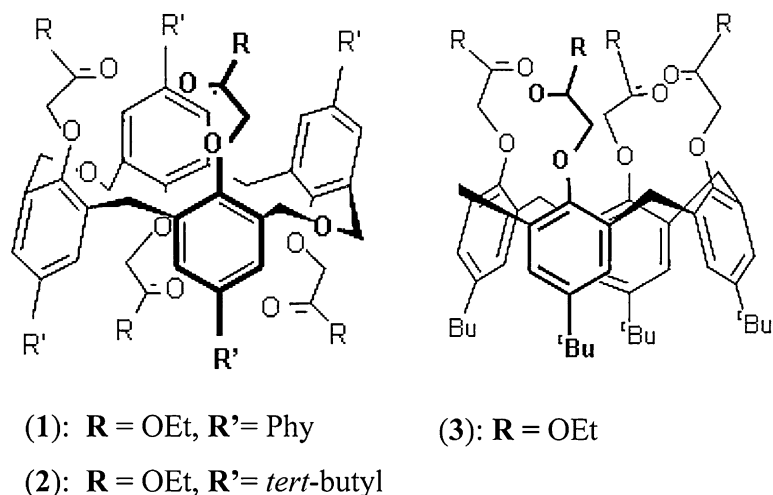
Extraction experiments

The extraction experiments from water into dichloromethane were performed according to the following procedure: 5 mL of 2.5×10^{-4} M aqueous picrate solution and 5 mL of 2.5×10^{-4} M solution of ligand (**1**) in CH₂Cl₂ were mechanically shaken in stoppered glass tube for 3 min, then magnetically stirred in a thermoregulated water bath at 20 ± 0.1 °C for 30 min and finally left standing for a further 30 min in order to obtain good separation of the two phases. The absorbance *A* of the metal

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Fig. 1 Structures of dioxacalix[4]arenes (1) and (2) and calix[4]arene (3)



picrates remaining in the aqueous phase was then determined spectrophotometrically at 355 nm. The extraction percentage, %*E*, are derived from expression $100(A_0 - A)/A_0$, where A_0 is the absorbance of the aqueous solution of a blank experiment without ligand.

Stability constant determination

The stability constants β_{xy} being the concentration ratio $[M_xL_y^{xn+}]/([M^{n+}]^x[L]^y)$ (where M^{n+} = metal ion and L = ligand) were determined in acetonitrile (Riedel-de-Haën, analytical reagent) by UV absorption spectrophotometry at 25 °C and constant ionic strength provided by 0.01 M Et_4NClO_4 (Fluka, purum) or Et_4NNO_3 (Acros) according to the procedure already described [22]. The spectra were recorded on a Perkin Elmer Lambda 11. The ligand concentrations 10^{-5} M and the increasing concentration of metal ion were recorded between 230 and 310 nm. The results data were treated by the program Letagrop-Spefo [23]. The metal salts used were perchlorates or nitrate in acetonitrile: $LiClO_4$, $Ca(ClO_4)_2 \cdot 4H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$ and $Hg(NO_3)_2$ (Fluka, purum), $KClO_4$ and $Ba(ClO_4)_2$ (Prolabo), $NaClO_4$ and $RbClO_4$ (Sigma), $CsClO_4$ and $Sr(ClO_4)_2 \cdot 6H_2O$ (Alfa Aesar), $Zn(ClO_4)_2 \cdot 6H_2O$ and $Pb(ClO_4)_2$ (Johnson Matthey Alfa Products), $AgNO_3$ (Strem Chemicals), $Mg(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ and $Mn(NO_3)_2 \cdot 4H_2O$ (Merck). All these salts were dried under vacuum for at least 24 h before use. The concentrations of the stock solutions of the cations (except alkali cations and Ag^+) were standardized by complexometry using the appropriate coloured indicators [24]. The concentration of the Ag^+ was determined by potentiometry with addition of NaCl.

1H NMR titration experiments

The 1H NMR spectra were recorded on a Bruker SY300 spectrometer. The temperature of the NMR probe was kept constant at 22 °C.

Results and discussion

Extraction studies

The ionophoric properties of ethylester derivative (1) towards metal cations were first evaluated by the standard picrate extraction method [25]. The results concerning alkali cations, expressed as a percentage of cation extracted (%*E*), are reported in Table 1. The corresponding values for (2) and (3) are included for comparison.

The data reveal that the ligand (1), in the C-1,2-alternate conformation, presents generally a low extraction levels for all alkali cations (%*E* ≤ 5.5). However, a slight affinity is observed towards K^+ . The extraction profile is generally similar to one of *p*-*tert*-butyltetrahomodioxacalix[4]arene

Table 1 Percentages of extraction of alkali and alkaline-earth picrates, from water to dichloromethane, at 20 °C

Ligands	% <i>E</i> ^a								
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺
(1)	≤1	1.2	5.5	2.5	3.1	≤1	1.3	≤1	≤1
(2) [9]	2.1	3.0	16.2	16.8	12.6	1.5	1.0	–	1.2
(3) [19, 20, 21]	7.2	29.0	4.7	3.6	5.6	–	4.3	–	5.1

^a Percentage errors: $\pm\sigma_{n-1} = 1$

tetraethylester (2), with a preference to large cations [9]. The substitution of *tert*-butyl group in *para* by a phenyl group seems to decrease the extraction levels for ligand (1), in particular for large cations.

It is noteworthy that cone-shaped calix[4]arene tetraethylester (3) exhibits high extractability for Na^+ because of the hole-size selectivity and the rigid of the ionophoric cavity, but with poor extractability for Pb^{2+} [19–21]. The comparison of its ionophoric properties with those of ligand (1), shows the influence of the presence of the dioxo bridge and the conformation in the extraction profile and in the selectivity (Fig. 2). In fact, in the C-1,2-alternate conformation only six donating sites can surround the cation, compared to the twelve sites in the cone conformation.

In the alkaline earth cation series, a low extraction affinity is observed for ligand (1) and the percentages of extraction can not exceed 1.3% (Table 1). This result is in agreement with literature showing a weak extraction affinity of esters derivatives towards alkaline-earth cations [26]. Low extraction levels were observed with transition and heavy metal cations ($\%E \leq 1$).

Complexation studies

The stability constants β of metal complexes were determined in acetonitrile by UV absorption spectrophotometry. The procedure consisted of adding increasing amounts of metallic perchlorates to a solution of (1). The resulting changes were analysed by the program Letagrop-Spefo [27]. The treatment of spectra variation consisted in establishing the nature of complexes formed in solution and their stability constant. The UV spectra of ligand (1) and its complexes have been recorded between 230 and 310 nm. A maximum of absorption was observed at 257 nm in the ligand spectra. The metal cation complexation is generally manifested by a hypochromic displacement, and the

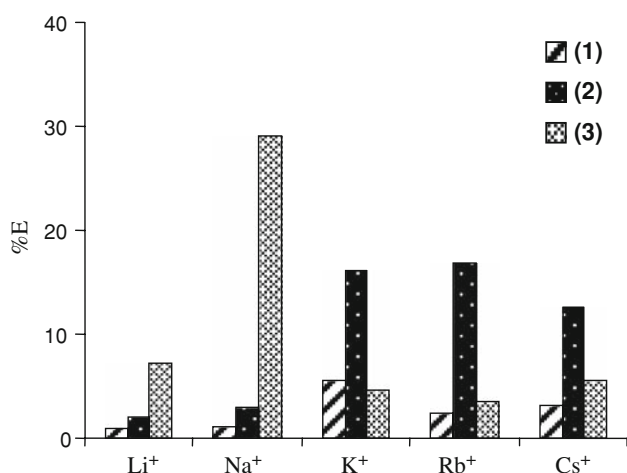


Fig. 2 Extraction profile (%E) of alkali cations by ligands (1)–(3)

complexes spectra are similar to those of ligand. An isobestic points were observed at 255 nm in the case of Ca^{2+} (Fig. 3), Sr^{2+} and Ba^{2+} and at 257 nm in the case of Pb^{2+} . The UV spectra enhance also hypsochrome displacements of $\Delta\lambda = 7$ nm for alkaline earth metal and $\Delta\lambda = 4$ nm for heavy metal. These displacements were following to R ($R = C_M/C_L$) close to 1.

In Table 2, the stability constants of complexes M_2L formed with alkali cations are regrouped.

For the alkali cation series, the stability constants vary between 6.4 and 7.5 logarithmic units, slightly more important for large cations (K^+ , Rb^+ and Cs^+). The stability profile is in agreement with those of extraction ones. The training of the binuclear species may correspond to the presence of the two equivalent coordination sites and opposites in the ring. 2:1 Stoichiometries were not found with ligand (2), only ML complexes were established [9].

Upon the complexation of alkaline-earth cations by the ester derivative (1), ML complexes are formed. Their stability constants, illustrated in Table 3, show significantly enhanced affinities towards Ca^{2+} and Ba^{2+} with selectivities $S_{(\text{Ca}^{2+}/\text{Mg}^{2+})}$ and $S_{(\text{Ba}^{2+}/\text{Mg}^{2+})}$ close to 3.9×10^3 and of 4.9×10^3 , respectively.

It was difficult to compare the stability profile of complexes of two ester derivatives (1) and (2). However, these two ligands have formed a stable complexes with Ca^{2+} et Ba^{2+} , reminding the *p-tert*-butylcalix[6]arene hexaester derivative behaviour, having a better affinity for large cations [26]. The presence of CH_2OCH_2 groups instead of methylene bridges, enlarging the cavity size of (1), allows to have binding properties similar to calixarenes with larger ring [9].

In the case of transition and heavy metal cations, ML complexes were formed as well as with alkaline-earth metal cations. The results are illustrated in Table 4.

The affinity of ligand (1) decreases from Mn^{2+} to Ni^{2+} , enhances for Cu^{2+} and decreases again for Zn^{2+} . This sequence exhibits a selectivity $S_{(\text{Mn}^{2+}/\text{Zn}^{2+})}$ close to 100.

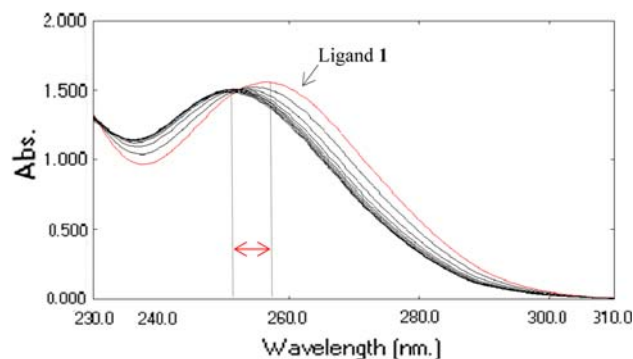


Fig. 3 UV spectra of Ca^{2+} complexation by ligand (1) in acetonitrile, $\theta = 25^\circ\text{C}$, $I = 10^{-2}$ M (Et_4NClO_4), ($C_L = 1.12 \times 10^{-5}$ M, $0 \leq R \leq 82$)

Table 2 Stability constants ($\log \beta_{21}$) of complexes M_2L of alkali cations in acetonitrile, $I = 10^{-2}$ M (Et_4NClO_4) at 25 °C

Ligand	$\log \beta_{21}$				
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
(1)	6.61 ± 0.02	6.40 ± 0.09	7.10 ± 0.03	7.5 ± 0.1	7.10 ± 0.02

Table 3 Stability constants ($\log \beta_{11}$) of complexes ML of alkaline-earth cations in acetonitrile, $I = 10^{-2}$ M (Et_4NClO_4), at 25 °C

Ligands	$\log \beta_{11}$			
	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺
(1)	2.24 ± 0.01	5.30 ± 0.02	3.39 ± 0.06	5.93 ± 0.06
(2)	2.2	>6	–	>6

Although the absence of extraction power, ligand (1) shows significant complexation affinity towards transition metal cations in particular for Mn^{2+} .

The stability constants of ML complexes of heavy metal cations vary between 3.1 and 5.44 logarithmic units and keep almost the same order than those of transition metal complexes. It's important to note the strong affinity of ligand (1) towards Ag^+ . The complexes $[Ag.1]^+$ is 28 and 219 times more stable than those of Cd^{2+} and Hg^{2+} , respectively.

¹H NMR studies

To obtain further information on the extraction of picrate metal cations by ethylester (1), particularly concerning the binding sites, ¹H NMR studies were performed. We have studied the reactions of (1) with hard cations Ca^{2+} , Ba^{2+} and Pb^{2+} . For this purpose $CDCl_3$ solutions of (1) were reacted with the different solid metal picrates, $M^{2+}(Pic^-)_2$. The ratio of extracted cation to ligand in solution was estimated by integration of picrate proton resonances versus those of aromatic protons of the dioxacalixarene unit. On the other hand, the variations of chemical shifts, $\Delta\delta$, of the protons of complexes versus the protons of the free ligand ($\Delta\delta = \delta_{complex} - \delta_{ligand}$) gave us indications on the location of the cation in the cavity of the ligand. Only variations $|\Delta\delta| \geq 0.05$ ppm were considered as significant. Figure 4 shows the ¹H NMR spectra of the free ligand (1) and its Ca^{2+} , Ba^{2+} and Pb^{2+} complexes, recorded at 300 MHz.

Table 4 Stability constants ($\log \beta_{11}$) of complexes ML of transition and heavy metal cations in acetonitrile, $I = 10^{-2}$ M (Et_4NClO_4 or Et_4NNO_3), at 25 °C

Ligand	$\log \beta_{11}$								
	Mn ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺	Ag ⁺
(1)	4.99 ± 0.01	4.3 ± 0.1	3.2 ± 0.2	3.90 ± 0.08	3.00 ± 0.02	4.0 ± 0.1	3.10 ± 0.01	5.0 ± 0.1	5.44 ± 0.08

The structure of ligand (1) was identified by ¹H and ¹³C NMR spectra and elemental analysis by No and co-worker [15]. They reported that (1) in C-1,2-alternate conformation has a pseudo center of symmetry in which two adjacent phenyl rings connected by methylene group are inverted.

The integrations of the picrate proton signals, appears upon the cations extraction by (1), showing evidence the formation of ML complexes in the case of Ca^{2+} and Pb^{2+} cations. This stoichiometry 1:1 is in agreement with the UV spectrophotometry results shown previously in acetonitrile.

In order to locate the cations, we have calculated the variations of chemical shifts, $\Delta\delta$ expressed in ppm, relative to ligand (1) protons and its complex of Ca^{2+} and of Pb^{2+} . Significant variations are illustrated in Table 5.

The ¹H NMR spectrum of ligand (1) in its Ca^{2+} and Pb^{2+} complexes keeps all its peaks, more or less shifted upon complexation. These kinds of variations as well as the conservation of the symmetry of the ligand in its complex suggest the location of these cations respectively in the central cavity of the macrocycle, in interaction with the phenolic oxygen atoms, the carbonyl groups and the oxygen atom of the bridge, as shown on Fig. 4. However, in the case of Ba^{2+} , a closer examination of the spectral changes indicates that the ¹H NMR spectrum is more complex. The mainly modifications are the multiplicity of signals indicating the lost of symmetry of the ligand in its complex and the formation of ML complex. Consequently, an “unsymmetrical” position of the cation in the macrocycle was suggested.

Conclusion

The spectrophotometric study of ethylester derivative (1), in acetonitrile, shows the formation of M_2L species with alkali cations and ML with all other cations. Although the poor affinity of extraction ($\%E \leq 5.5$), the complexant

Fig. 4 ^1H NMR spectra of ligand **(1)** and its complexes $[\text{Ca}(\mathbf{1})]^{2+}$, $[\text{Ba}(\mathbf{1})]^{2+}$ and $[\text{Pb}(\mathbf{1})]^{2+}$, in CDCl_3^*

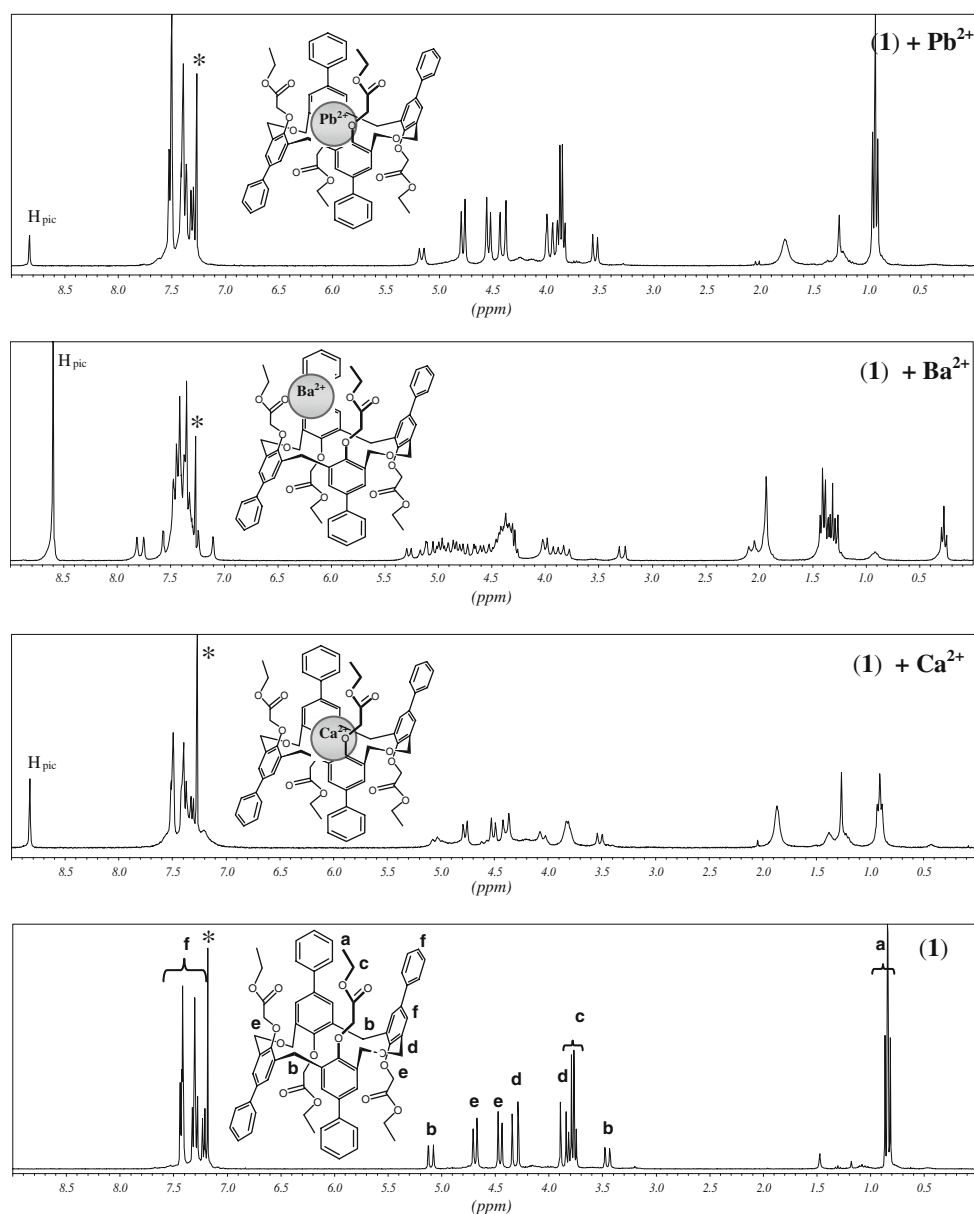


Table 5 Chemical shifts (in ppm) of tetrahomodioxacalix[4]arene tetraethylester (**1**) and its complex of Ca^{2+} and of Pb^{2+} in CDCl_3

	$\Delta\delta(\text{CH}_3)$	$\Delta\delta(\text{ArCH}_2\text{Ar})$	$\Delta\delta(\text{ArCH}_2\text{OCH}_2\text{Ar})$	$\Delta\delta(\text{ArCH}_2\text{Ar})$
$[\text{Ca}(\mathbf{1})]^{2+}$	0.36	-0.13	0.18	0.06
$[\text{Pb}(\mathbf{1})]^{2+}$	-0.04	0.06	0.18	0.06

power is higher with selectivity in favour to large size alkali cations, to Ca^{2+} , Ba^{2+} , Mn^{2+} and to Ag^+ . In other hand, the stability profiles of alkali and alkaline-earth complexes follow those of **(2)**. The presence of CH_2OCH_2 groups in the bridge, increasing the ligand size, gives to this ligand binding properties close to large size calixarenes.

The ^1H NMR study of Ca^{2+} , Ba^{2+} and Pb^{2+} complexation by ligand **(1)** in CDCl_3 exhibits the formation of ML complexes, in agreement with spectrophotometric results. The variations of chemical shift suggest the inclusion of Ca^{2+} and Pb^{2+} in the middle of cavity of ligand which keeps its symmetry, despite of Ba^{2+} which is located in asymmetry manner.

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