ORIGINAL ARTICLE

Interaction between *p*-tetraphenyl tetrahomodioxacalix[4]arene amide derivatives and alkali and alkaline-earth metal cations

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Abstract The binding properties of four amido derivatives of *p*-tetraphenyl tetrahomodioxacalix[4]arene towards alkali and alkaline-earth metal cations using UV-absorption spectrophotometry, ^{1}H NMR and ESI-mass spectrometry techniques are reported.

Keywords Tetrahomodioxacalixarenes ·
Amido derivatives · 1,2-alternate · 1,3-alternate ·
Binding properties · Alkali and alkaline-earth metal cations

Introduction

Due to the variety of properties that can offer the calixarenes 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, have been widely explored in last decade, especially the calix[4]arene derivatives [2–9]. The substituent

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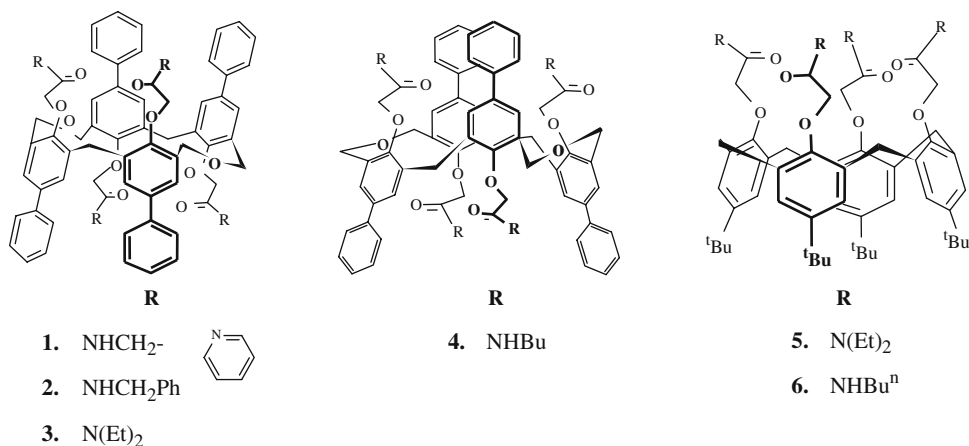e-mail: abidi_rym@yahoo.fr

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groups, the conformation adopted and the size of the cavity of the derivatives are important factors in the efficiency of the calix[4]arene derivative as a host or carrier for a given guest [4, 10].

Among the calix[4]arene derivatives, homooxacalix[4]arenes, bearing extra oxygen atoms in the macrocyclic ring, have been also interest organic chemists because of their conformational flexibility [11–13]. No and co-workers synthesised a series of *p*-tetraphenyl tetrahomodioxacalix[4]arene derivatives containing ester, alkyl and amide functional groups.

We report here our recent results concerning the binding of alkali and alkaline-earth metal ions by *p*-tetraphenyl tetrahomodioxacalix[4]arene amido derivatives differing by the nature of the amide groups at the lower rim: pyridinylamide (**1**), phenylamide (**2**), diethylamide (**3**) and *N*-butylamido (**4**). These ligands were synthesised by No and co-workers. Their extraction properties towards Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Sr^{2+}, Ba^{2+}, NH$_4^+$, Pb^{2+} and Ag$^+$ from water to 1,2-dichloroethane were also studied. They reported that the *p*-tetraphenyl tetrahomodioxacalix[4]arene pyridinamide **1** exhibited a significant affinity, more important than those of the *p*-tetraphenyl tetrahomodioxacalix[4]arene phenylamide **2**, towards all studied cations, in particular for Ag$^+$ (%E = 70.1). They explained these results by the contribution of the nitrogen atom, of pyridine group, in the cation coordination [14]. They reported also that *p*-tetraphenyl tetrahomodioxacalix[4]arene *N*,*N*-diethyl tetraamide **3** selectively encapsulates Pb^{2+} over metal ions in such manner that the lead ion is bound to the carbonyl oxygen atoms of two adjacent amide substituents and to one of aryl–alkyl ether oxygen [15]. Compounds **1–3** are blocked in C-1,2-alternate conformation [14, 16, 17], in contrast to **4** which is maintained in the 1,3 alternate conformation [15]. This last conformation is due to stable

Fig. 1 Structure of studied ligands (1–4) and related calixarenes (5, 6)

R

1. NHCH₂- [pyridine structure]

2. NHCH₂Ph

3. N(Et)₂

4. NHBu

5. N(Et)₂

6. NHBuⁿ

intramolecular hydrogen bonding established between N–H and the facing oxygen atom of the carbonyl C=O groups. This hydrogen bonding will decrease the metal ion complexation ability [18]. No and co-workers reported also that compound 4 gave a low extractability towards Pb^{2+} ion [18, 19].

The present studies of the binding properties have been established by determining the stability constants in acetonitrile and conducted by UV-absorption spectrophotometry and by ESI-mass spectrometry titrations. The solid–liquid extraction has been followed by ¹H-NMR. The data are discussed in the light of those obtained with already known and related ligands 5 and 6 containing diethylamide and N-butylamide, respectively, blocked in cone conformation. Figure 1 illustrates the structure of our ligands and the related calixarenes.

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 5 in CH_2Cl_2 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 picrates remaining in the aqueous phase was then determined spectrophotometrically at 355 nm. The percentage extraction, %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 $[M_x L_y^{xn+}]/([M^{n+}]^x[L]^y)$ (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 [20]. 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 220 and 320 nm. The results data were treated by programs Letagrop-Spefo [21]. The metal salts used were perchlorates or nitrate in acetonitrile: $LiClO_4$ and $Ca(ClO_4)_2 \cdot 4H_2O$ (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), $Mg(NO_3)_2 \cdot 6H_2O$ (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) were standardized by complexometry using the appropriate coloured indicators [22].

ESI-mass spectrometry experiments

Stock solutions of the ligand (3×10^{-6}) and the metal salts were prepared in acetonitrile and mixed in the given ratios (0.5, 1, 2 and 10) and immediately analyzed with the ESI-TOF (electrospray ionization time of flight) mass spectrometer.

High-resolution ESI mass spectra in positive mode were acquired on a time of flight mass spectrometer (microTof, Bruker Daltonics, Bremen, Germany). The instrument was calibrated using multiprotonated ions from horse heart myoglobin. The ESI-source was heated to 200 °C. Sample cone voltage (capillary exit) was varied from 60 to 160 V.

Sample solutions were introduced into the mass spectrometer source with a syringe pump (Cole Parmer, Vernon

Hills, Illinois, USA) with a flow rate of 5 μL/min. Scanning was performed on a m/z range from 100 to 3,000, data was averaged for 1 min and then smoothed using the Gaussian algorithm.

Proton NMR titration experiments

The ^{1}H 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 and complexation of alkali metal cations

UV-spectrophotometric study

The binding properties of amides derivatives **1–4** towards metal cations, from water into dichloromethane, were first evaluated by the standard picrate extraction method [23]. The results concerning alkali cations expressed as a percentage of cation extracted (%E), are reported in Table 1 and illustrated in Fig. 2.

The ligands **1**, **2** and **4**, present generally weak percentages of extraction ($1 \leq \%E \leq 3.5$). The ligand **4** exhibit an extraction power comparable to its homologue the *p-tert*-butylcalix[4]arene tetra-*n*-butylamide **6**, in cone conformation ($0 \leq \%E_6 \leq 5.2$). All this ligands bring secondary amide function groups which present a weak extraction power as observed previously by other authors [20, 24, 25].

However, ligand **3**, carrying tertiary amides functions at the lower rim, is a perfect extractant of these cations, namely Li$^+$, Na$^+$ and K$^+$. Although, its extraction power

Table 1 Percentages of alkali picrates extraction, from water to dichloromethane by ligands **1–4** at 20 °C, and stability constants of alkali cations complexes (log β_{xy}) in acetonitrile, I = 10^{-2} M (Et$_4$NClO$_4$) at 25 °C

Ligands		Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
1	%E^a	2.9	≤ 1	3.0	1.1	3.3
	log β_{21}^b	7.5	8.2	8.8	7.8	7.8
2	%E^a	1.1	1.2	3.3	3.5	1.1
	log β_{21}^b	6.3	6.5	6.6	7.1	7.1
3	%E^a	37.6	37.2	40.0	15.0	7.9
	log β_{11}^b	6.7	6.2	6.3	5.8	4.9
4	%E^a	≤ 1	≤ 1	≤ 1	≤ 1	3.4
	log β_{21}^b	7.7	8.0	8.5	7.5	7.8

^{a} Percentages error: $\pm\sigma_{N-1} = 1$
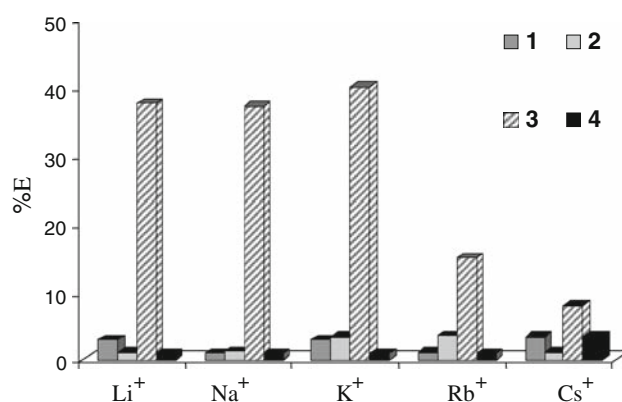
^{b} $0.01 \leq \sigma_{N-1} \leq 0.2$

Fig. 2 Extraction profile (%E) of alkali cations by ligands **1–4**

stay weak than its homologue, the *p-tert*-butylcalix[4]arene tetradiethylamide **5**, in cone conformation ($12 \leq \%E(5) \leq 95.5$). This can be explained by its conformation 1,2-alternate and by the presence of two bridges CH$_2$OCH$_2$ leading to a wider cavity.

The complexation of alkali cations by the amido derivatives followed by UV spectroscopy manifest generally a hypochromic displacement. In the case of ligand **3**, the spectral variations are accompanied by an hypsochrome displacement ($\Delta\lambda = 3$ nm) until a ratio R close to 1 and in the same time by an isobestic point which appears at 255 nm in the case of cations Li$^+$, Na$^+$, K$^+$ and Rb$^+$ (Fig. 3).

The stability constants log β_{xy} determined in acetonitrile for alkali metal series are collected in Table 1. The complexes formed are M$_2$L for the secondary amides **1**, **2** and **4** and ML for the tertiary amide **3**. Figure 4a shows the stability profiles of M$_2$L complexes. A similar profile is observed for ligands **1** and **4** despite their difference in conformation and substituents, with notable selectivity towards K$^+$ (S$_{K/Li}^{++} = 20$ for **1** and S$_{K/Rb}^{++} = 10$ for **4**). Though their structures are similar, the stability of the complexes with ligand **2** is lower than that of ligand **1**, particularly for Li$^+$, Na$^+$ and K$^+$. The presence of the nitrogen atoms as donor sites in pyridine can explain this behaviour. Otherwise no significant selectivity is observed in the case of ligand **2**.

The affinity of the tertiary amide derivative **3** is higher towards little size cations namely for Li$^+$ (S$_{Li/Cs}^{++} \approx 70$). This behaviour remind us the calix[4]arene diethylamide **5** one, in cone conformation. The stability of its complexes of Li$^+$, Na$^+$ and K$^+$ exceed 8.5 logarithmic units (Fig. 4b) [26].

ESI–MS study

In order to check the stoichiometry, a titration of some ligands has been carried out by mass spectrometry.

Fig. 3 UV spectra of Rb$^+$ complexation by ligand **3** in acetonitrile, $\theta = 25$ °C, I = 10^{-2} M (Et$_4$NClO$_4$) (C$_L$ = 1.51 × 10^{-5} M, $0 \leq R \leq 2$)
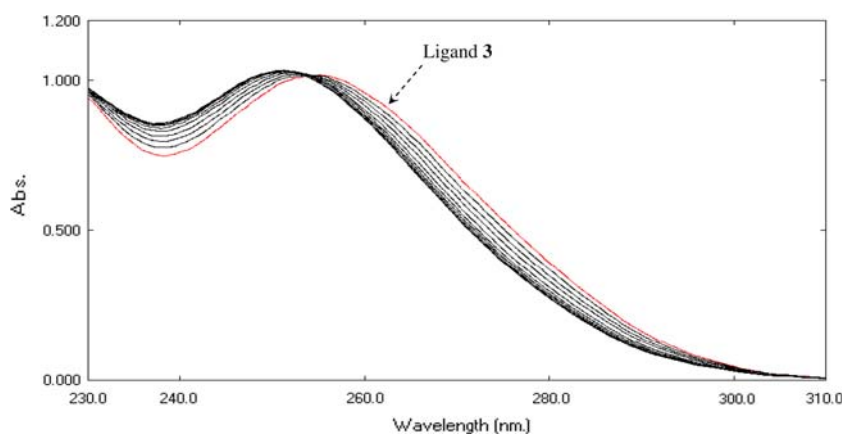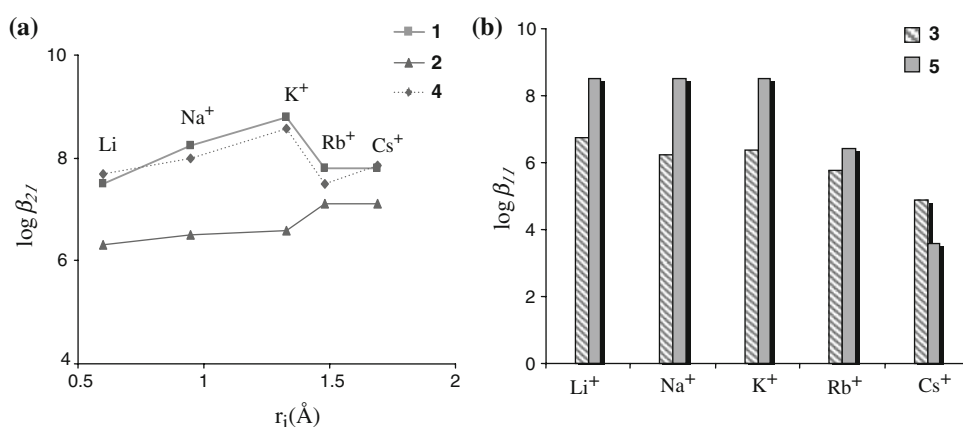

Fig. 4 Stability profiles of complexes M$_2$L of ligands **1**, **2** and **4** (**a**) and ML of ligands **3** and **5** (**b**) in the series of alkali cations, in acetonitrile

Complexation of Rb$^+$ by phenylamide derivative 2 The ESI–MS spectra of ligand **2** shows several peaks corresponding to NH$_4^+$, Na$^+$ and K$^+$ complexes already present as impurities in materials, as shown in Fig. 5. The titration by Rb$^+$ makes in evidence the formation of M$_2$L complex at 774.28, present as 15% and ML complex, major upon R equal to 1, at 1,463.1 m/z. However, the peak relative to the complex [Na.**2**]$^+$ kept the same intensity as the complex [Rb.**2**]$^+$. The weak intensity of the peak of the complex [Rb$_2$.**2**]$^{2+}$, observed from one equivalent of Rb$^+$, can be explained by the lost of the second cation upon the bombardment of the sample. In fact, the electricity voltage of the cone was 40 V, generating collisions with the molecules of nitrogen in the mass spectrometer and can cause the dissociation of the non-covalent complex.

Complexation of K$^+$ by n-butylamide derivative 4 The complexation of K$^+$ by ligand **4** (Fig. 6) shows the formation of binuclear complexes [K$_2$.**4**]$^{2+}$ at 659.7 m/z, [K.Na.**4**]$^{2+}$ at 651.7 m/z and mononuclear complexes [K.**4**]$^+$ at 1,280.5 m/z, [K.H.**4**]$^{2+}$ at 640.7 m/z.

At the ratio of 1, complexes [K.**4**]$^+$ and [K$_2$.**4**]$^{2+}$ appear. Upon addition of K$^+$, the intensity of the peaks relatives to
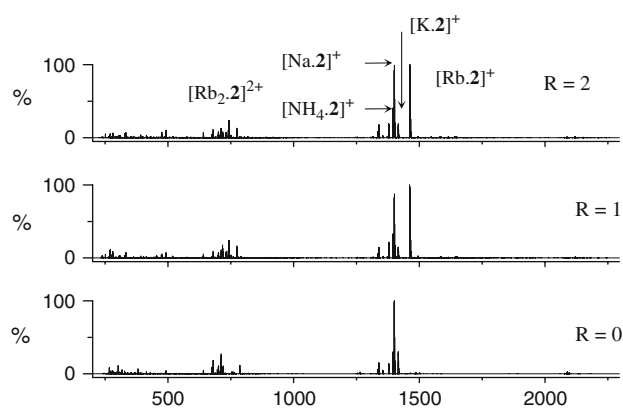

Fig. 5 ESI–MS spectra (40 V) relative to the complexation of Rb$^+$ by **2** in acetonitrile, R = 0, 1, 2

the K$^+$ complexes increase to the detriment of the [Na.**4**]$^+$ one. At 10 equivalents, the peaks of [Na.**4**]$^+$ and [K.**4**]$^+$ have the same intensity, which suggest an affinity comparable of the ligand towards Na$^+$ and K$^+$. In other hand, these results show the ability of the ligand **4** to form a binuclear species with the same or two different cations.
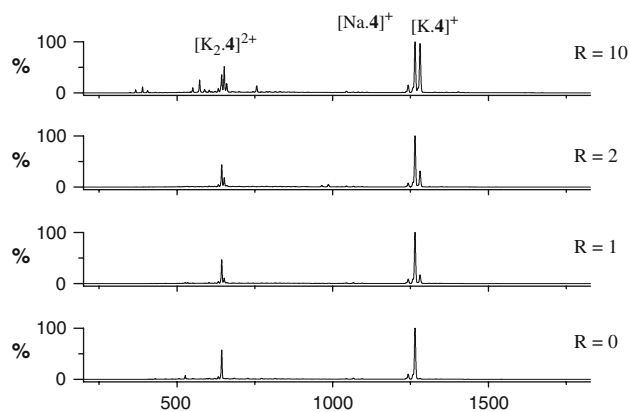
Fig. 6 ESI–MS spectra (40 V) relative to the complexation of K^+ by **4** in acetonitrile, R = 0, 1, 2, 10

Extraction and complexation of alkaline-earth metal cations

UV-spectrophotometric study

The percentages of extraction of alkaline-earth picrates cations by amido derivatives **1–4** are illustrated in Table 2, as well as the stoichiometry and stability constants of formed complexes. As shown in Table 2, ligands **1–2** and **4** are weak extractant (%E ≤ 1). However, the tertiary amide **3** exhibits an important extraction power towards Ca^{2+}, Sr^{2+} and Ba^{2+}. Its extraction profile is similar to the *p-tert*-butylcalix[4]arene tetradiethylamide **5** one, despite the difference of their conformation and the presence of the two oxa bridges in ligand **3** (Fig. 7a) [20].

The amide derivative **3** presents selectivity towards Sr^{2+} and Ba^{2+}. However, its homologue **5** exhibits selectivity

Table 2 Percentages of extraction of alkaline-earth picrates, from water to dichloromethane by ligands **1–4** at 20 °C, and stability constants of alkaline-earth cations complexes (log β_{xy}) in acetonitrile, I = 10^{-2} M (Et$_4$NClO$_4$) at 25 °C

Ligands		Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
1	%E[a]	≤1	≤1	≤1	≤1
	log β_{11}[b]	3.8	4.8	3.8	4.7
2	%E[a]	≤1	≤1	≤1	≤1
	log K_{11}[b]	3.4	–	4.6	3.8
	log β_{21}[b]	–	6.5	8.2	–
3	%E[a]	5.6	85.4	94.7	96.3
	log β_{11}[b]	6.2	4.3	5.2	7.7
4	%E[a]	≤1	≤1	≤1	≤1
	log K_{11}[b]	–	–	4.4	4.3
	log β_{21}[b]	6.5	8.9	7.6	–

[a] Percentages error: $\pm\sigma_{N-1} = 1$

[b] $0.01 \leq \sigma_{N-1} \leq 0.2$

towards Ca^{2+}. The cation Mg^{2+} is the less extracted cation by the two ligands.

The complexation of alkaline-earth cations by ligands **1** and **3** leads to the formation of complex with 1:1 stoichiometry. On the other hand, the phenylamide **2** and the *n*-butylamide **4** form species with various stoichiometries depending on the cation. In fact, and for Mg^{2+}/**2**, Ba^{2+}/**2** and Ba^{2+}/**4** systems, ML species are formed, while 2:1 species appear during the complexation of Ca^{2+} by ligand **2** and Mg^{2+} and Ca^{2+} by **4**. With these later ligands, two complexes, ML and M$_2$L, were formed simultaneous in the presence of Sr^{2+}. The stability constants, log K_{21}, relative to the formation of M$_2$L from ML are equal to 3.6 and 3.2 logarithmic units for ligands **2** and **4**, respectively. The log K_{21} values are lower than those of log K_{11}, showing up the absence of a cooperative effect for the M$_2$L complex formation.

It is noteworthy that the nature of species formed in the case of ligand **4** depends on the cation size. In fact, this ligand form M$_2$L complex with the less bulky cations, presents selectivity towards Ca^{2+}. For Sr^{2+}, two complexes 1:1 and 2:1 co-exist, and for the largest cation Ba^{2+} only 1:1 complex was formed.

The Fig. 7b presents the stability profiles of mononuclear complexation of **1**, **3** and **4** derivatives. Except for Ca^{2+}, the complexes formed by the diethylamide derivative **3** with alkaline-earth cations, are more stable than those obtained by ligand **1**. Significant selectivity have been noted towards Mg^{2+} and Ba^{2+} for **3** ($S_{Mg/Ca}^{2+/2+} = 10^2$; $S_{Ba/Ca}^{2+/2+} = 2.8 \times 10^3$). The complexation of alkaline-earth cations is strongly depends on the nature of substituent and the conformation of the ligand. These results confirm the higher affinities of the tertiary amide than those of secondary amides for cation complexation [25] (Figs. 8, 9).

In general, the affinity of calix[4]arenes amides towards alkaline-earth cations, as known in literature [27], is more important than the ester and ketone derivative. In general, the same conclusion can be given when binding properties of tetrahomodioxacalix[4]arene tetraethylester are compared to those of ligand **3**.

ESI–MS study

Complexation of Sr^{2+} by n-butylamide derivative 4 The follow of the ESI–MS titration of ligand **4** by Sr^{2+}, shows the appearance of a weak signal since the ratio R equal to 2, corresponding to the mononuclear complex [Sr.**4**]$^{2+}$. From R = 10, the signal become clear and intense and those of complex [Na.**4**]$^+$ present previously in the spectra of free ligand disappear.

Complexation of Ba^{2+} by n-butylamide derivative 4 The complexation of Ba^{2+} by ligand **4** reveal a signal which

Fig. 7 Profiles of extraction **a** of alkaline-earth cations by ligands **3** and **5** and of stability **b** of ML complexes of ligands **1**, **3** and **4**
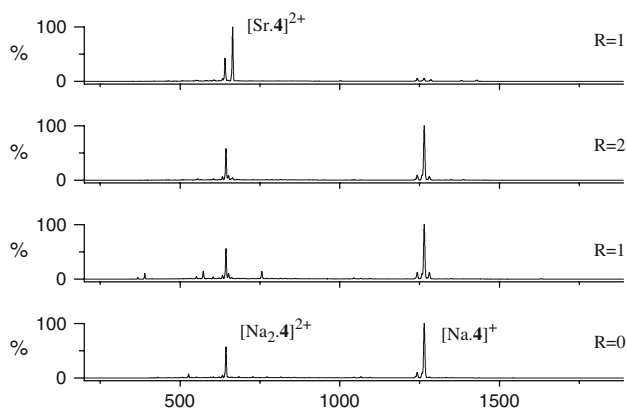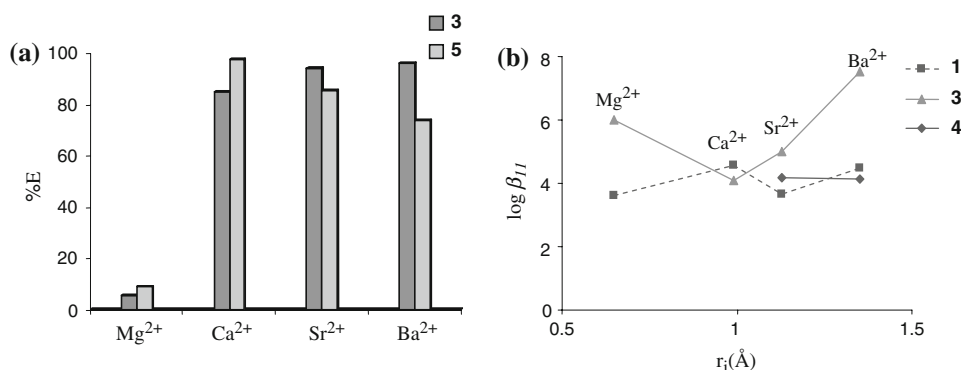

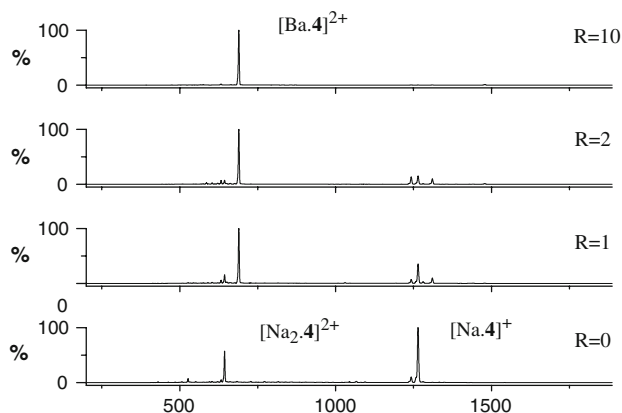**Fig. 8** ESI–MS spectra (40 V) corresponding to the complexation of Sr^{2+} by **4** in acetonitrile, $C_L = 1.52 \times 10^{-5}$ M, R = 0, 1, 2, 10

Fig. 9 ESI–MS spectra (40 V) corresponding to the complexation of Ba^{2+} [Ba.**4**]$^{2+}$ by **4** in acetonitrile, $C_L = 1.52 \times 10^{-5}$ M, R = 0, 1, 2, 10

appear at 689.4 m/z and corresponding to [Ba.**4**]$^{2+}$complex. This signal becomes unique and majority from the ratio these results confirm the formation of 1:1 complexes, found previously by spectrophotometric study in the case of Sr^{2+} and Ba^{2+}. Although, the binuclear complex with Sr^{2+}: [Sr$_2$.**4**]$^{4+}$, can not be identified by ESI–MS.

^{1}H-NMR study

To obtain further information mainly about the position of the cation in the macrocycle, ^{1}H NMR study was performed. This study is based on the picrate extraction by ligand dissolved in CDCl$_3$. The picrate ion, having two protons, appear as peak on the NMR spectra and the ratio of extracted cation by ligand was estimated by the integration of picrate proton resonances versus those of aromatic protons of the dioxacalixarene unit. In other hand, the variations of the chemicals shifts $\Delta\delta$ of the different protons of the ligand ($\Delta\delta = \delta_{complex} - \delta_{ligand}$) up to the complexation, can give us an idea about the location of the cation. In this context, we present as example, the NMR spectra of Ca^{2+}/**3** and Ca^{2+}/**4** systems recorded at 300 MHz in CDCl$_3$.

Complexation of Ca^{2+} by diethylamide derivative 3 On Fig. 10 and Table 3, we present respectively the NMR spectra and chemical shifts $\Delta\delta$ (ppm) of ligand **3** and its Ca^{2+} complex in CDCl$_3$.

The integration of the picrate proton signal makes in evidence the ML complex formation with Ca^{2+}. This result is in agreement with UV-spectrophotometric results conducted in acetonitrile.

The complexation of Ca^{2+} leads to the variations of almost all protons of the ligand. The AB systems, previously superposed in the free ligand spectra, stand out clearly and become more resolved on the complex spectra. The main variations of chemical shifts, observed for ArCH$_2$Ar and CH$_2$OCH$_2$ protons ($\Delta\delta = -0.7$ and -0.27, respectively), suggest the location of the Ca^{2+} cation in the central cavity, in interaction with phenolic oxygen atoms, carbonyles and oxa bridge (Fig. 11).

Complexation of Ca^{2+} by n-butylamide derivative 4 The chemical shifts corresponding to the protons of ligand **4** are collected in the Table 4. The ratio of the integration of picrate proton signal towards those of **4** exhibits the formation of M$_2$L complex. Though, the complexation of

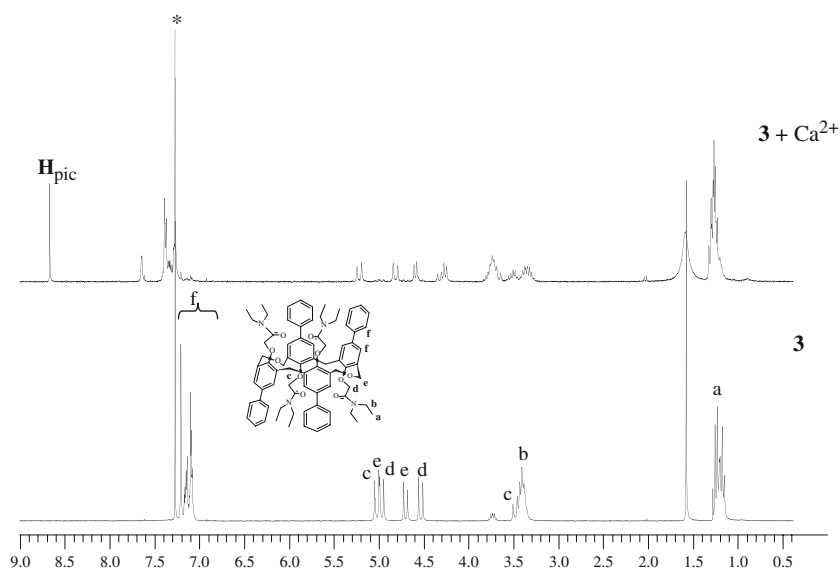**Fig. 10** NMR spectra of ligand **3** and its complex [Ca. **3**]$^{2+}$, in CDCl$_3$

Table 3 Chemical shifts (ppm) of different signals of free ligand **3** and its calcium complex in CDCl$_3$

Type of proton	δ (3)	δ [Ca. 3]$^{2+}$
NCH$_2$**CH$_3$**	1.17	1.25
NCH$_2$**CH$_3$**	1.23	1.26
N**CH$_2$**CH$_3$	3.40	3.73
Ar**CH$_2$**Ar	3.47	3.66
CH$_2$OCH$_2$	4.53	4.26
O**CH$_2$**CON	4.70	4.59
CH$_2$OCH$_2$	4.96	4.81
O**CH$_2$**CON	5.04	5.21
Ar**CH$_2$**Ar	5.02	4.32
H$_{Phy}$	7.08	7.36
Ar**H$_{meta}$**	7.15	7.38
H$_{Phy}$	7.20	7.64

Table 4 Chemical shifts (ppm) of ligand **4** in CDCl$_3$

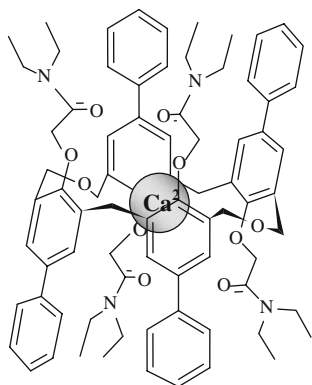| **H$_{corresponding}$**	δ (4)
CH$_3$	0.91
CH$_2$CH$_2$CH$_3$	1.36
NH	1.7
Ar**CH$_2$**Ar	3.53
N**CH$_2$**	3.87
CH$_2$OCH$_2$	3.94
CH$_2$OCH$_2$	4.39
O**CH$_2$**CON	4.53
O**CH$_2$**CON	4.53
Ar**CH$_2$**Ar	4.76
H$_{Phy}$ + **H$_{meta}$**	7.32–7.52

Fig. 11 Position of Ca^{2+} in the middle of the cavity of ligand **3**

Ca^{2+} affects all the protons with an enlargement of some signals. Then, it was difficult to get out information about the coordination and the location of the cation within the cavity of ligand **4**.

However, seen the structure of the ligand with an 1,3-alternate conformation, and the stoichiometry 2:1 of the complex, it is likely that each cations Ca^{2+}, is located in one of both cavity of the macrocycle, defined by two para phenyl substituent and two amide arms like presented on the Fig. 12.

Conclusion

The extraction study shows a weak extractant power of the secondary amides: pyridine **1**, phenyl **2** and *n*-butyl **4** derivatives towards alkali and alkaline-earth picrates cations. In contrast, the tertiary amide diethyl **3** derivative exhibits a high extraction power and the percentages %E range between 5.6 and 96%, showing a significant
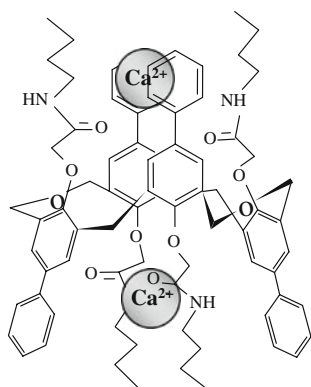
Fig. 12 Position of Ca^{2+} in the cavities of ligand **4**

selectivity in favour to Sr^{2+}, Ba^{2+} and Pb^{2+}. However, the extraction power of ligand **3** remains lower than the related calixarene **5**, in cone conformation. It may be assigned to the difference of the conformation or to the larger cavity of **3** due to the presence of two oxa bridges.

The spectrophotometry study shows the formation of M$_2$L and/or ML complexes with ligands **1**, **2** and **4** depend on cation nature. For example, in the case of the Sr^{2+}/**2** and Sr^{2+}/**4** systems, the species ML and M$_2$L are formed simultaneous. The formation of 2:1 stoichiometry in the case of Rb$^+$ complex with ligand **2** and K$^+$ complex with ligand **4** is confirmed by ESI–MS spectrometry. This later technique pointed out also the formation of supplementary species with 1:1 stoichiometry in the case of Rb$^+$/**2** systems.

In the case of ligand **3**, ML complexes were formed with all cations in the acetonitrile. Selectivities were pointed out in favour of Li$^+$($S^{++}_{Li/Cs} \approx 70$) and Ba^{2+} ($S^{2+2+}_{Ba/Ca} = 2.8 \times 10^3$) with high selectivity factors. The 1:1 stoichiometry of Ca^{2+} complex, in the chloroform, was detected by ^{1}H NMR and the variations of chemicals shifts upon the complexation suggest the location of this cation within the central macrocycle cavity.

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