June 2009 Volume 4 Issue 2

Inorganic CHEMISTRY

An Indian Journal

Trade Science Inc.

Full Paper

ICAIJ, 4(2), 2009 [71-77]

Binding properties of p-tetraphenyl tetrahomodioxacalix[4]arenes amides derivatives towards alkali and alkaline-earth metal cations

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Received: 16th February, 2009 ; Accepted: 21st February, 2009

ABSTRACT

We report 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. © 2009 Trade Science Inc. - INDIA

KEYWORDS

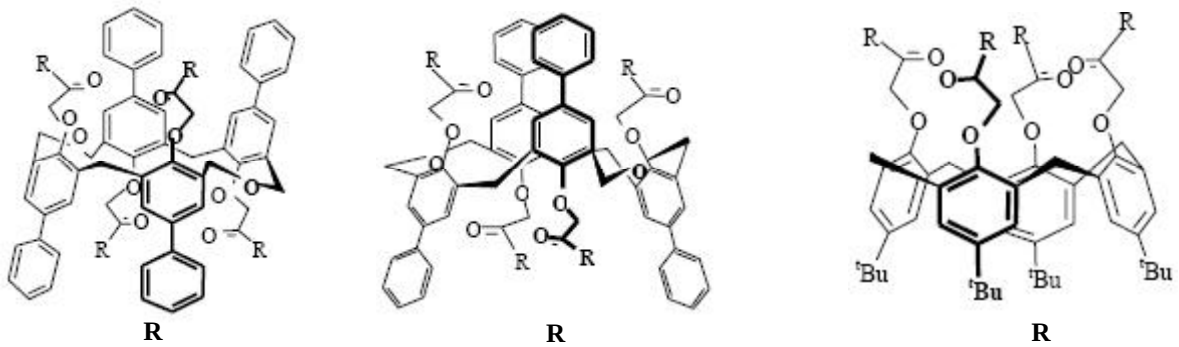
Tetrahomodioxacalixarenes;
Amido derivatives;
1,2-Alternate;
1,3-Alternate;
Binding properties;
Selectivity;
Alkali;
Alkaline-earth.

INTRODUCTION

Due to the variety of properties that calixarenes can offer 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 [2-8]. The substituent 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[4,9].

Among the calix[4]arene derivatives, homooxacalix [4]arenes, bearing extra oxygen atoms in the macrocyclic ring, have been also interesting to organic chemists because of their conformational flexibility[10-12]. No and co-workers synthesised a series of p-tetraphenyl tetrahomodioxacalix[4]arene derivatives containing ester, alkyl and amide functional groups.

In a continuation of our research on tetrahomodio xacalix[4]arene derivatives, 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 amides 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



R R R

1. $NHCH_2$-, 2. $NHCH_2Ph$, 3. $N(Et)_2$ 4. NHBu, 5. $N(Et)_2$, 6. $NHBu^n$

Figure 1: Structure of studied ligands (1-4) and related calixarenes (5, 6)

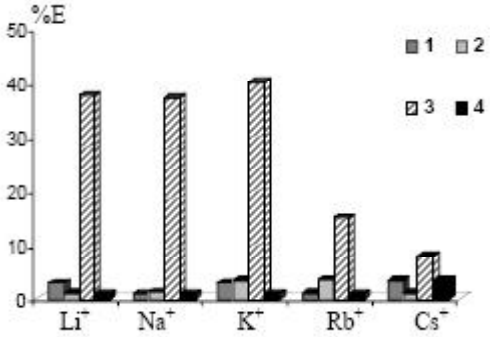


Figure 2 : Extraction profile (%E) of alkali cations by ligands 1-4

TABLE 1: Percentages of extraction of alkali picrates, from water to dichloromethane, at 20°C and stability constants of complexes ($\log\beta_{xy}$) of alkali cations by ligands 1-4 in acetonitrile, I = 10^{-2}M (Et_4NClO_4) at 25°C.

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

[a]Percentages error: ± σ_{n-1}= 1, [b]0.01 ≤σ_{N-1} ≤ 0.2

important than those of the p-tetraphenyl tetrahomodio xacalix[4]arene phenylamide 2, towards all studied cations, in particular toward Ag^+ (%E = 70.1). They explained this by the presence of the nitrogen atom of the pyridine participating in the cation complexation [13]. They reported also that p-tetraphenyl tetrahomodioxa calix [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 aryl-alkyl ether oxygen of one of them[14]. Compounds 1-3 are blocked in C-1,2-alternate conformation[13,15,16], in contrast to 4 which is maintained in the 1,3 alternate conformation[14]. This last conformation is due to -stable intramolecular hydrogen bonding between N-H and the facing oxygen atom of the carbonyl C=O groups. This hydrogen bonding will decrease the metal ion complexation ability[17]. No and co-workers reported also that compound 4 gave a low extractability towards Pb^{2+} ion[17,18].

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

RESULTS AND DISCUSSION

Extraction and complexation of alkali metal cations

The ionophoric properties of amides derivatives 1-4 towards metal cations, from water to dichloromethane, were first evaluated by the standard picrate extraction method[19]. The result concerning alkali cations expressed as a percentage of cation extracted (%E), are reported in TABLE 1 and illustrated in figure 2.

The ligands 1, 2 and 4, present generally weak percentages of extraction (1≤%E≤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≤%E(6) ≤ 5.2). All this ligands bring amide secondary functions groups which present a weak extraction power observed previously by other authors[20-22].

Ligand 3, carrying tertiary amides functions at the lower rim, is a perfect extractant of these cations, namely Li^+, Na^+ and K^+. However, its extraction power stay weak than its homologue, the p-tert-butylcalix[4]arene tetradiethyamide 5, in cone conformation (12 = %E(5) ≤95.5). This can be explained by the existence of two bridges CH_2OCH_2 and by its conformation 1,2-alternate.

The complexation of alkali cations by the amido derivatives is manifested generally by a hypochrome displacement. In the case of ligand 3, the spectral variations are produced in the same time as a hypsochrome displacement of $\Delta\lambda$ = 3 nm until a ratio R close to 1. An isobestic point appears at 255 nm in the case of cations Li^+, Na^+, K^+ and Rb^+ (figure 3).

The stability constants log β_{xy} determined in acetonitrile for alkali metal series are grouped in TABLE 1. The complexes formed are M_2L by the secondary amides 1, 2 and 4 and ML by the tertiary amide 3. Figure 4(a) show the stability profiles of complexes M_2L which are similar in the case of ligands 1 and 4 although their difference in conformation and substituents. They display selectivity towards K^+ (S_{K^+/Li^+} = 20 for 1 and S_{K^+/Rb^+} = 10 pour 4). Despite the similarity of the structure of ligand 1 and 2, the stability of complexes of ligand 2 is lower in particular for Li^+, Na^+ and K^+. The presence of the nitrogen atoms as donor sites in pyridine can explain this behaviour. Any significant selectivity is observed in the case of ligand 2 although the light increases in stability in the series.

The affinity of the tertiary amide derivative 3 is higher towards little size cations namely for Li^+ (S_{Li^+/Cs^+}≈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 figure 4 (b)[23].

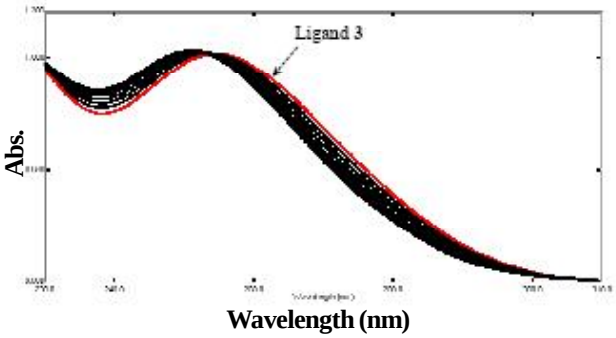


Figure 3 : UV spectra of Rb^+ complexation by ligand 3 in acetonitrile, θ = 25°C, I = 10^{-2} M (Et_4NClO_4), (C_L = 1.51× 10^{-5} M, 0 ≤ R ≤ 2)

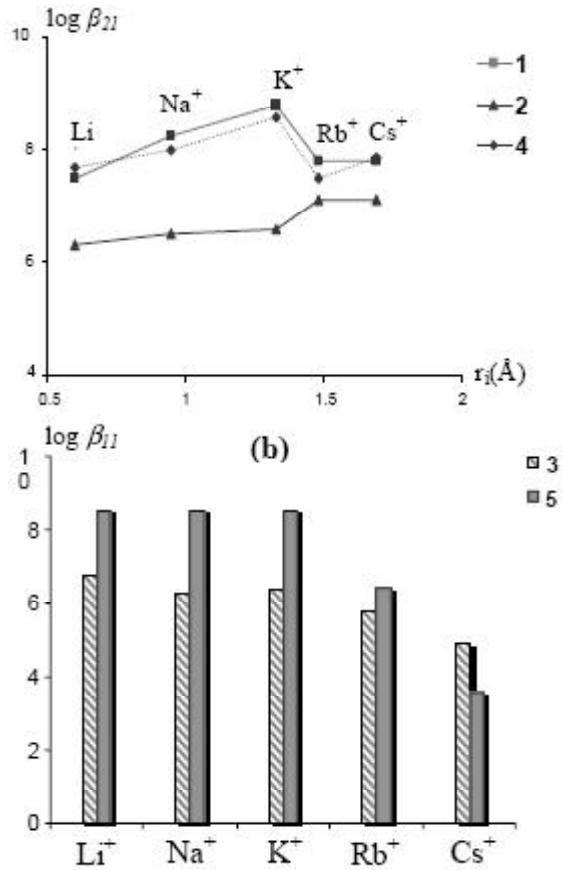


Figure 4 : Stability profiles of complexes M_2L of ligands 1, 2 and 4 (a) and ML of ligands 3 and 5 (b) in the series of alkali cations, in acetonitrile

Complexation of Rb^+ by phenylamide derivative 2

The ESI-MS spectra of ligand 2 show several peaks corresponding to NH_4^+, Na^+ and K^+ complexes already present as impurities in materials, as shown in figure 5. The titration by Rb^+ makes in evidence the formation of ML complex, major upon R equal to 1, at 1463.1 m/z and M_2L complex at 774.28, present as 15 %. 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 (figure 6) shows the formation of complexes $[K.\underline{9}]^+$ at 1280.5 m/z, $[K.H.4]^{2+}$ at 640.7, $[K.Na.4]^{2+}$ at 651.7 and $[K_2.4]^{2+}$ at 659.7.

At the ratio of 1, complexes $[K.4]^+$ and $[K_2.4]^{2+}$ appeared. Upon addition of K^+, the intensity of the peaks relatives to 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.

Extraction and complexation of alkaline-earth metal cations

The percentages of extraction of alkaline-earth picrates cations by amido derivatives 1-4 are illustrated in TABLE 2, as well as the stoechiometry and stability constants of complexes formed. 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 as 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 figure 7(a)[20].

The amide derivative 3 present selectivity towards

TABLE 2: Percentages of extraction of alkaline-earth picrates, from water to dichloromethane, at 20°C and stability constants of complexes (log β_{xy}) of alkaline earth cations by ligands 1-4 in acetonitrile, I = 10^{-2}M (Et_4NClO_4) at 25°C

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

[a]Percentages error: ± σ_{n-1}= 1, [b]0.01 ≤ σ_{N-1} ≤ 0.2

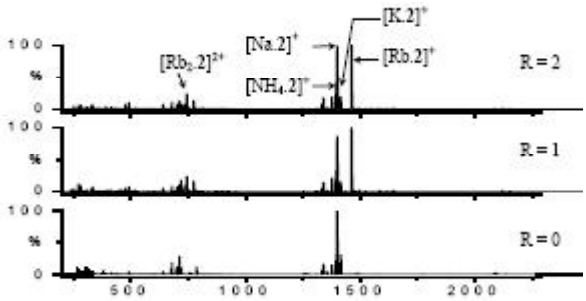


Figure 5 : ESI-MS spectra (40V) relative to the complexa tion of Rb^+ by 2 in acetonitrile, R = 0, 1, 2

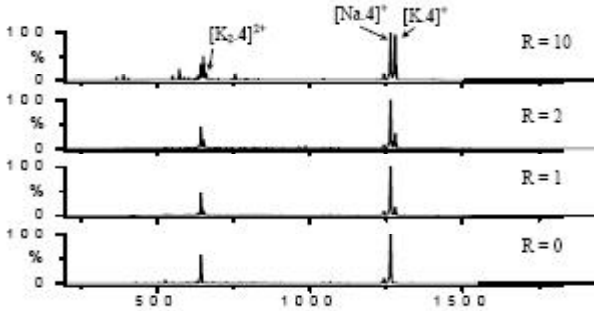


Figure 6: ESI-MS spectra (40V) relative to the complexa tion of K^+ by 4 in acetonitrile, R=0, 1, 2, 10

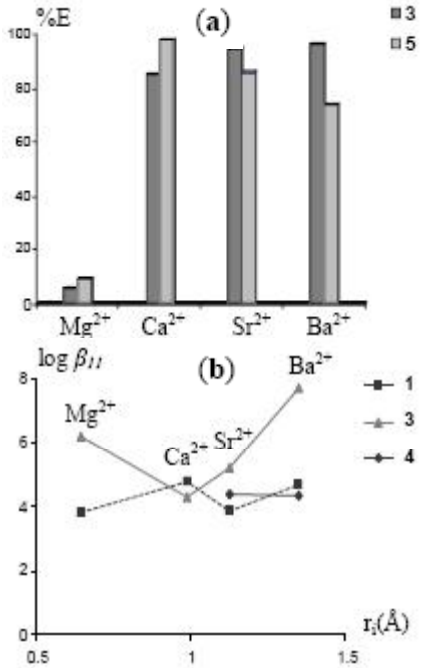


Figure 7: Profiles of extraction (a) of alkaline-earth cations by ligands 3 and 5 and of stability (b) of ML complexes of ligands 1, 3 and 4

Sr^{2+} and Ba^{2+} however its calixarene parent 5 exhibit a selectivity 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 lead to the formation of complex with 1:1 stoechiometry. On the other hand, the phenylamide 2 and the n-butylamide 4 form species with various stoechiometry depending on the cation. In fact, and for systems Mg^{2+}/2, Ba^{2+}/2 and Ba^{2+}/4, species ML 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_2L, were formed simultaneous in the presence of Sr^{2+}. The stability constants, log K_{21}, relative to the formation of M_2L from ML are equal to 3.6 and 3.2 logarithmic units respectively for ligands 2 and 4. They are lower than those of ML (log β_{11}). This shows the absence of the cooperative effect for the formation of M_2L complexes.

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_2L complex with less bulky cations and present 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 figure 7(b) presents the stability profiles of ML species formed by 1, 3 and 4. Only for Ca^{2+}, the complexes formed by the diethylamide derivative 3 are more stable than those obtained by ligand 1 and significant selectivity appears towards Mg^{2+} and Ba^{2+} for 3 ($S_{Mg^{2+}/Ca^{2+}}=10^2$; $S_{Ba^{2+}/Ca^{2+}} = 2.8\times10^3$). The complexation of alkaline-earth cations strongly depends on the nature of substituent and the conformation of the ligand. These results confirm that the complexation affinities of the tertiary amides are higher than those of secondary amides[21].

In general, the affinity of calix[4]arenes amides towards alkaline-earth cations, as known in literature, is more important than the ester and ketone derivative one. This is proved in the case of tetrahomodioxacalix [4]arene tetraethylester, studied also by us, and of ligand 3, excepted for Ca^{2+}[24].

To obtain further informations about the stoechiometry and 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 *vs* those of aromatic protons of the dioxacalixarene unit. In the other hand, the variations of the chemicals shifts $\Delta\delta$ of protons of complex towards those of ligand ($\Delta\delta = \delta_{complex}-\delta_{ligand}$) can give us idea about the location of the cation. In this context, we present here as example the spectra of the system Ca^{2+}/3 which has been recorded at 300 MHz in $CDCl_3$.

TABLE 3: Chemicals shifts (ppm) of ligand 3 and its complex of Ca^{2+} in $CDCl_3$

H correspondant	δ (3)	δ [Ca . 3]$^{2+}$
NCH_2CH_3	1.17	1.25
NCH_2CH_3	1.23	1.26
NCH_2CH_3	3.40	3.73
$ArCH_2Ar$	3.47	3.66
CH_2OCH_2	4.53	4.26
OCH_2CON	4.70	4.59
CH_2OCH_2	4.96	4.81
OCH_2CON	5.04	5.21
$ArCH_2Ar$	5.02	4.32
H_{Phy}	7.08	7.36
ArH_{meta}	7.15	7.38
H_{Phy}	7.20	7.64

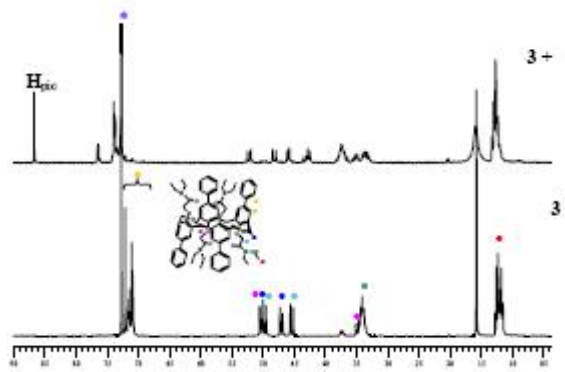


Figure 8 : NMR spectra of ligand 3 and its complex [Ca. 3]$^{2+}$, in $CDCl_3$

Complexation of Ca^{2+} by diethylamide derivative 3

Figure 8 present the NMR spectra of ligand 3 and its complex of Ca^{2+}.

The integration of the picrate proton signal makes in evidence the formation of ML complex of Ca^{2+}. This result is in agreement with those of spectrophotometric study in acetonitrile. However, the variations of chemicals shifts ($\Delta\delta$) are presented on TABLE 3.

The complexation of Ca^{2+} leads the variations of almost all protons of the ligand. The AB systems, previously superposed on the ligand specta, stand out

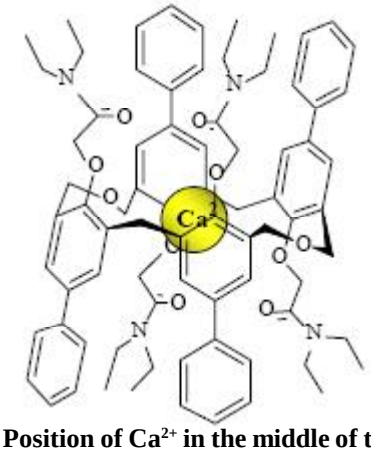


Figure 9 : Position of Ca^{2+} in the middle of the cavity of ligand 3

clearly and become more resolved on the complex spectra. The main variations of chemicals shifts of protons of $ArCH_2Ar$ and CH_2OCH_2 groupements ($\Delta\delta$ = -0.7 and -0.27, respectively) suggest the location of the cation Ca^{2+} in the middle of the macrocycle, in interaction with the phenolic oxygen atoms, the carbonyles and the oxa bridge (figure 9).

EXPERIMENTAL

Extraction experiments

The extraction experiments from water into dichloromethane were performed according to the following procedure: 5 ml of 2.5 $\times 10^{-4}$ 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 stroppered glass tube for 3 min, then magnetically stirred in a thermoregulated water bath at 20 ± 0.1^{0}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 spectrophoto metrically at 355 nm. The percentage extraction, %E, are derived from expression $100(A_0\text{-}A)/A_0$, 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-deHaën, analytical reagent) by UV absorption spectrophotometry at 25^{0}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 220 and 320 nm. The results data were treated by programs Letagrop-Spefo[25]. The metal salts used were perchlorates or nitrate in acetonitrile: $LiClO_4$ and $Ca(ClO_4)_2\cdot4H_2O$ (Fluka, purum), $KClO_4$ and $Ba(ClO_4)_2$ (Prolabo), $NaClO_4$ and $RbClO_4$ (Sigma), $CsClO_4$ and $Sr(ClO_4)_2\cdot6H_2O$ (Alfa Aesar), $Mg(NO_3)_2\cdot6H_2O$ (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 complexo metry using the appropriate coloured indicators[26].

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^{0}C. Sample cone voltage (capillary Exit) was varied from 60-160 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 5µl/min. Scanning was performed on a m/z range from 100-3000, data was averaged for 1 minute and then smoothed using the Gaussian algorithm.

Proton NMR titration experiments

The ^{1}H NMR spectrums were recorded on a Bruker SY300 spectrometer. The temperature of the NMR probe was kept constant at 22^{0}C.

CONCLUSION

The extraction study shows the 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 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 complexes M_2L and/or ML by ligands 1, 2 and 4 depending to the cation. For example, in the case of the systems Sr^{2+}/2 and Sr^{2+}/4, the species ML and M_2L are formed simultaneous. The 2:1 stoechiometry of the Rb^+ complex by ligand 2 and of the K^+ one by ligand 4 were confirmed by ESI-MS spectrometry. This later technique pointed also the formation of supplementary species with 1:1 stoechiometry in the case of Rb^+/2 systems.

In the case of ligand 3, ML complexes were formed with all cations in the acetonitrile. Selectivity were pointed off in favour to Li^+($S_{Li^+/Cs^+} \approx 70$) and Ba^{2+} ($S_{Ba^{2+}/Ca^{2+}} = 2.8\times10^3$). The 1:1 stoechiometry of Ca^{2+}complex, in the chloroform, was detected by ^1H NMR and the variations of chemicals shifts upon the complexation suggest a location of this cation in the middle of the macrocycle.

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