Journal of Inclusion Phenomena and Macrocyclic Chemistry (2006) 55:51–57
DOI 10.1007/s10847-005-9017-6

Synthesis and Complexation Studies of a Tetra(*N*,*N*-dimethyl) Aminoethylamide *p-tert*-butyl Calix[4]arene and Its Tetramethylammonium Derivative

J.K. CHERIF[1], M. MAHOUACHI[2], R. ABIDI[2,*] and J. VICENS[3]
[1]*I.P.E.I.T, Université de Tunis, Montfleury, Tunis, Tunisie;* [2]*Faculté des sciences de Bizerte, 7021 Zarzouna, Bizerte, Tunisie;* [3]*ECPM Groupe de Chimie des Interactions Moléculaires Spécifiques, associé au CRNS, 25, Rue Becquerl, F-67087, Strasbourg Cedex 2, France*

(Received: 13 May 2005; in final form: 5 September 2005)

Key words: calix[4]arenes, amide, amine, ammonium, complexation, ^{1}H-NMR, UV spectrophotometry

Abstract

We describe the synthesis of two functionalised *p-tert*-butyl calix[4]arenes: tetra(*N*,*N*-dimethyl) aminoethylamide derivative **1** and related tetramethylammonium **2**. Their complexation properties towards alkali and zinc metal cations are reported along with complexation of perchlorate anion by **2**.

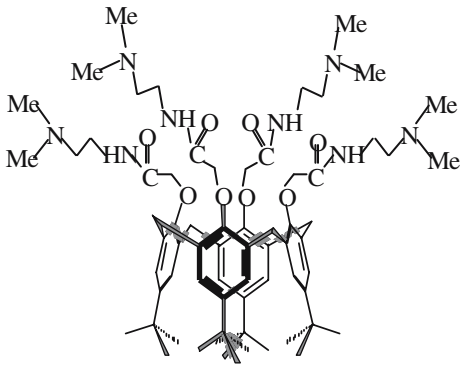
Introduction

In the last two decades, much attention has been paid to the synthesis of *O*-functionalised calixarenes and their use in chemical separation techniques [1–4]. This great attention results from important applications of calixarenes in the selective separation of chosen metals and their supramolecular properties as molecular inclusion compounds [1–4]. Moreover, the design of molecules with high ionic affinities remains important in many other utilisations such as chromatography, catalysis, industry and environmental fields.

The calix[4]arenes prepared by base-catalysed condensation of *para* substituted phenols with formaldehyde are attractive platform, their four phenolic OH at the lower rim can be further functionalised to give rise to selective metal cations receptors [6, 7]. Introduction of chosen functionalities on the phenolic hydroxyl's of calix[4]arenes gives derivatives with different shapes and subsequent selectivities of complexation. The ionophoric activity of amide [8, 9] and amine [10, 11] derivatives of *p-tert*-butyl calix[4]arene have been analysed towards alkali, alkaline-earth, transition metals and lanthanide cations. Arnaud *et al.* [12] have shown that the extraction ratio of metal picrates from aqueous solution into an organic phase varies with the nature of the amide substituent.

Few works have been devoted to calixarenes with mixed functionalities [13] and/or multipoint receptors [14, 15]. Two ways have been adopted to introduce the different functions: first, functions are distributed over phenolic groups and second, all functions are grouped together on the same pendant group. That type of host receptors widespread interest because of their potential properties. For example, additional binding centers in the calixarene may further influence the coordination behaviour of the host and can show cooperativity between the neighbouring sites that can be appended both for associating two types of soft and hard cations and/or accompanying counter-anion.

In the present study, we describe the synthesis of two functionalised *p-tert*-butyl calix[4]arenes: tetra(*N*,*N*-dimethyl) aminoethylamide **1** and its tetramethylammonium derivative **2**. Their complexation properties toward alkali and zinc metal cations are reported along with complexation of perchlorate anion by **2**.

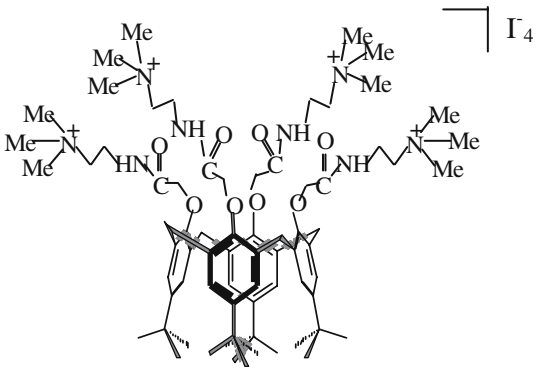


Scheme 1.

Results and discussion

The synthesis of ligand **1** was achieved by reacting *O*-tetramethyl ester *p-tert*-butyl calix[4]arene with an

* Author for correspondence. E-mail: abidi_rym@yahoo.fr



Scheme 2.

excess of commercial *N*-*N*-dimethyl-ethylen-diamine in a 1:1 mixture of methanol–toluene with a reflux of 3 days. **1** was isolated in 76% yield. Ligand **2** was obtained in 75% yield by dissolving **1** in an excess of commercial methyl iodide and gentle heating with stirring for 4 h. Ligands **1** and **2** were fully characterised and the cone conformation was deduced from their ^{1}H-NMR spectra since AB systems were observed for the ArCH_2Ar protons at 3.22 ppm and 4.47 ppm with J = 13.1 Hz for **1** and at 3.25 ppm and 4.42 ppm with J = 8.6 Hz respectively for **2**. The formation of four amido functions and the symmetry of ligand **1** was evidenced by the presence of a triplet at 7.68 ppm with J = 5.2 Hz, for CONH, and singlets at 6.76 ppm, 4.52 ppm, 2.21 ppm, and 1.07 for Ar–H_m, –CH_2OAr, –N(CH_3)$_2$ and –C(CH_3)$_3$ protons, respectively. Methylation of ligand **1** induces signals shifts to the low field of –NH–CH_2–CH_2–N(CH_3)$_2$ protons and high field shifts of –CH_2–O–Ar–C(CH_3)$_3$ protons. Another consequence is a general broadening of the signals. FAB (positive) mass spectra of ligand **2** shows the formation of a 1:1 sodium complex **2.Na**$^+$ at m/z = 1751.4.

Receptors **1** and **2** present two cavities. The first one is delineated by the four carbonyl and the four phenolic oxygen atoms. This cavity should interact with hard cations such as alkali metals as shown in previous works [15, 17]. The second cavity is formed by the four amine functions probably able to complex soft cations (Zn^{2+}, Ag^+....)

To gain information on the interaction between ligands **1** and **2** and alkali and zinc cations, solutions of the ligands were titrated, in acetonitrile, with perchlorate of alkali and zinc cations. The titration studies were conducted by UV spectrophotometry and in some cases by ^{1}H-NMR spectroscopy. As complementary study, extraction of alkali and zinc metal picrates, from the solid state or from aqueous solutions, by **1** and **2** dissolved in chloroform or dichloromethane, were realised and monitored by means of ^{1}H-NMR and UV spectrophotometry, consecutively.

Binding properties of ligands 1 and 2 UV-study

Complexation properties

The binding ability of ligands **1** and **2** towards hard cations (such as alkali metals) and soft cations (such as zinc metal cation) as their perchlorate salts has been evaluated by UV-spectrophotometry titrations in acetonitrile. The absorbance variation results revealed the formation of mono- (ML) and binuclear (M_2L) species for most of the complexes with a fairly strong complexation particularly with ligand **1** (Table 1).

In fact, the addition of alkali salts to ligand **1** produces important and a similar changes in the UV spectra with a formation of one or two isobestic points. Nonetheless, the interpretation of different data by the Letagrop program [18] indicates the simultaneous formation of mono- and binuclear species with cations from Li^+ to Rb^+. With Cs^+ it seems to be formed only a binuclear species. As shown in Table 1, ML complexes are more stable, $1 \times 10^4 < K_{11} < 6 \times 10^6$, than M_2L species with constant values (K_{ij}) oscillating between $2 \times 10^3 < K_{21} < 1.5 \times 10^4$ (Figure 1). However, ligand **1** has a high affinity for sodium cation supported by the larger global constants ($\log\beta_{11}$ = 6.79, $\log\beta_{21}$ = 10.81) within the alkali cations series. The first complexed sodium (in ML complex) must be located in the 'hard cavity' delimited by phenolic and carboxylic oxygens in agreement with

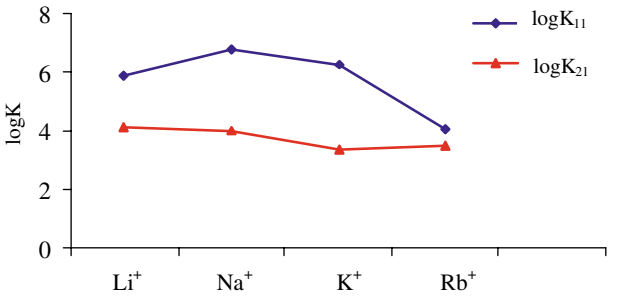


Figure 1. Stability constants of M^+.**1** and $(M^+)_2$.**1** species formed in acetonitrile.

Table 1. Stability constants, log β_{ij}, of the complexes formed with ligands **1** and **2** toward alkali and zinc metal, in acetonitrile at 25 °C

		Li^+	Na^+	K^+	Rb^+	Cs^+	Zn^{2+}
1	ML	5.86 ± 0.01	6.79 ± 0.15	6.29 ± 0.15	4.05 ± 0.06		6.27 ± 0.14
	M_2L	10.00 ± 0.01	10.81 ± 0.14	9.62 ± 0.02	7.53 ± 0.14	6.19 ± 0.01	11.18 ± 0.01
	ML_2						15.49 ± 0.06
2	ML	4.70 ± 0.06	5.06 ± 0.09	a	a	a	4.45 ± 0.10
							8.82 ± 0.02

(a) Variation to small to be interpreted.

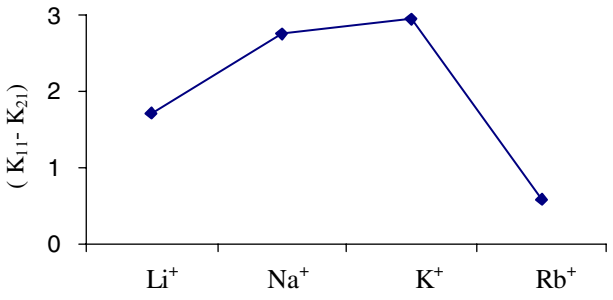


Figure 2. Negative cooperativity for recognition of alkali cations by ligand **1**.

previous results observed for the tetra amidocalix[4]arene [15, 17]. The complexation of a second Na^+ cation is less favourable than the first one, indicating a negative cooperativity and predominance of ML species in a solution. Same conclusion could be drawn for Li^+, K^+ and Rb^+ with more or less important negative cooperativity between the first and the second inclusion (Figure 2). It is interesting to note the decrease of the negative cooperativity effect for Rb^+ cation, to become positive for the caesium, since a binuclear species was formed over the mononuclear complex. While the stability of M_2L complex decreases with the increase of positive cooperativity. Formation of M_2L complexes could be a consequence of two factors:

- The first complexation particularly of the larger cations could induce an important reorganisation of ligand **1** conformation favouring the interaction with a second cation.
- The first complexation of metal cation could be accompanied by anion complexation which becomes responsible of the interaction of the ML complex with a second cation.

Until 1 equivalent, addition of zinc perchlorate to ligand **1** first induces a decrease of absorbance with a formation of two isobestic points, each of them corresponding to an equilibrium. Up to 1 equivalent, absorbance starts to increase with a hypsochrom shift of the maximum of absorbance (278.0–276.5 nm) (Figure 3). The observed variation indicates the formation at least of three species as confirmed by Letagrop analysis. Ligand **1** appears to form ML, ML_2 and M_2L complexes simultaneously with relatively high stability comparable to those obtained with Na^+. The simultaneous formation of the three species may indicate that the first complexed cation is located at the external soft cavity delimited by nitrogen atoms [15]. That means that the second cation in M_2L species may be located outside the ligand cavities.

Ligand **2** forms complexes only with small size cations as Li^+ and Na^+ in the alkali cations series. The formed mononuclear species appears less stable (14 and 50 times) than those formed with ligand **1** showing up the effect of the positive charges due to the ammonium $-N^+(CH_3)_3$. The repulsion between the two positive charge of Li^+ and Na^+ and the four supported $-N^+(CH_3)_3$ and/or the steric effect of the three methyl groups are the main features of the accessibility of the cations to the oxygen cavity inducing a decrease of the stability constants. Same observation can be done concerning the stability of the ML and M_2L complexes formed by ligand **2** and zinc cation. In addition, compared to **1**, the doublets of the tertiary nitrogens are no more available. The mononuclear and binuclear species are 60 and 200 times less stable than those formed with **1**. The absence of ML_2 species with zinc and ligand **2** can reveal and confirm the steric effect of the three methyl groups.

Liquid–liquid extraction

The liquid–liquid extraction of alkali metal picrates, by ligand **1** from water to dichloromethane are conducted by UV spectrophotometry as devised by Pedersen [19].

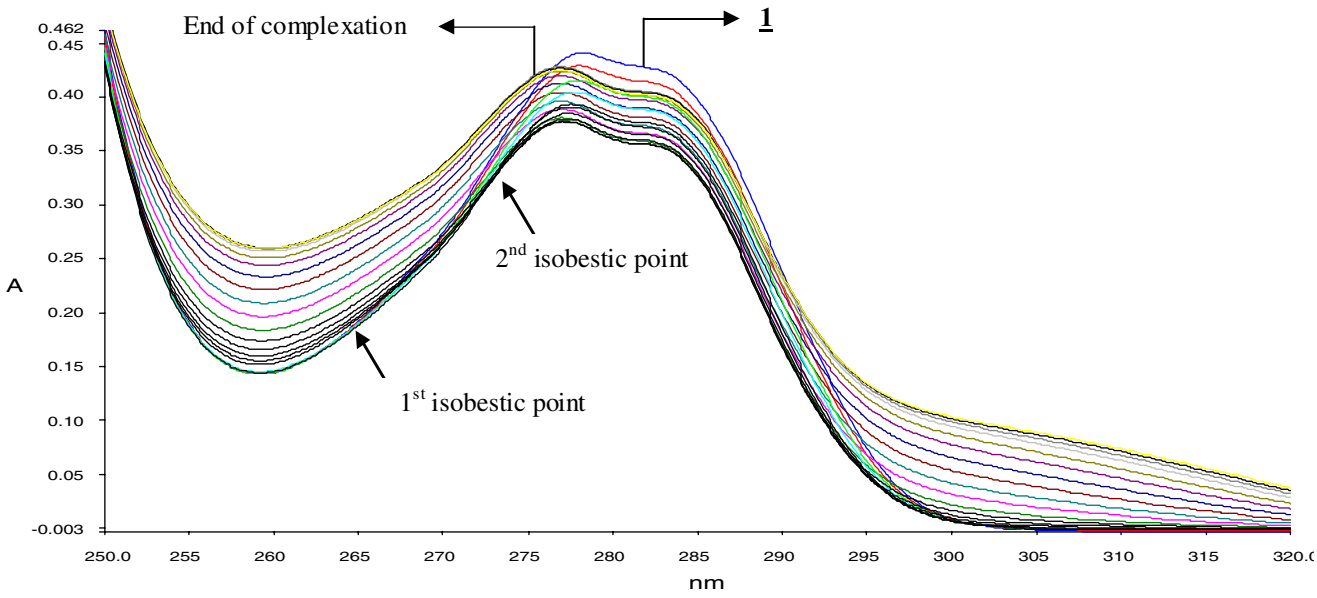


Figure 3. UV spectral change corresponding to zinc perchlorate complexation by ligand **1**.

The analysis of water phase (remaining picrate cation) allows the determination of extraction percentage (% E) of different cations which are given in Table 2. The values are obtained from at least two experiences.

From Table 2 we can notice the efficiency of ligand **1** for alkali extraction with percentage average up to 76% while no selectivity is denoted.

^{1}H-NMR study

Solid–liquid extraction

Solutions of **1** prepared in $CDCl_3$ are mixed with respective solid metal picrates: MPic with M = Li, Na, K, Rb and Cs and $M(Pic)_2$ with M = Zn. The ratio of the extracted cation to ligand in solution was estimated from ^{1}H-NMR spectra by integration of the picrate proton resonance vs those of the ligand.

In the presence of LiPic, NaPic, and $Zn(Pic)_2$ the ^{1}H-NMR spectra of ligand **1** are affected and reveal the appearance of new signals corresponding to picrate units at 8.89 ppm and 8.90 ppm for Li^+, 8.76 ppm for Na^+ and 8.69 ppm for Zn^{2+}. The stoichiometry of the complexes, after 48 h (unchanged spectra were obtained), estimated from integration ratio of the picrate protons resonance vs those of N*H* seems to correspond to ML species for Na^+ and M_2L for Li^+ and Zn^{2+} complexes. In the case of the lithium complexation, the splitting of the picrate singlet could display a difference in binding mode of the two picrate anions. The proximity of the shift values (8.89 ppm and 8.90 ppm) indicates that the binding difference is quite small to be considered. The formation of NaPic and $ZnPic_2$ complexes with ligand **1** in $CDCl_3$ broadened the most of ^{1}H-NMR signals. This observation can be interpreted by a slow intermolecular cation-ligand exchange of the cation between two free ligand units in the case of ML complex and between the free and coordinated ligand in the case of M_2L complex as suggested by UV-complexation results showing the coexistence of equilibria between L $\leftrightarrow$ ML and ML $\leftrightarrow$ M_2L. For LiPic, from the first extracted amounts, new signals appears superimposed with those of free ligand **1** indicating that there is no exchange contrary to Na^+ and Zn^{2+} systems. In a second step, the gradual formation of binuclear complex from the mononuclear species, show a split of signals only for, –N*H*; Ar–H_m, ArCH_2Ar and –C(CH_3)$_3$ protons. This variation could be a consequence of a reorganisation of the calixarene, after the first complexation, to allow the second inclusion.

Noteworthy is that the presence of KPic, RbPic and CsPic with ligand **1** did not show changes in the ^{1}H-NMR spectra indicating that the cations K^+, Rb^+ and Cs^+ are not extracted. We can conclude that **1** is selective for smaller cations within the alkaline series. Contrary to liquid–liquid extraction, solid–liquid extraction shows a selectivity of ligand **1** for the small cations. This difference is coming up from experimental conditions.

Table 2. Percentage extraction of metal picrates into CH_2Cl_2 at 20 °C

Metal		Li	Na	K	Cs
%*E*	**1**	89.5	76.3	91.1	–

Titration

Ligand 1 with $NaClO_4$ and $Zn(ClO4)_2$

Ligand **1**, dissolved in a 1:1 mixture of $CDCl_3$ and CD_3CN, has been titrated by a solution of $NaClO_4$ in the same mixture to reach 1:1 ratio. During the titration, ^{1}H-NMR variations show the coexistence of two spectra corresponding to L and ML species. When 1:1 ratio is attained, ligand signals disappear to give advantage to complex spectra. Considering chemical shift variations, and particularly the more affected protons, location of the cation inside the oxygen cavity delimited by phenolic and carbonyl oxygen is confirmed (Table 3).

On the other hand, we titrated ligand **1** in the same condition by $Zn(ClO_4)_2$ to reach 1:1 ratio. The observed shift in the ^{1}H-NMR spectra indicates that the complexation of Zn^{2+} affects most of ligand protons, those of the soft cavity present the more important shifts indicating the location of the zinc cation (Table 3).

In order to have more insight into the affinity properties of **1** for soft and hard cations we have been interested to a simultaneous inclusion of sodium and zinc cations on the same calixarene unit. In this case the mononuclear sodium complex has been titrated by $Zn(ClO_4)_2$. The ^{1}H-NMR results show an important shift of almost all δ (0.04 ppm $< \delta <$ 0.35 ppm) (Figure 4). The observed ^{1}H-NMR behaviours of Na^+.**1** in response to Zn^{2+} cation and regarding to the fact that the obtained spectra is quite different from those of **1** and **1.Zn^{2+}**, may indicate a considerable reorganisation of the ligand for the second inclusion **1.Zn^{2+}.Na$^+$** complex is then obtained.

Ligand 2 with NaI and $NaClO_4$

The fact that ligand **2** exist as 'an ion pair' (**2.I$_4$**), addition of metal cation with a counter ion, other than iodide, can induce an exchange between anions up to cation complexation. To headlight this exchange we first added Na I to ligand **2** a 1:1 mixture of $CDCl_3$ and CD_3CN. The cavity of ligand is then saturate with sodium, after that, $NaClO_4$ is added to the solution. The two studies are conducted by proton ^{1}H-NMR. The first analysis shows that the complexation of sodium cation affects significantly the protons of oxygen cavity and those of calixarene skeleton except those of CH_2–NH and *equatorial* Ar–CH_2–Ar (Table 4) which should pointing out of the cavity. For the second step $NaClO_4$ is added to the 1:1 formed complex, an unexpectedly precipitation occur. In this case the ^{1}H-NMR spectra of the filtered solution shows a slight and uniform difference of chemical shift for most protons (difference

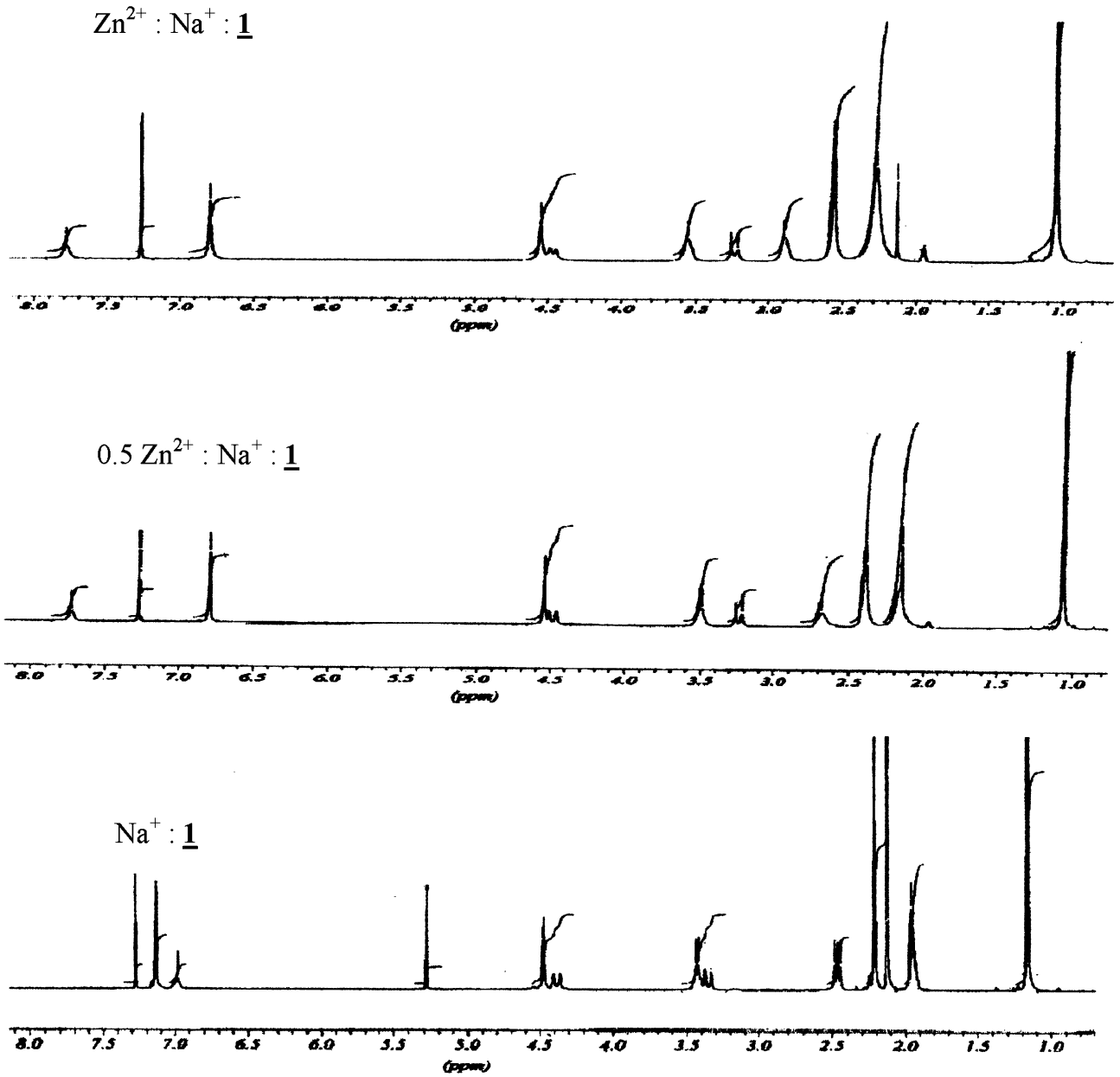


Figure 4. Proton NMR spectra corresponding to the titration of Na^+.**1** by $Zn(ClO_4)_2$ in a mixture of $CDCl_3/CD_3CN$.

between the shift of $NaClO_4$ complex and Na I complex). Nonetheless, the marked variation of N*H* and $N^+(CH_3)_3$ protons shifts (successively 0.80 ppm and 0.18 ppm) could indicate an exchange of iodide by perchlorate anion. The isolated precipitate presented as a thin powder could be attribute to the insoluble part of

Table 3. Variation of chemical shift induced by complexation of $NaClO_4$, $Zn(ClO_4)_2$ successively and simultaneously by ligand **1**

Proton	$\Delta\delta_{Na+.1}$	$\Delta\delta_{Zn2+.1}$	$\Delta\delta_{Na+\ Zn2+.1}$
NH	−0.9	−0.78	0.9
*Ar–**H**$_m$*	+0.35	+0.02	−0.35
*–**CH**$_2$OAr*	−0.03	−0.1	+0.04
*Ar**CH**$_2$Ar*	−0.1	+0.21	+0.08
*–**CH**$_2$–NH–*	−0.06	−0.08	+0.13
*Ar**CH**$_2$Ar*	+0.1	+0.08	−0.14
*–**CH**$_2$–N(CH$_3$)$_2$*	0	+0.08	+0.11
*–N(**CH**$_3$)$_2$*	−0.02	+0.05	+0.35
*–C(**CH**$_3$)$_3$*	+0.05	0	0

Table 4. Variation of shift corresponding to the titration of ligand **2** by NaI and $NaClO_4$

Proton	$\Delta\delta_{(Na.2)I}$	$\Delta\delta_{(Na.2)ClO4}$
NH	−0.43	−0.8
*Ar–**H**$_m$*	+0.35	+0.01
*–**CH**$_2$OAr*	−16	−0.06
*Ar**CH**$_2$Ar*	−0.24	+0.06
*–**CH**$_2$–NH–*	−0.03	−0.07
*Ar**CH**$_2$Ar*	+0.01	+0.07
*–**CH**$_2$–N(CH$_3$)$_3^+$*	0.12	+0.06
*–N$^+$(**CH**$_3$)$_3$*	+0.05	+0.18
*–C(**CH**$_3$)$_3$*	+0.08	+0.03

2.Na.$(ClO_4)_5$ complex or a mixed complex (ClO_4^- and I^-) insoluble at high concentration. In conclusion and comparing to cation complexation, anion exchange presents generally less important effect and then less important changes in NMR spectra.

As general conclusion, the derivative *p-tert*-butylcalix[4]arene tetraamide **1** extracts efficiently alkali and alkaline earth cations from water to dichloromethane efficiently with up to 76% average. The complexation of hard cations as alkaline and soft cations as zinc shows a formation of mono and binuclear species with almost all the cation with biligand species in addition with Zn^{2+}. In the case of mononuclear complexes, sodium have been localised in the oxygenated cavity and zinc in the nitrogenated one. Positive cooperativity has been exhibited only in the case of caesium with **1** since simply binuclear species is formed. Formation of binuclear species could be explained throw the reorganisation of the ligand after the first complexation or the simultaneously complexation of cation and anion favour the interaction of mononuclear species with a second cation. On the other hand ligand **1** seems able to complex simultaneously hard and soft cation. The exploration of this property can open a large field of applications. The methylation of tertiary amine of ligand **1** into ammonium reduce the affinity of the ligand **2** to Li^+ and Na^+ with a formation of only mononuclear species, their stability are also reduced. However, the use of counter ion other than iodide can induce an exchange of anion without affecting to mach the complexation property of ligand **2**. In ^{1}H-NMR condition (high concentration) the exchange of iodide by perchlorate anion of sodium complex (Na^+.**2**) induce a precipitation. This results means that the compound Na.**2**.I_5 can be used for treatment of waste water where anions as perchlorate can be extracted by simple precipitation at high concentration.

Experimental section

Synthesis

Melting points (mps) were taken on a Büchi 500 apparatus in a capillary sealed under nitrogen. TLC plates silica gel 60 F 254 Merck Elemental were used for monitoring the reaction course. Microanalyses were carried out at the service de Microanalyse of the Ecole de Chimie de Strasbourg. ^{1}H-NMR spectra were recorded at 200 MHz on a Bruker SY 200 spectrometer. The FAB mass spectrum was obtained on a VG-Analytical ZAB apparatus.

Preparation of compound 1

A mixture of tetramethyl ester **3** (1.87 g; 2.00 mmol), prepared according to a previously reported method [16] and *N*-*N*-dimethyl-ethylen-diamine (1.76 g, 20.00 mmol) were refluxed in 1:1 mixture of methanol–toluene (40 ml) for 3 days. After evaporation of the solvents, the crude residue was precipitated with acetone to give **1** in 76% yield; Mp > 260 °C. ^{1}H-NMR ($CDCl_3$), δ?are given in ppm from TMS, *J* are given in Hz): 7.68 (t, *J* = 5.2 Hz, 4H, N*H*), 6.76 (s, 8H, Ar–H_m), 4.52 (s, 8H, –CH_2OAr), 4.47 (AB system, *J* = 13.1 Hz, 4H, ArCH_2Ar), 3.44 (q, 8H, *J* = 6.2 Hz, 8H, –CH_2–NH), 3.22 (AB system, *J* = 13.1 Hz, 4H, ArCH_2Ar), 2.46 (t, *J* = 6.5 Hz, 8H, –CH_2–N$(CH_3)_2$), 2.21 (s, 24H, N(CH_3)$_2$), 1.07 (s, 36H, –C(CH_3)$_3$). FAB(+)MS *m*/*z* = 1161.62. Anal. Calcd for $C_{68}H_{104}N_8O_8$: C, 70.22; H, 8.95. Found C, 68.70; H, 9.10.

Preparation of compound 2

1 (2.32 g; 2.00 mmol) was dissolved in an excess of methyl iodide (7.10 g; 50 mmol), heated and stirred of 4 h. Solvents were evaporated to yield **2** in 75%. Mp > 270 °C. ^{1}H-NMR (CD_3CN): 8.30 (broad s, 4H, N*H*), 6.63 (s, 8H, Ar–H_m), 4.49 (s,8H, –CH_2OAr), 4.42 (AB system, *J* = 8.6 Hz, 4H, ArCH_2Ar), 3.72 (broad m, 8H, –CH_2–CH_2–NH–), 3.66 (broad m, 8H,–CH_2–CH_2–NH–); 3.25 (AB system, *J* = 8.6 Hz, 4H, ArCH_2Ar), 3.13 (s, 8H, –CH_2–$N^+(CH_3)_3$, 2.20 (s, 36H, N^+(CH_3)$_3$), 0.93 (s, 36H, –C(CH_3)$_3$) ppm. FAB(+)MS cald for $C_{72}H_{116}N_8O_8I_4$, mw = 1728.5, found *m*/*z* (%) = 1751.4 (10) [**1** + Na^+], 1623.5 (10).[**1**–I^- + Na^+], 1601.50 (55) [L–I], Anal. Calcd for $C_{72}H_{116}N_8O_8I_4$: C, 50.00; H, 6.76; Found C, 50.02, H.6.97.

^{1}H-NMR spectroscopy of complexes

For diphase complexation, samples of metal picrate complexes were prepared by adding un excess of metal picrate in $CDCl_3$ containing the ligand The ^{1}H-NMR (200 MHz) spectra are run at different time until spectra remained unchanged. The monophase complexation consists to add an increasing amount of metal perchlorate solution to a $CDCl_3$ or CD_3CN solution containing 5 mg of ligand.

1.[Li(Pic)]$_2$: ^{1}H-NMR($CDCl_3$), δ = 8.71 (s, 4H, *Pic*), 7.56 (t, 4H, N*H*), 6.81 (s, 8H, Ar–H_m), 4.58 (s, 8H, –CH_2OAr), 4.41 (AB system, *J* = 13.0 Hz, 4H, ArCH_2-Ar), 3.47 (q, 8H, *J* = 5.2 Hz, –CH_2–NH–), 3.18 (AB system, *J* = 13.0 Hz, 4H, ArCH_2Ar); 2.48 (t, *J* = 5.1 Hz, 8H, –CH_2–N$(CH_3)_2$), 2.16 (s, 24H, N(CH_3)$_2$), 1.06 (s, 36H,–C(CH_3)$_3$).

1.Na(Pic): ^{1}H-NMR($CDCl_3$): δ = 8.76 (s, 2H, *Pic*), 7.56 (t, 4H, N*H*),6.89 (s, 8H, Ar–H_m), 4.51 (s, 8H, –CH_2OAr), 4.39 (AB system, *J* = 12.9 Hz, 4H, ArCH_2-Ar), 3.42 (q, *J* = 5.4 Hz, 8H, –CH_2–NH–), 3.22 (AB system, *J* = 12.9 Hz, 4H, ArCH_2Ar); 2.44 (t, *J* = 5.0 Hz, 8H, –CH_2–N$(CH_3)_2$), 2.19 (s, 24H, N(CH_3)$_2$), 1.06 (s, 36H, –C(CH_3)$_3$).

1.[Zn(Pic)$_2$]$_2$: ^{1}H-NMR($CDCl_3$): δ = 8.84 (s, 8H, *Pic*), 7.86 (t, 4H, N*H*), 6.75 (s, 8H, Ar–H_m), 4.52 (s, 8H, –CH_2OAr), 4.47 (AB system, *J* = 13.0 Hz, 4H, ArCH_2Ar), 3.57 (q, 8H, *J* = 5.1 Hz, –CH_2–NH–), 3.22 (AB system, *J* = 13.0 Hz, 4H, ArCH_2Ar); 2.74 (t, *J* = 5.0 Hz, 8H, –CH_2–N$(CH_3)_2$), 2.44 (s, 24H, N(CH_3)$_2$), 1.06 (s, 36H, –C(CH_3)$_3$).

1.Na(ClO_4): ^{1}H-NMR($CDCl_3$): $\delta = 6.90$ (t, 4H, N*H*), 7.15 (s, 8H, Ar–H_m), 4.49 (s, 8H, –CH_2OAr), 4.4 (AB system, J = 12 Hz, 4H, ArCH_2Ar), 3.42 (q, J = 5.2 Hz, 8H, –CH_2–NH–), 3.35 (AB system, J = 12.0 Hz, 4H, ArCH_2Ar); 2.48 (t, J = 5.0 Hz, 8H, –CH_2–N(CH_3)$_2$), 2.20 (s, 24H, N(CH_3)$_2$), 1.15 (s, 36H, –C(CH_3)$_3$).

1.Zn(ClO_4)$_2$: ^{1}H-NMR($CDCl_3$): $\delta = 6.92$ (t, 4H, N*H*), 7.1 (s, 8H, Ar–H_m), 4.42 (s, 8H, –CH_2OAr), 4.29 (AB system, J = 10.0 Hz, 4H, ArCH_2Ar), 3.4 (q, 8H, J = 5.1 Hz, –CH_2–NH–), 3.30 (AB system, J = 10.0 Hz, 4H, ArCH_2Ar); 2.58 (t, J = 5.0 Hz, 8H, –CH_2–N(CH_3)$_2$), 2.30 (s, 24H, N(CH_3)$_2$), 1 (s, 36H, –C(CH_3)$_3$).

1.Na(ClO_4).Zn(ClO_4)$_2$: ^{1}H-NMR $\delta = 7.8$ (t, 4H, N*H*), 6.8 (s, 8H, Ar–H_m), 4.53 (s, 8H, –CH_2OAr), 4.48 (AB system, J = 12.0 Hz, 4H, ArCH_2Ar), 3.55 (q, 8H, J = 5.1 Hz, –CH_2–NH–), 3.21 (AB system, J = 12.0 Hz, 4H, ArCH_2Ar); 2.59 (t, J = 5.0 Hz, 8H, –CH_2–N(CH_3)$_2$), 2.55 (s, 24H, N(CH_3)$_2$), 1.05 (s, 36H, –C(CH_3)$_3$).

2.NaI: ^{1}H-NMR (CD_3CN): $\delta = 7.87$ (broad s, 4H, N*H*), 7.04 (s, 8H, Ar–H_m), 4.33 (s, 8H, –CH_2OAr), 4.18 (AB system, J = 8.0 Hz, 4H, ArCH_2Ar), 3.69 (broad m, 8H, –CH_2–CH_2–NH–), 3.65 (broad m, 8H, –CH_2–CH_2–NH–); 3.13 (AB system, J = 8.0 Hz, 4H, ArCH_2Ar), 3.18 (s, 8H, –CH_2–N$^+$(CH_3)$_3$, 0.93 (s, 36H, –C(CH_3)$_3$).

2.NaI.$NaClO_4$: ^{1}H-NMR (CD_3CN): $\delta = 7.07$ (s, 4H, N*H*), 7.03 (s, 8H, Ar–H_m), 4.27 (s, 8H, –CH_2OAr), 4.12 (AB system, J = 8.2 Hz, 4H, ArCH_2Ar), 3.62 (broad m, 8H, –CH_2–CH_2–NH–), 3.38 (t, 8H, –CH_2–CH_2–NH–), 3.19 (AB system, J = 8.2 Hz, 4H, ArCH_2Ar), 3.00 (s, 36H, N$^+$(CH_3)$_3$), 0.99 (s, 36H, –C(CH_3)$_3$).

Liquid–liquid extraction

The extraction experiments of alkali metal picrates from water into dichloromethane were performed according to a procedure described in the literature [17]. Equal volumes (5 ml) of neutral aqueous solution of alkali metal picrate (2.5×10^{-3} mol l^{-1}) and CH_2Cl_2 solution (5 ml) of calixarene derivatives (2.5×10^{-3} mol l^{-1}) were mixed and magnetically shaken in a thermoregulated water bath at 20 °C for 30 min and then left standing for 1 h in order to obtain a complete separation of the two phases. The concentration of metal picrate remaining in the aqueous phase was determined from the absorbance A at 355 nm. The percentage extraction $\%E$ was derived from the following expression in which A_0 is the absorbance of the aqueous solution of a blank experiment without calixarene:

$$\%E = 100(A_0 - A)/A_0$$

UV-complexation studies

The stability constants β_{xy} being the concentration ratios $[M_xL_y{}^{xn+}]/[M^{n+}]^x[L]^y$ and corresponding to the general equilibrium:

$$yL + xM^{n+} \rightleftarrows M_xL_y^{xn+}$$

(where M^{n+} = metal ion, L = ligand) were determined in acetonitrile by UV-absorption spectrophotometry at 25 °C. The ionic strength was been maintained at 0.01 mol l^{-1} using Et_4NClO_4. The spectra of ligand solutions of concentrations ranging between 10^{-4} and 2×10^{-4} mol l^{-1} and increasing concentration of metal ion, were recorded between 250 nm and 350 nm, the equilibria were quasi-instantaneous for all the systems. Addition of the metal ion to the ligand induced enough changes in the spectra to allow the analysis of the resulting data using the ''Letagrop'' program [18]. Best values for the formation constants β_{xy} of the various complex species and their molar absorptivity coefficients for various wavelengths are deduced from the best fit between the experimental and calculated UV spectra.

References

1. *Calixarenes A Versatile Class of Macrocyclic Compounds*, J. Vicens, and V. Böhmer (eds.), Kluwer Academic Publishers, Dordrecht, Holland (1991).
2. J.L. Atwood and S.G. Bott: in: J. Vicens and V. Böhmer (eds.), Calixarenes A Versatile Class of Macrocyclic Compounds, Kluwer Academic Publishers, Dordrecht, Holland (1991).
3. A. Ikeda and S. Shinkai: Chem. Rev. **97**, 1713 (1997).
4. G.P. Xue, J.S. Bradshaw, N. Su, K.E. Krakowiak, P.B. Savage, and R.M. Izatt: *J. Heterocyclic Chem.* **37**, 1 (2000).
5. V.V. Kronia, H.J. Wirth, and M.T.W. Hearn: *J. Chromatogr. A* **852**, 261 (1999).
6. M.L. Chen and J.W. Rathke: *Trends Inorg. Chem.* **5**, 29 (1998).
7. *Calixarenes Revisited*, in: C.D. Gutsche (ed.), The Royal Society of Chemistry, Cambridge (1999).
8. M.J. Schwing and A. McKervey: in: J. Vicens and V. Böhmer (eds.), *Calixarenes A Versatile Class of Macrocyclic Compounds*, Kluwer Academic Publishers, Dordrecht, Holland (1991).
9. F. Arnaud-Neu, G. Barrett, S. Cremin, M. Deazy, G. Ferguson, S. Harris, A. Lough, L. Guerra, M. McKervey, M.J. Schwing, and P. Schwinte: *J. Chem. Soc. Pekin Trans.* **2**, 1119 (1992).
10. *Calixarenes 2001*, in: Z. Asfari, V. Böhmer, J. Harrowfield, and J. Vicens (eds.), Kluwer Academic Publishers, Dordrecht, Holland (2001).
11. F. Arnaud-Neu and M.J. Schwing-Weill: *Synthetic Metals* **90**, 157 (1997).
12. F. Arnaud-Neu, G. Barrett, S. Fanny, D. Marrs, W. McGregor, M.A. McKervey, M.J. Schwing-Weil, V. Vetrogon, and S. wechsler: *J. Chem. Soc. Pekin Trans.* **2**, 453 (1995).
13. L. Baklouti, J. Cherif, R. Abidi, F. Arnaud-Neu, J. Harrowfield, and J. Vicens: *Org. Biomol. Chem.* **2**, 2786 (2004).
14. T. Saiki, J. Iwabuchi, S. Akine, and T. Nabeshima: *Tetrahed. Lett.* **45**, 7007 (2004).
15. A. Hamdi, R. Abidi, M. Trabelsi Ayadi, P. Thuéry, M. Nierlich, Z. Asfari, and J. Vicens: *Tetrahed. Lett.* **42**, 359 (2001).
16. A. Hamdi, R. Abidi, Z. Asfari, and J. Vicens: *J. Incl. Phenom. Macrocy. Chem.* **45**, 99 (2003).
17. R. Ungaro and A. Pochini: in: J. Vicens and V. Böhmer (eds.), Calixarenes A Versatile Class of Macrocyclic Compounds, Kluwer Academic Publishers, Dordrecht, Holland (1991).
18. B. Sillen and B. Warnquist: *Ark. Kemi.* **31**, 377 (1968).
19. (a) C. Pedersen: *J. Am. Chem. Soc.* **92**, 391 (1970); (b) H. Frensdorff: *J. Am. Chem. Soc.* **93**, 4684 (1971).