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Tetra(diethyl)amide-*p-tert*-butyl-thiacalix[4]arene in Cone Conformation: Synthesis and Binding Properties with Alkali, Alkaline Earth, Heavy and Transition Metal Ions

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Tetra(diethyl)amide-*p-tert*-butylthiacalix[4]arene 1a in the cone conformation was synthesized and its binding properties towards a large variety of metal ions were established on the basis of liquid–liquid and solid–liquid extraction as well as complexation experiments. This compound is a less efficient and selective compound than the "classical" tetra(diethyl)amide-*p-tert*-butylcalix[4]arene 3 in the cone conformation for alkali and alkaline earth metal ions. However, Pb^{2+} is selectively extracted and complexed within heavy and transition metal ions.

Keywords: Thiacalix[4]arene; Alkali metal ions; Alkaline earth metal ions; Heavy and transition metal ions; Phase transfer; Stability constants

INTRODUCTION

Thiacalixarenes are recent macrocycles belonging to the family of calixarenes. The presence of S atoms instead of the usual CH_2 bridges make them attractive to supramolecular chemists because different complexation behaviour is expected for these molecules [1–3]. Lamartine *et al*. [4] reported the synthesis of a *p-tert*-butyl-tetrakis[(diethylamide)-methoxy]tetrathiacalix[4]arene **1b**. The 1,3-alternate conformation was attributed to this compound on the basis of X-ray diffraction methods. However, the structure could not be refined anisotropically because the crystals were of poor quality [4]. **1b** showed significant extraction of a series of cations with maximum levels for K^+, Rb^+ and Ag^+. Its behaviour was different from the 'classical' *p-tert*-butyl-tetrakis[(diethylamide)methoxy]calix[4]arene **3** in the cone conformation which strongly extracts Na^+, K^+, Ca^{2+} and Ba^{2+}[5].

The replacement of bridging CH_2 groups by sulphur atoms introduces additional sites of chelation and modifies the dimension of the cavity [6]. The presence of sulphur atoms as potential chelation sites with a soft character should favour the interaction with soft metal ions, like for instance heavy metal ions.

We report herein the synthesis of the tetraamido derivative of *p-tert*-butylthiacalix[4]arene **1a**. Its cone conformation has been demonstrated by transforming **1a** into the tetramethylester derivative **2** whose conformation is known to be cone. First estimation of its ability to form complexes with alkali and alkaline earth metal ions and some heavy and transition metal ions (Ag^+, Cd^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+}) has been assessed through liquid-liquid extraction of the corresponding picrate salts from water into dichloromethane. Complexation in a single medium, methanol, with the same metal ions including also Hg^{2+} has been followed using UV absorption spectrophotometric and potentiometric titrations. Solid–liquid extraction experiments in deuteriated chloroform have also been performed allowing in some cases to localize the metal ion in the complex. The results are compared to those obtained previously [5] and in the present work with the corresponding "classical" calixarene **3**.

EXPERIMENTAL

Materials

The solvents dichloromethane (Prolabo, R.P. Normapur) and methanol (Riedel de Haën, water content

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max. 0.03%) were used without further purification. Metal picrates were prepared according to the different procedures mentioned in the literature [5,7,8,9]. The metal salts for complexation experiments were the following chlorides, perchlorates and nitrates used without further purification: LiCl (Fluka, MicroSelect), NaCl (Merck, p.a.), KCl (Merck, p.a.), RbCl (Merck, p.a.), CsCl (Fluka, puriss.), $MgCl_2$, 6 H_2O (Merck, p.a.) and $CuCl_2$ (Merck, p.a); $Ca(ClO_4)_2$, 4 H_2O, (Fluka, purum), $Sr(ClO_4)_2$, 4 H_2O (Alfa), $Ba(ClO_4)_2$ (Prolabo, R.P. Normapur) and $Zn(ClO_4)_2$, 6 H_2O (Alfa); $AgNO_3$ (Acros), $Pb(NO_3)_2$ (Merck, p.a.), $Cd(NO_3)_2$ (Merck, p.a.) and $Hg(NO_3)_2$, H_2O (Prolabo, p.a.). All these salts were dried under vacuum at ambient temperature before use. Silver stock solutions were standardized by potentiometry using NaCl. Complexometry with EDTA and the appropriate coloured indicators was used for the other cations except alkali ions. The ionic strength of all solutions was maintained constant by use of 10^{-2} M Et_4NCl (Fluka, purum), Et_4NClO_4 (Fluka, purum) or Et_4NNO_3 (Acros) according to the nature of the metal salts used, chlorides, perchlorates or nitrates.

Synthesis

Melting points (mps) were taken on Büchi 500 apparatus in tubes sealed under nitrogen. ^{1}H-NMR spectra ($CDCl_3$) were recorded on a Bruker SY 200 (δ in ppm, J in Hz). FAB(+)MS spectra were obtained on a VG-Analytical ZAB HF. Elemental analyses were performed at the Service de Microanalyse of the Institut de Chimie de Strasbourg. All the reactions were run under nitrogen atmosphere. All reagents were commercial and used without further purification. *p-tert*-Butylthiacalix[4]arene has been prepared according to reference [10].

Tetra(diethyl)amide p-tert-butylthiacalix[4]arene 1a

p-tert-butylthiacalix[4]arene (1.701 g; 2.36 mmol), K_2CO_3 (5.014 g: 36.27 mmol) in acetonitrile (100 ml) were stirred at room temperature for 2 h. Then $ClCH_2CONEt_2$ (3.245 g; 21.88 mmol) and NaI (1.067 g; 7.11 mmol) were added and the resulting mixture was refluxed for 15 h. The solvents were removed under vacuum. The residue was dissolved in CH_2Cl_2 (100 ml) and H_2O (100 ml). HCl was added until pH = 2. The organic layer was dried over sodium sulphate. After filtration the solvents were removed under reduced pressure and the medium was precipitated with methanol during evaporation. **1** (1.140 g; 0.97 mmol) was obtained pure as a white solid. Yield: 41%. A similar reaction was carried out by replacing K_2CO_3 by Cs_2CO_3: *p-tert*-butylthiacalix[4]arene (0.431 g; 0.59 mmol), Cs_2CO_3 (2.95 g; 9.05 mmol), $ClCH_2CONEt_2$ (3.186 g; 21.29 mmol), NaI (1.025 g; 6.83 mmol), **1** (0.318 g; 0.27 mmol). Yield: 46%; mp = 263–264°C; ^{1}H-NMR ($CDCl_3$) δ (in ppm from TMS) 7.66 (s, 8H, Ar-*H*), 4.81 (s, 8H, OCH_2CONEt_2), 3.43 (q, 8H, $J = 7.0$ Hz, $CONCH_2CH_3$), 3.22 (q, 8H, $J = 7.0$ Hz, $CONCH_2CH_3$), 1.23 (t, 12H, $J = 7.0$ Hz, $CONCH_2CH_3$), 1.19 (t, 12H, $J = 7.0$ Hz, $CONCH_2CH_3$), 1.17 (s, 36H, $C(CH_3)_3$); Elemental analysis Calc. for $C_{64}H_{92}N_4O_8S_4$. 3 CH_2Cl_2: C, 56.33; H, 6.91; Found: C, 57.06; H, 7.01.; Mass spectrum (FAB +): $m/z = 1195.7$ $[M + Na]^+$.

Tetramethylester p-tert-butylthiacalix[4]arene 2

Tetraamide *p-tert*-butylthiacalix[4]arene **1** (0.500 g; 0.42 mmol), 37% HCl (3 ml) in CH_3OH (50 ml) were refluxed for 48 h. The reacting mixture was evaporated to dryness. The resulting solid was dissolved in a mixture of CH_2Cl_2 and water. The organic layer was dried over sodium sulphate. After filtration, **2** was obtained as a white solid by precipitation with methanol during evaporation of the solvent; mp = 211–212°C; ^{1}H-NMR ($CDCl_3$) δ (in ppm from TMS) 7.31 (s, 8H, Ar-*H*), 3.78 (s, 8H, $OCH_2CO_2CH_3$), 2.96 (s, 12H, $OCH_2CO_2CH_3$), 1.26 (s, 36H, $C(CH_3)_3$); Mass spectrum (FAB +): $m/z = 949.5$ $[M + 3H]^+$.

Picrate Extraction Experiments

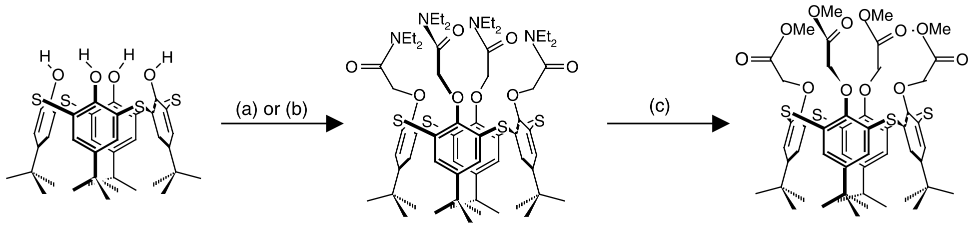
The percentages of metal picrate extracted from water into dichloromethane have been determined at 20 °C according to the procedure already described [5]. Solid-liquid extractions of the solid alkali, alkaline-earth and Ag^+, Cd^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} metal picrates into $CDCl_3$ solutions (10^{-3} M) of **1** were conducted until the ^{1}H-NMR spectra of the resultant solutions remained unchanged. The stoichiometry of the complexes was deduced from the integration ratio between the singlet of the picrate and the aromatic protons of the ligand. The ^{1}H-NMR ($CDCl_3$) spectra are as follows:

1 + Ca(Pic)$_2$

1.19 (s, 36H, *tert*-butyl), 1.26 (t, 12H, $J = 7.5$ Hz, $-CH_2-CH_3$), 1.26 (t, 12H, $J = 7.2$ Hz, $-CH_2-CH_3$), 3.32 (q, 8H, $J = 7.5$ Hz, $N-CH_2-CH_3$), 3.53 (q, 8H, $J = 7.2$ Hz, $N-CH_2-CH_3$), 4.90 (s, 8H, $O-CH_2-CON$), 7.85 (s, 8H, Ar-*H*).

1 + Ag(Pic)

1.12 (s, 36H, *tert*-butyl), 1.19 (t, 12 H, $J = 7.0$ Hz, $-CH_2-CH_3$), 1.23 (t, 12 H, $J = 7.0$ Hz, $-CH_2-CH_3$), 3.25 (q, 8H, $J = 7.0$ Hz, $N-CH_2-CH_3$), 3.34 (q, 8H, $J = 7.0$ Hz, $N-CH_2-CH_3$), 5.25 (s, 8H, $O-CH_2-CON$), 7.44 (s, 8H, Ar-*H*)



1a **2**

SCHEME 1 Synthesis of **1a** and **2**. (a) $ClCH_2CONEt_2/K_2CO_3$/NaI/acetonitrile/reflux 15 h; (b) $ClCH_2CONEt_2/Cs_2CO_3$/NaI/acetonitrile/reflux 15 h; (c) CH_3OH/HCl/reflux 48 h.

1 + Pb(Pic)$_2$

1.17 (s, 36H, *tert*-butyl),1.27 (t, 12H, $J = 7.2$ Hz, $-CH_2-CH_3$), 1,34 (t, 12H, $J = 6.7$ Hz, $-CH_2-CH_3$), 3.36 (q, 8H, $J = 7.2$ Hz, $N-CH_2-CH_3$), 3.53 (q, 8H, $J = 6.7$ Hz, $N-CH_2-CH_3$), 5.05 (s, 8H, $O-CH_2-$CON), 7.85 (s, 8H, Ar-*H*)

1 + Cu(Pic)$_2$

1.2 (s, 36H, *tert*-butyl), 1.27 (broad s, 24 H, $-CH_2-CH_3$), 3.27 (broad s, 8H, $N-CH_2-CH_3$), 3.50 (broad s, 8H, $N-CH_2-CH_3$), 4.82 (s, 8H, $O-CH_2-$CON), 7.70 (s, 8H, Ar-*H*)

1 + Zn(Pic)$_2$

1.16 (s, 36H, *tert*-butyl), 1.21 (broad t, 12 H, $-CH_2-CH_3$), 1.23 (t, 12 H, $J = 7.2$ Hz, $-CH_2-CH_3$), 3.28 (broad s, 8H), 3.49 (d, 8H, $J = 7.2$ Hz, $N-CH_2-CH_3$), 4.82 (s, 8H, $O-CH_2-$CON), 7.64 (s, 8H, Ar-*H*)

Stability Constant Determination

The stability constants β_{xy} corresponding to the concentration ratios $[M_xL_y]/([M]^x[L]^y)$ have been determined by UV absorption spectrophotometry following the procedure already described [5]. The absorbances were treated using programme Specfit [11]. In the case of Ag^+ the stability constants were confirmed by potentiometry using a silver electrode. Details on such experiments have been published elsewhere [12].

RESULTS AND DISCUSSION

Synthesis and Characterization of Tetraamide *p-tert*-butylthiacalix[4]arene 1a

The synthesis of **1a** is shown in Scheme 1. *p-tert*-Butylthiacalix[4]arene was reacted with ca. 10 equivalents of $ClCH_2CONEt_2$ in the presence of ca. 15 equivalents of K_2CO_3 (or Cs_2CO_3) and an excess of NaI in refluxing acetonitrile for 15 h.[†]After the work up, **1a** was precipitated pure with methanol in 41% (or 46%) yield.

Tetraalkylation was deduced from the ^{1}H-NMR spectrum of **1a** in $CDCl_3$. The ^{1}H-NMR spectrum was highly symmetrical presenting one singlet at 7.66 ppm (8 H) for the Ar-*H*, one singlet at 4.81 ppm (8 H) for the OCH_2CO, and one singlet at 1.17 ppm (36 H) for the *tert*-butyl groups. Two quadruplets at 3.43 ppm and 3.22 ppm with $J = 7.0$ Hz were attributed to the $CONCH_2CH_3$ while the two triplets at 1.23 ppm and 1.19 ppm with $J = 7.0$ Hz were attributed to the $CONCH_2CH_3$. Because of the high symmetry it was impossible to determine the conformation of the thiacalix[4]arene unit. As the conformations of the tetraalkylester *p-tert*-butylthiacalix[4]arenes are known we decided to transform **1a** into the tetramethylester derivative **2**. Thus, **1a** was refluxed in CH_3OH in the presence of HCl for 48 h (Scheme 1). After the work up, the ^{1}H-NMR spectrum of **2** was observed to be the same as the one of a sample already prepared in the laboratory whose X-ray structure showed the thiacalix unit to be in cone conformation [13]. Then **1a** was assumed to be in the cone conformation too.

Binding Properties

The extraction percentages of metal picrates together with the stability constants of the complexes formed in methanol are given in Tables I to III for alkali, alkaline earth, heavy and transition metal ions, respectively. Data for the related (thia)calixarenes **1b** in 1,3-alternate conformation [4] and **3** in cone conformation [5] have been included for comparison. The results are also illustrated in Figures 1–3.

With alkali metal ions, it can clearly be seen that the replacement of the bridging CH_2 by sulphur atoms leads to a significant decrease of the extraction levels for the smallest alkali cations Li^+, Na^+ and K^+ and to an increase of the extraction of the larger

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[†] In this work acetonitrile was used instead of acetone as reaction solvent (see reference [4]).

TABLE I Extraction percentages (E%) of alkali picrates from water into dichloromethane at 20°C by ligands **1a**, **1b** and **3** and stability constants (log β) of the corresponding complexes in methanol (I = 0.01 M Et_4NCl at 25°C)

	E%			log β	
Cations	**1a***	**1b**†	**3**‡	**1a***	**3**‡
Li^+	44.0 ± 0.4	22.9	62.0	2.4 ± 0.1	3.9
Na^+	50.0 ± 0.4	55	95.5	3.5 ± 0.1	7.9
K^+	41.0 ± 0.3	80.1	73.7	2.6 ± 0.1	5.8
Rb^+	33.5 ± 0.4	78	24.0	2.3 ± 0.1	3.8
Cs^+	33.4 ± 0.1	56.4	11.8	2.5 ± 0.1	2.4

*precision: $\pm\sigma_{n-1}$, σ_{n-1} being the standard deviation on the mean of n ($n \geq 3$) independent experiments; † from ref. [4]; ‡ from ref. [5].

cations Rb^+ and Cs^+. This observation may be related to the larger size [2] of the thiacalix[4]arene derivative **1a** with respect to its calix[4]arene counterpart **3**. Consequently, the thiacalix[4]arene derivative **1a** is less selective, although it still presents a small preference for Na^+ along the series.

The interpretation of the spectral changes of **1a** upon complexation in methanol showed the formation of 1:1 complexes whose stability is lower than that of the corresponding complexes with the calix[4]arene **3**.

As regards alkaline earth metal ions, the same trends were observed in extraction as in complexation, i.e. a decrease of the extraction percentages and log β values with the thiacalixarene derivative and all the cations of the series except Mg^{2+}. Calcium still remains the best extracted (E% = 53) and the best complexed ion (log $\beta = 5.17$) among the alkaline earth series. This leads to a drastic decrease of the Ca^{2+} over Mg^{2+} selectivity (expressed as the ratio of the extraction percentages) from 10.9 to 1.8 in extraction and from more than 7.8 to 1.7 log units in complexation, in going from **3** to **1a**.

As regards heavy and transition metal ions, the presence of sulphur atoms in the thiacalixarene framework leads also to strong decreases in the extraction percentages, especially for Ag^+ and Cd^{2+}. On the contrary the extraction levels of Cu^{2+} and Zn^{2+} are significantly enhanced, e.g. from 8 to 29.4 for Zn^{2+} [14]. Whereas calixarene **3** extracts almost quantitatively the three cations Ag^+, Pb^{2+} and Cd^{2+} (E% ≥ 97), **1a** displays a marked selectivity for Pb^{2+} vs. Ag^+ and Cd^{2+} which, expressed as the ratio of the extraction percentages, amounts to 1.8 and 3.7, respectively.

TABLE II Extraction percentages (E%) of alkaline earth picrates from water into dichloromethane at 20°C by ligands **1a**, **1b** and **3** and stability constants (log β) of the corresponding complexes in methanol (I = 0.01 M Et_4NCl or Et_4NClO_4, at 25°C)

	E%			log β	
Cations	**1a***	**1b**†	**3**‡	**1a***	**3**‡
Mg^{2+}	28.8 ± 0.6	39.7	9	3.5 ± 0.3	1.2
Ca^{2+}	53.0 ± 0.2	29.8	98	5.17 ± 0.04	≥9
Sr^{2+}	48.0 ± 0.3	–	86.3	4.51 ± 0.08	≥9
Ba^{2+}	27.3 ± 0.3	24.1	74.2	3.7 ± 0.1	7.2

*precision: $\pm\sigma_{n-1}$, σ_{n-1} being the standard deviation on the mean of n ($n \geq 3$) independent experiments; † from ref. [4]; ‡ from ref. [5].

TABLE III Extraction percentages (E%) of heavy and transition metal picrates from water into dichloromethane at 20°C by ligands **1a**, **1b** and **3** and stability constants (log β) of the corresponding complexes in methanol (I = 0.01 M Et_4NCl, Et_4NNO_3 or Et_4NClO_4, at 25°C)

	E%			log β	
Cations	**1a***	**1b**†	**3**‡	**1a***	**3**¶
Ag^+	46.3 ± 0.1	95.9	97	4.4 ± 0.3	7.2
Pb^{2+}	83.1 ± 0.2	32.6	97	5.18 ± 0.08	8.4
Cd^{2+}	22.2 ± 0.2	–	99	4.6 ± 0.1	8.5
Hg^{2+}	§	–	§	4.2 ± 0.1	3.82 ± 0.02‖ 9.5 ± 0.1‖,#
Cu^{2+}	47.6 ± 0.1	40.5	14	4.2 ± 0.1	6.5
Zn^{2+}	29.4 ± 0.5	–	8	3.92 ± 0.01	2.5

*precision: $\pm\sigma_{n-1}$, σ_{n-1}being the standard deviation on the mean of n ($n \geq 3$) independent experiments; † from ref. [4]; ‡ from †; ¶ from ref. [13]; § Values not reported as attempts to obtain pure mercury (II) picrate failed (see ref. [9]). ‖ this work; # 2:1 (M:L) complex.

Complexation of heavy metal ions has been followed in methanol with the thiacalix[4]arene **1a** by UV absorption spectrophotometry. Similar experiments were also performed with Hg^{2+} and the related calix[4]arene **3** for which no complexation data was available. **1a** forms only 1:1 complexes with all the cations studied. They are all, except Zn^{2+} and Hg^{2+} complexes, less stable than the 1:1 complexes

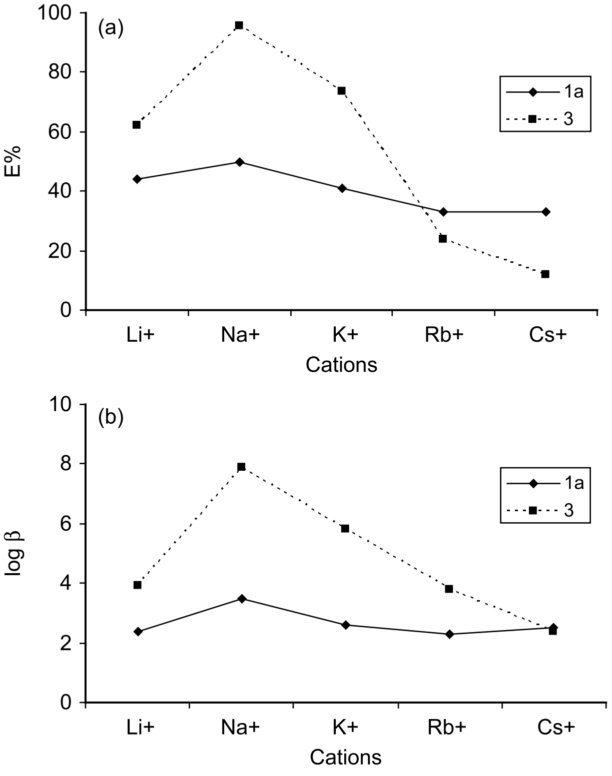


FIGURE 1 Comparison of extraction (a) and complexation (b) profiles of alkali metal ions with thiacalixarene amide **1a** and calixarene amide **3**.

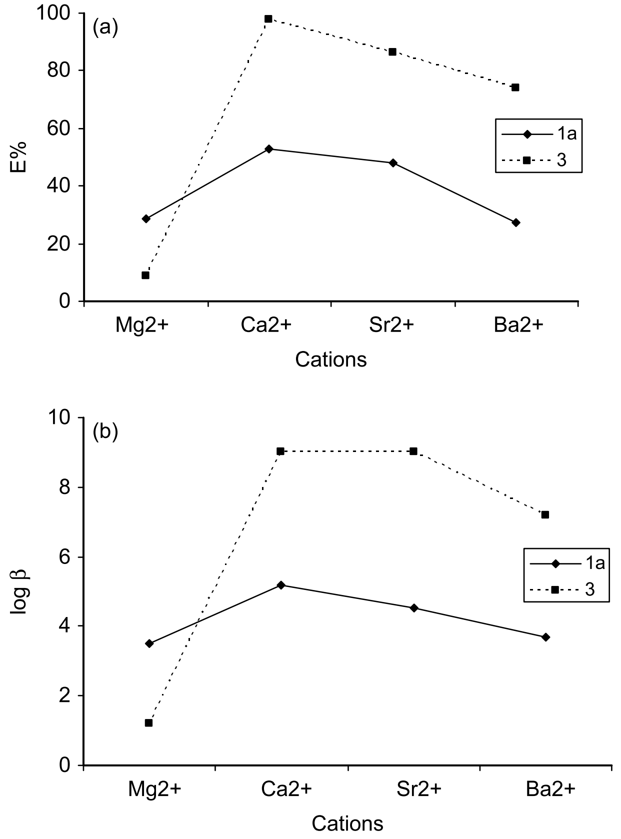


FIGURE 2 Comparison of extraction (a) and complexation (b) profiles of alkaline earth metal ions with thiacalixarene amide **1a** and calixarene amide **3**.

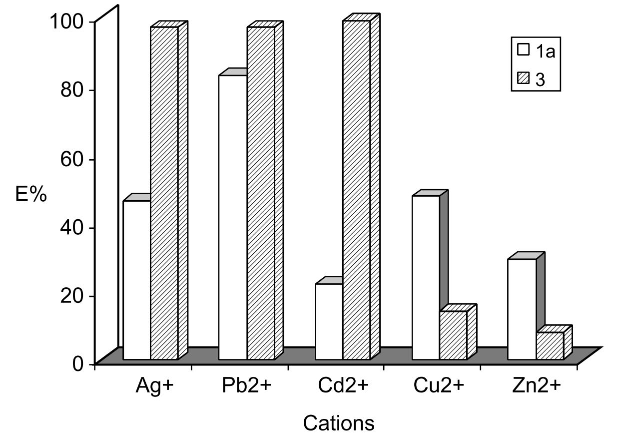


FIGURE 3 Comparison of the extraction percentages of heavy and transition metal picrates by thiacalixarene amide **1a** and calixarene amide **3**.

also formed with calixarene **3** [15]. As could be foreseen from the extraction studies, Pb^{2+} forms the most stable complex ($\log \beta = 5.18$).

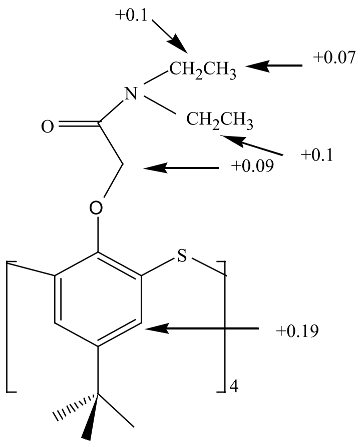
Significant differences were observed between the behaviour of both cone and 1, 3-alternate conformers of **1** towards K^+, Rb^+ and Ag^+. Much higher extraction percentages were found with the 1, 3-alternate conformer **1b** [4], which may be explained by the presence of two binding sites instead of one in the cone conformer **1a**.

Solid–liquid extraction experiments of alkali, alkaline-earth and Ag^+, Cd^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} picrates into $CDCl_3$ solutions (10^{-3} M) of **1a** were performed until the ^{1}H-NMR spectra of the resultant solutions remained unchanged. The stoichiometry of the complexes was deduced from the integration ratio between the singlet of the picrate and the aromatic protons of the ligand. The singlet of picrate appeared for Ca^{2+}, Ag^+, Pb^{2+}, Cu^{2+} and Zn^{2+} indicating the 1:1 stoichiometry of the complexes. The complexation of the metal cations was also deduced by the occurence of chemical shifts of the signals in the ^{1}H-NMR spectrum of **1a** which are shown in Table IV. If one assumes the chemical shifts are induced by the presence of the metal cation in the ligand, the larger shifts can be attributed to the localisation of the metal close to protons corresponding to the shift. In Chart 1 we present the $\Delta\delta > 0.05$ ppm of the shift of the proton signals giving the position of the cation in ligand **1a**.

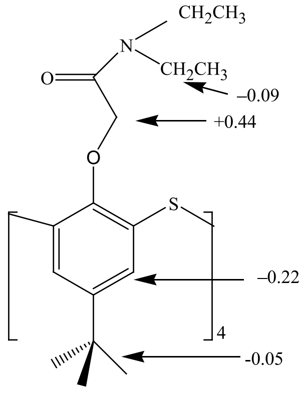
The larger shifts were observed for $N(CH_2CH_3)_2$, $N(CH_2CH_3)_2$ and OCH_2CON for Ca^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} indicative of interactions between the metal and the carbonyl functions of the amido groups and the phenolic oxygen atoms of the thiacalix[4]arene. For Ag^+ the larger shifts were observed for the OCH_2CON and the Ar*H* protons of the thiacalix[4]arene which can be attributed to a cation more deeply enclosed with interactions with the sulfur atoms and the aromatic rings of the macrocycle. For Zn^{2+} only shifts were observed for the $N(CH_2CH_3)_2$. This can be due to

TABLE IV ^{1}NMR chemical shift changes of the signals of **1a** after extraction of solid picrates (Δδ in ppm, *J* in Hz)

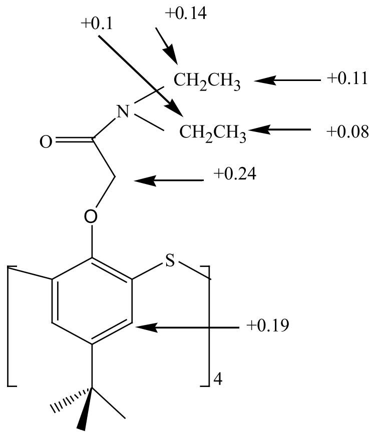
	$H_{\text{tert-butyl}}$	$-CH_2-CH_3$	$-CH_2-CH_3$	$N-CH_2-CH_3$	$N-CH_2-CH_3$	$O-CH_2-CON$	Ar-*H*	H_{Pic}
1a	1.17 s	1.19 t, $J = 7.0$	1.23 t, $J = 7.0$	3.22 q, $J = 7.0$	3.43 q, $J = 7.0$	4.81 s	7.66 s	
1a.Ca^{2+}	1.19 s	1.26 t, $J = 7.5$	1.26 t, $J = 7.2$	3.32 q, $J = 7.5$	3.53 q, $J = 7.2$	4.90 s	7.85 s	8.81
Δ δ	+0.02	+0.07	+0.03	+ 0.1	+0.1	+0.09	+0.19	–
1a.Ag$^+$	1.12 s	1.19 t, $J = 7.0$	1.23 t, $J = 7.0$	3.25 q, $J = 7.0$	3.34 q, $J = 7.0$	5.25 s	7.44 s	8.85
Δ δ	−0.05	+0.02	+0.004	+0.03	−0.09	+0.44	−0.22	
1a.Pb^{2+}	1.17 s	1.27 t, $J = 7.2$	1.34 t, $J = 6.7$	3.36 q, $J = 7.2$	3.53 q, $J = 6.7$	5.05 s	7.85 s	8.80
Δ δ	−0.001	+ 0.08	+0.11	+0.14	+ 0.1	+ 0.24	+0.19	–
1a.Cu^{2+}	1.2 s	1.27 broad s	1.27 broad s	3.27 broad s	3.50 broad s	4.82 s	7.70 s	–
Δ δ	+0.03	+0.08	+0.04	+0.05	+0.07	+0.01	+0.04	–
1a.Zn^{2+}	1.16 s	1.21 broad t	1.23 t, $J = 7.2$	3.28 broad s	3.49 d, $J = 7.2$	4.82 s	7.64 s	8.76
Δ δ	−0.01	0.03	+0.002	+0.06	+0.06	+0.01	+0.02	–



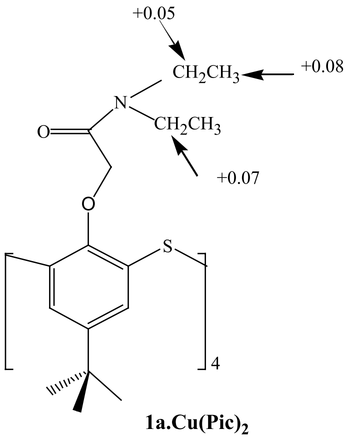
1a.Ca(Pic)$_2$



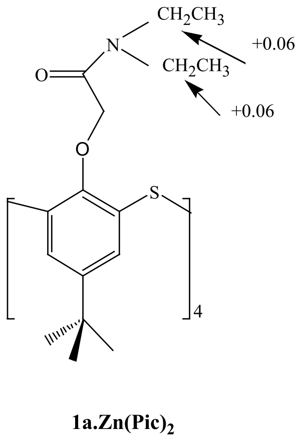
1a.AgPic



1a.Pb(Pic)$_2$



1a.Cu(Pic)$_2$



1a.Zn(Pic)$_2$

a lower affinity of the zinc cation for the carbonyl functions which can also be detected by a broadening of the whole ^{1}H-NMR spectrum of the zinc complex expected for a rapid metal-ligand exchange. In conclusion, the thiacalixarene counterpart of the tetra(diethyl)amide *p-tert*-butylcalix[4]arene was synthesized. Its cone conformation was proved from its conversion into the related ethyl ester derivative. The replacement of the bridging CH$_2$ units of the calix[4]arene by sulphur atoms led to a loss of selectivity within the alkali and the alkaline earth series which may be attributed to a size effect. In contrast the thia derivative turned to be selective for Pb^{2+} among heavy and transition metal ions.

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