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Sami Ben Maamar[a][b]; Natsagma Jadambaa[a]; Francis Vocanson[c]; Faouzi Meganem[b]; Caroline Felix[d]; Isabelle Dumazet-Bonnamour[d]
[a] Université de Lyon, Lyon, France [b] Faculté des Sciences de Bizerte, Jarzouna, Bizerte, Tunisia [c] Université Jean Monnet, Saint Etienne, France [d] UFR de chimie, Université Lyon 1, Villeurbanne, France

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Synthesis and complexation properties towards metal ions of new tri-substituted thiacalix[4]arenes

Sami Ben Maamar[a,c], Natsagma Jadambaa[a], Francis Vocanson[b1], Faouzi Meganem[c], Caroline Felix[d]* and Isabelle Dumazet-Bonnamour[d2]

[a]*Université de Lyon, Lyon, France;* [b]*Université Jean Monnet, Saint Etienne, France;* [c]*Faculté des Sciences de Bizerte, Jarzouna, Bizerte, Tunisia;* [d]*UFR de chimie, Université Lyon 1, Villeurbanne, France*

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New thiacalix[4]arenes appended with three amide functions have been prepared. Their conformations have been solved thanks to ^{1}H NMR 2D correlation spectroscopy (COSY) and nuclear overhauser and exchange spectroscopy (NOESY). The complexation ability of these ligands towards various metal ions (Cd^{2+}, Pb^{2+}, Pd^{2+}, Ni^{2+}, Hg^{2+}, Hg^{+}, Ag^{+}, Zn^{2+} and Cu^{2+}) has been investigated by the UV–vis absorption and the stoichiometry of the metal–ligand complexes was determined.

Keywords: thiacalix[4]arene; synthesis; conformation; metal complexation

Introduction

Toxic heavy metals such as copper, mercury, lead, nickel or cadmium can have a serious impact on the aqueous environment. Therefore, the detection and treatment of these toxic metal ions still remain an important topic. In this field, calixarenes, the well-known cyclic oligomers of *p*-substituted phenols and formaldehydes, have attracted increased interest. Since the conventional calix[4]arenes have poor coordination ability towards metal ions, chemical modifications have taken place by introducing functional groups having metal-binding ability. Recently, a new class of macrocycles named thiacalixarenes has emerged. The presence of sulphur atoms (which possess lone pairs and vacant 3d orbitals) instead of methylene bridges opens new possibilities, especially in the field of metal complexation. The parent thiacalix[4]arene was found to extract a wide range of transition metal ions from water, in contrast to the classical calix[4]arene (*1*). For many years, our group was interested in metal ion complexation and extraction (*2–4*). Hence, we have previously reported the synthesis of a thiacalix[4]arene with tetra-amide functions at the lower rim (*4*). Extraction experiments have evidenced a remarkable binding ability of this ligand towards a wide range of metal cations.

With the aim of supplementing this study, we wondered about the role of the number of chelating groups. The lower rim functionalisation of thiacalix[4]arene is becoming better understood following the work of Lhotak (*5*, *6*) and Yamamoto (*7*). A few articles report the odd functionalisation of thiacalixarenes. Among them, for example, the trimethylation of the hydroxyls of thiacalix[4]arene (*5*) was described (*5*) using K_2CO_3 in acetonitrile.

In this paper, we describe the preparation of thiacalix[4]arenes substituted with triamide functions at the lower rim. The complexation ability of these new ligands towards various metal ions has been investigated by the UV–vis titration. The goal of this work is to dispose of a macrocycle that could be grafted on a surface without losing its complexation properties.

Preparation and characterisation of the ligands

The synthetic route for the ligands **TC1–3** is depicted in Scheme 1. The *O*-alkylation of the lower rim of the parent *p*-*tert*-butylthiacalix[4]arene was achieved by the action of Na_2CO_3 (3 eq.) in acetone in the presence of NaI, followed by 2-chloro-*N*,*N*-diethylacetamide. The reaction was refluxed 3 days and the crude product was purified by chromatography on silica gel to afford the pure **TC1**. ^{1}H and ^{13}C NMR spectra of **TC1** in $CDCl_3$ showed the presence of the expected triamide derivative. However, it was difficult to determine the conformation of **TC1**. To complete the structural analysis, 2D COSY and NOESY experiments were performed. The ^{1}H NMR shows two doublets and one singlet for the $O{-}CH_2{-}C{=}O$ signal. The 2D COSY confirms the presence of an AB system for two $O{-}CH_2{-}C{=}O$ groups and a singlet for the third one (Figure 1). This AB system results from the rigidity of the calixarene conformation and of the prochirality of two of the CH_2 groups. The 2D NOESY shows correlation spots between

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*Corresponding author. Email: caroline.felix@univ-lyon1.fr

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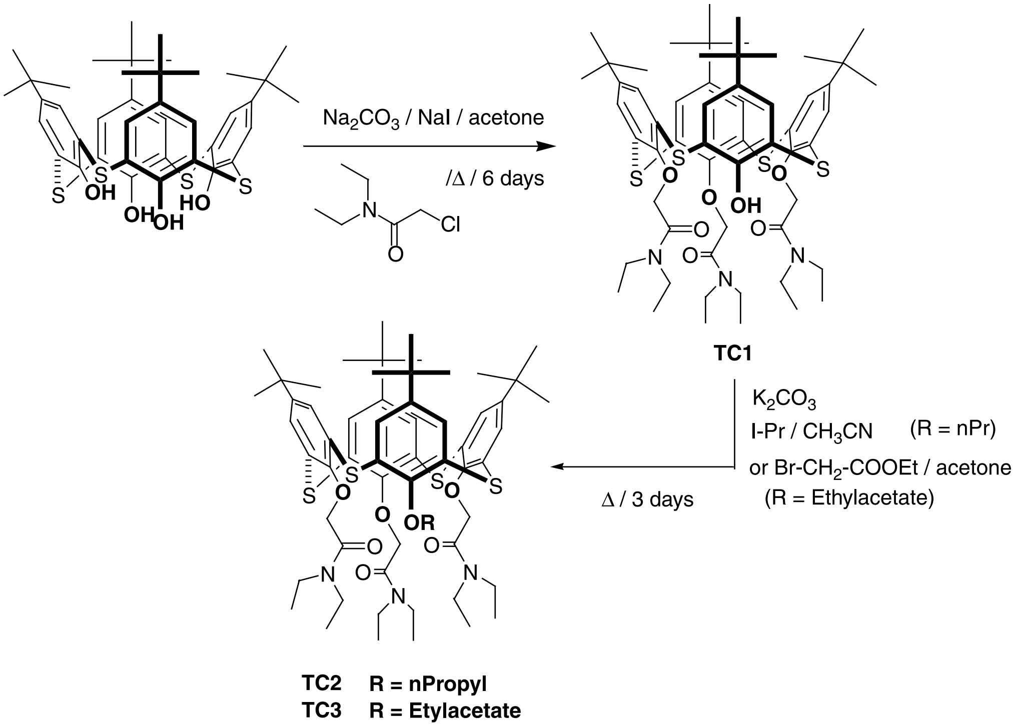


Scheme 1. Synthesis of triamide ligand derivatives.

the aromatic hydrogens of neighbouring phenyl moieties. A correlation spot is also present between one O—C*H*$_2$—C═O group (corresponding to the singlet signal) and the *OH* function (Figure 1). With the sight of these results, we can conclude that the tri-substituted thiacalix[4]arene **TC1** adopts a cone conformation in solution. Then, the derivatisation of the thiacalixarene **TC1** was researched to establish the influence of the substitution of the phenolic group on the complexation of metallic cations. At first, **TC1** was alkylated with 1-iodopropane in refluxing acetonitrile in the presence of K$_2$CO$_3$ as a base. The desired product **TC2** bearing three amide groups and one propyl group was obtained after chromatographic separation. **TC1** was also alkylated with ethylbromoacetate in refluxing acetone in the presence of K$_2$CO$_3$ as a base. The desired product **TC3** bearing three amide groups and one ethylacetate group was also obtained after the chromatographic separation. The compounds **TC2** and **TC3** were identified by ^{1}H and ^{13}C NMR, and ES-MS. The NMR analysis showed that the cone conformation was conserved for the two macrocyclic derivatives.

Complexation study

The UV–vis spectra of **TC1–3** show characteristic bands between 290 and 340 nm in CH$_3$CN/H$_2$O (3 v/v). Complexation properties of **TC1–3** were studied towards various metal salts (Cd^{2+}, Pb^{2+}, Pd^{2+}, Ni^{2+}, Hg^{2+}, Hg^{+}, Ag^{+}, Zn^{2+} and Cu^{2+}) by UV–vis titrations. In all cases, upon addition of metal cation solutions to a solution of **TC1–3**, spectra undergo clear changes and show the presence of isobestic points, indicating the existence of complex species. The addition of aliquots of Pb^{2+} (from 0.2 to 1 eq.) to a solution of **TC1** in a mixture of acetonitrile and water (3 v/v) led to a decrease in the absorption bands at 280 nm and to the appearance of a new absorption band centred at 335.5 nm that is characteristic of a metal–ligand charge transfer (MLCT) band between Pb^{2+} and the nitrogen and oxygen atoms of the amide functions on the

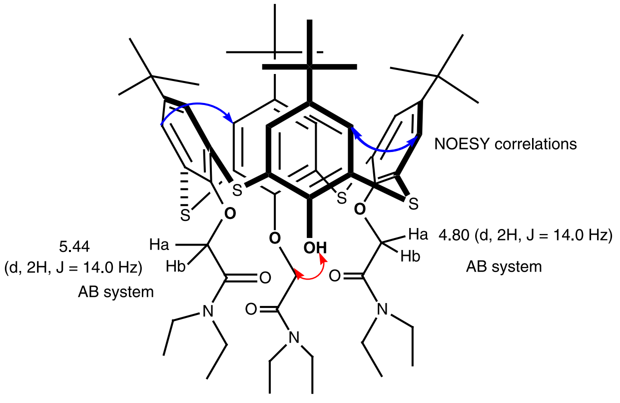


Figure 1. Conformational analysis of **TC1**. CH$_3$CN resulting from additions of Pb(NO$_3$)$_2$ (5 × 10^{-4} M in acetonitrile/water, 3 v/v).

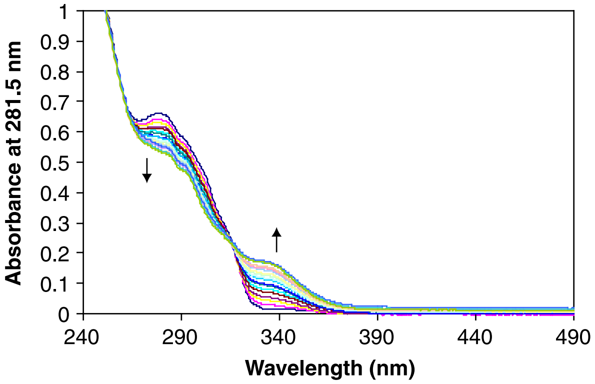
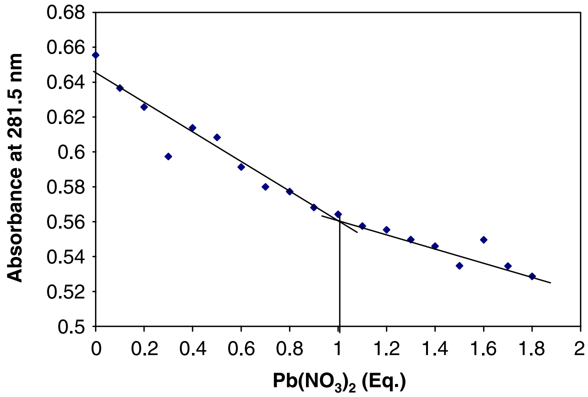


Figure 2. Changes in the absorbance spectrum of a 5 × 10^{-5} M solution of ligand **TC1** in CH_3CN resulting from additions of $Pb(NO_3)_2$ (5 × 10^{-4} M in acetonitrile/water, 3 v/v).

macrocycle (Figure 2). The isobestic point centred at 315.5 nm shows the formation of a new complex. Similar effects were observed upon addition of Ag^+, Cd^{2+}, Hg^+, Zn^{2+}, Pd^{2+} and Cu^{2+}. Upon addition of cations solutions, we can observe in all cases a hypsochromic effect of the band at 285 nm and MLCT bands.

The stoichiometry of metal–ligand (M–L) complexes was determined by both the molar ratio (*8*) and the Job plot (*9*) methods (Figure 3). The results are given in Table 1. They indicate a 1:1 stoichiometry for five complexes (Ag^+, Cd^{2+}, Pb^{2+}, Ni^{2+} and Pd^{2+}) in accordance with the literature data (*10*). We observed the formation of M_x–L_y complexes with Hg^+, Cu^{2+} and Zn^{2+}. It should be outlined that no complexation was observed for **TC1** with Hg^{2+}. For comparison, the complexation of mercury salts by the tetra-amide-thiacalix[4]arene derivative was studied: this macrocycle does not retain Hg^+(S. Ben Maamar, unpublished results.) ions, but a complex is obtained between Hg^{2+} ions and the receptor in acetonitrile as solvent (*5*). Complexation properties of **TC2** are reported in Table 1. ML-type complexes are obtained for Ag^+, Zn^{2+}, Pb^{2+}, Ni^{2+} and Pd^{2+}. Compared with the ligand **TC1**, we can highlight the formation of a monovalent complex with Zn^{2+}. No complexation occurs with Hg^+ whereas the addition of Hg^{2+} ions in a solution of **TC2** leads to the formation of a multivalent complex. The ligand **TC3**, bearing an ester group instead of a propyl chain, affords ML-type complexes with Cd^{2+}, Zn^{2+}, Pb^{2+}, Hg^{2+} and Pd^{2+}. An ML_2-type complex is observed with Ag^+.

(a) Mole ratio method of Pb^{2+}-**TC1** mixture



(b) Job plot of the titration of Pb^{2+} with **TC1**.

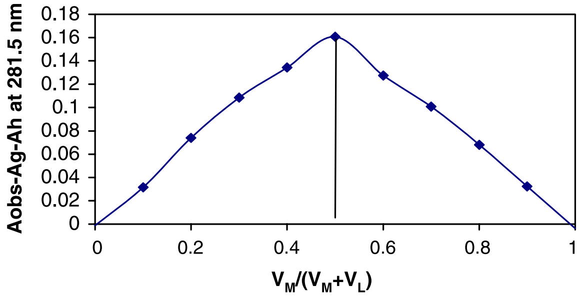


Figure 3. Determination of the stoichiometry of the Pb–ligand complex.

The stability constants *K* are defined as the concentration ratio, which are as follows [Equation (1)]:

$$K = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} \tag{1}$$

K can be correlated with the change in absorbance due to the formation of the ML complex. Further modifications of the Benesi–Hildebrand method (*11*) result in an equation, where a double reciprocal plot can be made with $1/\Delta A$ as a function of 1/[M], which is as follows [Equation (2)]:

$$\frac{1}{\Delta A} = \left[\frac{1}{\Delta\varepsilon[\mathrm{L}]_0 K}\right]\left[\frac{1}{[\mathrm{M}]}\right] + \frac{1}{\Delta\varepsilon[\mathrm{L}]_0} \tag{2}$$

The logarithms of the stability constants (Log *K*) are collected in Table 2. The values of the stability constants seem to indicate that the cation Cd^{2+} is strongly complexed with ligand **TC1** undoubtedly because of its great affinity for N and O atoms. **TC2** and **TC3** ligands exhibit affinity in the same range for all metal cations. This indicates that the introduction of an ester function instead of a propyl chain does not affect their binding ability. These results also show that it will be possible to introduce on the ligand **TC1** a spacer with a terminal function as silane or thiol allowing the grafting on a surface without loss of recognition. In this way, **TC1** is more interesting than the thiacalixarene with the four tetra-amide functions.

Conclusion

New thiacalix[4]arene derivatives appended with three amide functions have been prepared and their conformation described. The complexation ability of these ligands towards various metal ions has been investigated by the UV–vis absorption. These receptors exhibit similar

Table 1. Stoichiometry of metal–ligand complexes.

	Cd^{2+}	Pd^{2+}	Pb^{2+}	Hg^{+}	Hg^{2+}	Zn^{2+}	Cu^{2+}	Ni^{2+}	Ag^{+}
TC1	ML	ML	ML	–[a]	–[b]	–[a]	–[a]	ML	ML
TC2	–[a]	ML	ML	–[b]	–[a]	ML	–[a]	ML	ML
TC3	ML	ML	ML	–[b]	ML	ML	–[a]	–[a]	ML_2

[a] M_x–L_y complexes are observed.
[b] No complexation was observed.

Table 2. Stability constants of (1:1) metal–ligand complexes. Log K [λ (nm)].

	Cd^{2+}	Pd^{2+}	Pb^{2+}	Hg^{2+}	Zn^{2+}	Ni^{2+}	Ag^{+}
TC1	8.04 (281.5)	2.69 (244.5)	4.51 (281.5)	–	–	4.42 (278)	4.14 (281)
TC2	–	3.21 (242.5)	4.76 (294.5)	–	4.28 (236)	4.07 (284)	3.78 (294)
TC3	4.20 (283)	3.21 (242.5)	2.82 (284.5)	4.61 (282.5)	2.28 (292)	–	–

It should be noted that these values are approximations of the ligand affinity. Indeed, error in our calculations due to the uncertainties involved in ε determination and concentration of the solutions cannot be neglected.

complexation ability and selectivity except for Cd^{2+}. The main difference is observed for mercury salts. **TC1** binds selectively Hg^{+} (versus Hg^{2+}), whereas **TC2** forms selectively a multivalent complex with Hg^{2+} (versus Hg^{+}) and **TC3** gives only an ML-type complex with Hg^{2+}. It seems that the number of amide groups does not play a crucial role (*4*), but the presence of an OH function directs the selectivity towards the complexation of Hg^{+}. The extraction ability of the **TC1** derivative for noble metals such as Pd^{2+} and Au^{3+} has been investigated by means of liquid–liquid extraction experiments (*12*). It has been observed that a similar behaviour is exhibited in the case of gold for the ligand **TC1** and for the thiacalix[4]arene tetra-amide. In the case of palladium, the extraction efficiency increases with the **TC1** ligand. Moreover, the new **TC1** derivative has been successfully used as a carrier for Pd^{2+} and Au^{3+} transport in a supported liquid membrane.

Experimental section

General methods

Solvents were purified and dried by standard methods prior to use. All reactions were carried out under nitrogen. Column chromatography was performed with silica gel 60 (0.040–0.063 nm). Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained at 300.13 and 75 MHz ($CDCl_3$, trimethylsilane (TMS) as the internal standard, chemical shifts in ppm and J in Hertz). Mass spectra were obtained by the electrospray technique (positive mode).

*5,11,17,23-Tetra-*p-tert*-butyl-25,26,27-N,N-diethylaminocarbonyl-28-hydroxythia-calix[4]arene* ***TC1*** *(cone conformer)*

To a solution of 0.4 g (5.55×10^{-4} mol) of *p-tert*-butylthiacalix[4]arene and 0.176 g (1.66×10^{-3} mol) of Na_2CO_3 in acetone (60 ml), under nitrogen flux, was added 0.25 g (1.66×10^{-3} mol) of NaI and 0.24 ml (1.66×10^{-3} mol) of 2-chloro-*N,N*-diethylacetamide. The mixture was refluxed for 3 days. The solvent was removed under vacuum. To the residue was added $CHCl_3$ (40 ml). The organic layer was separated, washed with water (2 × 20 ml) and dried over Na_2SO_4. After the removal of the solvent, the residue was purified by chromatography on silica gel (0.04–0.063 mm from Merck; eluted with heptane/$CHCl_3$ 1:1) to afford pure **TC1** (286 mg, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.18$ (s, H, Ar—O*H*), 7.53 (s, 2H, Ar—*H*), 7.38 (s, 2H, Ar—*H*), 7.12 (s, 4H, Ar—*H*), 5.54 (s, 2H, Ar—O—CH_2—CO—), 5.44 (d, 2H (AB system), $^{2}J = 14.0$, Ar—O—CH_2—CO—), 4.82 (d, 2H (AB system), $^{2}J = 14.0$, Ar—O—CH_2—CO—), 3.51–3.34 (m, 12H, —CO—N(CH_2—CH_3)$_2$), 1.32–0.94 (m, 54H, Ar—C(CH_3)$_3$, —CO—N(CH_2—CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.70$ and 167.72 (—CH_2—*C*O—N—), 157.28 and 157.83 (Ar*C*—O), 147.12, 145.57 and 142.03 (Ar—*C*(CH_3)$_3$), 135.53, 134.48 and 133.37 (Ar*C*—H), 129.42 and 122.14 (Ar*C*—S), 72.71 and 69.39 (Ar—O—*C*H_2—CO—), 41.37 and 40.17 (—CO—N(*C*H_2—CH_3)$_2$), 34.39 (Ar—*C*(CH_3)$_3$), 31.67 (Ar—C(*C*H_3)$_3$), 14.82 and 13.56 (CO—N(CH_2—*C*H_3)$_2$). ES-MS. (positive mode): mass (*m/z*) = 1060 $[M + H]^{+}$, 1082.4 $[M + Na]^{+}$. M.p. = 138°C.

*5,11,17,23-Tetra-*p-tert*-butyl-25,26,27-N,N-diethylaminocarbonyl-28-propyloxythia-calix[4]arene* ***TC2*** *(cone conformer)*

To a solution of 0.1 g (0.094 mmol) of **TC1** and 0.065 g (0.471 mmol) of K_2CO_3 in acetonitrile (5 ml), under nitrogen flux, was added 0.092 ml (0.943 mmol) of 1-iodopropane. The mixture was refluxed for 3 days. The solvent was removed under vacuum. To the residue was added $CHCl_3$ (10 ml) and an aqueous solution of 1 N HCl

(10 ml). The organic layer was separated, washed with water (3 × 10 ml) and dried over Na_2SO_4. After the removal of the solvent, the residue was purified by chromatography on silica gel (0.04–0.063 mm from Merck; eluted with heptane/$CHCl_3$ 60:40) to afford pure **TC2** (23 mg, 22%) as white powder. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.43$ and 7.45 (d, 4H, $Ar{-}H$), 7.11 (s, 4H, $Ar{-}H$), 5.45 (s, 2H, $O{-}CH_2{-}CO{-}N(CH_2{-}CH_3)_2$), 5.04 (s, 4H, 2 $-O{-}CH_2{-}CO{-}N(CH_2{-}CH_3)_2$), 4.28 (t, 2H, $^3J = 7.72$, $O{-}CH_2{-}CH_2{-}CH_3$), 3.36–3.54 (m, 12H, 3 $O{-}CH_2{-}CO{-}N(CH_2{-}CH_3)_2$), 1.94–1.97 (m, 2H, $O{-}CH_2{-}CH_2{-}CH_3$), 1.04, 1.16 and 1.25 (m, 57H, $O{-}CH_2{-}CH_2{-}CH_3$, 3 $O{-}CH_2{-}CO{-}N(CH_2{-}CH_3)_2$ and $Ar{-}C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.52$ ($Ar{-}O{-}CH_2{-}CO{-}$), 158.01 ($ArC{-}O$), 146.92 ($ArC{-}C(CH_3)_3$), 134.85, 135.57 and 135.96 ($ArC{-}H$), 128.50, 129.17 and 130.96 ($ArC{-}S{-}$), 70.28 and 72.69 ($Ar{-}O{-}CH_2{-}$), 40.26, 41.56 and 41.78 ($O{-}CH_2{-}CO{-}N(CH_2{-}CH_3)_2$), 34.41 and 34.57 ($Ar{-}C(CH_3)_3$), 31.48, 31.67 and 31.83 ($Ar{-}C(CH_3)_3$), 24.23 ($O{-}CH_2{-}CH_2{-}CH_3$), 14.52 and 14.89 ($O{-}CH_2{-}CO{-}N(CH_2{-}CH_3)_2$), 13.44 ($O{-}CH_2{-}CH_2{-}CH_3$). ES-MS (positive mode): mass (m/z) = 1102.5 $[M + H]^+$, 1124.5 $[M + Na]^+$. M.p. = 200°C.

5,11,17,23-Tetra-p-tert-*butyl-25,26,27-N,N-diethylaminocarbonyl-28-ethoxycarbonylthiacalix[4]arene* ***TC3*** *(cone conformer)*

To a solution of 0.15 g (0.141 mmol) of **TC1** and 0.011 g (0.08 mmol) of K_2CO_3 in acetone (5 ml), under nitrogen flux, was added 0.031 ml (0.283 mmol) of ethylbromoacetate. The mixture was refluxed for 3 days. The solvent was removed under vacuum. To the residue was added $CHCl_3$ (20 ml) and an aqueous solution of 1 N HCl (10 ml). The organic layer was separated, washed with water (3 × 10 ml) and dried over Na_2SO_4. After the removal of the solvent, the residue was purified by chromatography on silica gel (0.04–0.063 mm from Merck; eluted with heptane/$CHCl_3$ 60:40) to afford pure **TC3** (81 mg, 50%) as white powder. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.36$, 7.52 and 7.64 (m, 6H, $Ar{-}H$), 7 (s, 2H, $Ar{-}H$), 4.73, 4.98 and 5.37 (m, 8H, 3 $O{-}CH_2{-}CO{-}N(CH_2{-}CH_3)_2$ and $O{-}CH_2{-}CO{-}O{-}CH_2{-}CH_3$), 4.21 (q, 2H, $^3J = 7.32$, $O{-}CH_2{-}CO{-}O{-}CH_2{-}CH_3$), 3.21 and 3.41 (m, 12H, 3 $O{-}CH_2{-}CO{-}N(CH_2{-}CH_3)_2$), 1.10, 1.18, 1.25, 1.28 and 1.31 (m, 57H, 3 $O{-}CH_2{-}CO{-}N(CH_2{-}CH_3)_2$, $Ar{-}C(CH_3)_3$ and $O{-}CH_2{-}CO{-}O{-}CH_2{-}CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 166.43$ and 167.29 ($Ar{-}O{-}CH_2{-}CO{-}$), 156.03 and 158.44 ($ArC{-}O$), 149.82 ($Ar{-}C(CH_3)_3$), 136.80, 136.99 and 137.02 ($ArC{-}H$), 128.32, 130.43 and 130.94 ($ArC{-}S{-}$), 71.74 and 75 ($Ar{-}O{-}CH_2{-}$), 61.74 ($O{-}CH_2{-}CO{-}O{-}CH_2{-}CH_3$), 40.44, 41.44 and 41.92 ($O{-}CH_2{-}CO{-}N(CH_2{-}CH_3)_2$), 34.83 ($Ar{-}C(CH_3)_3$), 31.32 and 31.52 ($Ar{-}C(CH_3)_3$), 14.72 ($O{-}CH_2{-}CO{-}O{-}CH_2{-}CH_3$), 13.40 and 14.57 (3 $O{-}CH_2{-}CO{-}N(CH_2{-}CH_3)_2$). ES-MS (positive mode): mass (m/z) = 1146.4 $[M + H]^+$, 1168.4 $[M + Na]^+$. M.p. = 215°C.

Complexation

The stability constants K defined as the concentration ratio [ML]/([M][L]) (where M = cation and L = ligand) were determined at 18°C, in acetonitrile or a mixture of acetonitrile/water (3 v/v) by UV absorption spectrophotometry. The spectra were recorded on a Shimadzu UV-2401-PC. The procedure consisted of adding increasing amounts of metallic salts (5×10^{-4} M) to a solution of **PC1–3** ([**PC1–3**] = 5×10^{-5} M). The metal salts used were chlorides, perchlorates, nitrates or trifluoroacetates according to their solubility in the solvents used. The following salts were used in pure acetonitrile: $Cd(ClO_4)_2{\cdot}H_2O$, CF_3COOAg, $Zn(ClO_4)_2{\cdot}6H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$, $PdCl_2$ $(CF_3COO)_2Hg$. In a mixture of acetonitrile/water (3 v/v), the following salts were used: $Pb(NO_3)_2$, $NiCl_2{\cdot}6H_2O$, $Hg(ClO_4)_2{\cdot}4H_2O$.

Notes

1. Email: francis.vocanson@univ-st-etienne.fr
2. Email: isabelle.bonnamour@univ-lyon1.fr

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