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Thiacrowncalix[4]arene Derivatives: Synthesis and Complexing Properties

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The synthesis of new thiacrowncalix[4]arenes containing four sulfur atoms in the crown moiety is reported. The complexation properties of these molecules towards soft metal cations such as Cd^{2+}, Hg^{2+} and Pb^{2+} were investigated by ^1H NMR and solvent extraction experiments that reveal their interest as extracting ligands.

Keywords: Thiacrowncalixarene; Complexation; Solvent extraction; Crystal structure

INTRODUCTION

The selective removal of highly toxic heavy metals is a major environmental concern. One of the strategies explored in this context consists of incorporating complexing ligands into solid materials, leading to an increasing interest in the design of cation-complexing ligands. Calixarenes represent an interesting class of compounds with a three-dimensional cavity that can host a large variety of molecules and ions [1]. Among them, calixcrowns have been widely studied as they show unique complexing properties towards alkali, alkaline earth and ammonium cations [2]. The idea of incorporating sulfur atoms in the crown of such calixarenes was dictated by the need to form more stable complexes with soft metal cations, such as Cd^{2+}, Hg^{2+} and Pb^{2+}. Indeed, thiacrownethers have already proved their ability to complex such cations [3–6]. A few studies have dealt with thiacrowncalixarene derivatives and focused on their complexation properties towards heavy metals such as Ag^{+}, Hg^{2+}, Pb^{2+} and Cu^{2+} [7–10]. However, the size of the crown of these calixarenes was limited by the commercial availability of the sulfur reagent. The aim of that work was to provide a ligand complexing heavy metals that could be incorporated into various solid materials. The covalent linkages of such calixarenes require modifications to dispose of suitable anchoring functions, affecting their complexing capacities as little as possible.

We report here the synthesis of two novel thiacrowncalix[4]arene derivatives bearing larger loops (four sulfur atoms). Their complexation properties towards Cd^{2+}, Hg^{2+} and Pb^{2+} ions were also studied by either ^1H NMR or solvent extraction experiments.

RESULTS AND DISCUSSION

Synthesis of the Thiacrowncalix[4]arenes

The synthesis of the thiacrowncalix[4]arenes $\mathbf{L^1}$ and $\mathbf{L^2}$ is illustrated in Fig. 1.

The calixarene $\mathbf{L^1}$ was obtained via a two-step synthesis. The calixarene derivative **1** was prepared in 65% yield by selective O-alkylation of calix[4]arene with 2.1 equivalents of chloroethoxy-*p*-toluenesulfonate in the presence of K_2CO_3 in refluxing acetonitrile during 7 days. The cone conformation of this compound was revealed by the presence in the ^1H NMR spectrum of an AB system at 4.36 and 3.38 ppm ($J = 13$ Hz), attributed to the methylenic protons ArCH_2Ar.

Intramolecular bridging on the lower rim of calixarene **1** was then achieved by condensation of

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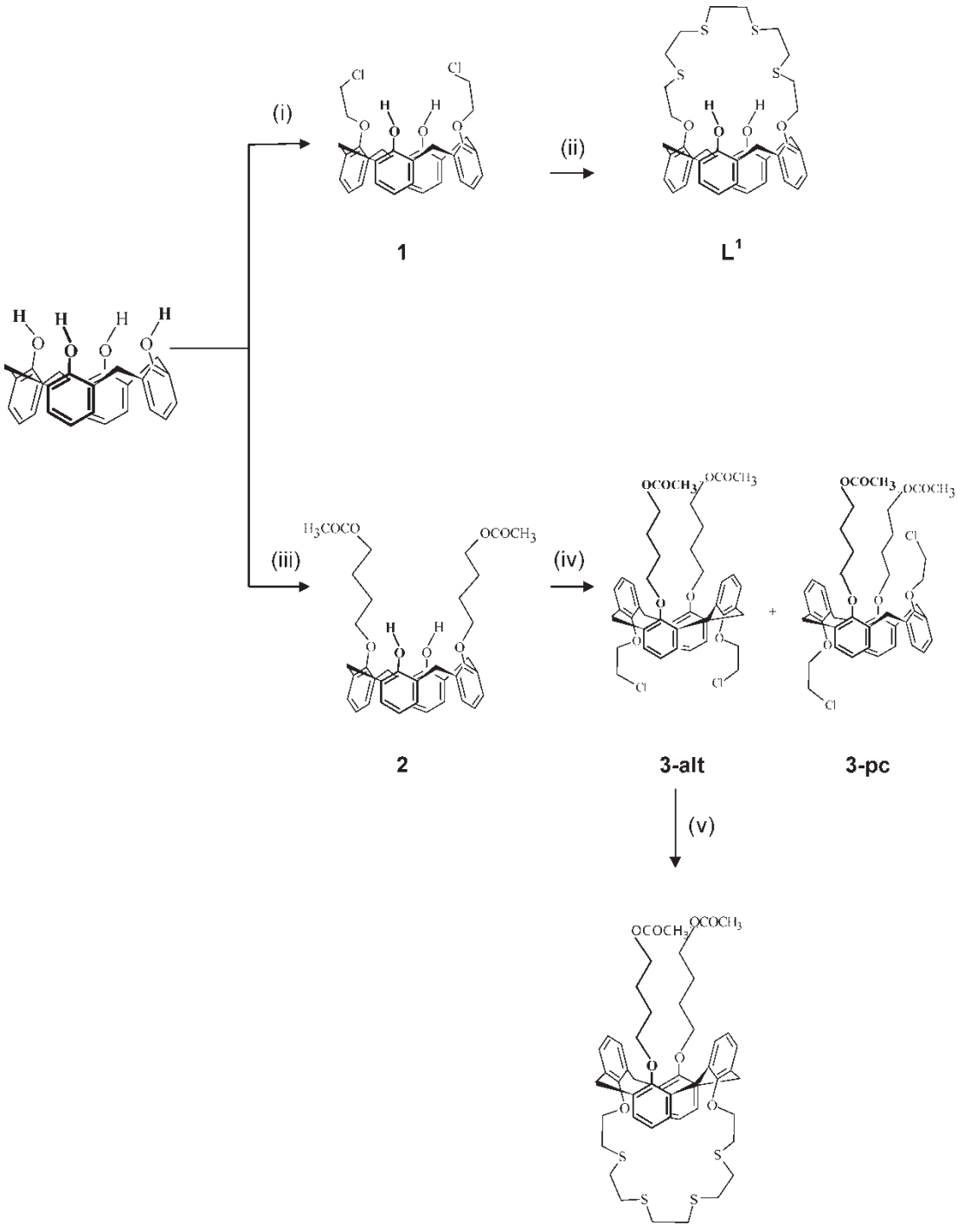

FIGURE 1 Synthetic pathways for ligands $\mathbf{L^1}$ and $\mathbf{L^2}$.

1.2 equivalents of 3,6-dithia-1,8-dithiooctane, previously treated by KOH in a refluxing benzene/DMF mixture for 10 min, and reflux of the mixture for 4 h. Finally, compound $\mathbf{L^1}$ was obtained, after purification, in 62% yield. The cone conformation was confirmed by the presence in the ^{1}H NMR spectrum of an AB system at 4.34 and 3.41 ppm ($J = 13$ Hz), attributed to the methylenic protons ArCH_2Ar.

The synthesis of $\mathbf{L^2}$ was accomplished using a three-step procedure. The calixarene derivative **2** was prepared in 42% yield by selective 1,3-*O*-alkylation of calix[4]arene with 2 equivalents of

4-bromobutylacetate in the presence of K_2CO_3 in refluxing acetone during 5 days. The cone conformation of this compound was revealed by the presence in the ^{1}H NMR spectrum of an AB system at 4.28 and 3.38 ppm ($J = 13$ Hz), attributed to the methylenic protons ArCH_2Ar.

Chloroethoxy-*p*-toluenesulfonate (2.5 equiv) was then added in the presence of K_2CO_3 in refluxing acetonitrile during 14 days for the O-alkylation of the two free phenolic functions of calixarene **2**. The solvent was removed by evaporation under reduced pressure and the crude product was purified by chromatography (SiO_2, CH_2Cl_2). 1,3-Dichloroethoxy-2,4-dioxabutyl acetate calix[4]arene **3** was obtained in both 1,3-alternate conformation, **3-alt** (singlet at 3.81 ppm for the ArCH_2Ar; 50% yield), and partial cone conformation, **3-pc** (AB system at 3.98 ppm and 3.12 ppm with $J = 13.0$ Hz and a singlet at 3.71 ppm for ArCH_2Ar; 39% yield).

Cyclization of compound **3-alt** was achieved by addition of 1 equivalent of 3,6-dithia-1,8-dithiooctane in the presence of KOH in a refluxing mixture of benzene/DMF during 20 days to give calixarene $\mathbf{L^2}$ in 26% yield. The 1,3-alternate conformation of the final compound was confirmed by ^{1}H NMR, where a singlet corresponding to the methylenic protons ArCH_2Ar was observed at 3.83 ppm.

Crystal Structure of 3-pc

The conformation of **3-pc** was confirmed by the determination of its crystal structure, shown in Fig. 2. The two independent, but nearly identical, molecules A and B are in the partial cone conformation, one of the rings bearing a CH_2CH_2Cl substituent being reversed with respect to the others. The four methylene carbon atoms linking the aromatic rings define a plane within ± 0.048 Å in both molecules. The dihedral angles between the aromatic rings and these reference planes are 84.3(2), 33.4(2), 83.5(2) and 88.3(2)° in molecule A and 84.7(2), 32.6(1), 86.7(2) and 86.5(2)° in molecule B. In each case, the ring closest to the reference plane is the one diametrically opposed to the reversed one and its substituent is directed towards the inside of the calixarene, whereas the other substituents are spread outside.

Complexation Studies

Preliminary complexation studies of $\mathbf{L^1}$ and $\mathbf{L^2}$ with the ions Cd^{2+}, Hg^{2+} and Pb^{2+} were carried out by either ^{1}H NMR or solvent extraction experiments.

For the ^{1}H NMR studies, $CDCl_3$ solutions of $\mathbf{L^1}$ and $\mathbf{L^2}$ were reacted at room temperature with solid metal picrate salts. The formation of a complex with ligand $\mathbf{L^1}$ was evidenced upon addition of $Pb^{2+}(Pic^-)_2$ and $Cd^{2+}(Pic^-)_2$.

Modifications of the chemical shifts ($\Delta\delta$) of the free ligand $\mathbf{L^1}$ in $CDCl_3$ in the presence of an excess of $Pb^{2+}(Pic^-)_2$ were observed. The two doublets of the aromatic protons (*meta* position) shifted upfield from 7.09 and 6.86 ppm to 6.94 and 6.74 ppm and the triplet of the aromatic protons at 6.70 ppm (*para* position) was split into two triplets at 6.59 and 6.54 ppm. The chemical shifts corresponding to the methylenic protons also shifted upfield. The doublets attributed to the AB system shifted from 4.34 and 3.41 ppm to 4.19 and 3.28 ppm. The methylenic protons of the crown shifted from 3.05–2.97 ppm to 2.98–2.87 ppm. The hydroxyl protons shifted from 7.53 ppm to 5.20 ppm. The integral ratio between the aromatic protons of the picrate anion (8.75 ppm) and the aromatic protons of $\mathbf{L^1}$ might indicate the formation of a binuclear complex $\mathbf{L^1}\cdot 2Pb^{2+}$.

Upon addition of $Cd^{2+}(Pic^-)_2$, the ^{1}H NMR spectrum of $\mathbf{L^1}$ only exhibited a small signal corresponding to the aromatic protons of the picrate anion (8.73 ppm) indicating a slight complexation.

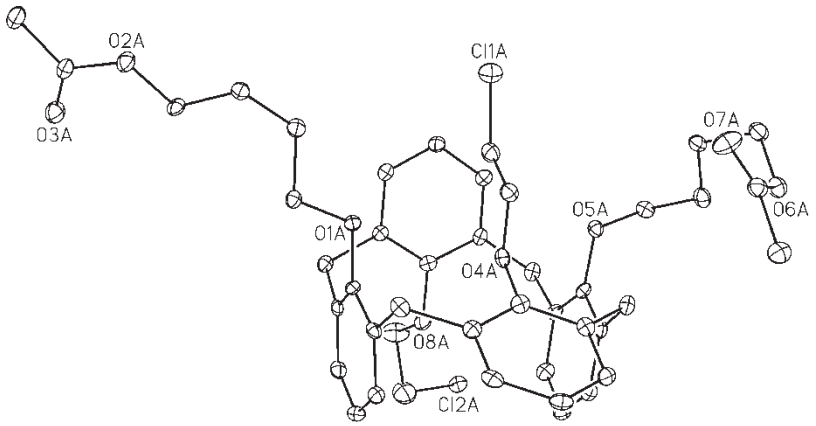

FIGURE 2 View of molecule A in compound **3-pc**. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level.

No modification of the chemical shifts of the free ligand $\mathbf{L^1}$ was observed upon addition of an excess of $Hg^{2+}(Pic^-)_2$ to $\mathbf{L^1}$.

The formation of a complex with ligand $\mathbf{L^2}$ was evidenced upon addition of $Cd^{2+}(Pic^-)_2$ or $Hg^{2+}(Pic^-)_2$. The overall spectra showed a coalescence effect at 20°C in the presence of the metal. Moreover, a small singlet corresponding to the aromatic protons of the picrate anion was noticed at 8.91 and 9.18 ppm when adding $Cd^{2+}(Pic^-)_2$ or $Hg^{2+}(Pic^-)_2$, respectively. Unlike ligand $\mathbf{L^1}$, the addition of an excess of $Pb^{2+}(Pic^-)_2$ to ligand $\mathbf{L^2}$ did not lead to any modifications of the chemical shifts of the free ligand $\mathbf{L^2}$.

Solvent extractions of Cd^{2+} and Pb^{2+} from different sodium nitrate media were carried out at 26°C by magnetically stirring the aqueous phase containing the metal with a chloroform phase containing ligand $\mathbf{L^1}$ or $\mathbf{L^2}$ for 1 h. Metal concentrations in both phases were then determined using atomic emission spectrometry. The results are presented on Figs. 3 and 4.

For all aqueous phases, ligand $\mathbf{L^1}$ exhibits a better extracting power than ligand $\mathbf{L^2}$ for both cadmium and lead. The results also indicate a more pronounced extraction of lead for both ligands compared with cadmium. $\mathbf{L^1}$ allows the extraction of 88% Pb^{2+} initially present in pure water compared to 66% Cd^{2+}. Extractions performed using $\mathbf{L^2}$ as ligand led to an extraction of 67% Pb^{2+} and 54% Cd^{2+}.

However, these extracting abilities are drastically decreased in the presence of sodium nitrate. Extractions performed from a 0.1 M sodium nitrate aqueous medium allow the extraction of only 25 and 20% Pb^{2+} and 10 and 4% Cd^{2+} when using ligands $\mathbf{L^1}$ and $\mathbf{L^2}$, respectively. This might be explained by competitive sodium extraction as 2×10^{-4} mol L^{-1} Na^+ was recovered in the stripping aqueous phase for experiments performed from a 0.1 M sodium nitrate medium.

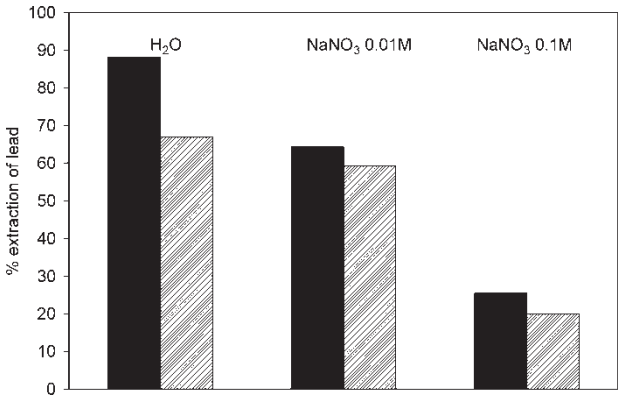

FIGURE 3 Extraction of Pb^{2+} (initial concentration: 1×10^{-5} mol L^{-1}) using ligands $\mathbf{L^1}$ (■) and $\mathbf{L^2}$ (▨), 2×10^{-3} mol L^{-1} in chloroform.

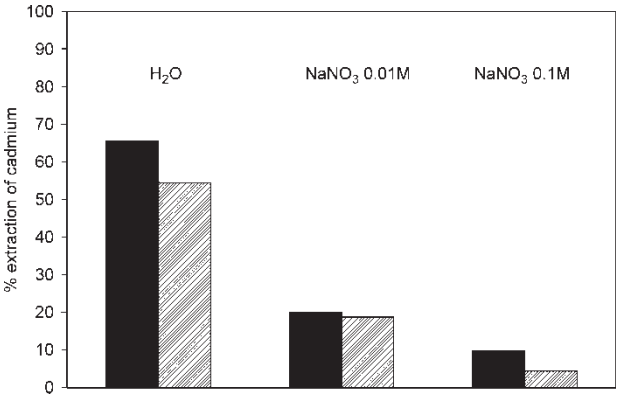

FIGURE 4 Extraction of Cd^{2+} (initial concentration: $\times 10^{-5}$ mol L^{-1}) using ligands $\mathbf{L^1}$ (■) and $\mathbf{L^2}$ (▨), 2×10^{-3} mol L^{-1} in chloroform.

CONCLUSIONS

The synthesis of two novel thiacrowncalix[4]arenes with four sulfur atoms, one in the cone and the other in the 1,3-alternate conformation, was achieved. These compounds allowed a very good extraction of Pb^{2+} and Cd^{2+} from aqueous media, compared to ligands bearing fewer sulfur atoms [7,8]. The presence of anchoring arms as well as the conformation change in ligand $\mathbf{L^2}$ seems to decrease heavy metal recognition. However, this ligand was still found to complex Cd^{2+} and Pb^{2+} efficiently. It should also be noted that the results observed for lead complexation by either ^{1}H NMR or solvent extraction experiments evidenced some differences for ligand $\mathbf{L^2}$, which might reflect an important role for water in the complexation.

EXPERIMENTAL

Synthesis

All reagents and solvents were commercial and used without further purification. Calix[4]arene was prepared according to the literature [11]. The melting points were taken on a Büchi 500 apparatus in capillaries sealed under nitrogen. Chromatography was performed using SiO_2 columns with Kieselgel Merck (art.11567). ^{1}H NMR measurements were carried out in $CDCl_3$ using a Bruker SY200 instrument (δ in ppm, J in Hz). FAB(+) mass spectra were recorded using a VG-Analytical ZAB HF instrument. Elemental analyses were performed at the Service de Microanalyse of the Institut de Chimie de Strasbourg.

1,3-Di(chloroethoxy)calix[4]arene (1)

Calix[4]arene (4.25 g, 10.0 mmol) and potassium carbonate (1.45 g, 10.5 mmol) were dissolved in

acetonitrile (200 mL) at room temperature and stirred under N_2 for 1 h. Chloroethoxy-*p*-toluenesulfonate (4.91 g, 21.0 mmol) was then added and the mixture was refluxed for 7 days. After cooling to room temperature, the solvents were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and acidified with 1 N HCl. The organic phase was dried over Na_2SO_4, filtered and evaporated to dryness. The residue was treated with ethanol to obtain the calixarene derivative **1** as a white solid.

Yield: 3.60 g (65%); mp = 207–208°C; ^{1}H NMR (200 MHz, $CDCl_3$): 7.69 (s, 2H, ArO*H*), 7.08 (d, 4H, J = 7.5 Hz, Ar*H*), 6.92 (d, 4H, J = 7.5 Hz, Ar*H*), 6.79–6.64 (m, 4H, Ar*H*), 4.36 (d, 4H, J = 13.0 Hz, ArCH_2Ar), 4.30 (t, 4H, J = 6.5 Hz, OCH_2CH$_2$), 4.08 (t, 4H, J = 6.5 Hz, OCH$_2$CH_2), 3.38 (d, 4H, J = 13.0 Hz, ArCH_2 Ar). Anal. J = 6.5 Hz, Calcd. for $C_{32}H_{30}O_4Cl_2$(%): C, 69.95; H, 5.52. Found: C, 70.01; H, 5.48. Mass spectrum (FAB + , NAB): m/z = 550.41 [MH$^+$].

1,3-Dihydroxycalix[4]arene-monothiacrown-6 (L^1)

3,6-Dithia-1,8-dithiooctane (0.26 g, 1.2 mmol) and potassium hydroxide (0.14 g, 2.4 mmol) were refluxed in a mixture of benzene (100 mL) and DMF (50 mL) for 10 min under a nitrogen atmosphere. Compound **1** (0.55 g, 1.0 mmol) was then added and the reaction mixture was refluxed for 4 h. Compound $\mathbf{L^1}$ was recovered after purification by chromatography (SiO_2, CH_2Cl_2) as a white solid.

Yield: 0.43 g (62%); mp = 167–168°C; ^{1}H NMR (200 MHz, $CDCl_3$): 7.53 (s, 2H, ArO*H*), 7.09 (d, 4H, J = 7.5 Hz, Ar*H*), 6.86 (d, 4H, J = 7.5 Hz, Ar*H*), 6.70 (t, 4H, J = 7.0 Hz, Ar*H*), 4.34 (d, 4H, J = 13.0 Hz, ArCH_2Ar), 4.17 (t, 4H, J = 6.5 Hz, OCH_2CH$_2$SCH$_2$CH$_2$), 3.41 (d, 4H, J = 13.0 Hz, ArCH_2Ar), 3.21 (t, 4H, J = 6.5 Hz, OCH$_2$CH_2SCH$_2$CH$_2$), 3.05–2.97 (m, 8H, OCH$_2$CH$_2$SCH_2CH_2SCH$_2$), 2.91 (s, 4H, OCH$_2$CH$_2$SCH$_2$CH$_2$SCH_2). Anal. Calcd. for $C_{38}H_{42}O_4S_4$(%): C, 66.05, H, 6.13. Found: C, 66.10; H, 6.16. Mass spectrum (FAB + , NAB): m/z = 691.1 [MH$^+$].

1,3-Di(4-oxabutylacetate)calix[4]arene (2)

Calix[4]arene (8.49 g, 20.0 mmol) and potassium carbonate (2.90 g, 21.0 mmol) were dissolved in acetone (700 mL) and stirred for 1 h at room temperature under a nitrogen atmosphere. 4-Bromobutylacetate (7.80 g, 40.0 mmol) was then added and the reaction mixture was refluxed for 5 days. After cooling to room temperature, the solvents were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and acidified with 1 N HCl. The organic phase was dried over Na_2SO_4, filtered and evaporated to dryness. After purification by chromatography (SiO_2, CH_2Cl_2), the calixarene derivative **2** was obtained as a white solid.

Yield: 5.50 g (42%); mp = 121–122°C; ^{1}H NMR (200 MHz, $CDCl_3$, δ in ppm): 8.02 (s, 2H, ArO*H*), 7.07 (d, 4H, J = 7.5 Hz, Ar*H*), 6.91 (d, 4H, J = 7.5 Hz, Ar*H*), 6.78–6.62 (m, 4H, Ar*H*), 4.28 (d, 4H, J = 13.0 Hz, ArCH_2Ar), 4.25 (s br, 4H, CH_2OCOCH$_3$), 4.04 (s br, 4H, OCH_2CH$_2$), 3.38 (d, 4H, J = 13.0 Hz, ArCH_2Ar), 2.11–2.09 (m, 8H, OCH$_2$CH_2CH_2), 2.09 (s, 6H, OCOCH_3). Anal. Calcd. for $C_{40}H_{44}O_8$(%): C, 73.60; H, 6.79. Found: C, 73.57; H, 6.86. Mass spectrum (FAB + , NAB): m/z = 653.3 [MH$^+$].

1,3-Di(4-oxabutylacetate)-2, 4-di(chloroethoxy)calix[4]arene (3)

Calixarene derivative **2** (2.60 g, 4.0 mmol) and potassium carbonate (5.53 g, 40.0 mmol) were dissolved in acetonitrile (400 mL) and stirred at room temperature for 1 h. Chloroethoxy-*p*-toluenesulfonate (2.34 g, 10.0 mmol) was then added and the reaction mixture was refluxed for 14 days. After evaporation of acetonitrile to dryness, the residue was dissolved in CH_2Cl_2 and acidified with 1 N HCl. The organic phase was dried over Na_2SO_4, filtered and concentrated. After purification by chromatography (SiO_2, CH_2Cl_2), calixarene derivatives **3-alt** and **3-pc** were recovered as white solids.

Analytical Data for Compound 3-alt

Yield: 1.55 g (50%); mp = 123–124°C. ^{1}H NMR (200 MHz, $CDCl_3$): 7.08–7.00 (m, 8H, Ar*H*), 6.79–6.64 (m, 4H, Ar*H*), 3.99 (t, 4H, J = 6.5 Hz, CH_2OCOCH$_3$), 3.81 (s, 8H, ArCH_2Ar), 3.59 (t, 4H, J = 6.5 Hz, ArOCH_2), 3.48 (t, 4H, J = 6.5 Hz, ArOCH_2), 2.91 (t, 4H, J = 6.5 Hz, OCH$_2$CH_2), 2.08 (s, 6H, OCOCH$_3$), 1.42–1.27 (m, 8H, OCH$_2$CH_2CH_2). Anal. Calcd. for $C_{44}H_{50}O_8Cl_2$(%): C, 67.95; H, 6.48. Found: C, 68.14; H, 6.43. Mass spectrum (FAB + , NAB): m/z = 776.1 [MH$^+$].

Analytical Data for Compound 3-pc

Yield: 1.20 g (39%); mp = 90–91°C. ^{1}H NMR (200 MHz, $CDCl_3$): 7.26–6.93 (m, 8H, Ar*H*), 6.50 (t, 2H, J = 7.0 Hz, Ar*H*), 6.36–6.31 (m, 2H, Ar*H*), 4.18 (t, 4H, J = 7.0 Hz, CH_2OCOCH$_3$), 4.07 (t, 2H, J = 7.0 Hz, CH_2CH$_2$Cl), 3.98 (d, 2H, J = 13.0 Hz, ArCH_2Ar), 3.87–3.75 (m, 4H, ArOCH_2), 3.71 (s, 4H, ArCH_2Ar), 3.68–3.55 (m, 4H, CH$_2$CH_2Cl and CH_2CH$_2$Cl), 3.25–3.19 (m, 2H, CH$_2$CH_2Cl), 3.12 (d, 2H, J = 13.0 Hz, ArCH_2Ar), 2.09 (s, 6H, OCOCH$_3$), 1.99–1.86 (m, 8H, OCH$_2$CH_2CH_2). Anal. Calcd. for $C_{44}H_{50}O_8Cl_2$(%): C, 67.95; H, 6.48. Found: C, 68.14; H, 6.43. Mass spectrum (FAB + , NAB): m/z = 776.1 [MH$^+$].

1,3-Di(4-oxabutylacetate)calix[4] arene-monothiacrown-6 (L^2)

3,6-Dithia-1,8-dithiooctane (0.26 g, 1.0 mmol) and potassium hydroxide (0.12 g, 2.1 mmol) were

refluxed in a mixture of benzene (100 mL) and DMF (50 mL) for 10 min under a nitrogen atmosphere. Compound **3** (0.78 g, 1.0 mmol) was then added and the reaction mixture was refluxed for 20 days. After cooling to room temperature, the solvents were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and acidified with 1 N HCl. The organic phase was dried over Na_2SO_4, filtered and evaporated to dryness. Compound $\mathbf{L^2}$ was recovered after purification by chromatography (SiO_2, CH_2Cl_2) as a white solid.

Yield: 0.23 g (26%); mp = 89–90°C. ^{1}H NMR (200 MHz, $CDCl_3$): 7.21–7.02 (m, 8H, Ar*H*), 6.99–6.78 (m, 4H, Ar*H*), 3.91 (t, 4H, $J = 6.5$ Hz, CH_2 OCOCH$_3$), 3.83 (s, 8H, ArCH_2Ar), 3.53–3.39 (m, 8H, ArOCH_2CH$_2$ and ArOCH_2CH$_2$S), 2.87 (s, 4H, SCH_2 CH_2S), 2.86–2.70 (m, 12H, CH$_2$SCH_2CH_2S), 2.07 (s, 6H, OCOCH$_3$), 1.32–1.21 (m, 8H, CH_2CH_2CH$_2$). Anal. Calcd. for $C_{50}H_{62}O_8S_4$(%): C, 65.33; H, 6.80. Found: C, 65.27; H, 6.91. Mass spectrum (FAB +, NAB): $m/z = 919.2$ [MH$^+$].

Crystal Structure of Compound 3-pc

Crystal Data for 3-pc

$C_{44}H_{46}Cl_2O_8$, $M = 773.71$, triclinic, space group $P\bar{1}$, $a = 15.661(2)$, $b = 17.087(2)$, $c = 17.419(2)$ Å, $\alpha = 107.673(8)$, $\beta = 97.630(8)$, $\gamma = 111.601(8)°$, $V = 3969(1)$ Å^3, $Z = 4$, $D_c = 1.295$ g cm^{-3}, $\mu = 0.217$ mm^{-1}, $F(000) = 1632$. $R_1 = 0.100$, $wR_2 = 0.228$, $S = 0.992$ for 13 793 independent reflections ($R_{int} = 0.099$) and 993 parameters.

Data were collected at 100(2) K on a Nonius Kappa CCD area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and processed with DENZO-SMN [12]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXTL [13]. One chlorine atom in each of the two independent molecules was found to be disordered over two positions that were refined with occupancy factors constrained to sum to unity. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced at calculated positions (except in the disordered parts) and were treated as riding atoms, with an isotropic displacement parameter equal to 1.2 (CH, CH$_2$) or 1.5 (CH$_3$) times that of the parent atom. Crystal data have been deposited with the Cambridge Crystallographic Data Centre (CCDC reference number 249648).

^{1}H NMR EXPERIMENTS

Picrate salts were prepared according to the procedure described in the literature [14, 15]. $\mathbf{L^1}$ or $\mathbf{L^2}$ (0.016 g) in $CDCl_3$ solution (0.5 mL) was reacted with an excess of Cd^{2+}, Hg^{2+} or Pb^{2+} picrate salts for 24 h at room temperature. ^{1}H NMR spectra were then recorded.

Solvent Extraction Experiments

Five mL of either a 10–100 mM sodium nitrate or a pure water aqueous phase containing $Cd(NO_3)_2{\cdot}4H_2O$ or $Pb(NO_3)_2$ (1×10^{-5} mol L^{-1}) and 5 mL of a water-saturated chloroform phase containing $\mathbf{L^1}$ or $\mathbf{L^2}$ (2×10^{-3} mol L^{-1}) were magnetically stirred for 1 h at 26.0 ± 0.2°C. Before and after extraction, the pH of the aqueous phase was measured using a Jenco Electronics Ltd pH meter and a combined Ag/AgCl electrode. Both phases were separated and aliquots were analyzed by atomic emission spectrometry (ICP/AES JY38) at $\lambda = 228.8$, 220.3 and 589.6 nm for Cd^{2+}, Pb^{2+} and Na^+, respectively. Prior to the analysis, the metal contained in the organic phase was stripped with a 0.1 M HNO_3 solution.

References

[1] Gutsche, C. D. In *Calixarenes Revisited*; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge, 1998.
[2] Casnati, A.; Ungaro, R.; Asfari, Z.; Vicens, J. In *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Eds.; Kluwer Academic: Dordrecht, 2001; pp 365–384.
[3] Baumann, T. F.; Reynolds, J. G.; Fox, G. A. *Chem. Commun.* **1998**, 1637.
[4] Tsuchiya, T.; Shimizu, T.; Hirabayashi, K.; Kamigata, N. *J. Org. Chem.* **2002**, *67*, 6632.
[5] Tsuchiya, T.; Shimizu, T.; Kamigata, N. *J. Am. Chem. Soc.* **2001**, *123*, 11534.
[6] Williams, S. M.; Brodbelt, J. S.; Marchand, A. P.; Cal, D.; Mlinaric-Majerski, K. *Anal. Chem.* **2002**, *74*, 4423.
[7] Sim, W.; Lee, J. K.; Kwon, J.; Kim, M. J.; Kim, J. S. *Bull. Korean Chem. Soc.* **2002**, *23*, 879.
[8] Akkus, G. U.; Memon, S.; Yilmaz, M. *Polycycl. Arom. Comp.* **2002**, *22*, 1075.
[9] Xie, J.; Zheng, Q.-Y.; Zheng, Y.-S.; Chen, C.-F.; Huang, Z.-T. *J. Inclusion Phenom.* **2001**, *40*, 125.
[10] Tabakci, M.; Memon, S.; Yilmaz, M.; Roundhill, D. M. *J. Polym. Sci. Part* **2004**, *42*, 186.
[11] Gutsche, C. D.; Levine, J. A.; Sujeeth, P. K. *J. Org. Chem.* **1985**, *50*, 5802.
[12] Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.
[13] Sheldrick, G.M. SHELXTL, Version 5.1, University of Göttingen, distributed by Bruker-AXS Inc., Madison, WI, 1999.
[14] Aggarwal, R. C.; Singh, N. K. *Def. Sci. J.* **1975**, *25*, 153.
[15] Arnaud-Neu, F.; Swing-Weill, M.-J.; Ziat, K.; Cremin, S.; Harris, S. J.; McKervey, M. A. *New J. Chem.* **1991**, *15*, 33.