Calixarenes Derivatized with Sulfur-Containing Functionalities as Selective Extractants for Heavy and Precious Metal Ions

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The calix[4]arenes 5,11,17,23-*tert*-butyl-25,26,27,28-(2-methylthioethoxy)calix[4]arene, 25,26,27,28-(2-methylthioethoxy)calix[4]arene, and 5,11,17,23-*tert*-butyl-25,26,27,28-(2-(2-thiophenecarboxy)ethoxy)calix[4]arene have been prepared. The structure of 25,26,27,28-(2-methylthioethoxy)calix[4]arene has been verified by X-ray crystallography. The crystals with the empirical formula $C_{40}H_{48}O_4S_4$ are monoclinic $C2/c$ with $a = 20.428(2)$ Å, $b = 10.581(1)$ Å, $c = 20.445(2)$ Å, $\beta = 118.461(5)°$, $Z = 4$. These calix[4]arenes are effective extractants for transferring heavy metal ions from aqueous solution into chloroform. The extraction of Sn(II), Hg(II), Ag(I), Pd(II), Au(III), MeHg(II), Pb(II) and Cd(II) into chloroform with these calix[4]arenes is compared with that performed with 5,11,17,23-*tert*-butyl-25,26,27,28-(2-*N*,*N*-dimethyldithiocarbamoylethoxy)calix[4]arene, 25,26,-27,28-(2,*N*,*N*-dimethyldithiocarbamoylethoxy)calix[4]arene, and 5,11,17,23-*tert*-butyl-25,26,27,28-(2-mercaptoethoxy)-calix[4]arene.

Introduction

From an environmental and economic viewpoint, there remains a need to discover more selective and effective extractants for toxic heavy metals from waters and soils.[1−3] The challenge is to find complexants that selectively extract commercially useful metals from a mixture and allow them to be released in pure form. In view of these considerations, we have targeted new complexants for mercury, methylmercury,[4] cadmium, lead, copper, thallium, tin, palladium, and silver.

Treatment methods for heavy-metal-containing waste include precipitation, solvent extraction, activated carbon adsorption, treatment with ion-exchange resins, bioremediation, reverse osmosis, electrolysis, cementation, irradiation, zeolite adsorption, evaporation, membrane processes, and ion flotation.[5] Solvent extraction with chelate and macrocyclic ligands requires rapid selective complexation, high stability against hydrolysis, minimal affinity for alkali or alkaline earth ions, high metal-extractant binding strength, and reversible complexation allowing for metal recovery.[6−8] The complexant donor atoms are usually oxygen, nitrogen and sulfur, but others are possible.[9,10] For extraction into nonpolar solvents the metal complex should be hydrophobic. Extractants include macrocycles, crowns, lariat ethers, cryptands, and calixarenes. In general, oxygen macrocycles are effective extractions for alkali and alkaline earth metals,[11−14] with nitrogen analogues being ineffective for alkali metals. Since heavy metals form strong bonds with sulfur, favored functionalities are hydrogen sulfides (HS^-), thiolates (RS^-), thioethers (RSR′), dithiocarbamates ($R_2NCS_2^-$), and substituted thioureas (RNHC(S)NHR′).[15]

Extractants must be selective for heavy metals against alkali, alkaline earth, or other common metals such as iron. Calixarenes with sulfur-derivatized functionalities potentially meet these requirements because they are multidentate preorganized macrocyclic type ligands with appended arms. Our chosen calix[4]arenes have sulfur groups appended to the lower rim (Figure 1).

Experimental Section

A. Synthesis and Characterization. Synthesis of Sulfur-Derivatized Calixarene Ligands. All materials and solvents were standard reagent grade and were used without further purification unless otherwise noted. Dry THF was distilled from the ketyl prepared from sodium and benzophenone. Acetone was dried over K_2CO_3. DMF was stored over molecular sieves (4 Å). Pyridine was dried over KOH pellets prior to use. The compounds 5,11,17,23-*tert*-butyl-25,26,27,-28-(2-*N*,*N*-dimethyldithiocarbamoylethoxy)calix[4]arene (**1**), 25,26,27,-28-(2,*N*,*N*-dimethyldithiocarbamoylethoxy)calix[4]arene (**2**), 5,11,17,23-*tert*-butyl-25,26,27,28-(2-mercaptoethoxy)calix[4]arene (**3**), 5,11,17,23-*tert*-butyl-25,26,27,28-(2-hydroxyethoxy)calix[4]arene, 5,11,17,23-*tert*-butyl-25,26,27,28−2-(bromoethoxy)calix[4]arene, and 25,26,27,28-(2-

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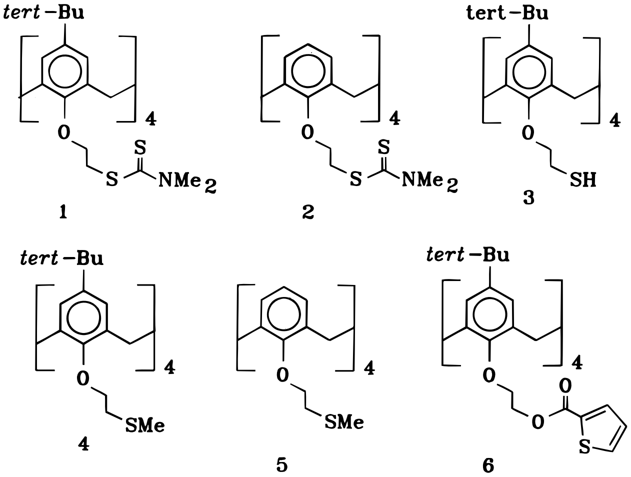

Figure 1. Structures of calix[4]arenes **1**−**6**.

bromethoxy)calix[4]arene were prepared using literature procedures.[16−18] Fast atom bombardment (FAB) mass spectra were obtained using a Kratos concept 1H spectrometer with the samples introduced in an *m*-nitrobenzyl alcohol matrix. Melting points were obtained on a hot-stage apparatus. ^{1}H and ^{13}C NMR spectra were measured using either a GE Omega 400 MHz or Bruker 200 or 300 MHz spectrometers. Infrared spectra were recorded as KBr pellets with a Mattson Cygnus 100 FT-IR instrument. Electronic spectra were recorded as aqueous or chloroform solutions, unless otherwise noted, with a Hewlett-Packard 8452A diode array UV/visible spectrometer. X-ray diffraction data were collected on a Siemens model P4 automated diffractometer using Mo Kα radiation. Elemental analyses were performed by Galbraith Inc., Knoxville, TN. All reactions were carried out under a nitrogen atmosphere. The presence of solvent in samples for elemental analysis was confirmed by ^{1}H NMR spectroscopy.

5,11,17,23-*tert*-Butyl-25,26,27,28-(2-methylthioethoxy)calix[4]arene (4). To a solution of 5,11,17,23-*tert*-butyl-25,26,27,28-(2-bromoethoxy)calix[4]arene (2.0 g, 1.8 mmol) in dry pyridine (40 mL) was added sodium thiomethoxide (1.0 g, 14.4 mmol). The reaction mixture was stirred at room temperature for 3 h and then poured slowly into ice-cold HCl (400 mL of 2N). *Stench! Methanethiol is evolved!* The solid was collected by filtration, dissolved in benzene (200 mL), and washed successively with HCl (200 mL) and water (200 mL). The reaction mixture was dried over $MgSO_4$, the solvent was evaporated almost to dryness, and methanol was added. The solution was then allowed to stand at 0 °C for 24 h. The compound was filtered and dried in vacuo. The compound can be recrystallized from a mixed solution of chloroform and methanol. Yield 1.10 g (63%), mp 194 °C. Anal. Calcd for $C_{56}H_{80}O_4S_4$: C, 71.1; H, 8.53; S, 13.6. Found: C, 71.0; H, 8.57; S, 12.5. ^{1}H NMR ($CDCl_3$): δ 1.05 (s, 36 H, *tert*-Bu); 2.19 (s, 12 H, CH_3S); 3.00−3.25 (m, 12 H, CH_2, CH_2S); 4.04 (t, 8 H, CH_2O); 4.36 (d, 4 H, CH_2); 6.77 (s, 8 H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 15.8 (q, ^1J(CH) = 138.4 Hz, CH_3S); 28.8−35.2 (m, CH_2, CH_2S, CCH_3, CCH_3); 73.5 (t, ^1J(CH) = 145.0 Hz, CH_2O); 125.1 (d, ^1J(CH) = 153.2 Hz, ArCH); 133.6 (s, Ar*C*); 144.9 (s, Ar*C*); 152.8 (s, Ar*C*).

25,26,27,28-(2-Methylthioethoxy)calix[4]arene (5). To a solution of 25,26,27,28-(2-bromethoxy)calix[4]arene (2.4 g, 2.8 mmol) in dry pyridine (40 mL) was added sodium thiomethoxide (1.6 g, 22.4 mmol). The reaction mixture was stirred at room temperature for 3 h and then poured slowly into ice-cold HCl (400 mL of 2 N). *Stench! Methanethiol is evolved!* The solid was collected by filtration, dissolved in benzene (200 mL), and washed successively with HCl (200 mL) and water (200 mL). After the reaction mixture was dried over $MgSO_4$ the solvent was evaporated almost to dryness, and methanol was added. The solution was then allowed to stand at 0 °C for 24 h. The compound was filtered and dried in vacuo. The compound can be recrystallized from a mixed solution of chloroform and methanol. Yield 1.40 g (68%), mp 145 °C. Anal. Calcd for $C_{40}H_{48}O_4S_4$: C, 66.6; H, 6.71; S, 17.8. Found: C, 67.0; H, 6.84; S, 17.6. ^{1}H NMR ($CDCl_3$): δ 2.17 (s, 12 H, CH_3S); 2.98 (t, 8 H, CH_2S); 3.17 (d, 4 H, CH_2); 4.04 (t, 8 H, CH_2O); 4.42 (d, 4 H, CH_2); 6.40−6.70 (m, 8 H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 15.8 (q, ^1J(CH) = 138.1 Hz, CH_3S); 30.9 (t, ^1J(CH) = 129.5 Hz, CH_2); 33.4 (t, ^1J(CH) = 140.6 Hz, CH_2); 73.3 (t, ^1J(CH) = 148.0 Hz, CH_2O); 122.5 (d, ^1J(CH) = 162.8 Hz, ArCH); 128.3 (d, ^1J(CH) = 155.4 Hz, Ar*C*); 134.83 (s, Ar*C*); 155.7 (s, Ar*C*).

5,11,17,23-*tert*-Butyl-25,26,27,28-(2-(2-thiophenecarboxy)ethoxy)calix[4]arene (6). To a solution of 5,11,17,23-*tert*-butyl-25,26,27,28-(2- hydroxyethoxy)calix[4]arene (1.30 g, 1.60 mmol) in dry pyridine (40 mL) was added 2-thiophene carbonyl chloride (1.90 g, 1.40 mL, 12.8 mmol) at 0 °C. The homogeneous solution was stored at 0 °C for 24 h. The reaction mixture was poured into ice-cold HCl (400 mL of 2 N). The solid was extracted with benzene (200 mL) and washed successively with HCl (200 mL) and 10% $NaHCO_3$ (3 × 200 mL). After the reaction mixture was dried over $MgSO_4$, the solvent was evaporated under reduced pressure to give a viscous oil. The addition of cold methanol caused the precipitation of a white solid which was collected by filtration. Yield 1.40 g (69%), mp 172 °C. Anal. Calcd for $C_{72}H_{80}O_{12}S_4{\cdot}CH_3OH$: C, 67.7; H, 6.31; S, 9.9. Found: C, 67.3; H, 6.41; S, 9.9. ^{1}H NMR ($CDCl_3$): δ 1.05 (s, 36H, *tert*-Bu); 3.16 (d, 4H, CH_2); 4.32 (t, 8H, CH_2O); 4.45 (d, 4H, CH_2); 4.77 (t, 8H, CH_2O); 6.77 (s, 8H, Ar*H*); 6.95−6.99 (m, 4H, Ar*H*); 7.40−7.47 (m, 4H, Ar*H*); 7.60−7.65 (m, 4H, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 31.0 (t, ^1J(CH) = 129.0 Hz, CH_2); 31.4 (q, ^1J(CH) = 116.2 Hz, CCH_3); 33.7 (s, CCH_3); 65.1 (t, ^1J(CH) = 148.4 Hz, CH_2O); 72.4 (t, ^1J(CH) = 143.8 Hz, CH_2O); 125.2 (d, $+_{\mathrm{ive}}$, ArCH); 127.6 (d, $+_{\mathrm{ive}}$, ArCH); 132.3 (d, $+_{\mathrm{ive}}$, ArCH); 133.5 (d, $+_{\mathrm{ive}}$, ArCH); 145.0 (s, Ar*C*); 153.0 (s, Ar*C*); 162.1 (s, $C{=}O$).

B. Crystal Structure Determination for 25,26,27,28-(2-Methylthioethoxy)calix[4]arene (5). Pale orange crystals of **5** were grown by slow evaporation of a solution of the compound in a mixture of $CHCl_3$ and MeOH. A suitable crystal was sealed in a thin-walled glass capillary under an atmosphere of dry nitrogen saturated with chloroform and methanol vapors. Data collection was performed on a Siemens model P4 automated diffractometer using Mo Kα radiation. The unit cell parameters were determined and refined by a least-squares fit of 24 high-angle reflections. Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction based upon a check of the Laue symmetry and systematic absences present was performed and was confirmed by the structure solution. The structure was determined by direct methods followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using the SHELXTL-IRIS software package provided by Siemens Analytical X-ray Instruments, Inc. The parameters refined included the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms, except for the disordered carbon atom positions of the side chain of one of the aromatic rings, which were refined isotropically. Hydrogen atoms were placed in calculated positions but were not refined. The crystallographic data are collected in Table 1, and selected bond distances and angles in Table 2. An ORTEP representation of **5** is shown in Figure 2.

Unit cell parameters and systematic absences indicated a choice of either the centrosymmetric group, $C2/c$, or the noncentrosymmetric group, Cc. Initial attempts to solve the structure by direct methods in $C2/c$ did not yield meaningful results. Changing the space group to Cc provided all of the non-hydrogen atom positions for one molecule; however, examination of the atomic coordinates revealed that one-half of the molecule was related to the other half by rotation about a 2-fold axis at 1, y, $^1/_4$. The coordinates for one-half of the molecule were then successfully refined in $C2/c$. At this stage, a large number of residual peaks were observed in the region of the side chain of one of the aromatic rings. These were found to correspond to an approximate 50/50 2-fold disorder of the sulfur and the three carbon atoms of the side chain, although a third position that formed reasonable bond distances and angles to atoms in both conformations was refined for

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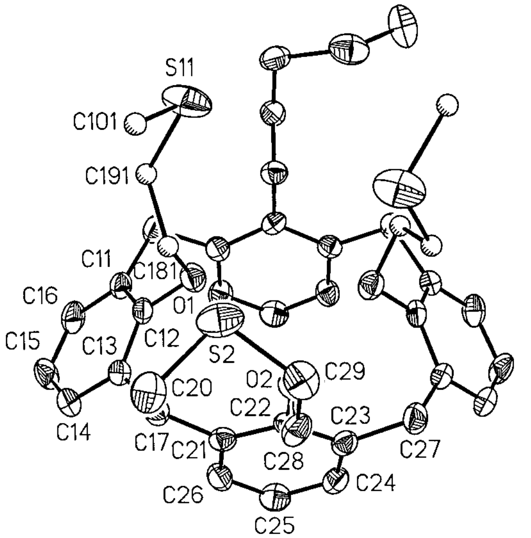


Figure 2. ORTEP representation (30% ellipsoids) of **5**.

Table 1. Crystallographic Data for 25,26,27,28-(2-Methylthioethoxy)calix[4]arene (**5**)

chemical formula	$C_{40}H_{48}O_4S_4$
formula weight	721.0
a, Å	20.428(2)
b, Å	10.581(1)
c, Å	20.445(2)
β, deg	118.461(5)
volume, Å^3	3885.0(8)
Z	4
space group	*C*2/*c* (No. 15)
T, °C	21
λ, Å	0.71073
ρ_{calcd}, g cm^{-3}	1.233
μ, cm^{-1}	2.83
R (%)[a]	7.69
R_w (%)[b]	10.35

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w|F_o|^2]^{1/2}$ $w = 1/\sigma^2(F)$.

Table 2. Selected Bond Distances (Å) and Angles (deg)

C101−S11	1.867(53)	C20−S2−C29	100.8(5)
S11−C191	1.915(47)	S2−C29−C28	116.5(7)
C191−C181	1.504(60)	C29−C28−O2	108.9(5)
C181−O1	1.465(36)	C28−O2−C22	112.8(5)
C20−S2	1.808(10)	C101−S11−C191	94.5(20)
S2−C29	1.792(10)	S11−C191−C181	115.3(35)
C29−C28	1.483(12)	C191−C181−O1	109.5(27)
C28−O2	1.439(7)	C181−O1−C12	111.0(22)

one of the carbon atoms. The two disordered sulfur positions (S11 and S12) were refined anisotropically, while the seven positions for the three carbon atoms were refined isotropically. The largest peaks in the final difference Fourier map corresponded to hydrogen atoms on the aromatic rings.

As a final check, the full molecule was refined in the noncentrosymmetric space group *Cc* in order to determine whether the residual peaks observed for the side chain were truly the result of disorder, or instead computer-generated artifacts caused by imposition of additional symmetry constraints that were not actually present in the structure. This procedure confirmed that the side chain was indeed disordered.

Description of the Crystallographic Disorder in the Aromatic Side Chain. The general numbering scheme for the chain, starting from the aromatic ring, is O1−C18−C19−S1−C10. All of the atoms in the chain are disordered except for O1; therefore, atom C18 occupies positions C181 and C182; atom C19 occupies positions C191, C192, and C193; atom S1 occupies positions S11 and S12; and atom C10 occupies positions C101 and C102. As shown in the tables of bond distances and angles, every one of the positions forms chemically reasonable bond distances and angles to at least one set of adjacent atoms, and some positions are common to more than one conformation of the chain. There are eight possible, chemically reasonable conformations that are described by these positions. The various sites may be included in anywhere from one to five of these configurations, and some configurations may be preferred over others. Hence, the site occupancy factors for any one position are not necessarily required to be the same as those for another position in the chain. The eight configurations, with the relevant bond distances and angles, are given below.

atom	connectivity
O1	attached to C181 (1.465 Å) and C182 (1.457 Å)
C181	attached to C191 (1.504 Å) and C192 (1.562 Å)
C182	attached to C192 (1.455 Å) and C193 (1.391 Å)
C191	attached to S11 (1.915 Å) and S12 (1.959 Å)
C192	attached to S11 (1.817 Å)
C193	attached to S12 (1.987 Å)
S11	attached to C101 (1.867 Å) and C102 (1.581 Å)
S12	attached to C102 (1.693 Å)

configuration	O1−C18−C19	C18−C19−S1	C19−S1−C10
O1−C181−C191−S11−C101	109.5°	115.3°	94.5°
O1−C181−C191−S11−C102	109.5°	115.3°	113.2°
O1−C181−C191−S12−C102	109.5°	105.0°	106.2°
O1−C181−C192−S11−C101	101.3°	117.8°	103.6°
O1−C181−C192−S11−C102	101.3°	117.8°	102.3°
O1−C182−C192−S11−C101	107.1°	107.9°	103.6°
O1−C182−C192−S11−C102	107.1°	107.9°	102.3°
O1−C182−C193−S12−C102	115.0°	106.4°	102.5°

Atoms C18, S1, and C10 were each found to occupy two positions. The site occupancy factors (SOF) for these atoms were refined independently, and the two factors for each atom were constrained to add up to a total of 1. Atom C19 occupies three positions, and these were refined with three independent, unconstrained site occupancy factors. A rigorous treatment requires that these three parameters also add up to 1; however, this treatment is beyond our capabilities. Faced with the choice of assigning fixed SOFs to these positions or allowing them to refine unconstrained, we chose the latter. The three parameters added to give a total of 1.74 atoms; however, it is our judgment that it is more preferable to use experimentally determined figures than to assign arbitrary numbers in this case. The site occupancy factors for all for the positions are given below.

C181 (0.460 78), C182 (0.539 22), C191 (0.607 48),
C192 (0.676 87), C193 (0.459 04), S11 (0.452 60),
S12 (0.547 40), C101 (0.230 67), C102 (0.769 33)

C. Metal Ion Extraction. Solution Preparation. The solutions used for the liquid−liquid extractions were prepared as follows: 10^{-4} mol of each of compound **1**−**6** was dissolved in chloroform (100 mL). In a similar manner 10^{-3} M solutions were prepared from $HgCl_2$ and $CH_3HgOCOCH_3$ in 0.1 M HNO_3; Na_2PdCl_4 and $SnCl_2$ in 0.1 M NaCl; K_2PtCl_4 in 0.1 M KCl; Li_2PdBr_4 in LiBr; $AuCl_3$ in 0.1 M HCl; $AgNO_3$, $Pb(NO_3)_2$, $Cd(NO_3)_2{\cdot}4H_2O$, $TlPF_6$, $Mn(NO_3)_2{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}2.5H_2O$, $Zn(NO_3)_2.6H_2O$, and H_2PtCl_6 in distilled water. Buffer solutions were either purchased from Aldrich (Hydrion, pH 3) or prepared by dissolving equimolar amounts of maleic acid and sodium hydroxide in distilled water to give a buffer with a pH of 6 and a concentration of 0.08 M.

Liquid−Liquid Extraction. Equal volumes from each phase (5 mL) were shaken for 1 min. An aliquot (2 mL) from the aqueous phase was then diluted to a volume of 10 mL with nitric acid (0.1 M), and the metal concentration was compared to that of the initial solution. Initial and final concentrations of the metals were measured on an Optimum 3000 ICP-AES spectrometer. Radiofrequency power: 1200 W. Nebulizer flow: 1.000 L/min. Auxiliary flow: 0.5 L/min. Plasma flow: 15 L/min. Pump rate: 1.0 mL/min. Equilibration time: 15 s. Read delay: 50 s. Rinse time: 20 s. Replicates: 3. The analytical wavelengths used are given in Table 3.

Table 3. Analytical Wavelengths for Analyses

Ag	328 nm*	338 nm	Pb	216 nm	220 nm*
Au	242 nm*	267 nm	Pd	324 nm	340 nm*
Cd	214 nm*	228 nm	Pt	204 nm	214 nm*
Hg	404 nm	253 nm*	Sn	189 nm*	235 nm
Ni	221 nm	341 nm*			

* Used for metal concentration determination.

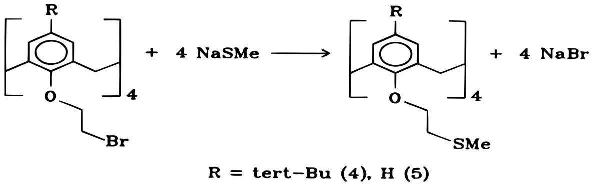
Those lines marked with an asterisk gave calibration curves with greater slopes and thus were used for metal concentration determination.

UV−Vis Measurements. Equal volumes of each phase (2 mL) were shaken for 1 min. A 1 mL aliquot from the organic phase was then diluted to a volume of 25 mL with chloroform, and a UV−vis spectrum of that solution in the region 200−500 nm was taken. If the absorbance of the highest intensity peak was >2.00, the sample was further diluted until the highest absorbance was <2.00.

^{1}H NMR Measurements. A sample of the calix[4]arene (∼4 mmol) was dissolved in $CDCl_3$ (1 mL), and this solution was shaken with the stoichiometric volume of the corresponding metal salt for 1 min. The phases were left to separate completely, a portion of the organic phase was pipetted into an NMR tube, and its ^{1}H NMR spectrum was measured. The organic layer was shaken again with a solution of thiourea in water, the organic phase was separated, and the ^{1}H NMR spectrum of the sample was again measured.

Results and Discussion

Synthesis. The carbamoyl derivatives **1** and **2** and the mercaptoethoxy-*tert*-butylcalix[4]arene **3** have been prepared by the literature procedure from the 2-bromoethoxy derivatives.[16,17] Treatment of the 2-bromoethoxy derivatives with sodium thiomethoxide in dry pyridine yields **4** and **5** that have thioether functionalities on their lower rim (eq 1). The compounds **4** and **5** differ only by having a *tert*-butyl or a hydrogen in the para position of the upper rim. Acylation of 5,11,17,23-*tert*-butyl-25,26,27,28-(2-hydroxyethoxy)calix[4]-arene with 2-thiophene carbonyl chloride in dry pyridine at 0 °C leads to the formation of **6** having both sulfur and oxygen binding sites bound to the lower rim (eq 2). The calix[4]arenes **4**−**6** have been characterized by a combination of ^{1}H and ^{13}C NMR spectroscopy. Although there are examples in the literature of metal complexes of thiophenes, to our knowledege, no extractions with thiophene-functionalized ligands have been reported. This prompted us to explore the extraction properties of **6** in order to make comparisons with the calix[4]arenes **1**−**5**.



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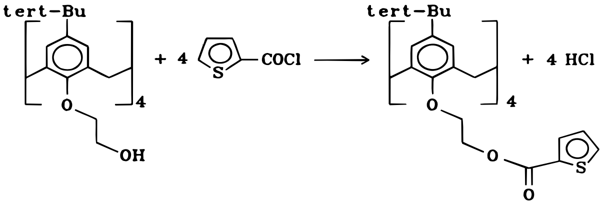

(2)

6

X-ray Crystallography. The structure of **5** confirms that proposed from spectroscopy. Selected bond distances and angles are collected in Table 2. No unusual bond distances or angles are observed. An ORTEP drawing of **5** is shown in Figure 2. The compound crystallizes in the flattened cone conformation with two of the phenyl rings in the calixarene unit almost parallel to each other, while those in the the other pair flip toward each other. The O−O distances between two opposite phenolic oxygen atoms are 3.583 Å (O1−O1′) to 5.642 Å (O2−O2′). One pair of opposite methylthioethoxy arms are situated above the cavity (the distance S11−S11′ is 4.496 Å), while the other pair points outside the cavity (the distance S2−S2′ is 7.684 Å). In the latter pair of side arms, the thioether sulfur atoms come into closer contact with sulfur atoms from another molecule (S2−S2″ = 4.434 Å). There is a crystallographically imposed C_2 axis passing through the center of the molecule.

Table 4. Extraction (%) of Heavy Metals by Calix[4]arenes **1**−**6**

	calix[4]arene					
metal (Å, CN)	**1**	**2**	**3**	**4**	**5**	**6**
Sn(II) 1.18, 3	10		17	<5	<7	<2
Hg(II) 1.02, 2	81	85	86	6	62	46
Ag(I) 1.15, 4	74	60	60	65	97	39
Pd(II) 0.86, 4	100	100	41	70	63	31
Au(III) 0.85, 4	100	97	64	100	99	8
MeHg(II) −, 4	38	2	81			
Pb(II) 1.19, 6	<3	11	<6			
Cd(II) 0.95, 4−6	<4	9	<3			

Metal Extractabilities. The extraction data with **1**−**6** show that they are selective extractants of heavy and precious metal ions into chloroform from water. The extractability data for Sn(II), Hg(II), Ag(I), Pd(II), Au(III), MeHg(II), Pb(II), and Cd(II) are collected in Table 4. The ionic radius and preferred coordination number of each is included. These calix[4]arenes do not extract the lighter metals Fe(II), Mn(II), Co(II), Ni(II), and Zn(II) nor do they extract Pt(II) and Pt(IV). Although the short extraction times do not necessarily yield equilibrium extraction conditions, the comparative values are valid insofar as they reflect the relative effectiveness of the extractants under short contact time conditions. Furthermore, in several cases where the compounds are stable, we have carried out extractions over several hours and find essentially the same results.

Our data show that, whereas **1** is an effective complexant for the heavy metals Hg(II) and MeHg(II), it is ineffective for Pb(II) and Cd(II) and only slightly effective for Sn(II). For **3** at low pH, similar results are obtained. For precious metals, both **1** and **3** are effective extractants for Au(III) but ineffective for Ni(II) and Pt(II). Compound **1** is effective for Pd(II), but **3** is only moderately effective. These extractabilities do not correlate well with size effects when the ionic radii for either 4- or 8-coordinate ions are used.[19] If platinum were to be excluded, a case could be made for the second series of metal ions that an ionic radius of 0.8 was favored for **1**. This exclusion of platinum is justifiable because it is likely that its poor extraction is due to the kinetic inertness of Pt(II).[20] Nevertheless, this premise fails for the first series of metals because Hg(II) (with an ionic radius of 1.10 Å) is efficiently extracted by **1**. Similarly, in octacoordination, Hg(II) and Cd(II) have closely similar ionic radii, yet they are on the opposite ends of the

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Table 5. Ligand Selectivities

	1	2	3	4	5	6
Au/Ag	1.4	1.6	1.1	1.5	1.0	0.2
Ag/Hg	0.9	0.7	0.7	10.8	1.6	0.9
Au/Pd	1.0	1.0	1.6	1.4	1.6	0.3
Hg/Au	0.8	0.9	1.3	0.06	0.6	5.8
Hg/Sn	8.1		5.1	>1.2	>8.8	>23
Hg/Cd	>20.3	9.4	>28.7			

extractability scale. Apparently all three factors—size, polarizability effects, and kinetics—play a role in the selective complexation of these metals. The de-*t*-butylated dithiocarbamoyl analogue **2** shows a similar extractability pattern, except that it extracts MeHg(II) only poorly. This selectivity pattern may be due to conformational differences in the calixarene ligand because, whereas the *tert*-butyl-substituted calix[4]arene **1** adopts the symmetric cone conformation, the unsubstituted analogue **2** adopts an elongated cone conformation.[17]

The thioether-functionalized ligands **4** and **5** show a slightly different pattern. The extractability order for Hg(II) and Ag(I) is reversed, and Pd(II) is only ~70% extracted. Thioethers as ligands are softer than dithiocarbamates, and the bulky alkyl groups attached directly to the donor atom in thioethers make them more space-demanding. The softness is a possible explanation for the preferable extractability of Ag(I) over Hg(II). Again, the conformational changes caused by the presence or absence of *tert*-butyl groups on the upper rim may explain the incresed extractability of **2** over **1**. Also, **2** may have a larger oxygen-rich cavity at the lower rim which may allow the etheral-oxygens to participate in the coordination process and thus to increase the extractability for Hg(II) and Ag(I). Both ligands extract Pd(II) moderately and Au(III) almost completely.

Ligand **6** with four thiophene rings appended onto the lower rim shows somewhat low extractability and selectivity. Thiophene alone does not form strong complexes which is likely due to the involvement of the unshared electron pairs of the sulfur atom in the formation of a stable π electron sextet. Nevertheless, **6** does extract some metal ions, even though all of the extractabilities are below 50%. In Table 5 is a summary of some selected selectivities of our sulfur-derivatized calixarene ligands.

At our present state of knowledge of calix[4]arene complexation chemistry with heavy metals, it is difficult to make any definitive statements about the reasons for this observed selectivity. Neither ionic radius nor preferred coordination number shows any strong correlation with the selectivity data. Although further data will be required to fully answer these questions, it is clear that good selectivities are obtainable with calix[4]arenes.

Characterization of Ligands and Their Metal Extracts. ^{1}H and ^{13}C NMR Spectra. In addition to ^{1}H resonances due to the *tert*-butyl groups at approximately δ 1.00 for the *tert*-butyl compounds **1**, **3**, **4,** and **6**, all compounds show two sets of doublets around δ 3.19 and 4.36 for the ring methylenes. These resonances support the compounds being in the cone conformation.

Compounds **1** and **2** have triplet ^{1}H NMR resonances for the methylenes of the 2-*N*,*N*-dimethyldithiocarbamoylethoxy group at δ 3.93 and 3.87 (CH_2S for **1** and **2**) and δ 4.24 and 4.22 (CH_2O for **1** and **2**). The corresponding N(CH_3)$_2$ resonances are observed as broad singlets at δ 3.38 and 3.53 for **1**, and at δ 3.37 and 3.52 for **2**. In the ^{13}C NMR spectrum of **1** and **2** resonances for the 2-*N*,*N*-dimethyldithiocarbamoylethoxy groups are found at δ 73.2 (*C*H$_2$O), 37.1 (*C*H$_2$S), 197.2 (*C*=S), 41.6 (N*C*H$_3$), and 45.3 (N*C*H$_3$) for **1**, and at δ 73.0 (*C*H$_2$O), 37.3 (*C*H$_2$S), 196.8 (*C*=S), 41.7 (N*C*H$_3$), and 45.4 (N*C*H$_3$) for **2**.

Table 6. ^{1}H NMR Spectra of **2** and Its Metal Complexes

metal salt	shift (δ)
none	3.37, 3.52 (N(CH_3)$_2$) 3.87 (CH_2S)
$HgCl_2$ (L/M = 2/1)	3.41, 3.58 (N(CH_3)$_2$)
$HgCl_2$ (L/M = 1/1)	3.43, 3.62 (N(CH_3)$_2$) 3.91 (CH_2S)
$AuCl_3$ (L/M = 1/1)	3.42, 3.61 (N(CH_3)$_2$)
$AgNO_3$ (L/M = 2/1)	3.39, 3.57 (N(CH_3)$_2$)
$AgNO_3$ (L/M = 1/1)	3.40, 3.60 (N(CH_3)$_2$)
$PdCl_4^{2-}$ (L/M = 1/1)	3.75, 3.85 (N(CH_3)$_2$)

Compound **3** is characterized by a quadruplet resonance at δ 3.08 (CH_2SH) and a triplet resonance at δ 1.60 (S*H*). Compound **4** is characterized by a multiplet at δ 3.00−3.25 (CH_2S), a triplet at δ 4.04 (CH_2O), and a singlet at δ 2.19 (CH_3S). Compound **5** shows a triplet at δ 2.98 (CH_2S), a triplet at δ 4.04 (CH_2O), and a singlet at δ 2.17 (CH_3S). Compound **6** is characterized by triplets at δ 4.34 (CH_2O) and 4.78 (CH_2O). The ^{13}C{^{1}H} NMR spectrum of **6** shows resonances at δ 125.2 (*C*H), 127.6 (*C*H), 132.3 (*C*H), 133.6 (*C*H),145.0 (*C*), 153.0 (*C*), and 162.1 (*C*=O). A DEPT spectrum was used to distinguish resonances belonging to tertiary or quaternary carbons. The presence of the ^{13}C resonances for the *C*H$_2$ groups in the vicinity of δ 31 supports the solution structures of **4**−**6** being in the cone conformation.[21]

It is possible that shifts in the complexant protons will be detectable for Hg(II), Ag(I), and Au(III) where significant extraction into the organic phase occurs. Free **2** shows a triplet at δ 3.87 (CH_2S) and broad peaks at δ 3.37 and 3.52 for the inequivalent N(CH_3)$_2$ methyls. After extraction of Hg(II) into $CHCl_3$ with a 1:1 ligand/metal ratio the N(CH_3)$_2$ resonances shift to δ 3.43 and 3.62, and the CH_2S resonance shifts to 3.91. After extraction with a 2:1 ligand/metal ratio, again only two N(CH_3)$_2$ resonances appear, this time at δ 3.41 and 3.58. The downfield shifts observed for CH_2S and N(CH_3)$_2$ upon complexation of Hg(II) are suggestive of binding of the metal to the sulfurs of the *N*,*N*-dimethylcarbamoyl group. The observation of only a single set of resonances in solutions of **2** and Hg(II) and the progressive downfield shifts as the metal/ligand ratio is increased can be explained by a fast metal−ligand exchange rate. Similarly when Ag(I) is extracted with **2** in a 1:1 ligand/metal ratio, N(CH_3)$_2$ shifts to δ 3.40 and 3.60, and with a 2:1 ligand/metal ratio, N(CH_3)$_2$ shifts to δ 3.39 and 3.57. Extraction of Au(III) causes downfield shifts to δ 3.42 and 3.61 for N(CH_3)$_2$. These spectral data are collected in Table 6. Although the ^{1}H NMR spectrum of extracted Au(III) with **2** remains unchanged over a considerable period of time, the presence of excess $AuCl_3$ in a solution of **1** or **2** in $CDCl_3$ results in a mixture of unidentifiable products that are likely due to oxidation of **1** and **2** by Au(III). For extracted Pd(II), N(CH_3)$_2$ now shifts to δ 3.75 and 3.85. Calix[4]arene **1** shows similar coordination behavior. These spectral changes upon metal complexation are due to metal binding via the sulfur atoms of the *N*,*N*-dimethylcarbamoyl moiety.

Although **4** and **5** extract Hg(II), Ag(I), and Pd(II), no significant shifts are observed in the solutions; therefore, ^{1}H

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Table 7. Electronic Absorption Spectra of Ligands and Complexes

compd	metal salt	λ (nm)
2		250, 280
2	$AuCl_3$	250, 280, ∼330
2	$PdCl_4^{2-}$	250, 280, 354
2	$PdBr_4^{2-}$	250, 280, 374
2	$HgCl_2$	250, 280, 312
2	$AgNO_3$	250, 280, ∼310 sh
5		242, 270
5	$AuCl_3$	242, 270, 320
5	$PdCl_4^{2-}$	242, 270, 362
5	$PdBr_4^{2-}$	242, 270, 378
5	$HgCl_2$	242, 270
5	$AgNO_3$	242, 270

NMR provides no insight regarding binding sites on these calixarenes. Additional information has therefore been sought from UV−vis spectroscopy of the chloroform extracts.

Electronic Absorption Spectra. UV−vis spectroscopy on the chloroform extracts of **2** and **5** are collected in Table 7, although for cases where little metal extraction occurs, no data were collected.

Calix[4]arene **2** shows two absorptions in the UV−vis at 250 and 280 nm due to transitions in the phenyl and *N*,*N*-dimethyldithiocarbamoyl groups. Extraction of $AuCl_4^-$, $PdCl_4^{2-}$, $PdBr_4^{2-}$, $HgCl_2$, and $AgNO_3$ leads to the appearance of a third band at longer wavelength. The respective positions of these additional bands are ∼330, 354, 374, 312, and ∼310 nm. This difference between $PdCl_4^{2-}$ and $PdBr_4^{2-}$ indicates that all four halides are not substituted. Calix[4]arene **5** shows one absorption at 242 nm due to a $n \rightarrow \pi^*$ transition in the thioether group, and a less intense shoulder at 270 nm due to $\pi \rightarrow \pi^*$ transitions in the calixarene aromatic ring. Extractions of Hg(II) and Ag(I) show no new long wavelength bands. Extraction of $PdCl_4^{2-}$ leads to a new absorption band at 362 nm, which is observed at 378 nm when $PdBr_4^{2-}$ is used. For $AuCl_4^-$ a new band appears at 320 nm.

The absorptions of **2** at 250 and 280 nm are likely due to $\pi \rightarrow p^*$ and $n \rightarrow s^*$ (or $n \rightarrow p^*$) transitions, respectively.[22] The additional red-shifted bands for **2** in the presence of Pd(II), Au(III), Hg(II), and Ag(I) are likely due to charge transfer. Similar bands have been found previously in analogous complexes, and the direction of the charge transfer in dithiocarbamate complexes has been assigned to both LMCT and MLCT transitions between sulfur and the metal center.[23,24] The additional red-shifted bands for **5** in the presence of Pd(II) and Au(III) are likely due to LMCT since their wavelengths are in the region expected for such a S → M transition.[25−28] These data support the premise that **2** and **5** are complexed to the metal ions via metal−sulfur bonds.[29] For Pd(II), where incomplete halide substitution occurs, literature precedent suggests that complexes of type PdX_2L_2 are formed (eq 3), where X is Cl, Br, and L is a sulfur donor group in **2** or **5**.[30] Gold(III) is also kinetically inert, and it is again unlikely that all chlorides are substituted in the extraction.[31] For Hg and Ag, literature precedent suggests metal extraction occurs as homoleptic complexes,[32] although polymeric species may also be present.[33−35] Nevertheless, both ^1H NMR and UV−vis spectroscopy of the metal extracts show the presence of metal−sulfur binding.

$$PdX_4^{2-} + 2L \rightarrow PdX_2L_2 \qquad (3)$$

Metal removal from these calix[4]arene extracts can be accomplished with thiourea. For **2**, with Hg(II), Ag(I), and Au(III), when the chloroform layer is washed with a thiourea solution in D_2O, the ^1H NMR spectrum of the chloroform layer verifies that it contains free **2**. For Pd(II) and Au(III), the solution color also transfers into the upper aqueous layer upon washing the lower chloroform layer with aqueous thiourea.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and bond angles, anisotropic displacement coefficients, and H-atom coordinates for **5** (6 pages). Ordering information is given on any current masthead page.

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