

Notes

Synthesis of Heavy Metal Ion Selective Calix[4]arenes Having Sulfur Containing Lower-Rim Functionalities

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Introduction

Calixarene based ligands with functionalities binding *via* their oxygen or nitrogen sites have been widely employed as selective complexants for group I and II metal ions.¹ By contrast, little has been published on the preparation of calixarene derivatives which coordinate to a metal center *via* other heteroatoms.^{2–4} Such compounds are particularly important if selective complexants for heavy metals are to be developed. We report here the preparation of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(2-bromoethoxy)calix[4]arene, along with its application for the synthesis of calixarene derivatives having sulfur containing functionalities appended to the lower rim, and the use of two of these derivatives as selective complexants for heavy metals.

Experimental Section

All materials and solvents were standard reagent grade and were used without further purification unless otherwise noted. Reagents were purchased from Aldrich Chemical Co. and used as supplied. Melting points were obtained on a hot-stage apparatus. ¹H and ¹³C NMR spectra were measured using a GE Omega 400-MHz spectrometer. Fast atom bombardment (FAB) mass spectra were obtained using a Kratos Concept 1H spectrometer with samples introduced in a *m*-nitrobenzyl alcohol matrix. Elemental analyses were performed by Galbraith Inc., Knoxville, TN.

All compounds were of reagent purity and were used as supplied. The compound 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(2-hydroxyethoxy)calix[4]arene (**1**) was prepared according to the published procedure.⁵ Extractions were carried out with chloroform solutions (1 mM) of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(2-(*N,N*-dimethyldithiocarbamoyl)ethoxy)calix[4]arene (**6**) or 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(2-mercaptoethoxy)calix[4]arene (**8**) and aqueous solutions (1 mM in 0.1 M HNO₃) of the metal salts. Equal volumes from each phase (5 mL) were shaken for approximately 1 min. A 2-mL aliquot from the aqueous phase was then diluted to a volume of 10 mL with 0.1 M HNO₃, 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.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(2-bromoethoxy)calix[4]arene (3**).** Following the published procedure **1** (6.0 g, 7.2 mmol) was converted first into the tosylate derivative **2**.³ The crude tosylate was then dissolved in acetone (80 mL) and a large excess of LiBr (5.0 g, 57.6 mmol) added. The reaction mixture was refluxed for 4 h and the solvent evaporated. The solid residue was then distributed between chloroform and water. The organic layer was separated, washed with water, and dried over MgSO₄. The volume of the solution was reduced to 10 mL and methanol added. After 48 h at approximately 0 °C colorless crystals were deposited. The crystals were collected by filtration and washed with cold methanol, yield 6.5 g (83%), mp 222 °C. Anal. Calcd for C₅₂H₆₈O₄Br₄: C, 58.0; H, 6.36; Br, 29.7. Found: C, 58.4; H, 6.57; Br, 29.9. FAB mass spectrum: *m/z* 1076. ¹H NMR (CDCl₃): δ 1.07 (s, 36H, *tert*-Bu); 3.19 (d, 4 H, CH₂), 3.85 (t, 8 H, CH₂Br), 4.23 (t, 8 H, CH₂O), 4.36 (d, 4 H, CH₂), 6.79 (s, 8 H, ArH). ¹³C NMR (CDCl₃): δ 30.08 (t, ¹J(CH) = 151.7 Hz, CH₂Br), 31.04 (t, ¹J(CH) = 129.5 Hz, CH₂), 31.29 (q, ¹J(CH) = 125.8 Hz, CCH₃), 33.83 (s, CCH₃), 74.58 (t, ¹J(CH) = 148.0 Hz, CH₂O), 125.30 (d, ¹J(CH) = 155.4 Hz, ArCH), 133.36 (s, ArC), 145.49 (s, ArC), 152.19 (s, ArCO).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(2-isothiuroniumethoxy)calix[4]arene Tetrabromide (4**).** Compound **3** (3.0 g, 2.8 mmol) was heated with a 40% excess of thiourea (1.2 g, 11.2 mmol) in acetone (60 mL). After 24-h reflux a white crystalline solid formed which was filtered, washed with several small aliquots of cold acetone, and dried *in vacuo*, yield 3.1 g (82%), mp 251 °C. Anal. Calcd for C₅₆H₈₄O₄N₈S₄Br₄: C, 48.7; H, 6.13; N, 8.11; S, 9.29; Br, 23.1. Found: C, 47.4; H, 6.29; N, 7.59; S, 8.61; Br, 21.6. FAB mass spectrum: *m/z* 1057 (M_{tetracation} - 3H)⁺. ¹H NMR (DMSO), δ 1.01 (s, 36 H, *tert*-Bu), 3.22 (d, 4 H, CH₂), 3.66 (t, 8 H, CH₂S), 4.18 (t, 8 H, CH₂O), 4.28 (d, 4 H, CH₂), 6.80 (s, 8 H, ArH), 9.11 (br s, 16 H, D₂O exchangeable, NH₂). ¹³C NMR (pyridine-*d*₅): δ 31.33 (q, *J* = 122.1 Hz, CCH₃), 31.63 (t, CH₂), 32.29 (t, CH₂), 33.91 (s, CCH₃), 73.26 (t, *J* = 146.5 Hz, CH₂O), 125.78 (d, *J* = 146.5 Hz, ArCH), 133.58 (s, ArC), 145.42 (s, ArC), 152.78 (s, ArCO), 171.31 (s, C=N).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(2-thiocyanatoethoxy)calix[4]arene (5**).** To a solution of **3** (1.0 g, 0.9 mmol) in acetone (25 mL) was added a 100% excess of potassium thiocyanate (0.7 g, 7.2 mmol). The reaction mixture was refluxed for 6 h and the solvent evaporated. The solid residue was then distributed between chloroform and water. The organic layer was separated, washed with water, and dried over MgSO₄. The solvent was evaporated almost to dryness, and then a quantity of methanol was added to cause precipitation. If a precipitate did not form immediately, the solution was allowed to stand at approximately 0 °C for 24 h. The precipitate was filtered and dried *in vacuo*, yield 0.7 g (78%), mp 204 °C. Anal. Calcd for C₅₆H₆₈O₄N₄S₄: C, 68.0; H, 6.93; N, 5.66; S, 13.0. Found: C, 68.0; H, 7.12; N, 5.16; S, 13.1. ¹H NMR (CDCl₃): δ 1.08 (s, 36 H, *tert*-Bu), 3.29 (d, 4 H, CH₂), 3.47 (t, 8 H, CH₂S), 4.20–4.30 (m, 12 H, CH₂O and CH₂), 6.81 (s, 8 H, ArH). ¹³C NMR (CDCl₃): δ 30.96 (t, *J* = 133.2 Hz, CH₂), 31.22 (q, *J* = 125.8 Hz, CCH₃), 32.36 (t, CH₂), 33.83 (s, CCH₃), 72.30 (t, *J* = 148.0 Hz, CH₂O), 111.73 (s, ArC), 125.63 (d, *J* = 148.0 Hz, ArCH), 132.99 (s, ArC), 146.23 (s, ArCO), 151.67 (s, SCN). IR (KBr), 2156 cm⁻¹ (ν(CN)).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(2-(*N,N*-dimethyldithiocarbamoyl)ethoxy)calix[4]arene (6**).** To a solution of **3** (1.0 g, 0.9 mmol) in acetone (25 mL) was added a 100% excess of sodium *N,N*-dimethyldithiocarbamate dihydrate (1.0 g, 7.2 mmol). The reaction mixture was refluxed for 6 h and the solvent evaporated. The solid residue was then distributed between chloroform and water. The organic layer was separated, washed with water, and dried over MgSO₄. The solvent was evaporated almost to dryness and then sufficient amount of methanol added to cause precipitation. If a precipitate did not form immediately, the solution was allowed to stand at ap-

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Table 1. Crystal Data for 3

cryst size	0.56 × 0.46 × 0.56 mm ³	<i>T</i> (K)	293
space group	trigonal <i>P</i> ₃ 21	<i>D</i> _c (g·cm ⁻³)	1.40
<i>a</i> (Å)	13.160(1)	radiation	Mo Kα
<i>b</i> (Å)	13.160(2)	no. reflcns measd	5938
<i>c</i> (Å)	25.595(6)	no. independent reflcns	2391
<i>V</i> (Å ³)	3839(2)	no. obsd reflcns	1591
<i>Z</i>	3	<i>R</i> _F ^a	0.061
		<i>R</i> _{wF} ^b	0.075

^a $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F)$.

Table 2. Positional Parameters and Their Estimated Standard Deviations^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Br1a	1.0261(3)	0.9798(2)	0.8978(2)	14.6(1)
Br1b	0.9967(5)	0.9630(4)	0.9590(4)	19.0(3)
Br2	0.5672(1)	0.6933(1)	0.92493(8)	10.67(4)
O1	0.7857(4)	0.5808(5)	0.8734(3)	4.1(2)
O2	1.0503(5)	0.6949(6)	0.9021(3)	4.5(2)
C1	0.7790(7)	0.4729(7)	0.8700(4)	2.9(2)*
C2	0.8119(7)	0.4323(7)	0.9136(3)	3.0(2)*
C3	0.8024(7)	0.3231(8)	0.9110(4)	3.7(2)*
C4	0.7613(8)	0.2505(8)	0.8689(4)	3.7(2)*
C5	0.623(1)	0.037(1)	0.8616(8)	10.8(5)
C7	0.796(1)	0.098(1)	0.9164(6)	10.7(5)
C(8)	0.813(1)	0.117(1)	0.8220(6)	12.2(5)
C9	0.7314(8)	0.2942(7)	0.8263(4)	3.4(2)*
C10	0.7424(8)	0.4039(8)	0.8268(4)	3.4(2)*
C11	1.2801(7)	0.7308(8)	0.8944(4)	3.9(2)*
C12	1.1983(8)	0.6527(7)	0.9345(4)	3.4(2)*
C13	1.2299(7)	0.5890(7)	0.9664(4)	3.2(2)*
C14	1.1489(8)	0.5017(8)	0.9999(4)	3.8(2)*
C15	1.1785(7)	0.4272(7)	1.0328(3)	3.3(2)
C16	1.124(1)	0.306(1)	1.0104(7)	10.8(5)
C17	1.139(1)	0.416(1)	1.0874(5)	14.5(5)
C18	1.309(1)	0.472(1)	1.0333(6)	10.6(5)
C19	1.0355(9)	0.4814(9)	0.9980(5)	4.9(3)*
C20	0.9988(8)	0.5449(7)	0.9662(4)	3.5(2)*
C21	1.0836(8)	0.6312(8)	0.9360(4)	3.7(2)*
C22	1.067(1)	0.8000(9)	0.9240(6)	9.5(4)
C23a	1.036(2)	0.847(2)	0.887(2)	15(1)
C23b	0.973(3)	0.836(2)	0.971(2)	10(1)
C24	0.6803(9)	0.5738(9)	0.8906(5)	6.2(3)
C25	0.697(1)	0.694(1)	0.8984(7)	11.1(6)
C26	0.8697(8)	0.5082(8)	0.9623(4)	3.8(3)

^a Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

proximately 0 °C for 24 h. The compound was filtered and dried *in vacuo*, yield 1.05 g (91%), mp 216 °C. Anal. Calcd for C₆₄H₉₂O₄N₄S₈: C, 62.1; H, 7.9; N, 4.53; S, 20.7. Found: C, 62.05; H, 7.56; N, 4.37; S, 20.6. FAB mass spectrum: *m/z* 1237 (M + H)⁺. ¹H NMR (CDCl₃), δ 1.06 (s, 36 H, *tert*-Bu), 3.17 (d, 4 H, CH₂), 3.38 and 3.53 (br s, 24 H, N(CH₃)₂), 3.93 (t, 8 H, CH₂S), 4.24 (t, 8 H, CH₂O), 4.50 (d, 4 H, CH₂), 6.78 (s, 8 H, ArH). ¹³C NMR (CDCl₃): δ 31.33 (t, ¹J(CH) = 125.8 Hz, CH₂), 31.36 (q, ¹J(CH) = 125.8 Hz, CCH₃), 33.76 (s, CCH₃), 37.07 (t, ¹J(CH) = 140.6 Hz, CH₂S), 41.63 (q, ¹J(CH) = 138.1 Hz, NCH₃), 45.31 (q, ¹J(CH) = 138.1 Hz, NCH₃), 73.19 (t, ¹J(CH) = 148.0 Hz, CH₂O), 125.04 (d, ¹J(CH) = 148.0 Hz, ArCH), 133.65 (s, ArC), 144.68 (s, ArC), 152.85 (s, ArCO), 197.21 (s, C=S).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(2-thioacetatoethoxy)-calix[4]arene (7). Compound **3** (2.6 g, 2.4 mmol) was dissolved in hot DMF (60 mL). A 100% excess of potassium thioacetate (2.2 g, 19.2 mmol) was then added and the reaction mixture stirred at 90 °C for 2 h. The solution was cooled and distributed between diethyl ether and water. The organic layer was separated, washed with water several times, and dried over MgSO₄. The solution volume was then reduced to about 10 mL and methanol added. After 48 h at 0 °C yellow crystals were deposited. The crystals were collected by filtration and washed with cold methanol. Subsequent recrystallization did not improve the purity, yield 1.6 g (65%), mp 162 °C dec. Anal. Calcd for C₆₀H₈₀O₈S₄: C, 68.1; H, 7.62; S, 12.1. Found: C, 68.5; H, 8.14; S,

12.8. ¹H NMR (CDCl₃): δ 1.06 (s, 36 H, *tert*-Bu), 2.35 (s, 12 H, CH₃), 3.16 (d, 4 H, CH₂), 3.48 (t, 8 H, CH₂S), 4.04 (t, 8 H, CH₂O), 4.38 (d, 4 H, CH₂), 6.77 (s, 8 H, ArH). ¹³C NMR (CDCl₃): δ 28.98 (t, ¹J = 144.3 Hz, CH₂), 30.67 (q, CH₃), 31.11 (t, CH₂), 31.37 (q, ¹J = 125.8 Hz, CCH₃), 33.83 (s, CCH₃), 73.19 (t, ¹J = 144.3 Hz, CH₂O), 125.19 (d, ¹J = 148.0 Hz, ArCH), 133.58 (s, ArC), 145.05 (s, ArC), 152.63 (s, ArCO), 195.44 (s, C=O).

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(2-mercaptoethoxy)-calix[4]arene (8). To a solution of **7** (1.3 g, 1.2 mmol) in hot ethanol (40 mL) was added 37% HCl (3 mL). After 2 h of refluxing, approximately half of the ethanol was evaporated and a sufficient quantity of water was added to cause precipitation. The white precipitate was collected by filtration, washed with water, and dried *in vacuo*. All attempts to purify the product by recrystallization gave intractable oils, yield 0.96 g (88%), mp 204 °C. Anal. Calcd for C₅₂H₇₂O₄S₄: C, 70.2; H, 8.16; S, 14.4. Found: C, 72.05; H, 8.72; S, 14.1. ¹H NMR (CDCl₃): δ 1.07 (s, 36 H, *tert*-Bu), 1.60 (t, 4 H, SH), 3.08 (q, 8 H, CH₂SH), 3.17 (d, 4 H, CH₂), 4.01 (t, 8 H, CH₂O), 4.34 (d, 4 H, CH₂), 6.78 (s, 8 H, ArH). ¹³C NMR (CDCl₃): δ 23.98 (t, ¹J = 140.6 Hz, CH₂), 31.04 (t, ¹J = 129.5 Hz, CH₂), 31.37 (q, ¹J = 125.8 Hz, CCH₃), 33.83 (s, CCH₃), 76.79 (t, ¹J = 148.0 Hz, CH₂O), 125.19 (d, ¹J = 148.0 Hz, ArCH), 133.43 (s, ArC), 145.13 (s, ArC), 152.56 (s, ArCO).

X-ray Crystallography. A colorless crystal of **3** in the shape of a flat pyramid was obtained by the slow diffusion of methanol into a solution of **3** in 1,2-dichloroethane. The crystal was mounted on a thin glass fiber and coated with a film of epoxy cement. General procedures for crystal orientation, unit cell determination, and refinement and data collection on the CAD-4 diffractometer have been published.⁶ Details specific to the present determination are given in Table 1. The CAD-4 software indicated a primitive hexagonal unit cell, but careful consideration of the intensities of possibly equivalent reflections showed only trigonal symmetry. A search for systematic absences revealed only the condition $000l$ ($l = 3n$) which is consistent with the space groups *P*₃, *P*₃21, *P*₃12, and their enantiomorphs. Further consideration of the intensity relationships indicated the space group to be *P*₃21 or its enantiomorph. A full quadrant ($h, -k, \pm l$) of data was collected and corrected for Lorentz and polarization effects and an anisotropic 24% decay in the intensity monitors. The data were corrected for absorption using Ψ scans on three reflections with χ near 90°. The structure was solved by direct methods (MULTAN 80)⁷ and refined by full-matrix, least-squares procedures. It was immediately obvious that one of the bromoethyl side chains was disordered over two sites with the bromine (Br(1)) and its attached carbon (C(23)) having occupancies of 0.59 (site "a") and 0.41 (site "b") based on refinement of occupancy parameters. The refined geometries for the two orientations were not very satisfactory, particularly for the minor orientation, which is at least in part due to the inability to distinguish separate sites for the α -carbon (C(22)) of this chain. A considerably elongated peak for this atom appeared in a $\Delta\rho$ map consistent with the presence of two overlapping sites for this atom. Despite this difficulty, however, the remainder of the molecule was satisfactory, leaving no doubt that the structure was essentially correct. Refinement of the final model in both *P*₃21 and *P*₃12 resulted in significantly (98% confidence level) lower values for *R* and *R*_w in the latter space group, indicating it to be the correct space group. In the late stages of the refinement most hydrogen atoms could be located and these were included as fixed contributions in calculated positions (C-H = 0.95 Å) with isotropic thermal displacement parameters 20% larger than those of the attached carbon atoms. These were updated periodically during the refinement. Exceptions were those attached to C(11), which were placed in the positions indicated by the $\Delta\rho$ map and allowed to ride on C(11), and those associated with the disordered bromoethyl group. The refinement converged satisfactorily except for some of the anisotropic thermal displacement parameters of the disordered atoms which showed a tendency to oscillate. All calculations were performed

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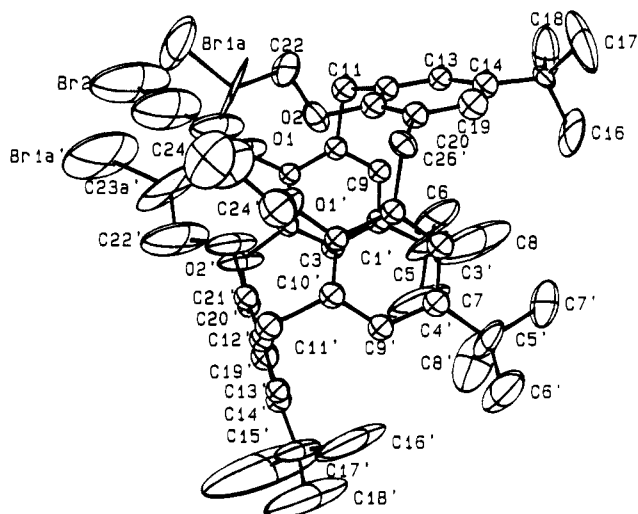
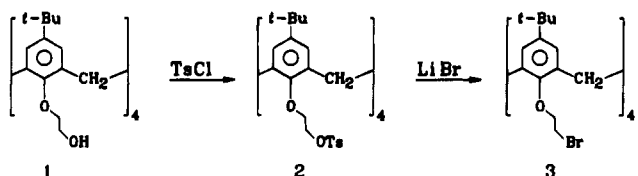


Figure 1. ORTEP view of (tetrabromoethoxy)-*tert*-butylcalix[4]arene (**3**) with 30% ellipsoids.

Table 3. Selected Bond Distances (Å) and Angles (deg)

Bond Distances (Å)			
Br2—C25	1.83(2)	Br1a—C23a	1.84(3)
C25—C24	1.50(3)	Br1b—C23b	1.57(4)
C24—O1	1.41(2)	C23a—C22	1.31(4)
O1—C1	1.38(1)	C22—O2	1.40(2)
Bond Angles (deg)			
Br2—C25—C24	114(1)	Br1a—C23a—C22	122(4)
C25—C24—O1	111(1)	C23a—C22—O2	104(2)
C24—O1—C1	113.4(9)	C22—O2—C21	113(1)

Scheme 1



on a VAX station 3100 with the MolEN⁸ suite of programs. Neutral atom scattering factors include the corrections for the real and imaginary components of the effects of anomalous dispersion.⁹ Final refined atomic coordinates are given in Table 2. Additional crystallographic data are included as Supplementary Material. Selected bond distances (Å) and angles (deg) are given in Table 3.

Results and Discussion

We have reported previously the synthesis of calixarene alcohols with either 2-hydroxyethoxy or 3-hydroxypropoxy groups appended onto the lower rim.⁵ Similarly Reinhoudt has prepared **1** and converted it into the tosylate derivative **2**.³ This compound has been used for nucleophilic substitution reactions. However, we find that **2** cannot be effectively used to prepare a full range of calix[4]arenes with sulfur containing lower-rim functionalities. We have therefore replaced the tosylate group with bromide (Scheme 1), thereby allowing the isolation of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(2-bromoethoxy)-calixarene (**3**). We have now used **3** for the introduction of a range of sulfur containing groups onto the lower calixarene rim. Compound **3** has been prepared in good yield by treating the calixaryl tosylate³ with an excess of LiBr in acetone at 60 °C.

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Scheme 2

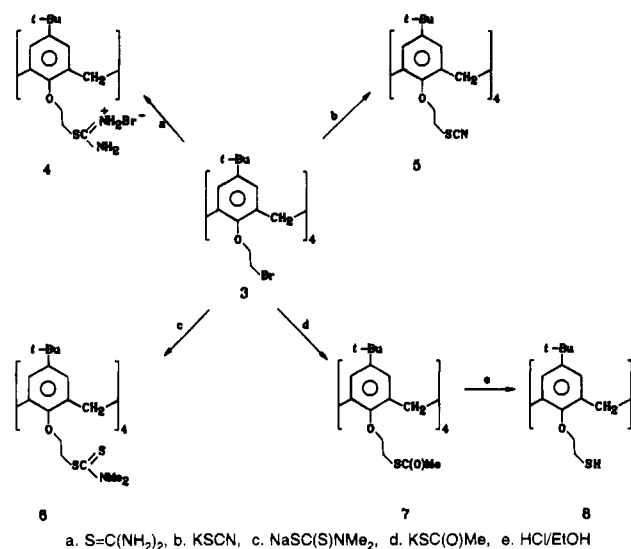


Table 4. Extraction of Pb²⁺, Cd²⁺, Hg₂²⁺, Hg²⁺, and MeHg⁺ with **6**

ion	metal concn (μg/mL)		
	before extractn	after extractn	extractn (%)
Pb ²⁺	30.5	30.9	0
Cd ²⁺	24.2	24.2	0
Hg ₂ ²⁺	51.4	9.6	81
Hg ²⁺	244.0	52.0	78
MeHg ⁺	37.5	23.4	38

The compound can be purified by slow crystallization from a mixture of CH₃OH and CHCl₃. The ¹H NMR data show that **3** exists in the cone conformation, and this has been confirmed by X-ray crystallography (Figure 1). The bond distances and angles of **3** do not show any unusual values (Table 3).

We have treated **3** with different sulfur containing nucleophiles to yield the tetraisothiuronium salt **4**, the tetrathiocyanato derivative **5**, the tetracarbamoyl derivative **6**, and the tetrathiol ester **7** (Scheme 2). All reactions have been carried out in acetone at 60 °C except for the preparation of the tetrathiol ester **7** which was carried out in DMF solvent. The IR spectrum of **5** shows a sharp absorption band at 2156 cm⁻¹ which shows that isomerization to the tetraisothiocyanate does not occur. Attempts to prepare **7** directly from **2** gave only intractable oils. Both base hydrolysis or LiAlH₄ reduction of compounds **4**–**7** leads to complex mixtures containing significant amounts of elimination products resulting from the cleavage of the ether bond.¹⁰ Under acidic conditions, however, **7** can be deacylated to give the (tetramercaptoethoxy)-*tert*-butylcalix[4]arene **8** in good yield.

Preliminary data with **6** and **8** show that they can potentially be used as selective extractants of heavy metal ions into chloroform from water. The extractability data for Pb²⁺, Cd²⁺, Hg₂²⁺, Hg²⁺, and MeHg⁺ are given in Tables 4 and 5, and those for Ni²⁺, Ag⁺, Pd²⁺, Pt²⁺, and Au³⁺, in Tables 6 and 7. These data shows that whereas **6** is an effective complexant for Hg₂²⁺, Hg²⁺, and MeHg⁺, it is completely ineffective as a complexant for Pb²⁺ and Cd²⁺. For **8** at low pH similar results are obtained. For the second series of metals both **6** and **8** are effective extractants for Au³⁺ and ineffective for Ni²⁺ and Pt²⁺.¹¹ Compound **6** is effective for Pd²⁺, but **8** is only moderately effective. These extractabilities do not correlate well with size

(10) Bacon, R. In *Organic Sulfur Compounds*; Kharasch, N., Ed.; Pergamon Press: Oxford, U.K., 1961; Vol. 1, Chapter 27.

(11) We cannot discount the possibility that Au³⁺ will be reduced by **8**.

Table 5. Extraction of Pb²⁺, Cd²⁺, Hg₂²⁺, Hg²⁺ and MeHg⁺ with **8**

ion	pH	metal concn ($\mu\text{g/mL}$)		extracn (%)
		before extracn	after extracn	
Pb ²⁺	1 ^a	38.7	38.0	2
	6 ^b	38.6	24.8	36
Cd ²⁺	1	28.1	28.6	0
	6	27.3	0.8	97
Hg ²⁺	1	43.5	6.1	86
	3 ^c	42.0	5.1	88
Hg ₂ ²⁺	1 ^d	303.7	50.4	83
MeHg ⁺	1	45.8	8.6	81
	3	40.3	6.0	85

^a 0.1 M HNO₃. ^b 0.08 M maleate buffer. ^c Hydron buffer (Aldrich).

^d Hg₂²⁺ precipitates in the buffer solution with pH 3.

Table 6. Extraction of Ni²⁺, Ag⁺, Pd²⁺, Pt²⁺, and Au³⁺ with **6**

ion	metal concn ($\mu\text{g/mL}$)		extracn (%)
	before extracn	after extracn	
Ni ²⁺	10.1	9.9	2
Ag ⁺	20.3	5.2	74
Pd ²⁺	18.1	0	100
Pt ²⁺	30.3	30.3	0
Au ³⁺	29.6	0	100

effects when the ionic radii for either 4- or 8-coordinate ions are used.¹² 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 **6**. This exclusion of platinum is justifiable because it is likely that its poor extraction is due to the kinetic

(12) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988. Yordanov, A. T.; Roundhill, D. M. *New J. Chem.*, submitted for publication.

Table 7. Extraction of Ni²⁺, Ag⁺, Pd²⁺, Pt²⁺, and Au³⁺ with **8**

ion	metal concn ($\mu\text{g/mL}$)		extracn (%)
	before extracn	after extracn	
Ni ²⁺	10.1	11.5	0
Ag ⁺	20.3	8.0	60
Pd ²⁺	18.1	10.6	41
Pt ²⁺	30.3	34.1	0
Au ³⁺	29.6	0	100

inertness of PtCl₄²⁻.¹³ Nevertheless, this premise fails for the first series of metals because Hg²⁺ (with an ionic radius of 1.10 Å) is efficiently extracted by **6**. Similarly, in octacoordination, Hg²⁺ and Cd²⁺ have closely similar ionic radii, yet they are on the opposite ends of the extractability scale. At present it is unclear as to what precise role size and polarizability effects are playing in this selective complexation of these metals.

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Supporting Information Available: Tables of crystallographic data, positional parameters, calculated hydrogen positional parameters, general displacement parameter expressions (*U*s), bond distances, and bond angles (8 pages). Ordering information is given on any current masthead page.

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(13) Yordanov, A. T.; Mague, J. T.; Roundhill, D. M. *Inorg. Chim. Acta.*, in press.