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(Methylthio)methyl and (*N*,*N*-Dimethylcarbamoyl)methyl Upper-Rim-Substituted Calix[4]arenes as Potential Extractants for Ag(I), Hg(II), Ni(II), Pd(II), Pt(II), and Au(III)

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We have previously reported the synthesis of calix[4]arenes with sulfur containing lower-rim functionalities and their application as selective heavy metal ion extractants.[1−3] Calixarenes were chosen because of their potential preorganization for complexation with metal ions, and because of the avalability of multiple sites for incorporating ligating functional groups.[4] The derivatives that were chosen had thiolate or (*N*,*N*-dimethylcarbamoyl)methyl functionalities appended to the lower rim. This choice was made because of the strong affinity of these functionalitites for metal ions such as Hg(II), Pd(II), Au(III), and Ag(I). From this work, it became apparent that the strong complexant ability of the thiolate group was accompanied by a low selectivity. In contrast, the (*N*,*N*-dimethylcarbamoyl)methyl functionality conferred both strong and rapid binding in addition to good selectivity. This improved selectivity may be a consequence of the (*N*,*N*-dimethylcarbamoyl)methyl ligating moiety on the calixarene being uncharged, because anionic dithiocarbamate salts are analogous to anionic thiolates in showing low selectivity between heavy metals.[5−8] We have decided, therefore, to further investigate (*N*,*N*-dimethylcarbamoyl)methyl-substituted calix[4]arenes as selective extractants. Furthermore, we have decided to use (methylthio)methyl derivatives instead of thiolates, even though they are expected to show lower binding, on the premise that the uncharged (methylthio)methyl ligating group may show higher selectivity for heavy metal ions. This premise is also supported by literature precedent where (methylthio)methyl-substituted calix[4]arenes have been used as silver-selective chemically modified field effect transistors.[9]

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. 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). Melting points were measured on a hot stage and are uncorrected. ^1H and ^{13}C NMR spectra were measured using either GE Omega 400 MHz or Bruker AC200 or 300 spectrometers with solutions dissolved in $CDCl_3$. 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 either by Galbraith Laboratories, Inc., Knoxville, TN, or by QTI Inc., Whitehouse, NJ. The compounds 5,11,17,23-tetrachloromethylcalix[4]arene and 25,26,27,28-tetramethoxycalix[4]arene (**1**) were prepared according to the published procedures.[10] Extractions were carried out with chloroform solutions (1 mM) of **1**−**5** and aqueous solutions (1mM in 0.1 M HNO_3) of the metal salts. 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 0.1 M HNO_3, and the metal concentration was compared to that of the initial solution. Initial and final concentrations of the metals were measured on either Perkin-Elmer Optimum 3000 or Plasma 400 ICP-AES spectrometers.

5,11,17,23-Tetrakis((methylthio)methyl)calix[4]arene (2). To a solution of **1** (1.1 g, 1.8 mmol) in dry THF (30 mL) was added a 100% excess of sodium thiomethoxide (1.0 g, 14.4 mmol). The reaction mixture was refluxed for 10 h, and the solvent was evaporated. The solid residue was then partitioned between water and chloroform (Stench!). The organic layer was separated, washed twice with water, and dried over $MgSO_4$. The solvent was evaporated almost to dryness, and then a quantity of methanol was added to cause precipitation. The precipitate was filtered and dried *in vacuo.* Yield: 37%. Mp: 207−210 °C. Anal. Calcd for $C_{36}H_{40}O_4S_4 \cdot 1.5C_4H_8O$: C, 65.3; H, 6.73; S, 16.6. Found: C, 65.2; H, 6.70; S, 16.4. MS: *m/z* 663 ($M - H^+$). ^1H NMR ($CDCl_3$): δ 1.96 (CH_3), 3.47 (CH_2), 4.26 (CH_2), 6.98 (CH), 10.15 (OH). ^{13}C NMR ($CDCl_3$): δ 15.1 (*q*, CH_3, $^1J(CH) = 140$ Hz), 31.7 (t, $^1J(CH) = 130$ Hz), 37.7 (t, $^1J(CH) = 140$ Hz), 128.6 (Ar*C*), 128.1 (Ar*C*), 130.1 (d, Ar*C*, $^1J(CH) = 148$ Hz), 131.7 (Ar*C*).

5,11,17,23-Tetrakis((methylthio)methyl)-25,26,27,28-tetramethoxycalix[4]arene (3). To a solution of 5,11,17,23-tetrachloromethyl-25,26,27,28-tetramethoxycalix[4]arene (310 mg, 0.49 mmol) in dry THF (9 mL) was added sodium thiomethoxide (280 mg, 9.8 mmol). The mixture was refluxed for 12 h. The solution was evaporated to dryness on a rotary evaporator to give a solid. This residue was extracted with chloroform (50 mL), and the extract was washed with water (3 × 50 mL). The chloroform solution was dried over $MgSO_4$, and the solvent was evaporated to give a yellow viscous liquid. Crystallization from a mixture of chloroform and hexane gave the product as pale yellow crystals. Yield: 190 mg, 61%. mp: 131−2 °C. Anal. Calcd for $C_{40}H_{48}O_4S_4$: C, 66.6; H, 6.71; S, 17.8. Found: C, 65.4; H, 6.92; S, 17.0. ^1H NMR ($CDCl_3$): 80 °C, averaging to the 1,3-alternate conformer δ 6.81 (8H, br, Ar*H*), 3.47−3.75 (28H, br, $ArCH_2Ar + CH_2S + OCH_3$), 1.87 (12H, s, SCH_3); 20 °C cone conformer (58%) δ 6.63 (8H, s, Ar*H*), 3.97 (4H, d, $^2J(HH) = 13$ Hz, $ArCH_2Ar$), 3.10 (4H, d, $^2J(HH) = 13$ Hz, $ArCH_2Ar$), 3.31 (8H, s, CH_2S), 3.62 (12H, s, OCH_3), 1.68 (12H, s, SCH_3); partial cone conformer (42%) δ 7.17 (2H, s, Ar*H*), δ 6.98 (2H, s, Ar*H*), δ 6.37 (2H, s, Ar*H*), δ 6.13 (8H, s, Ar*H*), 4.26 (4H, d, $^2J(HH) = 13$ Hz, $ArCH_2Ar$), 3.07 (4H, d, $^2J(HH) = 13$ Hz, $ArCH_2Ar$), 3.67 (4H, s, CH_2S), 3.62 (2H, s, CH_2S), 3.36 (2H, s, CH_2S), 3.35 (6H, s, OCH_3), 3.31 (3H, s, OCH_3), 3.07 (3H, s, OCH_3), 2.13 (2H, s, SCH_3), 2.00 (2H, s, SCH_3), 1.75 (4H, s, SCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 80 °C, 1,3-alternate conformer δ 157.1 (ArCOMe), 134.2 ($ArCCH_2S$), 131.6 ($ArCCH_2$), 129.5 (ArCH), 60.1 (OCH_3), 38.3 ($ArCH_2S$), 32.2 ($ArCH_2Ar$), 14.8 (SCH_2); 20 °C, cone conformer δ 156.8 (ArCOMe), 133.5 ($ArCCH_2S$), 131.5 ($ArCCH_2$), 128.5 (ArCH), 61.4 (OCH_3), 37.8 ($ArCH_2S$), 30.6 ($ArCH_2Ar$), 14.6 (SCH_2); partial cone conformer δ 156.8 (ArCOMe), 136.1, 132.5, 132.0 ($ArCCH_2S + ArCCH_2$), 130.9, 131.5 (ArCH), 60.6, 59.8, 58.5 (OCH_3), 37.8, 36.6 ($ArCH_2S$), 30.6 ($ArCH_2Ar$), 14.6 (SCH_2).

5,11,17,23-Tetrakis((*N*,*N*-dimethyldithiocarbamoyl)methyl)calix[4]arene (4). To a solution of **1** (0.6 g, 1.0 mmol) in dry DMSO (25 mL) was added a 100% excess of sodium *N*,*N*-dimethyldithiocarbamate dihydrate (1.2 g, 8.0 mmol). The reaction mixture was stirred at 60 °C for 10 h, after which it was distributed between water and chloroform (DMSO stays in the water layer). The organic layer was separated, washed twice with water, and dried over $MgSO_4$. The solvent was

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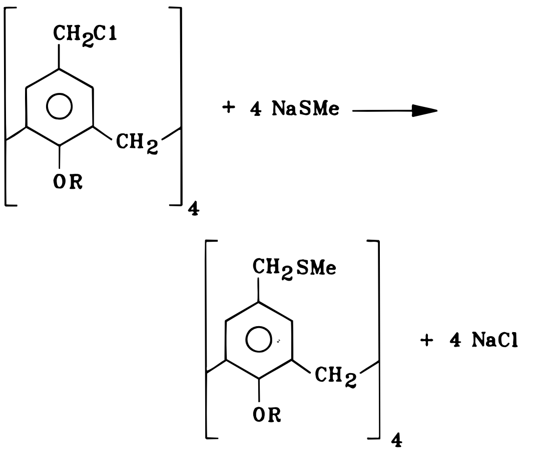
evaporated almost to dryness, and a sufficient quantity of methanol was added to cause precipitation. The precipitate was filtered and dried *in vacuo*. Anal. Calcd for $C_{44}H_{52}N_4O_4S_8{\cdot}2CHCl_3$: C, 46.2; H, 4.55; N, 4.68; S, 21.4. Found: C, 45.9; H, 5.55; N, 4.55 S, 21.5. ^{1}H NMR ($CDCl_3$): δ 10.08 (O*H*), 3.32 (C*H*$_2$), 3.53 (NC*H*$_3$), 4.34 (C*H*$_2$), 7.08 (Ar*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 31.5 (*C*H$_2$), 41.3 (*C*H$_2$), 41.9 (N*C*H$_3$), 128.1 (Ar*C*), 129.8 (Ar*C*), 130.0 (*C*H), 148.1 (Ar*C*O), 196.6 (*C*=S).

5,11,17,23-Tetrakis((*N*,*N*-dimethyldithiocarbamoyl)methyl)-25,26,27,28-tetramethoxycalix[4]arene (5). To a solution of sodium *N*,*N*-dimethyldithiocarbamate dihydrate (214 mg, 1.4 mmol) in dry acetone (15 mL) was added 5,11,17,23-tetrachloromethyl-25,26,27,28-tetramethoxycalix[4]arene (550 mg, 0.82 mmol). This mixture was refluxed for 1.5 h. The precipitated sodium chloride was removed by fitration. Removal of the acetone using a rotary evaporator yielded a white fluffy residue. The residue was triturated with chloroform, and the solid residue was removed by filtration. The chloroform was removed by evaporation to give the product as a brown oil. This oil was chromatographed on a silica gel column by eluting first with an ethyl acetate/petroleum ether (3/7) mixture and then with ethyl acetate. The pure ethyl acetate fraction was evaporated to give an oily residue, which was triturated with methanol to give the product. Recrystallization from ethyl acetate gave a colorless solid. Yield: 557 mg, 0.55 mmol, 67%. Mp: 105−107 °C. Anal. Calcd for $C_{48}H_{60}N_4O_4S_8$: C, 56.9; H, 5.97; N, 5.53; S, 25.3. Found: C, 57.0; H, 5.96; N, 5.37; S, 25.1. ^{1}H NMR ($CDCl_3$): 22 °C, slightly broad signals, conformer mixture δ 7.22 (Ar*H*, 2H), 7.04 (Ar*H*, 2H), 6.94 (Ar*H*, 2H), 6.71 (Ar*H*), 6.42 (Ar*H*, 2H), 4.47−3.03 (m, ArC*H*$_2$Ar, ArC*H*$_2$S, OC*H*$_3$, N(C*H*$_3$)$_2$); −20 °C partial cone conformer (67%) δ 7.24 (Ar*H*, 2H), 7.05 (Ar*H*, 2H), 6.93 (Ar*H*, 2H), 6.39 (Ar*H*, 2H), 4.45 (ArC*H*$_2$, 2H), 4.43 (ArC*H*$_2$, 2H), 4.19 (ArC*H*$_2$, 2H), 3.96 (ArC*H*$_2$Ar, 2H, ^2J(HH) = 14 Hz), 3.05 (ArC*H*$_2$Ar, 2H, ^2J(HH) = 14 Hz), 3.59 (OC*H*$_3$, 3H), 3.55 (OC*H*$_3$, 3H), 3.55 (OC*H*$_3$, 6H), 3.33 (NC*H*$_3$, 6H), 3.32 (NC*H*$_3$, 12H), 2.94 (NC*H*$_3$, 6H); 1,3-Alternate conformer (33%) δ 6.70 (Ar*H*), 4.21 (ArC*H*$_2$S), 3.72 (ArC*H*$_2$Ar), 3.38 (OC*H*$_3$), 3.36 (NC*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): 22 °C δ 197.2 (*C*S), 157.2 (Ar*C*OCH$_3$),156.9 (Ar*C*OCH$_3$), 136.3−127.6 (m, Ar*C*H, Ar*C*CH$_2$S, Ar*C*CH$_2$Ar), 61.4 (O*C*H$_3$), 60.6 (O*C*H$_3$), 59.9 (O*C*H$_3$), 58.8 (O*C*H$_3$), 45.0 (Ar*C*H$_2$S, Ar*C*H$_2$Ar), 42.7 (Ar*C*H$_2$S, Ar*C*H$_2$Ar), 41.4 (Ar*C*H$_2$S, Ar*C*H$_2$Ar), 35.9 (N*C*H$_3$), 30.4 (N*C*H$_3$), 29.6 (N*C*H$_3$); −20 °C, partial cone conformer δ 196.8−196.5 (*C*S), 157.1 (Ar*C*OCH$_3$), 156.6 (Ar*C*OCH$_3$), 136.3−126.7 (m, Ar*C*H, Ar*C*CH$_2$S, Ar*C*CH$_2$Ar), 60.7 (O*C*H$_3$), 59.8 (O*C*H$_3$), 58.9 (O*C*H$_3$), 45.3−41.5 (m, Ar*C*H$_2$S, Ar*C*H$_2$Ar), 35.7 (N*C*H$_3$), 30.0 (N*C*H$_3$); 1,3-alternate conformer δ 156.9 (Ar*C*OCH$_3$), 61.4 (O*C*H$_3$). Other peaks are coincident with those of the partial cone conformer.

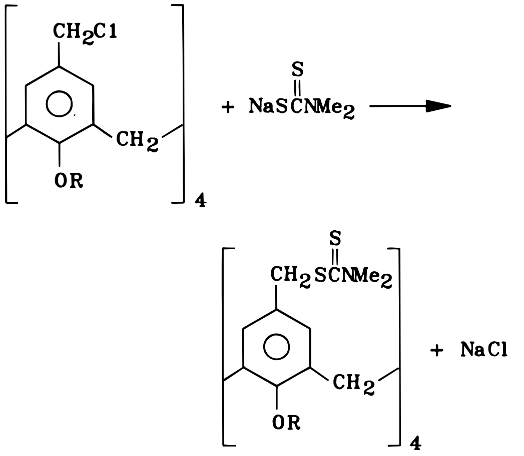
Results and Discussion

Our earlier work with calix[4]arenes was entirely focused on derivatives with functionalities appended to the lower rim.[1−3] For comparison with these lower-rim derivatives, and in order to examine complementary effects, we have now introduced sulfur-containing groups onto the upper calixarene rim. The lower rims are functionalized with either hydroxy or methoxy groups, and in order to determine whether the methoxy group affects the extractabiltities, we have used for comparison calix[4]arene **1** having only a methoxy group as a possible appended ligand. We have treated 5,11,17,23-tetrachloromethylcalix[4]arene and 5,11,17,23-tetrachloromethyl-25,26,27,28-tetramethoxycalix[4]arene with sodium thiomethoxide to yield the tetrathioether derivatives **2** and **3** (eq 1) and with sodium *N*,*N*-dimethyldithiocarbamate to give the tetracarbamoyl derivatives **4** and **5** (eq 2). The reactions were carried out in dry THF (**2** and **3**), DMSO (**4**), and acetone (**5**). Calix[4]arenes **3** and **5** differ from **2** and **4** in that they have methoxy rather than hydroxy groups on the lower rim. In the ^{1}H NMR spectra of both **3** and **5**, the bridging methylene protons appear as singlets, suggesting that both compounds are conformationally mobile at ambient temperature. The extraction data for compounds **1**−**5** (Figure 1) with the series of metal ions Ag(I), Hg(II), Ni(II), Pd(II), Pt(II), and Au(III) are collected in Table 1. These data show that **1**, with only a methoxy group on the lower rim, is a relatively poor extractant for these metals, having some effectiveness but only for Pd(II) and Ag(I).[11] In contrast, the sulfur-derivatized calix[4]arenes are effective extractants for Pd(II) and Au(III) and selective in that there is no observable extraction of Ni(II) or Pt(II) with any of these calix[4]arenes, and Hg(II) may or may not be extratced, depending on the particular derivative. For the case of Hg(II), both **3** and **5** are good extractants, whereas for Pd(II) and Au(III), **2**, **3**, and **5** are all effective for transferring the metals from water into a chloroform phase. For the case of calix[4]arenes **1**, **2**, **3**, and **5**, the phases both before and after the extractions are homogeneous, but for **4**, blueish-colored gelatinous precipitates with Hg(II), Pd(II), and Au(III) are observed during the extractions.[12] For Ni(II) and Pt(II) with **4**, where we do not observe a gelatinous precipitate, we have not analyzed the solutions for these metals because we cannot exclude the possibility that colloidal precipitates are present. The failure to observe extraction of Ni(II) with these compounds is to be expected by comparison with *lower-rim*-substituted (*N*,*N*-dimethylcarbam-



(1)

R = H(**2**); Me(**3**)



(2)

R = H(**4**); Me(**5**)

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[11] There is precedence for methyl ether derivatized calix[4]arenes being extractants for Ag(I), see: Xu, W.; Puddephatt, R. J.; Muir, K. W.; Torabi, A. A. *Organometallics* **1994**, *13*, 3054.

[12] This observation suggests the possibility that a polymeric material is formed where both sulfur and phenoxide donor sites coordinate to the metal centers.

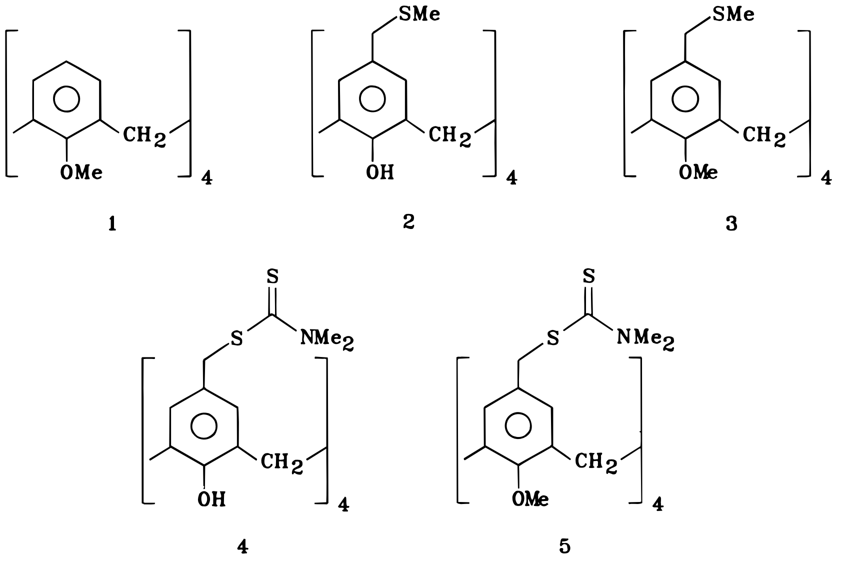


Figure 1. Structures of calix[4]arenes **1**−**5**.

Table 1. Extraction of Ag(I), Hg(II), Ni(II, Pd(II), Pt(II), and Au(III) with Calix[4]arenes **1**−**5**

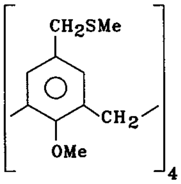
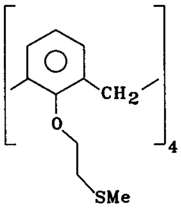
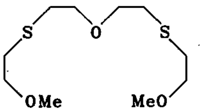
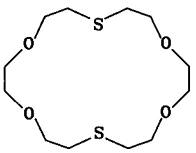
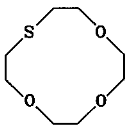
	1 extr %	**2** extr %	**3** extr %	**4** extr %	**5** extr %
Ag(I)	11	14	<1	gel	14
Hg(II)	<1	<1	92	gel	73
Ni(II)	<1	<1	<1	no gel	<1
Pd(II)	13	63	100	gel	100
Pt(II)	<1	3	<1	no gel	<1
Au(III)	<1	97	100	gel	99

oyl)methyl- and (methylthio)methylcalix[4]arenes where in no case do we observe the extraction of this metal. Apparently, these sulfur-donor groups have a relatively low affinity for Ni(II). Again for Pt(II), these donor groups on either rim do not yield calix[4]arene extractants; in this case, however, kinetic selectivity may be responsible.

The extraction of Hg(II) with **3** has also been carried out in the presence of group I and II metal ions in order to investigate whether complexation of such metal ions on the lower-rim methoxy group can lead to conformational changes in the calix[4]arene that influence the binding of the heavy metal on the upper rim. The respective percent extractions of Hg(II) in the presence of Na^+, K^+, Mg^{2+}, and Ca^{2+} are 99, 98, 86, and 98%. Since our data are probably not reliable to better than 5%, this variation means that there is no evidence for a complementary effect whereby complexation of a group I or II ions to the methoxy groups on the lower rim can cause a difference in the binding of Hg(II) to the upper rim.

The *N*,*N*-dimethyldithiocarbamoyl derivative **5** shows selectivity for Au(III) over Ag(I) and very good selectivity for Pd(II) and Hg(II) over Ni(II). In contrast, simple anionic dithiocarbamates extract both Ni(II) and Ag(I), in addition to Hg(II) and Pd(II). In general, these anionic dithiocarbamate complexants show little extraction selectivity between these individual heavy metals.[6,7,13−15] The high selectivity of **5**, therefore, represents a marked improvement from the extraction characteristics of simple dithiocarbamate salts.[16] The extraction selectivity of **5** is closely similar to that of the lower-rim-substituted compound 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(2-*N*,*N*-dimethyldithiocarbamoyl)ethoxy)calix[4]arene.[1] This correspondence indicates that the difference in cavity size between the upper and lower rims, and the possibility that with the lower-rim-substituted derivative the ether oxygen could be in chelation, are not significant factors in the extraction selectivities for this pair of compounds.

Table 2. Comparative Extraction and Binding Data for Thioether Ligands

	Au(III) = Pd(II) > Hg(II) >> Ag(I)	This work
	Au(III) = Ag(I) > Pd(II), Hg(II)	19
	Hg(II) > Ag(I)	20
	Hg(II) > Ag(I)	20
	Hg(II) > Ag(I)	20

Calix[4]arenes **2** and **3** with (methylthio)methyl groups appended to the upper calix[4]arene rim are effective extractants for Pd(II) and Au(III) but ineffective for Ni(II) and Pt(II). For **2** there is some extraction of Ag(I), but not for **3**. The failure

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(14) Hsieh, T.-P.; Liu, L. K. *Anal. Chim. Acta* **1993**, *282*, 221.

(15) Yamane,T.; Mukoyama, T.; Sasamoto, T. *Anal. Chim. Acta* **1974**, *69*, 347.

(16) Literature precedent confirms the high affinity of dithiocarbamates for Pd(II), see: Lo, J. M.; Lin, Y. P.; Lin, K. S. *Anal. Sci.* **1991**, *7*, 455.

of the upper-rim-substituted thioether compounds to effectively extract Ag(I) is surprising because the more hydrophobic derivative **3** is in general a somewhat better extractant than **2** and also because of the strong complexation of Ag(I) that has been observed with the lower-rim-substituted thioether-derivatized calix[4]arenes.[1,17] This difference between upper- and lower-rim-substituted calix[4]arenes may be a consequence of the Ag(I) being involved in chelating with both the O and S functionalities in the latter compounds, although we have little data at present to arrive at any firm conclusions.[11]

As ligands, calixarenes have generally not been placed in any particular classification category. The selectivity patterns of thioether-substituted calix[4]arenes, preorganized ligands with potential complementarity,[18-20] can, however, be possibly compared with chelates, macrocycles, and lariat macrocycles. In Table 2 we show some selectivity comparisons of the hydrophobic calix[4]arene **3** with groups of such ligands. Calix[4]arene **3** shows the same Hg(II) > Ag(I) selectivity as both the acyclic and macrocyclic thioethers. For the lower-rim-substituted derivative, however, this selectivity is reversed. No simple explanation for this difference is apparent at this time, but cavity size, the number and type of the donor atoms, and conformational aspects of the ligand are all likely important factors.

An aspect of the complexation chemistry of calixarenes that is difficult to address at this time is whether there is a conformational preference for metal binding. Since calix[4]arenes **2**, **3**, and **5** are present as a mixture of conformers, we are using a combination of NMR and molecular mechanics methods to investigate this possibility.

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