

Novel calix[4]arene-thiacrown ether for selective and efficient extraction of Ba(II), Pb(II), and Hg(II)

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Received: 31 October 2006 / Accepted: 8 December 2006 / Published online: 6 February 2007
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Abstract A di-ionizable *p*-*tert*-butylcalix[4]arene-1,3-thiacrown-5 ether extractant was synthesized. Its cone conformation and polyether ring attachment regioselectivity were verified by NMR spectroscopy. The metal ion-complexing properties of this ligand were evaluated by solvent extractions of metal cations from aqueous solutions into chloroform. The ligand was found to be an efficient extractant with Ba²⁺ selectivity in competitive solvent extraction of alkaline earth metal cations. It also exhibits high extraction ability for Pb²⁺ and for Hg²⁺ in single species solvent extractions.

Keywords Calixarenes · Crown compounds · Molecular recognition · Metal ion extraction

Introduction

Calix[4]crown compounds, generated by introduction of a polyether loop at the lower rim of calix[4]arenes, have been widely used in metal cation separations during the last two decades [1]. The common calix[4]-crowns reported in literature contain crown ether rings with only oxygen donor atoms and exhibit high affinity and selectivity toward metal ions classified as hard acids [2–5]. Recently, for treatment of environmental contamination caused by heavy metal cations, a few calix[4]arene-azacrown and -thiacrown ethers were synthesized [6–9]. These ligands showed high efficiency in detection and complexation of heavy metal cations.

However, these neutral ligands must extract both the metal cation and one or more anions from the aqueous phase into the organic diluent to preserve electroneutrality in the extraction complex. Due to the low distribution coefficients of common anions, such as Cl[−] and NO₃[−], from an aqueous phase into an organic phase, these ligands may suffer from poor extraction efficiency [10–12].

Incorporating pendant proton-ionizable groups (PIG)s into calix[4]crown ethers can dramatically enhance their extraction ability toward metal cations compared with their non-ionizable analogues. The ionized groups not only participate in cooperative metal ion coordination, but also eliminate the need to transfer aqueous phase anions into the organic phase by operating in a cation-exchange mode with the metal cation [13–15]. Herein we report the preparation of a novel di-ionizable *p*-*tert*-butylcalix[4]arene compound in the cone conformation with a thiacrown-5 ether ring attached to the lower rim of the calixarene scaffold. Hg²⁺ and Pb²⁺, and alkaline earth metal cation (AEMC) complexation by the ligand are evaluated in solvent extractions from aqueous solutions into chloroform.

Experimental

General

Reagents were obtained from commercial suppliers and used directly, unless otherwise noted. Acetonitrile (MeCN) was dried over CaH₂ and distilled immediately before use. THF was dried over sodium wire with benzophenone ketyl as an indicator. Infrared spectral

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analyses were performed with a Perkin-Elmer 1600 FT-IR spectrophotometer as deposits from CH_2Cl_2 solution onto a NaCl plate. The absorptions are given in wavenumbers (cm^{-1}). NMR spectra were measured with a Varian Unity Inova FT-500 spectrometer (499.7 MHz for ^1H , 125.7 MHz for ^{13}C) at 296 K in CDCl_3 with TMS as the internal standard. Chemical shifts (δ) are expressed in ppm downfield from TMS and coupling constants (J) values are given in Hz. Melting points were determined with a Mel-Temp apparatus. Elemental analysis was performed by Desert Analytics Laboratory of Tucson, Arizona.

Synthesis of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-dihydroxycalix[4]arene-thiacrown-5 (**2**)

A mixture of K_2CO_3 (1.05 eq, 0.23 g, 1.64 mmol), *p*-tert-butylcalix[4]arene (**1**) (1.0 eq, 1.01 g, 1.56 mmol), 1,4,10,13-tetraoxa-7-thiatridecane di-*p*-toluenesulfonate [16, 17] (1.05 eq, 0.85 g, 1.64 mmol), and 74 ml of MeCN was refluxed under nitrogen for 24 h. The solid was filtered and the filtrate was evaporated in vacuo. After addition of 50 ml of CH_2Cl_2 to the residue, the resulting solution was washed with water (50 ml), 2 N HCl (50 ml), and water (2×50 ml) and then dried over MgSO_4 . After evaporation of the solvent in vacuo, the residue was purified by column chromatography on silica gel with hexanes-EtOAc (9:1) as eluent to give 0.17 g (13%) of white solid with mp 272–274 °C. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3354 (br, OH), 1266, 1128, 1053 (C–O); δ_{H} (CDCl_3 , 500 MHz) 7.07 (s, 4H, ArH), 6.99 (s, 2H, OH), 6.74 (s, 4H, ArH), 4.35 (d, $J=13.1$, 4H, ArCH_2Ar , *ax*), 4.08–4.04 (m, 4H, $\text{ArOCH}_2\text{CH}_2\text{O}$), 4.02–4.00 (m, 4H, $\text{ArOCH}_2\text{CH}_2\text{O}$), 3.97 (t, $J=7.6$, 4H, $\text{OCH}_2\text{CH}_2\text{S}$), 3.30 (d, $J=13.2$, 4H, ArCH_2Ar , *eq*), 2.89 (t, $J=7.3$, 4H, $\text{OCH}_2\text{CH}_2\text{S}$), 1.31 (s, 18H, $\text{C}(\text{CH}_3)_3$), 0.90 (s, 18H, $\text{C}(\text{CH}_3)_3$); δ_{C} (CDCl_3 , 126 MHz) 150.6, 149.8, 146.8, 141.3, 132.4, 127.8, 125.4, 125.0 (Ar), 76.4 ($\text{ArOCH}_2\text{CH}_2\text{O}$), 72.9 ($\text{OCH}_2\text{CH}_2\text{S}$), 70.0 ($\text{ArOCH}_2\text{CH}_2\text{O}$), 33.9, 33.8 ($\text{C}(\text{CH}_3)_3$), 32.3 ($\text{OCH}_2\text{CH}_2\text{S}$), 31.7 ($\text{C}(\text{CH}_3)_3$), 31.2 (ArCH_2Ar), 31.0 ($\text{C}(\text{CH}_3)_3$); Calc. for $\text{C}_{52}\text{H}_{70}\text{O}_6\text{S}_1$: C, 75.87; H, 8.57; S, 3.89. Found: C, 75.50; H, 8.50; S, 3.87%.

Synthesis of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis[(ethoxycarbony)methoxy]-calix[4]arene-thiacrown-5 in the cone conformation (**3**)

A mixture of NaH (8.00 eq, 0.18 g, 7.29 mmol), **2** (1.00 eq, 0.75 g, 0.91 mmol), ethyl bromoacetate (6.00 eq, 0.91 g (0.61 ml), 5.47 mmol), and THF (13 ml) was stirred under nitrogen for 24 h. The excess NaH was destroyed by careful addition of 10% HCl

(5 ml) at 0 °C. The solvent was evaporated in vacuo and CH_2Cl_2 (50 ml) was added to the residue. The resulting solution was washed with H_2O (2×30 ml), dried over MgSO_4 , and evaporated in vacuo. Addition of MeOH to the residue gave 0.73 g (80%) of white solid with mp 238–240 °C. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 1760 (C=O), 1273, 1127, 1027 (C–O); δ_{H} (CDCl_3 , 500 MHz) 7.11 (s, 4H, ArH), 6.47 (s, 4H, ArH), 4.45 (s, 4H, $\text{OCH}_2\text{C}(\text{O})$), 4.44 (d, $J=12.6$, 4H, ArCH_2Ar , *ax*), 4.28 (q, $J=7.1$, 4H, OCH_2CH_3), 4.28–4.26 (m, 4H, $\text{ArOCH}_2\text{CH}_2\text{O}$), 4.22–4.19 (m, 4H, $\text{ArOCH}_2\text{CH}_2\text{O}$), 3.92 (t, $J=6.6$, 4H, $\text{OCH}_2\text{CH}_2\text{S}$), 3.16 (d, $J=12.7$, 4H, ArCH_2Ar , *eq*), 2.98 (t, $J=6.6$, 4H, $\text{OCH}_2\text{CH}_2\text{S}$), 1.33 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.32 (t, $J=7.1$, 6H, OCH_2CH_3), 0.82 (s, 18H, $\text{C}(\text{CH}_3)_3$); δ_{C} (CDCl_3 , 126 MHz) 169.4 (C=O), 154.5, 152.0, 145.2, 144.9, 135.2, 131.6, 125.6, 124.8 (Ar), 72.5 ($\text{ArOCH}_2\text{CH}_2\text{O}$), 72.4 ($\text{OCH}_2\text{CH}_2\text{S}$), 72.3 ($\text{OCH}_2\text{C}(\text{O})$), 68.5 ($\text{ArOCH}_2\text{CH}_2\text{O}$), 60.8 (OCH_2CH_3), 34.1, 33.6 ($\text{C}(\text{CH}_3)_3$), 31.7, 31.1 ($\text{C}(\text{CH}_3)_3$), 31.0 (ArCH_2Ar), 30.1 ($\text{OCH}_2\text{CH}_2\text{S}$), 14.3 (OCH_2CH_3); Calc. for $\text{C}_{60}\text{H}_{82}\text{O}_{10}\text{S}$: C, 72.40; H, 8.30; S, 3.22. Found: C, 72.48; H, 8.54; S, 3.00%.

Synthesis of 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-bis(carboxymethoxy)calix[4]arene-thiacrown-5 in the cone conformation (**4**)

A solution of **3** (0.33 g, 0.33 mmol) in THF (10 ml) was mixed with 10% aq Me_4OH (10 ml) and refluxed for 24 h. After cooling to room temperature, 6 N HCl (6 ml) was added and the mixture was stirred for 1 h. The solvent was evaporated in vacuo. The white precipitate in the aqueous solution was filtered and added to CH_2Cl_2 (30 ml). (Some of the solid did not dissolve in the CH_2Cl_2). The mixture was washed with water. (There was solid at the interface between the two layers.) The organic layer was separated, dried over MgSO_4 , and evaporated in vacuo to give a solid. The solid in the aqueous phase was filtered, combined with the solid from the organic phase, and dried under high vacuum to give 0.29 g (94%) of white solid with mp 250–251 °C. IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3396 (br, CO_2H), 1738 (C=O), 1249, 1120, 1025 (C–O); δ_{H} (CDCl_3 , 500 MHz) 8.24 (br s, 2H, CO_2H), 6.98 (s, 4H, ArH), 6.63 (s, 4H, ArH), 4.67 (s, 4H, $\text{OCH}_2\text{C}(\text{O})$), 4.39 (d, $J=12.7$, 4H, ArCH_2Ar , *ax*), 4.25–4.23 (m, 4H, $\text{ArOCH}_2\text{CH}_2\text{O}$), 4.16–4.13 (m, 4H, $\text{ArOCH}_2\text{CH}_2\text{O}$), 3.88 (t, $J=5.6$, 4H, $\text{OCH}_2\text{CH}_2\text{S}$), 3.20 (d, $J=12.9$, 4H, ArCH_2Ar , *eq*), 2.94 (t, $J=5.5$, 4H, $\text{OCH}_2\text{CH}_2\text{S}$), 1.20 (s, 18H, $\text{C}(\text{CH}_3)_3$), 0.95 (s, 18H, $\text{C}(\text{CH}_3)_3$); δ_{C} (CDCl_3 , 126 MHz) 172.9 (C=O), 153.5, 152.0, 145.4, 145.4, 134.2, 132.3, 125.6, 125.2 (Ar), 72.8 ($\text{ArOCH}_2\text{CH}_2\text{O}$), 72.3 ($\text{OCH}_2\text{C}(\text{O})$), 71.6 ($\text{OCH}_2\text{CH}_2\text{S}$), 69.3 ($\text{ArOCH}_2\text{CH}_2\text{O}$), 34.0, 33.7

($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$ & OCH_2CH_2S), 31.0 ($ArCH_2Ar$); Calc. for $C_{56}H_{74}O_{10}S$: C, 71.61; H, 7.94; S, 3.41. Found: C, 71.97; H, 8.17; S, 3.10%.

Procedure for competitive extraction of alkaline earth metal cations

An aqueous solution of the alkaline earth metal chlorides with hydroxides for pH adjustment (2.0 ml, 10.0 mM in each alkaline earth metal cation species) and 2.0 ml of 1.0 mM ligand in chloroform in a capped, polypropylene, 15-ml centrifuge tube was vortexed with a Glas-Col Multi-Pulse Vortexer for 10 min at room temperature. The tube was centrifuged for 10 min for phase separation with a Becton-Dickinson Clay Adams Brand® Centrifuge. A 1.5-ml portion of the organic phase was removed and added to 3.0 ml of 0.10 M HCl in a new, 15-ml, polypropylene centrifuge tube. The tube was vortexed for 10 min and then centrifuged for 10 min. The alkaline earth metal cation concentrations in the aqueous phase from stripping were determined with a Dionex DX-120 Ion Chromatograph with a CS12A column. The pH of the aqueous phase from the initial extraction step was determined with a Fisher Accumet AR25 pH meter with a Corning 476157 combination pH electrode.

Procedure for single species extraction of Pb(II)

The procedure followed that for competitive extraction of AEMC with the following changes. The aqueous phase contained 1.0 mM $Pb(NO_3)_2$ with the pH adjusted using either HNO_3 or tetramethylammonium hydroxide (TMAOH) solutions. For stripping of the extracted Pb^{2+} from the chloroform phase, 1.0 M HNO_3 was utilized. The Pb^{2+} concentrations in the aqueous stripping solutions were determined with a Perkin-Elmer Model 5000 atomic absorption spectrophotometer.

Procedure for single species extraction of Hg(II)

An aqueous solution (3.0 ml) of 0.25 mM $Hg(NO_3)_2$ with HNO_3 or TMAOH for pH adjustment and 3.0 ml of a 0.25 mM solution of the ligand in chloroform were placed in a capped, polypropylene, 15-ml centrifuge tube. The mixture was vortexed for 10 min at room temperature. The tube was centrifuged for 10 min for phase separation. A 0.50-ml sample of the aqueous phase was removed and diluted to 5.0 ml with water. A 1.5 ml aliquot of the diluted solution was shaken for 10 min with 3.0 ml of a 14 ppm solution of dithizone

and 1.5 ml of 1.0 M citric acid solution for which the pH had been adjusted to 3.15 using 1.0 M NaOH. The mixture was centrifuged for 10 min. The organic phase was then analyzed by using the absorbance at 496 nm for mercury dithizonate complex and a Shimadzu Model 260 UV-Vis spectrophotometer. The pH of the remaining aqueous phase from the initial extraction step was determined with a Fisher Accumet AR25 pH meter with a Corning 476157 combination pH electrode.

Results and discussion

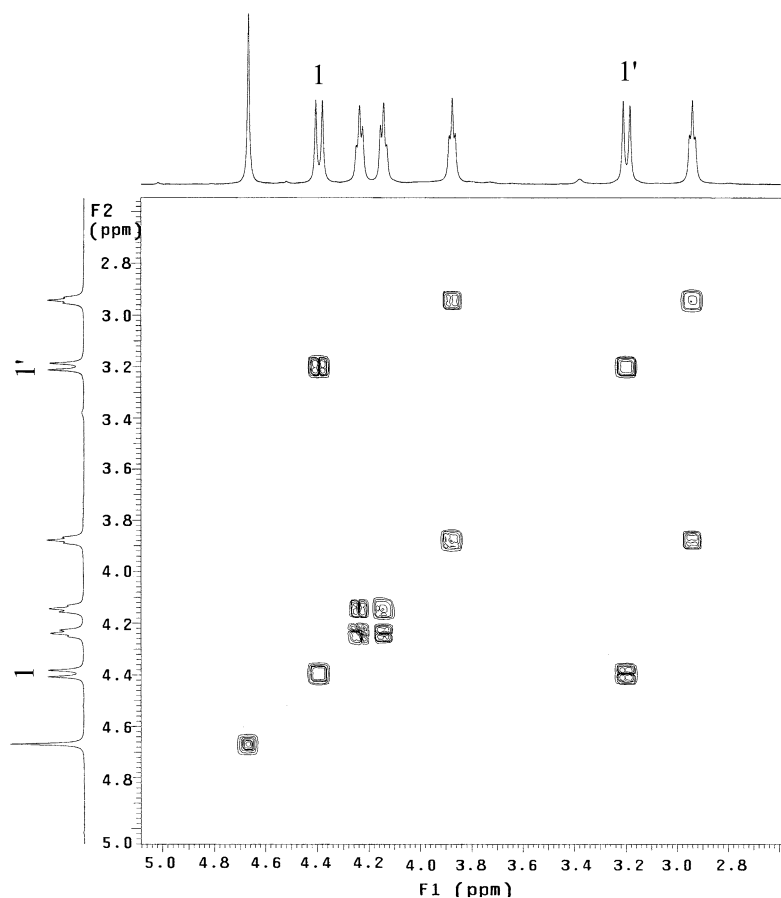
The 1,4,10,13-tetraoxa-7-thiatridecane di-*p*-toluenesulfonate was prepared according to the reported method [16, 17]. Compound **2** was synthesized in low yield by refluxing *p*-*tert*-butylcalix[4]arene (**1**), K_2CO_3 , and the ditosylate in THF. *p*-*tert*-Butylcalix[4]arene-1,3-thiacrown-5 ether **2** was reacted with ethyl bromoacetate and NaH in THF at room temperature to give diester **3** in 80% yield. Subsequent hydrolysis of diester **3** with Me_4NOH in H_2O -THF (1:1) gave diacid **4** in nearly quantitative yield.

The conformation of the calix[4]arene unit and regioselectivity of the crown linkage attachment were verified by NMR spectra. Take compound **4** as an example. There are no peaks between 36–40 ppm in the ^{13}C NMR spectrum, demonstrating that all four benzene rings have *syn*-arrangements [18]. In the 1H NMR spectrum, the bridging methylene proton signals are split into a pair of doublets with the same integration, marked as 1 (axial) and 1' (equatorial). As shown in Fig. 1, they are correlated with each other. These results demonstrate that the polyether ring is attached to the calix[4]arene in the distal phenolic units (Scheme 1). The correlated peaks 1 and 1' are separated by more than 1 ppm, which provides further evidence that the calix[4]arene molecule is in the cone conformation [18, 19].

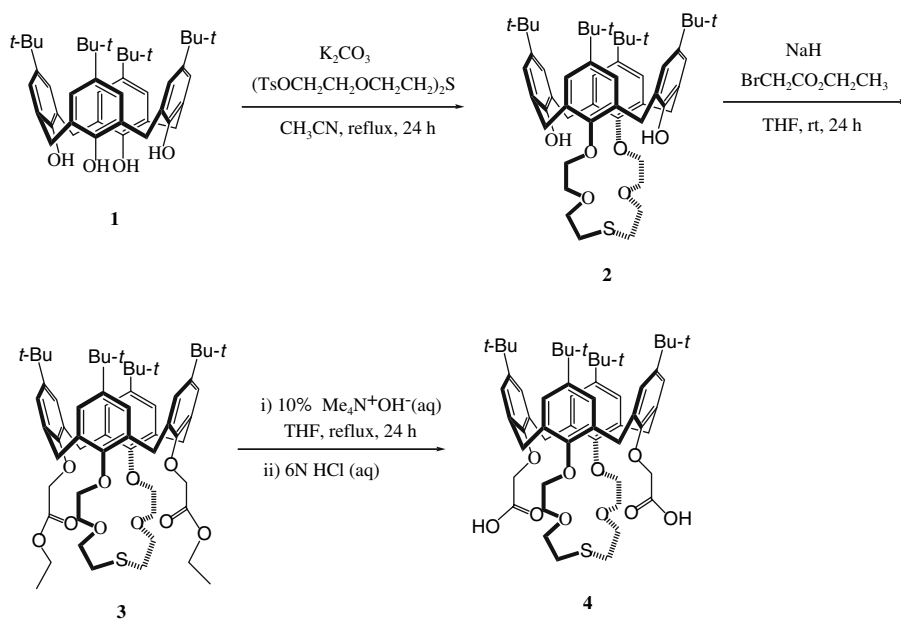
Competitive solvent extraction of AEMC and single species solvent extraction of Pb^{2+} and of Hg^{2+} from aqueous solutions into chloroform by ligand **4** were performed. For comparison, the single species solvent extractions of Pb^{2+} and of Hg^{2+} by the all-oxygen crown ligand **5** (Fig. 2) were also performed. Results from competitive AEMC solvent extractions by ligand **5** have been reported previously [20].

Results from competitive solvent extraction of AEMC by ligand **4** are presented in Fig. 3a. Ligand **4** exhibits high selectivity for Ba^{2+} over the other three AEMC species and 100% maximum metals loading (for formation of a 1:1 metal ion-diionized ligand extraction complex). The extraction selectivity order is

Fig. 1 ^1H - ^1H COSY NMR spectrum of **4**



Scheme. 1 Synthesis of di-ionizable *p*-*tert*-butylcalix[4]arene-1,3-thiacrown-5 ether **4** in the cone conformation



$\text{Ba}^{2+} \gg \text{Sr}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+}$. Under the same conditions, ligand **5** exhibited pronounced extraction selectivity for Ba^{2+} and Sr^{2+} over Ca^{2+} and Mg^{2+} [20]. The single species solvent extraction results for Pb^{2+} and

Hg^{2+} by ligands **4** and **5** are shown in Fig. 3b and c, respectively. For Pb^{2+} , ligand **4** is a somewhat weaker extractant than ligand **5**, but 100% maximum metal loading was reached for both ligands. For Hg^{2+} , the

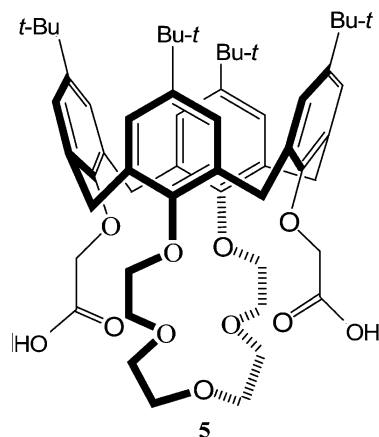


Fig. 2 Structure of di-ionizable calix[4]arene-crown-5 analogue **5**

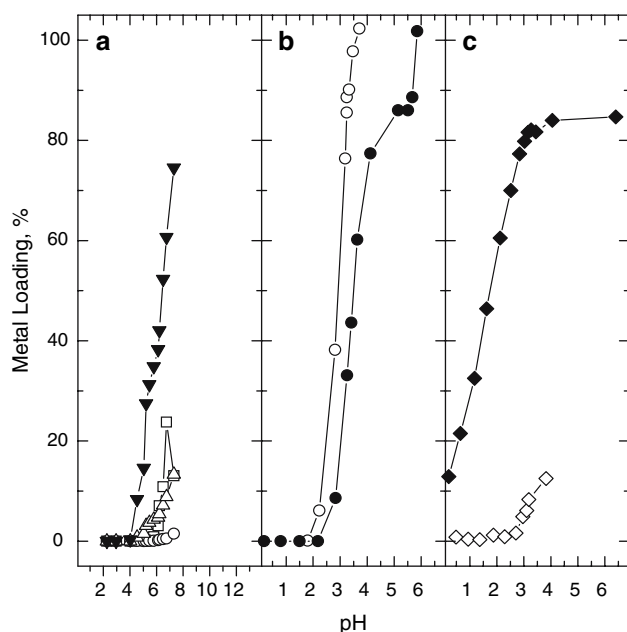


Fig. 3 Percent metal loading of the organic phase versus the equilibrium pH of the aqueous phase for: (a) competitive solvent extraction of alkaline earth metal cations by ligand **4** (\square — Mg^{2+} ; \circ — Ca^{2+} ; Δ — Sr^{2+} ; \blacktriangledown — Ba^{2+}); (b) single species solvent extraction of Pb^{2+} by ligands **4** (\bullet) and **5** (\circ); and (c) single species solvent extraction of Hg^{2+} by ligands **4** (\blacklozenge) and **5** (\diamond)

difference in the extraction results for ligands **4** and **5** is striking. Replacing one of the five hard oxygen in **5** by a soft sulfur atom in the crown ether ring of **4** leads to a dramatic change in the extraction ability of the ligand towards Hg^{2+} . The maximum Hg^{2+} loading was 84% for ligand **4**, but only 16% for ligand **5**.

Upon ionization, the fixed cone conformation for the calix[4]arene units controls the spatial relationship for a crown-complexed divalent metal ion with respect to the two anionic centers required for electroneutrality in the extraction complex. The di-ionizable

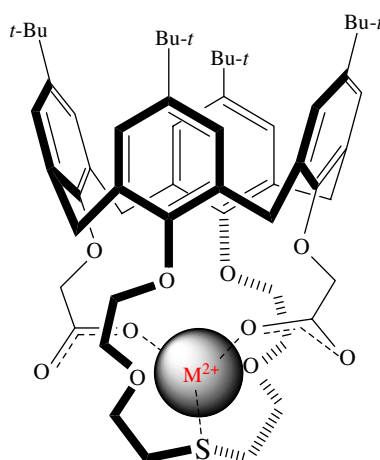


Fig. 4 Depiction of spatial relationship between a crown-complexed divalent metal ion and the anionic centers formed by ionization of ligand **4** (complex **6**)

calix[4]arene-1,3-crown-5 compounds **4** and **5** form metal ion complexes with an anionic center over each face of the crown unit, as depicted in Fig. 4 for the ionized form of ligand **4**. The differences between the extraction behaviors of ligands **4** and **5** clearly establish binding interactions between the complexed divalent metal ion and the sulfur atom of the crown ring.

Further investigations of the metal ion separation properties of this novel type of di-ionizable calix[4]arene-thiacrown ether are in process.

Acknowledgement We thank the Division of Chemical Sciences, Geosciences and Biosciences of the Office of Basic Energy Sciences of the U.S. Department of Energy (Grant DE-FG02-90ER14416) for support of this research.

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