Di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 ligands in cone and 1,2-alternate conformations: synthesis and metal ion extraction†

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Novel di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 ligands in cone and 1,2-alternate conformations were prepared as potential metal ion extractants. Selective bridging of proximal hydroxyl groups of the calix[4]arene platform by a crown-3 polyether unit was achieved under Mitsunobu reaction conditions. In addition to the carboxylic acid group, the acidity tunable *N*-(X)sulfonyl oxyacetamide functions [$OCH_2C(O)NHSO_2X$] with X group variation from methyl to phenyl to *p*-nitrophenyl to trifluomethyl were used as the proton-ionizable groups. Conformations and regioselectivities of the new ligands were established by ^1H and ^{13}C NMR spectroscopy. Competitive solvent extractions of alkali metal cations and of alkaline earth metal cations from aqueous solutions into chloroform were performed, as were single species extractions of lead(II) and mercury(II).

Introduction

In calixarene–crown ether compounds, also called calixcrowns, a calixarene platform is combined with a crown ether unit which bridges two phenolic oxygens of the former with a polyether chain.[1,2] Connection of distal phenolic oxygens in a calix[4]arene gives a 1,3-bridged calix[4]crown, while linking the proximal oxygens produces a 1,2-bridged calix[4]crown. It has been found that the 1,3-bridged calix[4]crowns exhibit high binding affinity and selectivity toward alkali and alkaline earth metal cations.[3–5] On the other hand, research on 1,2-bridged calix[4]crowns lags far behind, probably because of the low cation binding efficiency for the first-reported members.[6–8]

Syntheses of 1,2- and 1,3-bridged calix[4]crowns were generalized by Shinkai and coworkers.[9] A weak base was employed for *O*-alkylation of distal hydroxyl groups and a strong base facilitated formation of calix[4]arene-1,2-crown ethers. Based on this generalization, members of the Bartsch Research Group synthesized series of di-ionizable calix[4]arene-1,2-crown-4, -crown-5, and -crown-6 ligands in the cone conformation and studied their extraction behavior toward alkaline earth metal cations.[10,11] Di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-4 ligands exhibited unexpectedly high selectivity for Ba^{2+} over the other alkaline earth metal cations in competitive extraction from aqueous solutions into chloroform. Two examples of the studied calix[4]crowns are shown in Fig. 1.

Combining a crown ether with a calix[4]arene platform often enhances the cation binding ability of the parent calixarene. The selectivity can be affected by the crown ether size, identity of donor atoms on the crown ether moiety and the conformation of the calixarene platform. Attachment of proton-ionizable groups to calixcrowns further improves their metal ion extraction properties because the ionized group not only participates in metal ion coordination, but also eliminates the need to transfer one or more aqueous phase anions into the organic phase during extraction.

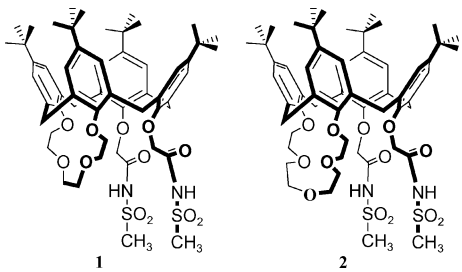
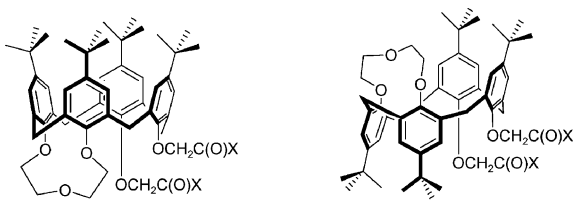


Fig. 1 Di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-4 and -crown-5 ligands **1** and **2**, respectively.

To further explore the influence of the crown ether ring size and to probe the effect of conformational variation on the extraction characteristics of *p-tert*-butylcalix[4]arene-1,2-crown ethers toward metal ions, two series of di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 compounds in the cone and 1,2-alternate conformations (Fig. 2) have now been synthesized. In



	X	
3	OH	**8**
4	$NHSO_2CH_3$	**9**
5	$NHSO_2C_6H_5$	**10**
6	$NHSO_2C_6H_4$-4-NO_2	**11**
7	$NHSO_2CF_3$	**12**

Fig. 2 Structures of di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 ligands in the cone (**3–7**) and 1,2-alternate (**8–12**) conformations.

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† Electronic supplementary information (ESI) available: IR, ^1H NMR and ^{13}C NMR spectral data for compounds **4–7** and **9–12**. See DOI: 10.1039/b700072c

addition to the carboxylic acid group, the acidity tunable *N*-(X)sulfonyl oxyacetamide functions [-C(O)NHSO$_2$X] with variation of X were used as the proton-ionizable groups.

Results and discussion

Synthesis of di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 ligands in the cone conformation

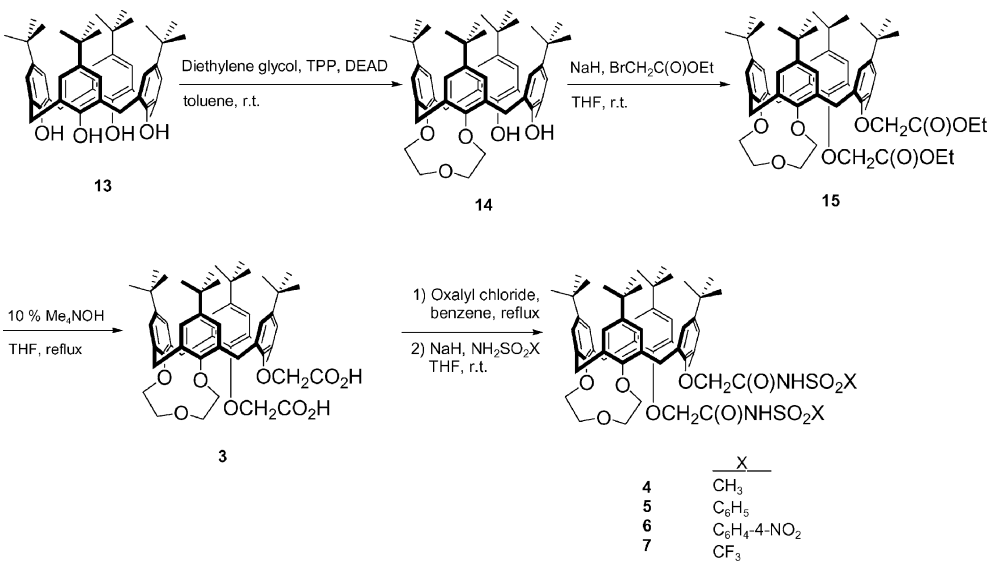
Preparation of the di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 ligands in the cone conformation is illustrated in Scheme 1. For synthesis of the calixcrown platform, the commonly employed method for preparation of calixcrowns with larger crown ether ring sizes was unsuccessful. Thus reaction of *p-tert*-butylcalix[4]arene (**13**), diethylene glycol ditosylate and a strong base failed to give the desired *p-tert*-butylcalix[4]arene-1,2-crown-3 (**14**). Variations of the base, as well as reaction temperature, were performed, but no **14** was detectable in the product mixtures. An entirely different method[12] was utilized for the synthesis of *p-tert*-butylcalix[4]arene-1,2-crown-3 (**14**) (Scheme 1). Under Mitsunobu reaction conditions, *p-tert*-butylcalix[4]arene (**13**), triphenylphosphine (TPP), diethyl azodicarboxylate (DEAD) and diethylene glycol were combined to form **14** in 54% yield. Calixcrown **14** was reacted with NaH in THF and then with ethyl bromoacetate to form cone *p-tert*-butylcalix[4]arene-1,2-crown-3 diester **15** in 61% yield. Diester **15** was hydrolyzed with aqueous Me$_4$NOH in THF at reflux to give diacid **3** in 88% yield. Diacid **3** was converted into the corresponding di(acid chloride) by reaction with oxalyl chloride at reflux in benzene. The di(acid chloride) was reacted with the appropriate sulfonamide anions in THF to afford compounds **4–7** in 78–96% yields.

Verification of the conformation and regioselectivity for di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 compounds **3–7** was provided by their ^{1}H and ^{13}C NMR spectra.[13,14] There were no peaks between 35–40 ppm in the ^{13}C NMR spectra revealing that all four benzene rings in each ligand have *syn* arrangements. In the ^{1}H NMR spectra, the protons of the bridging methylene groups (ArCH$_2$Ar) were split into three pairs of widely separated doublets with an integration ratio of 1 : 2 : 1. Due to the C_s symmetry and structural rigidity, the methylene protons in the ionizable side arms [-OCH$_2$C(O)-], as well as the methylene protons on the small crown ether ring, were diastereotopic. These data demonstrated that the crown rings are attached to the calix[4]arene platform *via* the proximal phenolic oxygens and the compounds are in the cone conformation.

Synthesis of di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 ligands in the 1,2-alternate conformation

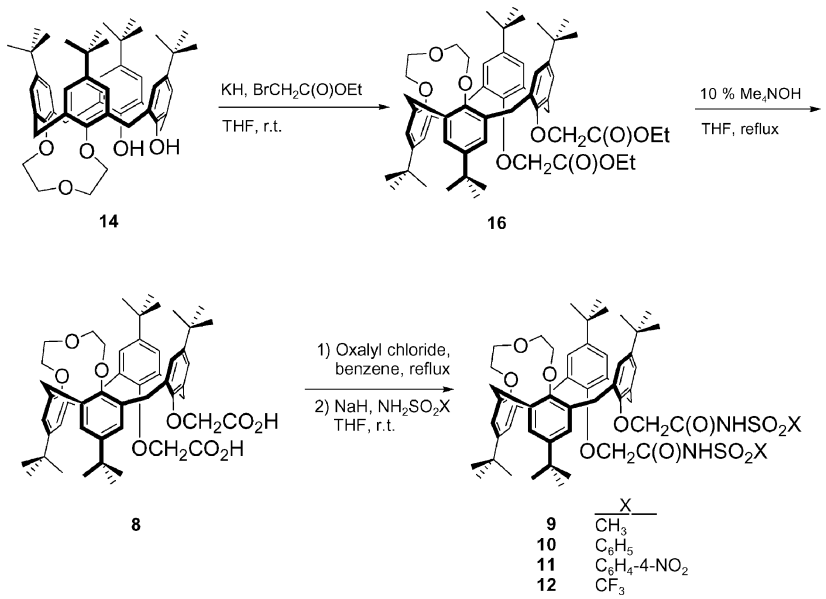
As shown in Scheme 2, *p-tert*-butylcalix[4]arene-1,2-crown-3 (**14**) was reacted with KH in THF and then with ethyl bromoacetate to produce *p-tert*-butylcalix[4]arene-1,2-crown-3 diester **16** in the 1,2-alternate conformation in 48% yield. Diester **16** was hydrolyzed with aqueous Me$_4$NOH in THF to give diacid **8** in 96% yield. Diacid **8** was converted into the corresponding di(acid chloride) by reaction with oxalyl chloride at reflux in benzene overnight. The di(acid chloride) was reacted with the appropriate sulfonamide anions in THF to afford ligands **10–12** in 87–91% yields. Compound **9** was obtained in only 20% yield due to formation of the mono-substituted byproduct.

Conformations for the di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 compounds **8–11** were established by their ^{1}H and ^{13}C NMR spectra.[13,14] The ^{13}C NMR spectra showed peaks at 31 and 38 ppm, revealing that the benzene rings have both *syn* and *anti* arrangements. In the ^{1}H NMR spectra, the protons of the bridging methylene groups were split into three pairs of doublets, with an integration ratio of 1 : 1 : 2. Two pairs of doublets were widely separated in an AX pattern and the other pair of doublets showed an AB pattern. Locked by the short polyether chain, the structure with C_s symmetry is rigid. Therefore, the two methylene protons in the ionizable side arms [-OCH$_2$C(O)-] and the methylene protons on the small crown ring are all diastereotopic. Compared with the cone conformers, these protons were shifted downfield due to de-shielding by the neighboring benzene rings.



13 14 15 3

Scheme 1 Synthesis of cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-di(*N*-(X)sulfonyl carbamoylmethoxyl)calix[4]arene-crown-3 ethers **4–7**.



Scheme 2 Synthesis of 1,2-alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-25,26-di(*N*-(X)sulfonyl carbamoylmethoxy)calix[4]arene-crown-3 ethers **9–12**.

Our attempts to grow suitable crystals of the 1,2-alternate and cone ligands for solid-state structure determination have been unsuccessful to date.

Competitive solvent extraction of alkali metal cations by di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 ligands 3–7 in the cone conformation and analogues 8–12 in the 1,2-alternate conformation

For competitive solvent extraction of aqueous alkali metal cation (Li^+, Na^+, K^+, Rb^+, Cs^+) (10.0 mM in each) solutions by 1.0 mM solutions of cone di-ionizable calix[4]arene ligands **3–7** in chloroform, plots of metal ion loading of the organic phase *vs.* the equilibrium pH of the aqueous phase are presented in Fig. 3.

For alkali metal cation extractions by cone conformers **3–7**, the total loadings of alkali metal cations were all near 200%, which is consistent with a 2 : 1 ratio of metal ion to ligand in the extraction complexes. At pH higher than 5–7, all five alkali metal cations were detectably extracted into the chloroform phase. Ligands **3–7** exhibited very good selectivity for Na^+ over the other four alkali metal ion species. Ligands **5** and **6** extracted a fair amount of Li^+ in the pH range of 5–7. Interestingly, the amount of Li^+ extracted diminished as the pH increased. This reveals that the binding of different alkali metal cation species by the ligands was influenced by the identity of the pendent proton-ionizable group and the equilibrium pH. The selectivity order for dicarboxylic acid **3** at pH above 11 was $Na^+ \gg Li^+ > K^+ \sim Cs^+ \sim Rb^+$, with a Na^+/Li^+ selectivity of 12 under conditions of high loading. The selectivity order for di-[*N*-(X)sulfonyl oxyacetamide] ligands **4–6**

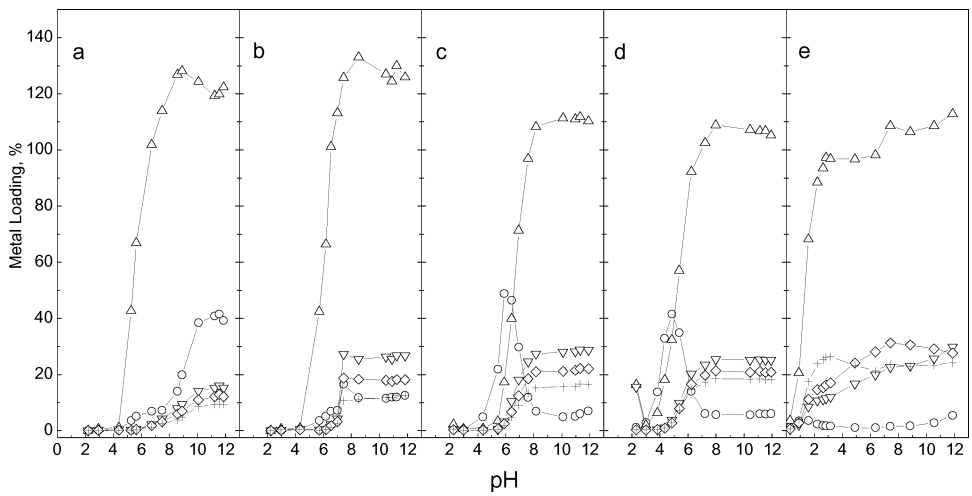


Fig. 3 Percent metal loading *vs.* the equilibrium pH of the aqueous phase for competitive solvent extraction of alkali metal ions into chloroform by cone *p-tert*-butylcalix[4]arene-1,2-crown-3 ethers: (a) **3**; (b) **4**; (c) **5**; (d) **6**; (e) **7**. ○ = Li^+, △ = Na^+, ▽ = K^+, ◇ = Rb^+, + = Cs^+.

at pH above 11 was $Na^+ \gg K^+ > Rb^+ > Cs^+ \geq Li^+$, with Na^+/K^+ ratios of 3.9–4.3. For all five of the cone conformers, the Na^+ loading exceeded 100%. This can be rationalized by a polyether ring-facilitated binding of one Na^+ by one ionized side arm plus unselective binding of all alkali metal ions by a second side arm pointing away from the crown ether ring, as illustrated in Fig. 4.

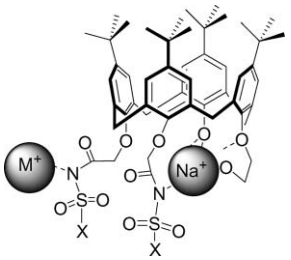


Fig. 4 Proposed binding of alkali metal cations by cone di-[*N*-(X)sulfonyl oxyacetamide] calix[4]arene-1,2-crown-3 ligands.

Di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 ethers **8–12** in the 1,2-alternate conformation exhibited markedly different behavior in competitive solvent extractions of aqueous alkali metal cations (Fig. 5) than that observed for the corresponding cone isomers (Fig. 3). All five of the alkali metal cation species were appreciably extracted into the chloroform phase with total metal ion loadings reaching 200%. However, no significant selectivity for any one of the alkali metal ions by the ligands was observed. Compared with cone ligands **3–7**, the 1,2-alternate ligands **8–12** will have the anionic side arms pointing away from the polyether subunits, resulting in poor selectivity for binding of alkali metal cations. This demonstrates that the spatial relationship of the ionizable groups and polyether ring has a pronounced influence upon the complexation of alkali metal cations by these di-ionizable calix[4]arene-1,2-crown-3 ligands.

Competitive solvent extraction of alkaline earth metal cations by di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 ligands 3–7 in the cone conformation and analogues 8–12 in the 1,2-alternate conformation

For competitive solvent extraction of aqueous alkaline earth metal cation (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) (2.0 mM in each) solutions by 1.0 mM solutions of di-ionizable calix[4]arene ligands **3–7** in chloroform, plots of metal ion loading of the organic phase *vs.* the equilibrium pH of the aqueous phase are presented in Fig. 6.

In competitive extraction of alkaline earth metal cations, di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 ligands **3–7** exhibit very different selectivity from their Ba^{2+}-selective, cone *p-tert*-butylcalix[4]arene-1,2-crown-4 and -crown-5 analogues.[10,11] Although the cone, di-ionizable calix[4]arene-1,2-crown-3 compounds could form metal ion complexes with two anionic centers on the same side of the crown ether unit, apparently the crown-3 ring is too small to hold Ba^{2+} between the ionized groups and the polyether oxygens. All four alkaline earth metal cations are appreciably extracted into the chloroform phase. The extraction selectivity order is $Mg^{2+} > Ca^{2+} > Ba^{2+} > Sr^{2+}$ for dicarboxylic acid **3**. The ordering is $Ba^{2+} \geq Ca^{2+} > Sr^{2+} > Mg^{2+}$ for ligands **4–6** and $Ca^{2+} \gg Ba^{2+} > Sr^{2+} > Mg^{2+}$ for ligand **7**. The pH for half loading, $pH_{0.5}$, is a qualitative measure of the ligand acidity. For compounds **4–7**, the $pH_{0.5}$ values were 8.9, 7.9, 7.3 and 6.0, respectively, in accord with the electron-withdrawing power of the X group.

For competitive solvent extractions of aqueous alkaline earth metal cations by 1,2-alternate, di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 analogues **8–12** in chloroform, plots of metal ion loading of the organic phase *vs.* the equilibrium pH of the aqueous phase are presented in Fig. 7. For dicarboxylic acid **8**, very little differentiation among the four alkaline earth metal ion species was evident. For ligands **9–12**, Ba^{2+} was the best extracted alkaline earth metal cation, although the selectivity was modest at best. It is interesting to note that the selectivity in competitive alkaline earth metal cation extractions is greater for the 1,2-alternate calix[4]arene-1,2-crown-3 ethers with two

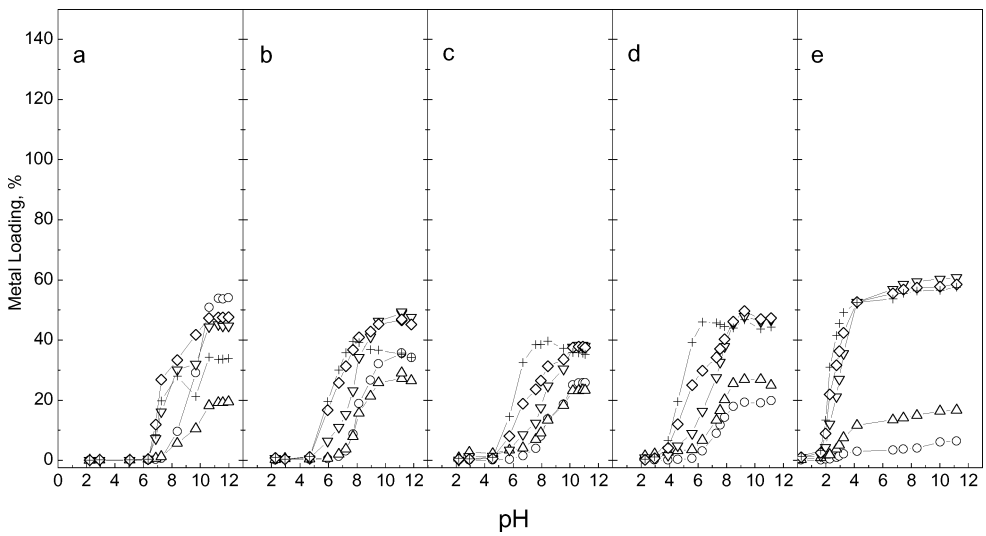


Fig. 5 Percent metal loading *vs.* the equilibrium pH of the aqueous phase for competitive solvent extraction of alkali metal ions into chloroform by 1,2-alternate *p-tert*-butylcalix[4]arene-1,2-crown-3 ethers: (a) **8**; (b) **9**; (c) **10**; (d) **11**; (e) **12**. ○ = Li^+, △ = Na^+, ▽ = K^+, ◇ = Rb^+, + = Cs^+.

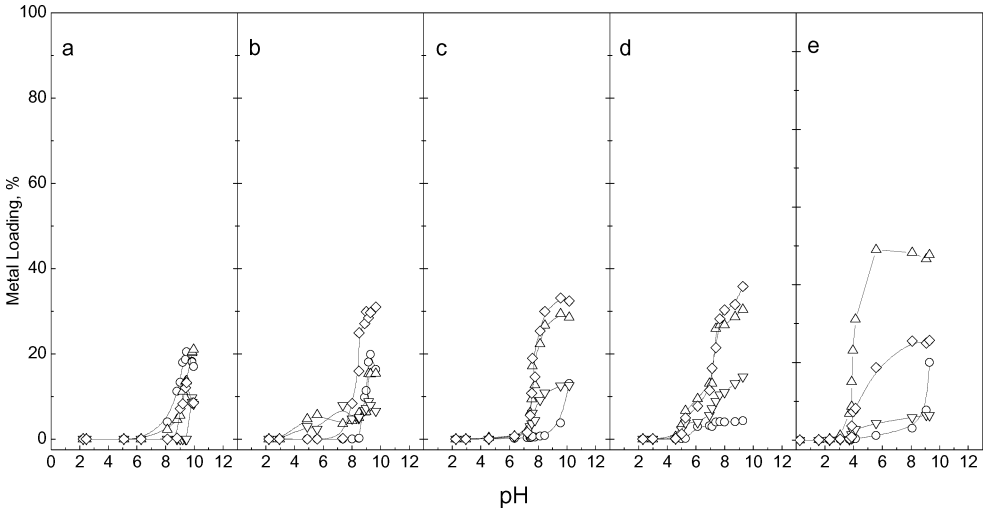


Fig. 6 Percent metal loading *vs.* the equilibrium pH of the aqueous phase for competitive solvent extraction of alkaline earth metal ions into chloroform by cone *p-tert*-butylcalix[4]arene-1,2-crown-3 ethers: (a) **3**; (b) **4**; (c) **5**; (d) **6**; (e) **7**. ○ = Mg^{2+}, △ = Ca^{2+}, ▽ = Sr^{2+}, ◇ = Ba^{2+}.

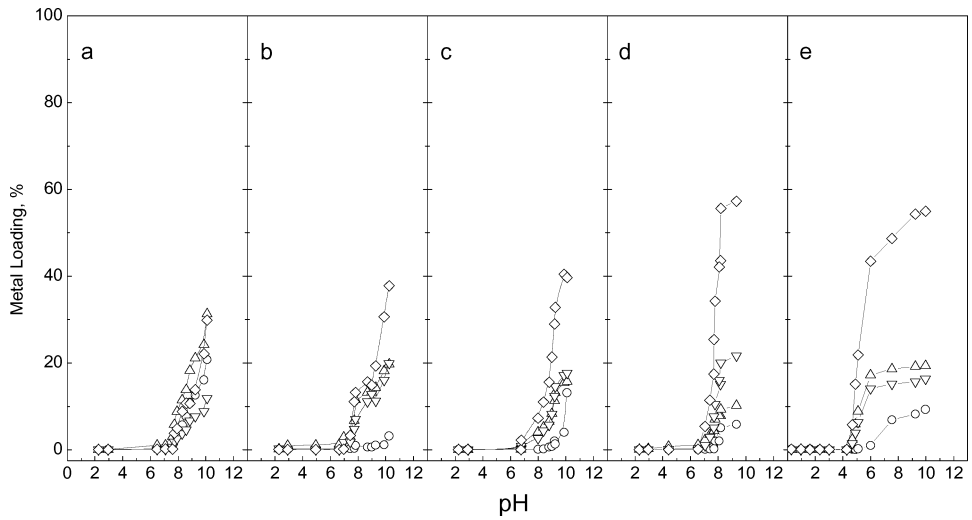


Fig. 7 Percent metal loading *vs.* the equilibrium pH of the aqueous phase for competitive solvent extraction of alkaline earth metal cations into chloroform by 1,2-alternate *p-tert*-butylcalix[4]arene-1,2-crown-3 ethers **8–12**: (a) **8**; (b) **9**; (c) **10**; (d) **11**; (e) **12**. ○ = Mg^{2+}, △ = Ca^{2+}, ▽ = Sr^{2+}, ◇ = Ba^{2+}.

N-(X)sulfonyl oxyacetamide groups than for the analogous cone conformers. For ligands **9–12**, the $pH_{0.5}$ values were 9.4, 9.1, 7.7, and 5.4, respectively, which is in accord with the electron-withdrawing power of the X group.

Solvent extraction of Pb^{2+} by di-ionizable *p-tert*-butylcalix[4]arene-1,2-crown-3 ligands 3–7 in the cone conformation and analogues 8–12 in the 1,2-alternate conformation

Earlier we reported that conformationally mobile *p-tert*-butylcalix[4]arenes with two pendant *N*-(X)sulfonyl oxyacetamide groups exhibited strong extraction propensity towards Pb^{2+} and Hg^{2+}.[15,16] Therefore, the study of metal ion extractions by di-ionizable calix[4]arene-1,2-crown-3 ligands **3–12** was expanded to include borderline Pb^{2+} and soft Hg^{2+}, in addition to the hard alkali and alkaline earth metal cations.

Single species solvent extractions of aqueous 1.00 mM Pb^{2+} solutions by 0.50 mM solutions of di-ionizable calix[4]arene ligands **3–12** in chloroform were conducted. Plots of Pb^{2+} loading of the organic phase *vs.* the equilibrium pH of the aqueous phase are presented in Fig. 8a. Cone dicarboxylic acid **3** and di-[*N*-(X)sulfonyl oxyacetamide] ligands **6** and **7** with X = 4-nitrophenyl and trifluoromethyl, respectively, all exhibited high efficiencies for Pb^{2+} extraction. Interestingly, ligands with X = methyl and phenyl gave only very low levels of Pb^{2+} extraction. In this case, the acidity of the di-[*N*-(X)sulfonyl oxyacetamide] ligand markedly influenced the metal ion extraction ability. Ligand **7** showed quantitative Pb^{2+} loading with a $pH_{0.5}$ value of 3.0.

All five of the 1,2-alternate analogues **9–12** showed very high extraction propensity for Pb^{2+} (Fig. 8b). The $pH_{0.5}$ values for the di-[*N*-(X)sulfonyl oxyacetamide] ligands **9–12** were 3.6, 3.9, 2.8, and 1.1, respectively. Thus, with X = trifluoromethyl, ligand **12** was found to be a very strong Pb^{2+} extractant. Compared with the

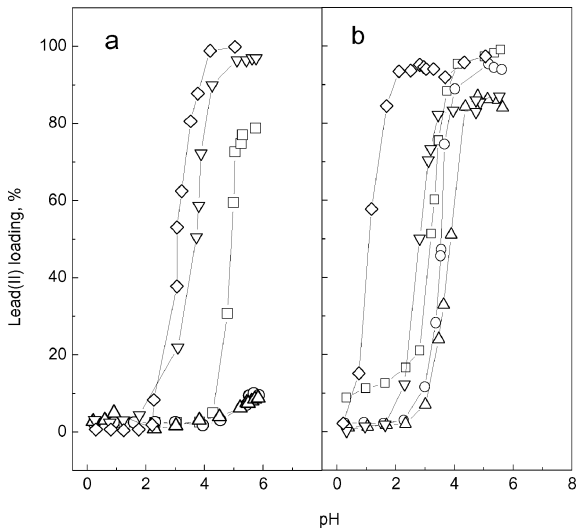


Fig. 8 Percent Pb^{2+} loading *vs.* the equilibrium pH of the aqueous phase for single species Pb^{2+} extraction into chloroform by *p-tert*-butylcalix[4]arene-1,2-crown-3 ethers: a) cone conformers **3–7** (□ = **3**, ○ = **4**, △ = **5**, ▽ = **6**, ◇ = **7**); b) 1,2-alternate conformers **8–12** (□ = **8**, ○ = **9**, △ = **10**, ▽ = **11**, ◇ = **12**).

cone ligands **3–7** (Fig. 8a), the extraction profiles showed that the 1,2-alternate conformation was favored for complexation of Pb^{2+}.

Solvent extraction of Hg^{2+} by di-ionizable *p-tert*-butylcalix[4]-arene-1,2-crown-3 ligands 3–7 in the cone conformation and ligands 8–12 in the 1,2-alternate conformation

For solvent extractions of aqueous 0.25 mM Hg^{2+} solutions with 0.25 mM solutions of di-ionizable calix[4]arene ligands **3–12** in chloroform, plots of Hg^{2+} loading of the organic phase *vs.* the equilibrium pH of the aqueous phase are presented in Fig. 9.

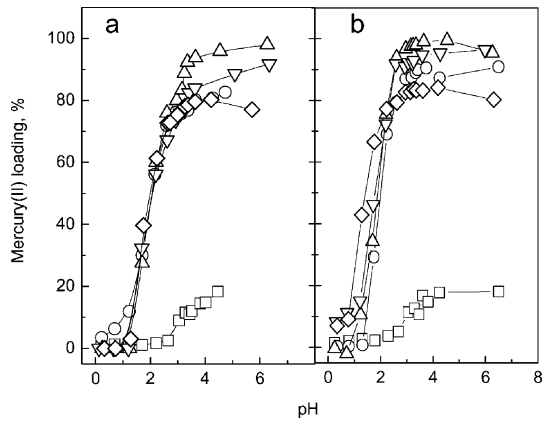


Fig. 9 Percent Hg^{2+} loading *vs.* the equilibrium pH of the aqueous phase for single species Hg^{2+} extraction into chloroform by *p-tert*-butylcalix[4]arene-1,2-crown-3 ethers: a) cone conformers **3–7** (□ = **3**, ○ = **4**, △ = **5**, ▽ = **6**, ◇ = **7**); b) 1,2-alternate conformers **8–12** (□ = **8**, ○ = **9**, △ = **10**, ▽ = **11**, ◇ = **12**).

The four cone di-[*N*-(X)sulfonyl oxyacetamide] ligands **4–7** exhibited much higher Hg^{2+} extraction than did dicarboxylic acid **3** (Fig. 9a). This underscores the importance of *N*-(X)sulfonyl oxyacetamide functions as an important addition to the more customary proton-ionizable groups. The $pH_{0.5}$ values for ligands **4–7** were all in the range of 2.0–2.2. Thus, the identity of X had little apparent influence on the extraction ability of the four di-[*N*-(X)sulfonyl oxyacetamide]-containing ligands.

The 1,2-alternate di-[(X)sulfonyl oxyacetamide] ligands **9–12** also showed much greater Hg^{2+} extraction propensity than the analogous dicarboxylic acid **8** (Fig. 9b). The $pH_{0.5}$ values for ligands **9–12** were all in the range of 1.5–2.0. Visual comparison of Fig. 9a and b suggests that complexation of Hg^{2+} by an 1,2-alternate di-[(X)sulfonyl oxyacetamide] ligand may be slightly stronger than that for a cone conformation analogue.

Conclusions

For solvent extraction of hard (alkaline earth metal cations), intermediate (Pb^{2+}) and soft (Hg^{2+}) divalent metal ions by di-[*N*-(X)sulfonyl oxyacetamide] calix[4]arene-1,2-crown-3 ligands, the 1,2-alternate conformations were found to exhibit greater extraction selectivity or efficiency compared with their cone conformation analogues. For Hg^{2+} extraction, *N*-(X)sulfonyl oxyacetamide acidic groups markedly surpassed analogous ligands with carboxylic acid functions. The strength of divalent metal cation complexation, as assessed by solvent extraction, increased in the order: alkaline earth metal cations < Pb^{2+} < Hg^{2+}.

Experimental

Melting points were determined with a Mel-Temp melting point apparatus. Infrared (IR) spectra were recorded with a Perkin-Elmer Model 1600 FT-IR spectrometer as deposits from CH_2Cl_2 solution on NaCl plates. The ^1H and ^{13}C NMR spectra were recorded with a Varian Unity INOVA 500 MHz FT-NMR (^1H 500 MHz and ^{13}C 126 MHz) spectrometer in $CDCl_3$ with Me_4Si as internal standard unless mentioned otherwise. Chemical shifts (δ) are given in ppm downfield from TMS and coupling constant (J) values are in Hz. Elemental analysis was performed by Desert Analytics Laboratory of Tucson, Arizona. Analytical TLC was performed on Analtech Uniplate silica gel or alumina plates. Silica gel 150 (Mallinckrodt SiliCAR®, 60–200 mesh) was used for column chromatography.

Reagents were obtained from commercial suppliers and used directly, unless otherwise noted. Tetrahydrofuran (THF) was dried over sodium with benzophenone as an indicator and distilled just before use.

p-tert-Butylcalix[4]arene-1,2-crown-3 (14)

To a mixture of *p-tert*-butylcalix[4]arene (6.50 g, 10 mmol), diethylene glycol (1.59 g, 15 mmol) and TPP (8.00 g, 30 mmol) in 200 mL of toluene, a 40% solution of DEAD (5.22 g, 30 mmol) in toluene was added dropwise. The mixture was stirred at room temperature for 0.5 h. Then the solution was evaporated *in vacuo* to dryness and the residue was extracted with hexane (3 × 30 mL) followed by evaporation of the combined hexane extracts *in vacuo* and subsequent stirring of the residue in hexane and ethyl acetate. The precipitate was filtered and the filtrate was chromatographed on silica gel with hexane–EtOAc (9 : 1) as eluent to give a white solid (3.90 g, 54%) with mp 198–199 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3342 (O–H), 1249 and 1124 (C–O); ^1H NMR ($CDCl_3$): δ 1.20 (s, 18 H, CH_3), 1.21 (s, 18 H, CH_3), 3.26–3.45

(m, 4 H, $ArCH_2Ar$), 4.01 (t, $J = 10.5$ Hz, 2 H, OCH_2CH_2O), 4.12 (t, $J = 11.0$ Hz, 2 H, OCH_2CH_2O), 4.28–4.46 (m, 7 H, OCH_2CH_2O, $ArCH_2Ar$), 4.82 (d, $J = 12.0$ Hz, 1 H, $ArCH_2Ar$), 6.94–7.06 (m, 6 H, ArH), 7.15 (d, $J = 2.0$ Hz, 2 H, ArH), 8.87 (s, 2 H, OH); ^{13}C NMR ($CDCl_3$): δ 31.30, 31.50, 32.66, 33.01, 33.90, 34.18, 75.32, 125.31, 125.58, 125.60, 126.45, 128.32, 128.84, 129.15, 133.88, 134.62, 142.81, 147.42, 149.14, 150.34. Anal. Calcd for $C_{48}H_{62}O_5$: C, 80.18; H, 8.69. Found: C, 80.08; H, 8.37%.

Cone *p-tert*-butylcalix[4]arene-1,2-crown-3 diester 15

p-tert-Butylcalix[4]arene-1,2-crown-3 (**14**) (5.00 g, 6.95 mmol) in 50 mL of THF was added dropwise into a mixture of NaH (0.85 g, 35.4 mmol) in 50 mL of THF. After stirring for 2 h, ethyl bromoacetate (6.95 g, 41.7 mmol) was added and the reaction mixture was stirred overnight. The reaction was monitored by TLC. After 48 h, the reaction was quenched by careful addition of dilute HCl and evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2. The solution was washed with dilute HCl and water, dried over $MgSO_4$, and the evaporated *in vacuo*. Chromatography of the residue on silica gel with hexane–EtOAc (1 : 4) as eluent gave an oil (3.81 g, 61%). IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 1760 (C=O), 1253 and 1128 (C–O); ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 18 H, CH_3), 1.12 (s, 18 H, CH_3), 1.34 (t, $J = 7.0$ Hz, 6 H, OCH_2CH_3), 3.09 (d, $J = 12.0$ Hz, 1 H, $ArCH_2Ar$), 3.18 (d, $J = 12.0$ Hz, 2 H, $ArCH_2Ar$), 3.24 (d, $J = 13.0$ Hz, 1 H, $ArCH_2Ar$), 3.83–3.92 (m, 2 H, OCH_2CH_2O), 4.07 (d, $J = 12.0$, 2 H, OCH_2CH_2O), 4.20 (m, 2 H, OCH_2CH_2O), 4.27 (q, $J = 7.0$, 4 H, OCH_2CH_3), 4.42 (d, $J = 10.5$ Hz, 2 H, OCH_2CH_2O), 4.54–4.65 (m, 3 H, $ArCH_2Ar$, OCH_2CO), 4.73 (d, $J = 12.5$ Hz, 2 H, $ArCH_2Ar$), 4.88 (d, $J = 15.5$ Hz, 2 H, OCH_2CO), 4.96 (d, $J = 12.0$ Hz, 1 H, $ArCH_2Ar$), 6.76–6.84 (m, 4 H, ArH), 6.86 (d, $J = 2.5$ Hz, 2 H, ArH), 6.92 (d, $J = 2.0$ Hz, 2 H, ArH); ^{13}C NMR ($CDCl_3$): δ 14.33, 31.02, 31.32, 31.42, 33.82, 33.88, 53.42, 60.62, 72.03, 73.04, 75.24, 124.35, 125.39, 125.55, 132.72, 134.03, 134.35, 134.81, 144.84, 145.34, 152.88, 152.93, 170.28. Anal. Calcd for $C_{56}H_{74}O_9$: C, 75.47; H, 8.37. Found: C, 75.22; H, 8.23%.

Cone *p-tert*-butylcalix[4]arene-1,2-crown-3 diacid 3

p-tert-Butylcalix[4]arene-1,2-crown-3 diester **15** (3.00 g, 3.05 mmol) in 60 mL of THF and 60 mL of 10% Me_4NOH was refluxed overnight. The solvent was evaporated *in vacuo* and the residue was dissolved in 100 mL of CH_2Cl_2. The organic layer was washed with 1 N HCl solution until pH 1, and then washed with 60 mL of brine and 60 mL of water, dried over $MgSO_4$, and evaporated *in vacuo* to give a white solid (2.49 g, 88%) with mp 255–256 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3217 (O-H), 1761 (C=O), 1203 and 1121 (C–O); ^{1}H NMR ($CDCl_3$): δ 1.07 (s, 18 H, CH_3), 1.11 (s, 18 H, CH_3), 3.12 (d, $J = 12.0$ Hz, 1 H, $ArCH_2Ar$), 3.22–3.36 (m, 3 H, $ArCH_2Ar$), 3.81–3.92 (m, 2 H, OCH_2CH_2O), 4.11 (d, $J = 12.5$ Hz, 2 H, OCH_2CH_2O), 4.20 (t, $J = 11.0$ Hz, 2 H, OCH_2CH_2O), 4.25–4.38 (m, 4 H, OCH_2CH_2O, $ArCH_2Ar$), 4.49 (d, $J = 13.0$ Hz, 1 H, $ArCH_2Ar$), 4.58 (d, $J = 16.5$ Hz, 2 H, OCH_2CO), 4.79 (d, $J = 16.5$ Hz, 2 H, OCH_2CO), 5.19 (d, $J = 12.5$ Hz, 1 H, $ArCH_2Ar$), 6.83–6.91 (m, 4 H, ArH), 6.93 (d, $J = 2.0$ Hz, 2 H, ArH), 6.99 (d, $J = 2.5$ Hz, 2 H, ArH); ^{13}C NMR ($CDCl_3$): δ 30.30, 30.60, 30.80, 31.24, 31.34, 33.90, 33.98, 53.41, 71.62, 73.63, 124.49, 125.47, 126.11, 126.19, 133.12, 133.25, 133.54, 134.94, 145.45, 146.80, 151.23, 152.71, 171.56. Anal. Calcd for $C_{52}H_{66}O_9$: C, 74.79; H, 7.97. Found: C, 74.50; H, 7.95%.

General procedure for preparation of 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di[*N*-(X)sulfonyl carbamoylmethoxy]calix-[4]arene-25,26-crown-3 compounds 4–7 in the cone conformation

Oxalyl chloride (1.03 mL, 12.0 mmol) was added to *p-tert*-butylcalix[4]arene-1,2-crown-3 diacid 3 (1.00 g, 1.20 mmol) in 50 mL of benzene and the mixture was refluxed for 6 h. After verifying the conversion by IR spectroscopy, the solvent was evaporated *in vacuo*. The appropriate sulfonamide (3.0 mmol) in 5 mL of THF was added to NaH (0.36 g, 15 mmol) in 20 mL of THF and the mixture was stirred at room temperature for 2 h. The acid chloride was added and the mixture was stirred overnight. The excess NaH was destroyed by careful addition of water. The THF was evaporated *in vacuo* and the residue was washed with 6 N HCl until pH 1 and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. IR, ^{1}H NMR and ^{13}C NMR spectra for compounds **4–7** are given in the ESI.†

Cone 5, 11, 17, 23 - tetrakis (1, 1 - dimethylethyl) - 27, 28 - di [*N* - (methane)sulfonyl carbamoylmethoxy]calix[4]arene-25,26-crown-3 (4). Obtained as a white solid (0.93 g, 79%) with mp 185–187 °C. Anal. Calcd for $C_{54}H_{72}N_2O_{11}S_2 \cdot 0.8C_6H_6$: C, 67.15; H, 7.36; N, 2.66. Found: C, 67.08; H, 7.65; N, 2.51%.

Cone 5, 11, 17, 23 - tetrakis(1, 1 - dimethylethyl) - 27, 28 -di [*N* - (benzene)sulfonyl carbamoylmethoxy]calix[4]arene-25,26-crown-3 (5). Obtained as a white solid (1.14 g, 95%) with mp 138–140 °C. Anal. Calcd for $C_{64}H_{76}N_2O_{11}S_2 \cdot 0.5H_2O$: C, 68.48; H, 6.91; N, 2.51. Found: C, 68.33; H, 6.75; N, 2.61%.

Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di[*N*-(4-nitro-benzene)sulfonyl carbamoylmethoxy]calix[4]arene-25,26-crown-3 (6). Obtained as yellow solid (0.97 g, 96%) with mp 275–277 °C. Anal. Calcd for $C_{64}H_{74}N_4O_{15}S_2$: C, 63.87; H, 6.20; N, 4.66. Found: C, 63.84; H, 6.48; N, 4.54%.

Cone 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di[*N*-(trifluoromethane)sulfonyl carbamoylmethoxy]calix[4]arene-25,26-crown-3 (7). Obtained as white solid (1.12 g 86%) with mp 214 °C (decomp.). Anal. Calcd for $C_{54}H_{66}F_6N_2O_{11}S_2$: C, 59.11; H, 6.06; N, 2.55. Found: C, 59.55; H, 6.36; N, 2.47%.

1,2-Alternate *p-tert*-butylcalix[4]arene-1,2-crown-3 diester 16

Calix[4]arene-1,2-crown-3 (**14**) (6.00 g, 8.34 mmol) in 60 mL of THF was added dropwise to a mixture of KH (4.17 g, 40% in mineral oil, 41.7 mmol) in 60 mL of THF. After stirring for 2 h, ethyl bromoacetate (8.34 g, 50.04 mmol) was added and the reaction mixture was stirred for 3 d. The reaction was quenched by careful addition of dilute HCl. The mixture was washed with dilute HCl and water, dried over $MgSO_4$, and evaporated *in vacuo*. Chromatography of the residue on silica gel with hexane–EtOAc (1 : 19) as eluent gave a white solid (3.60 g, 48%) with mp 205–206 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 1760 (C=O), 1205 and 1132 (C–O); ^{1}H NMR ($CDCl_3$): δ 1.09 (t, $J = 7.0$ Hz, 6 H, SO_2CH_3), 1.31 (s, 18 H, CH_3), 1.33 (s, 18 H, CH_3), 2.48, (t, $J = 10.0$ Hz, 2 H, OCH_2CH_2O), 3.15, (d, $J = 12.5$ Hz, 1 H, $ArCH_2Ar$), 3.30–3.44 (m, 3 H, $ArCH_2Ar$,

OCH_2CH_2O), 3.53–3.65 (m, 6 H, OCH_2CH_2O, OCH_2CO), 3.83 (d, $J = 17.0$ Hz, 2 H, OCH_2CO), 3.89–4.04 (m, 6 H, OCH_2CH_3, OCH_2CO), 4.07 (d, $J = 16.5$ Hz, 2 H, $ArCH_2Ar$), 4.54 (d, $J = 12.0$ Hz, 1 H, $ArCH_2Ar$), 4.77 (d, $J = 13.5$ Hz, 1 H, $ArCH_2Ar$), 6.97 (d, $J = 2.5$ Hz, 2 H, ArH), 7.07 (d, $J = 2.0$ Hz, 2 H, ArH), 7.32 (d, $J = 2.5$ Hz, 2 H, ArH), 7.42 (d, $J = 2.0$ Hz, 2 H, ArH); ^{13}C NMR ($CDCl_3$): δ 14.12, 29.20, 31.54, 31.58, 31.73, 34.07, 34.10, 39.14, 60.14, 69.37, 73.01, 74.43, 125.12, 125.43, 125.73, 125.89, 132.47, 133.06, 134.20, 135.24, 144.57, 145.57, 152.84, 152.96, 170.14. Anal. Calcd for $C_{56}H_{74}O_9$: C, 75.47; H, 8.37. Found: C, 75.50; H, 8.06%.

1,2-Alternate *p-tert*-butylcalix[4]arene-1,2-crown-3 diacid 8

The *p-tert*-butylcalix[4]arene-1,2-crown-3 diester **16** (4.00 g, 4.07 mmol) in 150 mL of THF and 150 mL of 10% Me_4NOH was refluxed overnight. The solvent was evaporated *in vacuo* and the residue was dissolved in 200 mL of CH_2Cl_2. The organic layer was washed with 1 N HCl until pH 1, and then with brine (100 mL) and water (100 mL), dried over $MgSO_4$, and evaporated *in vacuo* to give a white solid (3.60 g, 96%) with mp >300 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3391 (O-H), 1760 (C=O), 1207 and 1128 (C–O); ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 18 H, CH_3), 1.33 (s, 18 H, CH_3), 2.38, (t, $J = 11.0$ Hz, 2 H, OCH_2CH_2O), 3.19, (d, $J = 12.5$ Hz, 1 H, $ArCH_2Ar$), 3.24, (d, $J = 13.0$ Hz, 1 H, $ArCH_2Ar$), 3.49, (t, $J = 10.0$ Hz, 2 H, OCH_2CH_2O), 3.54–3.66 (m, 4 H, OCH_2CH_2O), 3.85 (d, $J = 17.5$ Hz, 2 H, $ArCH_2Ar$), 3.94 (t, $J = 17.0$ Hz, 2 H, $ArCH_2Ar$), 4.09 (d, $J = 15.5$ Hz, 2 H, OCH_2CO), 4.15 (d, $J = 16.0$ Hz, 2 H, OCH_2CO), 4.55 (d, $J = 12.0$ Hz, 1 H, $ArCH_2Ar$), 4.71 (d, $J = 12.5$ Hz, 1 H, $ArCH_2Ar$), 6.98 (d, $J = 2.0$ Hz, 2 H, ArH), 7.00 (d, $J = 2.0$ Hz, 2 H, ArH), 7.34 (d, $J = 2.5$ Hz, 2 H, ArH), 7.38 (d, $J = 2.0$ Hz, 2 H, ArH); ^{13}C NMR ($CDCl_3$): 29.54, 31.40, 31.59, 34.13, 34.20, 38.98, 68.32, 72.80, 74.47, 124.40, 125.22, 125.57, 126.54, 131.40, 131.86, 134.18, 134.84, 146.49, 146.52, 151.45152.13, 170.37. Anal. Calcd for $C_{52}H_{66}O_9 \cdot 1.0C_6H_6$: C, 76.29; H, 7.95. Found: C, 76.28; H, 8.11%.

General procedure for preparation of 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-bis[*N*-(X)sulfonyl carbamoylmethoxy]-calix[4]arene-25,26-crown-3 compounds 9–12 in the 1, 2-alternate conformation

Oxalyl chloride (1.03 mL, 12.0 mmol) was added to *p-tert*-butylcalix[4]arene-1,2-crown-3 diacid **8** (1.00 g, 1.2 mmol) in 50 mL of benzene and the mixture was refluxed for 6 h. After verifying the conversion by IR spectroscopy, the solvent was evaporated *in vacuo*. The appropriate sulfonamide (3.0 mmol) in 5 mL of THF was added to NaH (0.36 g, 15 mmol) in 20 mL of THF. The reaction mixture was stirred at room temperature for 2 h. The acid chloride was added and the mixture was stirred overnight. The excess NaH was destroyed by careful addition of water. The THF was evaporated *in vacuo* and the residue was washed with HCl until pH 1 and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. IR, ^{1}H NMR and ^{13}C NMR spectral data for compounds **9–12** are included in the ESI.†

1,2-Alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di-[*N*-(methane)sulfonyl carbamoylmethoxy]calix[4]arene-25,26-crown-3 (9). Purified by chromatography on silica gel with EtOAc–hexanes (2 : 23) as eluent to give a white solid (0.24 g, 20%) with mp 252–254 °C. Anal. Calcd for $C_{54}H_{72}N_2O_{11}S_2 \cdot 1.5C_6H_6$: C, 68.39; H, 7.38; N, 2.53. Found: C, 68.02; H, 7.52; N, 2.61%.

1,2-Alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di-[*N*-(benzene)sulfonyl carbamoylmethoxy]calix[4]arene-25,26-crown-3 (10). Obtained as a white solid (0.92 g, 90%) with mp 250–253 °C. Anal. Calcd for $C_{64}H_{76}N_2O_{11}S_2$: C, 69.04; H, 6.88; N, 2.52. Found: C, 68.89; H, 6.72; N, 2.78%.

1,2-Alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di-[*N*-(4-nitrobenzene)sulfonyl carbamoylmethoxy]calix[4]arene-25, 26-crown-3 (11). Obtained as a yellow solid (0.91 g, 91%) with mp 169–172 °C. Anal. Calcd for $C_{64}H_{74}N_4O_{15}S_2$: C, 63.87; H, 6.20; N, 4.66. Found: C, 63.69; H, 6.09; N, 5.08%.

1,2-Alternate 5,11,17,23-tetrakis(1,1-dimethylethyl)-27,28-di-[*N*-(trifluoromethane)sulfonyl carbamoylmethoxy]calix[4]arene-25, 26-crown-3 (12). Obtained as a white solid (1.03 g, 87%) with mp 235–236 °C. Anal. Calcd for $C_{54}H_{66}F_6N_2O_{11}S_2 \cdot 1.5C_6H_6$: C, 62.31; H, 6.22; N, 2.31. Found: C, 62.06; H, 6.10; N, 2.47%.

Procedure for competitive alkali metal cation extraction

An aqueous solution of the alkali metal chlorides with hydroxides and 0.01 M HCl for pH adjustment (for **7** and **12**, 1.0 M HCl was utilized for pH adjustment) (2.0 mL, 10.0 mM in each alkali 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. A sample of the aqueous phase from stripping was diluted 10 times with DI water and the alkali metal cation concentrations were determined using 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 Scientific Accumet AR25 pH meter and a Corning 476157 combination pH electrode.

Procedure for competitive alkaline earth metal cation extraction

The procedure was identical to that given above for the alkali metal cation extractions, except for replacement of the five alkali metal cations in the aqueous solutions with four alkaline earth metal cations at concentrations of 2.0 mM in each.

Procedure for lead(II) extraction

An aqueous solution (2.0 mL) of 1.0 mM $Pb(NO_3)_2$ with Me_4NOH or 0.01–1.00 M HNO_3 for pH adjustment and 2.0 mL of 0.50 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 4.0 M HNO_3 in a new, 15 mL, polypropylene centrifuge tube. The tube was vortexed for 10 min and then centrifuged for 10 min. Of the aqueous phase after stripping, 2.0 mL was diluted to 10 mL with DI water and the

Pb^{2+} concentration was determined with either a Perkin-Elmer Model 5000 atomic absorption spectrophotometer or a Leeman inductively coupled plasma (ICP) spectrophotometer using the absorption at 283.3 nm. The pH of the aqueous phase from the initial extraction step was determined with a Fisher Scientific Accumet AR25 pH meter and a Corning 476157 combination pH electrode.

Procedure for mercury(II) extraction

An aqueous solution (3.0 mL) of 0.25 mM $Hg(NO_3)_2$ with Me_4OH or 4 mM–1 M HNO_3 for pH adjustment and 3.0 mL of 0.25 mM solution of the 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 then centrifuged for 10 min for phase separation with a Becton-Dickinson Clay Adams Brand® centrifuge. A 0.50 mL sample of the aqueous phase was removed and diluted to 5.0 mL with DI water. A 1.5 mL aliquot of the diluted solution was mixed with 1.5 mL of buffer solution (1.0 M citric acid + 1.0 M NaOH solution; pH = 3.15). To this was added 3.0 mL of a 14 ppm solution of dithizone in chloroform. The mixture was vortexed for 5 min and then centrifuged for 5 min.

The organic phase was then analyzed by use of 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 Scientific AR25 pH meter and a Corning 476157 combination pH electrode.

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