Effect of upper rim *para*-alkyl substituents on extraction of alkali and alkaline earth metal cations by di-ionizable calix[4]arenes

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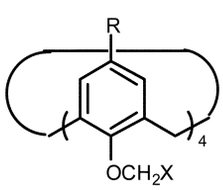
A series of new di-ionizable calix[4]arene *N*-(X-sulfonyl)carboxamides (X = CF_3, Me, Ph and C_6H_4-4-NO_2) and carboxylic acids with partially and completely removed upper rim *p-tert*-butyl groups was synthesized and utilized for competitive solvent extractions of alkali and alkaline earth metal cations. Removal of the *para*-alkyl substituents changes significantly both the efficiency and selectivity of metal ion separations by the carboxamide calix[4]arene extractants, while no such effect is observed for corresponding carboxylic acids.

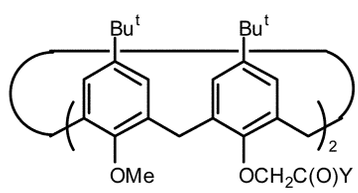
Introduction

Calix[4]arenes containing various functional groups on the lower rim have been utilized widely in metal ion separations. The literature data show that the capability of a calixarene ligand to complex a specific cationic species is determined by structural factors, in particular, the type of donor groups and shape of the cavity.[1] Identity of the *para* substituents on the upper rim, *i.e.*, substituents in *para*-positions relative to the phenolic oxygens, also influences the ionophoric propensities of these ligands for metal cations, although this feature has been much less explored. For example, tetraesters **1**[2] and tetraamide **2**[3] containing four *para-tert*-butyl groups on the upper rims of the calix[4]arene moieties exhibited substantially higher levels of extraction of alkali[2,3] and alkaline earth[3] metal picrates than analogs without substituents on the upper rim, while retaining the same selectivity patterns. Replacement of upper-rim hydrogen atoms with *para-tert*-butyl groups in carbamoyl phosphine oxide CMPO-containing ligands **3** for extraction of lanthanide and actinide ions increased both the distribution coefficients and selectivity of the separations.[4] In contrast, extraction efficiency of calix[4]arene tetrakis(phosphine oxides) **4** for trivalent lanthanides was enhanced when *para-tert*-butyl groups were replaced with hydrogens.[5]



1: X = C(O)OAlk; R = Bu^t, H
2: X = $C(O)NEt_2$; R = Bu^t, H
3: X = $(CH_2)_mNHC(O)CH_2P(O)Ph_2$; R = Bu^t, H
4: X = $CH_2P(O)Ph_2$; R = Bu^t, H

Earlier, we reported a series of *para-tert*-butyl-substituted di-ionizable calix[4]arene *N*-(X-sulfonyl)carboxamides **5** as extractants for hard and soft metal ions.[6] In particular, ligands **5** provided efficient and selective extraction of Pb^{2+}.[6a] In a preliminary study, it was observed that removal of the *para-tert*-butyl groups from **5a** resulted in a decrease of Pb^{2+} binding.[6c] To investigate further the *para* substituent effect on extraction of metal ions, in particular, cations of alkali and alkaline earth metals, we prepared a series of proton-ionizable ligands with no (**8**) or two (**10**) *para-tert*-butyl groups on the calix[4]arene upper rims. Herein we report their synthesis ‡ and extraction behavior compared with the fully *para-tert*-butylated analog. To examine the influence of the lower-rim proton-ionizable group identity on the upper-rim *para*-substituent effect, we included in this study the corresponding calix[4]arene dicarboxylic acids **6**, **7** and **9**.



5: Y = $NHSO_2X$
5a: X = CF_3
5b: X = Me
5c: X = Ph
5d: X = C_6H_4-4-NO_2
6: Y = OH

Results and discussion

Synthesis of *para*-dealkylated di-ionizable calix[4]arene *N*-(X-sulfonyl)carboxamides

Calix[4]arene *N*-(X-sulfonyl)carboxamides **8** without *para-tert*-butyl groups on the upper rim were obtained as shown in Scheme 1 from the dimethoxy derivative **11** which was synthesized by a reported procedure.[8] Reaction of **11** with methyl bromoacetate and caesium carbonate gave diester **12** which was hydrolyzed with tetramethylammonium hydroxide in aqueous THF at reflux to the corresponding dicarboxylic

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‡ Recently compounds **5b** and **5c** were reportedly utilized in separations of heavy metal cations (see ref. 7). However, the synthesis of these calixarenes has not been published to date.

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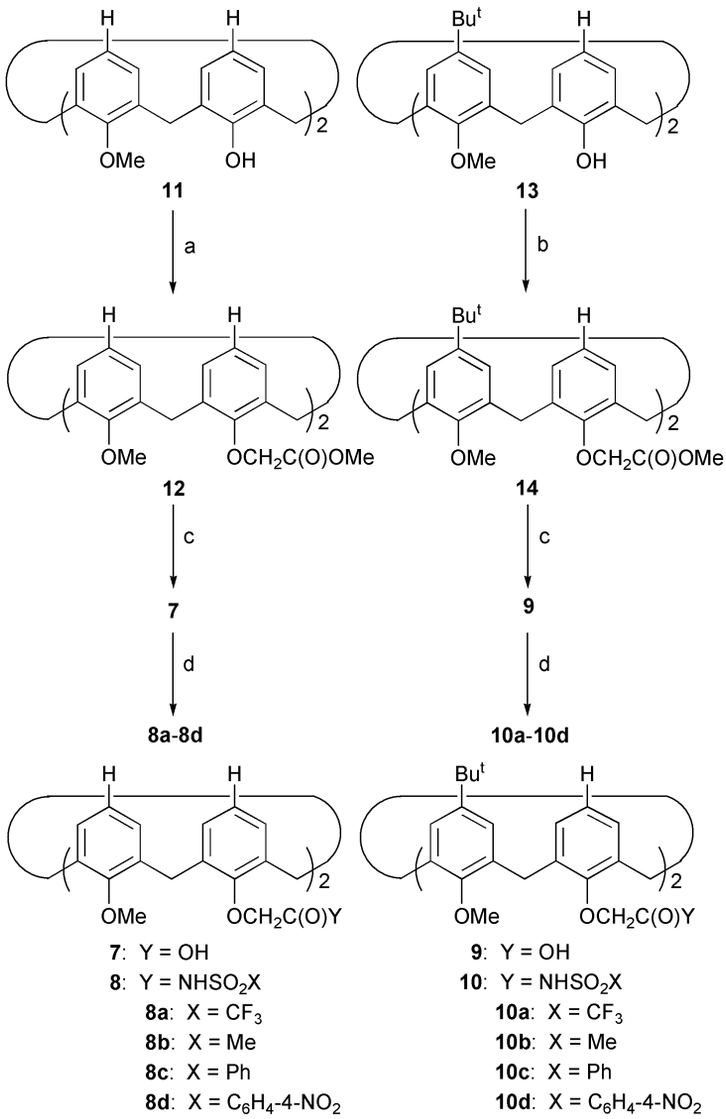

Scheme 1 Synthesis of di-ionizable calix[4]arenes **8a**–**8d** and **10a**–**10d**. *Reagents and conditions:* a) $BrCH_2CO_2Me$, Cs_2CO_3, MeCN, reflux; b) $BrCH_2CO_2Me$, NaH, DMF, 70 °C; c) Me_4NOH, THF–H_2O, reflux; d) i) $(COCl)_2$, C_6H_6, 70 °C; ii) XSO_2NH_2, NaH, THF, rt.

acid **7**. We found that diacid **7** could be readily purified *via* its caesium salt, since the salt appeared to be completely insoluble in $CHCl_3$ (see Experimental).§ Treatment of **7** with oxalyl chloride in benzene at reflux followed by reaction of the resultant acid chloride with the appropriate sulfonamide and sodium hydride in THF at room temperature[10] gave the calix[4]arene *N*-(X-sulfonyl)carboxamides **8a**–**8d**.

For preparation of ligands **10** (Scheme 1), selective removal of two of four *p*-Bu^t groups on the upper rim by a reported method[8] gave **13**. This compound was reacted with methyl bromoacetate and sodium hydride in DMF to give diester **14**. Hydrolysis of **14** with tetramethylammonium hydroxide in THF gave rise to dicarboxylic acid **9** which was converted into the corresponding *N*-(X-sulfonyl)carboxamides **10a**–**10d** as described above.

Extraction of alkali and alkaline earth metal cations by *p-tert*-butyl and *p*-dealkylated di-ionizable calix[4]arenes

Calix[4]arene-based ligands containing *N*-(X-sulfonyl)carboxamide groups with X variation from CF_3 to Me to Ph and C_6H_4-NO_2-4 possess "tunable" acidity of the NH-group due to different electron-withdrawing abilities of X.[6,10] Within the series, ligands with X = CF_3 exhibit the greatest acidity and highest propensities for extraction of various metal cations, without changing the selectivity patterns. Therefore, for comparison of the efficiency and selectivity of alkali metal cation (AMC) and alkaline earth metal cation (AEMC) extractions by tetra-*para*-alkylated, 1,3-bis(*para*-alkylated) and tetra-*p*-dealkylated calix[4]arenes, we have chosen the CF_3-containing representatives of each group of *N*-(X-sulfonyl)carboxamides (**5a**, **10a** and **8a**, respectively) and the corresponding dicarboxylic acids (**6**, **9** and **7**, respectively).

AMC and AEMC extraction into chloroform by the calix[4]arene *N*-(trifluoromethylsulfonyl)carboxamides

The results obtained for competitive extraction of five AMC species (Li^+, Na^+, K^+, Rb^+ and Cs^+) by ligands **5a**, **10a** and **8a** as a function of the aqueous phase pH are presented in Fig. 1. As is obvious from the plots of metal loading¶ *vs*. pH, removal of Bu^t groups from the upper rim significantly changed the complexing ability of the calix[4]arene *N*-(trifluoromethylsulfonyl)carboxamides for AMC. In particular, ligand **5a** was

§ Earlier, we reported a similar purification procedure for a 1,3-alternate calix[4]arene diacid *via* its caesium salt (see ref. 9).

¶ The loading percentage was calculated as (concentration of the metal ion extracted)/(concentration of the ligand) × 100%. For the monovalent AMC extraction with the di-ionizable calixarenes, total loadings approached 200%.

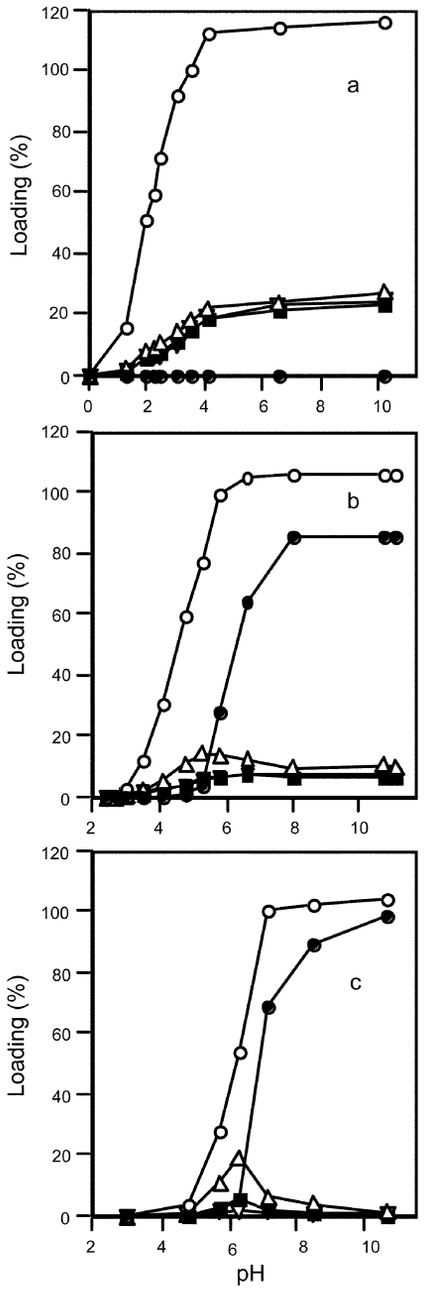

Fig. 1 pH profiles for competitive extractions of Li^+ (●), Na^+ (○), K^+ (Δ), Rb^+ (■) and Cs^+ (▽) from 10.0 mM (in each cation) aqueous chloride solutions by 1.00 mM calix[4]arene *N*-(trifluoromethylsulfonyl)carboxamides (a) **5a**, (b) **10a** and (c) **8a** in chloroform.

capable of extracting the metal ions from acidic aqueous solutions (pH for half-extraction of Na^+ was about 2), while ionophores **10a** and **8a** needed higher pH values. Thus, the pH for half-extraction of Na^+ varied from about 2 for **5a** to 4 for **10a** to 6 for **8a**.

Although high affinity for Na^+ (the best-extracted AMC) was observed for all three calixarenes, *para*-dealkylation led to a marked increase in the extraction of Li^+. Interestingly, with an aqueous phase pH under 5–6, none of the ligands showed a significant Li^+-binding. However, at higher pH, when the ionophore loading with Na^+ reached 40–50%, Li^+-uptake by the the partially dealkylated **10a** and, to an even larger extent, by completely dealkylated **8a** was enhanced dramatically, while Li^+-loading of the tetra-(*p*-*tert*-butyl)-containing compound **5a** remained undetectable.

Additionally, the pH-profiles of K^+, Rb^+ and Cs^+-extractions by **8a** (Fig. 1c) are quite different from those for **5a** (Fig. 1a). In particular, K^+-loading for **8a** showed a pronounced maximum at pH 6 and decreased abruptly to almost zero at higher pH as the Li^+ extraction was increasing dramatically. Rb^+ and Cs^+-loadings of **8a**, in contrast with **5a**, did not exceed 2%. The pH-dependence of K^+, Rb^+ and Cs^+-extractions observed for the partially *para*-dealkylated ligand **10a** (Fig. 1b) was intermediate between those for **5a** and **8a**. The unusual shape of the AMC-extraction pH profiles for **8a** suggests that binding of Na^+ changes the calixarene conformation to one favorable for Li^+, but unfavorable for K^+, Rb^+ and Cs^+.

For competitive AEMC extraction with the three calix-[4]arene *N*-(trifluoromethylsulfonyl)carboxamides from basic (pH 9.8) aqueous solution, the total metal loading of the ligand decreases on going from **5a** to **10a** to **8a** (Fig. 2). The *para*-

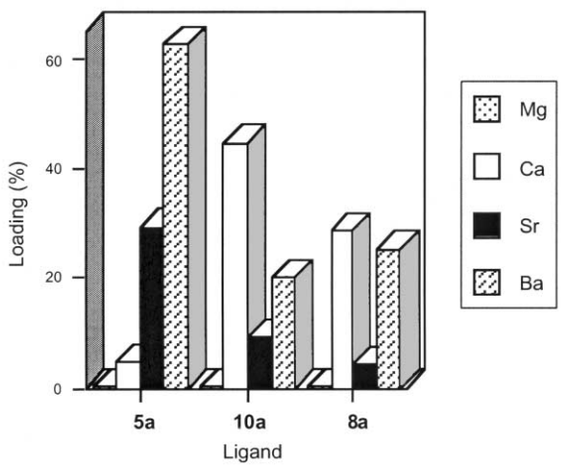

Fig. 2 Competitive AEMC extractions from 10.0 mM (in each cation) aqueous chloride/hydroxide solution at pH 9.8 by 1.00 mM calix[4]-arene *N*-(trifluoromethylsulfonyl)carboxamides **5a**, **10a** and **8a** in chloroform.

dealkylation also affected the extraction selectivities of the ionophores. The tetra-(*para*-*tert*-butyl)-substituted **5a** favored Ba^{2+}, while the dealkylated calixarenes **10a** and **8a** showed different degrees of Ca^{2+}-selectivity.

AMC and AEMC extraction into chloroform by the calix[4]-arene carboxylic acids

To explore a potential influence of the lower-rim functional group identity on the upper-rim *para*-dealkylation effect for calix[4]arene ionophores, competitive AMC and AEMC extractions from basic aqueous solutions by ligands **6**, **7** and **9** were performed (Figs. 3 and 4).

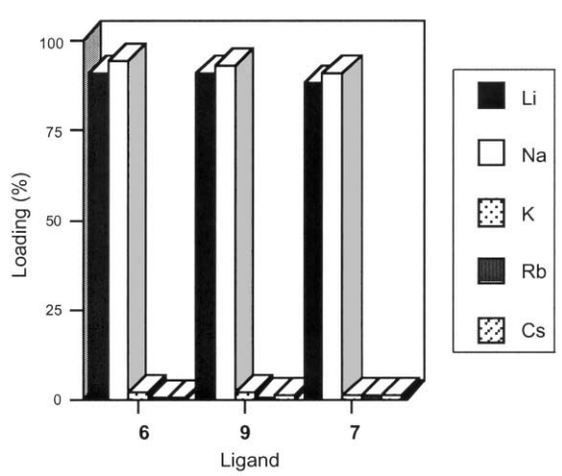

Fig. 3 Competitive AMC extraction from 10.0 mM (in each cation) aqueous chloride/hydroxide solution at pH 11.6 by 1.00 mM calix[4]-arene carboxylic acids **6**, **9** and **7** in chloroform.

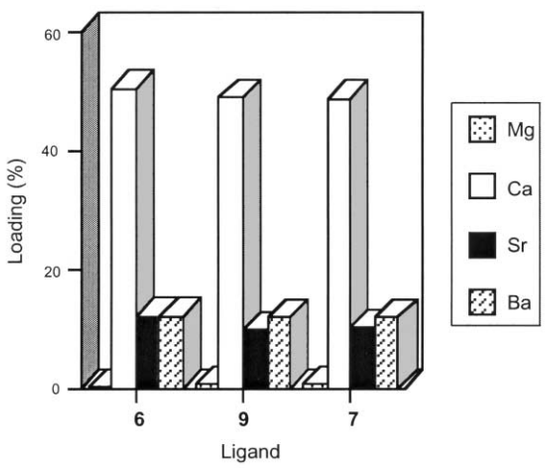

Fig. 4 Competitive AEMC extraction from 10.0 mM (in each cation) aqueous chloride/hydroxide solution at pH 9.8 by 1.00 mM calix[4]-arene carboxylic acids **6**, **9** and **7** in chloroform.

For AMC extraction (Fig. 3), all three ligands strongly favored binding of Li^+ and Na^+ over K^+, Rb^+ and Cs^+. The Na^+-loadings of **6**, **7** and **9** were only slightly larger than those observed for Li^+. It should be pointed out that during the AMC extraction with tetra-(*para*-H) compound **7**, considerable precipitation in the organic phase was observed.‖ Therefore, the metal loadings of **7** were calculated from differences of the AMC concentrations in the aqueous phase after and before extraction and are estimates. As is evident from the data in Fig. 3, the efficiencies of calix[4]arene carboxylic acids **6**, **7** and **9** as AMC extractants are not significantly affected by variation in upper-rim substituent.

Similarly, neither the metal loading nor the selectivity pattern for AEMC extraction by **6**, **7** and **9** (Fig. 4) exhibited appreciable changes with *para*-dealkylation of the calixarene extractant. All three ligands favored Ca^{2+} binding with the metal loading decreasing in the order $Ca^{2+} >> Ba^{2+} \geq Sr^{2+} >> Mg^{2+}$.

It is interesting that the metal ion-extraction profiles of all calix[4]arene dicarboxylic acids resembled more closely those of *para*-dealkylated *N*-(trifluoromethylsulfonyl)carboxamides **8a** and **10a** rather than their tetra-(*para*-*tert*-butyl)-containing analog **5a**.

Concluding remarks

Removal of upper-rim *para*-*tert*-butyl groups from di-ionizable calix[4]arenes may alter significantly the efficiency and selectivity of their AMC and AEMC extractions, with the effect depending strongly on the identity of the lower rim proton-ionizable group. In particular, the *para*-dealkylation resulted in a dramatic variation of the extraction propensities of calix[4]arene *N*-(X-sulfonyl)carboxamides, while those of the corresponding carboxylic acids remained almost unchanged.

Experimental

General

^{1}H NMR spectra were measured with a Varian Unity INOVA spectrometer (499.7 MHz). Chemical shifts (δ) are expressed in ppm downfield from TMS and coupling constant (J) values are given in Hz. pH was measured with a Fisher Scientific Accumet® 50 pH/ion/conductivity meter. Concentrations of alkali metal cations in aqueous solutions were determined with a Dionex DX-120 ion chromatograph. Samples for solvent extraction were shaken with a Glas-Col® Multi-Pulse Vortexer.

Materials

Anhydrous alkali metal chlorides, LiOH and $Ba(OH)_2$ were used as received from chemical suppliers. Hydrated alkaline earth metal chlorides were oven-dried, dissolved in deionized water and concentrations of metal cations in the aqueous solutions were checked by ion chromatography. Calixarenes **5a**,[6a] **6**,[11] **11**[8] and **13**[8] were prepared by reported procedures.

Synthesis of the di-ionizable calix[4]arene ligands

25,27-Bis(carboxymethoxy)-26,28-dimethoxycalix[4]arene (7). A mixture of **11** (2.17 g, 4.80 mmol), Cs_2CO_3 (6.26 g, 19.2 mmol), methyl bromoacetate (2.94 g, 19.2 mmol) and dry MeCN (130 cm^3) was refluxed under N_2 for 48 h, then the solvent was evaporated *in vacuo* and CH_2Cl_2 (150 cm^3) was added. The organic solution was washed with 1 M aqueous HCl and then water, dried ($MgSO_4$) and evaporated *in vacuo* to give crude **12** as a yellow oilish solid. This crude product was dissolved in THF (50 cm^3) and 25 cm^3 of 25% aqueous Me_4NOH and 50 cm^3 of H_2O were added. The mixture was refluxed for 24 h and then acidified with 10% aqueous HCl to pH 1. The solvent was removed *in vacuo*, then CH_2Cl_2 (100 cm^3) was added. The organic layer was washed with 10% aqueous HCl and then water, dried ($MgSO_4$) and the solvent was evaporated *in vacuo*. The residue was dissolved in $CHCl_3$ (80 cm^3) and Cs_2CO_3 (4.7 g, 14.4 mmol) was added. After stirring the mixture at room temperature for 4 h, the precipitate was filtered and washed with $CHCl_3$. To the precipitate, CH_2Cl_2 and 10% aqueous HCl were added to pH < 1. After stirring the mixture for 0.5 h, the resultant organic layer was separated, washed with 10% aqueous HCl and then water, dried over $MgSO_4$ and evaporated *in vacuo* to provide **7** as a colorless solid, yield 1.85 g (68%), mp 246–247 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3300 (OH), 1760 (C=O); δ_H ($CDCl_3$) 3.38 (d, J = 13.2, 4H), 3.85 (s, 6H), 4.27 (d, J = 13.2, 4H), 4.71 (s, 4H), 6.48–6.60 (m, 6H), 7.03 (t, J = 7.5, 2H), 7.19 (d, J = 7.5, 4H). Anal.Calcd. for $C_{34}H_{32}O_8$: C 71.82, H 5.67. Found: C 71.73, H 5.89%.

5,17-Bis(1,1-dimethylethyl)-25,27-bis(methoxycarbonylmethoxy)-26,28-dimethoxycalix[4]arene (14). NaH (0.46 g, 19 mmol) was added to a mixture of **13** (3.00 g, 4.44 mmol) and methyl bromoacetate (2.77 g, 18.0 mmol) in dry DMF (120 cm^3). The mixture was stirred under N_2 at 70 °C for 30 h, then additional amounts of NaH (0.23 g, 9.5 mmol) and methyl bromoacetate (1.40 g, 9.0 mmol) were added. The mixture was stirred for another 24 h and water (70 cm^3) was added. The solvents were evaporated *in vacuo* and CH_2Cl_2 (150 cm^3) was added. The resultant organic layer was washed with water, dried ($MgSO_4$) and evaporated *in vacuo*. Crystallization of the residue from MeOH gave **14** as a colorless solid, 2.56 g (72%), mp 116–118 °C. δ_H ($CDCl_3$): 1.25–1.39 (br m, 18H), 3.00–4.60 (br m, 24H), 6.20–6.58 (m, 4H), 6.80–7.38 (m, 6H). Anal.Calcd. for $C_{44}H_{52}O_8$: C 74.55, H 7.39. Found: C 74.64, H 7.50%.

5,17-Bis(1,1-dimethylethyl)-25,27-bis(carboxymethoxy)-26,28-dimethoxycalix[4]arene (9). A mixture of **14** (1.37 g, 1.9 mmol), THF (80 cm^3), 25% aqueous Me_4NOH (30 cm^3) and H_2O (60 cm^3) was refluxed overnight. The mixture was acidified with 10% aqueous HCl to pH ~1. The solvent was removed *in vacuo* and CH_2Cl_2 (100 cm^3) was added. The organic layer was washed with water, dried ($MgSO_4$) and the solvent was evaporated *in vacuo* to give **9** as a colorless solid (1.27 g, 97%), mp

‖ The solubility of AMC- and AEMC-complexes in chloroform was noted to generally decrease with calixarene upper-rim dealkylation. This effect was much more pronounced for the carboxylic acid derivatives than for the corresponding *N*-(X-sulfonyl)carboxamides.

217–219 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3200 (OH), 1758 (C=O); δ_H ($CDCl_3$) 0.85 (s, 18H), 3.36 (d, J = 13.1, 4H), 3.83 (s, 6H), 4.24 (d, J = 13.1, 4H), 4.68 (s, 4H), 6.59 (s, 4H), 7.03 (t, J = 7.6, 2H), 7.20 (d, J = 7.6, 4H), 11.50 (br s, 2H). Anal.Calcd. for $C_{42}H_{48}O_8 \cdot 0.5H_2O$: C 73.12, H 7.01. Found: C 73.09, H 6.98%.

General procedure for preparation of 25,27-bis[*N*-(X-sulfonyl)-carbamoylmethoxy]-26,28-dimethoxycalix[4]arenes 8a–8d and 5,17-bis(1,1-dimethylethyl)-25,27-bis[*N*-(X-sulfonyl)carbamoyl-methoxy]-26,28-dimethoxycalix[4]arenes 10a–10d

A solution of acid **7** or **9** (1.60 mmol) and oxalyl chloride (0.61 g, 4.80 mmol) in C_6H_6 (30 cm^3) was stirred under N_2 at 70 °C for 10 h and the solvent was removed *in vacuo* to provide the corresponding acid chloride. A solution of the acid chloride in THF (30 cm^3) was added to a mixture of the appropriate sulfonamide (4.0 mmol) and NaH (16.0 mmol) in THF (15 cm^3) and the mixture was stirred under N_2 at room temperature for 5 h for **8d** and **10d** and for 12 h for **8a**–**8c** and **10a**–**10c**. Then H_2O (2 cm^3) was added. The THF was evaporated *in vacuo* and CH_2Cl_2 (80 cm^3) was added to the residue. The organic layer was washed with aqueous Na_2CO_3 then water, dried (Na_2SO_4) and evaporated *in vacuo* to give the corresponding di-ionizable calix[4]arene as the Na salt. After purification (see below for individual compounds), the salts were dissolved in CH_2Cl_2, washed with 10% aqueous HCl then water, dried ($MgSO_4$) and evaporated *in vacuo*.

8a (X = CF_3). The Na salt was crystallized from $CHCl_3$–MeOH. Colorless solid, yield 67%, mp 216–217 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3380 (N–H), 1724 (C=O); δ_H ($CDCl_3$) 3.10–5.00 (br m, 18H), 6.10–7.30 (br m, 12H), 9.11 (br s, 2H). Anal.Calcd. for $C_{36}H_{32}F_6N_2O_{10}S_2$: C 52.05, H 3.88, N 3.27. Found: C 51.98, H 3.59, N 3.29%.

8b (X = Me). The Na salt was purified by column chromatography on silica gel with CH_2Cl_2–MeOH (49 : 1) as eluent. Colorless solid, yield 71%, mp 129–131 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3338 (N–H), 1725 (C=O); δ_H ($CDCl_3$) 3.10–5.00 (br m) + 3.41 (s) (24H), 6.10–7.30 (br m, 12H), 8.78 (br s, 1.4H), 10.43 (br s, 0.6H). Anal.Calcd. for $C_{36}H_{38}N_2O_{10}S_2$: C 59.82, H 5.30, N 3.88. Found: C 59.45, H 5.59, N 3.73%.

8c (X = Ph). The Na salt was purified by column chromatography on silica gel with CH_2Cl_2–MeOH (19 : 1) as eluent. Colorless solid, yield 58%, mp 128–130 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3336 (N–H), 1731 (C=O); δ_H ($CDCl_3$) 2.90–4.60 (br m, 18H), 6.15–7.30 (br m, 12H), 7.50–7.85 (m, 6H), 8.15–8.50 (m, 4H), 9.20 (br s, 2H). Anal.Calcd. for $C_{46}H_{42}N_2O_{10}S_2$: C 65.23, H 5.00, N 3.31. Found: C 65.31, H 4.83, N 3.30%.

8d (X = C_6H_4-4-NO_2). The Na salt was purified by column chromatography on silica gel with CH_2Cl_2–MeOH (97.5 : 2.5) as eluent. Light-yellow solid, yield 57%, mp 151–154 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 1735 (C=O), 3328 (N–H); δ_H ($CDCl_3$) 3.00–4.60 (br m, 18H), 6.35–7.30 (br m, 12H), 8.25–8.70 (br m, 8H), 9.54 (br s, 2H). Anal.Calcd. for $C_{46}H_{40}N_4O_{14}S_2$: C 58.97, H 4.30, N 5.98. Found: C 59.08, H 4.47, N 5.79%.

10a (X = CF_3). The Na salt was purified by column chromatography on silica gel with CH_2Cl_2–MeOH (19 : 1) as eluent. Colorless solid, yield 56%, mp 228–230 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 3375 (N–H), 1744 (C=O); δ_H (DMSO-d_6) 1.29 (s, 18H), 2.96–4.56 (br m, 18H), 6.20–6.56 (br m, 4H), 6.85 (br s, 2H), 7.00–7.46 (br m, 4H), 12.8 (br s, 2H). Anal.Calcd. for $C_{44}H_{48}F_6N_2O_{10}S_2$: C 56.04, H 5.14, N 2.97. Found: C 55.79, H 4.96, N 3.01%.

10b (X = Me). The Na salt was washed twice with MeOH. Colorless solid, yield 73%, mp 240–242 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 1730 (C=O), 3355 (N–H); δ_H (DMSO-d_6) 1.30 (s, 18H), 2.95–4.62 (br m, 24H), 6.20–6.60 (br m, 4H), 6.86 (s, 2H), 7.02–7.46 (br m, 4H), 11.85 (br s, 2H). Anal.Calcd. for $C_{44}H_{54}N_2O_{10}S_2$: C 63.28, H 6.52, N 3.35. Found: C 63.18, H 6.39, N 3.50%.

10c (X = Ph). The Na salt was washed twice with MeOH. Colorless solid, yield 84%, mp 179–181 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 1736 (C=O), 3352 (N–H); δ_H ($CDCl_3$) 1.36 (s, 18H), 3.22–4.30 (m, 24H), 6.19 (br s, 4H), 6.35 (br s, 2H), 7.13 (s, 4H), 7.54–7.64 (m, 4H), 7.64–7.74 (m, 2H), 8.26 (br d, 4H), 9.57 (br s, 2H). Anal.Calcd. for $C_{54}H_{58}N_2O_{10}S_2$: C 67.62, H 6.09, N 2.92. Found: C 67.92, H 6.05, N 3.32%.

10d (X = C_6H_4-4-NO_2). The Na salt was purified by column chromatography on silica gel with CH_2Cl_2–MeOH (49 : 1) as eluent. Yellow solid, yield 67%, mp 198 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1} 1738 (C=O), 3355 (N–H); δ_H ($CDCl_3$) 1.35 (s, 18H), 3.28 (br s, 4H), 3.52–4.18 (br m, 10H), 4.28 (br s, 4H), 6.10–6.75 (br m, 6H), 7.13 (s, 4H), 8.40–8.44 (br m, 4H), 8.45–8.51 (br m, 4H), 9.76 (br s, 2H). Anal.Calcd. for $C_{54}H_{56}N_4O_{14}S_2$: C 61.81, H 5.39, N 5.34. Found: C 61.79, H 5.58, N 5.63%.

Competitive extraction of alkali metal cations

An aqueous solution (10.0 mM each in Li^+, Na^+, K^+, Rb^+ and Cs^+ chlorides, with pH adjusted with dilute HNO_3 or LiOH) was extracted with an equal volume of 1.00 mM calixarene in $CHCl_3$. After extraction, the pH of the aqueous phase was measured, the organic phase was stripped with 0.10 M HCl and the AMC concentrations were determined by ion chromatography.

Competitive extraction of alkaline earth metal cations

An aqueous solution (10.0 mM each in Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} chlorides/hydroxides with pH 9.8) was extracted with an equal volume of 1.00 mM calixarene in $CHCl_3$. After extraction, the organic phase was stripped with 0.10 M HCl and the AEMC concentrations were determined by ion chromatography.

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