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New proton-ionizable, cesium-selective calix[4]arene-bis(crown-6-ethers) with markedly enhanced extraction efficiency

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Abstract

The first 1,3-alternate calix[4]arene-bis(crown-6-ethers) with a proton-ionizable group located in front of one crown ether cavity are synthesized. Compared with an analog that has no proton-ionizable group, the two new ligands possess markedly higher Cs^+ extraction efficiency.

Keywords: calixarenes; crown ethers; alkali metal cations; ligand design.

Calixcrowns,[1,2] macrocyclic compounds that combine calixarene and polyether units, are receiving considerable attention due to their highly selective metal ion recognition. Special interest in 1,3-alternate calix[4]arene-crown-6-ethers[3] (e.g. calix[4]arene-bis(crown-6-ether) **1**, Scheme 1) is based on their high Cs^+/Na^+ selectivity in solvent extraction and liquid membrane transport, which is a crucial feature for radioactive cesium separation from nuclear waste solutions.[4] Despite the high Cs^+ selectivity of such compounds, their applicability in practical separation processes is limited by low extraction efficiencies for their cesium salt complexes.[3] In earlier work, a bifunctional receptor which combined an anion-binding site with a calixcrown unit was utilized to enhance the transport of CsCl across a supported liquid membrane.[5]

We envisioned another approach to enhance Cs^+ extraction in which a proton-ionizable (cation-exchange) group is incorporated into the ligand. Appropriate positioning of this group would allow it to participate in cooperative metal ion complexation with the crown ether unit and the aromatic rings of the calix[4]arene. None of the previously reported[6–8] calixcrowns with proton-ionizable groups meet this requirement.

Herein, we report the first synthesis of 1,3-alternate calix[4]arene-bis(crown-6-ethers) with a proton-ionizable group located in front of one crown ether cavity and preliminary evaluation of their alkali metal cation (AMC) extraction efficiencies and selectivities.

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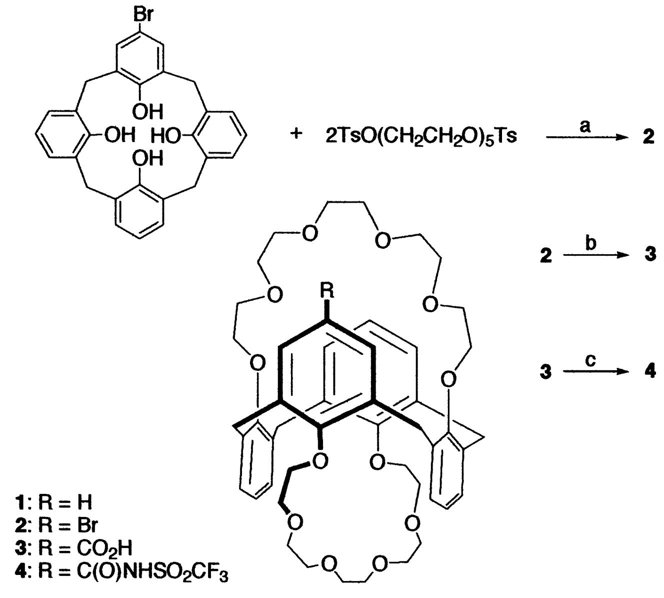

Scheme 1. (a) Cs_2CO_3, MeCN, reflux, 6 days, yield 65%; (b) i. BuLi, THF, −75°C, 10 min; ii. CO_2, THF, −75°C, 25 min, yield 70%; (c) i. $(COCl)_2$, C_6H_6, 70°C, 5 h; ii. $CF_3SO_2NH_2$, NaH, THF, rt, 16 h, yield 89%

Bromocalix[4]arene-bis(crown-6-ether) **2** was prepared from monobromocalix[4]arene[9] by reaction with pentaethylene glycol ditosylate (Scheme 1).[10] A 1,3-alternate conformation of the calix[4]arene moiety in **2** was verified by NMR spectroscopy, as a singlet at 3.84 ppm and two doublets at 3.75 and 3.79 ppm and two signals at 37.68 and 38.02 ppm were observed in the ^1H and ^{13}C NMR spectra, respectively, for the Ar–CH_2–Ar methylene groups of **2**.[11] Calixcrown carboxylic acid **3**[12] was synthesized by reaction of **2** with BuLi and then CO_2.[13,14] It should be noted that the carboxylic group in **3** is situated in front of the crown ether cavity where it should be able to interact with the complexed cation. To probe the effect of acidity of the proton-ionizable group on the metal ion-binding properties, carboxylic acid **3** was converted[15] into the corresponding acid chloride and then into the more acidic *N*-(trifluoromethylsulfonyl)-carboxamide **4**.[16]

The AMC separation abilities of the new proton-ionizable calixcrowns **3** and **4** relative to calix[4]arene-bis(crown-6-ether) **1**[10] were evaluated by competitive extractions of Li^+, Na^+, K^+, Rb^+, and Cs^+ from aqueous nitrate solution (0.10 mM in each AMC, pH 6.0) into 0.10 mM solutions of the ligand in chloroform.[17] *Under these conditions, AMC extraction by **1** was undetectable.* In contrast, calixcrown carboxylic acid **3** extracted 17.7% of Cs^+ with undetectable extraction of other AMC species. The more acidic calixcrown *N*-(trifluoromethylsulfonyl)carboxamide **4** gave 56.5 and 17.0% extractions of Cs^+ and Rb^+, respectively, with negligible extraction of Li^+, Na^+, and K^+. As shown in Fig. 1 for competitive extraction of Na^+, K^+, and Cs^+ by **4**, the Cs^+ extraction efficiency increases dramatically as the aqueous solution pH is increased from 0 to 7, while the extraction of Na^+ and K^+ remains low over the entire pH region.

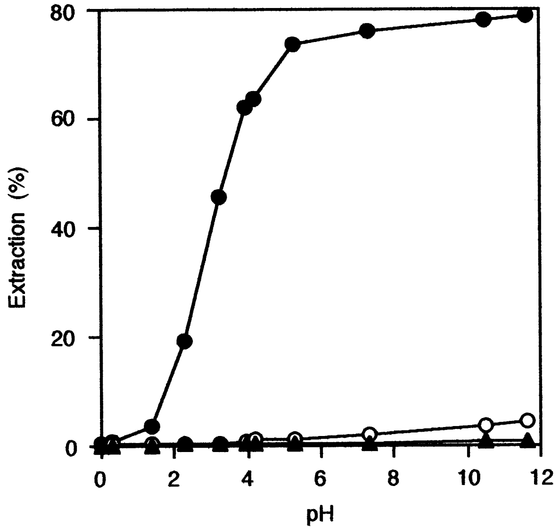

Figure 1. Extraction percentages for Na^+ (▲), K^+ (○), and Cs^+ (●) from 0.10 mM aqueous nitrate solutions into 0.10 mM solutions of **4** in chloroform

In summary, synthesis of the first 1,3-alternate calix[4]arene-bis(crown-6-ethers) with one proton-ionizable group is reported. An appropriate location of the proton-ionizable group is postulated to allow it to participate in cooperative metal cation complexation. The two new ligands exhibit enhanced efficiency in Cs^+ extraction compared to an analog with no proton-ionizable group, while retaining high Cs^+ selectivity.

Acknowledgements

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11. **2**: yield 65%, mp 115–116°C; ^{1}H NMR (499.7 MHz, CDCl$_3$, 23°C): δ 3.22–3.75 (m, 40 H), 3.75 (d, $^2J = 16.1$, 2 H; ArCH_2Ar), 3.79 (d, $^2J = 16.1$, 2 H; ArCH_2Ar), 3.84 (s, 4H, ArCH_2Ar), 6.87 (t, $^3J = 7.6$, 2 H), 6.91 (t, $^3J = 7.6$, 1 H), 7.05–7.15 (m, 6 H), 7.21 (s, 2 H); ^{13}C NMR (125.7 MHz, CDCl$_3$, 23°C): δ 37.68 (Ar$C\mathrm{H}_2$Ar), 38.02 (Ar$C\mathrm{H}_2$Ar), 69.38, 69.45, 69.52, 69.54, 69.60, 69.90, 70.87, 70.89, 70.93, 71.12, 71.16, 71.18, 71.21, 71.23, 114.88 (Ar*C*–Br), 122.75, 122.80, 129.59, 129.97, 132.12, 133.17, 133.65, 134.04, 136.37, 155.77, 156.44, 156.53. Anal. calcd for $C_{48}H_{59}BrO_{12}$: C 63.50, H 6.55, Br 8.80. Found: C 63.09, H 6.35, Br 8.78.
12. **3**: yield 70%, mp 89–90°C; IR (deposit from CH$_2$Cl$_2$ solution on a NaCl plate, cm^{-1}): ν 3300 (O–H), 1712 (C=O); ^{1}H NMR (499.7 MHz, CDCl$_3$, 23°C): δ 3.20–3.37 (m, 6 H), 3.37–3.47 (m, 4 H), 3.47–3.54 (m, 6 H), 3.54–3.77 (m, 24 H), 3.83 (s)+3.84 (d, $^2J = 16.0$) (6 H; ArCH_2Ar), 3.90 (d, $^2J = 16.0$, 2 H; ArCH_2Ar), 6.87 (t, $^3J = 7.3$, 1 H), 6.89 (t, $^3J = 7.3$, 2 H), 7.12 (d, $^3J = 7.3$, 6 H), 7.87 (s, 2 H); ^{13}C NMR (125.7 MHz, CDCl$_3$, 23°C): δ 37.88 (Ar$C\mathrm{H}_2$Ar), 69.40, 69.50, 69.54, 69.67, 70.06, 70.61, 70.77, 70.88, 70.93, 71.07, 71.14, 122.72, 123.11, 129.68, 130.01, 132.06, 133.13, 133.53, 134.04, 134.46, 156.40, 156.46, 161.51, 171.08 ($C\mathrm{O}_2$H). Anal. calcd for $C_{49}H_{60}O_{14}$: C 67.41, H 6.93. Found: C 67.21, H 6.93.
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16. **4**: yield 89%, mp 160–161°C; IR (deposit from CH$_2$Cl$_2$ solution on a NaCl plate, cm^{-1}): ν 1720 (C=O); ^{1}H NMR (499.7 MHz, CDCl$_3$, 23°C): δ 3.24–3.38 (m, 8 H), 3.43–3.56 (m, 8 H), 3.56–3.77 (m, 24 H), 3.79 (s)+3.80 (d, $^2J = 15.6$) (6 H; ArCH_2Ar), 3.87 (d, $^2J = 15.6$, 2 H; ArCH_2Ar), 6.85 (t, $^3J = 7.5$, 1 H), 6.89 (t, $^3J = 7.5$, 2 H), 7.09 (d, $^3J = 7.5$, 2 H), 7.13 (d, $^3J = 7.5$, 4 H), 7.56 (s, 2 H); ^{13}C NMR (125.7 MHz, CDCl$_3$, 23°C): δ 37.49 (Ar$C\mathrm{H}_2$Ar), 37.77 (Ar$C\mathrm{H}_2$Ar), 69.32, 69.50, 69.62, 69.88, 70.38, 70.56, 70.60, 70.73, 70.84, 70.92, 71.00, 71.09, 71.15, 71.25, 122.67, 122.76, 126.62, 129.80, 130.12, 130.35, 130.60, 132.75, 133.79, 133.97, 134.90, 156.24, 156.48, 161.53, 166.08 (*C*ONH). Anal. calcd for $C_{50}H_{60}F_3NO_{15}S$: C 59.81, H 6.02, N 1.39. Found: C 59.95, H 6.27, N 1.39.
17. After extraction, the organic phase was stripped with aqueous 0.01N HCl and the AMC concentrations were determined by ion chromatography.