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Rapid Metal Ions Shuttling through 1,3-Alternate Thiacalix[4]crown Tubes

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Several new thiacalix[4]monocrown and thiacalix[4]biscrown compounds were synthesized. Their metal ion extractabilities are found to be lower than those of conventional calix[4]crowns. By use of X-ray crystal structures and ^{1}H NMR spectroscopy, this result is explained by weaker electrostatic interactions of the polyether ring oxygen atoms with the metal ions and diminished π-metal ion interactions between the metal ions and the aromatic rings of the thiacalix[4]crowns. Temperature-dependent ^{1}H NMR spectroscopic measurements reveal coalescence temperatures T_c^{intra} and T_c^{inter} for metal ion exchange. In one case, this exchange was rationalized as metal ion shuttling through a thiacalix[4]biscrown tube. Since the metal ions are less tightly complexed by the polyether units in thiacalix[4]biscrowns than in conventional calix[4]biscrowns, more facile metal ion exchange between the two polyether units takes place in the former.

Introduction

Since viable synthetic routes to thiacalixarenes were first reported in 1997,[1] this class of macrocyclic ligands has attracted considerable interest as an alternative to “classic” calixarenes[2] by providing sites for functionalization not only on the aromatic rings but also on the bridging sulfur atoms. Thiacalixarenes possess additional coordination sites and the cavity dimensions are increased compared with analogous calixarenes. Unlike calix[4]arenes, thiacalix[4]arenes show affinity for transition metal ions because the sulfur atoms in the calixarene framework take part in the metal ion complexation.[3]

Lamare et al.[4] and Grün et al.[5] reported the synthesis of several 1,3-thiacalix[4]biscrowns-5 and -crowns-6, the first representatives of crown ether-bridged compounds in the thiacalixarene series. Investigation of their complexing abilities toward alkali metal cations (Na^+, K^+, Rb^+, and Cs^+) showed lower extraction efficiencies than those for related 1,3-calix[4]biscrowns-5 and -crowns-6. This behavior was attributed to a larger (about 0.5 Å) thiacalix[4]arene cavity as determined from X-ray crystal structures.[4] Molecular modeling indicated that Cs^+ is located close to the thiacalix[4]arene cavity, but does not interact with the crown ether unit leading to less efficient binding.[4] Recently, Csokai et al.[6] reported the synthesis of 1,3-thiacalix[4]monocrown-5 and -crown-6 in a 1,3-alternate conformation by condensing 1,3-dialkoxythiacalix[4]arenes with poly(ethylene glycol) ditosylates or diiodides. FAB-MS complexation studies along with two-phase extraction of alkali metal cations revealed select-

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(1) Kumagai, H.; Hasegawa, M.; Miyanari, S.; Sugawa, Y.; Sato, Y.; Hori, T.; Ueda, S.; Kamiyama, H.; Miyano, S. *Tetrahedron Lett.* **1997**, *38*, 3972.

(2) (a) Gutsche, C. D. C*alixarenes, Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge, UK, 1989; Vol. 1. (b) *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Vicens, J., Böhmer, V., Eds.; Kluwer: Dordrecht, The Netherlands, 1991. (c) Casnati, A.; Ungaro, R.; Asfari, Z.; Vicens, J. In *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001; pp 365−384. (d) Gutsche, C. D. In *Synthesis of Macrocycles: Design of Selective Complexing Agents*; Izatt, R. M., Christensen, J. J., Eds.; Wiley: New York, 1987; p 93. (e) Böhmer, V.; McKervey, M. A. *Chem. Z.* **1991**, 195. (f) Gutsche, C. D. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford University Press: New York, 1991; Vol. 4, pp 27−63. (g) Van Loon, J.-D.; Verboom, W.; Reinhoudt, D. N. *Org. Prep. Proced. Int.* **1992**, *24*, 437−462. (h) Ungaro. R.; Pochini, A. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Eds.; VCH: Weinheim, Germany, 1991; pp 57−81.

(3) (a) Iki, N.; Morohashi, N.; Narumi, F.; Miyano, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1597. (b) Iki, N.; Kumakai, H.; Morohashi, N.; Ejima, K.; Hasegawa, M.; Miyanari, S.; Miyano, S. *Tetrahedron Lett.* **1998**, *39*, 7559. (c) Hosseini, W. In *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001.

(4) Lamare, V.; Dozol, J.-F.; Thuéry, P.; Nierlich, M.; Asfari, Z.; Vicens, J. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1920.

(5) Grün, A.; Csokai, V.; Parlagh, G.; Bitter, I. *Tetrahedron Lett.* **2002**, *43*, 4153.

(6) Csokai, V.; Grün, A.; Parlagh, G.; Bitter, I. *Tetrahedron Lett.* **2002**, *43*, 7627.

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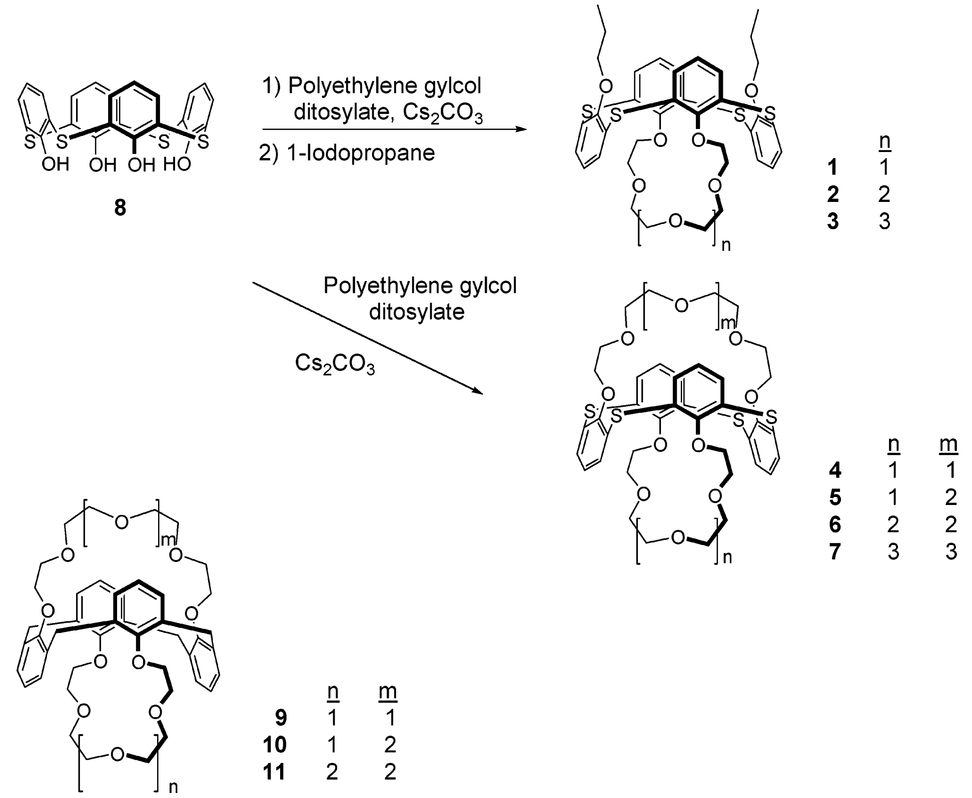
SCHEME 1. Schematic Representation of 1−11



ivities similar those observed earlier with analogous 1,3-thiacalix[4]biscrown compounds.

One of the most interesting features of the calixbiscrown compounds is metal ion shuttling though the central aromatic tube. Temperature-dependent ^{1}H NMR showed that K$^+$ oscillates in 1,3-alternate calix[4]biscrown-5 with T_c^{intra} (the coalescence temperature for intramolecular metal ion exchange) and T_c^{inter} (the coalescence temperature for intermolecular metal ion exchange) values of 378 and 398 K, respectively.[7]

With these observations in mind, we have prepared thiacalix[4]monocrown compounds **1**−**3** and thiacalix[4]biscrowns **4**−**7** (Scheme 1) and investigated metal ion shuttling across the central aromatic tube of the thiacalixcrown ether. Herein we compare the metal ion complexation behavior of ligands **1**−**7** and calix[4]biscrowns **9**−**11** as assessed by two-phase extraction of alkali metal (Na$^+$, K$^+$, Rb$^+$, and Cs$^+$), NH$_4^+$, Ag$^+$, Sr^{2+}, Ba^{2+}, and Pb^{2+} picrates. We also report the solid-state structures of **5**·K$^+$ and **6**·2Cs$^+$ that provide insight into the mode of metal complexation by these thiacalix[4]biscrown ligands.

Results and Discussion

Synthesis. 1,3-Alternate thiacalix[4]monocrowns **1**−**3** were prepared by reaction of thiacalix[4]arene (**8**) with the appropriate poly(ethylene glycol) ditosylate and Cs$_2$CO$_3$ followed by addition of 1-iodopropane (Scheme 1). For the thiacalix[4]biscrowns, reaction of **8** with the appropriate poly(ethylene glycol) ditosylate and Cs$_2$CO$_3$ gave **4**−**7** in moderate yields. The 1,3-alternate conformation of new compounds **1**−**7** was confirmed by ^{1}H NMR spectroscopy. For instance, in the ^{1}H NMR spectrum of **4**, chemical shifts for *p*- and *m*-hydrogen atoms of the benzene rings appeared at δ 6.98 (triplet) and δ 7.45 (doublet) with symmetrical patterns, which is consistent with the 1,3-alternate conformation. All of the compounds **1**−**7** exhibited similar ^{1}H NMR patterns. IR, ^{1}H, and ^{13}C NMR data for each new compound are shown in the Supporting Information.

TABLE 1. Extractability (*E*, %) of Cation Picrates by Ligands 1−7 and 9−11

	extractability (%)								
ligand	Na$^+$	K$^+$	Rb$^+$	Cs$^+$	NH$_4^+$	Ag$^+$	Sr^{2+}	Ba^{2+}	Pb^{2+}
1	2.1	25	32	10	18	4.6	3.3	0.5	1.3
2	0	0	8.1	25	0	15	0	0	0
3	0	0	0	0	0.4	35	0	0	2.5
4	0	32	30	3	13	0	0	0	0.5
5	2.2	28	33	28	12	16	2	1.7	0.8
6	0	0	8.5	27	1	0.9	0.7	3.9	0
7	0.7	2.5	4.6	10	3.1	10	2.6	1.9	7
9	6.2	115	117	64	108	96	3.6	4.7	11
10	5.9	119	116	104	103	106	6.2	4.8	8.7
11	4.3	12	25	113	22	88	2.3	4.9	8.1

Two-Phase Picrate Extraction. Extractabilities (*E*, %) of **1**−**7** and **9**−**11** toward alkali metal cations (Na$^+$, K$^+$, Rb$^+$, and Cs$^+$), NH$_4^+$, Ag$^+$, Sr^{2+}, Ba^{2+}, and Pb^{2+} were determined by two-phase picrate extraction.[8] The results are presented in Table 1. All of the ligands **1**−**7** gave lower extractabilities than the conventional 1,3-calix[4]biscrowns **9**−**11**. For alkali metal cation extraction,

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[7] Koh, K. N.; Araki, K.; Shinkai, S.; Asfari, Z.; Vicens, J. *Tetrahedron Lett.* **1995**, *36*, 6095.

[8] Bartsch, R. A.; Yang, I. W.; Jeon, E. G.; Walkowiak, W.; Charewicz, W. A. *J. Coord. Chem.* **1992**, *27*, 75.

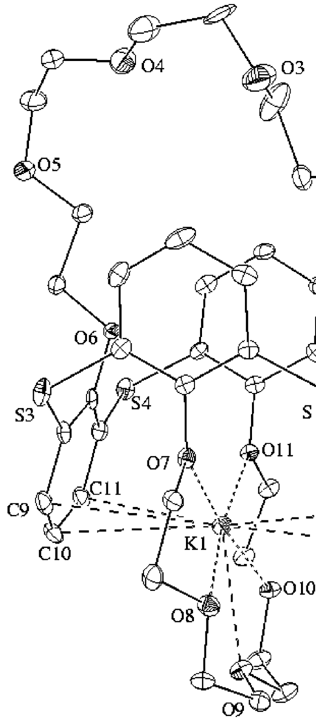

FIGURE 1. X-ray crystal structure of $\mathbf{5}\cdot K^+ClO_4^-$.

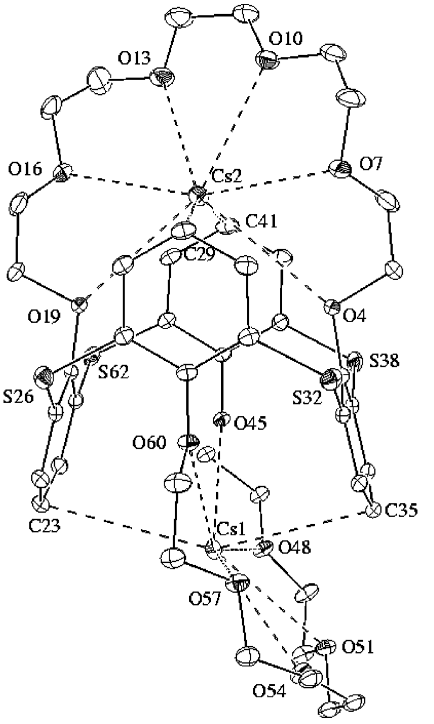

FIGURE 2. X-ray crystal structure of $\mathbf{6}\cdot 2Cs^+ClO_4^-$.

ligands **1** and **4** with crown-5 ring showed Rb^+ and K^+ selectivity, respectively. Ligands **2** and **6** with at least one crown-6 ring selectively extracted Cs^+. Similar trends were observed for the 1,3-thiacalix[4]monocrown-5 and -6 by Grün et al.,[5,6] in which a crown-5 ring was good for K^+ and a crown-6 ring was good for Cs^+. Ligand **3** with a singly crown-7 ring exhibited no propensity for alkali metal picrate extraction, while ligand **7** with two crown-7 units showed only low extractability. The crown-7 ring is known to be too large to fit with any metal cations.[9] Unexpectedly, ligand **3** gave excellent selectivity for Ag^+ among the nine metal ions evaluated.

Solid-State Structures. Selectivities for K^+ and Cs^+ by calix[4]biscrown-5 and for calix[4]biscrown-6, respectively, are attributed to two factors: a proper-sized cavity for the crown ether unit and a π-metal ion complexation effect[10] between two benzene rings with the metal ion. It was reported elsewhere that the sum of the half-thickness of the benzene π-electron cloud (1.70 Å) and the K^+ radius (1.33 Å) is 3.03 Å.[11] For Cs^+ (1.69 Å), this sum is 3.39 Å.[11] In the present work, we have probed the π-metal complexation effect in the thiacalix[4]crowns even though the macroring is enlarged by 0.5 Å compared to the conventional calix[4]arene.[4] As revealed in the solid-state structure of $\mathbf{5}\cdot K^+$ (Figure 1), K^+ is encapsulated by the crown-5 oxygens and two of the benzene rings. The K^+ is coordinated to five oxygen atoms of one polyether unit. The five oxygen atoms are roughly planar with an average atomic displacement of 0.063 Å, with K^+ lying below the plane by 0.1381 Å. Each diagonal pair of sulfide-bridged benzene rings has the dihedral angle of 22.8° (C1−C6 and C7−C12) or 22.3° (C13−C18 and C19−C24). The dihedral angles between adjacent aromatic rings are in the range of 86.1(3)−88.7(3)°. In previous work, we reported that *unsymmetrical* calix[4]biscrown-5;6 (**10**) entraps two K^+ in a 1:2 (ligand:metal) mode through the π-metal ion complexation.[12] However, *unsymmetrical* thiacalix[4]biscrown-5;6 (**5**) entraps only one K^+ in the crown-5 ring, which is a better binding site than the crown-6 ring. Presumably this is attributable to the larger cavity of the crown-6 unit of **5** compared to that of **10**, as well as the metal−metal ion repulsion.[12] Distances between K^+ and O7−O11 in the crown-5 ring of **5** are 2.816, 2.851, 2.851, 2.842, and 2.816 Å, respectively (average = 2.835 Å). Distances between K^+ and O7−O11 in the crown-5 ring of **10** are 2.791, 2.826, 2.803, 2.910, and 2.743 Å, respectively (average = 2.814 Å), which implies that the crown-5 ring of thiacalix[4]biscrown-5 (**4**) is somewhat wider than that of calix[4]biscrown-5. The π-metal complexation of **5** was investigated as well. Distances between K^+ and *p*-carbons (C4 and C10) of the two benzene rings of **5** are 3.294 and 3.469 Å, respectively. For *m*-carbons (C5;C3 and C9;C11), they are 3.341; 3.387 and 3.468;3.511 Å, respectively. The distances between K^+ and the *p*-carbons (C15 and C43) of the two benzene rings of **10** are 3.273 and 3.115 Å.[11] Distances between K^+ and the *m*-carbons (C14 and C16) of the two benzene rings of **10** are 3.331 and 3.379 Å, respectively. By comparison of these data, we conclude that the π-metal ion complexability of thiacalix[4]crown-5 (**4**) is somewhat weaker than that of calix[4]crown-5 (**10**).

Figure 2 shows the 1:2 complex of Cs^+ with **6**. The Cs^+ ion is coordinated to six oxygen atoms with distances

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[9] Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud-Neu, F.; Fanni, S.; Schwing, M.-J.; Egberink, R. J. M.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 2767.

[10] Gokel, G. W.; Barbour, L. J.; Ferdani, R.; Hu, J. *Acc. Chem. Res.* **2002**, *35*, 878.

[11] Ikeda, A.; Tsuzuki, H.; Shinkai, S. *Tetrahedron Lett.* **1994**, *35*, 8417.

[12] Kim, J. S.; Lee, W. K.; Kim, J. G.; Suh, I. H.; Yoon, J. Y.; Lee, J. H. *J. Org. Chem.* **2000**, *65*, 7215.

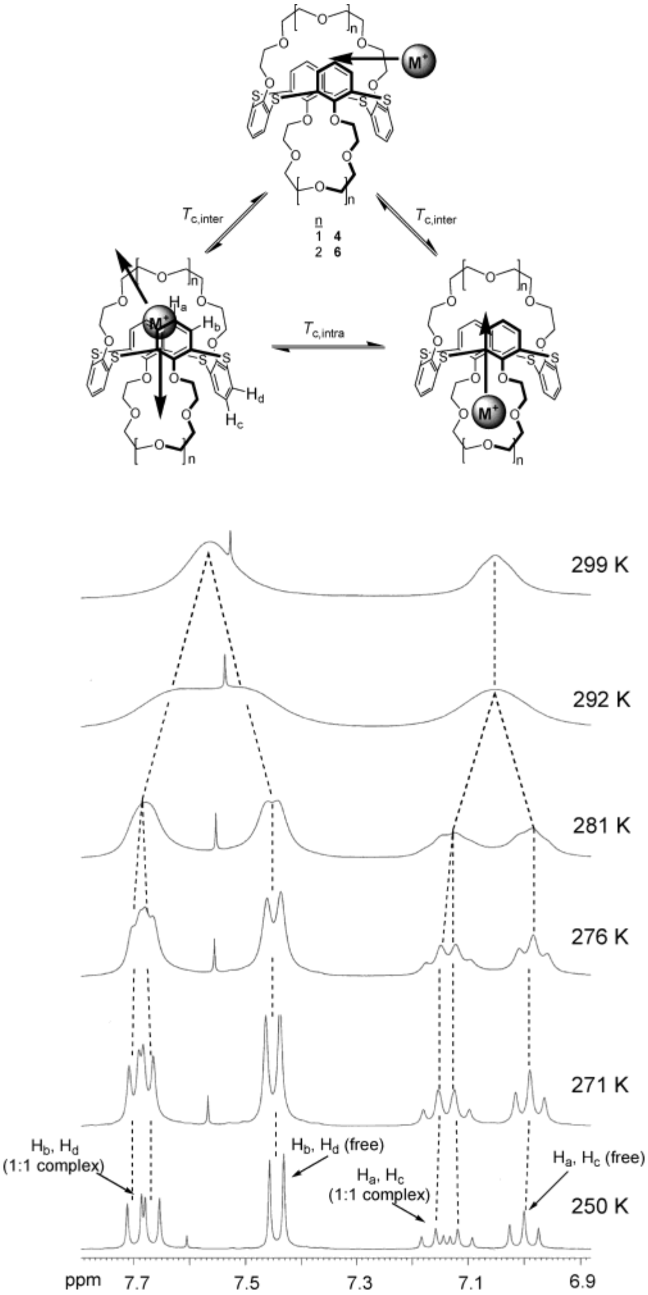

FIGURE 3. Effect of temperature on the ^{1}H NMR spectra (300 MHz) of **4** after addition 0.5 equiv of $KClO_4$ in $CDCl_3/CD_3OD$ (4/1).

ranging from 3.071(4) to 3.649(5) Å (mean value = 3.36 Å). In the Cs^+ complex of a 1,3-alternate calix[4]biscrown-6, the distances ranged from 2.995(4) to 3.570(1) Å (mean value = 3.29(14) Å).[13] In addition to these Cs^+-O interactions, distances between the *p*-carbons and Cs^+ are also indicative of π-metal ion complexation. For **6**, they ranged from 3.363(5) to 3.816(2) Å (mean value = 3.589 Å), which is a little longer than those of 1,3-alternate calix[4]biscrown-6 (**11**), 3.09(1)−3.89(4) Å (mean value = 3.54 Å).[13] As mentioned above, the weaker π-metal ion interactions deduced from longer distances between the metal ion and the *p*- and *m*-carbons for two of the benzene rings of the thiacalixcrown are due to an increase in the size of the calix[4]macroring frame by 0.5 Å.

^{1}H NMR Spectroscopy of the 4·K$^+$ Complex. To provide evidence of the π-metal ion interactions, we used ^{1}H NMR spectroscopic techniques of complex **4**·K^+, as shown in Figure S1 (Supporting Information). One triplet (H_{para}) at δ 6.98 and one doublet (H_{meta}) at δ 7.45 shifted to a lower field by $\Delta\delta = 0.13$ and 0.22 ppm, respectively, compared with the uncomplexed ligand verify that cation-π interactions are playing a role in metal ion complexation. In the case of calix[4]biscrown-5 (**9**), however, the corresponding *p*- and *m*-hydrogen atoms shifted downfield by $\Delta\delta = 0.17$ and 0.34 ppm, respectively.[12] These are larger shifts than those for **4**. In the same manner, *p*- and *m*-hydrogen atoms of calix[4]biscrown-6 (**6**) gave only a $\Delta\delta = 0.1$ ppm downfield shift upon the addition of 1.0 equiv of $CsClO_4$. This indicates that π-cation interactions in 1,3-alternate thiacalix[4]biscrown systems, although weaker, remain one of the factors that control cation complexation. These ^{1}H NMR spectroscopic observations regarding cation-π interactions are in good agreement with the solid-state structures of the complexes mentioned above.

Temperature-Dependent (TD) ^{1}H NMR Studies. Figure 3 shows TD ^{1}H NMR spectra of a solution of **4** (10^{-3} M in 4:1 $CDCl_3/CD_3OD$) upon addition of 0.5 equiv of $KClO_4$. The *m*-protons (H_b and H_d) in the 1:1 complex showed a downfield $\Delta\delta$ from 7.44 (free ligand) to 7.67 and 7.71 ppm (1:1 complex) due to π-metal interactions between K^+ and the *m*-protons of the calix-aromatic units. The other pair of free H_b and H_d did the same from 7.44 ppm with doublet splitting. As temperature increased to 281 K, the two doublets for complexed H_b and H_d began to coalesce and eventually became a broad singlet. In addition, the *p*-hydrogen atoms (complexed H_a and H_c) were also found to coalesce at 281 K. This coalescence temperature was found to be constant regardless of the metal ion concentration (0.5, 1.0, and 1.5 equiv). This coalescence temperature (T_c^{intra}) was assumed to be due to *intramolecular* metal ion shuttling through the calixtube.[14] With further temperature increase, complexed and free protons of both H_b and H_d shift together and coalesce at 299 K, indicating that an *intermolecular* metal ion exchange exists.

At this stage, it is instructive to compare the T_c^{intra} and T_c^{inter} values of **4**·K^+ with those of **9**·K^+. The **9**·K^+ complex (10^{-3} M in 4:1 $CDCl_3/CD_3OD$ solution) did not show coalescence of *m*- and *p*-protons even at 333 K. From those results, we can deduce that since the K^+ is more tightly encapsulated in **9** than in **4**, the shuttling rate of the metal ion through the calixtube in **9** is slower.

In the case of **6**·Cs^+ (Figure 4), we observed that two doublets for *m*-protons (H_b and H_d) in the 1:1 complex coalesce at 265 K, which is due to the *intramolecular* metal ion oscillation. At the same temperature, intermolecular metal ion exchange was also observed. For *p*-protons (H_a and H_c), we noted the same T_c^{intra} (265 K) and T_c^{inter} (265 K). The relatively low T_c^{intra} of **6**·Cs^+ compared to that of **4**·K^+ is ascribed to weaker binding of Cs^+ by **6** than that of K^+ by **4** and reflects more facile shuttling of the Cs^+ ion through the π-basic tube of **6**.

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(13) Thuéry, P.; Nierlich, M.; Lamare, V.; Dozol, J. F.; Asfari, Z.; Vicens, J. *J. Inclusion Phenom. Macrocyclic Chem.* **2000**, *36*, 375.

(14) Ikeda, A.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 3102.

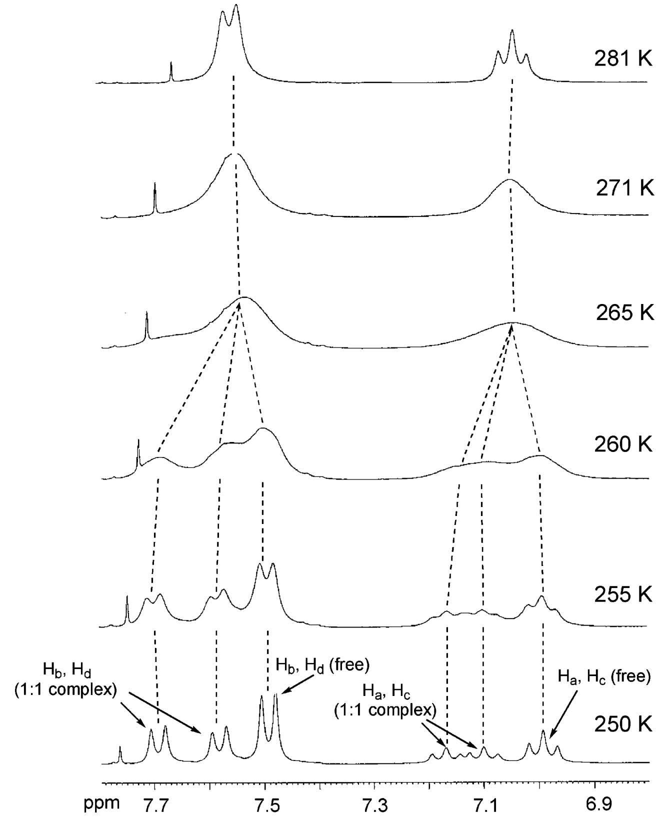

FIGURE 4. Effect of temperature on the ^{1}H NMR spectra (300 MHz) of **6** after addition 0.5 equiv of $CsClO_4$ in $CDCl_3/CD_3OD$ (4/1).

Figure 5 presents TD ^{1}H NMR spectra of **5**·Cs^+ for which two different crown units (crown-5 and crown-6) are attached to the thiacalix[4]arene framework. As the temperature increases, a pair of free H_d and complexed H_d collapsed at 281 K, implying there is an *intermolecular* metal ion exchange (T_c^{inter}) as explained above. We, however, could not observe the *intramolecular* metal ion shuttling (T_c^{intra}) across the calixtube **5**. This is obviously because the crown-5 ring is not suitable for Cs^+ so *intramolecular* tunneling of Cs^+ from the crown-6 ring to the crown-5 ring does not easily take place. On the contrary, the smaller ion, K^+, can freely shuttle through the calixtube of **5** because both crown-5 and crown-6 rings can accept K^+. As shown in Figure 6, T_c^{intra} and T_c^{inter} were found to be 286 and 305 K, respectively.

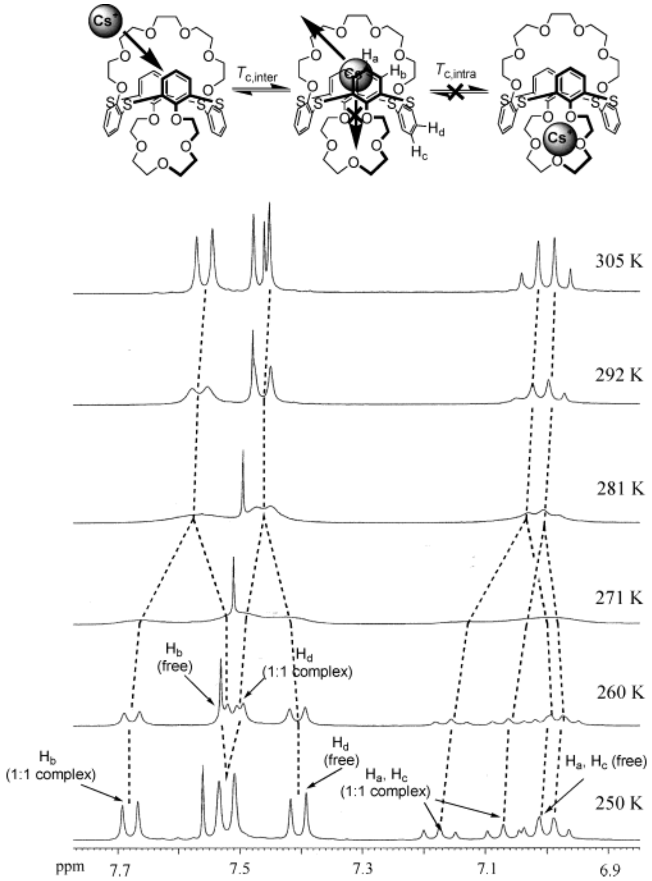

FIGURE 5. Effect of temperature on the ^{1}H NMR spectra (300 MHz) of **5** after addition of 0.5 equiv of $CsClO_4$ in $CDCl_3/CD_3OD$ (4/1).

Since the splitting patterns for the intermolecular and intramolecular metal ion exchange are distinct, the oscillation rate at the coalescence temperature can be measured. Calculated oscillation rates (k_c^{intra}) and activation energy ($\Delta G^*{}_c^{intra}$) for the metal ion transport through the calixtube are given in Table 2. From these data, it is clear that the oscillation rate (k_c^{intra}) is related to the metal ion binding ability of the ligand. Thus, Cs^+ oscillates more rapidly in **6** (about two times faster) than K^+ in **4** because Cs^+ is bound by thiacalix[4]biscrown-6 more weakly than is K^+ by the thiacalix[4]biscrown-5. Moreover, the oscillation rate (k_c^{intra}) of Cs^+ through calix[4]-biscrown-5 (**11**) could not be measured under the same experimental conditions, because the metal ion is complexed too tightly by the polyether unit. To the best of our knowledge, this is the first report of intramolecular metal ion shuttling through the π-basic tube of thiacalix[4]biscrowns.

Experimental Section

Materials. Metal picrates were prepared by reaction of picric acid with the appropriate metal carbonate.[8] Compounds **4**,[4] **6**,[4] **8**,[1] **9**,[12] **10**,[12] and **11**[9] were prepared by published methods.

2,8,14,20-Tetrathiacalix[4]-25,27-dipropylcrown-5 (1). A solution of thiacalix[4]arene (1.00 g, 2.01 mmol), tetraethylene glycol ditosylate (1.11 g, 2.20 mmol), and Cs_2CO_3 (3.28 g, 10.0 mmol) in CH_3CN (100 mL) and toluene (50 mL) was refluxed for 10 h under N_2. After the solution was cooled to room temperature, 1-iodopropane (1.36 g 8.00 mmol) was added and the mixture was refluxed for an additional 18 h under N_2. After solvent removal in vacuo, 300 mL of CH_2Cl_2 and 100 mL of 5% aqueous HCl solution were added. The organic layer was separated and dried over $MgSO_4$. Removal of the organic solvent in vacuo gave a brownish oil. Column chromatography on silica gel with ethyl acetate/hexane (1:5) as eluent gave **1** as a white solid. Yield 10%. Mp 138.8−139.1 °C. FAB MS, *m*/*z* (M^+) calcd 739.0, found 739.00. Anal. Calcd for $C_{38}H_{42}OS_4$: C, 61.70; H, 5.68. Found: C, 61.74; H, 5.65

2,8,14,20-Tetrathiacalix[4]-25,27-dipropylcrown-6 (2). The preparation method was the same as for **1**. A white solid. Yield 12%. Mp 107.8−108.0 °C. FAB MS, *m*/*z* (M^+) calcd 783.05, found 783.00. Anal. Calcd for $C_{40}H_{46}O_8S_4$: C, 61.30; H, 5.87. Found: C, 61.35; H, 5.85.

2,8,14,20-Tetrathiacalix[4]-25,27-dipropylcrown-7 (3). The preparation method was the same as for **1**. Column

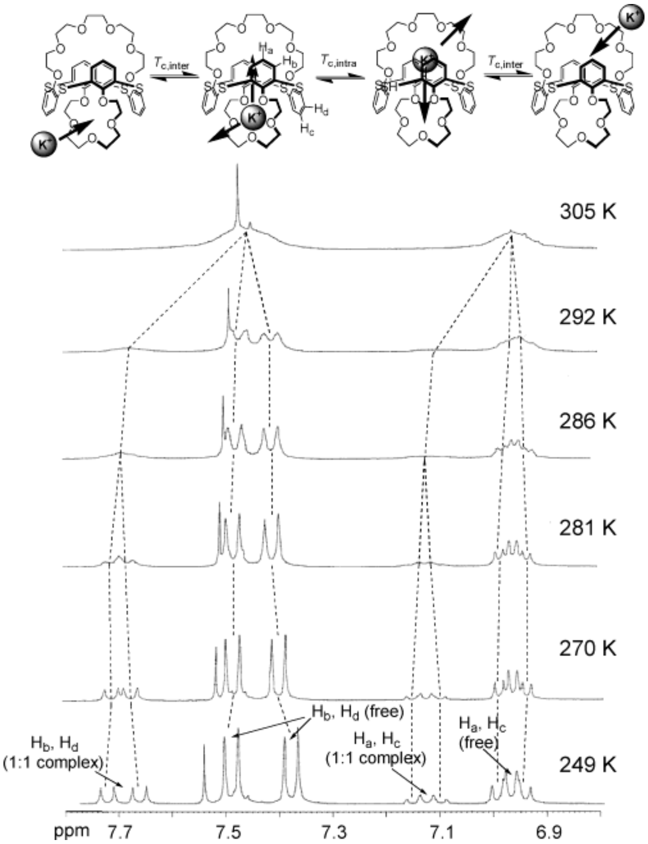

FIGURE 6. Effect of temperature on the ^{1}H NMR spectra (300 MHz) of **5** after addition of 0.5 equiv of $K^+ClO_4^-$ in $CDCl_3$/CD_3OD (4/1).

chromatography on silica gel with ethyl acetate/hexane (1:4) as eluent gave **3** as a colorless oil. Yield 34%. FAB MS *m*/*z*(M$^+$) calcd 827.11, found 827.05. Anal. Calcd for $C_{42}H_{50}O_9S_4$: C, 60.94; H, 6.05. Found: C, 60.96; H, 6.01.

2,8,14,20-Tetrathiacalix[4]biscrown-5;6 (5). A solution of thiacalix[4]arene (4.56 g, 9.22 mmol), tetraethylene glycol ditosylate (10.0 g, 19.9 mmol), pentaethylene glycol ditosylate (5.52 g, 1.00 mmol), and K_2CO_3 (6.34 g, 45.8 mmol) in CH_3CN (250 mL) and toluene (100 mL) was refluxed for 18 h under N_2. The workup procedure was the same as for **1**. Column chromatography on silica gel with ethyl acetate/hexane (1:3) as eluent gave **5** as a white solid. Yield 35%. Mp 192.6−193.4 °C. FAB MS *m*/*z* (M$^+$) calcd 857.09, found 857.01. Anal. Calcd for $C_{42}H_{48}O_{11}S_4$: C, 58.80; H, 5.60. Found: C, 58.84; H, 5.61.

2,8,14,20-Tetrathiacalix[4]biscrown-7 (7). The preparation method is the same as that for **5**. Column chromatography on silica gel with ethyl acetate/hexane (1:1) as eluent gave **7** as a white solid. Yield 15%. Mp 85.6−86.0 °C. FAB MS *m*/*z* (M$^+$) calcd 991.26, found 989.30. Anal. Calcd for $C_{48}H_{60}O_{14}S_4$: C, 58.24; H, 6.07. Found: C, 58.23; H, 6.05.

TABLE 2. Spectral Parameters, Coalescence Temperature, Exchange Rates, and Free Energies of Activation for Intramolecular Cation Exchanges in 4·K$^+$, 5·K$^+$, 5·Cs$^+$, and 6·Cs$^+$ Complexes[a]

compd	^{1}H signal	$\Delta\nu$, Hz (temp, K)	T_c^{intra} (K)	T_c^{inter} (K)	k_c^{intra}, s^{-1}	$\Delta G^*{}_c^{intra}$, kcal/mol
4·K$^+$	ArH(*p*)	12 (260)	281	299	26.7	14.7
5·K$^+$	ArH(*p*)	15 (260)	286	305	33.3	14.8
5·Cs$^+$	ArH(*p*)	32 (250)	*b*	281	*b*	*b*
6·Cs$^+$	ArH(*p*)	21 (250)	265	265	46.6	13.5

[a] $\Delta\nu$, separation of the ^{1}H NMR signals at the temperature indicated; T_c^{intra} and T_c^{inter}, coalescence temperature; k_c^{intra}, exchange rate at coalescence; $\Delta G^*{}_c^{intra}$, free energy of activation at coalescence calculated from T_c^{intra} and k_c^{intra} with use of the following equation: $\Delta G^*{}_c^{intra} = RT \ln(6.62 \times 10^{12}/k_c^{intra})$. The conditions are the same as those described in Figures 3−6. [b] Intramolecular exchange of metal cation could not be observed.

Two-Phase Extraction. Liquid−liquid two-phase extraction experiments were performed by contacting an aqueous solution (2.0 mL) containing the metal picrate (0.20 mM) and a chloroform solution (2.0 mL) of the ligand (0.10 mM) by shaking for 30 min at 25 °C. The concentration of picrate anion extracted from the aqueous phase into the organic layer was determined by UV spectrophotometry (λ_{max} = 373 nm). Three independent experiments were carried out for each combination of ligand and metal picrate.

Crystallography. Single crystals of **5**·$K^+ClO_4^-$ and **6**·$2Cs^+$-ClO_4^- were obtained by slow evaporation of CH_3OH/CH_2Cl_2 (1:9) solutions. All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite monochromator. All crystal data obtain by using SHELXTL software[15] for **5**·K$^+$ and **6**·2Cs$^+$ are listed in the Supporting Information.

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Supporting Information Available: Additional ^{1}H, ^{13}C NMR, IR spectra (Data S1−S5), and ^{1}H NMR for the complex (Figure S1), and crystal data (Tables S1 and S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Bruker *SHELXTL*; Structure Determination Software Programs; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1997.