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Heterogeneous Binuclear Complexation of 1,3-Alternate Calix[4]-Bis-Crown Bearing Two Different Crown Rings

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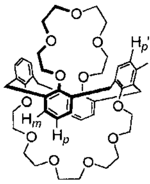
Introduction

Calixarenes, which are macrocyclic compounds available in a variety of ring sizes, are of particular interest as inclusion hosts for ions and specific molecules.[1,2] Calixcrown ethers in which the proper-sized crown rings are incorporated into the calixarene framework have also attracted intense interest as a specific metal-selective extractant.[3] 1,3-Alternate calix-bis-crowns[4] have particularly interesting molecular features including (i) HSAB-based complexation, “hard” oxygen atoms complementing the “hard” metal ion, (ii) a size-match between the crown ether cavity and a specific metal ion, (iii) two crown loops able to adopt 1:2 complexation, and (iv) cation interaction between two rotated benzene rings in the 1,3-alternate conformation and the metal ion.[5] With regard to iii, complexation studies have sometimes had conflicting results. For example, a 1:1 complex was suggested based on the results of a transport and two-phase extraction experiment.[6] However, a 1:2 complex has been reported from conductometric, spectroscopic, and X-ray crystallographic studies.[7−9] Although calix-bis-crowns have two cavities that can simultaneously capture two metal ions, they have been shown to have even worse extractability than calix-mono-crowns, probably due not only to electrostatic repulsion between the two metal ions, but also to an induced conformation change that does not favor binding of the second metal.[10] In the case of iv above, recent investigations have revealed that cation interaction plays a crucial role in various molecular interactions[11] but in some cases this role is limited, and this remains a controversial subject.[12]On the basis of previous studies, we recently investigated three topics regarding the complexation of calix-bis-crowns with metal ions: (i) the possibility of concomitant complexation of two different metal ions with a calix-bis-crown in which two different crown loops are attached to an 1,3-alternate calix[4]arene, (ii) cation-interactions of two metal ions with two pairs of benzene rings, and (iii) effects of cation−cation repulsion on cation interaction. We selected compound **1** as a 1,3-alternate calix-bis-crown with two different crown ether loops in which the crown-5 is suitable for K^+, and the crown-6 is suitable for Cs^+. We report here the crystal structure of a heterogeneous binuclear complex in which two different metal ions are encapsulated in a calix-bis-crown with different-sized crown loops and a detailed investigation regarding cation−π interaction.



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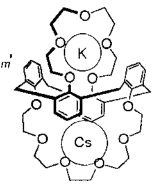
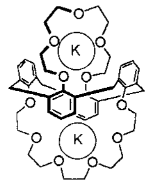


1K$^+$Cs$^+$



1K$^+$K$^+$

Results and Discussion

Previously, we reported that **1** can be prepared by reacting calix[4]arene and 2 equiv of tetraethylene glycol

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ditosylate in the presence of K_2CO_3, and then adding 2 equiv of pentaethylene glycol ditosylate and Cs_2CO_3 in acetonitrile.[13] The association constants (log K_a) of **1** for Na^+, K^+, Rb^+, and Cs^+ picrate were 7.94, 9.57, 9.18, and 8.74, respectively, which indicates rather low selectivity because of its two different-sized cavities. The X-ray crystal structure for a K^+-Cs^+ diperchlorate (**1**·K^+Cs^+) complex crystallized from the slow evaporation of a solution of MeOH and dichloromethane, and its crystal data are listed in Supporting Information. This conformation enables five oxygens on the upper ring and six oxygen atoms on the lower crown loop to be directed toward the central metal ions (K^+ and Cs^+ ions). The distances between Cs^+-(O1−O6) in the downward crown ring are 3.470, 3.196, 3.291, 3.402, 3.152, and 3.440 Å, respectively, which are greater than those between K^+-(O7−O11) in the upper ring (2.802, 2.824, 2.804, 2.907, and 2.746 Å) simply due to the difference in size of the two cavities of the calix-bis-crown. In this crystal structure, we can also clearly observe cation−π interaction between these two metal ions and the *para*-carbons of two rotated benzene rings. The distances for Cs^+−C37 (*para*-carbon of the benzene ring) and Cs^+−C21 are 3.556 and 3.307 Å, respectively, while those for K^+−C43 and K^+−C15 are 3.240 and 3.094 Å. The slightly greater distances for Cs^+−C37 and K^+−C43 compared with Cs^+−C21 and K^+−C15, respectively, are attributable to the sterically unfavorable perchlorate anions located near Cs^+−C37 and K^+−C43. The sum of the half-thickness of the benzene π-electron (1.70 Å) and the K^+ radius (1.33 Å) is 3.03 Å. For Cs^+ ion (1.69 Å), this sum is 3.39 Å.[14] Thus, the distances between the metal ion and the *para* carbons of the benzene rings in this study are close enough for cation−π interaction. Regarding the π−metal preference, the K^+ seems to be more tightly coordinated to the crown-5 ring than the cesium ion is to the crown-6 ring due to the presence of extra cation−π interactions between the K^+ and *meta*-carbons of the upper benzene rings (see the detail ORTEP diagram in Supporting Information).

^{1}H NMR investigation of **1**·Cs^+ K^+ was also carried out. Two sets of triplet peaks that appeared at 6.89 (H_p) and 6.91 (H_p') ppm in **1** were shifted to 7.01 ($\Delta = 0.12$) and 7.04 ($\Delta = 0.13$) ppm. More interestingly, two doublet peaks were shifted from 7.09 (H_m) and 7.12 (H_m') ppm to 7.26 ($\Delta = 0.17$) and 7.46 ($\Delta = 0.34$) ppm, respectively, implying that the *meta*-carbons of two pairs of benzene rings predominantly participate in the cation−π interactions. From this NMR behavior and the crystal structure, it is likely that the K^+ ion is more tightly coordinated with calixcrown-5 than the Cs^+ ion is coordinated with calixcrown-6. These results suggest that two different-sized metal ions can be encapsulated by the calix-bis-crown compound due to good size-matching and cation−π interaction despite electrostatic repulsion between the two metal cations. In the Cs^+ calixcrown-6 complex, *para*-carbons of the two benzene rings predominantly participate in cation−π interaction. However, for the K^+ calixcrown-5 complex, the *meta*-carbons are more likely to participate in cation−π complexation. To the best of our knowledge, this is the first example of an X-ray crystal structure in which one calix-bis-crown encapsulates two different-sized metal cations.

On the basis of these results, we were also interested in investigating the crystal structure of the K^+ complex with crown-6 loop, which has a relatively large cavity that does not complement K^+. For example, are there still cation−π interactions, although electrostatic repulsion is likely still present between the two metal ions? On the basis of a general "size-concept", we initially expected a 1:1 complexation. However, two K^+ ions were encapsulated in both the upper crown-5 ring and the lower crown-6 ring, apparently supporting 1:2 complexation although one of the K^+ ions does not fit in the crown-6 ring. The ORTEP structure of the potassium perchlorate (**1**·$2K^+$) complex and its crystal data are also described in Figure 2 and Table 2, respectively, in Supporting Information. This crystal structure is also the first example of two K^+ ions complexes with a calix-bis-crown with different-sized crown loops. The distances between K2 and O7−O11 in the upper crown ring are 2.789, 2.827, 2.807, 2.910, and 2.742 Å, respectively. The distances between K2 and the *para* carbons (C15 and C43) of the two benzene rings are 3.276 and 3.118 Å, respectively, which are similar to the results in Figure 1 of Supporting Information. In contrast, surprisingly, the distances for K1−O1 (3.806 Å) and K1−O6 (3.775 Å) for the two phenolic oxygens of the lower crown-6 ring are greater than those for K1−O2 (2.796 Å), K1−O3 (2.961 Å), K1−O4 (2.907 Å), and K1−O5 (2.861 Å) by more than 1.0 Å, clearly indicating that the two phenolic oxygens of the lower crown ring hardly take part in this coordination. More interestingly, the distances between K1 and the *para* carbons (C21 and C37) of the two benzene rings are 3.170 and 3.879 Å, respectively. The latter much longer distance makes the crown-6 ring slightly tilted to the left and distorted. Considering that the unusually greater distances for K1−O1 (3.806 Å) and K1−O6 (3.775 Å) for the two phenolic oxygens as well as K1−C37 for the *para* carbons of the benzene rings are unfavorable for cation interaction, we could expect that there is a critical electrostatic repulsion between the two metal ions. The distances for K−Cs (Figure 1) and K1−K2 (Figure 2) are 6.442 and 6.892 Å, respectively. The greater distance for K1−K2 may be due to the fact that since the crown-6 cavity is relatively wide to surround the K^+, the K1 can move slightly downward to reduce the metal−metal repulsion and is therefore no longer located in the center of the crown-6 cavity. In contrast to 3.170 Å, which is an appropriate length for cation−π interaction between K1 and C21, the greater distance of 3.879 Å for K1−C37 is unlikely to support cation−π interaction. In the ^{1}H NMR spectrum of the complex **1**·K^+K^+, one (H_p) of two triplet peaks at 6.89 ppm is shifted to a lower field by only 0.04 ppm, indicating that cation−π interaction plays only a minor role. In contrast, the other triplet peak (H_p') at 7.17 ppm is shifted by 0.29 ppm to a lower field, implying strong cation−π interaction. Two doublet peaks were observed to shift from 7.09 (H_m) and 7.12 (H_m') to 7.26 (broad) ppm, and we could not assign the exact shifting value due to peak broadening. These NMR behaviors are in good agreement with the solid-state structure regarding cation−π complexation (Figure 2 in Supporting Information). Thus, the weak complexation of calix-bis-crown-6 with K^+ ion is likely due to the size difference and the weak cation−π interaction due to electrostatic repulsion between the two cations.

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These results suggest that the driving force in metal ion complexation with calix-bis-crown is electrostatic interaction between the metal ion and the electron-donor oxygen atoms, while cation−π interaction between the metal ion and π-orbitals of the two rotated benzene rings plays a minor role. However, this cation−π interaction is considerably reduced by cation−cation repulsion between the two metal ions through the π-basic tunnel of the calix-bis-crown compound.

Experimental Section

Compound **1** was previously prepared by Kim's lab.[13] ^{1}H NMR samples for metal perchlorate complexes were prepared as follows. A mixture of **1** (20.0 mg) and excess metal perchlorate (at least 5 equiv) in $CDCl_3$ (1.0 mL) was stirred for 1 h. After filtration of the precipitated metal perchlorate, the resultant $CDCl_3$ solution runs with 400 MHz NMR. Crystals were mounted and aligned on a Cad-4 diffractometer.[14] The structures were solved by direct methods,[16] and the least-squares refinement of the structure was performed by the program SHELXL97.[17]

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Supporting Information Available: ORTEP diagrams and detailed crystal data of **1**·Cs^+K^+ and **1**·K^+K^+ are shown in Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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