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Calix[4]thiacrowns as Ditopic Hosts for Homo- and Heterobinuclear Accommodation: First Report of a Chopsticks-Type π-Coordination

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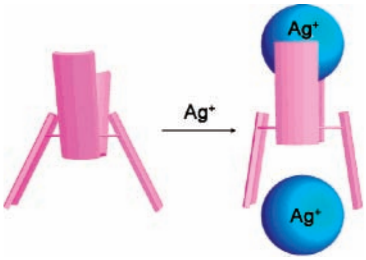
ABSTRACT



Calix[4]thiacrowns with hetero-L^1 and a homodonor set (L^2) were synthesized and characterized by X-ray analysis. From the reaction of L^2 with AgPF$_6$, disilver complex [Ag$_2$(L^2)](PF$_6$)$_2$ (1) was isolated. By comparing 1,3-alternate conformations of L^2 and 1, we found a considerable decrease of dihedral angles of two opposite aromatic rings upon complexation. This finding can be explained in terms of the “chopsticks process”, which illustrates how Ag$^+$–arene π-coordination occurs. Heterobinuclear complexation of L^1 in solution was also observed.

Calixarenes[1] and crown ethers[2] are extensively utilized as molecular scaffolds for the design and construction of elaborated supramolecular systems.[3] Calixcrowns offer particular promise because the fusion of calixarene and crown units by bridging through entities enables the divergent orientation of cavities of a size and nature sufficient to accommodate a variety of guests.[4]

A number of macrocyclic binuclear complexes fall into two main categories: linked macrocycles[5] and macrocycles with larger cavities.[6] From this point of view, the calixcrowns

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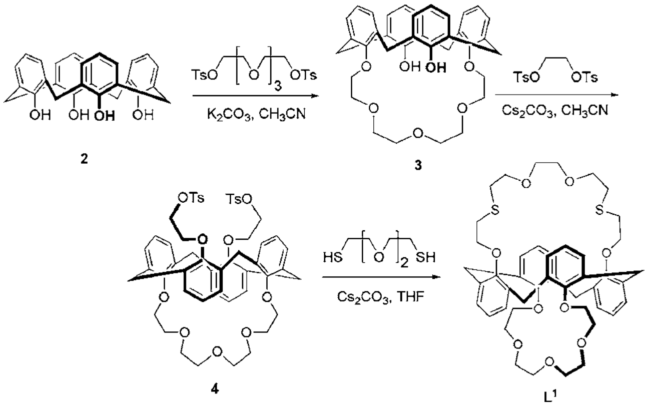
may be considered as a third category of macrocyclic binuclear ligands. In fact, the synthesis of calixcrowns together with aspects of their alkali metal coordination chemistry has been the focus of several studies.[4] For example, 1,3-dialkoxycalix[4]crown-6[7a] and calix[4]crown-5[7b] derivatives are selective ionophores for Cs^+ and K^+, respectively, not only due to the coordination of the crown ring but also with respect to the cation π-coordination,[8] especially in the 1,3-alternate conformation. Despite these promising features, no reports of either the preparation or the crystal structure of the calix[4]thiacrown receptors, which can accommodate the softer metal ions in their individual cavities, have appeared in the literature except in our previous work.[9] In particular, the calixcrowns, in which the crown and thiacrown rings are incorporated simultaneously into the calixarene unit, have not been reported.

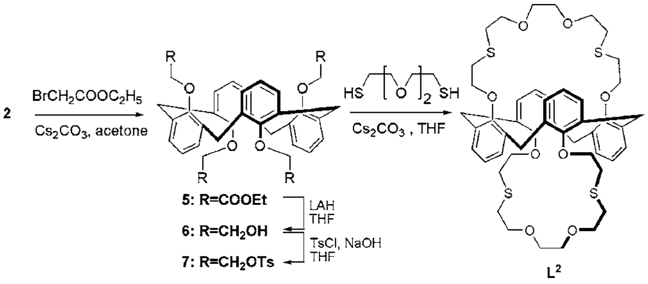
As part of ongoing efforts, we therefore focused our attention to the calix[4]crowns that would potentially contain two softer metals or one softer and one harder metal within the individual cavities, respectively. As can be seen in our heteroleptic donor macrocyclic system,[10] one possible strategy for the preparation of binuclear complexes with softer metal ions in this area is the use of a sulfur donor in the crown rings. With this consideration in mind, we explored the possibility of generating soft metal coordination products through the modification of the crown units. Herein, we present the synthesis and structural characterization of binuclear complexations of **L**^{1} and **L**^{2} (Schemes 1 and 2).

Scheme 1. Synthesis of **L**^{1}



L^1 was synthesized by a two-step cyclization (Scheme 1). First, the cyclization reaction of calix[4]arene **2** with tetraethyleneglycol ditosylate, employing K_2CO_3 as a base in acetonitrile, afforded the calix[4]-monocrown-5 **3**. Ditosylation of **3** with 2 equiv of ethyleneglycol ditosylate led to the 1,3-alternate ditosyl derivative **4**.[11] Once again, the cyclization of **4** with dithiol in the presence of Cs_2CO_3 afforded the desired asymmetric calix[4]crown **L**^{1}. The NMR spectra of **L**^{1} exhibit the expected increase in signal complexity arising from its unsymmetrical nature.

Scheme 2. Synthesis of **L**^{2}



Having successfully obtained **L**^{1} as an unsymmetric product, we proceeded to the synthesis of a symmetric analogue **L**^{2}, which has S_2O_4 rings on both sides (Scheme 2). The key precursor **7**, 1,3-alternate tetratosylate, was prepared using a known tosylation reaction of **6**.[12] Bicyclization by the coupling reaction of **7** with the corresponding dithiol in the presence of Cs_2CO_3 afforded the desired product **L**^{2} in reasonable yield (48%).

Unequivocal confirmation of **L**^{1} was provided by a single-crystal X-ray analysis. Single crystals of **L**^{1} for crystallography were prepared by vapor diffusion of diethyl ether into the acetonitrile solution. The crystal structure gave clear evidence of a saddle-shaped 1,3-alternate conformation of the calix[4]arene unit; the aromatic rings are tilted up (B and D) and down (A and C), alternately (Figure 1). The conformations of the two bridging rings, which connect two opposite xylyl groups, differ from the donor sets: the S_2O_4 ring is bent, and the O_5 ring is unfolded. The overall shape of the ring entities could be extracted by considering the

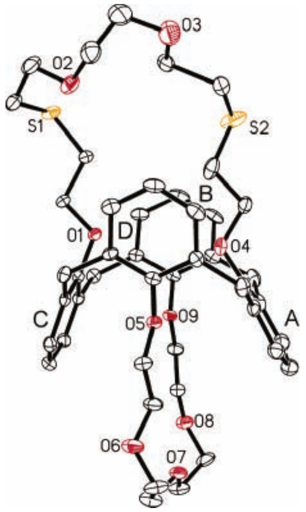


Figure 1. Crystal structure of **L**^{1}.

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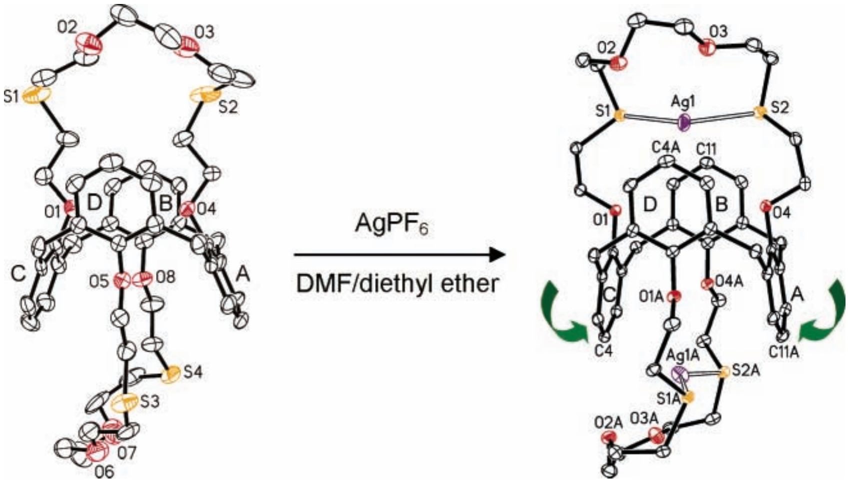

Figure 2. Crystal structures of $\mathbf{L^2}$ (left) and its disilver complex **1**, $[Ag_2(\mathbf{L^2})](PF_6)_2$ (right).

torsional angles associated with donor orientation. The conformation of the O_5 linkage (beginning from O5 to O9) can therefore be described as *t-g-g-t* (*t* = *trans*, *g* = *gauche*), whereas that of the S_2O_4 linkage (beginning from O1 to O4) shows a *t-g-g-t-t* arrangement.

Single crystals of $\mathbf{L^2}$ suitable for crystallography were prepared by slow evaporation of the acetonitrile−chloroform solution (v/v 3:1). The crystal structure also gave clear evidence of saddle-shaped 1,3-alternate conformations of the calix[4]arene unit (Figure 2, left). Both of the S_2O_4 rings in each side, which connect two opposite xylyl groups, are bent. In this case, the conformation of the S_2O_4 linkage between donors (beginning from O1 to O4 or from O5 to O8) can be described as a *t-t-g-g-t* arrangement.

Reaction of $\mathbf{L^2}$ in dichloromethane with 2 equiv of $AgPF_6$ in methanol afforded a colorless precipitate. The precipitate was isolated and dissolved in DMF. Vapor diffusion of diethyl ether into the DMF solution yielded the crystalline product **1** suitable for X-ray analysis. An X-ray analysis revealed that **1** is a binuclear silver(I) complex of formula $[Ag_2(\mathbf{L^2})](PF_6)_2(DMF)_2$ in which each metal atom is accommodated in the crown-ring cavities as if in a peanut shell. Unlike $\mathbf{L^2}$, the torsion angles between donors for the S_2O_4 ring unit fall in the range of 60.7−66.3°, in keeping with all *gauche* conformations.

In **1**, the Ag^+ coordination is completed by two strong Ag−S bonds [Ag−S1 2.481(1) and Ag−S2 2.510(1) Å]. However, there are some additional cation$\cdots\pi$ interactions.[8] For example, the Ag atom interacts with C atoms in the aromatic ring showing η^3-type cation$\cdots\pi$ interactions (Ag1$\cdots$C3A 3.283 Å, Ag1$\cdots$C4A 2.818 Å, and Ag1$\cdots$C5A 3.339 Å). These results suggest a synergic effect for the macrocyclic and π-coordination on the stabilization of **1**. Such a cation−π interaction in solution was also observed in calix[4]arene derivatives by NMR.[8]

Comparison of the dihedral angles of two opposite aromatic rings (B and D or A and C) of 1,3-alternate calix[4] units between $\mathbf{L^2}$ and its disilver complex **1** afforded a good case for illuminating the effect of π-coordination[13] because the dihedral angles show considerable changes before and after complexation with Ag^+ (Supporting Information Table S1). For example, the dihedral angles for free $\mathbf{L^2}$ (A−C, 42.83°; B−D, 44.35°, for $\mathbf{L^2}$) were found to be much reduced in their disilver complexes (14.47° for **1**). Such a conformation in **1** takes advantage of generating π-coordination between Ag^+ and the aromatic ring. The result can be explained in terms of a "chopsticks process", which illustrates how the π-coordination occurs through changes of the dihedral angles between the two aromatic rings (see Figure 3). With this first report, we were able to elucidate

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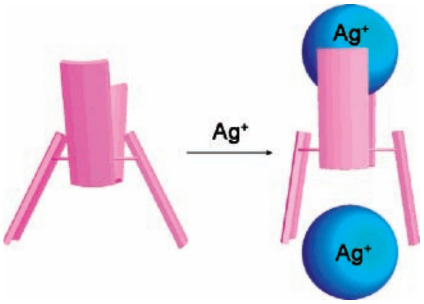

Figure 3. π-Coordination via the chopsticks process in **1**.

and visualize the stabilization of the calix[4]arene complexes with a 1,3-alternate by the π-coordination process.

The metal recognition of the calix[4]thiacrowns was examined by solvent extraction (Figure 4). Because the ionophores have two possible binding sites for the metal species, the maximum extractability can be defined as 200%. Commonly, the maximum amount of Ag^+ was extracted by both ionophores (**L^1**, 189%; **L^2**, 194%). In terms of the results for the per-crown-ring, each ionophore extracted more than one Ag^+, suggesting the formation of 1:2 complexes (ligand/metal), which was confirmed by X-ray analysis. The high Ag^+ extraction achieved by **L^1** is due to the affinity of O donors as well as S atoms for Ag^+, which was supported by NMR titration (Supporting Information Figure S8). It is noteworthy that some hard metal ions were also extracted by **L^1** to a high extent: K^+, 122%; Rb^+, 120%; NH_4^+, 120%; and Cs^+, 112%. This is attributed to the formation of binuclear complexes $[M_2(\mathbf{L^1})]^{n+}$ because the crown-5 ring in **L^1** promotes the complexation with these metal species.

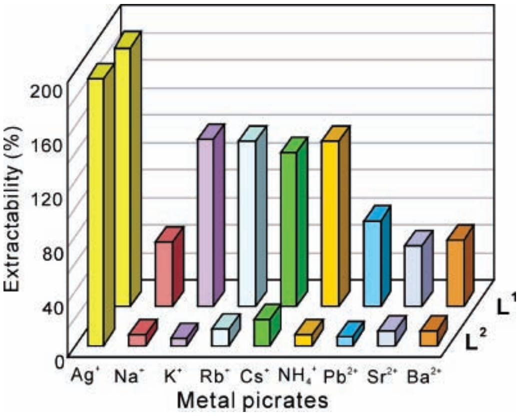

Figure 4. Extractability of metal picrates from the aqueous to the 1,2-dichloroethane phase by **L^1** and **L^2**. [ligand] = 0.10 mM. [MPic] = 0.20 mM. $V_{\text{ligand}} = V_{\text{MPic}} = 2.0$ mL.

The mass spectra of **L^1** with a mixture of 1 equiv of potassium and silver picrates were dominated by heterobinuclear species such as $[K(\mathbf{L^1})AgPic]^+$ (*m/z* 1192.9) and $[K(\mathbf{L^1})Ag]^{2+}$ (*m/z* 482.8). The mononuclear species $[Ag(\mathbf{L^1})]^+$ (*m/z* 925.9) and $[K(\mathbf{L^1})]^+$ (*m/z* 855.1) were also observed (Figure 5). The results of a comparative ^{1}H NMR study also suggested the formations of the $\mathbf{L^1}{-}K^+$ (Supporting Information Figure S5) and of the heterobinuclear $Ag^+{-}\mathbf{L^1}{-}K^+$ (Supporting Information Figure S6) complexation occurring in solution. The NMR spectrum of the potassium complex $\mathbf{L^1}{-}K^+$ showed the slow-exchange process on the NMR time scale (Supporting Information Figure S1). In contrast to the case of the K^+ complex, the silver complex $\mathbf{L^1}{-}Ag^+$ showed the fast-exchange process.

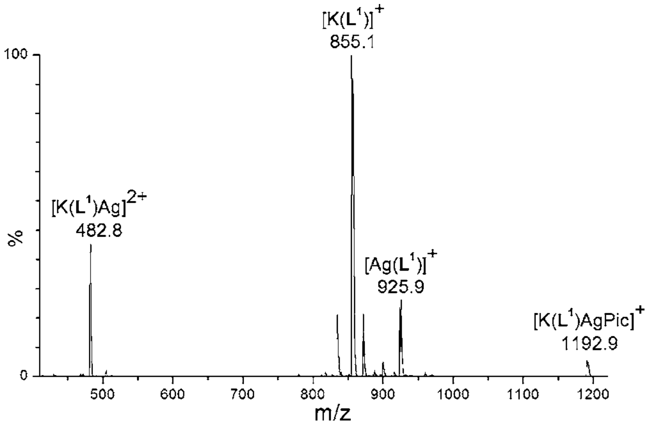

Figure 5. ESI-MS spectra of **L^1** in the presence of KPic (1.0 equiv) and AgPic (1.0 equiv) in acetonitrile.

In this work, we describe the synthesis of calix[4]crowns as homo- and heterobinucleating ligands and their complexing behaviors. In particular, we were successfully able to elucidate and visualize the stabilization of the calix[4]arene complex by the chopsticks-type π-coordination process. We expect these studies will be useful to estimate the existence or strength of the diverse types of π-coordination in similar systems.

Acknowledgment. This work was supported by a Korea Research Foundation Grant (2005-070-C00068).

Supporting Information Available: Syntheses of **L^1** and **L^2**; X-ray cystallographic files (CIF); and NMR and extraction data. This material is available free of charge via the Internet at http://pubs.acs.org.

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