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A Calix-bis-crown with Hard and Soft Crown Cavities: Heterobinuclear K⁺/Ag⁺ Complexation in Solid and Solution States

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Calixcrowns offer particular utility since the fusion of calixarene and crown ether units enables the divergent orientation of cavities of a size and nature sufficient to accommodate a variety of guests.^[1] Among them, calix[4]-bis-crowns^[2] with a 1,3-alternate conformation (or saddle-type) have interesting features including 1) two crown cavities able to undergo dinucleation and 2) HSAB-based complexation selectivity.^[3] Kim et al.^[4] reported the synthesis of a heterodinuclear complex of an unsymmetrical calix-bis-crown with two different size crown loops: a crown-5 and a crown-6 suitable for K⁺ and Cs⁺, respectively. We recently reported the examples of calix[4]-bis-dithiacrown based, *endo*-coordinated disilver(I) complexes as well as an *exo*-coordinated 3D network connected by CuI-based clusters.^[5]

Despite the existence of systems exhibiting 1) and 2) above, neither the preparation nor the crystal structure of any calixcrowns, which are designed to accommodate hard and soft metal ions in their individual cavities, has been reported previously. In view of this, we have focused our attention to the synthesis and characterization on a new calix-bis-crown system designed to bind both soft and hard metal ions within its respective cavities.

In preliminary work, we synthesized an unsymmetrical calix[4]-bis-crown, in which oxa- and thiaoxa-crown rings are simultaneously bound to the calixarene scaffold. Howev-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901580.

er, in this case the synthesized species with monothiaoxaand dithiaoxa-crown as the softer rings failed to accommodate Ag⁺ probably a result of K⁺-Ag⁺ repulsion rather than a lack of complexation affinity for Ag⁺. These results motivated us to optimize the ligand structure for this ion through the modification of the thiaoxa-crown unit and prepared the unsymmetrical calix[4]arene (4) incorporating O₅/ O₂S₃-bis-crown rings(Scheme 1). To the best of our knowl-



Scheme 1. Synthesis of ligand.

edge, the latter is the first macrocyclic ligand system to stabilize a heterobinuclear complex incorporating hard and soft metal ions in each cavity both in the solid and in solution.

The ligand 4 was synthesized by a two-step cyclization procedure (Scheme 1). First, cyclization of calix[4]arene 1 with tetraethyleneglycol ditosylate afforded the calix[4]-mono-crown-5 (2). Ditosylation of 2 with ethyleneglycol di-

Chem. Eur. J. 2009, 15, 8989-8992

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tosylate led to the 1,3-alternate ditosyl derivative (3).^[6] Once again, the cyclization of **3** with (HS–CH₂CH₂)₂S gave the desired unsymmetrical calix[4]-bis-crown (**4**). Unequivocal confirmation of **4** was provided by a single-crystal X-ray analysis employing a single crystal obtained by slow evaporation of a CH₃OH/CH₂Cl₂ solution of the complex. The crystal structure showed a saddle-shaped, 1,3-alternate conformation of the calix[4]arene unit; the aromatic rings in Figure 1(left) are tilted up (B and D) and down (A and C),



Figure 1. Crystal structures of $4 \cdot CH_3OH$ (left) and its heterobinuclear Ag⁺ and K⁺ complex 5, [Ag(4)K]·2PF₆·2CH₃CN (right). Hydrogen atoms, anions and solvent molecules are omitted.

alternately. Notably, all of the oxygen atoms in **4** are directed inwards, while the sulfur donors are directed outwards with respect to the ring cavities.

Reaction of KPF₆ and AgPF₆ in acetonitrile layered onto a dichloromethane solution of 4 yielded the crystalline product 5. X-ray analysis revealed that 5 is a heterodinuclear K⁺ and Ag⁺ complex of formula [K(4)Ag]·2PF₆·2CH₃CN in which both metal ions are accommodated in the crown-ring cavities (Figure 1(right)). The K⁺ is situated symmetrically within the O_5 -cavity, with K⁺–O lengths in the range 2.766-2.843 Å. The K⁺ is also stabilized by cation- π interactions with the aromatic rings A and C (K+...C12 3.220 and K+ ...C25 3.115 Å, dashed lines in Figure 1(right)). On the other hand, the Ag⁺ occupies the remaining ring and is in a fourcoordinated environment, with three coordination sites occupied by three S donors (Ag-S1 2.540, Ag-S2 2.855, and Ag-S3 2.496 Å) and the remaining site occupied by one aromatic C atom, yielding a cation $-\pi$ bond (Ag–C32 2.476 Å). No significant interaction was found between the Ag⁺ and C18 atom (4.393 Å).

Upon complexation, two major conformational changes are observed: 1) the orientation of three sulfur donors undergoes considerable rearrangement from *exo*- to endodentate and 2) the dihedral angles of each opposite pair of aromatic rings in the free ligand are much reduced ($\mathbf{x}A-\mathbf{C}$ 37.0° \rightarrow 23.4° and $\mathbf{x}B-\mathbf{D}$ 40.8° \rightarrow 27.6°). The former change is to some extent expected to be entropically unfavorable;

while the latter behavior may be considered to reflect a chopsticks-type π interaction, as proposed by us previously^[5a,b] (Figure S4 in the Supporting Information).

The ESI-mass spectrum of **4** mixed with one equivalent of each of KPF₆ and AgPF₆ was dominated by peaks for heterobinuclear species such as $[K(4)AgPF_6]^+$ (*m*/*z* 1081.9) and $[K(4)Ag]^{2+}$ (*m*/*z* 467.9) (Figure 2). The mononuclear species $[Ag(4)]^+$ (*m*/*z* 898.0) and $[K(4)]^+$ (*m*/*z* 828.1) were also observed.



Figure 2. ESI-MS spectrum of 4 in the presence of KPF_6 (1.0 equiv) and $AgPF_6$ (1.0 equiv) in acetonitrile.

In a comparative NMR study of the complexation behavior, the formation of the heterodinuclear complex was also confirmed (Figure 3). The signals of the aromatic protons (H_{a-d}) in 4 are well identified, exhibiting the characteristics of the 1,3-alternate conformation with the $C_{2\nu}$ symmetry (Figure 3A-a). Therefore, the peaks of aromatic ring protons H_a and H_b (red) adjacent to the sulfur donors appear farther upfield than those of H_c and H_d (blue) near the O₅cavity, respectively. Addition of one equivalent of silver(I) picrate causes larger downfield shifts of the peaks for H_a and H_b than for those of H_c and H_d (Figure 3A-b). On addition of one more equivalent of Ag+, however, more or less no further downfield shifts was observed (Figure 3A-c). This behavior confirms the different affinity of the donor sets the Ag⁺ is not bonded as strongly in the O₅-cavity as it is in the O₂S₃-cavity. However, addition of one equivalent of K⁺ to the above solution of Ag⁺ complex led to a much lager downfield shift, in accord with the formation of the heterodinuclear species $[Ag(4)K]^{2+}$ (Figure 3 A-d). Since both cavities were already saturated by their preferred metal species, no further shifts occurred on addition of additional K⁺ (Figure 3A-e).

The NMR spectra of **4** were also obtained under conditions involving the reverse order of salt addition (Figure 3B). According to the peak patterns and chemical shift changes shown in Figure 3B-b,c, the potassium ion is accommodated in the O5-ring cavity and then the added Ag⁺ occupies the O_2S_3 -ring cavity to form the heterodinuclear species $[Ag(4)K]^{2+}$ (Figure 3B-d). Interestingly, the NMR peaks in Figure 3B-e show the same pattern to those in Fig-

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Figure 3. Cation-induced ¹H NMR spectra of aromatic region for A: stepwise addition of silver(I) and potassium(I): a) **4**, b) **4**+1.0 equiv Ag⁺, c) **4**+2.0 equiv Ag⁺ d) **4**+2.0 equiv Ag⁺ + 1.0 equiv K⁺, c) **4**+2.0 equiv K⁺, c) **4**+2.0 equiv K⁺, c) **4**+2.0 equiv K⁺, c) **4**+2.0 equiv K⁺, d) **4**+2.0 equi

ure 3 A-e, suggesting that the respective structural conversions finally reach the same heterodinuclear complexation equilibrium position.

In this work, we describe the synthesis and structural characterization of a unsymmetrical calix[4]-bis-crown and its heterodinuclear K^+ and Ag^+ complex. We expect that the unsymmetrical calix-bis-crown system can offer potential design tool for engineering new receptors for heteronuclear guest system. Further investigation of the physical properties and related system is in progress.

Experimental Section

General: All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. The ¹H and ¹³C NMR spectra were recorded by using a Bruker Advance-300 (300 MHz) NMR spectrometer. Mass spectra were obtained by using a JEOL JMS-700 spectrometer. The FT-IR spectra were measured by using a Shimadzu FT-IR 8100 spectrometer. The elemental analysis was carried out by using a LECO CHNS-932 elemental analyzer.

Synthesis and characterization of 4: To a refluxed solution of K_2CO_3 (0.569 g, 4.12 mmol) in THF (100 mL) was added dropwise a solution of 3 (1.00 g, 1.10 mmol) and 2-mercapto ethyl sulfide (0.239 g, 1.55 mmol) in THF (50 mL) for 3 h under nitrogen, and the reaction mixture was refluxed for an additional 24 h. After cooling to room temperature, 10% HCl (10 mL) was added and the solvent was removed under reduced pressure. The reaction mixture was extracted with CH₂Cl₂ (3×50 mL), washed with water and then dried over anhydrous MgSO₄. The crude product was chromatographed on silica gel using ethyl acetate and *n*-

hexane (1:2) as eluent, and recrystallized from CH₂Cl₂/*n*-hexane (1:30, *v*/*v*) to give a white crystalline solid in 16% yield (0.12 g). Mp=259–260°C; ¹H NMR (CDCl₃, 300 MHz, 295 K): δ =7.07 (dd, 8H, Ar), 6.89 (tt, 4H, Ar), 3.89 (s, 8H, ArCH₂Ar), 3.48 (s, 8H, OCH₂CH₂O), 3.42 (t, 4H, ArOCH₂CH₂O), 2.64 (s, 8H, ArOCH₂CH₂CH₂O), 3.03 (t, 4H, ArOCH₂CH₂O), 2.64 (s, 8H, ArOCH₂CH₂SCH₂), 1.98 ppm (t, 4H, SCH₂CH₂S); ¹³C NMR (CDCl₃, 75 MHz, 295 K): δ =134.6, 133.9, 129.3, 129.1, 123.4, 122.5, 72.8, 71.1, 70.6, 68.6, 67.4, 38.3, 35.5, 33.8, 32.2 ppm; IR (KBr pellet): $\tilde{\nu}$ =2904, 1461, 1215, 1148, 1094, 764 cm⁻¹; MS (FAB, *m*/*z*): 812 [*M*⁺+Na], 788 [*M*⁺]; elemental analysis (%) calcd for C₄₄H₅₂O₇S₃: C 66.97, H 6.64, S 12.19; found: C 67.02, H 6.79, S 12.55.

Preparation of [Ag(4)K]·2PF₆·2CH₃CN (5): AgPF₆ (3.20 mg, 1.27 mmol) and KPF₆ (2.33 mg, 1.27 mmol) in acetonitrile (3 mL) were layered onto a dichloromethane solution (3 mL) of **4** (10.0 mg, 1.27 mmol) at room temperature. The X-ray quality single crystals were obtained in good yield (10.7 mg, 69%). IR (KBr pellet): $\bar{\nu}$ =2920, 2876, 2346 (CN), 2304 (CN), 1469, 1201, 1078, 756 cm⁻¹; MS (ESI): *m*/*z*: 1081.9 [K(4)Ag(PF₆)]⁺, 467.9 [K(4)Ag]²⁺; elemental analysis (%) calcd for C₄₈H₅₈AgF₁₂KN₂O₇P₂S₃: C 44.07, H 4.47, N 2.14, S 7.35; found: C 44.29, H 4.54, N 2.61, S 7.76.

Crystal data for **4** and **5** were collected at 100 K using synchrotron radiation ($\lambda = 0.85$ Å), employing a 6BX Bruker Proteum 300 CCD detector and a Pt-coated Si double-crystal monochromator located at the Pohang Accelerator Laboratory in Korea. The HKL2000 (*V*. 0.98.694)^[7] software package was used for data collection, cell refinement, reduction, and absorption correction. The intensity data were processed using the Saint Plus program. All of the calculations for the structure determination were carried out using the SHELXTL package (version 5.1).^[8] In most cases, hydrogen positions were input and refined in a riding manner along with the attached carbons. Relevant crystal data collection and refinement data for the crystal structures of **4** and **5** are summarized in Table S1. In the refinement procedure for **4**, the hydrogen atoms of the CH₃OH molecule in the lattice were not included to avoid the overlapping with hydrogen atoms in the ligand.

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CCDC 719416 (4) and 719415 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

Acknowledgements

This work was supported by grant No. R32-2008-000-20003-0 from the World Class University (WCU) project of the Ministry of Education, Science & Technology (MEST) and the Korea Science and Engineering Foundation (KOSEF) through Gyeongsang National University. Experiments at PLS were supported in part by MEST and POSTECH.

Keywords:	calixarenes	•	crown	compounds	•
heterobinuclear · potassium · silver					

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Received: June 10, 2009 Published online: August 19, 2009