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Unsymmetrical Calixcrowns Incorporating Hard and Soft Loops as a New Scaffold for Multinuclear Endo/Exocyclic Complexation and Networking

Jai Young Lee,[†,‡] So Young Lee,[†] Sunhong Park,[†] Jongchul Kwon,[‡] Wonbo Sim,[*,‡] and Shim Sung Lee[*,†]

[†]*Department of Chemistry (BK21) and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, South Korea, and* [‡]*Department of Chemistry, Konyang University, Nonsan 320-711, South Korea*

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Unsymmerical calix[4]crowns containing [(O_4S)(O_5)] (**L^1**) and [(O_4S_2)(O_5)] (**L^2**) as crown loops were employed as new scaffolds both for complexation studies and for network formation. Reactions of **L^1** and **L^2** with KI in the presence of CuI afforded a copper(I) iodide cluster linked 1D-type endocyclic dipotassium(I) complex [K_2(**L^1**)(Cu_7I_9)]$_n$ (**1**) and a copper(I) iodide cluster linked 1D-type endocyclic monopotassium(I) complex [K**L^2**(μ_2-Cu_3I_4)]$_n$ (**2**), respectively. By comparison, the reaction of **L^2** with KPF_6 in the presence of CuI and HgI_2 afforded the 1-D endocyclic potassium(I) complex [K(**L^2**)($CuHgI_4$)]$_n$ (**3**), linked with a $CuHgI_4$ cluster unit. The formation of homo- and heterodinuclear complexes in solution was also confirmed by comparative NMR studies.

Introduction

The design of organic receptors with divergent and carefully placed binding sites offers enormous potential for the fabrication of novel architectures incorporating interconnecting modules.[1] However, macrocyclic receptors or their discrete complexes have only seldom been employed as building blocks for the construction of such supramolecular networks.[2]

In the search for new receptor molecules optimized for the formation of new supramolecular networks having well-defined geometries, we have focused our attention on calixcrowns, the fusion of crown ether[3] and calixarene[4] units, which enables the divergent orientation of cavities of a size and nature sufficient to accommodate a variety of guests.[5] In particular, calix[4]-biscrowns[6] have been regarded as attractive building blocks due to their expected selectivity for specific metal ions based on size-matching[3] or hard and soft acids and bases[7] concepts as well as through dinuclear complexation by two crown loops and cation−π interactions.[8] As a consequence, research on binuclear complexes with diverse types of calix[4]-bis-crowns

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*To whom correspondence should be addressed. E-mail: sslee@gnu.ac.kr.

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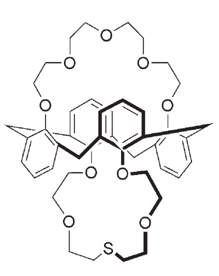
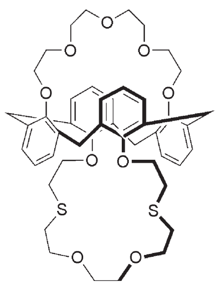
has been a recent area of considerable interest.[6] Kim et al.[7b] reported the heterobinuclear complex of an unsymmetrical calix-bis-crown with two different-sized crown loops in which a crown-5 loop is suitable for K$^+$ and a crown-6 loop is suitable for Cs$^+$. The developments in sensor chemistry based on calix[4]arene derivatives have been well reviewed by these authors.[9]

We have been interested in the assembly of supramolecular architectures based on the exocoordination of thiamacrocycles because the sulfur donor is expected to favor the binding of soft metal ions in an exocyclic mode.[10] In particular, self-assembly processes involving copper(I) halides and thiamacrocycles often lead to metal–organic frameworks because the copper(I) halides are capable of adopting a variety of coordination modes that include one- to three-dimensional polymeric networks containing a variety of structural motifs.[11] We have reported calix[4]-bis-dithiacrown-based endocoordinated disilver(I) complexes as well as an exocoordinated 3-D network connected by CuI-based clusters.[12] We also recently described the temperature-dependent assembly of 3-D CuI coordination polymers containing calix[4]-bis-dithiacrown.[12c,d] In this case, upon the removal of coordinated acetonitrile from the initial solvent-coordinated polymer, a unique crystal-to-crystal transformation accompanied by an irreversible photoluminescence change was demonstrated to occur.

Chart 1



$\mathbf{L}^1$



$\mathbf{L}^2$

In extending this work, we were interested in using a ligand-directed approach to achieve the synthesis of a new family of heteromultinuclear complexes as well as to achieve the construction of infinite networks. We therefore focused our attention on unsymmetrical calix[4]crowns in which oxygen donors on one side of the crown ring are replaced by sulfur atoms. Such a receptor would potentially bind two hard metals or one softer and one harder metal within the respective cavities. A further area of recent interest has been the synthesis and investigation of copper(I) halide cluster complexes of thiaoxa macrocycles involving both diverse networks and unusual photophysical properties.[13] As an extension of these studies, the unsymmetrical calix[4]thiacrowns, $\mathbf{L}^1$ and $\mathbf{L}^2$, simultaneously incorporating both crown and thiacrown rings on a calix[4]arene scaffold are now reported (Chart 1). In this paper, we describe the complexation and network formation behavior of the new unsymmetrical calix[4]-bis-crowns with hard and soft metal ions.

Experimental Section

General. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded with Bruker Advance-300 (300 MHz) and -500 (500 MHz) NMR spectrometers. The mass spectra were obtained on a JEOL JMS-700 spectrometer. The elemental analysis was carried out on a LECO CHNS-932 elemental analyzer. The FT-IR spectra of the coordination polymers were measured with a Shimadzu FT-IR 8100 spectrometer.

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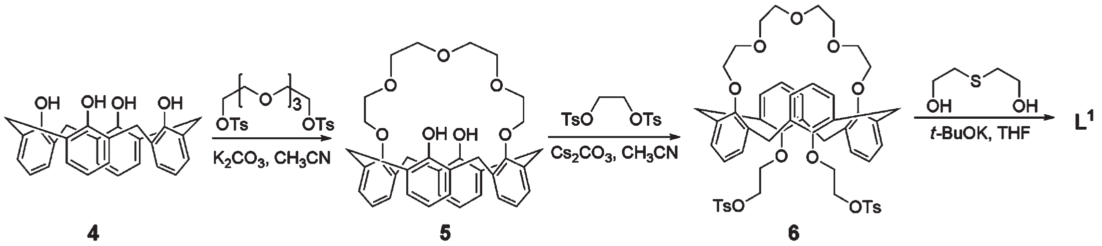
Scheme 1. Synthesis of L^1



25,27-Oxo-crown-5-26,28-monothiacrown-5-calix[4]arene (L^1). To a refluxed solution of *t*-BuOK (0.920 g, 8.20 mmol) in THF (200 mL) was added dropwise a solution of **6** (1.00 g, 1.03 mmol) and 2,2′-thiodiethanol (0.189 g, 1.55 mmol) in THF (100 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 CH_2Cl_2 (3 × 50 mL), washed with water, and then dried over anhydrous $MgSO_4$. The crude product was chromatographed on silica gel using ethyl acetate and *n*-hexane (1:3) as an eluent and recrystallized from CH_2Cl_2/*n*-hexane (1:30, v/v) to give a white crystalline solid in 16% yield (0.12 g). Mp: 243−244 °C. IR (pellet): 2915, 1460, 1214, 1177, 1093, 820 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.08 (dd, 4H, Ar), 6.88 (tt, 4H, Ar), 3.86 (s, 8H, $ArCH_2Ar$), 3.62−3.44 (m, 20 H, $ArOCH_2CH_2OCH_2CH_2O$, $ArOCH_2CH_2OCH_2CH_2S$), 3.31−3.09 (m, 8H, OCH_2CH_2O, OCH_2CH_2S), 2.66 (t, 4H, OCH_2CH_2S). ^{13}C NMR ($CDCl_3$): δ 156.9, 156.6, 134.2, 134.0, 129.5, 122.9, 122.8, 73.0, 72.3, 71.0, 69.9, 69.2, 68.1, 38.2, 30.0 ppm. MS (FAB, *m*/*z*): 780 ($M^+ + Na$), 757 (M^+).

Preparation of $\{[K_2(L^1)(Cu_7I_9)]\cdot 2CH_3CN\}_n$ (1). Copper(I) iodide (6.15 mg, 32.3 mmol) and potassium iodide (5.36 mg, 32.3 mmol) in acetonitrile (3 mL) were layered onto a dichloromethane solution (3 mL) of L^1 (10.0 mg, 13.2 mmol) at room temperature. The X-ray-quality single crystals were obtained in good yield (23.1 mg, 87%), Anal. Calcd for $C_{94}H_{104}Cu_{11}I_{15}K_4N_3O_{18}S_2$: C, 25.74; H, 2.39; N, 0.96; S, 1.46. Found: C, 25.68; H, 2.41; N, 1.02; S, 1.49. IR (KBr pellet): 2925, 2876, 2341, 2310, 1437, 1215, 1107.

Preparation of $\{[K(L^2)(Cu_3I_4)]\cdot 2CH_3CN\}_n$ (2). Copper(I) iodide (6.15 mg, 32.3 mmol) and potassium iodide (5.36 mg, 32.3 mmol) in acetonitrile (3 mL) were layered onto a dichloromethane solution (3 mL) of L^2 (10.0 mg, 12.2 mmol) at room temperature. The X-ray-quality single crystals were obtained in good yield (24.1 mg, 89%), Anal. Calcd for $C_{50}H_{62}Cu_3I_4KN_2O_9S_2$: C, 36.70; H, 3.82; N, 1.71; S, 3.92. Found: C, 36.52; H, 3.73; N, 1.69; S, 4.01. IR (KBr pellet): 2929, 2866, 2356, 2307, 1441, 1217, 1110.

Preparation of $\{[K(L^2)(CuHgI_4)]\cdot 2CH_3CN\cdot 2H_2O\}_n$ (3). Copper(I) iodide (6.15 mg, 32.3 mmol), potassium iodide (5.36 mg, 32.3 mmol), and mercury iodide (14.7 mg, 32.3 mmol) in acetonitrile (3 mL) were layered onto a dichloromethane solution (3 mL) of L^2 (10.0 mg, 12.2 mmol) at room temperature. The X-ray-quality single crystals were obtained in good yield (22.4 mg, 86%), Anal. Calcd for $C_{50}H_{62}CuHgI_4KN_2O_{11}S_2$: C, 34.47; H, 3.59; N, 1.61; S, 3.68. Found: C, 34.38; H, 3.57; N, 1.62; S, 3.70. IR (KBr pellet): 3401, 2931, 2872, 2338, 2312, 1447, 1223, 1104.

Comparative NMR Study. The NMR experiments were conducted on Bruker Avance 500 spectrometer at 298 K. For the NMR studies, a stock solution of Ag-Pic and K-Pic (0.1 M) dissolved in CD_3CN-$CDCl_3$ (v/v 1:1) was added incrementally, by using an automicropipet (0−25 μL), to the respective compound L (typically ~0.01 M) dissolved in CD_3CN-$CDCl_3$ (v/v 1:1, 0.75 mL) in the NMR tube.

Crystallographic Structure Determinations. Crystal data for **2** were collected at 100 K using synchrotron radiation (λ = 0.7500 Å), employing a 4AMXW ADSC Quantum-210 detector and a Pt-coated Si double-crystal monochromator located at the Pohang Accelerator Laboratory (PAL) in Korea. The HKL2000 (version 0.98.694)[14] software package was used for data collection, cell refinement, reduction, and absorption correction. Crystal data for L^1, **1**, and **3** at 173 K were collected on a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 45 collected frames) using the SMART program. 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 6.22).[15] Absorption corrections were applied by using XPREP and SADABS.[16] 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 L^1, **1**, **2**, and **3** are summarized in Table S1 (Supporting Information). In the crystal of **1**, hydrogen atoms of the CH_3CN solvents were not included. In the crystals of **2** and **3**, the treatment of disorder in O3, C6, C7, and C8 atoms and the CH_3CN solvent molecule for **2** and C44 for **3** are not impossible because of a nonpositive definite problem, although these atoms have large thermal vibration. In the crystal of compound **3**, hydrogen atoms of the water molecules were not included.

Results and Discussion

Ligand Synthesis. L^1 was synthesized in two successive cyclization steps as depicted in Scheme 1. Cyclization of calix[4]arene **4** with tetraethyleneglycol ditosylate afforded the calix[4]-*mono*-crown **5**. Ditosylation of **5** with ethyleneglycol ditosylate led to the ditosyl derivative **6**.[12a] The cyclization of **6** with 2,2′-thiodiethanol afforded the desired unsymmetrical calix[4]-*bis*-crown L^1. The NMR spectrum of L^1 exhibits the expected signal complexity arising from its unsymmetrical nature. L^2 was synthesized as reported previously by us.[12b]

Single crystals of L^1 were prepared by vapor diffusion of diethyl ether into the acetonitrile solution, and its saddle-type 1,3-alternate conformation was confirmed by X-ray analysis as shown in Figure 1. The sulfur atom is oriented in an exodentate fashion, while oxygen atoms are positioned endodentate except O4. From the torsion angles associated with donor orientation, the conformation of the O_4S-linkage (O1 to O4) can therefore can be described as g−g−t−t (t = trans, g = gauche), whereas that of the O_5 linkage (O5 to O9) shows a t−g−g−g arrangement.

Complex Study in Solid State. Reaction of L^1 with KI in the presence of CuI gave a yellow crystalline product, **1**,

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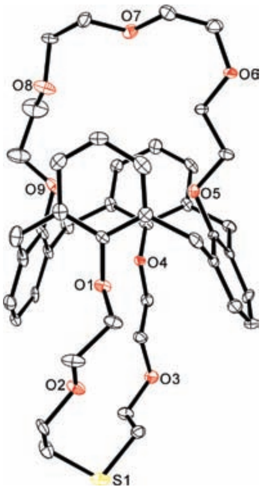

Figure 1. Crystal structure of $\mathbf{L^1}$.

that was suitable for X-ray analysis. The crystal structure of **1** showed the presence of the 1,3-alternate conformation of the calixarene unit and featured a 1-D array of formula $\{[K_2(\mathbf{L^1})(Cu_7I_9)]\cdot 2CH_3CN\}_n$ in which endocyclic dipotassium(I) complexes are linked by an exocyclic CuI cluster ribbon via Cu−S bonds (Figure 2a). Thus, the asymmetric unit contains one $\mathbf{L^1}$, two potassium atoms, and one Cu_7I_9 cluster (Figure 2b). The coordination of K2 involves five K2−O bonds (2.743−2.823 Å), while the environment of K1 is different and contains one S donor (S1) with its coordination being completed by four K1−O bonds (2.658−2.857 Å). The K1···S1 length (3.194 Å) is shorter than the sum of van der Waals radii (2.35 + 1.27); the S1 atom in the O_4S ring acts both as a weak donor for endocyclic K^+ and as a bridgehead for the exocyclic network via a Cu1−S1 bond (2.318 Å). In addition, K2 interacts with adjacent aromatic carbons to give an η^3-type cation···π interaction (K2···C = 3.160−3.389 Å, see dashed lines in Figure 1b). There are also η^3-type cation···π interactions with K1 involving carbon atoms (K1···C = 3.149−3.435 Å) of the B and D aromatic rings. The exocyclic CuI ribbon cluster consists of the fusion of Cu_2I_2 rhomboid units through edge sharing to form a 1-D backbone.

Since it gives direct information on the conformational changes upon complexation, a structural comparison of **1** with $\mathbf{L^1}$ is shown in Figure 2c. Notably, the dihedral angles for free $\mathbf{L^1}$ (A−C, 42.84°; B−D, 41.70°) are found to be much reduced in their dipotassium(I) complex **1** (A−C, 23.23°; B−D, 24.15°). From this comparison, it proved possible to rationalize the stabilization of the calix[4]arene complexes with 1,3-alternate configurations in terms of π-interaction processes. We recently proposed similar behavior for the disilver(I) complex of calix[4]-bis-S_2O_3-crown in terms of a "chopsticks" process.[12b] Upon complexation, all of the donors are directed toward the inside of the cavity, and the torsion angles between two adjacent donors correspond to a gauche conformation.

The reaction of $\mathbf{L^2}$ with KI in the presence of CuI afforded **2** as a yellow crystalline product which was suitable for X-ray analysis. Once again, the crystal structure showed a 1,3-alternate conformation of the calixarene unit. Compound **2** features a double-stranded 1-D array of formula $\{[K(\mathbf{L^2})(Cu_3I_4)]\cdot 2CH_3CN\}_n$ in which endocyclic potassium(I) complexes are linked with exocyclic CuI cluster ribbons via Cu−S bonds (Figure 3a). The asymmetric unit contains one $\mathbf{L^2}$, one potassium atom, and one Cu_3I_4 cluster (Figure 3b). The potassium atom is located in the center of the O_5-crown cavity, with its coordination involving five K1−O bonds (2.718−2.843 Å). In a similar manner to that of **1**, the potassium atom interacts with carbons in an adjacent aromatic ring to give an η^3-type cation···π interaction (K1···C = 3.220−3.304 Å, see dashed lines in Figure 3b). Unlike **1**, however, the O_4S_2-ring cavity is empty. The two sulfur donors act as a bridgehead via Cu−S bonds (2.346 Å) for the double-stranded exocyclic network. The exocyclic CuI cluster is made up of the fusion of Cu_2I_2 rhomboid units through edge sharing to form the 1-D backbone.

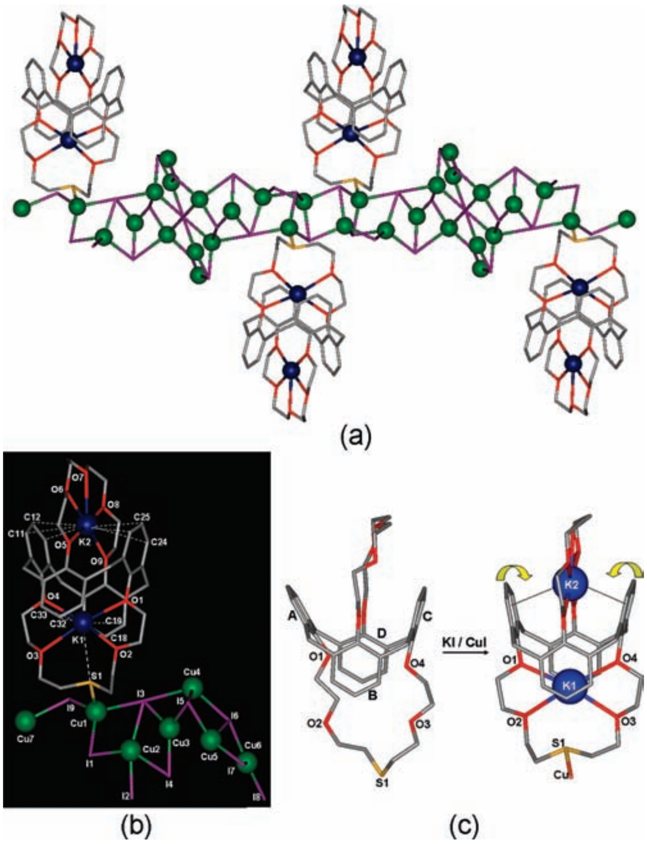

Figure 2. (a) 1-D polymeric network structure of **1**, $\{[K_2(\mathbf{L^1})(Cu_7I_9)]\cdot 2CH_3CN\}_n$, (b) asymmetric unit, and (c) conformational comparison of $\mathbf{L^1}$ (left) and **1** (right, calixcrown part). Hydrogen atoms and solvent molecules are omitted.

Reaction of $\mathbf{L^2}$ with KPF_6 in the presence of CuI and HgI_2 afforded a yellow crystalline product of type **3**, which proved suitable for X-ray analysis. Unlike the case of **2**, compound **3** features a single-stranded 1-D polymeric arrangement of formula $\{[K(\mathbf{L^2})(CuHgI_4)]\cdot 2CH_3CN\cdot 2H_2O\}_n$ consisting of $\mathbf{L^2}$ and a $CuHgI_4$ cluster with a −L−Cu−L−Cu− arrangement (Figure 4a). That is, the endocyclic monopotassium(I) complex of $\mathbf{L^2}$ is linked by exocyclic $CuHgI_4$ clusters via Cu−S bonds, with the asymmetric unit containing one $\mathbf{L^2}$, one potassium atom, and one $CuHgI_4$ cluster (Figure 4b). As expected, K1 coordination involves five K1−O bonds (2.753−2.854 Å) and is also stabilized by π interactions with carbons in the adjacent aromatic ring (K1···C =

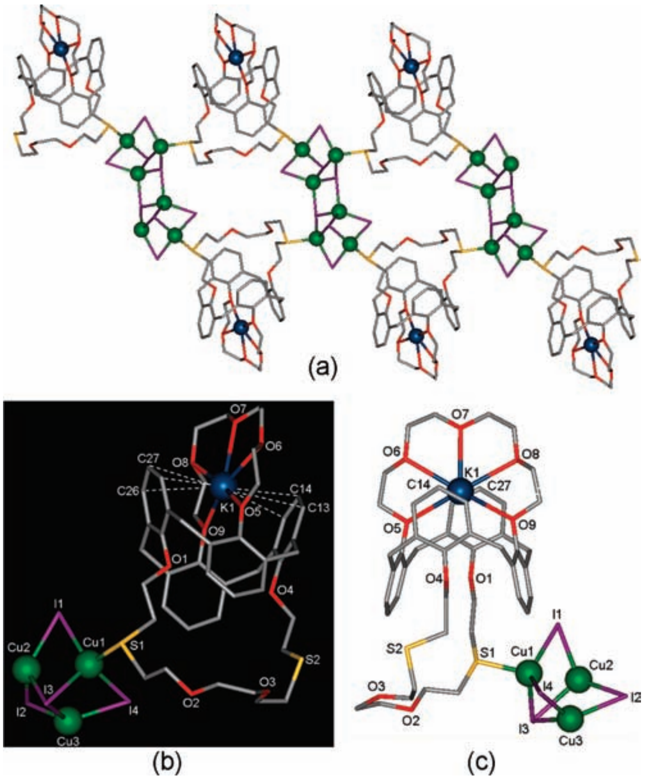

Figure 3. (a) Double-stranded 1-D polymeric network structure of **2**, $\{[K(\mathbf{L^2})(Cu_3I_4)]\cdot 2CH_3CN\}_n$, (b) asymmetric unit, and (c) 90° rotation of b. Hydrogen atoms and solvent molecules are omitted.

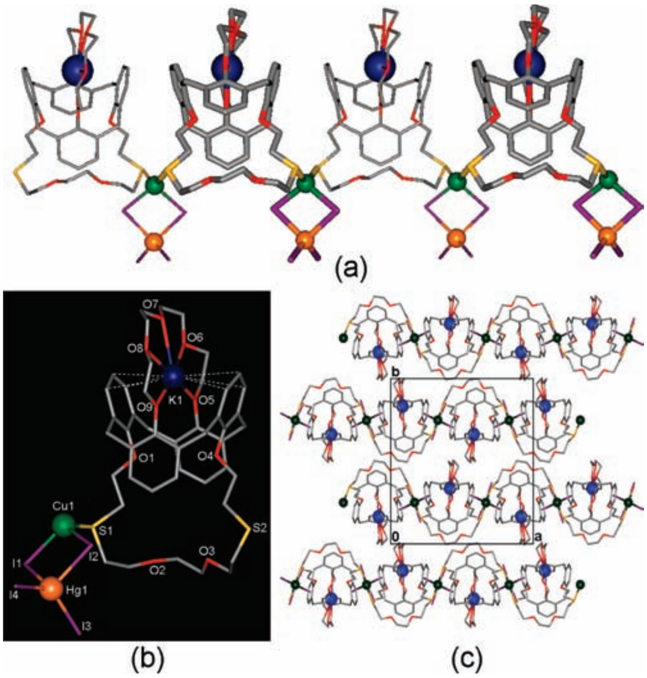

Figure 4. Single-stranded 1-D polymeric network structure of **3**, $\{[K(\mathbf{L^2})(CuHgI_4)]\cdot 2CH_3CN\cdot 2H_2O\}_n$, (b) asymmetric unit, and (c) *c*-axis packing structure. Hydrogen atoms and solvent molecules are omitted.

3.185−3.4876 Å, see dashed lines in Figure 4b). The Cu1 atom, which links two ligands via Cu−S bonds, shows distorted tetrahedral coordination, being bound to two S donors from two $\mathbf{L^2}$ and two I atoms. Related square-type heteronuclear Cu(II)−Hg(II)X_4 clusters have been reported previously.[17] To the best of our knowledge, this is the first characterized square-type heteronuclear cluster of a copper−mercury halide system containing copper(I).

Complex Study in Solution by Comparative NMR and ESI-Mass Spectrometry. In an extension of the solid-state study, comparative ^{1}H NMR experiments were performed, and the formation of homo- and heterodinuclear complexes in solution was confirmed (Figure 5 and Figures S5, S6, and S7, Supporting Information). The signals of the aromatic protons in $\mathbf{L^1}$ are well-resolved and readily identified, suggesting that the stabilization of the 1,3-alternate conformation occurs in solution [see Figure 5A-a; $H_{a,b}$: peaks occuring at higher field (marked in red) are located near the O_4S ring; $H_{c,d}$: peaks occuring at lower field (marked in blue) are located near the O_5 ring]. The complexation of silver(I) ions proceeds in two steps. First, the addition of 1 equiv of silver(I) picrate causes larger downfield shifts for the H_a and H_b signals than for those of H_c and H_d (Figure 5A-b). This behavior can be explained by the dissimilar affinity of the respective donor sets toward Ag^+,; it is not bonded as strongly in the O_5 cavity as it is in the OS_4 cavity. On the addition of one more equivalent of Ag^+, further downfield shifts of each peak were observed (Figure 5A-c), in keeping with the formation of a disilver(I) species $[Ag_2(\mathbf{L^1})]^{2+}$. Additions of 1 (Figure 5A-d) and 2 equiv (Figure 5A-e) of K^+ to the above disilver(I) complex solution led to a new set of peaks at lower field (marked in green) in accord with the formation of the heterodinuclear species $[Ag(\mathbf{L^1})K]^{2+}$. This observation suggests that the disilver and heterodinuclear complexes coexist and that the exchange process between them is slow on the NMR time scale.

Next, the NMR spectra of $\mathbf{L^1}$ were obtained under conditions involving the reverse order of salt addition. Upon the addition of 1 (Figure 5B-b) and 2 equiv (Figure 5B-c) of K^+ to $\mathbf{L^1}$, two sets of signals were present, one for free $\mathbf{L^1}$ and the second for its complex (primed, in lower field), reflecting a slow-exchange process. This is in contrast to the behavior observed for the above silver(I) system (Figure 5A). Additions of 1 (Figure 5B-d) and 2 equiv (Figure 5B-e) of Ag^+ to the dipotassium(I) complex solution (Figure 5B-c) also led to a new set of peaks at higher field corresponding to those of heterodinuclear species $[Ag(\mathbf{L^1})K]^{2+}$.

Interestingly, the NMR peak pattern in Figure 5B-e shows the same pattern as that in Figure 5A-e, suggesting that the respective structural conversions finally reach the same heterodinuclear complexation equilibrium. A comparative NMR study was also carried out for $\mathbf{L^2}$, and similar complexation behavior was observed (Figure S6, Supporting Information) for this system. The data for the crown rings also suggest the same results (Figure S5 and S7, Supporting Information).

The mass spectra of $\mathbf{L^1}$ mixed with 1 equiv each of potassium and silver picrates (Pic) were dominated by peaks for heterobinuclear species such as $[K(\mathbf{L^1})AgPic]^+$ (*m*/*z* 1132.0) and $[K(\mathbf{L^1})Ag]^{2+}$ (*m*/*z* 455.6). The mononuclear species $[Ag(\mathbf{L^1})]^+$ (*m*/*z* 865.9) and $[K(\mathbf{L^1})]^+$ (*m*/*z* 794.9) were also observed (Figure 6).

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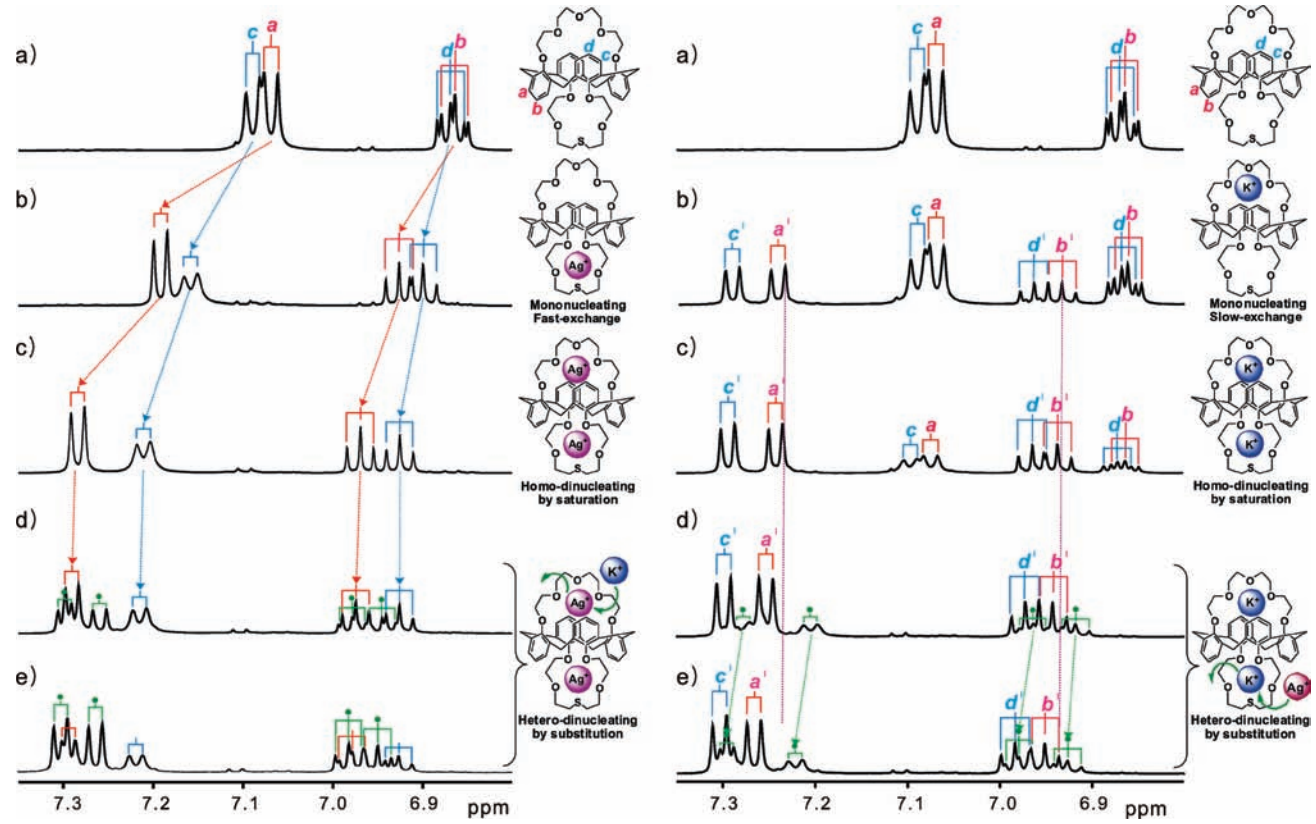

Figure 5. ^{1}H NMR (500 MHz) spectra of aromatic region for (A) (a) $\mathbf{L^1}$, (b) $\mathbf{L^1}$ + 1.0 equiv of Ag^+, (c) $\mathbf{L^1}$ + 2.0 equiv of Ag^+, (d) $\mathbf{L^1}$ + 2.0 equiv of Ag^+ + 1.0 equiv of K^+, (e) $\mathbf{L^1}$ + 2.0 equiv of Ag^+ + 2.0 equiv of K^+ and for (B) (a) $\mathbf{L^1}$, (b) $\mathbf{L^1}$ + 1.0 equiv of K^+, (c) $\mathbf{L^1}$ + 2.0 equiv of K^+, (d) $\mathbf{L^1}$ + 2.0 equiv of K^+ + 1.0 equiv of Ag^+, (e) $\mathbf{L^1}$ + 2.0 equiv of K^+ + 2.0 equiv of Ag^+ (as picrate salts) in CD_3CN-$CDCl_3$ (v/v 1:1).

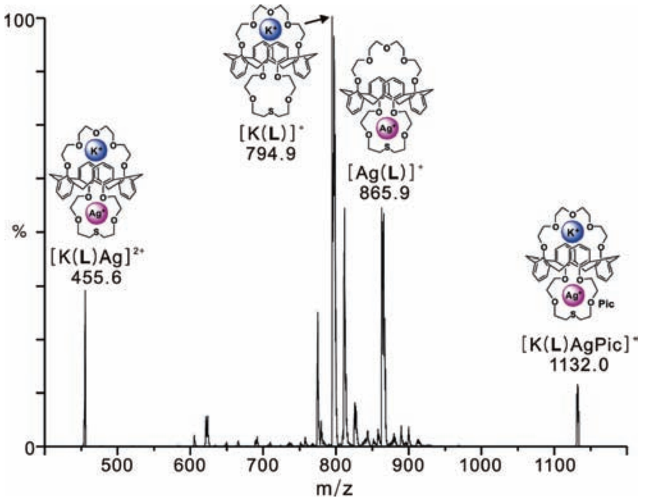

Figure 6. ESI-mass spectrum of $\mathbf{L^1}$ with AgPic and KPic in CH_3CN.

Conclusions

In summary, two unsymmerical calix[4]crowns containing $[(O_4S)(O_5)]$ ($\mathbf{L^1}$) and $[(O_4S_2)(O_5)]$ ($\mathbf{L^2}$) as crown loops were employed as new scaffolds both for complexation studies and for network formation. Interaction of $\mathbf{L^1}$ and $\mathbf{L^2}$ with KI in the presence of CuI afforded a 1-D copper(I) iodide cluster complex $[K_2(\mathbf{L^1})(Cu_7I_9)]_n$ (**1**), incorporating endocyclic dipotassium(I), and a copper(I) iodide cluster linked 1-D-type endocyclic monopotassium(I) complex $[K(\mathbf{L^2})(Cu_3I_4)]_n$ (**2**), incorporating endocyclic monopotassium(I), respectively. By comparison, the reaction of $\mathbf{L^2}$ with KPF_6 in the presence of CuI and HgI_2 afforded the 1-D endocyclic potassium(I) complex $[K(\mathbf{L^2})(CuHgI_4)]_n$ (**3**), linked with a $CuHgI_4$ cluster unit. The structure motifs observed represent not only new hard/soft binuclear coordination species but also endo/exocyclic network generation. The formation of homo- and heterodinuclear complexes in solution was also confirmed by comparative NMR studies. We think that the endo/exocyclic coordination networks based on the proposed unsymmetical calix[4]-bis-crowns derivatives in this work can open the unexplored research topics not only in the synthetic metallosupramolecules field but also in the related materials field.

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Supporting Information Available: Crystallographic data and CIF files of **L**, **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.