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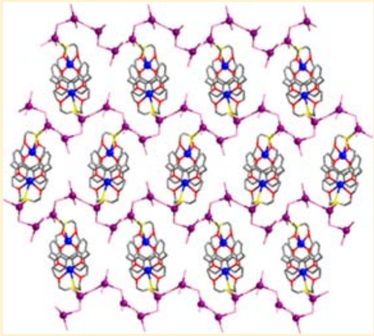
Hard and Soft Metal Complexes of Calix[4]-*bis*-monothiacrown-5: X-ray and NMR Studies of Discrete Homodinuclear Complexes and a Heteromultinuclear Network

Ja-Yeon Kim,[†] In-Hyeok Park,[†] Jai Young Lee,[‡] Joon-Hwa Lee,[†] Ki-Min Park,[†] and Shim Sung Lee*,[†]

[†]Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, S. Korea
[‡]Department of Chemistry, Konyang University, Nonsan 320-711, S. Korea

Supporting Information

ABSTRACT: Endocyclic homodinuclear complexation and endo/exocyclic heteronuclear networking of calix[4]-*bis*-monothiacrown-5 (**L**) are reported. First, dipotassium(I) and disilver(I) complexes of **L** were isolated and their solid state structures characterized. To probe the complexation behavior for these same systems in solution, the competition between potassium(I) and silver(I) for **L** was monitored by ^{1}H NMR. Potassium(I) showed a higher affinity to **L** than silver(I) both in the solid and solution states. The reaction of **L** with KI in the presence of HgI_2 afforded a two-dimensional coordination polymer with the endocyclic dipotassium(I) complex linked by an exocyclic mercury(II) iodide cluster backbone.

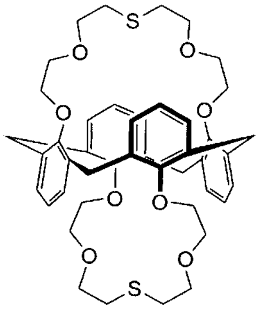


INTRODUCTION

Calix[4]-*bis*-crowns[1] comprising the calix[4]arene scaffold with a 1,3-alternate conformation and two crown units are one of the most widely investigated class of supramolecular host systems which display interesting features that include the capability to undergo dinuclear complexation,[2] to show size-matching between the crown cavity and the guest metal,[3] and HSAB[4]-based complexation selectivity. The calix[4]-*bis*-crown incorporating five oxygen donors in each crown unit has a loop size suitable for the complexation of potassium(I) and cesium(I).[5] Calix[4]-*bis*-thiacrowns[1j−o] with softer crown cavities due to the presence of sulfur heterodonors show affinity toward soft silver(I). In some cases, cation−π interactions also stabilize the dinuclear complexes of calix[4]-*bis*-(thia)crowns.[1i−k,6]

We have been interested in the assembly of new types of supramolecular architectures of thiamacrocycles, including calix[4]-*bis*-thiacrowns, which yield network products due to the sulfur donors favoring binding to a softer metal ion in an exodentate manner (that is, the metal is bound outside the macrocyclic cavity).[7] Such supramolecular networking of thiamacrocycles based on exocoordination has been reviewed by us.[8] Recently, we have reported endocyclic disilver(I) complexes of calix[4]-*bis*-dithiacrown-5 as well as a corresponding exocoordinated 3-D network connected by CuI-based clusters.[1k,l] The unsymmetrical calix-*bis*-crown-5 incorporating O_5 and O_2S_3 crown units and its discrete heterodinuclear (K^+/Ag^+) complex both in the solid and solution have been introduced by us.[9] We have also reported 3-D CuI networks incorporating the endocyclic dipotassium(I) complex of calix[4]-*bis*-monothiacrown-5 (**L**).[1n] In this case, on removal of coordinated acetonitrile, the solvent-coordinated network undergoes a single-crystal to single-crystal transformation accompanied by an irreversible photoluminescence change.

Scheme 1. Calix[4]-*bis*-monothiacrown-5 (L)



L

In this work, we selected calix[4]-*bis*-monothiacrown-5 (**L**) possessing one sulfur heterodonor in each ring as a potential bridgehead for exocoordination and also to introduce partial softness to the crown-5 cavity. Comparison of the reactivity of **L** toward hard and soft metal ions has been one of the core issues in this research area because of the conflicting expectation. In this view, potassium(I) and silver(I) were selected as an optimized cation system that might serve the informative results. Based on our previous results,[1m−o] we have

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also investigated the extension of our synthetic approach to obtain new supramolecular networks of **L** incorporating endocyclic dinuclear analogues of the above.

Consequently, we have isolated the dipotassium(I) and disilver(I) complexes of **L** and compared their reactivities and structural characteristics. Comparative NMR experiments for the competitive complexation with these hard and soft metal ions were also performed. In addition, the formation of an endo/exocyclic two-dimensional (2D) heteronuclear coordination network with an extended structure based on the dipotassium(I) complex of **L** is reported.

■ RESULTS AND DISCUSSION

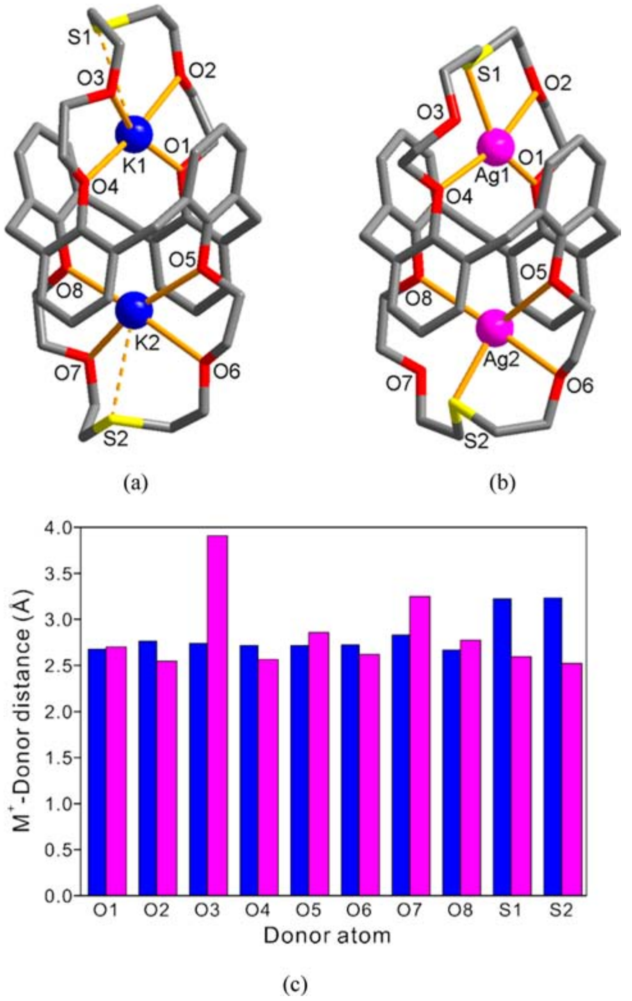
Calix[4]-*bis*-monothiacrown **L** was synthesized by a bicyclization of the 1,3-alternate tetratosylate with the corresponding dialcohol as reported by us previously.[1n]

Synthesis and Structural Comparison of Dipotassium(I) and Disilver(I) Complexes (1 and 2). Repeated attempts to isolate the potassium(I) complex of **L** in crystalline form were not successful. Our alternate approach was to react **L** with KI in the presence of CdI_2 in acetonitrile/dichloromethane. The resulting product was a desired endocyclic dipotassium(I) complex **1**, $[K_2\mathbf{L}][Cd_2I_6]\cdot CH_2Cl_2$ (Figure 1 does not show $[Cd_2I_6]^{2-}$), in which the square-type dicadmium(II) hexaiodide cluster $[Cd_2I_6]^{2-}$ exists as a separated counterion (see Figure S1 in the Supporting Information and Table 1). The crystal structure of the $[K_2\mathbf{L}]^{2+}$ cation in **1** confirms the presence of the 1,3-alternate conformation of the calixarene unit and shows that two potassium(I) ions are accommodated in the monothiaoxa-crown-ring cavities. The geometric parameters for the $[Cd_2I_6]^{2-}$ anion (see Figure S1 in the Supporting Information) are similar to those reported previously for this unit.[10]

Crystals of a corresponding silver(I) complex **2** were obtained from the reaction of **L** with $AgClO_4$ in methanol/dichloromethane. The X-ray analysis revealed that **2** is an endocyclic dinuclear complex of type $[Ag_2\mathbf{L}](ClO_4)_2$, with the silver(I) coordination approximating that observed in the potassium(I) complex **1** (Figure 1b, Figure S2 in the Supporting Information, and Table 2). Once again, the crystal structure of **2** confirmed a 1,3-alternate conformation for the calixarene unit but its overall structure is slightly less symmetrical than that of **1**.

In both complexes, the two metal ions that lie inside the crown cavities are crystallographically independent but their coordination environments are not significantly different. As expected, each potassium(I) ion in **1** coordinates to four O donors [K1−O 2.675−2.764 Å (av. 2.724 Å) and K2−O 2.668−2.832 Å (av. 2.734 Å)]. The K···S lengths (K1−S1 3.222 and K2−S2 3.233 Å) are shorter than the sum of the van der Waals radii (2.35 + 1.27 Å), suggesting that the S atoms are weaker donors for the endocyclic coordination of potassium(I) (Figure 1c). Although the coordination environment of each silver(I) in **2** is somewhat different and has one Ag−S bond [Ag1−S1 2.595 and Ag2−S2 2.521 Å] with its coordination being completed by three Ag−O bonds [Ag1−O 2.546−2.702 Å (av. 2.604 Å) and Ag2−O 2.619−2.858 Å (av. 2.751 Å)]. The lengths of Ag1···O3 (3.908 Å) and Ag2···O7 (3.249 Å) are longer than the sum of van der Waals radii (3.20 Å). The $Ag^+\cdots Ag^+$ separation [5.278 Å] in **1** is slightly longer than that of $K^+\cdots K^+$ [5.083 Å] in **2**.

In both cases, the metal ions are also stabilized by η^3-type cation···π interactions with the aromatic C atoms (Figure 2).



(a) (b)

(c)

Figure 1. Structural comparison of the dicationic complex parts of (a) **1**, $[K_2\mathbf{L}][Cd_2I_6]\cdot CH_2Cl_2$, and (b) **2**, $[Ag_2\mathbf{L}](ClO_4)_2\cdot 2CH_3OH\cdot H_2O$, and (c) M^+−donor distances in **1** (blue, M = K) and **2** (pink, M = Ag). Hydrogen atoms, noncoordinating solvent molecules, and anionic parts ($[Cd_2I_6]^{2-}$ in **1** and two ClO_4^- in **2**) are omitted.

Since the potassium(I) ions in **1** are situated almost at the center of ring A and ring C or ring B and ring D, the distances of the K···C interactions (K1···C 3.187−3.433 Å and K2···C 3.161−3.350 Å) are not so different to each other (Figure 2a). The positions of the silver(I) ions in **2**, however, are shifted toward ring C (Ag1···C 2.859−3.074 Å, dashed lines in Figure 2b) or ring D (Ag2···C 2.612−2.951 Å), resulting in a less symmetrical structure. Moreover, the distances for Ag1···ring A (C19−21) and Ag2···ring B (C11−13) are in range 3.410−3.909 Å and are longer than for typical cation···π interactions.[1i−k,6]

The structural comparison of **1** and **2** showing the synergic contribution of donor atoms and aromatic rings to stabilize the metal ions suggests that K^+ shows a higher affinity to **L** than Ag^+ in the solid state. To the best of our knowledge, these are the first structurally characterized examples of such homodinuclear complexes that can bind two hard metal ions as well as two soft metals ions.

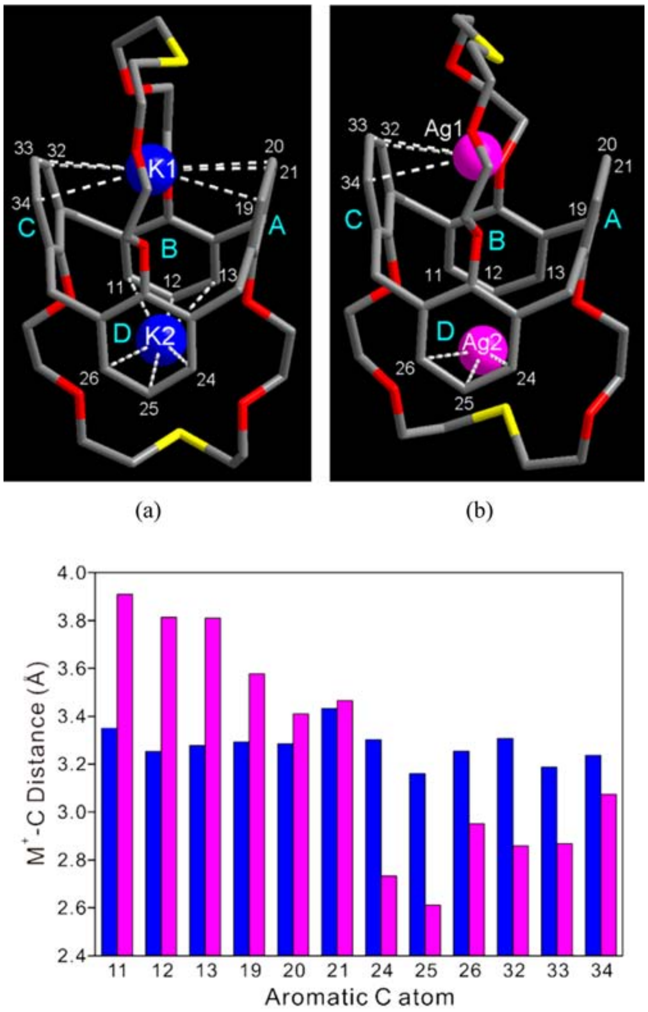
Synthesis and Structure of 2D Heteromultinuclear Network (3). Having investigated and compared the dipotassium(I) and disilver(I) cationic complex system in the solid state, we proceeded to the preparation of the

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 1

K1−O1	2.675(4)	K2−O5	2.713(4)
K1−O2	2.764(4)	K2−O6	2.723(5)
K1−O3	2.738(4)	K2−O7	2.832(5)
K1−O4	2.717(4)	K2−O8	2.668(4)
K1···S1	3.222(2)	K2···S2	3.233(2)
K1···C19	3.293(6)	K2···C11	3.350(6)
K1···C20	3.285(6)	K2···C12	3.253(7)
K1···C21	3.433(6)	K2···C13	3.278(7)
K1···C32	3.308(6)	K2···C24	3.302(6)
K1···C33	3.187(7)	K2···C25	3.161(6)
K1···C34	3.237(6)	K2···C26	3.254(7)
Cd1−I1	2.6999(8)	Cd2−I3	2.8647(7)
Cd1−I2	2.7317(7)	Cd2−I4	2.8519(7)
Cd1−I3	2.8617(8)	Cd2−I5	2.7368(7)
Cd1−I4	2.8709(7)	Cd2−I6	2.7163(8)
K1···K2	5.083(2)		
O1−K1−O2	60.41(12)	O5−K2−O6	60.40(13)
O1−K1−O4	126.80(12)	O6−K2−S2	64.51(11)
O2−K1−S1	63.16(10)	O7−K2−S2	61.49(10)
O3−K1−S1	63.09(10)	O8−K2−O5	126.25(13)
O4−K1−O3	60.10(13)	O8−K2−O7	60.93(13)
I1−Cd1−I2	119.69(3)	I4−Cd2−I3	95.74(2)
I1−Cd1−I3	112.93(3)	I5−Cd2−I3	109.29(2)
I1−Cd1−I4	107.55(2)	I5−Cd2−I4	111.89(2)
I2−Cd1−I3	106.17(2)	I6−Cd2−I3	109.65(3)
I2−Cd1−I4	112.50(3)	I6−Cd2−I4	112.73(3)
I3−Cd1−I4	95.38(2)	I6−Cd2−I5	115.67(3)

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 2

Ag1−S1	2.595(2)	Ag2−S2	2.521(2)
Ag1−O1	2.702(5)	Ag2−O5	2.858(5)
Ag1−O2	2.546(5)	Ag2−O6	2.619(6)
Ag1−O4	2.565(5)	Ag2−O8	2.776(5)
Ag1···C32	2.859(7)	Ag2···C24	2.733(7)
Ag1···C33	2.868(7)	Ag2···C25	2.612(7)
Ag1···C34	3.074(7)	Ag2···C26	2.951(7)
Ag1···O3	3.908(5)	Ag2···O7	3.249(6)
Ag1···C19	3.578(7)	Ag2···C11	3.909(8)
Ag1···C20	3.410(7)	Ag2···C12	3.813(8)
Ag1···C21	3.466(7)	Ag2···C13	3.810(8)
Ag1···Ag2	5.278(1)		
O2−Ag1−S1	75.51(13)	S2−Ag2−O6	77.62(13)
O2−Ag1−O1	63.14(15)	S2−Ag2−O8	99.10(11)
O4−Ag1−S1	92.75(12)	O6−Ag2−O5	61.21(16)
O4−Ag1−O1	125.67(14)	O8−Ag2−O5	115.50(14)



(a) (b)

(c)

Figure 2. Closer views of $M^+\cdots\pi$ interactions (dashed lines) in (a) **1** (M = K), (b) **2** (M = Ag), and (c) comparison of their distances.

corresponding heterometallic (K^+/M^{n+}) complex. This was achieved by employing Hg^{2+} in place of Cd^{2+}. On changing from CdI_2 to HgI_2 in a one-pot reaction with **L**, we obtained the heterometallic product. Thus, treatment of **L** with KI in the presence of HgI_2 afforded the 2-D framework species **3**, $[K_2\mathbf{L}Hg_4I_{10}]_n$ (Figure 3 and Table 3). The X-ray analysis revealed that **3** is made up of a 2-D network with neutral charge by cross-linking of 1-D "wavy" $-HgI_2-I-HgI-I-$ backbones with endocyclic dipotassium(I) complex $[K_2\mathbf{L}]^{2+}$ units via Hg−S bonds. The asymmetric unit of **3** consists of a half molecule of **L**, one K^+, two Hg^{2+}, and five I^-. In the resulting 2-D structure, the single block unit contains two $[K_2\mathbf{L}]^{2+}$, ten Hg^{2+}, and twenty six I^- (Figure 3b). Again, the potassium(I) ion that lies inside the crown cavity is four-coordinate, being bound to four oxygens. In this case, the K···S distance (3.186 Å) and the $K^+\cdots K^+$ separation (4.985 Å) are slightly shorter than those in **1**. The K^+ in **3** is also stabilized by η^3-type cation···π interactions ($K^+\cdots C$ 3.1−3.3 Å, not shown in the Figure 3) similar to those present in **1**.

In **3**, there are two crystallographically independent Hg atoms which are bridged by I atom (I3) with a Hg1−I3−Hg2 angle of 109.6° (Figure 3c). The Hg1 atom has a distorted tetrahedral environment with coordination sites occupied by one bridgehead sulfur donor from **L**, two terminal I atoms and one bridging I atom. The Hg2 atom is also situated in a roughly tetrahedral environment, bonding to two terminal I atoms and two bridging I atoms to provide the wavy backbone. The Hg−S bond length [2.759(2) Å] falls into the longer end of the normal range (2.5−2.8 Å)[11] for similar reported system. No solvent molecules are present in the crystal lattice. The size of each brick is ca. 13.8 × 15.1 Å.

The KI/HgI_2 complex **3** shows that the anion as a second coordinating species has a remarkable influence on the structure of the resulting product. Recently, one $Cu(NO_3)_2/HgI_2$ heteronuclear 1-D network complex of an NS_4-donor macrocycle with an endo/exo coordination mode has been reported by us.[12] As we understand, **3** is the first characterized

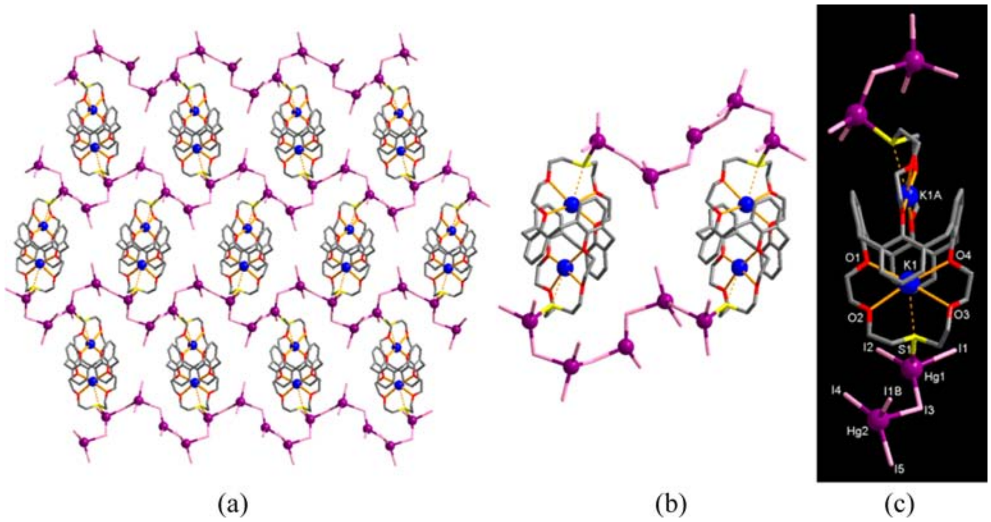


Figure 3. (a) 2D polymeric network **3**, $[K_2LHg_4I_{10}]_n$, (b) one block unit, and (c) core coordination component. Hydrogen atoms are omitted.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 3[a]

Hg1−I1	2.9189(6)	Hg1−I2	2.6429(6)
Hg1−I3	2.6803(6)	Hg2−I1B	2.9107(6)
Hg2−I3	3.1756(6)	Hg2−I4	2.6523(6)
Hg2−I5	2.6687(6)	Hg1−S1	2.7589(18)
K1−O1	2.691(5)	K1−O2	2.781(5)
K1−O3	2.93(2)	K1−O4	2.680(5)
K1···S1	3.186(2)		
K1···C11A	3.211(7)	K1···C19	3.317(7)
K1···C12A	3.150(7)	K1···C20	3.218(7)
K1···C13A	3.271(7)	K1···C21	3.293(7)
K1···K1A	4.985(2)		
S1−Hg1−I1	90.00(4)	I2−Hg1−S1	99.07(4)
I2−Hg1−I1	105.729(18)	I2−Hg1−I3	138.52(2)
I3−Hg1−S1	101.62(4)	I3−Hg1−I1	109.792(18)
I4−Hg2−I3	99.964(18)	I4−Hg2−I5	140.70(2)
I4−Hg2−I1B	108.959(19)	I5−Hg2−I3	93.140(18)
I5−Hg2−I1B	102.74(2)	I1A−Hg2-I3	105.585(17)
O1−K1−O2	60.94(13)	O2−K1−S1	61.85(11)
O3−K1−S1	59.8(4)	O4−K1−O1	127.97(14)
O4−K1−O3	57.6(4)		

[a] Symmetry operations: (A) $-x + 1, y, -z + 3/2$; (B) $-x + 1/2, -y + 1/2, z + 1/2$.

dinuclear macrocyclic complex exhibiting an infinite 2D connectivity pattern via the heterometal as well as anion.

NMR Study of the Competition Reactions of K^+ and Ag^+ toward L. To investigate the complexation behavior for dipotassium(I) and disilver(I) complexes of **L** in solution, we monitored the competition reactions of these two ions toward **L** by ^1H NMR. First, the ^1H NMR spectra of **L** were observed upon stepwise addition of KI (0−2.18 equiv.) (Figure 4 and Figure S3 in the Supporting Information).

The signals of the aromatic protons in **L** are well-resolved and readily identified, suggesting that a stable 1,3-alternate conformation occurs in solution [see the spectrum in Figure 4A-a; proton *a*: a doublet at lower field (marked in red); proton *b*: a triplet at higher field (marked in blue)]. Additions of 0.58 equiv. (Figure 4A-b) and 1.02 equiv. (Figure 4A-c) of K^+ to the solution of **L** led to two new sets of peaks at lower field: one set is denoted with primes (a' and b') to indicate the corresponding protons near the empty O_4S ring in the monopotassium(I) complex $[K\mathbf{L}]^+$ and another set denoted with the subscript K (a_K and b_K) indicate the corresponding protons near the K^+-filled O_4S ring in the same species (see top of Figure 4B). The latter set appears at lower field than that of the former due to complexation to the metal ion. This observation is in accord with free **L** and $[K\mathbf{L}]^+$ coexisting in this mole ratio range and that the exchange between them is slow on the NMR time scale (300 MHz, see the proposed corresponding slow exchange equilibrium at the top of Figure 4B).

Notably, the further addition of K^+ above the 1.46 equiv. (Figure 4A-d-g) led to the disappearance of the peaks for free **L** (denoted with *a* and *b*). Instead, a new set of peaks (denoted with subscript KK) appeared at a lower field which are assigned to the corresponding protons in the dipotassium(I) complex $[K_2\mathbf{L}]^{2+}$ formed in this mole ratio range.

Also this observation is in keeping with presence of the slow exchange between $[K\mathbf{L}]^+$and $[K_2\mathbf{L}]^{2+}$ (bottom of Figure 4B). The existence of the peaks corresponding to free **L** at 1.02 equiv. (see Figure 4A-c) and $[K\mathbf{L}]^+$ at 2.04 equiv. (see Figure 4A-f) suggest that the stepwise complexation of hard potassium(I) does not occur completely under the conditions employed due to the presence of a soft sulfur donor in each crown ring. As expected, the stepwise reaction from $[K\mathbf{L}]^+$ to $[K_2\mathbf{L}]^{2+}$ is less complete than that from **L** to $[K\mathbf{L}]^+$.

The competition complexation studies of **L** in the presence of potassium(I) and silver(I) (as hexafluorophosphate) were performed by ^1H NMR to obtain the further information on the behavior of the dipotassium(I) complexation of **L** and also the reactivity of the O_4S crown rings toward the hard and soft metal ion species (Figure 5 and Figure S4 in the Supporting Information).

First, the complexation of silver(I) proceeds by a two step process. As shown in Figure 5A-b, the addition of 1.0 equiv. of silver(I) causes downfield shifts for H_a and H_b. On addition of one additional equiv. of silver(I), further downfield shifts of each peak were observed, in keeping with the formation of a disilver(I) species $[Ag_2\mathbf{L}]^{2+}$ (Figure 5A-c). Unlike the mono- and dipotassium(I) complexation of **L** shown in Figure 4, the spectra indicate that mono- and disilver(I) complexation equilibria undergo fast exchange on the NMR time scale (see

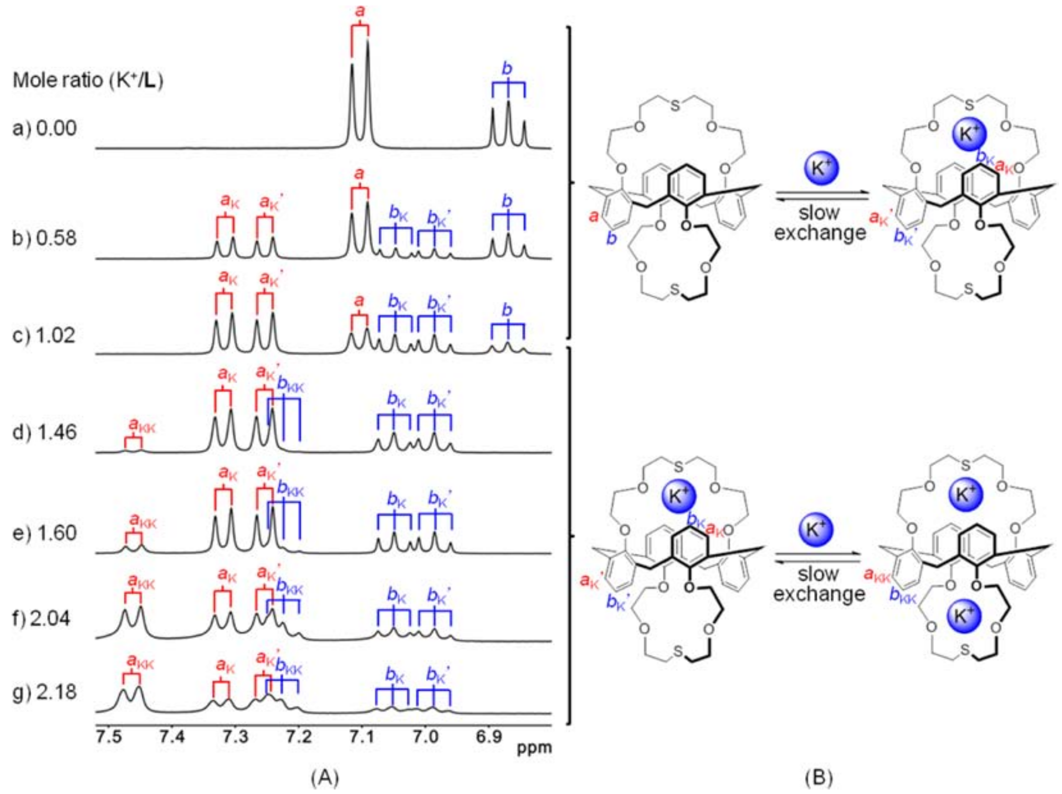


Figure 4. (A) Potassium(I)-induced ^{1}H NMR spectra of the aromatic region for **L** in $CD_3CN/CDCl_3/CD_3OD$ (v/v 6:3:1): [**L**] = 10 mM, KI (0–2.18 equiv.) and (B) the proposed equilibria with slow exchange in each mole ratio region.

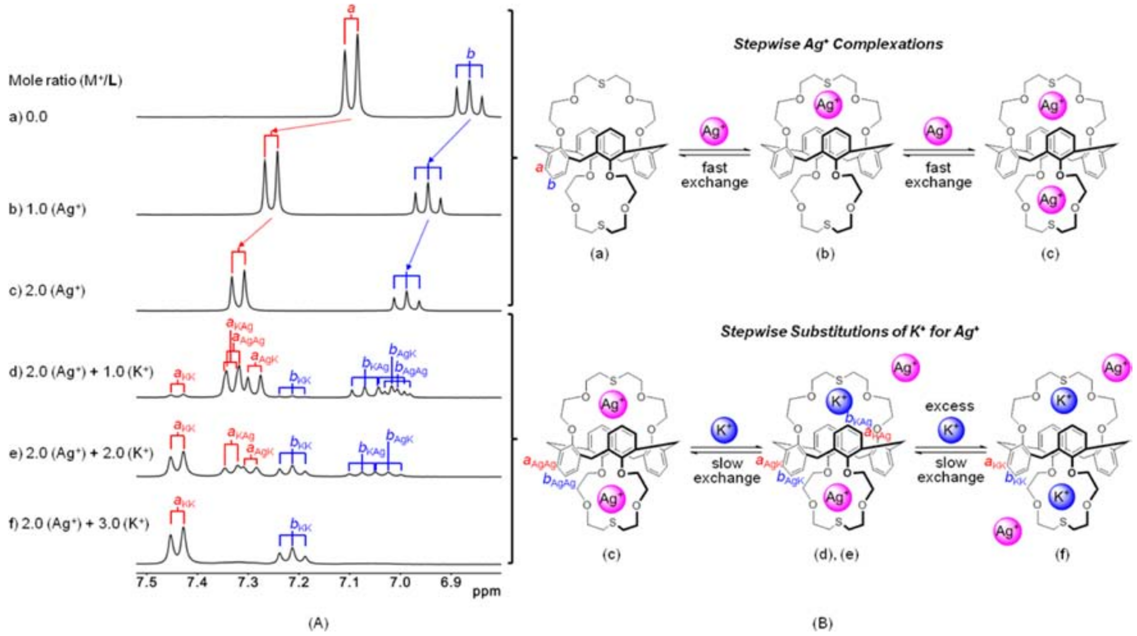


Figure 5. (A) Stepwise soft (Ag^+) and hard (K^+) metal ions-induced ^{1}H NMR spectra of the aromatic region for **L** in $CD_3CN/CDCl_3$ (v/v 7:3): [**L**] = 10 mM and (B) the proposed equilibria between corresponding species with fast or slow exchange in each mole ratio region.

the top of Figure 5B). Further, the addition of 1.0 equiv. of potassium(I) to the above disilver(I) complex solution led to three new sets of peaks (denoted with subscripts KAg, AgK and KK) near each disilver(I) complex peak (denoted with subscript AgAg) (Figure 5A-d). This observation is in accord with the formation of heterodinuclear $[AgLK]^{2+}$ as well as a dipotassium(I) $[K_2L]^{2+}$ species. In this case, the three possible dinuclear complexes $[Ag_2L]^{2+}$, $[AgLK]^{2+}$, and $[K_2L]^{2+}$ appear to coexist with their respective exchange processes being slow on the NMR time scale. On addition of one more equivalent of potassium(I), the signals for the disilver(I) complex (denoted with subscript AgAg) disappeared and, instead, the dipotassium(I) complex peaks (denoted with subscript KK) increase in intensity (Figure 5A-e). Interestingly, the addition of 3.0 equiv. of potassium(I) led to the above more complicated spectral pattern being reduced to two simple peaks, suggesting that the proposed competition reactions finally reach the formation of the dipotassium(I) species $[K_2\mathbf{L}]^{2+}$ (Figure 5A-f). Comparative NMR experiments for the competition system discussed above were also performed under conditions involving the reverse order of salt addition (see Figures S5 and S6 in the Supporting Information). From these results, the two potassium(I) ions which were added first are accommodated in two O_4S rings in a stepwise manner. The silver(I) then added resulted in almost no influence on the peak patterns for the dipotassium(I) complex. Once again, this result agrees with potassium(I) showing a higher affinity to **L** than silver(I), similar to the result suggested in the solid state.

■ CONCLUSION

We present the synthesis and crystal structures of the dipotassium(I) and disilver(I) complexes of **L** as representative complexes of hard and soft metals, respectively. The solution behaviors for the two dinuclear complexes were also investigated in a comparative NMR. Both in the solid and solution states, we demonstrated that potassium(I) shows a higher affinity to **L** than silver(I). In the solid state, the dipotassium(I) complex forms a unique 2D network in which an exocyclic mercury(II) iodide cluster backbone cross-linked by dipotassium(I) complex units.

■ EXPERIMENTAL SECTION

General. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. The ^1H NMR spectra were recorded by using a Bruker Advance-300 (300 MHz) NMR spectrometer. Mass spectra were obtained by using a Thermo Scientific LCQ Fleet spectrometer and JEOL JMS-700 spectrometer. The FT-IR spectra were measured by using a Thermo Fisher Scientific Nicolet *i*S 10 FT-IR spectrometer. The elemental analysis was carried out by using a LECO CHNS-932 elemental analyzer.

CAUTION! Perchlorate salts of metal complexes are potentially explosive and should be handled with great care.

Preparation of 1, $[K_2L][Cd_2I_6]CH_2Cl_2$. Cadmium iodide (13.4 mg, 32.3 mmol) and potassium iodide (5.7 mg, 32.3 mmol) in acetonitrile (1 mL) was added to a solution of **L** (10.6 mg, 12.9 mmol) in dichloromethane (1 mL). Slow evaporation of the solution afforded a colorless crystalline product suitable for X-ray analysis. Yield: 40%. Mp: 287−290 °C (decomp.). IR (KBr pellet): 2935, 2866, 2358, 1446, 1357, 1247, 1198, 1113, 1091, 1038, 1007, 926, 825, 777 cm^{-1}. Anal. Calcd for $[C_{44}H_{52}Cd_2K_2I_6O_8S_2]$: C, 28.76; H, 2.85; S, 3.49. Found: C, 29.16; H, 2.90; S, 3.26%. Mass spectrum *m*/*z* (ESI): 425.17 $[K_2(\mathbf{L})]^{2+}$.

Preparation of 2, $[Ag_2L](ClO_4)_2\cdot CH_3OH\cdot H_2O$. Silver perchlorate (6.8 mg, 32.3 mmol) in methanol (0.5 mL) was added to a solution of **L** (10.1 mg, 12.9 mmol) in dichloromethane (0.5 mL). The reaction mixture was stirred and slow evaporation of the solution afforded a colorless crystalline product suitable for X-ray analysis. Yield: 41%. Mp: 259−260 °C (decomp.). IR (KBr pellet): 2928, 1633, 1449, 1357, 1294, 1248, 1197, 1120, 1090, 926, 891, 825, 779, 623 cm^{-1}. Anal. Calcd for $[C_{44}H_{56}Ag_2Cl_2O_{18}S_2]$: C, 43.19; H, 4.61; S, 5.24. Found: C, 42.98; H, 4.36; S, 5.22%. Mass spectrum *m*/*z* (FAB): 493.11 $[Ag_2(\mathbf{L})]^{2+}$.

Preparation of 3, $[K_2LHg_4I_{10}]_n$. A small amount of toluene was added to a dichloromethane (1 mL) solution of **L** (10.3 mg, 12.9 mmol); then the required mercury(II) iodide (29.4 mg, 64.7 mmol) and potassium iodide (5.7 mg, 32.3 mmol) in methanol was layered on the toluene phase; the (layered) mixture afforded a yellow crystalline product suitable for X-ray analysis. Yield: 60%. Mp: 268−270 °C (decomp.). IR (KBr pellet): 2935, 2866, 1445, 1360, 1246, 1198, 1111, 1088, 1038, 1006, 925, 826 cm^{-1}. Anal. Calcd for $[C_{46}H_{60}Hg_4K_2I_{10}O_{10}S_2]$: C, 18.50; H, 2.02; S, 2.15. Found: C, 18.62; H, 1.80; S, 2.11%.

X-ray Crystallographic Analysis. Crystal data for **1**−**3** were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo K*α* radiation (λ = 0.71073 Å) generated by a rotating anode. The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 36 collected frames). Data collection, data reduction, and semiempirical absorption correction were carried out using the software package of APEX2.[13] All of the calculations for the structure determination were carried out using the SHELXTL package.[14] In all cases, all nonhydrogen atoms were refined anisotropically and all hydrogen atoms except coordinated water molecules were placed in idealized positions and refined isotropically in a riding manner along with their respective parent atoms. Relevant crystal data collection and refinement data for the crystal structures of **1**−**3** are summarized in Table S1 in the Supporting Information. In the crystal of compound **3**, O3 and C7 atoms in the crown ring were disordered into two positions, respectively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete NMR titration data. CCDC 929675 (**1**), 938988 (**2**), and 929676 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sslee@gnu.ac.kr (S.S.L.).

Notes

The authors declare no competing financial interest.

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