

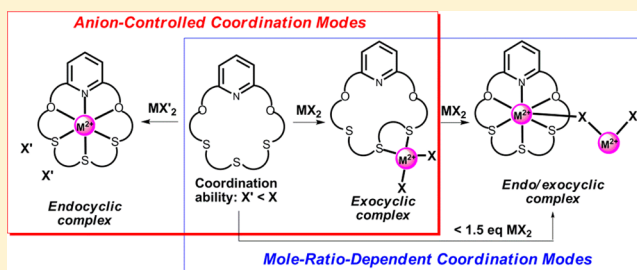
Cooperative Effect of Anion and Mole Ratio on the Coordination Modes of an  $\text{NO}_2\text{S}_3$ -Donor Macrocyclic

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## Supporting Information

**ABSTRACT:** Synthesis of an  $\text{NO}_2\text{S}_3$ -macrocyclic (**L**) incorporating a pyridine subunit and its anion and/or mole ratio-dependent coordination modes in the formations of mercury(II) complexes is reported. When the mercury(II) salts with different anions ( $\text{ClO}_4^-$  or  $\text{Br}^-$ ) were reacted with **L**, the  $\text{Hg}(\text{ClO}_4)_2$  afforded a typical endocyclic complex  $[\text{HgL}](\text{ClO}_4)_2$  (**1**). Meanwhile, the  $\text{HgBr}_2$  gave an exocyclic complex  $[\text{HgLBr}_2]$  (**2**) in which the metal ion exists outside the macrocyclic cavity. The observed anion effect on the coordination modes can be explained by the anion coordination ability toward the metal cation. In the mole ratio variation experiments, notably, the use of 1.5 equiv or above of  $\text{HgBr}_2$  in the same reaction condition gave a unique endo/exocyclic dumbbell-type complex **3**,  $[\text{Hg}_4\text{L}_2\text{Br}_6][\text{Hg}_2\text{Br}_6]$ . However, the formation of the endocyclic  $\text{Hg}(\text{ClO}_4)_2$  complex **1** shows no mole ratio dependency. To monitor the observed mole ratio-dependent exocoordination products as well as their reactivities and reversibility, systematic powder X-ray diffraction (PXRD) analysis was also applied. From single crystal X-ray and PXRD analyses, it was found that endocyclic complex **1** is not reactive, but complexes **2** and **3** are reactive and show the reversibility between them in the presence of the corresponding reactants.



## INTRODUCTION

Over the years, most macrocyclic ligands have been employed for endocyclic coordination (metal-in-cavity) toward the central metal ion species.<sup>1</sup> Thiamacrocyclics, however, frequently form exocyclic complexes in which the metal ion species exist outside the cavity because of the preferential exocyclic orientation of the sulfur donors respect to the cavity.<sup>2–6</sup> Because of this reason, the exocyclic coordination of macrocyclic ligands has proved to be a useful strategy for generating both discrete<sup>7a</sup> and polymeric<sup>7b</sup> metallo-supramolecular species that often exhibit unusual structures.

We have previously reported the exocoordination-based discrete and network structures of supramolecular complexes incorporating thiamacrocyclics, with such systems being attractive, not only because of their unusual topologies<sup>8</sup> but also because of their application as photophysical sensors.<sup>9</sup>

Our initial motivations to utilize exocoordination were that the isolated products are readily influenced by several factors involving ligands (donor atom) and anions that we can control. We have reported the anion-controlled endo- and exocyclic silver(I) complexes with an  $\text{O}_3\text{S}_2$ -macrocyclic, which are explained by the different anion coordination ability toward the metal cation.<sup>10</sup> On the other hand, we have introduced a mercury(II)-selective chromoionophoric macrocyclic exhibiting anion-controlled color changes due to the formation of endo- or exocyclic complexes depending on the coordination ability of the anions.<sup>9a</sup> Recently, a sulfur-rich macrocyclic incorporating one pyridine subunit and its  $\text{Hg}(\text{II})/\text{Cu}(\text{II})$  heteronuclear one-

dimensional (1D) network complex with an endo-/exocyclic coordination mode have also been introduced by us.<sup>11</sup>

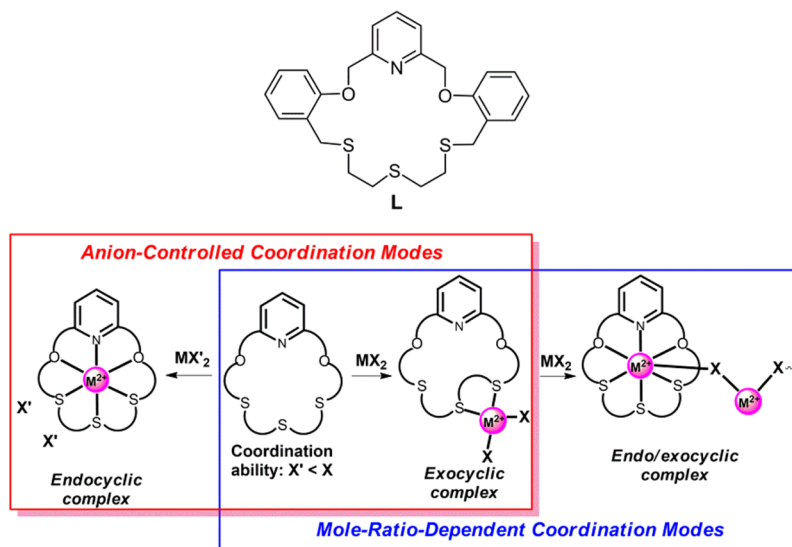
In the course of our ongoing studies to explore the controlling factors of the coordination modes for the macrocyclics,<sup>7b</sup> we have been interested in extending our research to involve a ligand- and anion-directed approach in terms of crystal engineering. In this work, we therefore proposed a sulfur-rich mixed donor macrocyclic **L** which employs a pyridine subunit to accommodate one metal cation in the cavity and two additional benzo subunits to enhance the structural rigidity (Chart 1). The 20-membered macrocyclic **L** is somewhat semiflexible due to the consecutive thioether segment as bridge heads for the required exocoordination, and this seems to induce the diversity of the coordination modes across their respective complexes.

For example, on coordination of a soft metal salt with a noncoordinating anion to the pyridine as well as other donors, **L** might be expected to favor the endocyclic product.<sup>11</sup> In contrast, a soft metal salt with a coordinating anion in the same condition could result in the formation of the exocyclic one. When the pyridine and the semiflexible nature of **L** associated with the thioether linkage are considered together, however, it is difficult to predict the coordination behavior in the presence of an excess amount of the reactants (e.g., mercury(II) salt). On the basis of this assumption, we have suggested whether minor factors such as the mole ratio of the reactants (that is, the

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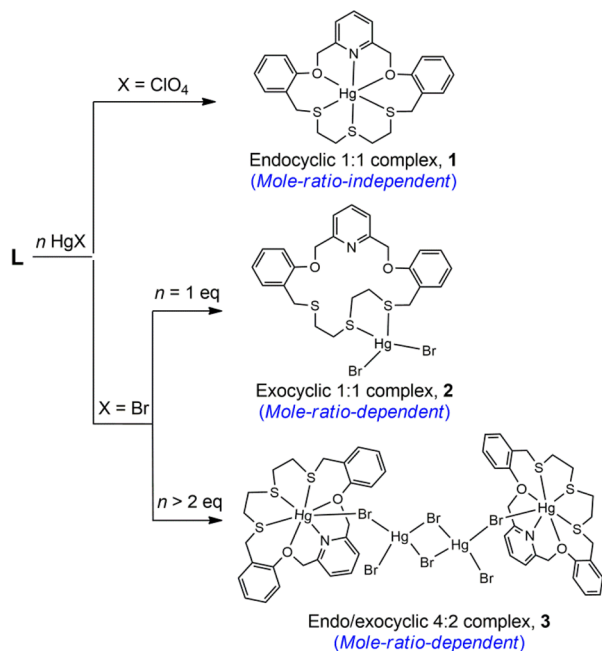
Chart 1. Diagram of Cooperative Effect of Anion and Mole Ratio on the Endocyclic and the Exocyclic Coordination Modes



metal-to-ligand ratio) might be employed to control the nature of the resulting complex type.<sup>12</sup> Furthermore, the mole ratio dependency on the formation of macrocyclic complexes has not been systematically investigated so far. Thus, we have coupled the anion approach with the use of the mole ratio variation to understand the controlling factors of the coordination mode of the proposed macrocycle.

In this work, we have prepared two mercury(II) complexes (1 and 2) of L with different coordination modes, depending on the anions ( $\text{ClO}_4^-$  and  $\text{Br}^-$ ) (Scheme 1). Interestingly, on increasing the mole ratio of  $\text{HgBr}_2$ , a new complex with the endo-/exocyclic coordination was isolated. However, the formation of the endocyclic product ( $\text{ClO}_4^-$  form) shows no mole ratio dependency. The structural characteristics of the complexes of L with the different coordination modes have

Scheme 1. Hg(II) Complexes of L, Showing Different Coordination Modes Depending on Anions and Mole Ratios



been probed by X-ray analysis. Powder X-ray diffraction (PXRD) analysis has also been applied to monitor the observed mole ratio dependent exocoordination products. To the best of our knowledge, the observation of mole ratio-dependent products coupled with such coordination mode has not been reported previously.

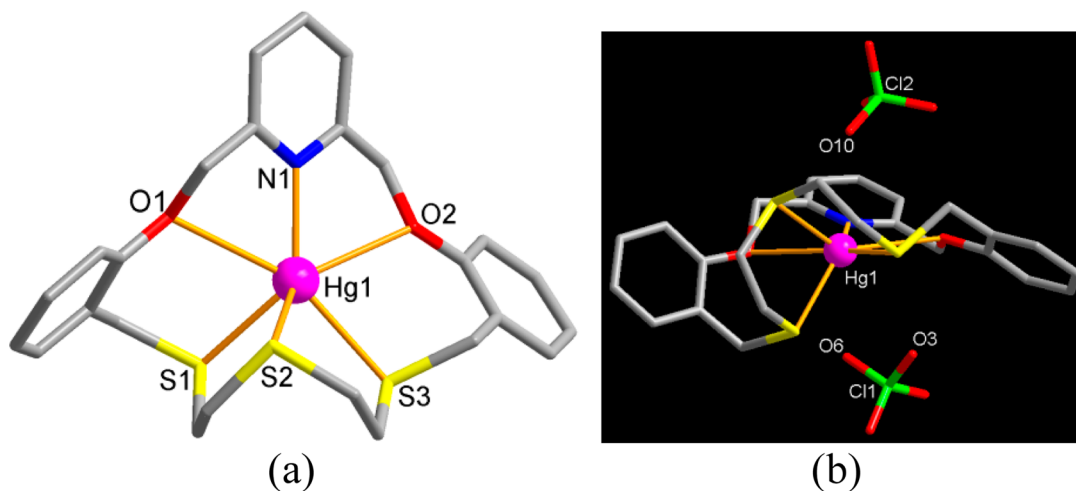
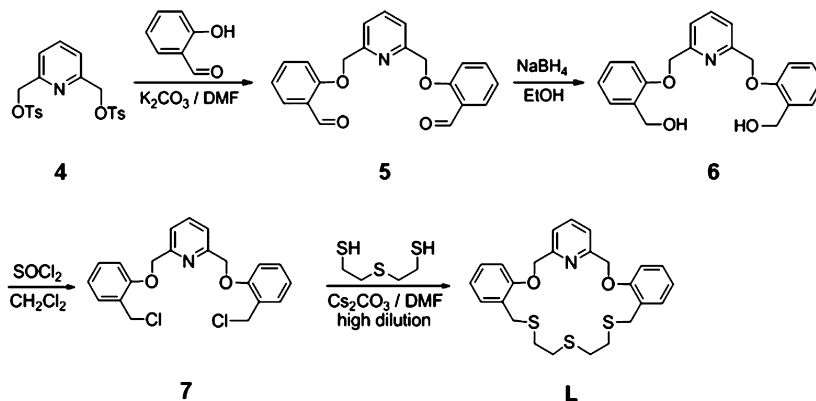
## RESULTS AND DISCUSSION

**Synthesis of Macrocyclic Ligand (L).** Synthesis of the target macrocycle L involved four steps starting from ditosylate 4 (Scheme 2), with each step proceeding smoothly in reasonable yield. Dichloride 7 was prepared from dialdehyde 5 and dialcohol 6 using a known procedure.<sup>13</sup> L was obtained by coupling macrocyclization reaction between 7 and dithiol in the presence of  $\text{Cs}_2\text{CO}_3$  under high dilution condition; a reasonable yield was obtained (25%). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Figure S6, Supporting Information) together with elemental analysis and mass spectra were all in clear agreement with the proposed structures.

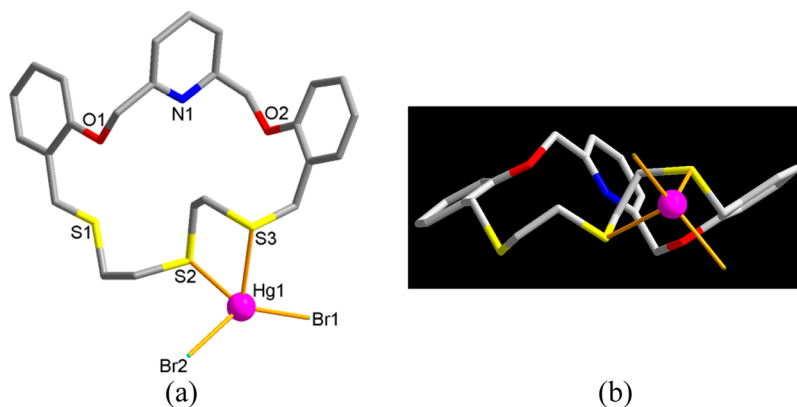
**Anion-Dependent Endo- and Exocyclic Complexes (1 and 2).** In an attempt to examine the anion dependency on the coordination modes of the mercury(II) complexes of L,  $\text{Hg}(\text{ClO}_4)_2$  and  $\text{HgBr}_2$  were used. L dissolved in dichloromethane was treated with 1 equiv of each mercury(II) salt in acetonitrile. Slow evaporation of the solutions afforded the crystalline products of 1 ( $\text{ClO}_4^-$  form) and 2 ( $\text{Br}^-$  form) suitable for X-ray analysis. Using these reaction systems, two complexes were prepared and structurally characterized (Figures 1 and 2).

The X-ray analysis revealed that 1 is a typical endocyclic mononuclear complex of formula  $[\text{HgL}](\text{ClO}_4)_2$  in which a mercury(II) ion is accommodated inside the macrocyclic cavity (Figure 1a). In 1, the mercury(II) center in the cavity is six-coordinate, being bound to all donor atoms from L, adopting a “tight-and-twisted” conformation. The Hg–S bond distances in 1 [2.5730(14)–2.6987(13) Å] are typical, and those of the Hg–O bonds [Hg1–O1 2.817(4) and Hg1–O2 2.790(3) Å] show somewhat elongated distances because of the larger cavity size of L for the mercury(II) complexation. The pyridine nitrogen appears to bind strongly to the mercury(II) center [Hg1–N1 2.221(4) Å], which largely contributes to the

Scheme 2. Synthesis of L



**Figure 1.** The mercury(II) perchlorate complex **1**,  $[\text{HgL}](\text{ClO}_4)_2$ , showing an endocyclic coordination mode: (a) front view (anions were omitted) and (b) side view.

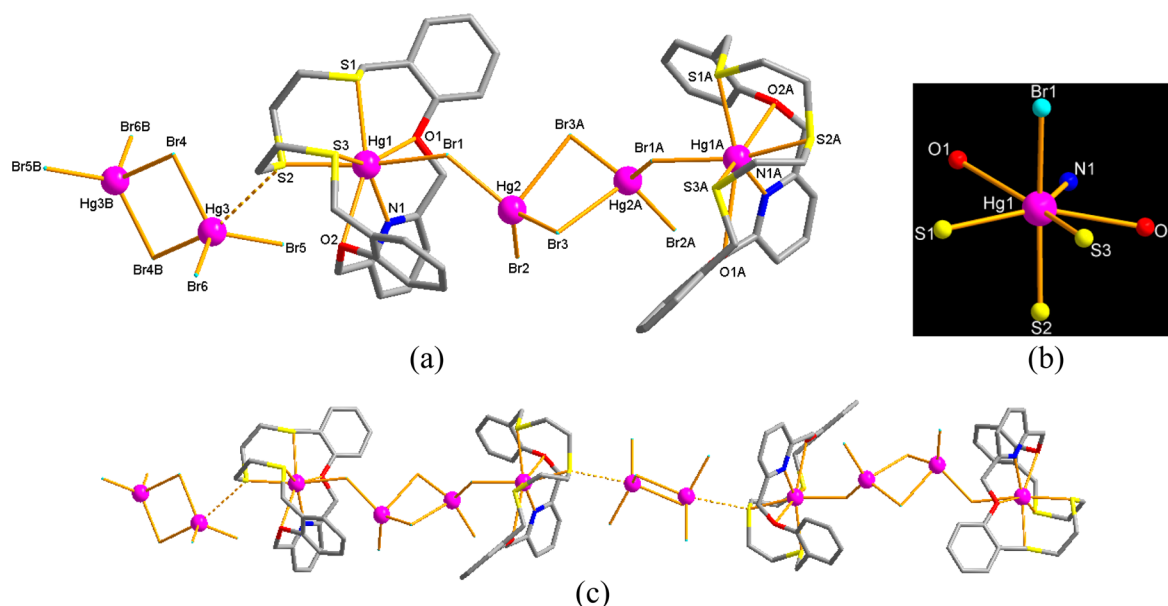


**Figure 2.** The mercury(II) bromide complex **2**,  $[\text{HgLBr}_2]$  showing an exocyclic coordination mode: (a) front view and (b) side view.

formation of the endocyclic complex with thiamacrocycles. The mercury(II) coordination in **1** cannot be described simply in terms of a regular geometry. The perchlorate anions in **1** remain uncoordinated, with the closest distance between the Hg and O atoms being av. 3.236(6) Å (Figure 1b). The adoption of this preferred anion/solvent-uncoordinated endocyclic mode in **1** is associated with the weaker coordinating affinity of the anion and solvent molecules themselves. Unlike other complexes obtained in this work

(see below), **1** shows no reactivity with the excess amount of reactants such as  $\text{Hg}(\text{ClO}_4)_2$  or **L** in solution.

A single crystal X-ray analysis revealed that **2** crystallized in the monoclinic space group  $P2_1/c$ . In marked contrast to the metal ion position in **1**, the bromide complex **2** shows an exocoordinated species of formula  $[\text{HgLBr}_2]$  (Figure 2). In this case, the Hg atom lies outside the cavity. Unlike the six-coordinate Hg center in **1**, the Hg1 atom in **2** is four-coordinate being bonded by two S donors (S2 and S3) from one **L** and two bromide ions to form a distorted tetrahedral



**Figure 3.** Crystal structure of mercury(II) bromide complex **3**,  $[\text{Hg}_4\text{L}_2\text{Br}_6][\text{Hg}_2\text{Br}_6]$ : (a) the dumbbell-type complex part and  $[\text{Hg}_2\text{Br}_6]$  part showing a weak interaction, (b) coordination environment of the endocyclic Hg1 atom showing a distorted pentagonal bipyramidal geometry, and (c) the pseudo-one-dimensional structure via the  $\text{Hg3}\cdots\text{S2}$  interaction (dashed lines, 3.528 Å).

environment, with tetrahedral angles falling in the range  $79.82(5)^\circ$  for  $\text{S3}-\text{Hg1}-\text{S2}$  to  $135.64(3)^\circ$  for  $\text{Br2}-\text{Hg1}-\text{Br1}$ . These large deviations are due to the formation of the presence of the five-membered chelate ring  $[\text{Hg1}-\text{S2}-\text{C}-\text{C}-\text{S13}]$  via two  $\text{Hg}-\text{S}$  bonds. The two O, one N, and one S (S1) donors remain uncoordinated. The  $\text{Hg}-\text{S}$  bond distances [ $\text{Hg1}-\text{S2}$  2.7329(17) and  $\text{Hg1}-\text{S3}$  2.6664(17) Å] are slightly longer than those in **1** [av. 2.6996(9) Å]. The  $\text{Hg}-\text{Br}$  bond distances [ $\text{Hg1}-\text{Br1}$  2.5066(9) and  $\text{Hg1}-\text{Br2}$  2.5002(8) Å] are typical. With respect to the anion-coordination ability, the preferred exocoordination mode of **2** is due to the stronger affinity of the  $\text{Br}^-$  ion toward the Hg center, inducing the metal positioned outside the cavity.

Recently, some examples of anion-controlled endo- and exocyclic silver(I)<sup>10</sup> and mercury(II)<sup>9a</sup> complexes with the macrocycles have been reported by us. Such anion-dependent endo- and exocoordination modes in the macrocycles are still rare.

**Mole Ratio-Dependent Coordination Modes: An Endo-/Exocyclic Complex (3).** The above anion-dependent Hg(II) complexes with different coordination modes encouraged us to study the possible preparation of the corresponding Hg(II) complexes both with the endo- and the exocoordination modes simultaneously. Since the exocyclic mercury(II) bromide complex **2** has an empty cavity, we assumed that the use of excess amount of  $\text{HgBr}_2$  as a reactant can lead to not only the exocoordination but also the endocoordination.

When 2 equiv of mercury(II) bromide was used in the reaction with **L**, as a preliminary condition, a colorless crystalline product **3** was isolated. Compound **3** features a discrete type complex with two separated parts of formula  $[\text{HgL}(\mu_2-\text{Hg}_2\text{L}_6)\text{HgL}][\text{Hg}_2\text{Br}_6]$  (Figure 3): one dumbbell-type macrocyclic mercury(II) complex cation part and one mercury(II) bromide cluster anion part. The asymmetric unit of the macrocyclic complex part contains one **L**, one endocyclic Hg atom (Hg1), one exocyclic Hg atom (Hg2), and three Br atoms.

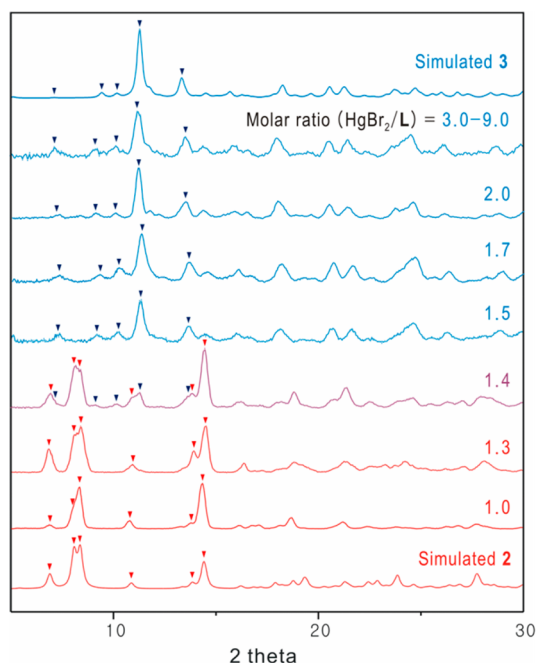
In the macrocyclic complex part, there are two crystallographically independent Hg atoms (Hg1 and Hg2) which are bridged by the Br1 atom to form a dumbbell-shape. The Hg1 atom which locates at the center of the macrocyclic cavity is seven-coordinate, being bound to a  $\text{NO}_2\text{S}_3$ -donor set from **L** in a highly twisted conformation. One remaining site is occupied by one Br atom (Br1). The coordination geometry can be best described as a distorted pentagonal bipyramid with  $\text{NO}_2\text{S}_2$  donors from **L** defining the pentagonal plane, and the axial positions occupied by one remaining sulfur atom (S2) and one Br atom (Br1). The  $\text{S2}-\text{Hg1}-\text{Br1}$  angle is  $165.05(12)^\circ$ .

In **3**, there are two rhomboidal clusters  $[\text{Hg}_2\text{Br}_6]^{2-}$ ; one links the two endocyclic mercury(II) complex units via  $\text{Hg1}-\text{Br1}$  bond [2.768(2) Å] resulting in the formation of the dumbbell-shape and another one is separated from the complex part with  $\text{Hg3}\cdots\text{S2}$  distance of 3.528 Å, which is shorter than the sum of the van der Waals radii.<sup>14</sup> Unlike the typical endo-/exocyclic complexes in which both metals inside and outside the cavity bind to the macrocyclic ligand;<sup>7,10</sup> in this case, the Hg2 atom outside the cavity is not directly coordinated by the macrocycle. The geometric parameters of the both rhomboid-type clusters are similar to those reported previously for this part.<sup>15</sup>

#### Systematic PXRD Studies: Mole Ratio Effect on the Formations of the Exo- and Endo-/Exocyclic Complexes.

The studies on the coordination modes of the products associated with the mole ratio of the reactants were provided by the consecutive PXRD patterns. We performed a series of experiments in the preparation of  $\text{HgBr}_2$  complexes with **L** by varying the mole ratio of  $\text{HgBr}_2/\text{L}$  from 1.0 to 9.0. The resulting PXRD patterns of the products obtained in each mole ratio were recorded and compared with the simulated PXRD patterns of **2** and **3** based on the single crystal X-ray analysis (Figure 4).

When the mole ratios are in the range of 1.0–1.3, the PXRD patterns of the products are coincident with the simulated pattern of the exocyclic complex **2**, suggesting that **2** is an only product in this region. When the mole ratio reaches 1.4, some new peaks (denoted with blue reciprocal triangles) are

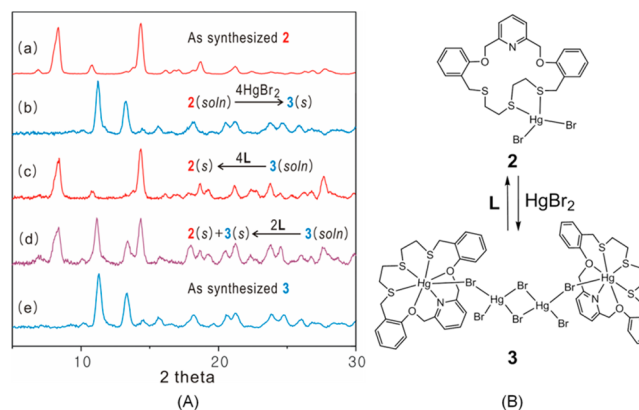


**Figure 4.** PXRD patterns of the products by varying the mole ratio of the reactants ( $\text{HgBr}_2/\text{L} = 1.0\text{--}9.0$ ). The data shown in the bottom and the top represent the simulated PXRD patterns of **2** and **3**, respectively, based on the single crystal X-ray analysis.

observed, which indicate **3**, suggesting a mixture of **2** and **3** was obtained. However, when the mole ratio increased above 1.5, the evidence of **2** disappeared and only **3** was obtained. Thus, we can conclude that as the content of  $\text{HgBr}_2$  increases, the exocyclic product **2** is further reacted with the existing excess salt to form the stable endo/exocyclic species **3**. The observed sudden conversion of the product near the mole ratio 1.4 could be associated with the conformational change of **L** from its flattened form to the highly twisted form as mentioned in Figures 2 and 3 since **L** is somewhat semiflexible.

Over recent years, our group has investigated the rationally designed macrocycles incorporating sulfur donors in conjunction with aromatic subunit to prepare diverse types homo- and heteronuclear endo-/exocyclic complexes from such system. The present result observed is the first case that the endo- and the endo-/exocoordinated macrocyclic complexes can be prepared by varying the mole ratio of the reactants.

**Reactivities and Reversibility of the Complexes.** As mentioned above, the endocyclic complex **1** shows no reactivity with both of the reactants. However, the complexes **2** and **3** which involve the exocyclic mode are reactive with the mercury(II) salt and **L**, respectively. The reversibility between **2** and **3** was examined by analyzing the isolated products for the forward and the reverse reactions in solution (Figure 5). When **2** was reacted with 4 equiv of  $\text{HgBr}_2$  in acetonitrile/dichloromethane, we obtained a colorless precipitate which was identified as **3** by the PXRD data (Figure 5Ab,e). Oppositely, when **3** was reacted with 4 equiv of **L** in the same condition, we confirmed that **2** was obtained as a colorless precipitate (Figure 5Ac,a), suggesting the reversible conversion between **2** and **3** in the presence of the corresponding reactants. Meanwhile, when the amount of  $\text{HgBr}_2$  (in the forward reaction) or **L** (in the reverse reaction) was reduced from 4 to 2 equiv, a mixture of **2** and **3** was obtained in both cases (Figure 5Ad).



**Figure 5.** (A) PXRD patterns for (a) **2**, (b) the solid product (identified as **3**) obtained from the forward reaction of **2** with 4 equiv of  $\text{HgBr}_2$ , (c) the solid product (identified as **2**) obtained from the reaction of **3** with 4 equiv of **L**, (d) The solid products (identified as a mixture of **2** and **3**) obtained from the reaction of **3** with 2 equiv of **L** and (e) **3**. (B) The reversible process between **2** and **3** in the presence of the corresponding reactants. All the reactions were carried out in acetonitrile/dichloromethane.

From the observed reactivities and the reversibility, it is found that the endocyclic complex **1** is not reactive, but both of the complexes **2** and **3** which involve the exocyclic metal ion are reactive. These phenomena might be considered as an indication that such macrocyclic complexes possessing the exocyclic metal ion could function as a metalloligand to undergo further complexation reactions.

## CONCLUSION

We have isolated and structurally characterized the anion-controlled endo- and exocoordinated mercury(II) complexes. Coupled with the observed anion dependency on the coordination modes, we found that the mole ratio of the reactants for the exocoordinated system undergoes further reaction resulting in an interesting endo-/exocoordinated species. The systematic PXRD study supports the observed dependency of the mole ratio as a controlling factor on the coordination modes. In addition, it was found that the endocyclic complex is not reactive, but both of the exo- and endo-/exocyclic ones are reactive and show the reversibility between them in the presence of the corresponding reactants. Hence, the combined approach of single crystal X-ray analysis and PXRD analysis has enabled in-depth information concerning of the coordination mode through changing the mole ratio of the reactants. We consider that the exocoordinated product is promising to be served as a platform or a metalloligand to construct the diverse metallosupramolecules. Further investigations on this and similar systems as well as on the potential applications are currently in progress.

## EXPERIMENTAL SECTION

**General.** All chemicals and solvents used in the syntheses were reagent grade and were used without further purification. Fourier transform infrared (FT-IR) spectra were recorded with a Thermo-Fisher Scientific Nicolet iS 10 FT-IR spectrometer. The elemental analysis was carried out on a LECO CHNS-932 elemental analyzer. The  $^1\text{H}$  NMR spectra were recorded by using a Bruker Advance-300 NMR spectrometer. Mass spectra were obtained by using a Thermo Scientific LCQ Fleet spectrometer.

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

Table 1. Crystallographic Data and Structure Refinement for 1–3

|  | 1   | 2  | 3  |
|--|---|--|--|
| formula                                      | C <sub>25</sub> H <sub>27</sub> HgCl <sub>2</sub> NO <sub>10</sub> S <sub>3</sub> | C <sub>25</sub> H <sub>27</sub> HgBr <sub>2</sub> NO <sub>2</sub> S <sub>3</sub> | C <sub>50</sub> H <sub>50</sub> Hg <sub>6</sub> Br <sub>6</sub> N <sub>2</sub> O <sub>4</sub> S <sub>6</sub> |
| formula weight                               | 869.15  | 830.07   | 3097.74  |
| temperature                                  | 173(2)  | 173(2)   | 173(2)   |
| crystal system                               | orthorhombic  | monoclinic   | monoclinic   |
| space group                                  | P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>                                     | P2 <sub>1</sub> /c   | C2/c   |
| Z  | 4   | 4  | 4  |
| a (Å)  | 12.2583(3)  | 4.9569(4)  | 34.6711(7)   |
| b (Å)  | 13.5867(3)  | 25.526(2)  | 13.2665(3)   |
| c (Å)  | 16.9143(4)  | 21.0651(16)  | 15.1019(3)   |
| α (deg)                                      | 90  | 90   | 90   |
| β (deg)                                      | 90  | 93.611(4)  | 96.8680(10)  |
| γ (deg)                                      | 90  | 90   | 90   |
| V (Å <sup>3</sup> )                          | 2817.07(11)   | 2660.1(4)  | 6896.5(2)  |
| D <sub>calc</sub> (g/cm <sup>3</sup> )       | 2.049   | 2.073  | 2.984  |
| 2θ <sub>max</sub> (deg)                      | 52.00   | 52.00  | 52.00  |
| R <sub>1</sub> , wR <sub>2</sub> [I > 2σ(I)] | 0.0307, 0.0568  | 0.0461, 0.0793   | 0.0710, 0.1966   |
| R <sub>1</sub> , wR <sub>2</sub> [all data]  | 0.0358, 0.0585  | 0.0790, 0.0898   | 0.0863, 0.2088   |
| goodness-of-fit on F <sup>2</sup>            | 0.825   | 1.012  | 1.069  |
| no. of reflection used [>2σ(I)]              | 5537 [R <sub>int</sub> = 0.0414]  | 5207 [R <sub>int</sub> = 0.0770]   | 6793 [R <sub>int</sub> = 0.0545]   |
| structure determination                      | SHELXTL   | SHELXTL  | SHELXTL  |
| refinement                                   | full-matrix   | full-matrix  | full-matrix  |

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 1

|           |            |           |            |
|-----------|------------|-----------|------------|
| Hg1–N1    | 2.221(4)   | Hg1–S1    | 2.5730(14) |
| Hg1–S2    | 2.6987(13) | Hg1–S3    | 2.6204(15) |
| Hg1–O1    | 2.817(4)   | Hg1–O2    | 2.790(3)   |
| N1–Hg1–S3 | 137.14(12) | N1–Hg1–S1 | 128.12(12) |
| N1–Hg1–O2 | 67.76(14)  | N1–Hg1–S2 | 119.32(11) |
| N1–Hg1–O1 | 65.55(13)  | O2–Hg1–O1 | 132.20(11) |
| S1–Hg1–S2 | 83.67(4)   | S1–Hg1–S3 | 88.05(5)   |
| S1–Hg1–O1 | 76.55(8)   | S1–Hg1–O2 | 128.59(8)  |
| S2–Hg1–O1 | 78.24(8)   | S2–Hg1–O2 | 135.94(9)  |
| S3–Hg1–O1 | 156.32(8)  | S3–Hg1–O2 | 71.48(8)   |
| S3–Hg1–S2 | 82.31(4)   |           |            |

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 2

|            |            |             |            |
|------------|------------|-------------|------------|
| Hg1–S2     | 2.7329(17) | Hg1–S3      | 2.6664(17) |
| Hg1–Br1    | 2.5066(9)  | Hg1–Br2     | 2.5002(8)  |
| Br1–Hg1–S3 | 103.23(4)  | Br1–Hg1–S2  | 102.20(4)  |
| Br2–Hg1–S3 | 116.56(4)  | Br2–Hg1–Br1 | 135.64(3)  |
| Br2–Hg1–S2 | 103.33(4)  | S3–Hg1–S2   | 79.82(5)   |

**Synthesis and Characterization of L.** Cesium carbonate (5.05 g, 15.5 mmol) was dissolved in DMF (2000 mL) in a 3 L round-bottom flask. 2-Mercaptoethyl sulfide (1.59 g, 10.3 mmol) and dichloride 7 (4.01 g, 10.3 mmol) were dissolved in DMF (30 mL) and placed in a 50 mL glass syringe. The contents of the syringe were added dropwise at a regular rate (0.6 mL·h<sup>-1</sup>) into the DMF solution under a nitrogen atmosphere with the aid of microprocessor controlled syringe pump at 45–50 °C over 50 h. After being cooled to room temperature, the reaction mixture was filtered and the solvent evaporated. Water (100 mL) was added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate and filtered and the solvent was removed to give yellow crude mixture. Flash column chromatography (SiO<sub>2</sub>, *n*-hexane/ethyl acetate = 8:2) afforded the product as a white solid in 25% yield. Mp: 119–121 °C. IR (KBr, pellet) 3021, 2927, 2873, 1596, 1491, 1450, 1288, 1237, 1097, 1012, 1096, 782, 753 cm<sup>-1</sup>. Anal. Calcd for C<sub>25</sub>H<sub>27</sub>NO<sub>2</sub>S<sub>3</sub>: C, 63.93; H, 5.79; N, 2.98; S, 20.48. Found: C, 63.81; H, 5.94; N, 3.03; S,

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for 3<sup>a</sup>

|              |            |              |            |
|--------------|------------|--------------|------------|
| Hg1–N1       | 2.375(14)  | Hg1–O1       | 2.941(13)  |
| Hg1–O2       | 2.765(13)  | Hg1–S1       | 2.761(6)   |
| Hg1–S2       | 2.641(5)   | Hg1–S3       | 2.710(5)   |
| Hg1–Br1      | 2.768(2)   | Hg2–Br2      | 2.485(3)   |
| Hg2–Br3      | 2.568(3)   | Hg2–Br1      | 2.627(2)   |
| Hg2–Br3A     | 2.924(3)   | Hg3–Br5      | 2.530(2)   |
| Hg3–Br4      | 2.656(2)   | Hg3–Br4B     | 2.8486(19) |
| Hg3–Br6      | 2.530(2)   | Br3–Hg2A     | 2.924(3)   |
| Br4–Hg3B     | 2.8486(19) |              |            |
| Hg2–Br3–Hg2A | 87.13(9)   | Hg2–Br1–Hg1  | 125.56(8)  |
| Hg3–Br4–Hg3B | 90.58(6)   | N1–Hg1–S2    | 99.2(4)    |
| N1–Hg1–S3    | 132.4(4)   | N1–Hg1–Br1   | 94.4(4)    |
| N1–Hg1–S1    | 137.6(4)   | N1–Hg1–O2    | 66.3(5)    |
| N1–Hg1–O1    | 65.3(4)    | O2–Hg1–O1    | 131.7(4)   |
| O2–Hg1–Br1   | 101.6(3)   | S1–Hg1–O2    | 72.3(3)    |
| S1–Hg1–Br1   | 84.74(12)  | S1–Hg1–O1    | 69.7(3)    |
| S2–Hg1–Br1   | 165.05(12) | S2–Hg1–S1    | 81.05(16)  |
| S2–Hg1–S3    | 82.12(15)  | S2–Hg1–O1    | 110.1(3)   |
| S2–Hg1–O2    | 78.5(3)    | S3–Hg1–S1    | 89.83(15)  |
| S3–Hg1–O1    | 154.3(3)   | S3–Hg1–O2    | 155.4(3)   |
| S3–Hg1–Br1   | 93.26(10)  | Br1–Hg1–O1   | 81.2(3)    |
| Br1–Hg2–Br3A | 88.86(8)   | Br2–Hg2–Br3A | 108.28(11) |
| Br2–Hg2–Br1  | 119.30(10) | Br2–Hg2–Br3  | 116.93(11) |
| Br3–Hg2–Br3A | 88.14(9)   | Br3–Hg2–Br1  | 121.53(9)  |
| Br4–Hg3–Br4B | 89.42(6)   | Br4–Hg3–S2   | 74.78(9)   |
| Br4B–Hg3–S2  | 159.01(10) | Br5–Hg3–Br4B | 97.59(7)   |
| Br5–Hg3–S2   | 80.01(10)  | Br5–Hg3–Br4  | 122.22(7)  |
| Br6–Hg3–Br5  | 120.38(7)  | Br6–Hg3–S2   | 89.71(11)  |
| Br6–Hg3–Br4B | 109.05(7)  | Br6–Hg3–Br4  | 110.65(7)  |

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

20.46. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.79–6.91 (11H, aromatic, see Figure S6a, Supporting Information), 5.11 (s, 4H, PyCH<sub>2</sub>O), 3.71 (s, 4H, ArCH<sub>2</sub>S), 2.235 (t, 4H, ArCH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>), 2.23 (t, 4H, ArCH<sub>2</sub>SCH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ) 156.5, 156.2, 137.7,

130.9, 128.5, 127.9, 122.6, 121.7, 112.3, 71.9, 32.4, 31.6, 29.5. Mass spectrum  $m/z$  (ESI): 492.33 (L + Na)<sup>+</sup>.

**Preparation of 1, [HgL](ClO<sub>4</sub>)<sub>2</sub>.** A dichloromethane (1 mL) solution of L (19.9 mg, 0.0424 mmol) was allowed to diffuse slowly into an acetonitrile (1 mL) solution of Hg(ClO<sub>4</sub>)<sub>2</sub> (16.9 mg, 0.0424 mmol) in a capillary tube (i.d. 5 mm). Slow evaporation of the solution gave colorless crystalline **1** that proved suitable for X-ray analysis (yield: 87%). Mp: 217–218 °C (decomp.). IR (KBr pellet): 2991, 2936, 1495, 1456, 1234, 1096 (ClO<sub>4</sub><sup>-</sup>), 805, 765, 735, 623 (ClO<sub>4</sub><sup>-</sup>), 1040, 777 cm<sup>-1</sup>; Anal. Calc for [C<sub>26</sub>H<sub>29</sub>HgCl<sub>4</sub>NO<sub>10</sub>S<sub>3</sub>]: C, 32.72; H, 3.06; N, 1.47; S, 10.08. Found: C, 32.76; H, 3.09; N, 1.70; S, 10.03%. Mass spectrum  $m/z$  (ESI): 335.4 [Hg(L)]<sup>2+</sup>.

**Preparation of 2, [HgBr<sub>2</sub>L].** A dichloromethane (1 mL) solution of L (20.2 mg, 0.0430 mmol) was allowed to diffuse slowly into an acetonitrile (1 mL) solution of HgBr<sub>2</sub> (15.5 mg, 0.0430 mmol) in a capillary tube (i.d. 5 mm). Slow evaporation of the solution gave colorless crystalline **2** that proved suitable for X-ray analysis (yield: 88%). Mp: 148–149 °C (decomp.). IR (KBr pellet): 3059, 2968, 2912, 1591, 1489, 1453, 1245, 1223, 1009, 798, 757, 750 cm<sup>-1</sup>; Anal. Calc for [C<sub>25</sub>H<sub>27</sub>HgBr<sub>2</sub>NO<sub>2</sub>S<sub>3</sub>]: C, 36.17; H, 3.28; N, 1.69; S, 11.59. Found: C, 36.29; H, 3.28; N, 1.66; S, 11.87%. Mass spectrum  $m/z$  (ESI): 749.9 [HgBrL]<sup>+</sup>.

**Preparation of 3, [Hg<sub>4</sub>Br<sub>6</sub>L<sub>2</sub>][Hg<sub>2</sub>Br<sub>6</sub>].** Preparation of **3**, HgBr<sub>2</sub> (20.1 mg, 0.0428 mmol) in acetonitrile was added to a solution of L (30.8 mg, 0.0856 mmol) in dichloromethane (1 mL). Slow evaporation of the solution afforded a colorless crystalline product **3** suitable for X-ray analysis (yield: 83%). Mp: 230–232 °C (decomp.). IR (KBr pellet): 3059, 2914, 1600, 1480, 1456, 1403, 1235, 1223, 1103, 1050, 1036, 790, 765 cm<sup>-1</sup>; Anal. Calc for [C<sub>20</sub>H<sub>34</sub>Hg<sub>6</sub>Br<sub>12</sub>N<sub>3</sub>O<sub>2.5</sub>S<sub>3</sub>]: C, 20.31; H, 1.93; N, 1.75; S, 6.02. Found: C, 20.72; H, 1.86; N, 1.54; S, 6.46%. Mass spectrum  $m/z$  (FAB): 750.1 [HgBrL]<sup>+</sup> (the molecular ion peak is not shown).

**X-ray Crystallographic Analysis.** All data were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo K<sub>α</sub> radiation ( $\lambda = 0.71073$  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.<sup>16a</sup> All of the calculations for the structure determination were carried out using the SHELXTL package.<sup>16b</sup> In all cases, all non-hydrogen 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, Supporting Information.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Analytical data, geometric parameters of crystalline complexes, PXRD patterns, and X-ray crystallographic files (CIFs). This material is available free of charge via the Internet at <http://pubs.acs.org>. The CIF files can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) CCDC Numbers 975092–975094 (for compounds **1–3**) for this paper.

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### ■ Notes

The authors declare no competing financial interest.

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