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Ligand- and Anion-Directed Assembly of Exo-Coordinated Mercury(II) Halide Complexes with O_2S_2-Donor Macrocycles

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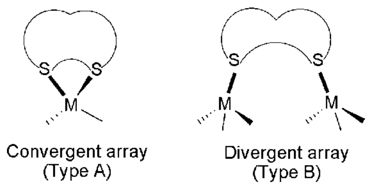
Assembly reactions of mercury(II) halides (Cl, Br, and I) with two O_2S_2 macrocycles (**L**^{1} and **L**^{2}) having different interdonor (S···S) distances were investigated, and four types of supramolecular complexes (**1**−**4b**) were obtained depending on the S···S distances as well as the size of the halide anions. Photoluminescence of these compounds was also studied.

Programmed self-assembly of supramolecular complexes has attracted intense interest for not only their fascinating structural topologies[1] but also potential applications.[2] In the view of ligand-directed metal−organic assembly, a rigid or semirigid bischelating ligand is beneficial in allowing the building of robust and, therefore, predictable products.[3] Nevertheless, to predict a given type of network structure, it is necessary to understand more representative examples.

Recently, we have reported the exo-coordination properties of dithiamacrocycles,[4] which afforded diverse types of supramolecular complexes, upon variation of the donor atoms, counterions, and solvents.[5] Additionally, we have proposed that simple tuning of sulfur-to-sulfur separation in dithiamacrocycles may add one possibility to the controlling factors.[6] The idea is that the length of the aliphatic chain separating two S donors may be effective to discriminate the products because of the different exo-binding modes toward the soft metal ion. For example, if the separation between two S donors is not big enough in the ring, the two S donors will cooperate to chelate one metal (type A; Chart 1). On the other hand, if the separation is large, each S donor tends to coordinate to individual metal ions (type B).

Chart 1



We are interested in extending this idea to a ligand-directed approach to prepare new supramolecular structures. At the same time, we have tried to merge the role of anions[7] (mainly the size effect) in this self-assembly. In this work, we examined the interdonor distances and anion size as combined controlling factors to direct the assembly of mercury(II) complexes. Based on these considerations, we chose two analogous O_2S_2 macrocycles **L**^{1} and **L**^{2} because these two macrocycles are expected to have discriminated sulfur-to-sulfur distances.

The synthesis and crystal structure of **L**^{1} were reported by us previously.[6] **L**^{2} was synthesized by a coupling reaction

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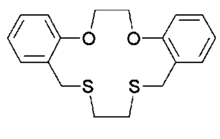
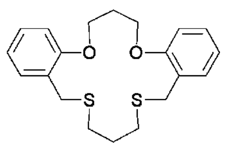


L^1



L^2

for macrocyclization from dibenzodichloride with 1,3-propanedithiol in the presence of Cs_2CO_3 under high dilution conditions in a reasonable yield (38%; see the Supporting Information). The single crystals of $\mathbf{L^2}$ were obtained by slow evaporation of an ethyl acetate solution, and its crystal structure was characterized (Figure 1). In crystal structures, $\mathbf{L^1}$ has an unfolded conformation,[6] but $\mathbf{L^2}$ is folded. In both cases, two O donors are oriented in an endo fashion, while two S donors are positioned exodendate. As expected, the S···S distance in $\mathbf{L^2}$ (5.035 Å) is larger than that of $\mathbf{L^1}$ (4.387 Å).[6]

Macrocyclic mercury(II) halides (X) complexes **1**–**4b** all have the basic mercury(II)-**L**-X_2 stoichiometry of $[Hg\mathbf{L}X_2]_y$ ($y = 1$, 2, or n). Each species was synthesized under slightly different conditions, giving rise to a different structure in each case. Complexes **1** (X = Cl) and **2** (X = I) based on $\mathbf{L^1}$ are discrete di- and mononuclear species, respectively, while complexes **3** (X = Cl) and **4** [**4a** (X = Br) and **4b** (X = I) are isostructural] based on $\mathbf{L^2}$ are both coordination polymers comprised of 1-D chains.

First, $\mathbf{L^1}$ dissolved in methanol/acetonitrile (1:1) was treated with equimolar amounts of mercury(II) halides in methanol, respectively. Slow evaporation of the reaction mixture of $HgCl_2$ and $\mathbf{L^1}$ afforded the single crystals of **1** suitable for X-ray analysis. In the case of HgI_2, a colorless precipitate was obtained, and single crystals of **2** were obtained by vapor diffusion of diethyl ether into a dimethyl sulfoxide solution of this complex. No X-ray-quality single crystals were obtained for $HgBr_2$.

As shown in Figure 2a, the chloro-type complex **1** crystallizes as a cofacial dimeric complex $[Hg_2(\mathbf{L^1})_2Cl_4]$, with two $\mathbf{L^1}$ molecules sandwiching an exodentate Hg−(μ-Cl)$_2$−Hg core.[8] In **1**, each Hg atom that lies outside the cavity is five-coordinate and is bonded to two S atoms of one $\mathbf{L^1}$, forming a five-membered ring. The coordination geometry around the Hg center can be described as a distorted trigonal bipyramid where Cl1, Cl2, and S1 form the trigonal plane while Cl1A and S2 atoms occupy the axial positions (∠S2−Hg1−Cl1A 164.4°).

Unlike **1**, the iodo-type complex **2** shows a half-sandwich-type structure[9] with formula $Hg(\mathbf{L^1})I_2$ (Figure 2b). In **2**, the Hg atom is in a distorted tetrahedral geometry with two coordination sites occupied by two S donors from $\mathbf{L^1}$ in a bent exo arrangement. Two I^- ions occupy two coordination sites on the Hg atom.

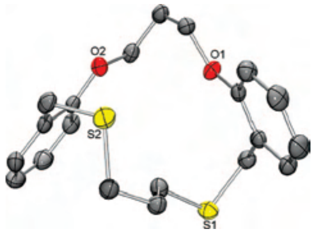
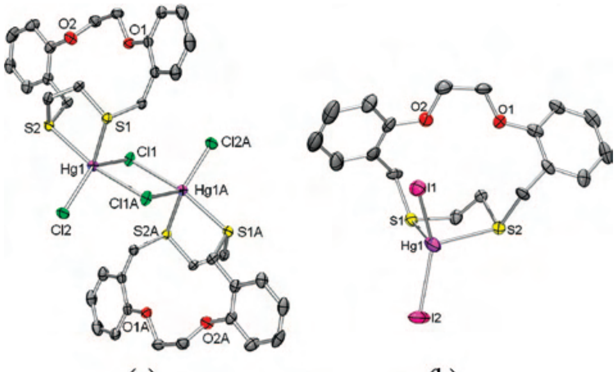


Figure 1. Crystal structure of $\mathbf{L^2}$.



(a) (b)

Figure 2. Crystal structures of (a) a dimercury(II) sandwich-type complex **1** $[Hg_2(\mathbf{L^1})_2Cl_4]$ and (b) a half-sandwich-type complex **2** $[Hg(\mathbf{L^1})I_2]$. Symmetry operations: (A) compound **1**, $2 - x, -y, -z$.

The S···S separation within each ligand is observed as 3.224 Å (for **1**) and 3.488 Å (for **2**). Considering the larger size of the I atom than the Cl atom, the difference is not significant. However, these are much more reduced from that of their free form ($\mathbf{L^1}$ 4.387 Å).[6] The different shapes between **1** and **2** are attributed to the anion size effect.[5] Unlike the dinuclear structure **1** linked with two Cl atoms, the bulk I atoms in **2** are sterically hindered by each other to form a larger molecule. Similar results were also observed for $\mathbf{L^2}$ (see Figure 3). While the half-sandwich-type macrocyclic complexes are not uncommon,[9] the interesting family of such dimercury(II) sandwich complexes based on the thiamacrocycle has not been reported. Consequently, the shorter sulfur-to-sulfur distance (4.387 Å)[6] in $\mathbf{L^1}$ leads to discrete complexes with a type A coordination mode (Chart 1). At the same time, the smaller Cl and larger I atoms resulted in the formation of dimercury(II) sandwich structure **1** and half-sandwich-type complex **2**, respectively, as depicted in Scheme S1 in the Supporting Information.

Having successfully obtained two different complexes of $\mathbf{L^1}$ with a type A coordination mode, we proceeded to the preparation of corresponding complexes by employing $\mathbf{L^2}$ with longer sulfur-to-sulfur distances. When equimolar amounts of $\mathbf{L^2}$ and $HgCl_2$ were used as reactants in methanol/acetonitrile/dichloromethane, colorless single crystals of **3**, $[Hg(\mathbf{L^2})Cl_2]_n$, were obtained. X-ray analysis reveals that **3** has a double-stranded polymeric chain structure (Figure 3a). The framework contains two exobidentate macrocycles bridging a dinuclear chloro-bridged mercury unit, Hg−(μ-Cl)$_2$−Hg. An alternating arrangement of a pair of macrocycles and a Hg−(μ-Cl)$_2$−Hg unit forms a large cyclic dimer,

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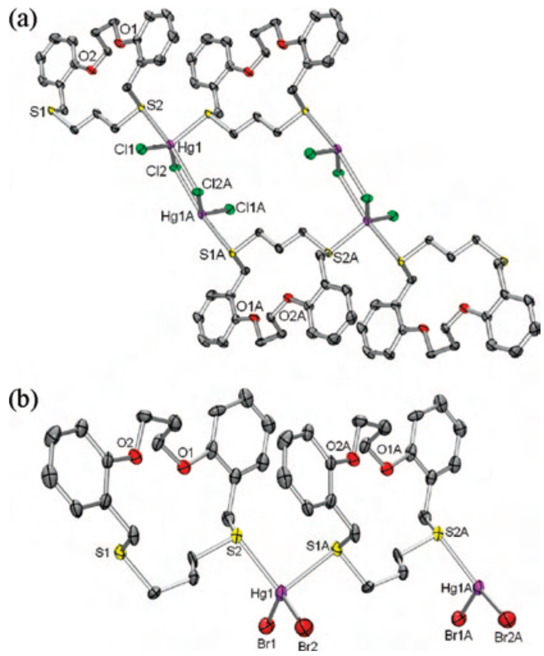

Figure 3. Crystal structures of (a) double-stranded 1-D polymer **3**, $[Hg(\mathbf{L}^2)Cl_2]_n$, and (b) single-stranded 1-D polymers of **4a** (X = Br) and **4b** (X = I), $[Hg(\mathbf{L}^2)X_2]_n$. Symmetry operations: (A) compound **3**, $-x - 1, -y + 1, -z$; (B) compounds **4a** and **4b**, $x - 1, y, z$.

corresponding to a 16-membered ring. The Hg atom has a distorted trigonal-bipyramidal environment with coordination sites occupied by the two exodentate S donors from two adjacent macrocycles. The remaining sites are occupied by three Cl atoms. The Cl1, Cl2, and S1B atoms define the trigonal plane, with the axial positions occupied by S2 and Cl2A atoms [∠S2−Hg1−Cl2A 169.04(5)°]. In packing, the double-stranded polymeric chain of **3** is also stabilized by $\pi\cdots\pi$ stacking interactions between intermolecular aromatic units (Figure S4 in the Supporting Information).

In the case of the reactions of $HgBr_2$ and HgI_2 with $\mathbf{L}^2$ in methanol/dichloromethane, colorless crystalline products **4a** (X = Br) and **4b** (X = I), $[Hg(\mathbf{L}^2)X_2]_n$, were obtained, respectively. Complexes **4a** and **4b** are isostructural and, unlike the $HgCl_2$ complex **3**, they adopt a single-stranded 1-D coordination framework consisting of $\mathbf{L}^2$ and $HgCl_2$ with a $-\mathbf{L}^2-Hg-\mathbf{L}^2-Hg-$ pattern (Figure 3b). The Hg atom that links two macrocycles via Hg−S bonds shows distorted tetrahedral coordination composed of two S donor atoms from two $\mathbf{L}^2$. In complexes **4a** (4.821 Å) and **4b** (4.849 Å), the sulfur-to-sulfur distance in each ring is much farther from those of complexes **1** (3.224 Å) and **2** (3.488 Å).

The results for $\mathbf{L}^2$ complexes also show that the halide anions as second coordinating species have a remarkable influence on the structures and topologies of the assembled products. Consequently, in contrast to **1** and **2**, the longer sulfur-to-sulfur distance in the macrocycle induces the exo-bridging coordination (type B) to produce the polymeric scaffold. Once again, as depicted in Scheme S1 in the Supporting Information, the topological changes with the halide anions in the 1-D polymeric structures, to some extent, are also due to the anion size effects on the formation of $X-Hg-X_2-Hg-X$ (X = Cl) or $X-Hg-X$ (X = Br or I) cluster units.

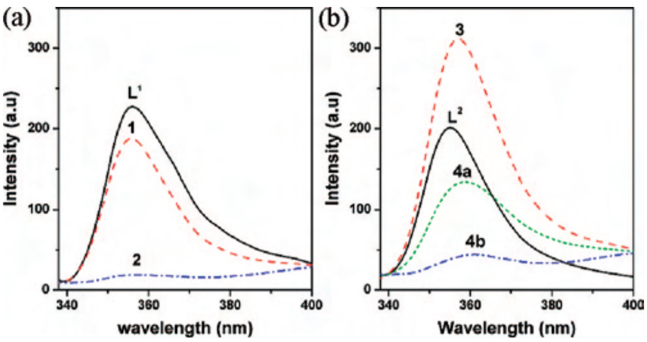

Figure 4. Solid-state photoluminescence spectra of (a) $\mathbf{L}^1$ and (b) $\mathbf{L}^2$ complexes.

Solid−state photoluminescence studies were carried out for **1**−**4b** at room temperature (Figure 4). The emissions for the complexes are found to be lower than that of each free ligand ($\mathbf{L}^1$, $\lambda_{em} = 355$ nm; $\mathbf{L}^2$, $\lambda_{em} = 355$ nm) except complex **3**. Upon complexation, slightly red-shifted emissions compared with those of free ligands [λ_{em} = 356 (**1**), 357 (**2**), 357 (**3**), 359 (**4a**), and 361 (**4b**) nm] are observed. Because no emissions originating from metal-centered excited states are expected for the d^{10} metal ion species such as Hg^{II}, the emissions of **1**-**4b** seem to attributed to the π-π* intraligand fluorescence.[10] The emission intensity of the complex is found to be dependent on the anion used, Cl > Br > I, which can be explained by a heavy-atom quenching effect.[11] In addition, the observed chelation-enhanced fluorescence for **3** may be attributed to the presence of a $\pi-\pi$ stacking interaction between intermolecular aromatic units (Figure S4 in the Supporting Information).

In summary, we have described the synthesis and structural characterization of mercury(II) halide complexes with two analogous dithiamacrocycles having different sulfur-to-sulfur distances. These results, as examples of programmed self-assembly, clearly indicate that the proposed interdonor distances together with the size of the halide ions play decisive roles cooperatively in the conformations or topologies of the supramolecular products. The complexes show ligand-centered photoluminescence properties.

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Supporting Information Available: X-ray crystallographic files in CIF formats, synthetic procedures, and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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