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Anion-Modulated Reversible Conversion of Molecular Assembly between a Macrocycle and a Linear Chain

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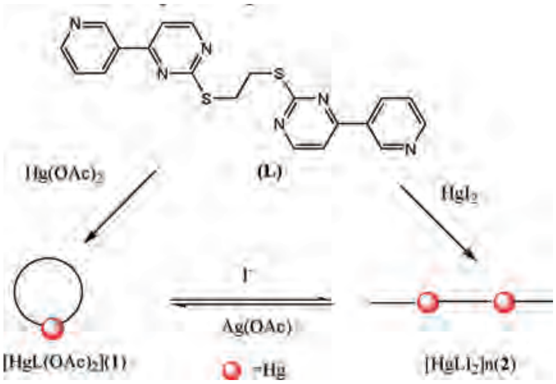
Interaction of a flexible thioether ligand with mercury(II) acetate and iodide, respectively, yielded two compounds with structural motifs of a macrocycle and a 1D polymer, whose structural patterns were dominated by anions and could be reversibly changed.

In the past decade, molecular-level motors or machines have gradually become a very interesting field,[1] in which reversible structural conversions are essential for these systems. So far, most of these reversible processes have been deliberately designed and driven via light[2] or electrons[3] in a fast way. It is noted that most of these processes have been implemented between tautomers and have no significant impact on the essential skeletons of the compounds during the conversion. However, such processes driven by chemical keys such as anions to modulate these reversible systems are scarce.[4] The reason is that chemically forced processes usually result in a complete change in the basic framework of the compounds and cannot be easily interchanged. Recently, we designed a system with a flexible thioether ligand and obtained two mercuric complexes, whose frameworks could be reversibly converted via anions. Herein reported is the system in which conversion between a macrocycle and a linear chain is adjusted by the nature of the anions (Scheme 1).

Scheme 1. Reversible Conversion between a Macrocyclic Motif and a Chain Motif via Chemical Forces



The ligand (L), prepared from the reaction of 1,2-dibromoethane with 4-(pyridin-3-yl)pyrimidine-2-thiol, offers the coordination flexibility required for undergoing the structural variety resulting from the metal salts used. Treatment of L with $Hg(OAc)_2$ or HgI_2 in CH_3OH gave two compounds whose structures have been determined by X-ray crystallography. The molecular structures of $[HgL(OAc)_2]$ (**1**) and $[HgLI_2]_n$ (**2**) are depicted in Figures 1 and 2, respectively.

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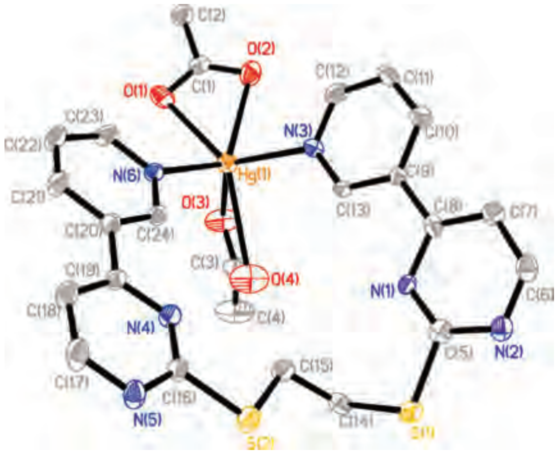

Figure 1. Perspective view of the molecular structure of complex **1** (thermal ellipsoids at the 30% probability level; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Hg1−O1, 2.428(4); Hg1−O2, 2.569(6); Hg1−O3, 2.179(6); Hg1−O4, 2.723(6); Hg1−N3, 2.295(6); Hg1−N6, 2.312(6); O1−C1, 1.245(9); O2−C1, 1.252(9); O3−C3, 1.229(11); O4−C3, 1.207(11); O3−Hg1−N6, 117.5(2); O3−Hg1−N3, 122.3(2); O2−Hg1−O3, 99.06(19); O1−Hg1−O3, 93.1(2); O1−Hg1−N3, 130.64(19); O1−Hg1−N6, 85.19(18); O2−Hg1−N3, 86.73(19); O2−Hg1−N6, 125.34(18); N3−Hg1−N6, 103.6(2); O1−Hg1−O4, 137.61(19); O2−Hg1−O4, 140.48(19).

Figure 2. Perspective view of the molecular structure of complex **2** with the atom-numbering scheme (thermal ellipsoids at the 30% probability level; H atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Hg1−I1, 2.6359(8); Hg1−I1a, 2.6359(8); Hg1−N3, 2.398(6); Hg1−N3a, 2.398(6); I1−Hg1−N3, 105.14(16); I1−Hg1−I1a, 138.35(3); I1−Hg1−N3a, 104.04(16); I1a−Hg1−N3, 104.04(16); N3−Hg1−N3a, 89.8(2); I1a−Hg1−N3a, 105.14(16). Symmetry code: $-x$, y, $^1/_2 - z$.

As shown in Figure 1, the configuration about the metal atom is distortedly octahedral. The Hg^{II} ion is chelated by two bidentate acetato ligands through their O atoms and two pyridine N atoms from the ligand. It is worth noticing that two acetate anions are not equivalent with different Hg−O bond distances.[5] Interestingly, the ligand twists so much as two terminal pyridine groups to chelate the Hg atom, forming a macrocycle, and the dihedral angle between the two pyridine rings is 71.047°. Meanwhile, in this structure, each pyridyl ring is almost coplanar to its neighboring pyrimidyl ring, and the corresponding dihedral angles between the two heterocyclic rings are ca. 2.853° and 3.179°, respectively.

The hydrogen-bond connectivity in **1** is very interesting (see the Supporting Information). Two O atoms from one acetate anion act as hydrogen-bonding acceptors and participate in an intermolecular hydrogen-bonding pattern [C−H···O]. Independent macrocycle molecules are connected to each other through the hydrogen bonding above in a head-to-tail pattern between donors and acceptors, forming an infinite 2D hydrogen-bonded puckered network. Synchronously, two noncoordinated N atoms in the macrocycle also form hydrogen bonds [C−H···N] to link the neighboring macrocycle, producing a 3D network. In addition, there exist aromatic $\pi\cdots\pi$ interactions (center-to-center distances: 3.624 and 3.814 Å) between macrocycles.

The crystal structure of **2** indicates that it has an infinite zigzag chain consisting of $[HgLI_2]_n$, in which Hg^{II} ions are bridged sequentially by pyridyl N atoms of ligands (shown in Figure 2).

Each Hg atom is tetracoordinated by two pyridine N donors from different ligands and two coordinated I^- counterions with a Hg−N distance of 2.398(6) Å and a Hg−I distance of 2.636(8) Å. Both Hg−N and Hg−I distances in the complex are in the range of those found in the other complexes.[6] Because Hg−N distances are obviously shorter than Hg−I distances, the tetrahedral environment is rather distorted. Unlike **1**, the pyridyl ring and its neighboring pyrimidyl ring in a ligand are not coplanar, with a dihedral angle of ca. 36.256°.

In the solid state, the adjacent zigzag chains are stacked through $\pi\cdots\pi$ interactions with short centroid−centriod distances of 3.389 and 3.482 Å. Furthermore, there are nontraditional hydrogen bonds, C−H···I contacts (C−H···I = 4.04 Å, H···I = 3.17 Å, and C−H···I = 158°)[7] and short S···I van der Waals contacts (S···I = 3.76 Å) that hold adjacent modules into a 3D supramolecular structure (see the Supporting Information).

In both **1** and **2**, all ligands only adopt a N,N′-bidentate bridging coordination pattern through two pyridyl N atoms to connect metal atoms. For complexes **1** and **2**, systematic variation in the dimensionality of coordination complexes, metallocycle and 1D framework, can be obtained probably because of the template role of different anions.

The formation of these two complexes prompted us to study whether there is an interconversion between two complexes starting from pure crystallized entities by deliberately varying anions in these complexes. Upon dissolution of the crystal samples of **1** and KI in methanol, the macrocyclic compound had a quick conversion (yield 70% after 6 h at 60 °C) into the chain compound (**2**), which was checked by powder X-ray diffraction (PXRD) spectra. A reverse chain-to-macrocycle conversion (yield 40% after 6 h at 60 °C in dark) was also observed by dissolving crystal samples of **2** and AgOAc in methanol.

Experimental and simulated PXRD patterns of polymorphic transformations between the two forms of complexes **1**

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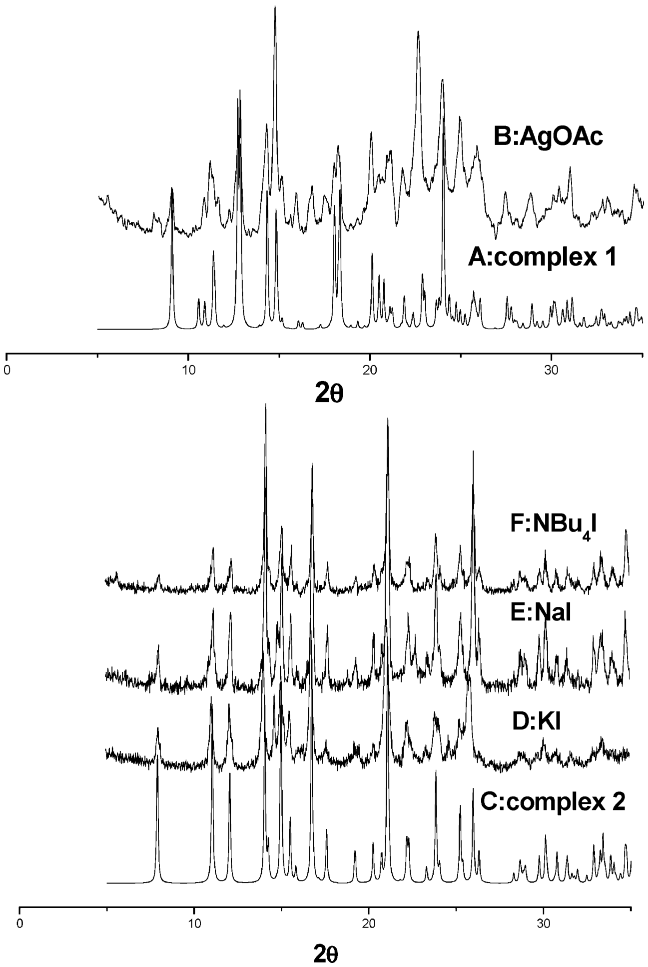

Figure 3. Comparison of the experimental and calculated PXRD patterns of **1** and **2**: calculated form (A) and experimental form (B) of complex **1**; calculated form (C) and experimental form (D−F) of complex **2**.

and **2** are presented in Figure 3. The PXRD patterns of **B** and **D** reveal that both compounds are pure single phases and are consistent with the simulation results from the single-crystal X-ray data of **1** and **2**. From Figure 3, it can be clearly seen that both **B** and **D** have molecular structures identical with those of **A** (complex **1**) and **C** (complex **2**), respectively. Additionally, IR spectral data and elemental analyses of **B** and **D** are almost identical with those of **1** and **2**, respectively. Substitution of NBu_4I or NaI for KI also afforded the conversion of **1** to **2**. The PXRD patterns (named **E** and **F,** respectively, in Figure 3) were similar to that of complex **2**. However, replacement of AgOAc with NaOAc or KOAc in the conversion of **2** to **1** did not produce the desired result. That is to say, any soluble iodide salts can change the macrocyclic motif into a chain motif. However, other acetate salts apart from AgOAc cannot work in the reverse conversion because only I^- anions were moved via Ag ions, which acetate anions can take the place of to coordinate with the metal ion. This means that reversible conversion between **1** and **2** is viable and successful.

Lehn and his co-workers reported an interconversion between a gridlike cobalt complex and a pincer-like cobalt complex, which was modulated by solvents with different coordination capacities for Co ions.[8] Our type of structural interconversion can be understood when taking into account of the flexibility of the thioether ligand and the different coordinative ability of anions. According to Pearson's hard and soft acids and bases principle,[9] the formation of the chain compound happens by using I^- anions, which are of strong coordinative capacity for Hg^{II}, to substitute for acetate anions, which are of low coordinative capacity for Hg^{II}. On the other hand, when silver acetate is used to react with the chain compound to get rid of I^- anions by forming silver iodide, acetate anions bind the Hg^{II} ion to generate the macrocycle.

In conclusion, the results of the current study support the presence of a reversible transition between 0D and 1D structures of mercury complexes using different chemical compounds as the driving force. The couple $[HgL(OAc)_2]$ (**1**)/$[HgLI_2]_n$ (**2**) represents an example of chemical interconversion by chemical keys, AgOAc and MI (M = Na, K, NBu_4).

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Supporting Information Available: Detailed experimental procedures, IR spectroscopic data, and additional ORTEP views of **L**, CIF files giving X-ray structural data for the ligand, **1**, and **2**, TGA diagrams, and ^1H NMR spectra and supramolecular structures of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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