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Networking of Tribenzo-O_2S_2-Macrocycles with Mercury Thiocyanate: Effect of Macrocyclic Isomers

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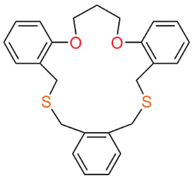
ABSTRACT: Tribenzo-O_2S_2-macrocyclic isomers incorporating a xylyl group in the ortho (***o*-L**), meta (***m*-L**), and para (***p*-L**) positions were employed to examine the effect of ligand isomers on supramolecular networking assembly with mercury(II) thiocyanate. ***o*-L** and ***p*-L** afforded 1-D linear $[Hg_2(\textbf{\textit{o}-L})(SCN)_4]_n$ (**1**) and 1-D zigzag $[Hg(\textbf{\textit{p}-L})(SCN)_2]_n$ (**3**) coordination polymer networks, respectively, while ***m*-L** gave a brick-wall type 2-D network polymer of type $[Hg_2(\textbf{\textit{m}-L})(SCN)_4]_n$ (**2**). All three polymeric structures show different thiocyanate binding motifs.

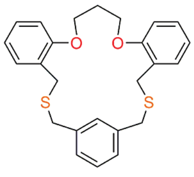
The structural modification of macrocyclic ligands has been an important strategy for the construction of novel supramolecular coordination species and has led to a very considerable variety of coordination geometries and metal bonding modes that are controlled to varying degrees by the conformational flexibility of the ligand.[1] In particular, the versatility of thioether-containing macrocycles makes them useful for generation of a range of network products because the sulfur donor is expected to favor binding to softer metals such as Ag(I) and Hg(II) in either an exo- or an endocyclic mode.[2,3] The nature of such network coordination polymeric structures incorporating thiamacrocycles quite often displays a strong dependence on the ring rigidity of the macrocyclic unit.[4]

In the course of our ongoing studies of the thiamacrocycles,[2,4,5] we explore the possibility of generating novel metallosupramolecular architectures through the structural modification of the macrocycles. Recently, we reported the influence of the use of positional isomers of three NS_2-macrocycles on the formation of their exo-coordination-based silver(I) and mercury(II) complexes that were shown to exhibit flower-, leaf-, and tree-shaped patterns.[5f]

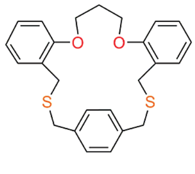
Motivated by these results, we were interested in extending these studies employing the use of the (17- to 19-ring) O_2S_2 tribenzomacrocycle isomers ***o*-L**, ***m*-L**, and ***p*-L**. These tribenzomacrocycle isomers contain two sulfur donors in the crown rings as possible bridging positions for proposed exocoordination-based network formation.[6] Since the order of their conformational ring flexibility is ***o*-L** > ***m*-L** > ***p*-L**, reflecting the position of the xylyl constituent,[4] we reasoned that the use of these positional isomers may also induce the formation of different (flexibility-controlled) products when reacted with a soft metal ion, such as the mercury(II) ion. Further, we have coupled this approach with the use of thiocyanate as a commonly bridging anion in an endeavor to achieve the construction of a new family of infinite networks. In particular, the different linker anions can induce different structural networking, and thus, this and the use of exosulfur coordination effects will most likely play important roles in forming resulting supramolecular architectures.[7]



***o*-L**

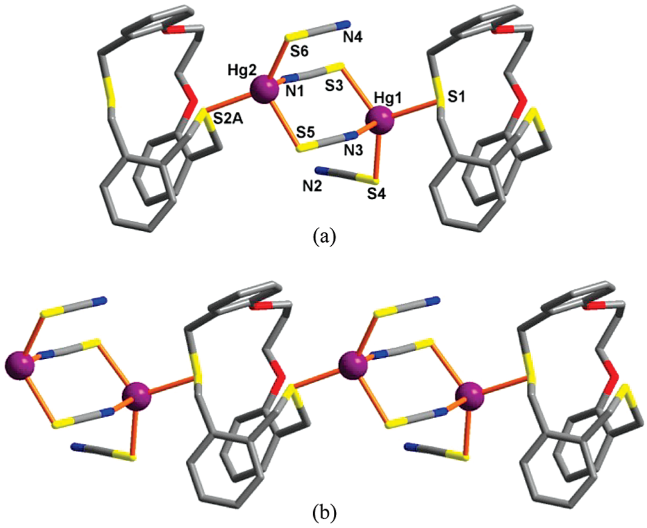


***m*-L**



***p*-L**

Herein, we present the synthesis and structural characterization of three supramolecular complexes for ***o*-L**, ***m*-L**, and ***p*-L** that involve the networking of the macrocycles by means of exocyclic coordination. In this work, an investigation of the effect of changing the macrocyclic ring flexibility across ***o*-L**, ***m*-L**, and ***p*-L** on the products obtained with mercury(II) thiocyanate was carried out. Using this strategy, we obtained the self-assembled supramolecular networks **1**−**3**, exhibiting different topologies (Scheme 1); all three structures were characterized by X-ray analysis (Figures 1−3).



(a)

(b)

Figure 1. Crystal structure of **1**, $[Hg_2(\textbf{\textit{o}-L})(SCN)_4]_n$: (a) core coordination unit and (b) 1-D "looped" network.

Synthesis of ***o*-L** involved four steps starting from salicylaldehyde, with each step proceeding smoothly (Scheme 2). Dichloride precursor **6** was prepared through dialdehyde **4** and dialcohol **5** using a known procedure.[8] The target macrocycle ***o*-L** was obtained by coupling reactions involving dichloride **6** and 1,2-benzenedimethanethiol in the presence of Cs_2CO_3 under high dilution conditions in a yield of 65%. The ^{1}H and ^{13}C NMR spectra together with elemental analysis and mass spectra were clearly in agreement with the proposed structures. ***m*-L** was synthesized as reported previously by us.[9] ***p*-L** was synthesized similarly except the use of 1,4-benzenedimethanethiol and its synthetic detail will be reported elsewhere.

Reaction of ***o*-L** in dichloromethane with $Hg(SCN)_2$ in acetonitrile afforded the colorless crystalline product **1**, suitable for X-ray analysis. Interestingly, compound **1** features a 1-D polymeric array of formula $[Hg_2(\textbf{\textit{o}-L})(\mu_{1,3}\text{-SCN})_2(SCN)_2]_n$, in which the three anions contribute to the coordination sphere of each Hg center

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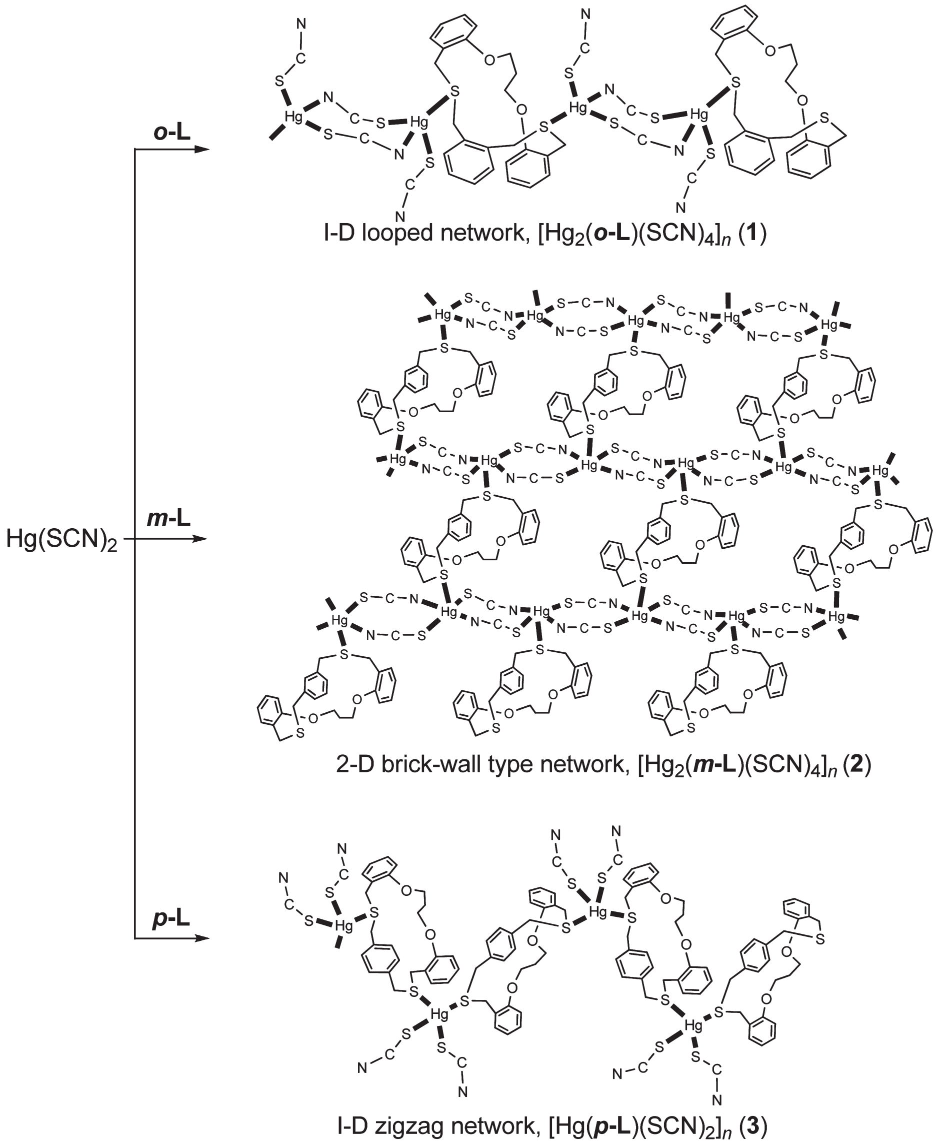
Scheme 1. Mercury(II) Thiocyanate Complexes Prepared

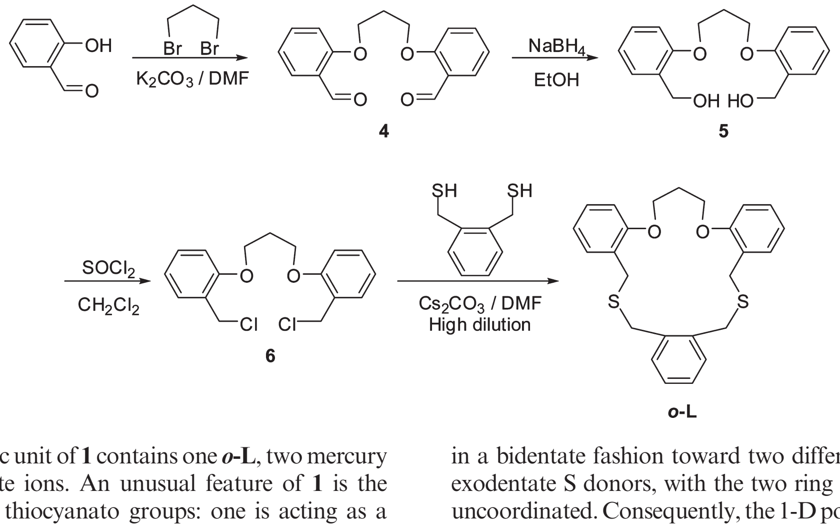


I-D looped network, $[Hg_2(\textbf{o-L})(SCN)_4]_n$ (**1**)

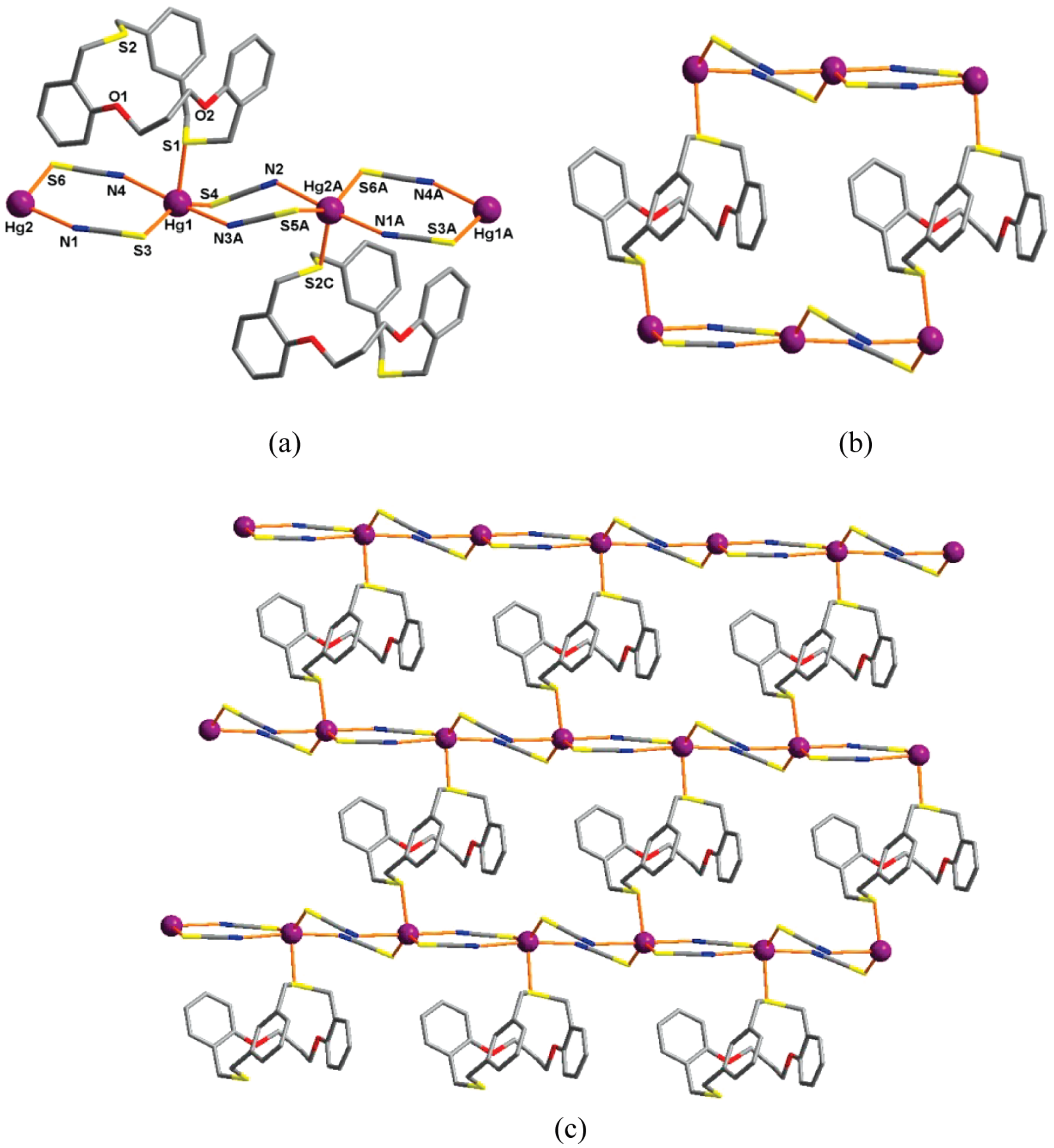
2-D brick-wall type network, $[Hg_2(\textbf{m-L})(SCN)_4]_n$ (**2**)

I-D zigzag network, $[Hg(\textbf{p-L})(SCN)_2]_n$ (**3**)

Scheme 2. Synthesis of *o*-L



(Figure 1). The asymmetric unit of **1** contains one ***o*-L**, two mercury ions, and four thiocyanate ions. An unusual feature of **1** is the presence of two types of thiocyanato groups: one is acting as a S-terminal ligand, and the other has a $\mu_{1,3}$-SCN bridging coordination mode through its N and S atoms. The macrocycle coordinates in a bidentate fashion toward two different metal centers via two exodentate S donors, with the two ring oxygen donors remaining uncoordinated. Consequently, the 1-D polymeric array of **1** consists of alternating linkages of one ***o*-L** and one eight-membered metallacycle, Hg1-($\mu_{1,3}$-SCN)$_2$-Hg2, with the end-to-end thiocyanate



(a)

(b)

(c)

Figure 2. Crystal structure of **2**, $[Hg_2(\textbf{\textit{m}}\text{-}\mathbf{L})(SCN)_4]_n$: (a) core coordination unit, (b) single brick unit, and (c) 2-D brick-wall type network.

bibridge in a "chair" conformation, with a Hg1···Hg2 distance of 5.852(4) Å.

The bond distances to the thioether sulfur donors (Hg1−S1, 2.577(3); Hg2−S2A, 2.528(3) Å) are reasonably similar and compare well with those found in other mercury(II)−thiamacrocyclic complexes.[10] Both of the Hg centers (Hg1 and Hg2) are four-coordinate and show similar coordination environments, being coordinated by one sulfur donor from one ***o*-L**, two bridging thiocyanate ions, and one terminal thiocyanate ion. The coordination sphere of each Hg center is distorted tetrahedral, with the "tetrahedral" angles falling in the range 93.4(2)−130.9(1)° for Hg1 and 91.7(1)−137.7(1)° for Hg2. The distortions from a regular tetrahedron result, in part, from the formation of the mercury(II) thiocyanate metallacycle with its presumably rigid NCS−Hg−NCS bond angles.

The eight-membered metallacycle formed by two mercury atoms and two bridging thiocyanate ions is nonplanar, with the mercury atoms being displaced 0.675 Å (Hg1) and 0.890 Å (Hg2) above and below the plane determined by the two coplanar thiocynate groups. The thiocyanate groups show small distortions [175.0(6) and 177.3(6)°] from linearity, as is usually observed.

Reaction of ***m*-L** with $Hg(SCN)_2$ under similar conditions to those employed for ***o*-L** afforded the colorless crystalline product **2**, which proved suitable for X-ray analysis. Unlike **1**, compound **2** features a 2-D polymeric arrangement of formula $[Hg_2(\textbf{\textit{m}}\text{-}\mathbf{L})(SCN)_4]_n$ (Figure 2). The asymmetric unit of **2** contains one ***m*-L**, two mercury ions, and four thiocyanate ions. The gross geometry of **2** can be described as an infinite brick-wall pattern (Figure 2c). The network of **2** is made up of the 1-D "looped" backbones composed of Hg1-$(\mu_{1,3}\text{-SCN})_2$-Hg2 repeating units. These linear "looped" chains are further cross-linked by ***m*-L** macrocycle via Hg−S(thioether) bonds, yielding the 2-D framework. The Hg−S(thioether) bond lengths [Hg1−S1 2.631(2), Hg2−S2C 2.585(2) Å] agree well with the corresponding values [2.5−2.8 Å] for related systems;[10] they are slightly shorter than those for $Hg-S_{SCN}$ (avg 2.431 Å).

Each Hg(II) ion is five-coordinate, being bound to one sulfur atom of ***m*-L** and four thiocyanate ions via two $Hg-S_{SCN}$ and two $Hg-N_{SCN}$ bonds. The coordination geometry can best be described as a distorted trigonal bipyramid with one S donor of ***m*-L**, two S atoms from two thiocyanate ions defining the trigonal plane, and the

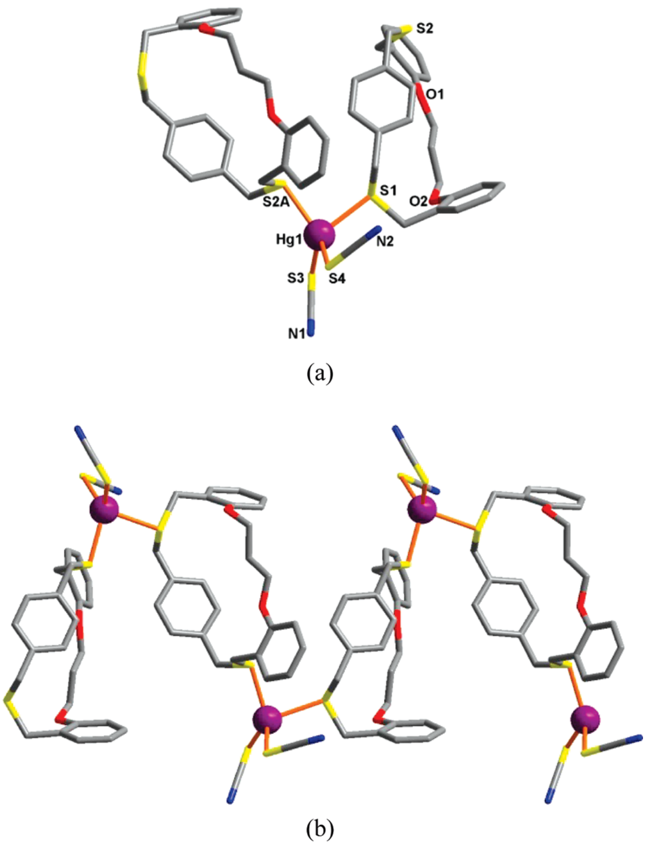


Figure 3. Crystal structure of **3**, [Hg(***p*-L**)(SCN)$_2$]$_n$: (a) core coordination unit and (b) 1-D zigzag-type network.

axial positions occupied by two N atoms from an additional two thiocyanate ions [∠N3A−Hg1−N4 172.9(2)°], with the macrocycle adopting a highly twisted configuration. Again, the ether oxygens do not coordinate. The layered structure in this case appears to be dominated by the presence of a linear Hg1-($\mu_{1,3}$-SCN)$_2$-Hg2 repeating unit, with the flexible ***m*-L** unit simply acting as a bridging component via its exocoordinated sulfur donor sites, which are bound orthogonally to the mercury-containing chain. To the best of our knowledge, **2** is the first structurally characterized 2-D network complex adopting such 1-D looped backbones in association with Hg1-($\mu_{1,3}$-SCN)$_2$-Hg2 repeating units. We know of only one other related structure incorporating similar infinite Hg(II) bridging thiocyanato chains that are linked in a similar manner by two nitrogens from a bridging bidentate hexamethylenetetramine ligand.[11]

Reaction of ***p*-L** with Hg(SCN)$_2$ under the same conditions as used above afforded a 1-D zigzag polymeric array of formula [Hg(***p*-L**)(SCN)$_2$]$_n$ (**3**) incorporating a -(***p*-L**)-Hg-(***p*-L**)-Hg- motif (Figure 3). The asymmetric unit of **3** contains one ***p*-L**, one mercury ion, and two thiocyanate anions. The structural unit shown in Figure 3 is generated through symmetry operations. The Hg1 atom which links two macrocycles via Hg−S bonds shows distorted tetrahedral coordination with the coordination shell composed of two S donor atoms from two ***p*-L** macrocycles and two S-bonded monodentate thiocynate ions. The Hg−S(thioether) distances [2.705(1), 2.576(1) Å] are appreciably longer than the Hg−N$_{\mathrm{SCN}}$ distances [2.487(1), 2.493(1) Å]. The largest deviations from tetrahedral coordination around Hg involve the angles S1−Hg1−S2A [86.7(1)°] and S2A−Hg1−S4 [125.0(1)°]. Once again, the two O donor atoms of the macrocycle remain uncoordinated. The conformation of ***p*-L** in **3** adopts a flatter conformation, suggesting that the ***p*-L** isomer is less flexible that those of ***o*-L** and ***m*-L** because of its enhanced ring rigidity, arising from the presence of the *p*-xylyl ring fragment. In this case, unlike the cases of **1** and **2**, the ring cavity of the macrocycle seems to be too rigid to adopt the stereochemical demand of any types of the bridging coordination modes for thiocyanate ion. Instead, the two thiocyante ions in the coordination sphere of **3** simply act as terminal ligands. The phase purities of the bulk materials for **1**−**3** were confirmed by XRPD (Figure S1 of the Supporting Information).

In summary, the present paper reports the assembly and structural characterization of three new mercury thiocyanate metallo-supramolecular structures with 1-D and 2-D coordination polymers. From these results, it is concluded that a combination of the binding behavior of the thiocyanate anion and the influence of the ring-rigidity of the macrocycles in complexation coupled with the tendency for the exocoordination of sulfur donors of the thiamacrocycle alters ligand behavior and has important consequences of the ligand binding modes for constructing new Hg(II)-supramolecular systems exhibiting different architectures.

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Supporting Information Available: Experimental details, crystal data, XRPD patterns, selected bond distances and angles, and a cif file. This material is available free of charge via the Internet at http://pubs.acs.org.

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