

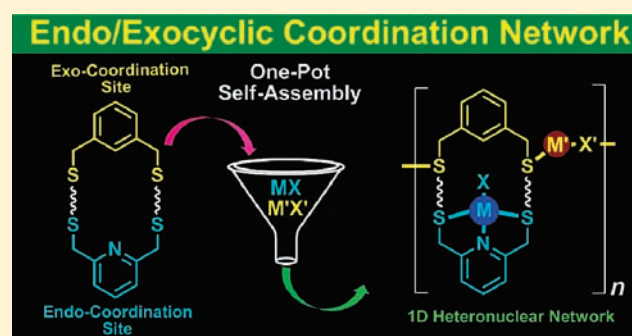
Rational Approach to Endo/Exocoordinated Heteronuclear Macrocyclic Network: Supramolecular Hg(II), Cu(II), and Hg(II)/Cu(II) Complexes of a NS₄ Macrocycle

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Supporting Information

ABSTRACT: A rationally designed sulfur-rich macrocycle **L** incorporating one pyridine and one benzo subunit was synthesized and structurally characterized. From the assembly reactions of **L** with copper(II) nitrate and mercury(II) iodide, an endocyclic monocopper(II) complex and an exocyclic dimercury(II) complex were prepared, respectively. On the basis of these results, the construction of a Hg(II)/Cu(II) heteronuclear 1D network complex with an endo/exocyclic coordination mode was achieved by one-pot assembly reaction of **L** with mercury(II) iodide in the presence of copper(II) nitrate.



INTRODUCTION

Due to their central cavities, macrocyclic ligands have frequently been employed to tune their subunits for an endocyclic metal recognition (metal-in-cavity).¹ Thiamacrocycles, however, often form exocyclic complexes in which the metal ions exist outside the cavity because of the preferential exo-orientation of the sulfur donors.²

We have reported the exocoordination-based discrete and continuous types of supramolecular complexes of the thiamacrocycles, which are attractive not only because of their unusual topologies³ but also due to their potential application as new photophysical sensor systems.⁴ For example, we recently proposed an *N*-azo-coupled NO₂S₂-macrocycle as a chromogenic receptor for mercury(II), which serves to illustrate how the coordinating ability of the anion controls the color change through the formation of endo- or exocyclic complexes.^{4a} More recently, we have reported the anion-controlled endo- and exocyclic complexes of an O₃S₂-macrocycle with AgPF₆ and AgClO₄, respectively.^{3d}

In the course of our ongoing studies of sulfur-containing mixed donor macrocycles,^{3,4} we are exploring the possibility of generating the ligand-directed approach to achieve the synthesis of a new family of heteromultinuclear network complexes with endo- and exocyclic coordination simultaneously. One possible strategy for the preparation of the endo/exocyclic heterobimetallic complexes is to use the macrocyclic system, which possesses the cavity site for endocoordination and the bridgehead donor site for exocoordination. In this work, we therefore proposed a ditopic macrocycle which employs a NS₂ donor set in one side to accommodate one metal cation in the cavity and the two sulfur donors as bridgeheads for the required exocoordination which, in

turn, serves the metal ion coordination from outside the cavity. Further, we have coupled this approach with the use of bridging anion to achieve the coordination network. This approach with a NS₄ macrocycle **L** (Scheme 1) and suitable choice of metal salts enabled us to prepare the endo/exocyclic heterobinuclear complex with networking structure via one-pot procedure.

RESULTS AND DISCUSSION

The bimolecular cyclization of dihalide–dithiol enables the synthesis of thiamacrocycles via C–S bond formation.⁵ Thus, the target macrocycle **L** was synthesized by coupling reactions between dichloride **5** and 2,6-pyridinedimethanethiol **6** in the presence of Cs₂CO₃ under high dilution condition (yield, 20%; Scheme 1). Compounds **4–6** were prepared using known procedures.⁶ The NMR spectrum of **L** exhibits the expected signal complexity arising from its unsymmetrical nature.

The structure of **L** was also characterized in the solid state by X-ray crystallography (Figure 1). The single crystals of **L** were grown by slow evaporation from its dichloromethane solution. In the crystal, two macrocycles with different conformations were found probably due to the intermolecular CH···π interaction in packing (see Figure S1). In both macrocyclic units, all sulfur atoms are oriented in an exo fashion, while pyridine nitrogen directs the cavity center. From the torsion angles associated with donor orientation, the conformation of the S₄N-linkage in one macrocycle unit with a chair shape (left side, S3–S4–N2–S3A–S4A) can be described as *t*–*g*–*g*–*t* (*t* = *trans*, *g* = *gauche*).

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Scheme 1. Synthesis of L

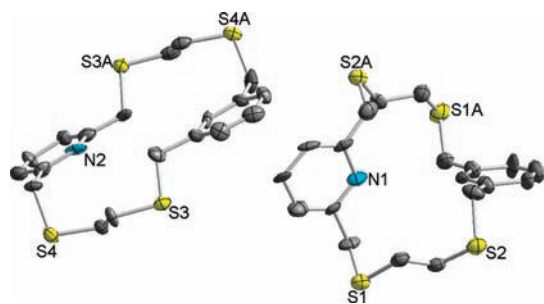
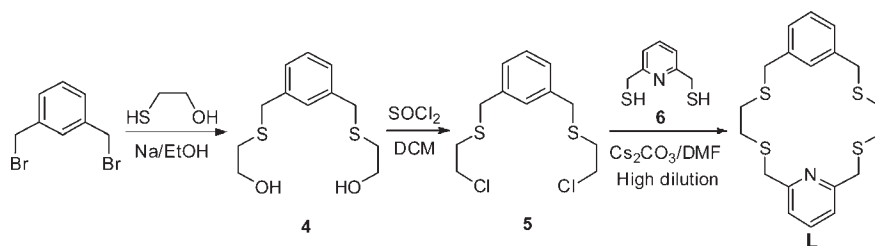
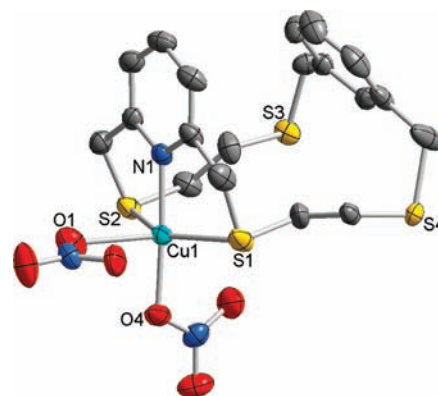
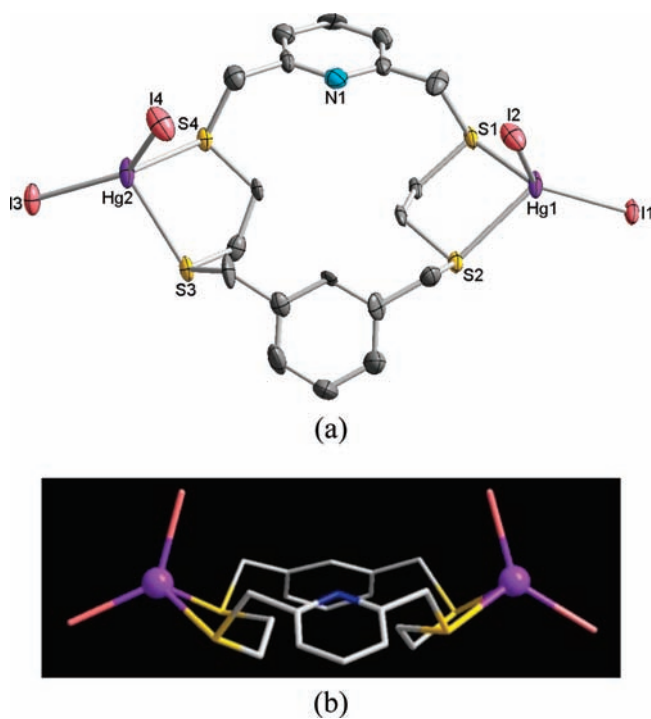


Figure 1. Crystal structure of L.

Figure 3. Endocyclic 1:1 [Cu(II)/L] complex 2, [Cu(L)(NO₃)₂]·CH₃OH. The noncoordinating solvent molecule was omitted.Figure 2. Exocyclic 2:1 [Hg(II)/L] complex 1, [Hg₂(L)₄]·0.5H₂O·0.5CH₂Cl₂: (a) top view and (b) side view. The noncoordinating solvent molecules were omitted.

Another macrocycle with a twisted-form (right side) also shows *t-g-g-t* arrangement (S2–S1–N1–S2A–S1A).

In complexation, mercury(II) and copper(II) salts were used to prepare the individual homonuclear complexes for L. First, the reaction of mercury(II) iodide with L in methanol/dichloromethane afforded colorless crystalline 1 suitable for X-ray analysis.

In marked contrast to the metal ion position in 2 (see later), the compound 1 shows the exocoordinated dinuclear complex of formula [Hg₂(L)₄]·0.5H₂O·0.5CH₂Cl₂ (Figure 2a). In 1, each Hg atom which lies outside the cavity is bonded to two sulfur donors and two I[−] to form a distorted tetrahedral environment, with “tetrahedral angles” falling in the range 80.5(1)° (S1–Hg1–S2) to 129.6(1)° (I1–Hg1–I2) for Hg1 and 80.0(1)° (S3–Hg1–S4) to 137.4(1)° (I3–Hg1–I4) for Hg2. These large deviations are due to formation of the five-membered chelate rings via Hg–S bonds. Unlike the *trans*-type torsion angles between two neighboring sulfur donors for the free L, those of 1 exhibit the *gauche* arrangement (Figure 2b). The Hg–S bond distances [2.711(2)–2.762(2) Å] fall into the longer end of the normal range (2.5–2.8 Å)⁷ for the similar system reported. Above all, the preferred bimetallic exocoordination mode of 1 can be explained due to the strong affinity of I[−] toward each mercury(II) center (av Hg–I 2.65 Å) with the pyridyl nitrogen remaining uncoordinated.

Next, the reaction of copper(II) nitrate trihydrate with L in methanol/dichloromethane afforded a dark green crystalline product 2. As we expected by employing the pyridine subunit, the X-ray analysis revealed that 2 is a typical endocyclic 1:1 copper(II) complex of formula [Cu(L)(NO₃)₂]·CH₃OH, in which the metal ion is accommodated inside the macrocyclic cavity (Figure 3). In 2, the Cu center that lies inside the cavity is five-coordinated, being bound facially to two sulfur donors and one nitrogen donor from one L that exhibits a folded arrangement unlike its free form shown in Figure 1. The coordination sphere is completed by two monodentate nitrate ligands, with the two ring sulfur donors (S3 and S4) remaining uncoordinated.

Addison et al.⁸ introduced the distortion parameter τ , which provides a measure of the degree of square pyramid (SP) versus

trigonal bipyramid (TBP) geometry adopted by the five-coordinate Cu(II) complexes. According to its definition [$\tau = (\theta_1 - \theta_2)/60$], where θ_1 is the largest and θ_2 is the second largest basal angle in the coordination sphere, an ideal SP is characterized by $\tau = 0$, while $\tau = 1$ means an ideal TBP. The experimental τ value for the Cu1 atom in **2** is 0.53. Thus, the copper coordination in **2**

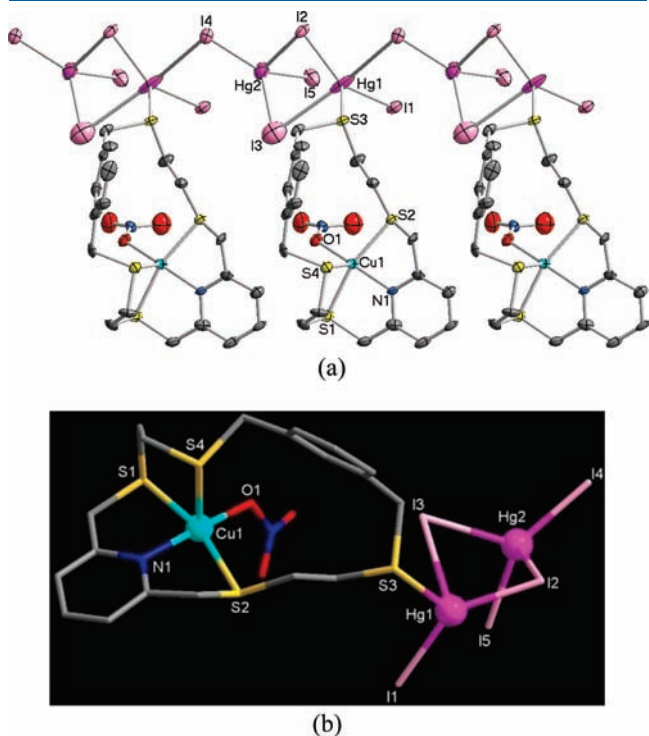


Figure 4. Endo/exocyclic 1D polymeric complex **3**, $\{[\text{Cu}(\text{L})(\text{NO}_3)_2\text{Hg}_2\text{I}_5] \cdot \text{CH}_2\text{Cl}_2\}_n$: (a) 1D network structure and (b) asymmetric unit. The noncoordinating solvent molecule was omitted.

has a geometry nearly intermediate between SP and TBP but can be best described as a distorted TBP, where S1, S2, and O1 atoms form the trigonal plane while N1 and O4 atoms occupy the axial positions [$\angle \text{N1}-\text{Cu1}-\text{O4} 176.5(1)^\circ$]. The bite angles around the Cu1 atom in the trigonal plane vary considerably, ranging from $84.6(1)^\circ$ (S2–Cu1–O1) to $144.9(1)^\circ$ (S1–Cu1–S2) partially due to the repulsive sulfur-to-sulfur interaction.

Having obtained the exocyclic dimercury(II) complex **1** and the endocyclic monocopper(II) complex **2** both in discrete form, as a main target, we proceeded to the preparation of the related Hg(II)/Cu(II) heteronuclear macrocyclic complex that would potentially influence the coordinated metal ion position as well as networking.

When 1 equiv of HgI_2 plus 1 equiv of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were used in one-pot reaction with **L**, the green crystalline product **3** was obtained. Compound **3** features a 1D array of formula $\{[\text{Cu}(\text{L})(\text{NO}_3)_2\text{Hg}_2\text{I}_5] \cdot \text{CH}_2\text{Cl}_2\}_n$ in which endocyclic copper(II) complex units are linked with exocyclic mercury iodide cluster backbone via Hg–S bonds (Figure 4a). The asymmetric unit contains one **L**, one copper atom, two Hg atoms, one nitrate ion, and five iodide ions (Figure 4b). Again, the Cu atom that lies inside the cavity is five-coordinated, being bound to one pyridyl nitrogen and three sulfur donors from one **L**. The coordination sphere is completed by one monodentate nitrate ligand. Unlike **2**, the Cu1 atom in **3** has the distortion parameter⁸ τ value 0.13, suggesting its distorted SP with NS_2 donors from **L** and one O atom from one monodentate nitrate ligand defining the square plane and the apex position occupied by the S4 atom from **L**.

In the exocyclic mercury(II) iodide part, there are two crystallographically independent Hg atoms (Hg1 and Hg2) which are bridged by μ_2 -I₂ and μ_2 -I alternately to form a 1D backbone. The Hg1 atom is five-coordinated by three bridging iodide ions, one terminal iodide ion, and one bridgehead sulfur donor from **L**. Since the distortion parameter⁸ $\tau = 0.35$, the coordination geometry of Hg1 atom can be best described as a distorted SP with four iodide ions defining the square plane and the apex

Table 1. Crystal and Experimental Data for **L**, **1**, **2**, and **3**

	L	1	2	3
formula	$\text{C}_{19}\text{H}_{23}\text{NS}_4$	$\text{C}_{19.5}\text{H}_{25}\text{ClHg}_2\text{I}_4\text{NO}_{0.5}\text{S}_4$	$\text{C}_{20}\text{H}_{27}\text{CuN}_3\text{O}_7\text{S}_4$	$\text{C}_{20}\text{H}_{25}\text{Cl}_2\text{Cu}_1\text{Hg}_2\text{I}_5\text{N}_2\text{O}_3\text{S}_4$
fw	393.62	1056.08	613.23	1639.78
<i>T</i>	173(2) K	173(2) K	173(2) K	173(2) K
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$C2/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
<i>Z</i>	8	4	2	2
<i>a</i> (Å)	31.93(3)	13.689(3)	8.5234(4)	8.5739(7)
<i>b</i> (Å)	5.602(6)	16.969(4)	10.5146(6)	13.8870(11)
<i>c</i> (Å)	22.55(2)	14.974(4)	15.8863(12)	15.6684(12)
α (deg)	90	90	96.754(4)	80.024(3)
β (deg)	97.035(14)	104.056(11)	102.105(4)	81.731(4)
γ (deg)	90	90	113.810(2)	89.926(3)
<i>V</i> (Å ³)	4005(7)	3374.4(13)	1240.61(13)	1817.7(2)
<i>D_x</i> (g/cm ³)	1.306	2.665	1.642	2.996
$2\theta_{\text{max}}$ (deg)	52.00	52.00	54.00	52.00
R1, wR2 [<i>I</i> > 2σ(<i>I</i>)]	0.0585, 0.1460	0.0492, 0.1398	0.0368, 0.1093	0.0888, 0.2094
R1, wR2 [all data]	0.1030, 0.1804	0.0579, 0.1483	0.0427, 0.1161	0.0975, 0.2145
no. refls used [<i>I</i> > 2σ(<i>I</i>)]	3911 [<i>R</i> _{int} = 0.0923]	6594 [<i>R</i> _{int} = 0.0585]	5362 [<i>R</i> _{int} = 0.0361]	7082 [<i>R</i> _{int} = 0.0577]
structure determination	SHELXTL	SHELXTL	SHELXTL	SHELXTL
refinement	full-matrix	full-matrix	full-matrix	full-matrix

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **1**, [Hg₂(L)I₄]·0.5H₂O·0.5CH₂Cl₂

Hg1–I1	2.659(1)	Hg2–I3	2.649(1)
Hg1–I2	2.669(1)	Hg2–I4	2.651(1)
Hg1–S1	2.729(2)	Hg2–S3	2.762(2)
Hg1–S2	2.711(2)	Hg2–S4	2.741(2)
I1–Hg1–I2	129.6(1)	I1–Hg1–S1	109.2(1)
I1–Hg1–S2	115.5(1)	I2–Hg1–S1	108.8(1)
I2–Hg1–S2	102.4(1)	S2–Hg1–S1	80.5(1)
I3–Hg2–I4	137.4(1)	I3–Hg2–S3	102.2(1)
I3–Hg2–S4	112.6(1)	I4–Hg2–S3	107.3(1)
I4–Hg2–S4	102.3(1)	S4–Hg2–S3	80.0(1)

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **2**, [Cu(L)(NO₃)₂]·CH₃OH

Cu1–N1	1.958(2)	Cu1–O1	2.240(3)
Cu1–S1	2.373(1)	Cu1–O4	1.939(2)
Cu1–S2	2.400(1)		
O4–Cu1–N1	176.5(1)	O4–Cu1–O1	85.1(1)
N1–Cu1–O1	91.7(1)	O4–Cu1–S1	95.7(1)
N1–Cu1–S1	85.4(1)	O1–Cu1–S1	129.6(1)
O4–Cu1–S2	95.0(1)	N1–Cu1–S2	86.0(1)
O1–Cu1–S2	84.6(1)	S1–Cu1–S2	144.9(1)

position occupied by the S3 atom from **L**. Unlike the Hg1, the Hg2 is four-coordinated by three bridging I[−] and one terminal I[−]. The bond distances of Hg–I_{bridging} (av 3.140 Å) are longer than those of Hg–I_{terminal} (av 2.634 Å), which is less than the sum of the van der Waals radii of 3.88 Å (Hg = 1.73, I = 2.15 Å).⁹ Previously, we have reported K(I)/Cu(I),^{3a} K(I)/Cu(I)/Hg(II),^{3a} and Pd(II)/Ag(I)^{3m,10} heteronuclear macrocyclic network complexes exhibiting the hard/soft or soft/soft types of the acid–base combination system based on HSAB concept. To our best understanding, this is the first characterized example of a binuclear macrocyclic network complex with the borderline/soft acids metal combination.

In summary, the rationally designed ditopic sulfur-rich macrocycle **L** and its discrete dimercury(II) and monocopper(II) complexes with exo- and endocyclic coordination modes were synthesized, respectively. The proposed ditopic macrocycle **L** also enabled us to prepare the endocyclic copper(II) complex linked with mercury iodide backbone as a first example of this type of macrocyclic complexes from the one-pot reaction. More generally, the tendency to adopt the observed endo- and exocyclic coordination modes shows the possibility that such infinite coordination networks based on the macrocycle can be prepared by controlling the arrangement of donor system in the macrocyclic ligand. Further investigations of the development and potential application of the similar system are in progress.

EXPERIMENTAL SECTION

General. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. NMR spectra were recorded on a Bruker 300 spectrometer (300 MHz). The FT-IR spectra were measured with a Nicolet iS 10 spectrometer. The mass spectrum was obtained on a Thermo Scientific LCQ Fleet spectrometer.

Table 4. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **3**, {[Cu(L)(NO₃)Hg₂I₃]·CH₂Cl₂]_n^a

Cu1–O1	1.952(1)	Cu1–S1	2.354(5)
Cu1–N1	2.013(2)	Cu1–S4	2.610(5)
Cu1–S2	2.350(5)	Hg1–I1	2.646(2)
Hg1–I2	2.633(2)	Hg1–I3	3.465(2)
Hg1–S3	2.681(5)	Hg1–I4A	3.597(2)
Hg2–I2	3.516(2)	Hg2–I3	2.939(3)
Hg2–I4	2.631(2)	Hg2–I5	2.617(2)
O1–Cu1–N1	170.0(6)	O1–Cu1–S2	99.1(4)
N1–Cu1–S2	81.8(4)	O1–Cu1–S1	90.9(4)
N1–Cu1–S1	86.0(4)	S2–Cu1–S1	163.0(2)
O1–Cu1–S4	100.1(4)	N1–Cu1–S4	89.4(5)
S2–Cu1–S4	103.1(2)	S1–Cu1–S4	88.5(2)
I2–Hg1–I1	140.5(1)	I2–Hg1–S3	113.1(1)
I1–Hg1–S3	104.1(1)	S3–Hg1–I3	87.3(1)
I2–Hg1–I3	90.2(1)	I1–Hg1–I3	104.8(1)
I4A–Hg1–I1	90.5(1)	I4A–Hg1–S3	78.2(1)
I4A–Hg1–I3	161.2(1)	I2–Hg1–I4A	84.7(1)
I5–Hg2–I4	145.4(1)	I5–Hg2–I3	96.6(1)
I4–Hg2–I3	117.5(1)	I3–Hg2–I2	84.4(1)
I2–Hg2–I4	88.3(1)	I2–Hg2–I5	101.0(1)

^aSymmetry operations: (A) 1 + x, y, z.

The elemental analysis was carried out on a LECO CHNS-932 elemental analyzer.

Synthesis and Characterization of **L.** Cesium carbonate (6.18 g, 18.9 mmol) was dissolved in DMF (1000 mL) in a 2-L round-bottom flask. 2,6-Pyridinedimethanethiol (2.32 g, 13.5 mmol) and dichloride (4.0 g, 13.5 mmol) were dissolved in DMF (40 mL), and this solution was added slowly over a period of 24 h with the reaction temperature maintained at 55–60 °C. The reaction mixture was rapidly stirred for a further 12 h, allowed to cool to room temperature, and then filtered. The filtrate was evaporated, and the residue was partitioned between water and dichloromethane. The aqueous phase was separated and extracted with two further portions of dichloromethane. The combined organic phases were dried with anhydrous sodium sulfate and then evaporated to dryness. The flash column chromatography (SiO₂; *n*-hexane/ethyl acetate 9:1) afforded the product as a white solid in 20% yield.

Mp: 176–178 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.94 (s, 1 H, Ar), 7.71 (t, *J* = 5.8 Hz, 1 H, Ar), 7.43–7.27 (m, 5 H, Ar), 3.77 (s, 4 H, ArCH₂S), 3.68 (s, 4 H, SCH₂CH₂), 2.69–2.51 (m, 8 H, SCH₂CH₂). ¹³C NMR (75 MHz, CDCl₃): 157.0, 131.3, 128.7, 127.7, 121.2, 112.7, 64.5, 31.0, 30.7, 30.2, 29.4. IR (KBr pellet): 2925, 2914, 2360, 2342, 1586, 1570, 1452, 1423, 1195, 1083, 991, 812, 752 cm^{−1}. Anal. Calcd for [C₁₉H₂₃N₁S₄]: C, 57.97; H, 5.89; N, 3.56; S, 32.58. Found: C, 57.67; H, 5.94; N, 3.36; S, 32.35%. Mass spectrum *m/z*: 394.08 [C₁₉H₂₄N₁S₄]⁺.

Preparation of **1, [Hg₂(L)I₄]·0.5H₂O·0.5CH₂Cl₂.** Mercury iodide (11.5 mg, 0.025 mmol) in methanol (2 mL) was added to a solution of **L** (10.0 mg, 0.025 mmol) in dichloromethane (2 mL). Slow evaporation of the solution afforded a colorless crystalline **1** that proved suitable for X-ray analysis. Mp: 184–186 °C (decomp). IR (KBr pellet): 2925, 2854, 2361, 2343, 1637, 1628, 1587, 1450, 1421, 1199, 1081, 815, 750, 707, 674 cm^{−1}. Anal. Calcd for [C₁₉H₂₃Hg₂I₄NS₄]: C, 17.52; H, 1.78; N, 1.08; S, 9.85. Found: C, 17.42; H, 1.66; N, 0.94; S, 9.84%.

Preparation of **2, [Cu(L)(NO₃)₂]·CH₃OH.** Copper(II) nitrate trihydrate (6.14 mg, 0.025 mmol) in methanol (2 mL) was added to a solution of **L** (10.0 mg, 0.025 mmol) in dichloromethane (2 mL). Slow evaporation of the solution afforded a dark green crystalline **2** that proved suitable for X-ray analysis. Mp: 192–194 °C (decomp). IR (KBr

pellet): 2922, 2427, 2361, 2342, 1637, 1587, 1571, 1454, 1421, 1384, 1196, 1083, 1046, 813, 752, 708, 678 cm^{-1} . Anal. Calcd for $[\text{C}_{19}\text{H}_{23}\text{-CuN}_3\text{O}_6\text{S}_4]$: C, 39.27; H, 3.99. Found: C, 39.55; H, 3.92%.

Preparation of 3, $\{[\text{Cu}(\text{L})(\text{NO}_3)\text{Hg}_2\text{I}_5]\cdot\text{CH}_2\text{Cl}_2\}_n$. Mercury(II) iodide (11.5 mg, 0.025 mmol) and copper(II) nitrate trihydrate (6.14 mg, 0.025 mmol) in methanol (4 mL) were added to a solution of **L** (10.0 mg, 0.025 mmol) in dichloromethane (2 mL). Slow evaporation of the solution afforded green crystalline **3** that proved suitable for X-ray analysis. Mp: 195–197 °C (decomp). IR (KBr pellet): 2910, 2361, 2341, 1603, 1491, 1464, 1384, 1283, 1025, 999, 731, 708, 697, 669, 652 cm^{-1} . Anal. Calcd for $[\text{C}_{19}\text{H}_{23}\text{CuHg}_2\text{I}_5\text{N}_2\text{O}_3\text{S}_4]$: C, 14.68; H, 1.49. Found: C, 14.21; H, 1.45%.

X-ray Crystallographic Analysis. All data were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) 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 APEX2.¹¹ All of the calculations for the structure determination were carried out using the SHELXTL package.¹² 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. In the cases of coordinated water molecules, the initial positions of the hydrogen atoms were obtained from difference electron density maps and refined with riding constraints. Relevant crystal data collection and refinement data for the crystal structures of **L**, **1**, **2**, and **3** are summarized in Tables 1, 2, 3, and 4.

■ ASSOCIATED CONTENT

S Supporting Information. X-ray data in CIF format, and crystal packing and NMR spectrum of **L** as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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