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Extra Large Macrocycle: 40-Membered Macrocycle via 2:2 Cyclization and Its Dimercury(II) Complex

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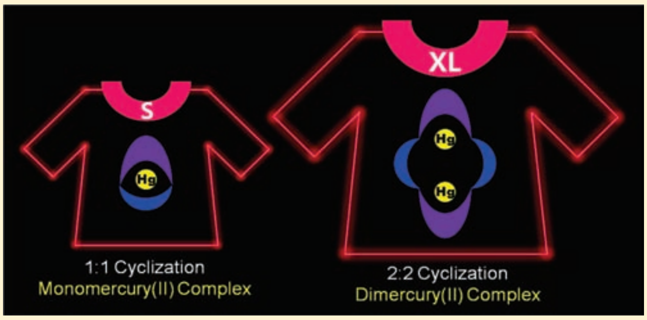
Supporting Information

ABSTRACT: A large 40-membered $N_4O_4S_4$ macrocycle ($\mathbf{L}^2$) was obtained through a 2:2 cyclization of the corresponding dithiol and dichloride as a minor product during the preparation of a 20-membered $N_2O_2S_2$ macrocycle ($\mathbf{L}^1$, 1:1 cyclization product). Each macrocycle was successfully separated from the mixed products and identified. The larger macrocycle $\mathbf{L}^2$ allowed the preparation of its dimercury(II) complex, adopting a one-dimensional (1D) stairway-like polymeric chain linked with the anion. A monomercury(II) complex of the smaller macrocycle $\mathbf{L}^1$ was also prepared. Both complexes and the larger macrocycle $\mathbf{L}^2$ were structurally characterized by the single crystal X-ray analysis.



INTRODUCTION

Binuclear macrocyclic complexes are one of the coordination systems of interest in diverse areas, such as electron transport, charge transfer, and allosteric behavior in biochemical systems.[1] Thus, particular attention has been devoted to the development of new macrocyclic ligand systems capable of forming binuclear complexes. In this regard, the macrocyclic ligand with a large cavity based on the 2:2 cyclization[2,3] and the linked macrocyclic ligands[1c,4] can permit complexing properties to bind two metal ions in defined positions. In contrast to the abundant reports on the Schiff base type large macrocycles based on the 2:2 cyclization which can accommodate two metal ions simultaneously,[2] the non-Schiff base type large macrocycles based on the 2:2 cyclization that can form binuclear soft metal complexes are very rare.[3a]

We have been involved in a program of preparing new type of binuclear macrocyclic complexes based on a mixed-donor macrocyclic system including thiacrown,[3a] calixcrown,[5] and calixthiacrown.[6] Recently, we have reported the isolation of a 24-membered N_2S_6-macrocycle from the 2:2 dithiol-dihalide cyclization and its disilver complex.[3a]

In this work, the cyclization of dichloride precursor **3** with *N*-Boc dithiol **4** led to both $N_2O_2S_2$ ($\mathbf{L}^1$) and $N_4O_4S_4$ ($\mathbf{L}^2$) macrocycles via 1:1 and 2:2 cyclization, respectively (Scheme 1). Fortunately, we were able to separate the larger 2:2 macrocyclic precursor **5b** with the 40-membered ring size. Herein we report the syntheses of the small and large macrocyclic ligands and their complexes, with emphasis on the complexation behavior of the large macrocycle.

RESULTS AND DISCUSSION

The bimolecular cyclization of dichloride-dithiol enables the synthesis of dithiamacrocycles through C−S bond formation.[7] In this work, the mixture of *N*-Boc macrocycle precursors **5a** and **5b** was obtained by the 1:1 and 2:2 cyclization reactions utilizing dichloride **3**[8] and *N*-Boc-protected dithiol **4**[9] in the presence of Cs_2CO_3 in tetrahydrofuran (THF), respectively (Scheme 1). Notably, the presence of the 2:2 cyclization product **5b** as a minor product (17%) was confirmed by the ^{1}H NMR peaks, indicating a general downfield shift compared to those of the 1:1 cyclization product **5a** (Figure 1b). We also confirm the formation of **5b** by an ESI-mass spectrum (Supporting Information, Figure S1). Separation of **5a** and **5b** was achieved by column chromatography on silica-gel. The ^{1}H NMR spectra of **5a** and **5b** clearly show the success of the two components from the mixture (Figure 1a and 1c). The deprotection of *Boc*-groups with trifluoroacetic acid afforded the target macrocycles $\mathbf{L}^1$ and $\mathbf{L}^2$ (Supporting Information, Figure S2).

Unequivocal conformation of the large macrocycle $\mathbf{L}^2$ and its precursor **5b** were provided by X-ray analysis (Figure 2, Supporting Information, Figures S3, and S4). Single crystals of $\mathbf{L}^2$ as an acid form suitable for X-ray analysis were obtained by slow evaporation of a dimethylformamide (DMF) solution of $\mathbf{L}^2$ with several drops of trifluoroacetic acid. The overall structure of $\mathbf{L}^2$ is quite planar and elongated, and the pyridine nitrogen is directed exo to the macrocyclic ring.

First, the reaction of mercury(II) perchlorate with $\mathbf{L}^1$ in methanol/dichloromethane yielded a colorless precipitate. Vapor diffusion of diethyl ether into an acetonitrile solution gave rise to a crystalline product **1**. The crystal structure shows that **1** is a 1:1 endocyclic complex of formula $[Hg(\mathbf{L}^1)](ClO_4)_2 \cdot CH_3CN$, in which no anion and solvent molecules are present in the coordination sphere (Figure 3). The Hg atom accommodated in the center

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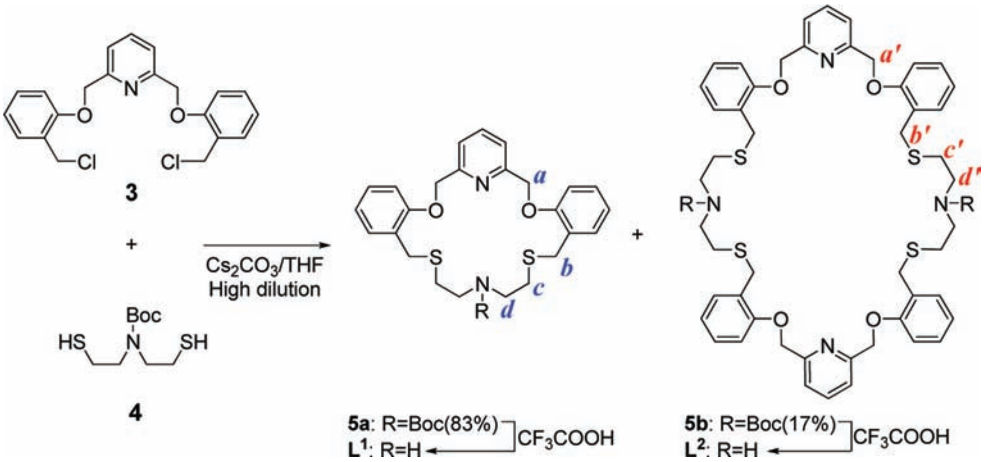
Scheme 1. Synthesis of L^1 and L^2 via 1:1 and 2:2 Cyclizations, Respectively



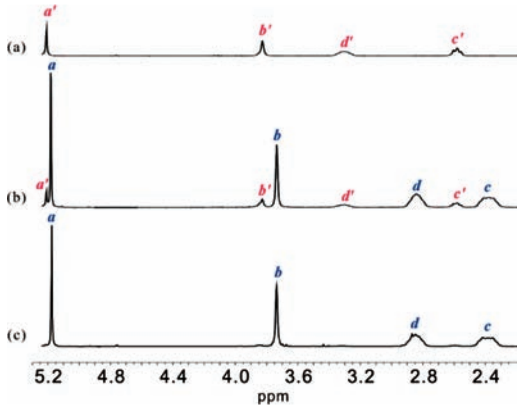


Figure 1. ^{1}H NMR spectra (aliphatic region) of (a) **5b**, (b) mixture of **5a** and **5b**, and (c) **5a** in $CDCl_3$.

of the ring cavity is effectively six-coordinated by $N_2O_2S_2$ donors of $\mathbf{L^1}$. In this case, the metal center is fully shielded by the 20-membered macrocycle, in which the macrocycle twists such that an unsymmetrical but apparently favorable cavity is formed (Figure 3b). Accordingly, the Hg center is bound to all donor atoms of $\mathbf{L^1}$ and adopts a "tight" conformation. The Hg atom coordination cannot be described simply in terms of a regular polyhedron. The Hg−N bond lengths [Hg−N1 2.205(3) and Hg−N2 2.367(3) Å] are within the normal literature range for this bond type.[10] As mentioned, the coordination about Hg center is not symmetric, for example, both sulfur donors being bound asymmetrically; the Hg1−S1 bond length is 2.570(1) Å while that for Hg1−S2 is 2.719(1) Å however, both of which are still typical.

Having obtained the mononuclear mercury(II) complex of $\mathbf{L^1}$, we proceeded to the preparation of a more challenging complex of $\mathbf{L^2}$ incorporating the large cavity. Initially, we were unable to obtain a meaningful crystalline complex of $\mathbf{L^2}$ with common mercury salts. Therefore, our attention was focused on the reaction conditions, employing bridging anions with high coordination ability including SCN^- ion to induce the formation of the related complex with a polymeric form, because coordination polymers are normally less soluble than their discrete analogs in common solvents. This approach was successful for isolating the $\mathbf{L^2}$ complex in a polymeric form. In fact, 4−5 drops of toluene were carefully added on the top

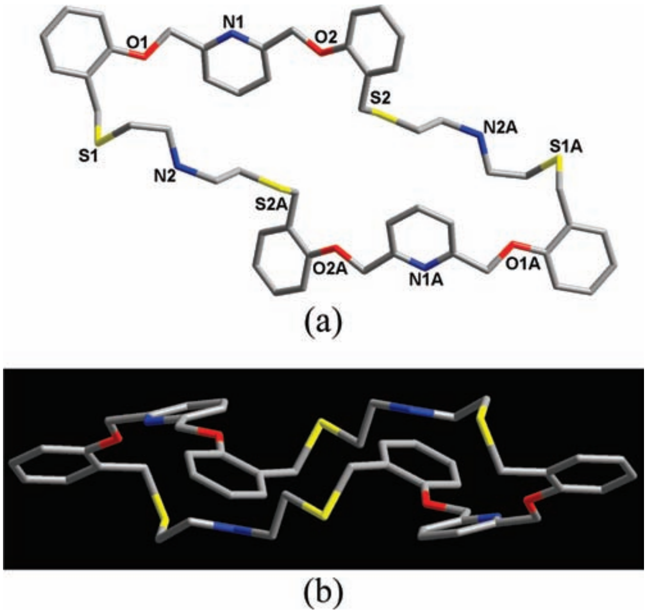


Figure 2. Crystal structure of $\mathbf{L^2} \cdot 2CF_3COOH$; (a) top view and (b) side view. Hydrogen atoms and anions are omitted.

of a dichloromethane solution of $\mathbf{L^2}$ and then the mixture of $Hg(SCN)_2$ and $Hg(CF_3COO)_2$ in acetonitrile/DMF was layered above the toluene and on standing, a colorless needle-type crystalline product **2** was obtained.

As illustrated in Figure 4, X-ray analysis revealed that **2** is an infinite dimercury(II) complex with formula $[Hg_2(\mathbf{L^2})(\mu_{1,3}\text{-}SCN)_2(CF_3COO)_2]_n$ that involves both coordinating anions. In the large cavity of $\mathbf{L^2}$, two mercury(II) ions occupy each NS_2 binding site. These dinuclear complex units are further doubly linked by two bridging thiocyanato ligands, adopting a one-dimensional (1D) polymeric array (Supporting Information, Figure S5). Since there is an imposed inversion at the center of the macrocyclic cavity, the asymmetric unit of **2** contains only a half molecule of $\mathbf{L^2}$, one mercury ion, one thiocyanate ion and one trifluoroacetate ion. The 1D chain of **2** consists of the alternating linkages of one $\mathbf{L^2}$ and one eight-membered metallacycle, Hg-$(\mu_{1,3}\text{-}SCN)_2$-Hg, to provide a "stairway" conformation

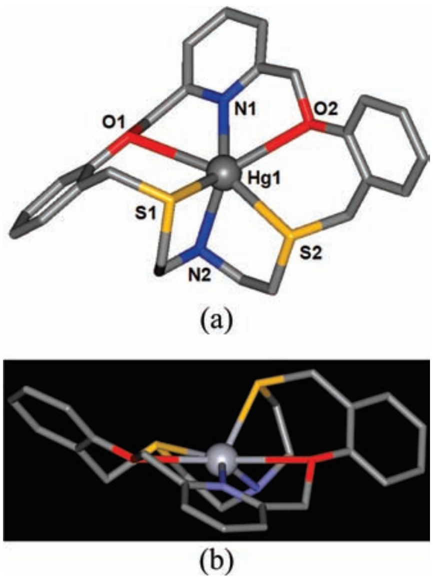


Figure 3. Crystal structure of **1**, $[Hg(\mathbf{L^1})](ClO_4)_2 \cdot CH_3CN$; (a) top view and (b) side view. Hydrogen atoms, noncoordinating anions, and solvent molecule are omitted.

(Figure 4c). The Hg···Hg distance in the large cavity is 8.208(2) Å and that in the Hg-($\mu_{1,3}$-SCN)$_2$-Hg metallacycle is 6.100(1) Å. One part of the macrocycle coordinates to the mercury ion in a tridentate fashion via NS_2 donors, and the coordination environment is completed by two bridging thiocyanate ions and one terminal trifluoroacetate ion. The coordination geometry can be best described as a distorted octahedron with the NS_2 donors from $\mathbf{L^2}$ and one sulfur atom from a thiocyanato ligand defining the square plane, and the axial positions occupied by the remaining thiocyanato nitrogen and an oxygen atom from the trifluoroacetate ion. The O3−Hg1−N3B angle is 165.5(4)°. Two pyridine nitrogen atoms in an exo form and four oxygen donors associated with an antiarrangement of the N−C−C-O segment unit remain uncoordinated.

In **2**, the bond distances of Hg−$S_{thioether}$ [2.781(4) and 2.759(4) Å] are also typical, and they are longer than that of Hg−S_{SCN} [2.474(3) Å] because of the sp hybridization of the thiocyanate ion. The coordination sphere of each Hg center is distorted octahedral. Distortions from the formation of a regular polyhedron result, in part, from two fused 5-membered metallacycles via Hg-donors bonds and the 8-membered Hg-$(SCN)_2$-Hg metallacycle. Overall, it seems that synergic contributions from the ligand, solvent, and two anions all contribute toward the stabilization of the observed unique dinuclear 1D networking behavior of the large macrocycle.

In summary, the 1:1 and 2:2 cyclization products with 20-membered and 40-membered ring cavities have been obtained from the dithiol-dichloride coupling reaction, respectively, and successfully separated. While the smaller macrocycle forms a typical discrete-type monomercury(II) complex, the large macrocycle allowed to prepare the 1D stairway-type polymeric dimercury(II) complex linked with anions. Since the large macrocycle represents the potential to display a wide range of binding properties, investigations aimed not only to obtain new binuclear species but also to synthesize metallo-supramolecules such as cascade and catenated complexes are in progress.

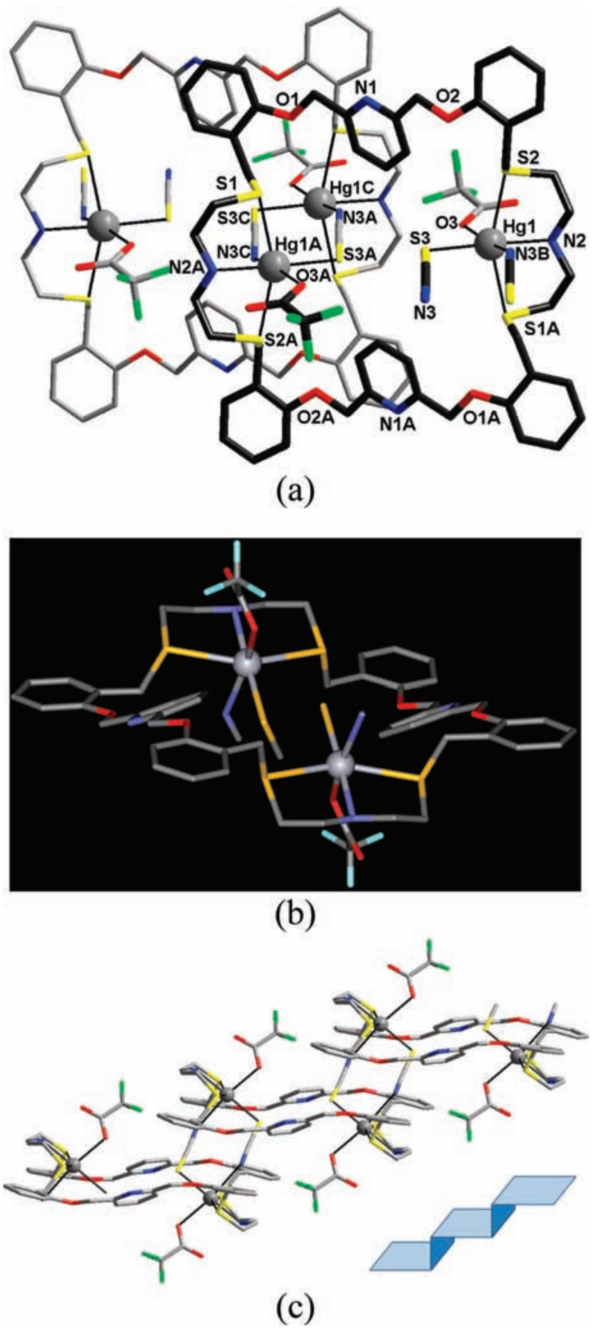


Figure 4. Crystal structure of **2**, $\{[Hg_2(\mathbf{L^2})(\mu_2\text{-}SCN)_2(CF_3COO)_2] \cdot CH_3CN\}_n$; (a) coordination environment, (b) side view, and (c) top view of 1D network. Hydrogen atoms and noncoordinating solvent molecule are omitted.

■ EXPERIMENTAL SECTION

General Procedures. 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 *i*S 10 spectrometer. The electrospray ionization (ESI) mass spectra were obtained on a Thermo Scientific LCQ Fleet spectrometer. The high resolution mass spectrum (HRMS) was obtained on a JEOL JMS-700 spectrometer. The elemental analysis was carried out on a LECO CHNS-932 elemental analyzer.

Table 1. Crystal and Experimental Data for 5b, L^2, 1, and 2

	5b	$L^2 \cdot 2CF_3COOH$	1	2
formula	$C_{60}H_{72}N_4O_8S_4$	$C_{54}H_{56}F_6N_4O_8S_4$	$C_{27}H_{30}Cl_2HgN_3O_{10}S_2$	$C_{60}H_{60}F_6Hg_2N_8O_8S_6$
fw	1105.46	1131.27	892.15	1728.70
T	173(2) K	173(2) K	173(2) K	173(2) K
cryst syst	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Z	1	1	4	2
a (Å)	11.1337(4)	8.5075(5)	13.3089(12)	9.7601(15)
b (Å)	11.4072(4)	11.7799(7)	25.372(2)	25.723(4)
c (Å)	12.8970(4)	13.6194(7)	9.3722(9)	14.0525(19)
α (deg)	65.292(2)	98.079(3)	90	90
β (deg)	89.483(2)	96.774(2)	102.543(5)	114.213(9)
γ (deg)	73.899(2)	95.124(3)	90	90
V (Å^3)	1419.04(8)	1334.12(13)	3089.2(5)	3217.6(8)
D_x (g/cm^3)	1.294	1.408	1.918	1.784
$2\theta_{max}$ (deg)	52	52	52	52
R_1, wR_2 [$I > 2\sigma(I)$]	0.0437, 0.1133	0.1068, 0.2439	0.0240, 0.0630	0.0937, 0.1602
R_1, wR_2 [all data]	0.0545, 0.1222	0.1226, 0.2548	0.0272, 0.0646	0.1316, 0.1917
GOF	1.024	1.106	1.042	1.044
data/restraints/parameters	5570/0/343	5253/0/361	6076/0/406	6311/36/434
no. reflns used [$>2\sigma(I)$]	5570 [R_{int} = 0.0297]	5253 [R_{int} = 0.0517]	6076 [R_{int} = 0.0420]	6311 [R_{int} = 0.3174]
structure determination	SHELXTL	SHELXTL	SHELXTL	SHELXTL
refinement	full-matrix	full-matrix	full-matrix	full-matrix

Synthesis and Characterization of Ligands (L^1 and L^2). Cesium carbonate (2.35 g, 7.21 mmol) was dissolved in THF (500 mL) in a 1 L round-bottom flask. *N*-Boc dithiol **4** (1.22 g, 5.14 mmol) and dichloride **3** (2.00 g, 5.15 mmol) were dissolved in THF (30 mL), and this solution was added to a 50 mL dropping funnel. The contents in the dropping funnel were added dropwise into a THF solution of Cs_2CO_3 at 55−60 °C for 50 h. The reaction mixture was rapidly stirred for a further 10 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 resulting solid was later shown to contain a mixture of **5a** (major, 83%) and **5b** (minor, 17%). This mixture was separated by column chromatography on silica gel (eluent: *n*-hexane-ethyl acetate 7:3). The *Boc*-groups of **5a** and **5b** readily were removed by treatment with trifluoroacetic acid to obtain $\mathbf{L^1}$ and $\mathbf{L^2}$, respectively. In each case, aqueous sodium bicarbonate solution was added to the residue, which was then extracted with dichloromethane. The combined organic phases were dried with anhydrous sodium sulfate and then evaporated to dryness. Both compounds were obtained as colorless solids.

$\mathbf{L^1}$: Mp 109−111 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.99−7.92 (*m*, 11 H), 5.17 (*s*, 4 H), 3.73 (*s*, 4 H), 2.81 (*t*, *J* = 6.8 Hz, 4 H), 2.58 (*t*, *J* = 6.7 Hz, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 156.2, 156.1, 138.4, 131.2, 128.9, 126.7, 123.7, 122.2, 112.0, 71.5, 46.2, 27.9, 26.6. IR (KBr, cm^{-1}): 2926, 2753, 2361, 2343, 1654, 1596, 1494, 1456, 1244, 761. Mass spectrum *m/z* (ESI): 453.3 ($\mathbf{L^1}$+1)$^+$. Anal. Calcd for $C_{25}H_{28}N_2O_2S_2$: C, 66.34; H, 6.24; N, 6.19. Found: C, 65.66; H, 6.23; N, 5.70.

$\mathbf{L^2}$: Mp 115−117 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82−7.67 (*m*, 11 H), 5.14 (*s*, 4 H), 3.73 (*s*, 4 H), 2.67 (*t*, *J* = 6.1 Hz, 4 H), 2.56 (*t*, *J* = 6.0 Hz, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 155.7, 154.9, 136.8, 129.4, 127.5, 126.0, 120.0, 119.1, 110.9, 69.5, 46.8, 30.8, 29.6. IR (KBr, cm^{-1}): 2918, 2810, 2361, 2344, 1595, 1493, 1452, 1243, 1110, 753. HRMS (FAB): Calcd. for $C_{50}H_{56}N_4O_4S_4$ (M$^+$): 904.3184. Found: 904.3181.

Preparation of [Hg(L^1)](ClO_4)$_2$·CH_3CN (1). $Hg(ClO_4)_2 \cdot xH_2O$ (15.2 mg) in methanol (3 mL) was added to $\mathbf{L^1}$ (15.0 mg, 33.1 mmol) in dichloromethane (3 mL). The colorless precipitate obtained was separated and dissolved in acetonitrile. Vapor diffusion of diethyl ether into the acetonitrile solution afforded colorless crystalline product suitable for X-ray analysis. Yield (40%); Mp 305−308 °C (decomp.). IR (KBr, cm^{-1}): 2994, 2928, 2870, 1604, 1499, 1231, 1085 (ClO_4^-), 760, 623. Mass spectrum *m/z* (ESI): 327.0 [Hg($\mathbf{L^1}$)]$^{2+}$.

Preparation of {[$Hg_2(L^2)(\mu_2\text{-}SCN)_2(CF_3COO)_2$]·$CH_3CN$}$_n$ (2). A mixture of mercury(II) thiocyanate (5.20 mg, 16.6 mmol) and mercury(II) trifluoroacetic acid (7.10 mg, 16.6 mmol) in acetonitrile/DMF (9:1) was layered onto a dichloromethane solution (3 mL) of $\mathbf{L^2}$ (15.0 mg, 16.6 mmol). Slow evaporation of the solution afforded crystalline product suitable for X-ray analysis. Yield (10%); Mp 155−158 °C. IR (KBr, cm^{-1}): 2924, 2375, 2109 (SCN^-), 1687 ($CF_3CO_2^-$), 1596, 1491, 1449, 1245 ($CF_3CO_2^-$), 754. Mass spectrum *m/z* (ESI): 1163.6 [Hg($\mathbf{L^2}$)SCN]$^+$.

Crystallographic Structure Determinations. Crystal data for **5b**, $\mathbf{L^2}$, **1**, and **2** were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 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.[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 the 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 **5b**, $\mathbf{L^2}$, **1**, and **2** are summarized in Table 1. Selected bond distances and bond angles for **1** and **2** are presented in Tables 2 and 3, respectively.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 1, $[Hg(L^1)](ClO_4)_2 \cdot CH_3CN$

Hg1−N1	2.205(3)	Hg1−N2	2.367(3)
Hg1−S1	2.570(1)	Hg1−S2	2.719(1)
Hg1−O1	2.882(2)	Hg1−O2	2.783(2)
N1−Hg1−S1	125.4(1)	N1−Hg1−S2	137.1(1)
N1−Hg1−O1	65.3(1)	N1−Hg1−O2	82.2(1)
N2−Hg1−S1	82.2(1)	N2−Hg1−S2	76.6(1)
N2−Hg1−O1	87.8(1)	N2−Hg1−O2	137.8(1)
S1−Hg1−O1	76.1(1)	S1−Hg1−O2	119.4(1)
S2−Hg1−O1	157.5(1)	S2−Hg1−O2	70.2(1)
S1−Hg1−S2	85.6(1)	N1−Hg1−N2	130.6(1)
O1−Hg1−O2	130.4(1)		

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 2, $\{[Hg_2(L^2)(\mu_2\text{-}SCN)_2(CF_3COO)_2] \cdot CH_3CN\}_n$[a]

Hg1−N2	2.310(9)	Hg1−N3B	2.745(11)
Hg1−S2	2.759(4)	Hg1−S3	2.474(3)
Hg1−S1A	2.781(4)	Hg1−O3	2.461(9)
N2−Hg1−O3	99.6(3)	N2−Hg1−S2	76.6(3)
N2−Hg1−S3	177.8(3)	N2−Hg1−S1A	79.4(3)
N2−Hg1−N3B	89.5(4)	N3B−Hg1−S3	90.8(3)
N3B−Hg1−S2	87.9(3)	N3B−Hg1−S1A	91.5(3)
N3B−Hg1−O3	165.5(4)	S3−Hg1−S2	105.6(1)
S2−Hg1−S1A	156.0(1)	S2−Hg1- O3	83.4(3)
S3−Hg1−S1A	98.4(1)	S3−Hg1- O3	80.5(2)
S1A−Hg1− O3	101.2(3)		

[a] Symmetry operations: (A) $-x, -y + 1, -z + 2$; (B) $-x-1, -y + 1, -z + 2$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Analytical data, crystal structures, and X-ray crystallographic files (CIFs). This material is available free of charge via the Internet at http://pubs.acs.org.

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