

Anion-Dependent Exocyclic Mercury(II) Coordination Polymers of Bis-dithiamacrocycle

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Synthesis and structural characterization of mercury(II) halides and perchlorate complexes (**1-4**) of bis-OS₂-macrocycle (**L**) are reported. **L** reacts with mercury(II) chloride and bromide to yield an isostructural 2D coordination polymers with type [Hg(**L**)X₂]_n (**1**: X = Cl and **2**: X = Br). In **1**, each Hg atom which lies outside the cavity is six-coordinate with a distorted octahedral geometry, being bound to four adjacent ligands *via* monodentate Hg-S bonds and two remaining sites are occupied by two terminal chlorido ligands to form a fishnet-like 2D structure. When reacting with mercury(II) iodide, **L** afforded a 1D coordination polymer {[Hg₂(**L**)I₄]·CHCl₃}_n (**3**) in which each exocyclic Hg atom is four-coordinate, being bound to two sulfur donors from different ligands doubly bridging the ligand molecules in a head-to-tail mode. The coordination sphere in **3** is completed by two iodo terminal ligands, adopting a distorted tetrahedral geometry. On reacting with mercury(II) perchlorate, **L** forms solvent-coordinated 1D coordination polymer {[Hg₂(**L**)(DMF)₆](ClO₄)₄·2DMF}_n (**4**) instead of the anion-coordination. In **4**, the Hg atom is five-coordinate, being bound to two sulfur donors from two different ligands doubly bridging the ligand molecules in a side-by-side mode to form a ribbon-like 1D structure. The three remaining coordination sites in **4** are completed by three DMF molecules in a monodentate manner. Consequently, the different structures and connectivity patterns for the observed exocyclic coordination polymers depending on the anions used are influenced not only by the coordination ability of the anions but also by anion sizes.

Key Words : Bis-OS₂-macrocycle, Coordination polymer, Exo-coordination, Mercury(II), Anion effect

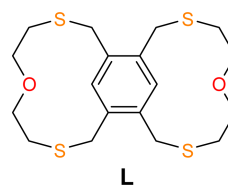
Introduction

The supramolecular coordination chemistry of sulfur-containing crown ethers (thiacrowns or thiamacrocycles) has been studied over the past four decades as a core research area in transition and post-transition metal chemistry.¹⁻⁶ In the thiamacrocycles, the electron sufficiency of sulfur donor atoms and the related S··S repulsion in the macrocyclic ring cavity stabilize the trans (or anti) torsion arrangement for the S-C-C-S unit. Such a trans torsion arrangement in the thiamacrocycles have a tendency to lead a metal coordination in an exocyclic (outside the cavity) mode.⁷⁻¹⁰ Thus, unlike the preference of the endocyclic coordination mode of O,N-donor-macrocycles, the thiamacrocyclic ligands tend to lead the formation of the exocyclic thiaphilic metal (M) complexes *via* multiple M-S bonds without accompanying the large distortion of the ring cavity, which is energetically unfavorable.¹¹ In practice, a range of exo-coordination-based thiamacrocyclic complexes adopting a discrete and polymeric structures have been reported by our group^{5,6,11} and other researchers.^{12,13}

Bis-macrocycles are one of the candidate ligand systems to accommodate two metal ions simultaneously.¹⁴ Loeb and Shimizu have reported the synthesis of meta-type bis-(oxa)thiamacrocycles including bis-OS₂-macrocycle (**L**) and their discrete type endocyclic binuclear complexes in which

two thiaphilic metal ions such as copper(I) or silver(I) exist inside the both cavities.^{15,16} Related to the controlled coordination mode, we have recently reported the synthesis of two regio-isomers of bis-O₂S₂-macrocycles and their selective formations of an endo- and an exocyclic complexes depending on the interdonor (sulfur-to-sulfur) distances in the isomers.¹⁷

In this study, we employed relatively small bis-OS₂-macrocycle, **L**, to investigate its coordination behaviors in the complexation with mercury(II) salts in the solid state because the study on the coordination products including network species for the bis-macrocycles is still very rare.¹⁵⁻¹⁷ Furthermore, the exo-coordination based products obtained in the present work show different connectivity patterns or dimensionalities depending on the anions used. We, herein, report several 1D and 2D network type coordination polymers by using **L** from the reactions with mercury(II) salts. And the resulting structures are discussed in terms of the anion effect such as coordination ability or anion sizes.^{18,19}



Experimental

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 electrospray ionization (ESI) mass spectra were obtained on a Thermo Scientific LCQ Fleet spectrometer. The elemental analysis was carried out on a LECO CHNS-932 elemental analyzer.

Preparation of $[\text{Hg}(\text{L})\text{Cl}_2]_n$ (1). Mercury(II) chloride (34 mg, 0.108 mmol) in methanol (1 mL) was added to **L** (10 mg, 0.025 mmol) in chloroform (1 mL). Slow evaporation of the solution afforded colorless crystalline product **1** suitable for X-ray analysis. mp 204–206 °C (decomp.). IR (KBr pellet): 3051, 2976, 2933, 2881, 2856, 2789, 2359, 2344, 1492, 1403, 1353, 1124, 1071, 1027, 918, 757 cm^{-1} . Anal. Calcd for $[\text{C}_{18}\text{H}_{26}\text{O}_2\text{S}_4\text{HgCl}_2]_n$: C, 32.07; H, 3.89; S, 19.02. Found: C, 32.20; H, 3.84; S, 19.09%.

Preparation of $[\text{Hg}(\text{L})\text{Br}_2]_n$ (2). Mercury(II) bromide (37 mg, 0.103 mmol) in methanol (1 mL) was added to **L** (10 mg, 0.025 mmol) in chloroform (1 mL). Slow evaporation of the solution afforded colorless crystalline product **2** suitable for X-ray analysis. mp 205–207 °C (decomp.). IR (KBr pellet): 3050, 2923, 2881, 2853, 2789, 2368, 2346, 1492, 1403, 1354, 1126, 1071, 1027, 917, 757 cm^{-1} . Anal. Calcd for $[\text{C}_{18}\text{H}_{26}\text{O}_2\text{S}_4\text{HgBr}_2]_n$: C, 28.33; H, 3.43; S, 16.81. Found: C, 28.03; H, 3.33; S, 16.73%.

Preparation of $[\text{Hg}_2(\text{L})\text{I}_4 \cdot \text{CHCl}_3]_n$ (3). Mercury(II) iodide (57 mg, 0.125 mmol) in methanol (1 mL) was added to **L** (10 mg, 0.025 mmol) in chloroform (1 mL). Slow

evaporation of the solution afforded colorless crystalline product **3** suitable for X-ray analysis. mp 201–203 °C (decomp.). IR (KBr pellet): 3003, 2921, 2884, 2360, 2343, 1432, 1358, 1213, 1065, 1029, 914, 764, 715 cm^{-1} .

Preparation of $[\text{Hg}_2(\text{L})(\text{DMF})_6](\text{ClO}_4)_4 \cdot 2\text{DMF}]_n$ (4). Mercury(II) perchlorate hydrate (50 mg, 0.125 mmol) in acetonitrile (1 mL) was added to **L** (10 mg, 0.025 mmol) in chloroform (1 mL). The colorless precipitate obtained was separated and dissolved in dimethylformamide (DMF). Vapor diffusion of diethyl ether into the DMF solution afforded colorless crystalline product **4** suitable for X-ray analysis. mp 160–162 °C (decomp.). IR (KBr pellet): 3019, 2922, 2865, 2366, 2345, 1671, 1387, 1255, 1088 (ClO_4^-), 1014, 792, 626, 797 cm^{-1} . Anal. Calcd for $[\text{C}_{27}\text{H}_{47}\text{O}_{21}\text{S}_4\text{N}_3\text{Hg}_2\text{Cl}_4]_n$ $\{[\text{Hg}_2(\text{L})(\text{DMF})_5](\text{ClO}_4)_4\}_n$: C, 22.82; H, 3.33; N, 2.96. Found: C, 22.30; H, 3.47; N, 2.50%.

X-ray Crystallographic Analysis. Crystal data for **L** and **1–4** were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ 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 semi-empirical absorption correction were carried out using the software package of APEX2.²⁰ All of the calculations for the structure determination were carried out using the SHELXTL package.²¹ 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. Relevant crystal data collection and

Table 1. Crystal and Experimental Data

	L	1	2	3	4
Formula	$\text{C}_{18}\text{H}_{26}\text{O}_2\text{S}_4$	$\text{C}_{18}\text{H}_{26}\text{Cl}_2\text{HgO}_2\text{S}_4$	$\text{C}_{18}\text{H}_{26}\text{Br}_2\text{HgO}_2\text{S}_4$	$\text{C}_{19}\text{H}_{27}\text{Cl}_3\text{Hg}_2\text{I}_4\text{O}_2\text{S}_4$	$\text{C}_{21}\text{H}_{41}\text{Cl}_2\text{HgN}_4\text{O}_{13}\text{S}_2$
Formula weight	402.63	674.12	763.04	1430.78	893.19
Temperature	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
Space group	<i>P</i> -1	<i>P</i> ₂ ₁ <i>2</i> ₁	<i>P</i> ₂ ₁ <i>2</i> ₁	<i>Pnma</i>	<i>P</i> -1
<i>Z</i>	2	4	4	4	2
<i>a</i> /Å	6.8542(2)	8.5870(2)	8.6121(4)	17.7998(7)	9.9612(3)
<i>b</i> /Å	9.2466(2)	13.3216(3)	13.4355(6)	21.5068(10)	12.0742(4)
<i>c</i> /Å	15.0388(3)	19.6156(5)	20.0467(7)	8.5661(4)	15.6108(5)
α /deg	97.4890(10)	90	90	90	97.450(2)
β /deg	94.5710(10)	90	90	90	104.965(2)
γ /deg	90.3810(10)	90	90	90	112.449(2)
<i>V</i> /Å ³	941.85(4)	2243.88(9)	2319.56(17)	3279.2(3)	1620.72(9)
<i>D</i> _{calc} / (g/cm ³)	1.420	1.995	2.185	2.898	1.830
$2\theta_{\text{max}}$ (°)	56.64	56.00	56.00	56.00	56.00
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0402, 0.0923	0.0284, 0.0541	0.0725, 0.1933	0.0486, 0.1050	0.0453, 0.0914
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0575, 0.0992	0.0363, 0.0564	0.0986, 0.2082	0.0645, 0.1160	0.0576, 0.0996
GOF	1.047	0.870	1.102	1.048	1.098
No. of reflns used [<i>I</i> > 2σ(<i>I</i>)]	4678 [<i>R</i> _{int} = 0.0384]	5395 [<i>R</i> _{int} = 0.0391]	5601 [<i>R</i> _{int} = 0.0876]	4067 [<i>R</i> _{int} = 0.1006]	7789 [<i>R</i> _{int} = 0.0519]
Structure Determination	SHELXTL	SHELXTL	SHELXTL	SHELXTL	SHELXTL
Refinement	full-matrix	full-matrix	full-matrix	full-matrix	full-matrix

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for **1**^a, [Hg(L)Cl₂]_n

Hg1-S1	2.929(1)	Hg1-S2A	2.956(1)
Hg1-S3B	3.025(1)	Hg1-S4C	3.038(1)
Hg1-Cl1	2.387(1)	Hg1-Cl2	2.379(1)
Cl2-Hg1-S1	92.4(1)	S1-Hg1-S2A	171.2(1)
Cl1-Hg1-S1	91.7(1)	S1-Hg1-S3B	82.3(1)
S1-Hg1-S4C	82.2(1)	S2A-Hg1-S4C	106.4(1)
S3B-Hg1-S4C	162.7(1)	S4C-Hg1-Cl1	89.3(1)
S4C-Hg1-Cl2	86.3(1)	S2A-Hg1-S3B	89.3(1)
Cl2-Hg1-S2A	89.9(1)	Cl2-Hg1-S3B	86.6(1)
Cl1-Hg1-S2A	86.9(1)	Cl1-Hg1-S3B	98.9(1)
Cl2-Hg1-Cl1	173.5(1)		

^aSymmetry operations: (A) $-x+1/2, -y+1, z+1/2$ (B) $-x+3/2, -y+1, z+1/2$ (C) $x-1, y, z$

Table 3. Selected Bond Lengths (Å) and Bond Angles (°) for **2**, [Hg(L)Br₂]_n

Hg1-S1	2.955(11)	Hg1-S2A	3.056(10)
Hg1-S3B	3.137(11)	Hg1-S4C	3.083(1)
Hg1-Br1	2.481(11)	Hg1-Br2	2.486(11)
Br2-Hg1-S1	92.2(1)	S1-Hg1-S2A	172.0(1)
Br1-Hg1-S1	93.1(1)	S1-Hg1-S3B	79.9(1)
S1-Hg1-S4C	85.2(1)	S2A-Hg1-S4C	87.3(1)
S3B-Hg1-S4C	163.7(1)	S4C-Hg1-Br1	88.1(1)
S4C-Hg1-Br2	97.8(1)	S2A-Hg1-S3B	108.0(1)
Br2-Hg1-S2A	86.2(1)	Br2-Hg1-S3B	89.4(1)
Br1-Hg1-S2A	89.2(1)	Br1-Hg1-S3B	86.2(1)
Br2-Hg1-Br1	172.4(1)		

^aSymmetry operations: (A) $-x-1/2, -y+1, z-1/2$ (B) $x-1, y, z$ (C) $-x-1/2, -y+1, z-0.5$

Table 4. Selected Bond Lengths (Å) and Bond Angles (°) for **3**^a, [Hg₂(L)₄]_n·CHCl₃

Hg1-I1	2.620(1)	Hg1-S1	3.023(2)
Hg1-I2	2.628(1)	Hg1-S2B	2.861(2)
I1-Hg1-I2	161.9(1)	I2-Hg1-S2B	96.6(1)
I1-Hg1-S2B	99.1(1)	I2-Hg1-S1	93.6(1)
I1-Hg1-S1	97.5(1)	S2A-Hg1-S1	82.2(1)

^aSymmetry operations: (B) $x, y, z-1$

Table 5. Selected Bond Lengths (Å) and Bond Angles (°) for **4**^a, {Hg₂(L)(DMF)₆}(ClO₄)₄·2DMF}_n

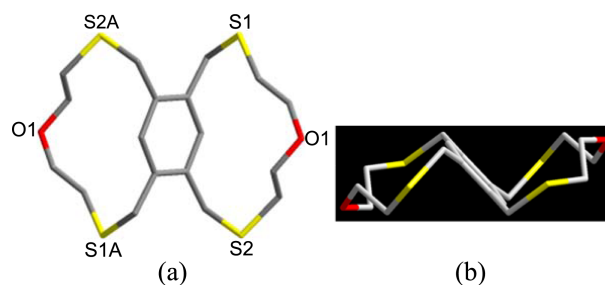
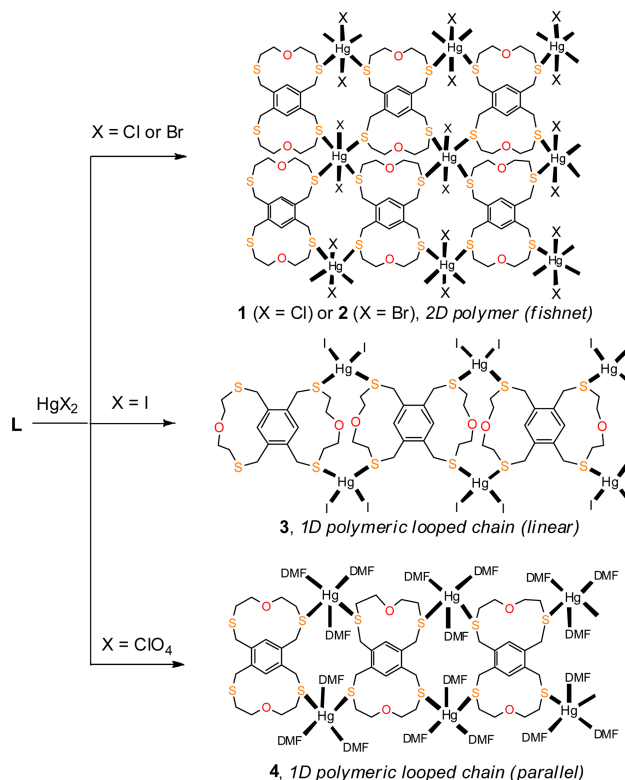
Hg1-S1	2.460(1)	Hg1-O3	2.480(5)
Hg1-S2B	2.471(1)	Hg1-O4	2.426(5)
Hg1-O2	2.472(4)		
S1-Hg1-S2B	156.5(1)	O2-Hg1-O3	78.6(2)
S1-Hg1-O2	87.5(1)	O4-Hg1-S1	101.8(1)
S1-Hg1-O3	104.5(1)	O4-Hg1-S2B	81.7(1)
S2B-Hg1-O2	99.7(1)	O4-Hg1-O2	153.4(2)
S2B-Hg1-O3	98.8(1)	O4-Hg1-O3	74.9(2)

^aSymmetry operations: (B) $x-1, y, z$

refinement data for the crystal structures of **L** and **1-4** are summarized in Tables 1-5.

Results and Discussion

Bis-OS₂-macrocycle **L** was prepared from 1,3-bis-cyclization reaction of 1,2,4,5-tetra(bromomethyl)benzene with 2,2'-oxydiethanethiol using a known procedure.¹⁵ The single crystals of **L** suitable for the X-ray analysis were grown by slow evaporation from the chloroform/methanol solution, and its X-ray crystal structure was characterized (Figure 1). In the crystal, all donor atoms are oriented in an exodentate fashion (Figure 1(a)). Each 12-membered macrocyclic ring in **L** is twisted and slightly folded showing a chair-like overall conformation (Figure 1(b)). The aliphatic segment between donor atoms spans anti arrangements with characteristic torsion angles [S1-C-C-O1 176.96° and O1-C-C-S2 174.97°]. The sulfur-to-sulfur separation in each macrocyclic cavity (S1...S2 6.587 Å) is larger than that between

**Figure 1.** Crystal structure of **L**; (a) top view and (b) side view.**Scheme 1.** Anion-dependent mercury(II) complexes of **L** prepared in this work.

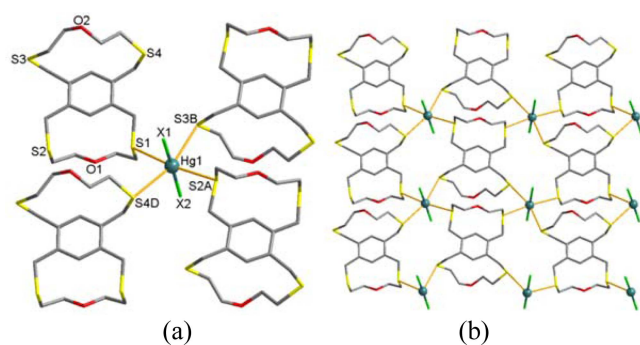


Figure 2. Isostructural 2D coordination polymers $[\text{Hg}(\text{L})\text{X}_2]_n$ (**1**: $\text{X} = \text{Cl}$ or **2**: $\text{X} = \text{Br}$); (a) core coordination unit and (b) 2D exocyclic fishnet-like network.

two macrocycles (S1...S2A 4.598 Å).

Assembly reactions of mercury(II) salts (halides and ClO_4) with **L** were accomplished. All of the macrocyclic mercury(II) complexes **1–4** with different anions shows the polymeric structures *via* the exocyclic coordination (Scheme 1). Each species was prepared under slightly different conditions, giving rise to a different structure except **1** (Cl form) and **2** (Br form) which have an isostructural 2D network structure.

As mentioned, the reactions of **L** with HgCl_2 and HgBr_2 in chloroform/methanol yielded isostructural 2D coordination polymers of type $[\text{Hg}(\text{L})\text{X}_2]_n$ (**1**: $\text{X} = \text{Cl}$ or **2**: $\text{X} = \text{Br}$) in which the mercury atom links the bis-macrocycles in two directions to form a fishnet like pattern (Figure 2). Since the geometrical parameters of the isostructure, **1** and **2**, are not significantly different, the discussion for only **1** is presented. The asymmetric unit of **1** contains one Hg atom, one ligand molecule, and two chloride ions. The Hg atom which lies outside the cavity is six-coordinate, being bound to four adjacent ligands in a monodentate manner *via* Hg-S bonds [2.929(1)–3.038(1) Å]. Two remaining coordinate sites are occupied by two chlorido ligands and the metal center adopts a distorted octahedral geometry with four sulfur donor atoms from four different ligands defining the square plane and the axial position occupied by the two chloride ions [Cl1–Hg1–Cl2 173.5(1)°].

The bulk purity and homogeneity of the products **1** and **2** were monitored by the powder X-ray diffraction (PXRD) patterns. For example, the PXRD pattern of the product **1** is shown at the top of Figure 3(a) together with the simulated pattern (bottom of Figure 3(a)) derived from the corresponding single-crystal X-ray analysis data. Both PXRD patterns in Figure 3(a) match well, indicating that **1** is the only product formed in this reaction. The comparison of the two PXRD patterns for **2** shown in Figure 3(b) also means that **2** is the only product in the given reaction.

On reaction with HgI_2 , **L** forms iodo complex $\{[\text{Hg}_2(\text{L})\text{I}_4]\cdot\text{CHCl}_3\}_n$ (**3**) (Figure 4). Unlike **1** or **2**, this complex is a 1D coordination polymer. The asymmetric unit of **3** for the complex part contains one Hg atom, a half molecule of one **L**, and two iodide ions. The bulk purity and homogeneity of the product **3** were also confirmed by comparison of the

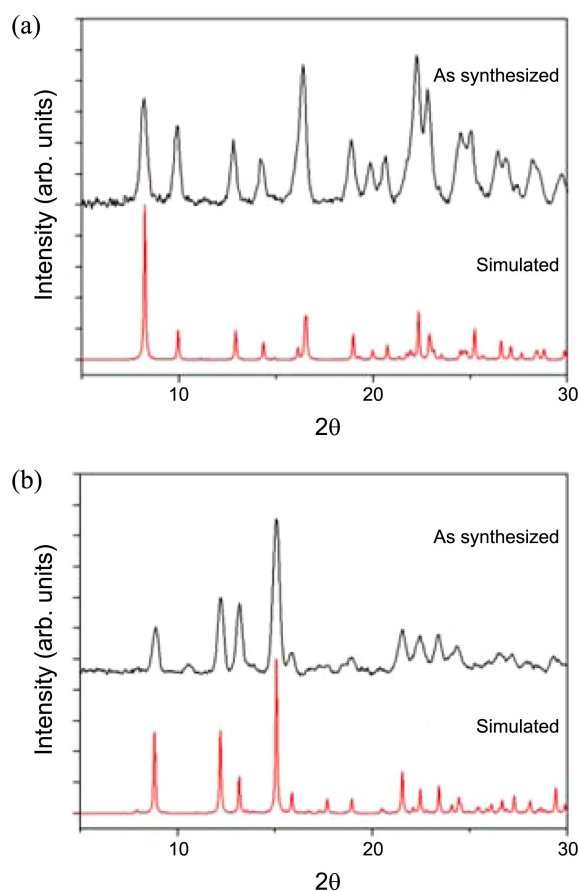


Figure 3. PXRD patterns for (a) **1** and (b) **2**.

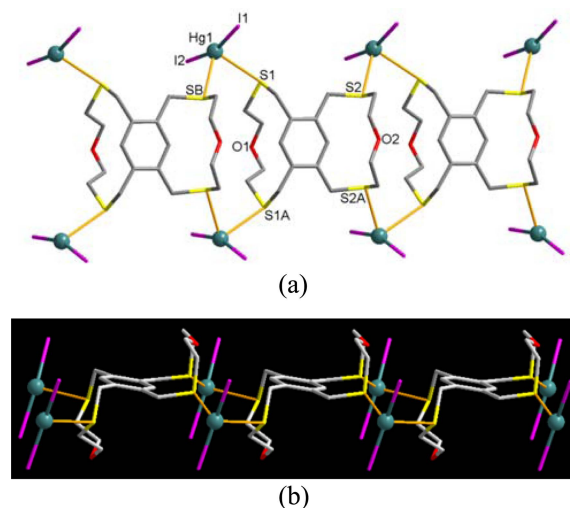


Figure 4. 1D polymeric looped chain $\{[\text{Hg}_2(\text{L})\text{I}_4]\cdot\text{CHCl}_3\}_n$ (**3**) with a linear linking pattern; (a) top view and (b) side view. Non-coordinating solvent molecule is omitted.

PXRD patterns (Figure 5).

In **3**, each Hg atom which lies outside the cavity is four-coordinate, being bound to two sulfur donors from different ligands doubly bridging the ligand molecules in a head-to-tail (or linear) mode *via* the Hg-S bonds [Hg1–S1 3.023(2), Hg1–S2B 2.861(2) Å] to form a 1D looped array. The

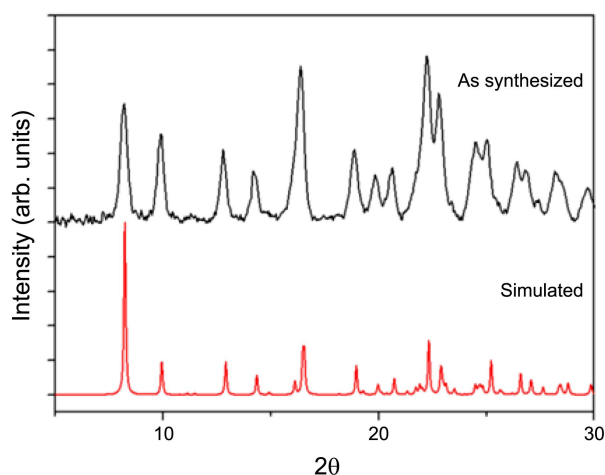


Figure 5. PXRD patterns for 3.

coordination sphere is completed by two iodo terminal ligands [Hg1-I1 2.620(1), Hg1-I2 2.628(1) Å] and the metal center adopts a distorted tetrahedral geometry. The bite angles around the metal center vary considerably from the regular tetrahedral geometry, ranging from 82.2(1)° (S1-Hg1-S2A) to 161.9(1)° (I1-Hg1-I2), presumably due to the large size of iodide ions. Thus, the preferred exocyclic 1D arrangement in 3 reflects the larger size and the strong affinity of the iodide ions toward the mercury(II) center resulting in the propagation of the polymerization into the head-to-tail type 1D array.

Having obtained the three halide-form complexes of **L** which show the anion-coordination, the preparation of related species with a weaker coordinating anion was proceeded. When mercury(II) perchlorate was employed in the reaction

with **L** in chloroform/methanol a colorless precipitate was yielded. The precipitate obtained was separated and dissolved in DMF. Vapor diffusion of diethyl ether into to the DMF solution afforded crystalline product **4** suitable for X-ray analysis. The X-ray analysis revealed that **4** is solvent-coordinated 1D coordination polymer $\{[\text{Hg}_2(\text{L})(\text{DMF})_6](\text{ClO}_4)_4 \cdot 2\text{DMF}\}_n$. The asymmetric unit of the complex part of **4** contains a half molecule of **L**, one mercury atom, and three DMF molecules.

In **4**, the Hg atom that lies outside the cavity is five-coordinate, being bound to two sulfur donors from two different ligands doubly bridging the ligand molecules in a side-by-side (or parallel) mode *via* the Hg-S bonds [Hg1-S1 2.460(1), Hg1-S2B 2.471(1) Å] to form a 1D looped ribbon-like array. The coordination sphere is completed by three DMF molecules in a monodentate manner *via* Hg-O bonds [av. Hg-O 2.459(8) Å]. The preferred solvent-coordinated 1D polymeric structure appears to reflect the weaker coordination affinity of ClO_4^- for mercury(II), allowing the solvent coordination to generate a 1D polymeric array.

Conclusion

In this study, a comparative investigation of the mercury(II) complexes of bis-OS₂-macrocycle, **L**, with different anions is reported. It is noteworthy to compare the structures of the three types of products in terms of the anions. With respect to anion-coordination ability, the formations of such coordination polymers **1-3** reflect the stronger affinity of halides to the mercury(II) centers in these complexes. Among the halides, the iodide anion in **3** probably induces the smaller coordination number ($n=4$) as well as the formation of the simple chain structure due to its larger size. Meanwhile, the reaction with mercury(II) perchlorate **L** favors formation of the solvent-coordinated complex **4** which propagates through one direction to generate a 1D ribbon-like structure. Consequently, it is realized that the coordination ability and size for the anions are key factors to control the resulting exocyclic coordination products.

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Supplementary Materials. Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-1012652-1012656 (**L** and **1-4**)).

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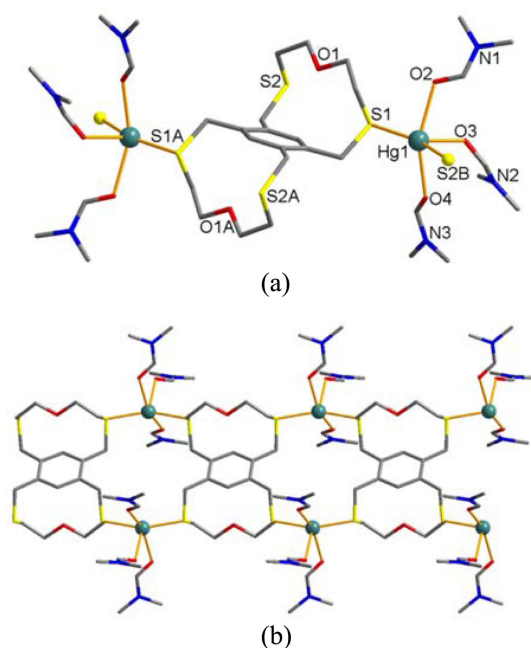


Figure 6. 1D polymeric looped chain $\{[\text{Hg}_2(\text{L})(\text{DMF})_6](\text{ClO}_4)_4 \cdot 2\text{DMF}\}_n$ (**4**) with a parallel linking pattern; (a) core coordination unit and (b) top view of the 1D chain. Non-coordinating anions and solvent molecules are omitted.

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