

An Unusual Pseudo-Coordination Polymer of Dithia-18-Crown-6 with Heavy Metal

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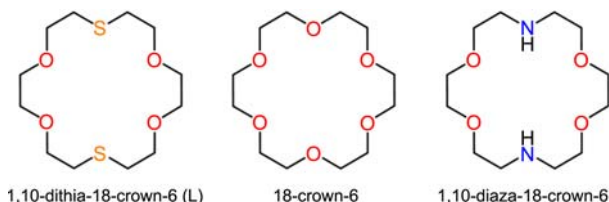
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18-Crown-6 and its mixed-donor analogue have been an important macrocyclic host system because their cavity sizes are comparable to the size of a range of the metal ions to form stable endocyclic (*metal-in-cavity*) complexes in solution and solid states.¹ Accordingly, 1,10-dithia-18-crown-6 (**L**)² and 1,10-diaza-18-crown-6³ can be considered as the representative ones which have the nature sufficient to accommodate a variety of guest metal ions, depending on the donor atom tuning. In practice, **L** as a potent hexadentate macrocyclic ligand has been expected to form stable complexes with some alkaline⁴ and soft metal⁵ ions in solid state. However, the preparation and structural characterization of the complexes of **L** have not been much investigated than expected,^{4,5} despite an importance of this macrocyclic host in the supramolecular coordination chemistry.

Recently, we have reported some divalent hard and soft metal (Ca, Co, Cu, Zn, Cd, Hg, and Pb) complexes of **L** with a discrete endocyclic mode.⁶ We also introduced on the networking of **L** that shows different topologies and connectivity patterns.⁷ The tendency to adopt this networking arrangement is mainly due to the exocyclic coordination of **L** and its oxidized analogue to the metal centers [Cu(I) and Cu(II)].

In this work, we report the synthesis and X-ray study of an extended series of new complexes of **L** incorporating heavy metal ions such as Hg(II) and Cd(II). The versatility of these results is highlighted by the formation of a pseudo-coordination polymer whose structure is similar to the ivy leaves.

**Results and Discussion**

First, when an equimolar amount of HgCl₂ was employed in the reaction of **L** in methanol/dichloromethane a colorless crystalline product **1** suitable for X-ray analysis was obtained. The crystallographic analysis revealed that the compound **1** has an unusual arrangement which is composed

of two discrete macrocyclic complex parts and one continuous mercury(II) chloride chain part with a formula $n\{[\text{Hg}(\text{L})\text{Cl}]_2\}[\text{Hg}_2\text{Cl}_6]_n$ (Figure 1(a)). The asymmetric unit of **1** contains four Hg atoms, two macrocycles, and eight Cl atoms. Interestingly, each macrocyclic complex part further interacts with the infinite mercury(II) chloride chain though the interaction between one sulfur donor in the macrocycle and the Hg atom in the chain [dashed lines in Figure 1(a), Hg3...S2 3.278(4) and Hg4...S4 3.235(3) Å]. Overall, the network pattern including **1** can be considered as the pseudo-coordination polymer which resembles the ivy leaves: the 1D zigzag array of Hg-Cl-Hg-Cl chain as a stem and the macrocyclic complexes as leaves.

The two crystallographically independent macrocyclic complex parts [Hg(L)Cl]₂ show no significant structural difference. Each Hg atom which lies inside the cavity is seven-coordinate, being bound to all the donors of **L** adopting a slightly folded conformation. One remaining site is occupied by one Cl atom (Figure 1(b)). The coordination geometry can be best described as a distorted monocapped trigonal prismatic geometry (Figure 1(c)). The trigonal faces of the monocapped trigonal prism are defined by O5–O8–S3 and O6–O7–S4 with O5 eclipsing O6, O8 eclipsing O7, and S3 eclipsing S4. One chloride atom (Cl2) caps the one rectangular face (O5–O6–O7–O8).

The Hg-S bond distances [2.468(4)-2.660(4) Å] fall in the lower part of the literature range for such bonds (2.5-2.8 Å).⁸ This preferential coordination by sulfur donor is usual since mercury(II) tends to bind to thioether sulfur donor strongly. The Hg-O bond distances [2.721(19)-3.055(10) Å] show longer than those of Hg-S, suggesting that mercury(II) is bonded weakly to the ether oxygen. In the 1D zigzag chain, the Hg3 and Hg4 atoms linked by Cl6 atom are situated in the distorted tetrahedral coordination environment, with the tetrahedral angles 91.7(1)-134.8(2)° for Hg3 atom and 91.4(1)-123.8(2)° for Hg4 atom. The large deviations from the regular tetrahedral geometry are due to the Hg...S interactions as mentioned above.

Recently, we have reported a series of the NS₂-macrocyclic (**m-L**) based metallosupramolecules including the ivy leaf-shaped product [Hg₂(**m-L**)₂Cl₄]_n, in which Hg(II) complex part is attached to a Hg-Cl-Hg-Cl single-chain backbone.⁹ To the best of our knowledge, the 1D type (Hg₂Cl₆)_n chain which interacts with the macrocyclic mercury(II) complex

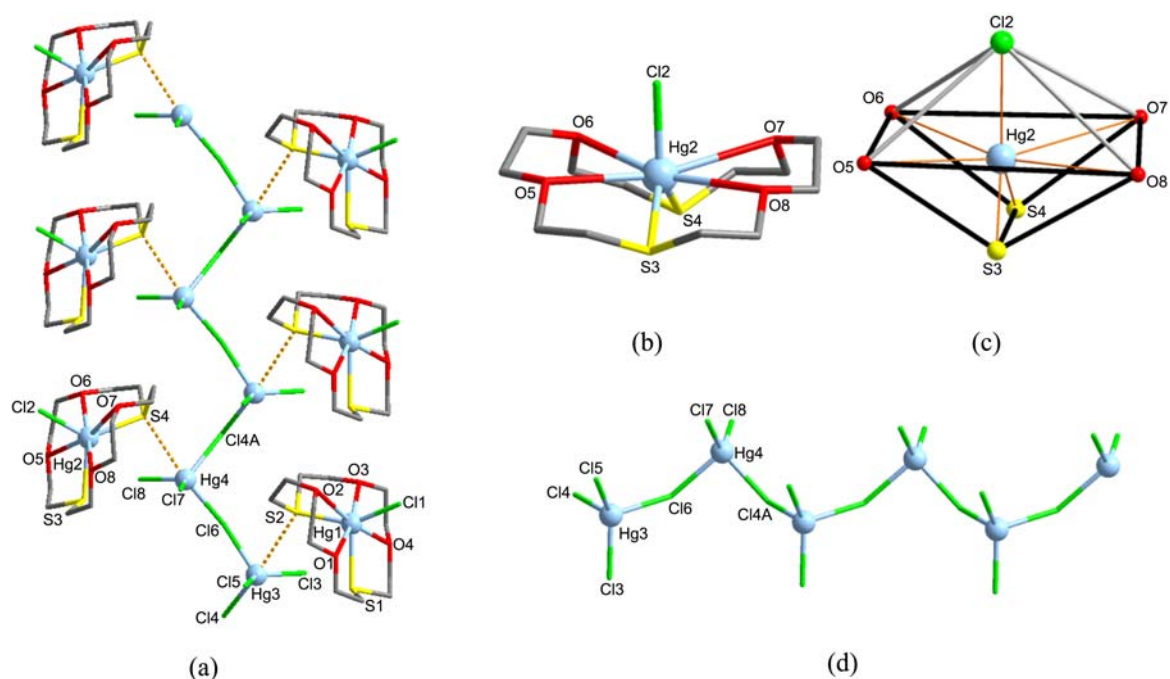


Figure 1. Crystal structure of **1**, $n\{[\text{Hg}(\text{L})\text{Cl}]_2\}[\text{Hg}_2\text{Cl}_6]_n$: (a) the ivy leaves shaped pseudo-coordination polymer network linked by Hg...S interaction, (b) coordination environment of the macrocyclic complex part associated with Hg2 atom, (c) coordination geometry around Hg2 atom showing a monocapped trigonal prismatic arrangement, and (d) the infinite zigzag-type $[\text{Hg}_2\text{Cl}_6]_n$ chain part. Symmetry code: (A) $-1+x, y, z$. Selected bond lengths (Å) and angles ($^\circ$): Hg1-S1 2.660(4), Hg1-S2 2.468(4), Hg1-O1 2.793(10), Hg1-O2 2.827(10), Hg1-O3 2.722(10), Hg1-O4 2.876(10), Hg1-Cl1 2.343(4), Hg2-S3 2.552(4), Hg2-S4 2.499(3), Hg2-O5 2.904(12), Hg2-O6 2.721(19), Hg2-O7 3.055(10), Hg2-O8 2.972(10), Hg2-Cl2 2.367(4), S1-Hg1-S2 97.57(12), S3-Hg2-S4 113.12(11), Hg3...S2 3.278(4), Hg4...S4 3.235(3).

part is the first example.

Having obtained the mercury(II) complex **1**, we then proceeded to undertake the identical reaction involving mercury(II) and cadmium(II) together. When one equivalent of HgI_2 plus one equivalent of CdI_2 were used in one-pot reaction with **L**, the yellow crystalline product **2** suitable for X-ray analysis was obtained. In **2**, unlike **1**, the cadmium(II) occupy the macrocyclic cavity, adopting a discrete structure with three separated parts of a formula $[\text{CdI}(\text{L})]_2[\text{Hg}_2\text{I}_6]$ (Figure 2): two macrocyclic cadmium(II) complex cation parts and one mercury(II) iodide cluster anion part. The asymmetric unit of **2** contains two Cd atoms, two Hg atoms, two macrocycles, and eight I atoms.

The two crystallographically independent macrocyclic cadmium(II) complex parts show no significant structural difference. Like Hg atom in **1**, each Cd atom in **2** is also seven-coordinate, being bound to all the donors of **L**, with its seventh site being occupied by one I atom. Again, the coordination geometry around each Cd atom in the center of the macrocyclic cation unit can be considered as a distorted monocapped trigonal prism, in which one I atom caps the one rectangular face (O1–O2–O3–O4) (Figure 2(c)). The bond distances of Cd-S [2.592(3)–2.671(3) Å] and Cd-O [2.34(2)–2.749(8) Å] are typical.

The geometric parameters of the square-type cluster $[\text{Hg}_2\text{I}_6]^{2-}$ in **2**, whose formation apparently aids the stabilization of the two macrocyclic cadmium(II) complex part, are similar to those reported previously for this part.¹⁰ So, the

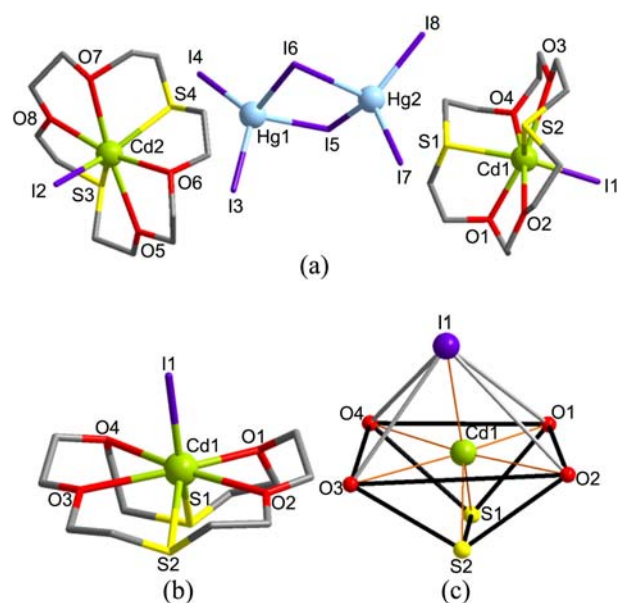


Figure 2. Crystal structure of **2**, $[\text{CdI}(\text{L})]_2[\text{Hg}_2\text{I}_6]$: (a) general view showing three separate parts, (b) coordination environment of the macrocyclic complex part associated with Cd1 atom, and (c) coordination geometry around Cd1 atom showing a monocapped trigonal prismatic arrangement. Selected bond lengths (Å) and angles ($^\circ$): Cd1-S1 2.592(3), Cd1-S2 2.659(2), Cd1-O1 2.34(2), Cd1-O2 2.65(4), Cd1-O3 2.681(7), Cd1-O4 2.749(8), Cd1-I1 2.6801(9), Cd2-S3 2.671(3), Cd2-S4 2.612(3), Cd2-O5 2.699(8), Cd2-O6 2.577(8), Cd2-O7 2.650(8), Cd2-O8 2.557(8), Cd2-I2 2.6902(10), S1-Cd1-S2 93.96(8), S3-Cd2-S4 94.61(11).

preferred endo-coordinated cadmium(II) complex part in **2** under the mixed heavy metal ions condition is due to high affinity of the iodide ion toward the mercury(II) to form the exocyclic $[\text{Hg}_2\text{I}_6]^{2-}$ cluster.

In summary, the assembly reactions of 1,10-dithia-18-crown-6 (**L**) with mercury(II) and/or cadmium(II) salts provide metallosupramolecules with the unusual arrangement due to the formation of the mercury(II) halides (chloride and iodide) clusters which locate outside the macrocyclic cavity. In the reaction with mercury(II) chloride, we were able to isolate the 1D pseudo-coordination polymer **1** which resembles the ivy leaves. In **1**, it is considered that the 1D zigzag array of Hg-Cl-Hg-Cl chain as a leaf-stem and the macrocyclic complexes as leaves. While, from the reaction of mercury(II) iodide and cadmium(II) iodide mixture, the discrete complex **2** with two macrocyclic cadmium(II) complex cation parts and one mercury(II) iodide cluster anion part was isolated. In both cases, each metal center is seven-coordinate, being bound to all the donors of **L**, with its seventh site being occupied by one halide atom, adopting a distorted monocapped trigonal prism.

Experimental Section

General. All chemicals were purchased from commercial sources and used as received. All solvents used were of reagent grade. Elemental analyses were carried out on a LECO CHNS-932 elemental analyzer. ESI-MS spectra were recorded in positive ion mode from acetonitrile solution with Thermo Scientific LCQ Fleet spectrometer. The FT-IR spectra were recorded using Thermo Fisher Scientific Nicolet iS 10 FT-IR spectrometer with KBr pellets.

Synthesis of 1. HgCl_2 (18.3 mg, 0.101 mmol) in methanol (1 mL) was added to a solution of **L** (30.0 mg, 0.101 mmol) in dichloromethane. Slow evaporation of the solution afforded a colorless crystalline product **1** suitable for X-ray analysis (42%). mp 143–145 °C. IR (KBr pellet) 2919, 2359, 1616, 1474, 1370, 1283, 1124, 1096, 1076, 1031, 920, 815 cm^{-1} . MS (ESI) m/z : 533.17 $[\text{Hg}(\text{L})\text{Cl}]^+$.

Synthesis of 2. CdI_2 (22.2 mg, 0.101 mmol) and HgI_2 (27.6 mg, 0.101 mmol) in methanol (1 mL) was added to a solution of **L** (30.0 mg, 0.101 mmol) in dichloromethane. Slow evaporation of the solution afforded a yellow crystalline product **2** suitable for X-ray analysis (51%). mp 169–171 °C. IR (KBr pellet) 2863, 2349, 1614, 1471, 1409, 1367, 1285, 1125, 1096, 1069, 905, 792 cm^{-1} . Anal. Calcd for $[\text{C}_{24}\text{H}_{48}\text{Cd}_2\text{Hg}_2\text{I}_8\text{O}_8\text{S}_4]$: C, 12.90; H, 2.17; S, 5.74. Found: C, 12.97; H, 1.99; S, 5.54%. MS (ESI) m/z : 537.00 $[\text{Cd}(\text{L})\text{I}]^+$.

X-Ray Crystallography Data. Single Crystals suitable for data collection were chosen under an optical microscope, mounted on glass fiber, and frozen under a stream of cryogenic nitrogen gas before data collection. Intensity data were collected on a Bruker SMART APEX II ULTRA diffractometer attached with a CCD detector and graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 36 collected frames).

Table 1. Crystal and experimental data for **1** and **2**

	1	2
formula	$\text{C}_{24}\text{H}_{48}\text{Cl}_8\text{Hg}_4\text{O}_8\text{S}_4$	$\text{C}_{24}\text{H}_{48}\text{Cd}_2\text{Hg}_2\text{I}_8\text{O}_8\text{S}_4$
temperature (K)	173(2)	173(2)
formula weight	1678.82	2234.04
crystal system	Triclinic	Monoclinic
space group	$P\bar{1}$	$P2_1/n$
<i>a</i> (Å)	7.3984(8)	7.6412(2)
<i>b</i> (Å)	17.3535(19)	20.9168(6)
<i>c</i> (Å)	17.4765(18)	31.5266(10)
α (deg)	104.620(6)	90
β (deg)	93.011(6)	94.078(2)
γ (deg)	101.573(6)	90
<i>V</i> (Å ³)	2121.03(13)	5026.1(3)
<i>Z</i>	2	4
<i>D</i> _{calc} (g/cm ³)	2.637	2.952
μ (mm ⁻¹)	15.222	12.041
$2\theta_{\text{max}}$ (deg)	52.00	52.00
reflections collected	31899	59621
independent reflections	8284	9886
goodness-of-fit on F^2	1.026	1.068
R_1, wR_2 [$I > 2\sigma(I)$]	0.0559, 0.1482	0.0472, 0.1234
R_1, wR_2 (all data)	0.0796, 0.1730	0.0636, 0.1350

Data collection, data reduction, and semi-empirical 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 **1**, the O2-C-C-S2-C-C and O6-C-C-S2 segments are disordered over two sites occupied in 53:47 and 72:28 ratios, respectively. In **2**, the O4-C-C-S1-C-C-O1-C-C-O2-C-C-S2 and S3-C-C-O8-C-C-O7-C-C-S4 segments are also disordered over two sites occupied in 41:59 and 48:52 ratios, respectively.

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Supplementary Materials. Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-894539 (**1**) and CCDC-894540 (**2**)). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk.

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