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## Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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# Synthesis, Crystal Structure, and Characterization of a Novel Coordinated Polymer [Hgl<sub>2</sub>L]<sub>2</sub> [L = Ethanediyl bis(isonicotinate)]

Hong-Mei Wang <sup>a</sup> , Mei Liu <sup>b</sup> , Qing-Li Wang <sup>a</sup> & Yun-Yin Niu <sup>a</sup>

<sup>a</sup> Department of Chemistry , Zhengzhou University , Zhengzhou, P. R. China

<sup>b</sup> Physical, Chemical and Biological Department, Henan Jiaozuo Teacher's College, Jiaozuo, P. R. China Published online: 04 Oct 2011.

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### Synthesis, Crystal Structure, and Characterization of a Novel Coordinated Polymer [HgI<sub>2</sub>L]<sub>2</sub> [L = Ethanediyl bis(isonicotinate)]

Hong-Mei Wang,<sup>1</sup> Mei Liu,<sup>2</sup> Qing-Li Wang,<sup>1</sup> and Yun-Yin Niu<sup>1</sup>

<sup>1</sup>Department of Chemistry, Zhengzhou University, Zhengzhou, P. R. China <sup>2</sup>Physical, Chemical and Biological Department, Henan Jiaozuo Teacher's College, Jiaozuo, P. R. China

A novel coordinated polymer  $[HgI_2L]_2$  was synthesized through the reaction of ethanediyl bis(isonicotinate) and HgI<sub>2</sub> in mixed MeOH–THF (5:2). The crystal structural analysis indicated that the complex crystallized in the monoclinic space group P2<sub>1</sub>/c, a = 10.8575(10), b = 19.8946(19), c = 8.8408(8),  $\beta$  = 95.4690(10), V = 1901.0(3) Å3, Z = 4. The complex possessed a novel three-dimensional supramolecular framework formed by hydrogen bonds among repeating  $[HgI_2L]_2$  dimeric units. Its decomposition process is very simple, and decomposition with an apparently endothermal process takes place at the same time.

**Keywords** coordinated polymer, HgI<sub>2</sub> adducts, metallamacrocycle, crystal structure, thermogravimetric analysis

#### INTRODUCTION

Metallosupramolecular species with fascinating structures and topology have become one of the most active areas of material science and chemical research, because of their potential applications on magnetism, electrical, conductivity, ion exchange, separation, and catalysis.<sup>[1-3]</sup> In the supramolecular compounds, coordination interactions between metal centers and multidentate organic ligands formed the primary structure, which could be further organized to supramolecular frameworks through weak noncovalent interactions, such as hydrogen bonding, halogen bonding, and  $\pi - \pi$  interactions.<sup>[4,5]</sup> It was found that the metallosupramolecule of mercuric iodide presented important utility in fields such as optical detection and superconducting materials, and the self-assembly of the metallosupramolecule of mercuric iodide attracted much attention.<sup>[6-8]</sup> Recently, some macrocyclic coordination polymers of mercuric iodide were designed and constructed with the introduce of the organic nitrogen-containing heterocyclic bridging ligands.<sup>[9-14]</sup>

In this study, a novel three-dimensional metallosupramolecular complex  $[HgI_2L]_2$  was obtained through the reaction of ethanediyl bis(isonicotinate) and  $HgI_2$  in mixed MeOH-THF (5:2). The crystal structural analysis indicated that the complex crystallized in the monoclinic space group P2<sub>1</sub>/c and was a binuclear metal macrocyclic complex with center of symmetry. Its decomposition process is very simple, and decomposition with an apparent absorption process takes place at the same time.

#### **EXPERIMENTAL**

#### **General Information and Materials**

Iso-nicotinic acid and anhydrous ethanediol were obtained from Aldrich Chemical Company. All other chemicals were of analytical reagent grade and used without further purification. The infrared (IR) spectrum was recorded on a Shimazu IR435 spectrometer as KBr disk (4000–400 cm<sup>-1</sup>).

#### Syntheses of the Ligand L

The ligand L is obtained by the simple reaction of heating the isonicotinic acid chloride with ethanediol.<sup>[15]</sup>

#### Syntheses of the Complex [Hgl<sub>2</sub>L]<sub>2</sub>

A solution of L (0.1 mmol) in CH<sub>3</sub>OH (5 ml) was added to a solution of HgI<sub>2</sub> (45.4 mg, 0.1 mmol) in THF (2 ml). The solution was then filtered and slowly evaporated in a vial at room temperature. Colorless crystals of the complex were obtained after approximately 3 days in about 51% yield. Analysis calculated for [HgI<sub>2</sub>L]<sub>2</sub>: C, 23.12; H, 1.65; N, 3.85%. Found: C, 23.15; H, 1.67; N, 3.89%.

#### X-Ray Crystallography

Suitable crystals were selected for the structure analysis. The diffraction data were collected on a Bruker APEX-II areadetector diffractometer operating at 50 kV and 40 mA using MoK $\alpha$  radiation (0.071–0.073 nm). Data collection and reduction were performed using the SMART and SAINT software.<sup>[16]</sup> The structures were solved by direct methods, and the nonhydrogen atoms were subjected to anisotropic refinement by

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Address correspondence to Yun-Yin Niu, Department of Chemistry, Zhengzhou University, Zhengzhou 450052, P. R. China. E-mail: niuyy@zzu.edu.cn

TABLE 1 Crystallographic data and structural refinement for compound  $[HgI_2L]_2$ 

Empirical formula	$C_{14}H_{12}Hg I_2N_2O_4$
Formula weight	726.65
Crystal system	Monoclinic
Space group	P2(1)/c
Crystal size(mm)	$0.31 \times 0.29 \times 0.18$
a, Å	10.8575(10)
b, Å	19.8946(19)
c, Å	8.8408(8)
$lpha,^{\circ}$	90
₿, °	95.4690(10)
$\gamma,^{\circ}$	90
$V, Å^3$	1901.0(3)
Dc, mg·cm <sup><math>-3</math></sup>	2.539
Z	4
$\mu$ , mm <sup>-1</sup>	11.362
Reflections collected/unique	14334/3531
R(int)	0.0249
Final R indices	R1 = 0.0218, wR2 = 0.0425
R indices (all data)	R1 = 0.0276, wR2 = 0.0443
Goodness-of-fit on F <sup>2</sup>	1.014
Largest peak, hole ( $e \cdot Å^{-3}$ )	0.721, -0.816
F(000)	1312
Temperature, K	291(2) K
-	

 ${}^{a}R_{1} = ||Fo| - |Fc||/|Fo|.$ 

 ${}^{b}wR_{2} = [w(Fo^{2} - Fc^{2})^{2}/w(Fo^{2})^{2}]^{1/2}.$ 

full-matrix least squares on F<sup>2</sup> using the SHELXTXL package.<sup>[17]</sup> The hydrogen atoms were generated geometrically and included in structure factor calculations. Crystal data and refinement details were summarized in Table 1. Selected bond lengths and bond angles were listed in Table 2.



FIG. 1. The binuclear metallamacrocycle of the complex  $[HgI_2L]_2$ . The hydrogen atoms are not displayed, for clarity.

#### **RESULTS AND DISCUSSION**

#### Crystal Structure of the Complex [Hgl<sub>2</sub>L]<sub>2</sub>

Single-crystal x-ray diffraction analysis revealed that the complex was a novel neutral binuclear metallamacrocycle with a crystallographic center of symmetry. As shown in Figure 1, the binuclear metallamacrocycle was composed of two Hg(II) ions, two bridging L ligands, and four terminal I anions. The distorted tetrahedral coordination center Hg(II) was bound to two iodide atoms and two N-donors from two L ligands, and the Hg1–I1, Hg1–I2, Hg1–N1, and Hg1–N2 bond lengths were 2.6462(4), 2.6498(4), 2.462(4), and 2.455(3) Å, respectively, which were similar to those of the related polymers [HgI<sub>2</sub>(4-bped)]<sub>2</sub> (Hg–I ranging from 2.6425(5) to 2.6391(5) Å and Hg–N from 2.457(5) to 2.454(4) Å). Additionally, the angles around Hg center ranged from 98.67(12) to 143.539(14)°. Two bridging L ligands and two

		TABLE 2			
Selected bond 1	enoths (Å)	and anoles (	°) for co	mnound	Hola

Selected bond lengths (Å) and angles (°) for compound $[HgI_2L]_2$					
Hg(1)–N(1)	2.462 (4)	O(3)–C(9)	1.339 (5)		
Hg(1)–N(2)#1	2.455 (3)	O(3)–C(8)	1.450 (5)		
Hg(1)-I(1)	2.6462 (4)	O(4)–C(9)	1.193 (5)		
Hg(1)-I(2)	2.6498 (4)	N(1)–C(5)	1.328 (5)		
O(1)–C(6)	1.197 (5)	N(1)-C(1)	1.336 (5)		
O(2)–C(6)	1.321 (5)	N(2)–C(12)	1.329 (5)		
O(2)–C(7)	1.445 (5)	N(2)–C(13)	1.329 (5)		
N(1)-Hg(1)-I(1)	102.55 (8)	C(9)–O(3)–C(8)	116.6 (3)		
N(1)-Hg(1)-I(2)	100.76 (8)	C(5)-N(1)-C(1)	117.5 (4)		
N(2)#1-Hg(1)-N(1)	98.67 (12)	C(1)-N(1)-Hg(1)	119.8 (3)		
N(2)#1 - Hg(1) - I(1)	100.27 (8)	C(5)-N(1)-Hg(1)	122.5 (3)		
N(2)-Hg(1)-I(2)	103.48 (8)	C(12)–N(2)–C(13)	117.7 (4)		
I(1)-Hg(1)-I(2)	143.539 (14)	C(12)–N(2)–Hg(1)#1	122.3 (3)		
C(6)–O(2)–C(7)	116.5 (3)	C(13)–N(2)–Hg(1)#1	120.0 (3)		

Symmetry transformations used to generate equivalent atoms: #1, -x + 1, -y + 2, -z + 1.

TABLE 3
D-HA interactions and their distances and angles parameters
for the compound $[HgI_2L]_2$

D–H…A interaction	$D_{D\cdots A}({\rm \AA})$	$D_{H\cdots A}({\rm \AA})$	∠DHA (°)
$C(11)-H(11A)\cdots O(1)$ $C(8)-H(8B)\cdots O(4)$ C(8)-H(8A)-I(1)	3.405 3.670 3.064	2.571 2.718 2.165	149.39 167.02

Hg atoms made up an interesting, ring-like structure unit with dimensions of 13.05 Å (Hg1–Hg1), which is smaller than that in its HgCl<sub>2</sub> complex (13.29 Å).<sup>[18]</sup>

In the solid-state structure, there existed three types of outer sphere intermolecular interactions: The terminal I1 atom had a C–H…I hydrogen bonding with the aliphatic C(8)H(8A)s group from the L ligand of the neighboring dimeric unit; on the other hand, there were aromatic C(11)–H(11A)…O(1) bonding and aliphatic C(8)–H(8B)…O(4) hydrogen bonding between L ligands of the neighboring dimeric unit. Although the C–H…I(O) hydrogen bonds (Table 3) were relatively weak, they were very important in holding crystal framework. As a result of these C–H…I(O) inducing contacts, the repeating  $[HgI_2L]_2$  dimeric units grow infinitely in the a, b, c directions, and then a final three-dimensional supramolecular structure was built (Figure 2). Indeed, all these intermolecular interactions are weak, we can't deny, but they may make this binuclear complex increase its melting point and become stable.

#### **Thermogravimetric Properties**

From DTG (Figure 3), it is observed that the decomposition process of the compound  $[HgI_2L]_2$  is very simple. At 107.8°C, compound  $[HgI_2L]_2$  reaches decomposition and the peak value of weightlessness rate appears at 167.1°C in the process of decomposition. On the basis of TG graphs, the complex begins to decompose at 107.8°C, indicating that its stability is very poor. Decomposition temperature of the complex is between 107.8 and 241.0°C. In this temperature range, the bonds, Hg–I and Hg–N break. Total weightlessness is 70.19% when the temperature reaches 700°C, with the last product HgO. Decomposition of the compound with an endothermic process occurs at the same time.

#### SUPPLEMENTAL MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC number 813846. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (e-mail: HYPERLINK "mailto:deposit@ccdc.cam.ac.uk" deposit@ccdc.cam.ac.uk, or URL: http://www.ccdc.cam.ac.uk).



FIG. 2. Three-dimensional supramolecular framework of compound  $[HgI_2L]_2$  (along c axis), with  $CH \cdots O(I)$  interaction showed by dotted lines.



FIG. 3. Thermal analysis curve of the compound [HgI<sub>2</sub>L]<sub>2</sub>.

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