



# Halide effects on formation and physicochemical properties of mercury(II) complexes containing Y-type tridentate N-donor



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## ABSTRACT

Self-assembly of  $\text{HgX}_2$  ( $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) with Y-type 2,6-bis[(2-isonicotinoyloxy-5-methylphenyl)methyl]-1-isonicotinoyloxy-4-methylbenzene (L) yields 2D consisting of alternate prismatic *P*- and *M*-helical-linked-layers, 1D consisting of *P*- and *M*-helices, and simple 2D sheet in a unique Y-type mode, respectively. The L/Hg(II) ratio of each product (3/3 for  $\text{Cl}^-$ ; 2/3 for  $\text{Br}^-$ ; 1/3 for  $\text{I}^-$ ) is dependent on the nature of the halide anions. The coordinating environments around of Hg(II) ion approximate to a square pyramid for  $\text{Cl}^-$ , a square planar and a distorted tetrahedral geometry for  $\text{Br}^-$ , and distorted tetrahedral arrangement for  $\text{I}^-$ , respectively. Photoluminescence wavelengths are strongly depending on the halide anions, and coordination ability to L is in the order of  $\text{X}^- = \text{Cl}^- > \text{Br}^- > \text{I}^-$ . Such physicochemical properties were explained by electronic and steric natures of halide anions.

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## 1. Introduction

Assemblies of desirable molecular topology via suitable combination of metal cations as an angle component and organic donors as a rigid spacer have been a hot issue for the past decade, owing to their task-specific applications in the fields of gas adsorption, mixed-valence system, photo-induced electron or energy transfer, magnetic exchange, semiconductors, catalysts, luminescent chemosensors, ion-exchangers, and super-array [1–10]. In particular, various new types of organic donors have been employed for the tailor-made construction of functional skeletons. To date, tridentate donors have generated a variety of coordination skeletons including coordination cages or triangular module coordination polymers owing to flexibility in bridging ability, bite angles, and conformation of the tridentate donor ligands [11–18], but the systematic coordination polymers containing interesting Y-type tridentate ligands are relatively rare [5]. Meanwhile, (counter)anions, directly and indirectly, play significant roles in formation and function of molecular skeletons owing to their non-innocent features such as negative charge, polarizability, size, geometry, strong solvent effects, weak interactions,

and pH dependence [19–23]. For instance, the ubiquitous  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  anions have both similarities and differences in shape, charge, size, coordinating ability, and metallophilicity [19].

In order to scrutinize the direct roles of halide anions and to confirm the proof-of-concept experiments on complexation of a Y-type tridentate N-donor ligand, self-assembly of  $\text{HgX}_2$  ( $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) with 2,6-bis[(2-isonicotinoyloxy-5-methylphenyl)methyl]-1-isonicotinoyloxy-4-methylbenzene (L) was carried out. Herein we report the halides' role and driving force behind the 1D and 2D coordination polymerization along with their physicochemical properties. Their different coordination chemistry including mole ratio, coordination numbers, and related photo-physical properties has been discussed. The environmentally problematic mercury(II) ion utilized herein has been known to act as various directional central metal units such as linear, T-shaped, tetrahedral, and octahedral geometries [24–26].

## 2. Experimental

### 2.1. Materials and measurements

All commercialized chemicals including  $\text{HgX}_2$  ( $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) were purchased from Aldrich, and used without further purification. 2,6-Bis[(2-isonicotinoyloxy-5-methylphenyl)methyl]-1-isonicotinoyloxy-4-methylbenzene (L) was prepared according

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to the literature [5]. Elemental microanalyses (C, H, N) were performed on solid samples by the Pusan center, KBSI, using a Vario-EL III. Thermal analyses were undertaken under a nitrogen atmosphere at a scan rate of 10 °C/min using a Labsys TGA-DSC 1600. Infrared spectra were obtained on a Nicolet 380 FT-IR spectrometer with samples prepared as KBr pellets. <sup>1</sup>H (300 MHz) NMR spectra were recorded on a Varian Mercury Plus 300. Photoluminescence spectra were acquired on a Hitachi F-7000.

## 2.2. Synthesis of [HgCl<sub>2</sub>(L)]·2CH<sub>2</sub>Cl<sub>2</sub> (**1**)

A methanol solution (2 mL) of HgCl<sub>2</sub> (0.05 mmol, 15.6 mg) was layered onto a dichloromethane solution (2 mL) of L (0.05 mmol, 33.2 mg). After 5 days, colorless crystals suitable for single crystal X-ray diffraction were obtained in an 82% yield (40.0 mg) based on Hg(II) salt. m. p. 250 °C (dec.). Anal. Calcd for C<sub>43</sub>H<sub>37</sub>N<sub>3</sub>O<sub>6</sub>Cl<sub>6</sub>Hg: C, 46.74; H, 3.37; N, 3.80%. Found: C, 45.90; H, 3.28; N, 3.85%. IR (KBr, cm<sup>-1</sup>): 1744 (s, ν(C=O)), 1559 (w), 1506 (w), 1415 (m), 1273 (s), 1260 (m), 1195 (m), 1129 (w), 1062 (m), 877 (w), 854 (w), 813 (w), 754 (m), 697 (m), 673 (w).

## 2.3. Synthesis of [Hg<sub>3</sub>Br<sub>6</sub>(L)<sub>2</sub>]·4H<sub>2</sub>O·2CH<sub>2</sub>Cl<sub>2</sub> (**2**)

An acetonitrile solution (2 mL) of HgBr<sub>2</sub> (0.06 mmol, 21.6 mg) was layered onto a dichloromethane solution (2 mL) of L (0.04 mmol, 26.5 mg). After 3 days, colorless crystals suitable for single crystal X-ray diffraction were obtained in an 80% yield (38.5 mg) based on Hg(II) salt. m. p. 215 °C (dec.). Anal. Calcd for C<sub>84</sub>H<sub>78</sub>N<sub>6</sub>O<sub>16</sub>Cl<sub>4</sub>Br<sub>6</sub>Hg<sub>3</sub>: C, 38.06; H, 2.97; N, 3.17%. Found: C, 38.20; H, 3.01; N, 3.12%. IR (KBr, cm<sup>-1</sup>): 1745 (s, ν(C=O)), 1606 (w), 1564 (w), 1495 (w), 1469 (w), 1416 (m), 1325 (w), 1272 (s), 1194 (s), 1130 (m), 1087 (w), 1062 (m), 1009 (w), 876 (w), 851 (w), 809 (w), 754 (m), 698 (w), 678 (w).

## 2.4. Synthesis of [Hg<sub>3</sub>(μ-I)<sub>3</sub>I<sub>3</sub>(L)] (**3**)

A methanol solution (1 mL) and acetonitrile solution (0.5 mL) of HgI<sub>2</sub> (0.06 mmol, 9.1 mg) was layered onto a chloroform solution (1 mL) of L (0.02 mmol, 13.3 mg). After 7 days, colorless crystals suitable for single crystal X-ray diffraction were obtained in an 81% yield (18.1 mg) based on Hg(II) salt. m. p. 205 °C (dec.). Anal. Calcd for C<sub>41</sub>H<sub>33</sub>N<sub>3</sub>O<sub>6</sub>I<sub>6</sub>Hg<sub>3</sub>: C, 24.30; H, 1.64; N, 2.07%. Found: C, 24.20; H, 1.66; N, 2.10%. IR (KBr, cm<sup>-1</sup>): 1754 (m, ν(C=O)), 1736 (s, ν(C=O)), 1604 (w), 1563 (w), 1498 (w), 1472 (w), 1415 (m), 1324 (w), 1282 (s), 1269 (s), 1195 (s), 1137 (w), 1114 (w), 1060 (m), 808 (w), 757 (m), 697 (w), 680 (w).

## 2.5. Crystal structure determinations

X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated Mo Kα (λ = 0.71073 Å) and a CCD detector at ambient temperature. Thirty-six frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the multi-scan method (SADABS) [27]. The structures were solved by the direct method (SHELXS 97) and refined by full-matrix least squares techniques (SHELXL 97) [28]. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined only for the isotropic displacement parameters. The crystal parameters and procedural information corresponding to the data collection and structure refinement are listed in Table 1.

**Table 1**  
Crystal data and structure refinement for **1–3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Formula	C <sub>43</sub> H <sub>37</sub> N <sub>3</sub> O <sub>6</sub> Cl <sub>6</sub> Hg	C <sub>84</sub> H <sub>78</sub> N <sub>6</sub> O <sub>16</sub> Cl <sub>4</sub> Br <sub>6</sub> Hg <sub>3</sub>	C <sub>41</sub> H <sub>33</sub> N <sub>3</sub> O <sub>6</sub> I <sub>6</sub> Hg <sub>3</sub>
M <sub>w</sub>	1105.05	2650.55	2026.87
Cryst. system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P2 <sub>1</sub> /c
a (Å)	8.9314(3)	8.8491(3)	17.2464(3)
b (Å)	12.8564(4)	16.4620(6)	12.8289(2)
c (Å)	20.9226(7)	16.7092(5)	27.4204(4)
α (°)	72.540(2)	99.204(2)	90
β (°)	88.950(2)	101.426(2)	125.851(1)
γ (°)	74.408(2)	96.218(2)	90
V (Å <sup>3</sup> )	2202.34(1)	2330.35(1)	4917.42(1)
Z	2	1	4
d <sub>calcd</sub> (g/cm <sup>3</sup> )	1.666	1.889	2.738
μ (mm <sup>-1</sup> )	3.909	7.680	13.155
R <sub>int</sub>	0.0363	0.0504	0.1277
F(000)	1092	1270	3624
GoF on F <sup>2</sup>	1.088	1.034	1.013
R <sub>1</sub> [I > 2σ(I)] <sup>a</sup>	0.0473	0.0658	0.0795
wR <sub>2</sub> (all data) <sup>b</sup>	0.1253	0.2170	0.1802

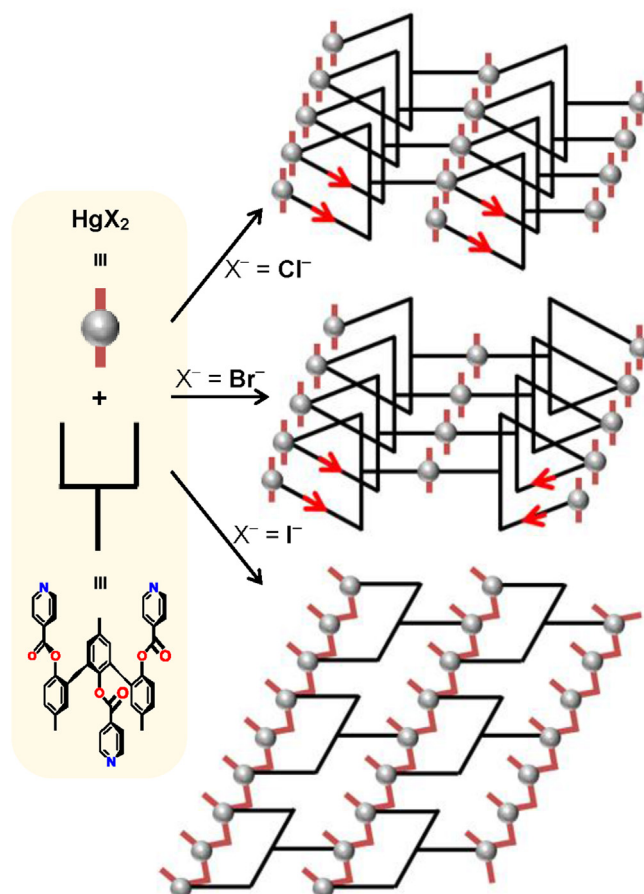
$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left( \frac{\sum w(F_o^2 - F_c^2)^2}{\sum wF_o^2} \right)^{1/2}$$

## 3. Results and discussion

### 3.1. Synthesis

Self-assembly of HgX<sub>2</sub> (X<sup>-</sup> = Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>) with 2,6-bis[(2-isonicotinoyloxy-5-methylphenyl)methyl]-1-isonicotinoyloxy-4-



**Scheme 1.** Synthetic procedure of **1** (X<sup>-</sup> = Cl<sup>-</sup>), **2** (X<sup>-</sup> = Br<sup>-</sup>), and **3** (X<sup>-</sup> = I<sup>-</sup>).

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