



## Non-covalent interaction in metal cation-directed assembly of supramolecular architectures: Synthesis, characterization and crystal structures

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### ABSTRACT

Three new complexes [Zn(NCS)<sub>2</sub>L<sub>2</sub>] (**1**), [Hg(SCN)<sub>2</sub>L<sub>2</sub>] (**2**) and [Mn(NCS)<sub>2</sub>L<sub>4</sub>] (**3**), have been synthesized by the self-assembly of 4-imidazolylchalcone (abbreviated as L) with M(SCN)<sub>2</sub> (M = Hg<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>). The complexes have been characterized by spectroscopic and crystallographic methods. <sup>1</sup>H NMR spectra of complexes **1–3** present that metal ions have effect on the chemical shifts of protons of coordinated groups. Three complexes illustrate different molecular structures due to the different coordinated modes of the metal ions. In the title complexes, the coordination geometries of Zn, Hg and Mn ions are tetrahedral N<sub>4</sub>, N<sub>2</sub>S<sub>2</sub> and octahedral N<sub>6</sub>, respectively. Finally, hydrogen bonding interactions assemble the different coordination units into higher-dimensional frameworks. The results show that the metal ion and weak non-covalent interactions play important roles in the construction of the final supramolecular structures.

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### 1. Introduction

During the past few decades, the design and synthesis of supramolecular structures based on strong coordinate bonds and multiple weak non-covalent forces, such as intermolecular hydrogen bonding interactions, has become one of the most active fields in coordination chemistry and crystal engineering due to their fascinating structural features and potential applications as functional materials [1–6]. The non-covalent forces are weaker than the coordinate bonds, however, they are common and play critical roles in forming the supramolecular structures due to their significant contribution to the self-assembly process [7–11]. More work has been focused on the weak non-covalent forces in the design and synthesis of supramolecular structures.

It is well known that the assembly process can be affected by many factors, such as the choice of ligands, anions, metal ions, and so on [12–16]. Carbonyl group, which widely exists in organic and biological systems, plays a crucial role in stabilizing both the extended crystal structures of small molecules and biological systems through various weak intermolecular interactions generated via carbonyl group [1]. Thus, we have designed and synthesized a

new chalcone derivative containing imidazolyl and carbonyl group via Claisen–Schmidt condensation of acetophenone with 4-imidazolylbenzaldehyde. The ligand is expected to create not only coordinate bond through imidazolyl nitrogen atom but also intermolecular non-covalent interaction via carbonyl oxygen atom in the assembly of the complexes.

At the same time, the rational selection of anions is very important because the anions can control and adjust the topologies of coordination frameworks through coordinate bonds or non-covalent interactions. In coordination chemistry, thiocyanate has been widely used as anion and coligand for the construction of the coordination complex [17–21]. It can coordinate to metals by either the sulfur or the nitrogen atom, or both. The most important is that, when thiocyanate acts as a terminal ligand, the uncoordinated sulfur or nitrogen atom is often involved in intermolecular or intramolecular hydrogen bonding and other weak interactions, which play extremely important roles to regulate and stabilize the supramolecular structure.

It is clear that different metal ions have different coordination modes. In construction of higher-dimensional complex architectures, Zn(II) often shows low coordination number of four with tetrahedral coordination geometry [12,13,22]. However, Mn(II) ion has attracted our interest, due to its high coordination number and the magnetic properties of its complex [23]. Hg(II) complexes have been widely studied because of their structural diversities and

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attractive optical properties [24]. In order to probe the influence of metal ions on the supramolecular construction, a study was carried out with different metal salts having the same thiocyanate ions. Herein, three different structural supramolecular complexes based on the reaction of 4-imidazolylchalcone and  $M(\text{SCN})_2$  ( $M = \text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ) were obtained by self-assembling. In the molecular structure of **1**, Zn(II) ion is four coordinated by two nitrogen atoms of the imidazolyl groups and two nitrogen atoms of thiocyanate ions. However, in the molecular structure of **2**, Hg(II) ion is four coordinated by two imidazolyl nitrogen atoms and two sulfur atoms of thiocyanate ions to form a  $\text{S}_2\text{N}_2$  distorted tetrahedral geometry. For that of **3**, Mn(II) ion is in a  $\text{N}_6$  distorted octahedral geometry. Finally, higher-dimensional structures are formed through different weak non-covalent forces due to the different coordination modes of metal ions. Here, we present the synthesis, spectroscopy characterization and crystal structures of complexes **1–3**.

## 2. Experimental

### 2.1. General

All commercially available chemicals are of analytical grade and used without further purification. The solvents were purified by conventional methods. 4-Imidazolylbenzaldehyde was synthesized according to the methods reported [25].

### 2.2. Synthesis

#### 2.2.1. Synthesis of 4-imidazolylchalcone (**L**)

A methanol solution (40 mL) of NaOH (4.00 g, 0.1 mol) was added dropwisely to a stirred methanol (20 mL) solution of 4-imidazolylbenzaldehyde (1.72 g, 10 mmol) and acetophenone (1.20 g, 10 mmol) in a round-bottom flask at room temperature. The yellow solid product formed immediately. After filtration, the product was washed by methanol and water, dried in vacuo. Yield: 2.33 g, 85%. *Anal. Calc.* for  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}$ : C, 78.81; H, 5.14; N, 10.21. Found: C, 78.50; H, 5.48; N, 10.01%.  $^1\text{H NMR}$ : (400 MHz,  $\text{CD}_3\text{COCD}_3$ ),  $\delta$  (ppm): 7.145 (s, 1H), 7.573, 7.592, 7.611 (t,  $J = 7.6$  Hz, 2H), 7.671, 7.690, 7.708 (t,  $J = 7.6$  Hz, 1H), 7.779, 7.800 (d,  $J = 8.4$  Hz, 2H), 7.815

(1H), 7.876 (s, 1H), 7.983, 8.022 (d,  $J = 15.6$  Hz, 1H), 8.053, 8.074 (d,  $J = 8.4$  Hz, 2H), 8.172, 8.191 (d,  $J = 7.6$  Hz, 2H), 8.405 (s, 1H).  $^{13}\text{C NMR}$ : (100 MHz,  $\text{CD}_3\text{COCD}_3$ ),  $\delta$  (ppm): 189.07 (C-5), 142.87 (C-7), 138.19 (C-4), 137.51 (C-11), 135.56 (C-12), 133.19 (C-1), 133.02 (C-8), 130.55 (C-10), 130.13 (C-13), 128.79 (C-2), 128.55 (C-3), 122.13 (C-6), 120.12 (C-9), 117.72 (C-14). IR  $\nu(\text{cm}^{-1})$ : 653(s), 699(s), 727(m), 778(s), 832(s), 985(s), 1019(m), 1058(s), 1108(m), 1185(m), 1219(s), 1308(s), 1336(s), 1486(m), 1552(s), 1574(s), 1600(s), 1663(s), 3093(s). MS (EI) ( $m/z$ ): *Anal. Calc.* for  $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}$ : 274.11  $[\text{M}]^+$ . Found: 274.11  $[\text{M}]^+$ . UV–Vis (DMF):  $\lambda_{\text{max}}$  (nm): 328.

#### 2.2.2. Synthesis of $\text{Zn}(\text{NCS})_2\text{L}_2$ (**1**)

Complex **1** was prepared by layering method at room temperature. A clear methanol solution (15 mL) of  $\text{Zn}(\text{NCS})_2$  (18.10 mg, 0.1 mmol) was carefully layered onto a solution of 4-imidazolylchalcone (54.86 mg, 0.2 mmol) in chloroform (15 mL). Yellow needle-shaped crystals suitable for X-ray diffraction were obtained by slow interlayer diffusion. Yield: 51.03 mg, 70%. *Anal. Calc.* for  $\text{C}_{38}\text{H}_{28}\text{ZnN}_6\text{O}_2\text{S}_2$ : C, 62.50; H, 3.86; N, 11.51. Found: C, 62.20; H, 3.53; N, 11.20%.  $^1\text{H NMR}$ : (400 MHz,  $\text{CD}_3\text{COCD}_3$ ),  $\delta$  (ppm): 7.176 (s, 1H), 7.574, 7.593, 7.612 (t,  $J = 7.6$  Hz, 2H), 7.672, 7.691, 7.709 (t,  $J = 7.6$  Hz, 1H), 7.795, 7.815 (d,  $J = 8.4$  Hz, 2H), 7.821 (1H), 7.919 (s, 1H), 7.992, 8.031 (d,  $J = 15.6$  Hz, 1H), 8.066, 8.087 (d,  $J = 8.4$  Hz, 2H), 8.173, 8.192 (d,  $J = 7.6$  Hz, 2H), 8.456 (s, 1H). IR  $\nu(\text{cm}^{-1})$ : 654(s), 694(s), 725(m), 777(s), 832(s), 982(s), 1018(s), 1067(s), 1220(s), 1311(m), 1338(s), 1525(s), 1577(w), 1604(s), 1663(s), 2093(s), 3120(m).

#### 2.2.3. Synthesis of $\text{Hg}(\text{SCN})_2\text{L}_2$ (**2**)

Complex **2** was prepared by the same synthetic procedure to complex **1** using  $\text{Hg}(\text{SCN})_2$  (31.70 mg, 0.1 mmol) instead of  $\text{Zn}(\text{NCS})_2$  to react with 4-imidazolylchalcone (54.86 mg, 0.2 mmol). Yellow rhomboid single crystals were obtained. Yield: 51.90 mg, 60%. *Anal. Calc.* for  $\text{C}_{38}\text{H}_{28}\text{HgN}_6\text{O}_2\text{S}_2$ : C, 52.74; H, 3.26; N, 9.71. Found: C, 52.43; H, 3.59; N, 9.48%.  $^1\text{H NMR}$ : (400 MHz,  $\text{CD}_3\text{COCD}_3$ ),  $\delta$  (ppm): 7.186 (s, 1H), 7.576, 7.595, 7.614 (t,  $J = 7.6$  Hz, 2H), 7.675, 7.694, 7.712 (t,  $J = 7.6$  Hz, 1H), 7.791, 7.812 (d,  $J = 8.4$  Hz, 2H), 7.823 (1H), 7.930 (s, 1H), 8.003, 8.042 (d,  $J = 15.6$  Hz, 1H), 8.072, 8.093 (d,  $J = 8.4$  Hz, 2H), 8.179, 8.198 (d,  $J = 7.6$  Hz, 2H), 8.460 (s, 1H). IR

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

Complex	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	$\text{C}_{38}\text{H}_{28}\text{ZnN}_6\text{O}_2\text{S}_2$	$\text{C}_{38}\text{H}_{28}\text{HgN}_6\text{O}_2\text{S}_2$	$\text{C}_{74}\text{H}_{56}\text{MnN}_{10}\text{O}_4\text{S}_2$
Formula weight	730.15	865.37	1268.35
$T$ (K)	298(2)	298(2)	298(2)
$\lambda$ (Å)	0.71069	0.71069	0.71069
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$
$a$ (Å)	19.13(3)	37.945(5)	34.425(5)
$b$ (Å)	5.798(8)	5.950(5)	10.949(5)
$c$ (Å)	16.58(2)	15.930(5)	17.827(5)
$\beta$ (°)	107.48(2)	105.259(5)	104.172(5)
$V$ (Å <sup>3</sup> )	1754(4)	3470(3)	6515(4)
$Z$	2	4	4
$D_{\text{calcd}}$ ( $\text{g cm}^{-3}$ )	1.382	1.657	1.293
$F(000)$	752	1704	2636
Crystal size (mm)	$0.30 \times 0.20 \times 0.20$	$0.30 \times 0.20 \times 0.20$	$0.30 \times 0.20 \times 0.20$
Reflections collected	9177	11 587	5727
Unique reflections	2989	3042	3063
Parameters	222	223	412
GOF on $F^2$	1.129	1.016	1.127
$R_1$ [ $I > 2\sigma(I)$ ]	0.0591	0.0300	0.0659
$wR_2$ [ $I > 2\sigma(I)$ ]	0.1324	0.0700	0.1780
$\Delta\rho_{\text{min/max}}$ ( $\text{e Å}^{-3}$ )	0.413/−0.359	0.726/−0.432	0.759/−0.559

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