

## Synthesis and Crystal Structures of Zn(II)- and Cd(II) - Isonicotinate Complexes

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### INTRODUCTION

Recently much attention has been paid to design and synthesis of metal-organic hybrid materials with fascinating network topologies<sup>1</sup> and potential applications as functional materials.<sup>2</sup>

Isonicotinic acid (HIN) have been widely used in synthesizing metal organic frameworks as asymmetrical rigid ligand. With regard to isonicotinic acid complex, hydrogen bonds (O-H...O) can be commonly found between uncoordinated carboxylic group and water in the complex and at the same time,  $\pi$ - $\pi$  stackings also exist in the coordination. As a consequence, a lot of isonicotinic acid complexes can form infinite extended three-dimensional network supramolecular compounds.<sup>3</sup> In the view of development of synthetic strategies and functional materials, the combination of carboxylate-containing ligands and neutral pyridyl-containing ligands can afford much more assembly process with metal ions through changing one of two types of organic ligands.<sup>4</sup>

During studies aimed at constructing cavity containing rectangular two- or three-dimensional networks using dicarboxylate and 4-pyridylcarbonitrile as spacer, we have isolated 3D-coordination polymers, [Zn(IN)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] (**1**) and [Cd(IN)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>] (**2**), respectively, using diphenic acid and 4-pyridylcarbonitrile as spacer. It is interesting that 4-pyridylcarbonitrile turned to isonicotinic acid by the acid hydrolysis in the process of reaction.<sup>5</sup> We report here the synthesis and crystal structures of the complex **1** and **2**.

### EXPERIMENTAL

All chemicals are commercially available and were used as received without further purification. Elemental analyses (C, H, N) were performed on a Carlo Erba EA-1106 Elemental Analyzer. Infrared spectra were recorded in the range

from 4000 to 400 cm<sup>-1</sup> on a Mattson Polaris FT-IR Spectrophotometer using KBr pellets. Thermogravimetric analysis (TG) was performed on a TA Discovery TGA instrument with a heating rate of 10 °C·min<sup>-1</sup>. All reactions were carried out in 23 ml Teflon-lined stainless-steel autoclave. The vessels were filled approximately to 40% capacity. The initial and final pH of the reaction was measured using Sentron 1001 pH meter.

#### Preparation of [Zn(IN)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] (**1**)

A mixture of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.111 g, 0.5 mmol), diphenic acid (0.121 g, 0.5 mmol), 4-pyridinecarbonitrile (0.052 g, 0.5 mmol), and H<sub>2</sub>O (10 mL) in the mole ratio of 1.0:1.0:1.0:1111 was placed in a 23 mL Teflon-lined Parr acid digestion bomb and heated for 3 d at 180 °C under autogenous pressure. After the mixture was removed from the oven and allowed to cool under ambient conditions for 3d., colorless needles of **1** suitable for X-ray diffraction were isolated in 57% (0.110 g) yield based on zinc. Initial pH, 4.0; final pH, 4.0. Anal. Calcd. for C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub>Zn: C, 37.77; H, 4.22; N, 7.34. Found: C, 38.35; H, 4.25; N, 7.22%. IR (KBr pellet, cm<sup>-1</sup>): 3283(m), 2972(s), 1614(m), 1579(s), 1536(s), 1444(m), 1406(s), 1054(m), 1033(m), 755(m), 710(m).

#### Preparation of [Cd(IN)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] (**2**)

A mixture of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.153 g, 0.5 mmol), diphenic acid (0.121 g, 0.5 mmol), 4-pyridinecarbonitrile (0.052 g, 0.5 mmol), and water (7 mL) was placed in a 23 ml Teflon-lined Parr acid digestion bomb and heated for 3 d at 165 °C under autogenous pressure. After the mixture was removed from the oven and allowed to cool under ambient conditions for 3d, colorless crystals (block) of **2** suitable for X-ray diffraction were isolated in 40.0% (0.083 g) yield based on Cd. Initial pH, 5.0; final pH, 5.0. Anal. Calcd. for C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>O<sub>8</sub>Cd: C, 33.62; H, 3.76; N, 6.54. Found: C, 34.23; H, 3.58; N, 6.42%. IR (KBr pellet, cm<sup>-1</sup>): 3309(s),

2975(w), 1586(s), 1541(s), 1417(s), 1384(s), 1229(m), 1058(m), 1021(m), 820(w), 770(m), 686(s).

### X-ray Structure Determination

Single crystals of **1** and **2** were obtained by the method described in the above procedures. Structural measurement for the complexes were performed on a Bruker SMART APEX CCD diffractometer using graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at the Korea Basic Science Institute. The structures were solved by direct method and refined on  $F^2$  by full-matrix least-squares procedures using the SHELXTL programs.<sup>6</sup> All non-hydrogen atoms were refined using anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with the DIAMOND program.<sup>7</sup> The crystallographic data for complex **1** and **2** is listed in Table 1.

## RESULTS AND DISCUSSION

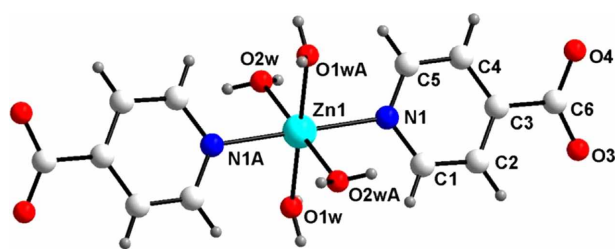
The compounds were isolated from the reaction mixture of Zn(OAc) $_2$ ·2H $_2$ O (**1**)/Cd(NO $_3$ ) $_2$ ·4H $_2$ O (**2**), diphenic acid, 4-pyridylcarbonitrile, and H $_2$ O in the mole ratio of 1.0:1.0:1.0:1111(**1**)/778(**2**) by the hydrothermal technique. The diphenic acid present in the initial reaction mixture was not found in the crystalline product and 4-pyridylcarbonitrile was changed to isonicotinic acid by the acid hydrolysis in the hydrothermal processes. However, the compound **1** was reported previously by the reaction of Zn(NO $_3$ ) $_2$  with isonicotinic acid.<sup>8</sup>

Our first aim in this work was to obtain the 2D or 3D network MOF complexes which metal centers are bridged by the dicarboxylate anion and N-donor system. Unfortunately, attempts to obtain such materials by varying stoichiometry, temperature, and other reaction parameters proved to be generally unsuccessful.

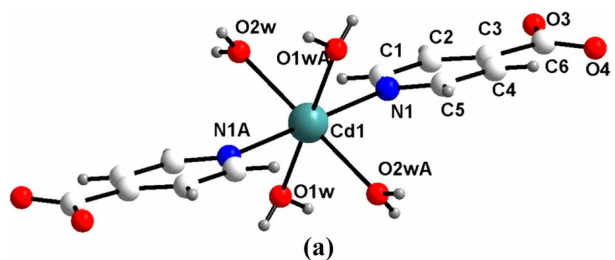
Complex **1** and **2** show essentially the same structure

Table 1. Crystal data and structure refinement for complexes **1** and **2**

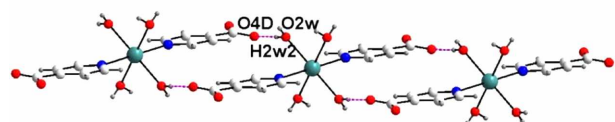
Complex	<b>1</b>	<b>2</b>
Empirical formula	C $_{12}$ H $_{16}$ N $_2$ O $_8$ Zn	C $_{12}$ H $_{16}$ N $_2$ O $_8$ Cd
Formula weight	381.64	428.67
T (K)	223(2)	223(2)
$\lambda$ (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
<i>a</i> (Å)	6.3286(4)	6.4300(3)
<i>b</i> (Å)	6.8862(4)	6.9164(4)
<i>c</i> (Å)	7.2749(6)	9.4100(5)
$\alpha$	96.098(2)	94.662(2)
$\beta$ (°)	105.005(2)	104.7583(19)
$\gamma$	112.995(2)	111.9290(19)
<i>V</i> (Å $^3$ )	349.83(4)	368.07(3)
<i>Z</i>	1	1
$\mu$ (mm $^{-1}$ )	1.803	1.529
<i>F</i> (000)	196	214
$\theta$ (°)	2.34 to 28.40	2.28 to 28.38
Absorption correction	Multi-scan, $T_{\min} = 0.7033$ , $T_{\max} = 0.8995$	Multi-scan, $T_{\min} = 0.7811$ , $T_{\max} = 0.9139$
Limiting indices	$-8 \leq h \leq 8$ , $-9 \leq k \leq 9$ , $-12 \leq l \leq 12$	$-8 \leq h \leq 8$ , $-9 \leq k \leq 9$ , $-12 \leq l \leq 12$
Reflections collected	14592	13957
Independent reflections	17493 [R(int) = 0.0504]	1836 [R(int) = 0.0386]
Observed reflections [ $I \geq 2\sigma(I)$ ]	1608	1794
Goodness-of-fit on $F^2$	1.134	1.155
$R_1$ [ $I \geq 2\sigma(I)$ ]	0.0245	0.0201
$wR_2$ [ $I \geq 2\sigma(I)$ ]	0.0542	0.0412
$R_1$	0.0308	0.0218
$wR_2$	0.0567	0.0421
Largest peak and hole (e Å $^{-3}$ )	0.416 and -0.325	0.435 and -0.331



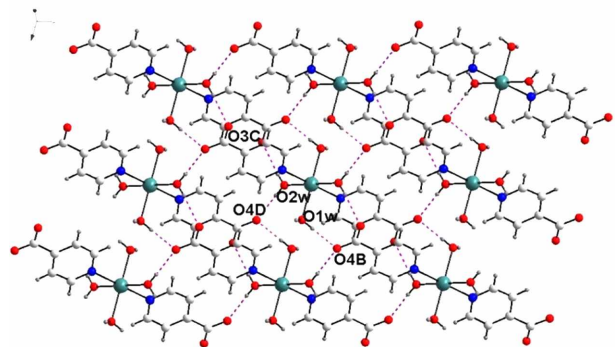
**Figure 1.** Coordination environment in **1** (Symmetry codes: A,  $-x, -y, -z$ ).



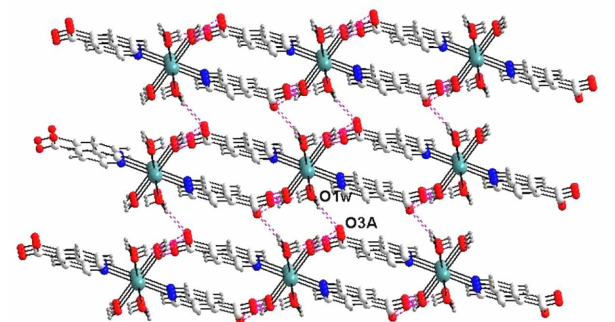
(a)



(b)



(c)



(d)

**Figure 2.** (a) Coordination environment in **2**. (b) 1D chain in **2**. (c) 2D layer in **2**. (d) 3D supramolecular framework formed by O-H...O hydrogen bond in **2**. Symmetry codes: (a) A,  $-x, -y, -z$ ; (b)-(d) A,  $x-1, y-1, z-1$ ; B,  $-x+1, -y, -z+1$ ; C,  $x-1, y, z-1$ ; D,  $x, y, z-1$ .

(Fig. 1 and 2). Selected bond lengths and angles for both complexes are listed in Table 2. Each metal(II) ion in both complexes is coordinated in a slightly distorted octahedral  $N_2O_4$  environment by two isonicotinic N-atoms and four O atoms of four coordinated water molecules. Each metal(II) ion lies in the equatorial plane (O2wO1wO1wAO2wA mean deviation, 0.000(1) Å). The M(II)-O (Zn-O; 2.096(1), 2.157(1) and Cd-O; 2.288(1), 2.328(2) Å) and M(II)-N distances (Zn-N; 2.135(1), Cd-N; 2.311(1) Å) are similar to those of  $[Zn(C_6H_4NO_2)_2(H_2O)_2] \cdot 0.5C_3H_7NO^9$  and  $[Cd(IN)_2(H_2O)] \cdot DMF^{10}$  respectively. The bond angles around the metal(II) ion are as follows: *trans*-L-M-L = 180(8) and *cis*-L-M-L = 86.61(5)–91.86(5) for Zn(II) and *trans*-L-M-L = 180(8) and *cis*-L-M-L = 86.16(5)–93.84(5)° for Cd(II) (Table 2). Due to delocalization of electron density in the carboxylate anion the C-O bond distances are the same within an experimental uncertainties (Table 2). The carboxyl groups in isonicotinic acid are deprotonated and the dihedral angle of pyridyl rings are 3.758(41)° for **1** and 0.000(85)° for **2**,

**Table 2.** Selected bond lengths (Å) and angles (°) for the Complexes **1** and **2**

Complex 1			
Zn1-O2w	2.096(1)	Zn1-O2wA	2.096(1)
Zn1-N1	2.135(1)	Zn1-N1A	2.135(1)
Zn1-O1w	2.157(1)	Zn1-O1wA	2.157(1)
C6-O3	1.256(2)	C6-O4	1.255(2)
O2w-Zn1-O2wA	180.00(8)	O2w-Zn1-N1	91.86(5)
O2wA-Zn1-N1	88.14(5)	O2w-Zn1-N1A	88.14(5)
O2wA-Zn1-N1A	91.86(5)	N1-Zn1-N1A	180.00(5)
O2w-Zn1-O1w	86.78(5)	N1-Zn1-O1w	88.61(5)
N1A-Zn1-O1w	91.39(5)	O2w-Zn1-O1wA	93.22(5)
O2wA-Zn1-O1wA	86.78(5)	N1-Zn1-O1wA	91.39(5)
N1A-Zn1-O1wA	88.61(5)	O1w-Zn1-O1wA	180.00(7)
O4-C6-O3	125.87(15)	O4-C8-O3	125.5(4)
Complex 2			
Cd1-O2w	2.328(2)	Cd1-O2wA	2.328(2)
Cd1-N1	2.311(1)	Cd1-N1A	2.311(1)
Cd1-O1w	2.288(1)	Cd1-O1wA	2.288(1)
C6-O3	1.255(2)	C6-O4	1.251(2)
O2w-Cd1-O2wA	180.00(8)	O2w-Cd1-N1	93.84(5)
O2wA-Cd1-N1	86.16(5)	O2w-Cd1-N1A	86.16(5)
O2wA-Cd1-N1A	93.84(5)	N1-Cd1-N1A	180.00(8)
O2w-Cd1-O1w	93.42(6)	N1-Cd1-O1w	92.61(5)
N1A-Cd1-O1w	87.39(5)	O2w-Cd1-O1wA	86.58(6)
O2wA-Cd1-O1wA	93.42(6)	N1-Cd1-O1wA	87.39(5)
N1A-Cd1-O1wA	92.61(5)	O1w-Cd1-O1wA	180.00(7)
O1w-Cd1-O2wA	86.58(6)	O4-C6-O3	125.84(16)

Symmetry transformations used to generate equivalent atoms: A)  $-x, -y, -z$ .

**Table 3.** Hydrogen bonds for **2** [ $\text{\AA}$  and  $^\circ$ ]

D-H...A	D-H	H...A	D...A	$\angle$ DHA
Complex <b>2</b>				
O1w-H1w1...O3A	0.79	2.00	2.778(2)	168
O1w-H2w1...O4B	0.79	1.87	2.652(2)	173
O2w-H1w2...O3C	0.77	2.05	2.808(2)	169
O2w-H2w2...O4D	0.79	1.98	2.769(2)	178

Symmetry transformations used to generate equivalent atoms: A,  $x-1, y-1, z-1$ ; B,  $-x+1, -y, -z+1$ ; C,  $x-1, y, z-1$ ; D,  $x, y, z-1$ .

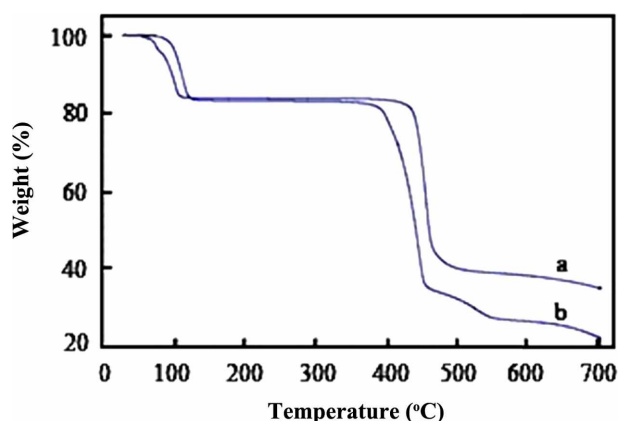
respectively.

The crystal packing is directed by hydrogen bond interactions with the participation of water H-donor atoms and carboxylic group O atoms acting as acceptors (Table 3). In a typical complex **2**, the hydrogen bonds (O2w-H2...O4D) form 1D chains along *c*-axis (Fig. 2(b)). The chains are inter-linked by hydrogen bonds (O1w-H2...O4B, O2w-H1...O3C) to form 2D network along *a*-axis (Fig. 2(C)). In addition, hydrogen bond (O1w-H1...O3A) between the water molecule and carboxyl oxygen atom of another adjacent ac-plane contribute significantly to the assembly of these 2D networks into supramolecular 3D network (Fig. 2(d)).

The IR spectra show a typical the antisymmetric and symmetric stretching bands of carboxylate groups at 1579 and 1406  $\text{cm}^{-1}$  for **1** and at 1541 and 1384  $\text{cm}^{-1}$  for **2**, respectively.<sup>11</sup> For the correlation of the infrared spectra with the structures of metal carboxylates the difference between the asymmetric and symmetric carboxylate stretches is often used.<sup>12</sup> The separation ( $\Delta$ ) between  $\nu_{\text{asym}}(\text{CO}_2)$  and  $\nu_{\text{sym}}(\text{CO}_2)$  is 173  $\text{cm}^{-1}$  for **1** and 157  $\text{cm}^{-1}$  for **2**, respectively. This value is similar to the observed values ( $170 \pm 10 \text{ cm}^{-1}$ ) for the compounds with the ionic  $\text{COO}^-$  group.<sup>11</sup> On the other hand, the  $\Delta$  values calculated from the structural data of the complex are 165.29  $\text{cm}^{-1}$  for **1** and 170.25  $\text{cm}^{-1}$  for **2**, respectively. ( $\Delta = 1818.1 \delta_r + 16.47 (\theta_{\text{OCO}} - 120) + 66.8$ , where  $\delta_r$  is difference between the two CO bond lengths ( $\text{\AA}$ ) and  $\theta_{\text{OCO}}$  is the OCO angle ( $^\circ$ )<sup>12</sup>

The  $\nu(\text{O-H})$  stretch was observed at  $\sim 3300 \text{ cm}^{-1}$  for both complex. The peaks at 1614–1536  $\text{cm}^{-1}$  are attributable to the  $\nu(\text{C-O})$ ,  $\nu(\text{C-N})$  or  $\nu(\text{C-C})$  of aromatic group.<sup>13</sup> In addition, the peaks between 820 and 686  $\text{cm}^{-1}$  can be assigned to the  $\nu(\text{C-H})$  of pyridine ring.<sup>14</sup>

TG analysis of compound **1** and **2** was performed to observe their thermal behaviors. As shown in Fig. 3, the TG curve of complex **1** shows the first weight loss of 16.00% (calcd. 18.88%) from 50  $^\circ\text{C}$  to 120  $^\circ\text{C}$  in accord with the release of four water molecules based on the chemical formula. Upon subsequent heating, the compound remains intact to 365 $^\circ\text{C}$ , followed by a rapid loss of 45.56% (calcd.



**Figure 3.** Thermogravimetric analysis of (a) **1** and (b) **2**.

63.99%), corresponding to the loss of two IN molecules in the temperature range of 365–600  $^\circ\text{C}$ . The total weight loss of 61.63% is less than the calculated value of 78.76% if the final product is assumed to be ZnO, which indicate that the decomposing process is not complete due to the use of nitrogen protection. For **2**, The first weight loss of 16.43% from 63 to 132  $^\circ\text{C}$  corresponds to the release of four water molecules (calcd. 16.81%). The second weight loss of 56.52% (calcd. 56.97%) from 275 to 600  $^\circ\text{C}$  corresponds to the release of two IN ligands. The final product is also assumed to be CdO (obsd. 26.4%, calcd. 29.95%).

In conclusion, two new polymeric complexes,  $[\text{M}(\text{IN})_2(\text{H}_2\text{O})_4]_n$  ( $\text{M} = \text{Zn}(\mathbf{1})$  and  $\text{Cd}(\mathbf{2})$ ) were successfully isolated by the hydrothermal technique, respectively. In the complex, monomeric metal (II) complex is interconnected by hydrogen bond between water H-donor atoms and carboxylic group O atoms to give 3D network. The isonicotinate ligand in the crystalline product was formed from 4-pyridylcarbonylnitrile as initial reactant by the acid hydrolysis in the process of reaction.

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**Supporting Information.** Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-1443978 (**1**) and CCDC-1443979 (**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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