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# Metal-controlled assembly tuning the topology and dimensionality of coordination polymers of Ag(I), Cd(II) and Zn(II) with the flexible 2-(1H-imidazole-1-yl)acetic acid (Hima)

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## Abstract

Three new, inorganic–organic coordination polymers based on a versatile linking unit 2-(1*H*-imidazole-1-yl)acetate (ima) and Ag<sup>I</sup>, Cd<sup>II</sup> and Zn<sup>II</sup> ions, exhibiting one to three dimensionalities and different topology structures, have been prepared in water medium and structurally characterized by single-crystal X-ray diffraction analysis. Reaction of AgNO<sub>3</sub> with Hima afforded a neutral one-dimensional (1-D) chains [Ag(ima)]<sub>n</sub> (1) which exhibits a pseudo two-dimensional (2-D) layered architecture through  $\pi$ - $\pi$  stacking interaction between imidazole rings and intermolecular Ag···Ag interactions. Reaction of CdCl<sub>2</sub> with Hima yielded neutral 2-D coordination polymers [Cd(ima)<sub>2</sub>]<sub>n</sub> (2) possessing (6, 3) topology structures, which further stack into 3-D supramolecular networks through C–H···O weak interactions. While Zn(NO<sub>3</sub>)<sub>2</sub> was used, a non-centric 3-D coordination polymer [Zn(ima)<sub>2</sub>]<sub>n</sub> (3) featuring a 3-fold interpenetrating diamondoid net was isolated. Among these polymers, the building block ima anion exhibits different coordination modes. These results indicate that the versatile nature of this flexible ligand, together with the coordination preferences of the metal ions, play a critical role in construction of these novel coordination polymers. The spectral, thermal and SHG (second-harmonic generation) properties of these new materials have also been investigated.

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Keywords: Coordination polymer; Silver metal; Zinc metal; Cadmium metal; 2-(1H-Imidazole-1-yl) acetic acid; X-ray

## 1. Introduction

Metal-organic frameworks (MOFs) have been successfully constructed and self-assembled by metal ions and well-designed organic ligands, which have attracted considerable attention currently in the field of supramolecular chemistry and crystal engineering, due to their unique electronic, magnetic, catalytic, optical and second-order NLOacitve properties [1–5]. So far, a variety of discrete and a wide range of 1D-3D MOFs have been achieved in the last decade [1–4], however, the crystal engineering of MOFs with desired topologies and specific properties still remains a difficult challenge since there are a variety of factors influ-

\* Corresponding author. Tel./fax: +86 531 82350869. *E-mail address:* ceswyt@sohu.com (Y.-T. Wang). encing the self-assembly process [6] such as the coordination geometry and the oxidation state of the metal ions [6], metal-to-ligand ratio [7], nature of the ligands [8], solvents [9] and/or counteranions [10], even the reaction temperature and pH value [11]. In general, the design of appropriate ligands as "building blocks", together with the coordination preferences of the metal ions as "nodes", is undoubtedly the most rational synthetic strategy in manipulating the MOF topologies and thus modifying the properties of these materials. In this context, the multi-functional linkers containing both imidazole and carboxylate groups have been much less used in the construction of MOFs, since they do not readily fit into predictable patterns due to their structural flexibility and conformational freedom, although some MOFs have recently been constructed by a few related flexible ligands [1a,12,13].

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Scheme 1. Coordination modes of ima in 1-3.

As a sequel work of our on-going investigation on the design and control of the self-assembly of MOFs based on asymmetric rigid ligands [8,14], we chose 2-(1*H*-imidazole-1yl) acetic acid (Hima) as a flexible multifunctional building block by considering its following advantages compared with the usual rigid ligands: (i) it possesses flexibility due to the presence of a  $-CH_2-$  spacer between the imidazole and carboxylate groups (see Scheme 1) which may lead to novel topological architectures upon metal complexation under appropriate conditions; (ii) it has three potential binding sites when coordinating to metal ions; (iii) no metal complex containing this ligand has been documented to date. We now report herein the preparations and characterizations of three new MOFs of ima, namely  $[Ag(ima)]_n$  (1)  $[Cd(ima)_2]_n$  (2) and  $[Zn(ima)_2]_n$  (3).

## 2. Experimental

#### 2.1. Materials and general methods

All the starting materials and solvents for syntheses were obtained commercially (ACROS) and used as received. Elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra as KBr discs were recorded pellets in range 400–4000 cm<sup>-1</sup> on a Nicolet 5DX spectrometer. Thermogravimetric analysis (TGA) data were collected with a Perkin-Elmer TGS-2 analyzer in N<sub>2</sub> at a heating rate of 10 °C min<sup>-1</sup>.

## 2.2. Nonlinear optical property measurement

Kurtz powder SHG measurements [15] were performed on ground samples of crystalline 1–3 with a synchroscan streak camera (Hamamatsu Model C1587, 8 ps resolution) connected to a polychromator as the detector system, and an optical parametric generator (Spectra Physics, Model:OPA-800C) pumped by a mode-locked Ti:sapphire laser oscillator–amplifier system (Spectra Physics, Model: Hurricane) as the pump source. The powder second-harmonic signals were compared to that of urea to determine the relative SHG efficiencies of 1–3.

## 2.3. Synthesis of $[Ag(ima)]_n$ (1)

To a solution of Hima (12.6 mg, 0.1 mmol) in water (5 mL) a dilute aqueous solution of NaOH was added with stirring to adjust the pH value of the mixture to ca. 7.

Then, a water solution (5 mL) of AgNO<sub>3</sub> (17 mg, 0.1 mmol) was added slowly to the above solution. The resultant colorless solution was filtered. Block colorless single-crystals suitable for X-ray diffraction were obtained by slow evaporation within one week in 65% yield. Anal. Calcd for C<sub>5</sub>H<sub>5</sub>AgN<sub>2</sub>O<sub>2</sub>: C, 25.78; H, 2.16; N, 12.02%. Found: C, 25.71; H, 2.18; N, 12.09%. IR (cm<sup>-1</sup>): 3109vs, 2977m, 1677m, 1578vs, 1515s, 1384vs, 1309vs, 1249s, 1240s, 1215m, 1190m, 1103vs, 1103vs, 1036vs, 975m, 942m, 923m, 911m, 866m, 830vs, 786s, 774m, 743s, 688m, 654m, 625m, 584m.

## 2.4. Synthesis of $[Cd(ima)_2]_n$ (2)

The solution of Hima (25 mg, 0.2 mmol) in water (5 mL) was added an aqueous solution (5 mL) of CdCl<sub>2</sub> (23 mg, 0.1 mmol) followed by dropwise addition of a dilute aqueous solution of NaOH, with stirring until the pH was *ca*. 7. Further stirring of the solution for *ca*. 30 min resulted in a small quantity of colorless precipitate, which was filtered off. The resultant colorless filtrate was left to stand at room temperature. Colorless block-like single-crystals suitable for X-ray diffraction were obtained by slow evaporation within three days in 75% yield. Anal. Calcd for C<sub>10</sub>H<sub>10</sub>CdN<sub>4</sub>O<sub>4</sub>: C, 33.12; H, 2.78; N, 15.45%. Found: C, 33.22; H, 2.75; N, 15.49 %. IR (cm<sup>-1</sup>): 3137vs, 1593vs, 1510m, 1442m, 1396vs, 1316vs, 1293m, 1235m, 1199m, 1095m, 1039, 982m, 939m, 917m, 877m, 834m, 781m, 693vs, 652m, 631m, 579m.

## 2.5. Synthesis of $[Zn(ima)_2]_n(3)$

The solution of Hima (25 mg, 0.2 mmol) in water (5 mL) was slowly added a water solution (5 mL) of Zn(NO<sub>3</sub>)<sub>2</sub> (30 mg, 0.1 mmol) under stirring for *ca.* 30 min. Then a dilute aqueous solution of NaOH was added dropwise with stirring to the above mixture until the pH was *ca.* 7. The resultant white precipitate was filtered off and the colorless solution was left to stand at room temperature. Block colorless single-crystals suitable for X-ray diffraction were obtained by slow evaporation within five days in 72% yield. Anal. Calcd for C<sub>10</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub>Zn: C, 38.06; H, 3.19; N, 17.75 %. Found: C, 37.94; H, 3.20; N, 17.82%. IR (cm<sup>-1</sup>): 3151vs, 3003m, 2921m, 1591vs, 1525m, 1400vs, 1351m, 1319m, 1292m, 1235m, 1113vs, 1091m, 1042m, 983m, 942m, 921m, 868m, 832m, 798m, 764m, 702s, 655s, 629m, 579m.

#### 2.6. X-ray crystallography

Single crystal X-ray diffraction measurements of 1-3 were carried out with a Bruker APEX II CCD diffractometer equipped with a graphite crystal monochromator. The lattice parameters were obtained by least-squares refinement of the diffraction data. All the measured independent reflections were used in the structural analysis, and semiempirical absorption corrections were applied using the SADABS program. The program SAINT [16] was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [17]. Metal atoms were located from the E-maps and other nonhydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for all the non-hydrogen atoms based on  $F^2$ . All the hydrogen atoms were first found in difference electron density maps, and then placed in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. The absolute structures for 3 have been determined with the Flack parameters of 0.032(19) [18]. Crystal data as well as details of data collection and refinement for the complexes 1-3 are given in Table 1.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data

Table 1

Cr	ystal	and	structure	refinement	for	comp	lexes	1-	3
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Centre, CCDC Nos. 291,258, 291,261, 291,263 for 1–3, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

# 3. Results and discussion

### 3.1. Preparation of complexes 1-3

All 1–3 were obtained as neutral complexes from aqueous solutions by reactions of Hima with different metal salts. Compound 1 could also be isolated when using AgBF<sub>4</sub> and Ag<sub>2</sub>SO<sub>4</sub> as the Ag(I) source, as confirmed by X-ray diffraction, IR spectra and elemental analyses. Similar cases were also observed for Zn<sup>II</sup> and Cd<sup>II</sup> complexes, which indicates that the final products are independent of the counter-anions in the metal salts. Furthermore, although 2 and 3 have the exact 2:1 ligand/metal compositions, our trials showed that the products do not significantly depend on the ligand-to-metal ratio, while higher yields were observed when increasing the ligand-to-metal ratio.

## 3.2. Crystal Structures

## 3.2.1. Structure analysis of 1

In 1, there is one  $Ag^{I}$  atom and one ima ligand in each independent crystallographic unit, as shown in Fig. 1a.

	1	2	3
Empirical formula	C <sub>5</sub> H <sub>5</sub> AgN <sub>2</sub> O <sub>2</sub>	$C_{10}H_{10}CdN_4O_4$	$C_{10}H_{10}N_4O_4Zn$
Formula weight	232.98	362.63	315.59
<i>T</i> /[K]	298	298	298
Wavelength/[Å]	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	Cc
	8.8134(17)	8.4289(16)	9.005(5)
b/[Å]	13.460(3)	5.1470(10)	16.512(9)
<i>c/</i> [Å]	5.2446(10)	12.466(2)	9.172(5)
β/[°]	106.399(2)	92.667(2)	117.276(7)
$V/[\text{Å}]^3$	596.9(2)	540.25(17)	1212.2(11)
Z	4	2	4
$\mu/[mm^{-1}]$	3.301	2.040	2.042
Crystal size [mm]	$0.32 \times 0.18 \times 0.09$	$0.30 \times 0.10 \times 0.10$	$0.30 \times 0.20 \times 0.20$
$\rho/[g  cm^{-3}]$	2.593	2.229	1.729
Reflections collected	3372	2878	3289
Independent reflections	1334	1197	1985
Reflections $[I > 2\sigma(I)]$	1244	1072	1855
<i>F</i> (000)	448	356	640
R <sub>int</sub>	0.0352	0.0150	0.0330
Data/restraints/parameters	1334/0/92	1197/0/88	1985/2/172
$\theta$ range	2.41 to 27.96	2.98 to 28.01	2.47 to 28.15
Goodness of fit on $F^2$	1.104	1.055	1.006
Largest peak and hole $[e Å^{-3}]$	0.666/-0.670	0.522/-0.287	0.603/-0.441
$R_1^{a}/wR_2^{b} [I > 2\sigma(I)]$	0.0257/0.0614	0.0202/0.0513	0.0411/0.0859
$R_1^{a}/wR_2^{b}$ (all data)	0.0276/0.0622	0.0235/0.0531	0.0447/0.0878

<sup>a</sup> 
$$R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$$

<sup>b</sup> wR<sub>2</sub> =  $\left[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\right]^{1/2}$ .



Fig. 1. (a) View of the coordination environment of  $Ag^{I}$  in 1 with thermal ellipsoids at 30% probability; (b) view of the 1-D chain and pseudo 2-D layer formed by  $Ag \cdots Ag$  interactions between adjacent chains.

Table 2

The coordination geometry of the two-coordinated Ag<sup>I</sup> center is slightly bent (O–Ag–N 156.30(9)°). Each ima anion act as a bridge between two Ag<sup>I</sup> atoms (Scheme 1(a)) with the Ag–N<sub>imidazole</sub> bond length of 2.154(2) Å normal for related Ag–N coordination bonds [19] and the slightly longer Ag–O<sub>carboxy</sub> bond (see Table 2) giving rise to a zigzag chain.

Additionally, short Ag···Ag<sup>i</sup> (i = x, -y + 3/2, z + 1/2) contacts between the adjacent chains is 3.149(3) Å result in the formation of pseudo 2D frameworks (Fig. 1b) which are stacked in an *ABAB* sequence with all ima ligands in a same layer arranged along the same plane [20] and exhibiting interlayer hydrogen-bonding interactions (Table 3) and  $\pi$ - $\pi$  packing interaction between imidazole rings (3.6291 Å) and C(3)-H(3A)··· $\pi$  (2.72 Å) (Fig. 2) [21].

## 3.2.2. Structural analysis of 2

Complex 2 is 2-D MOFs. In 2, each metal ion is six-coordinated by six ima ligands using their imidazole nitrogen or carboxylate oxygen donors. The coordination geometry of Cd<sup>II</sup> could be described as a nearly ideal octahedron, as shown in Fig. 3a and Table 2. For each carboxylate group of ima in 2, two C–O bond distances of the carboxylic group are almost equivalent, being consistent with its structural feature (*syn–anti* coordination) as shown in Scheme 1(b). Thus, Cd atom is coordinated by six distinct ima ligands and each ima bridges three Cd<sup>II</sup> centers to form a 2-D coordination polymer with (6,3) topology [22] along the crystallographic *ab* plane, as illustrated in Fig. 3b. Such coordination layers are parallel stacked with an *ABAB* sequence featuring interlayer hydrogen-bonding interactions (see Table 3 and Fig. 4).

#### 3.2.3. Structure analysis of 3

The local coordination geometry around the Zn1 center can be described as a distorted tetrahedron (Table 2). The

is (A) and angle	s () for complexes <b>I</b>	,
2.154(2)	$Ag(1)-Ag(1)^b$	3.1489(8)
2.244(2)	C(1)–O(1)	1.249(3)
2.651(2)	C(1)–O(2)	1.252(3)
156.30(9)	$O(1)^{a} - Ag(1) - O(2)^{c}$	85.50(7)
117.18(7)		
2.2731(18)	$Cd(1) - O(2)^{d}$	2.3487(16)
2.3501(16)	$Cd(1) - O(1)^{e}$	2.3501(16)
2.3487(16)	O(1)–C(1)	1.247(3)
2.2731(18)	O(2)–C(1)	1.246(3)
82.53(6)	$O(1)^{a}$ -Cd(1)-O(1) <sup>e</sup>	180.00
93.32(6)	$O(2)^{b}-Cd(1)-N(2)^{c}$	86.68(6)
180.00	$O(2)^{b}-Cd(1)-O(2)^{d}$	180.00
86.68(6)	$O(1)^{e}-Cd(1)-O(2)^{b}$	88.01(5)
97.47(6)	$O(2)^{d}$ -Cd(1)-N(2) <sup>c</sup>	93.32(6)
91.99(5)	$O(1)^{e}-Cd(1)-N(2)^{c}$	82.53(6)
97.47(6)	$O(1)^{e}-Cd(1)-O(2)^{d}$	91.99(5)
88.01(5)		
1.935(4)	O(1) - C(1)	1.262(7)
2.012(5)	O(2) - C(1)	1.204(7)
1.962(4)	O(3) - C(6)	1.258(7)
1.990(5)	O(4)–C(6)	1.229(7)
118.2(2)	O(3) <sup>a</sup> -Zn(1)-N(4)	96.28(19)
110.27(16)	$N(2)^{b}-Zn(1)-N(4)$	105.95(19)
109.99(17)	$O(3)^{a} - Zn(1) - N(2)^{b}$	115.86(19)
	2.154(2) 2.244(2) 2.651(2) 156.30(9) 117.18(7) 2.2731(18) 2.3501(16) 2.3487(16) 2.3487(16) 2.2731(18) 82.53(6) 93.32(6) 180.00 86.68(6) 97.47(6) 88.01(5) 1.935(4) 2.012(5) 1.962(4) 1.990(5) 118.2(2) 110.27(16) 109.99(17)	$\begin{array}{cccc} 1.5 & (-1) & \text{and angles () 101 complexes 1 } \\ \hline 2.154(2) & Ag(1)-Ag(1)^b \\ 2.244(2) & C(1)-O(1) \\ 2.651(2) & C(1)-O(2) \\ \hline 156.30(9) & O(1)^a-Ag(1)-O(2)^c \\ \hline 117.18(7) \\ \hline \\ \hline \\ 2.2731(18) & Cd(1)-O(1)^e \\ 2.3487(16) & O(1)-C(1) \\ 2.2731(18) & O(2)-C(1) \\ \hline \\ 82.53(6) & O(1)^a-Cd(1)-O(1)^e \\ \hline \\ 93.32(6) & O(2)^b-Cd(1)-N(2)^c \\ \hline \\ 180.00 & O(2)^b-Cd(1)-O(2)^d \\ \hline \\ 86.68(6) & O(1)^e-Cd(1)-O(2)^d \\ \hline \\ 97.47(6) & O(2)^d-Cd(1)-N(2)^c \\ 97.47(6) & O(1)^e-Cd(1)-N(2)^c \\ 97.47(6) & O(1)^e-Cd(1)-O(2)^d \\ \hline \\ 88.01(5) \\ \hline \\ \hline \\ 1.935(4) & O(1)-C(1) \\ 2.012(5) & O(2)-C(1) \\ 1.962(4) & O(3)-C(6) \\ \hline \\ 1.990(5) & O(4)-C(6) \\ \hline \\ 118.2(2) & O(3)^a-Zn(1)-N(4) \\ 110.27(16) & N(2)^b-Zn(1)-N(4) \\ 109.99(17) & O(3)^a-Zn(1)-N(2)^b \\ \hline \end{array}$

Symmetry codes: <sup>a</sup>1 + x, y, 1 + z; <sup>b</sup>x, 3/2 - y, -1/2 + z; <sup>c</sup>1 + x, 3/2 - y, 1/2 + z for 1; <sup>a</sup>5/2 - x, -1/2 + y, 3/2 - z; <sup>b</sup>5/2 - x, 1/2 + y, 3/2 - z; <sup>c</sup>2 - x, -y, 2 - z; <sup>d</sup>-1/2 + x, -1/2 - y, 1/2 + z; <sup>e</sup>-1/2 + x, 1/2 - y, 1/2 + z for 2; <sup>a</sup>-1 + x, -y, -1/2 + z; <sup>b</sup>-1/2 + x, 1/2 - y, 1/2 + z for 3.

Zn1 center coordinates to two imidazole nitrogen atoms and two carboxylate oxygen atoms [O(1) and O(3)] of four different ima ligands (Fig. 5a). Two Zn-N<sub>imidazole</sub> bond

Table 3 Hydrogen bond geometries in the crystal structure of 1-3

Complex	$D\!\!-\!\!H\!\cdot\cdot\cdot\!A^a$	$D{\cdots}A\;(\mathring{A})$	$H{\cdots}A\;(\mathring{A})$	D−H···A (°)
1				
	$C(2)-H(2A)\cdot \cdot \cdot O(1)^i$	3.453(4)	2.58	150
	$C(4)$ – $H(4A)$ ··· $O2^{ii}$	3.240(3)	2.59	127
2				
	$C(2)-H(2B)\cdots O(1)^{i}$	3.512(2)	2.57	163
	$C(3) - H(3A) \cdots O(1)^{ii}$	3.087(2)	2.57	115
	$C(4)-H(4A)\cdot\cdot\cdot O(2)^{iii}$	3.242(3)	2.45	144
	$C(5)–H(5A)\cdots O(2)^{iv}$	3.384(3)	2.53	153
3				
	$C(2)-H(2A)\cdot \cdot \cdot O(2)^{i}$	3.447(6)	2.54	156
	$C(2)-H(2B)\cdots O(2)^{ii}$	3.376(6)	2.42	169

<sup>a</sup> Symmetry codes: <sup>i</sup>x, y, 1 + z; <sup>ii</sup>1 + x, y, z for **1**; <sup>i7</sup>/2 - x, -1/2 + y, 3/2 - z; <sup>ii5</sup>/2 - x, -1/2 + y, 3/2 - z; <sup>iii-1/2 + x, 1/2 - y, 1/2 + z; <sup>iv7</sup>/2 - x, 1/2 + y, 3/2 - z for **2**; <sup>i1</sup>1/2 - x, 1/2 + y, z; <sup>iii</sup>1 - x, 1/2 + y, 1/2 - z for **3**.</sup>

lengths are nearly the same, and slightly longer than two similar Zn–O<sub>carboxy</sub> distances (see Table 2). For the ima carboxylic groups, the coordinated C–O bond lengths (1.262(7) and 1.258(7) Å) are significantly longer than those of the uncoordinated bonds (1.204(7) and 1.229(7) Å) being similar that in **1**.

The Zn(1) center is connected to four adjacent Zn centers through the ima bridges to result in a 3D diamondoid MOF (Fig. 5b) with the adjacent Zn–Zn separations of 9.054(3) and 8.784(3) Å and the Zn–Zn–Zn angles in the range of  $81.16^{\circ}$  to  $124.65^{\circ}$ , being significantly deviated from  $109.45^{\circ}$  expected for an idealized diamond network, thus the diamondoid network in **3** is distorted. With long Zn–Zn separations, large cavities are formed within each diamondoid net in **3** (Fig. 5b) which gives rise to the formation of 3-fold interpenetration. The crystal structure of **3** is very similar to those reported previously [5a]. Additionally, crystal structure have been further stabilized by hydrogen-bonding interactions (see Table 3 and Fig. 6).

## 3.3. IR spectra

The IR spectrum of 1 shows characteristic bands of the dicarboxylate groups in the usual region at  $1578 \text{ cm}^{-1}$  for the asymmetric stretching and at  $1384 \text{ cm}^{-1}$  for the symmetric stretching (Fig. S1). The difference between these wave numbers is  $194 \text{ cm}^{-1}$ , which is attributed to the existence of monodentate modes of the carboxylate groups (Scheme 1a) [23]. For 2, the bands are at  $1593 \text{ cm}^{-1}$  for the asymmetric stretching and at  $1396 \text{ cm}^{-1}$  for the symmetric stretching. The difference value of  $203 \text{ cm}^{-1}$  indicates that the bridging modes of ima is present (Scheme 1b). For 3, the bands are at 1591  $\text{cm}^{-1}$  for the asymmetric stretching and at 1400 cm<sup>-1</sup> for the symmetric stretching. The difference value of  $191 \text{ cm}^{-1}$  shows the existence of monodentate modes of the carboxylate groups (Scheme 1a). The IR spectra indicate that the ima carboxylate groups function in different coordination modes, being consistent with the crystal structures of 1-3, respectively.

## 3.4. Second harmonic generation efficiency

According to the principles proposed by Kurtz and Perry [15] the strength of second harmonic generation (SHG) efficiency of the compounds can be estimated by measuring powder samples. Only **3** is SHG-active, having an SHG intensities of 0.5 relative to that of urea, which confirm that it crystallizes in the polar space groups, in consistent with the structural analyses.

## 3.5. Thermogravimetric analysis (TGA)

High thermal stability is an important precondition in the conversion of coordination frameworks from laboratory curiosities to practical materials. Thus, TGA measurements were conducted to determine the thermal stability of 1-3. For 1, no obvious loss weight was



Fig. 2. Perspective of molecular packing in 1 along c axis. The dashed lines stand for hydrogen bond.



Fig. 3. (a) View of coordination environments of the metal atoms in 2 with thermal ellipsoids at 30% probability; (b) View of 2-D layer to (101) plane.



Fig. 4. Perspective of molecular packing in 2 along [010] direction, respectively. The dashed lines stand for hydrogen bond.

observed before at the range of 240 °C. A rapid weight loss occurred in the 240–284 °C region (peak: 270 °C). The remaining weight of 49.4% corresponds to the percentage (49.7%) of Ag<sub>2</sub>O. For **2**, the TGA shows MOFs remained intact until two consecutive weight losses occur in the range of 297–372 °C (peak: 348 °C). The remaining weight of 35.2% corresponds to the percentage (35.4%) of CdO. For **3**, the TGA indicates that the MOF remained intact until two consecutive weight losses occur in the 350–405 °C region (peak: 383 °C). The remaining weight of 26.0% corresponds to the percentage (25.8%) of ZnO.



Fig. 5. (a) Coordination environment of the metal atom in 3 with thermal ellipsoids at 30% probability; (b) Diamondoid network of 3.



Fig. 6. Perspective of molecular packing in 3 along a axis. The dashed lines stand for hydrogen bond.

## 4. Conclusions

New MOFs have been constructed from a multidentate flexible ligand 2-(1*H*-imidazole-1-yl)-acetic acid (Hima) and Ag<sup>I</sup>, Cd<sup>II</sup> and Zn<sup>II</sup> ions, and structurally characterized by X-ray diffraction analysis. These compounds show 1-D, 2-D and 3-D coordination frameworks, respectively. The present study demonstrates that the flexible ima anion is capable of coordination to metal centers with both imidazole nitrogen atoms and the carboxylate group oxygen atoms in variable coordination modes, and the MOFs exhibit different dimensionalities with different metal ions, as well as that the coordination geometry of the metal ions is very important for the formation of acentric crystal structures.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2006.07.021.

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