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# Syntheses, structures and photoluminescence of a series of coordination frameworks based on dicarboxylate anion and bis(imidazole) ligand

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# ABSTRACT

In this article, ten new coordination frameworks, namely,  $[Ni(H_2O)_6]\cdot(L3)$  (1),  $[Zn(L3)(H_2O)_3]$  (2),  $[Cd(L3)(H_2O)_3]$ -5.25H<sub>2</sub>O (3),  $[Ag(L1)(H_2O)]$ -0.5(L3) (4), [Ni(L3)(L1)] (5),  $[Zn(L3)(L1)_{0.5}]$ ·H<sub>2</sub>O (6),  $[Cd(L3)(L1)_{0.5}(H_2O)]$  (7),  $[CoCl(L3)_{0.5}(L1)_{0.5}]$  (8),  $[ZnCl(L3)_{0.5}(L2)_{0.5}]$  (9), and  $[CoCl(L3)_{0.5}(L2)_{0.5}]$  (10), where L1 = 1,1'-(1,4)-butanediyl)bis(imidazole), L2 = 1,1'-(1,4-butanediyl)bis(2-ethylbenzimidazole) and  $H_2-L3 = 3,3'-(p-xylylenediamino)$ bis(benzoic acid), have been synthesized by varying the metal centers and nitrogen-containing secondary ligands. These structures have been determined by single-crystal X-ray diffraction analyses, elemental analyses and IR spectra. In 1, the L3 anion is not coordinated to the Ni(II) center as a free ligand. The Ni(II) ion is coordinated by water molecules to form the cationic  $[Ni(H_2O)_6]^{2+}$  complex. The hydrogen bonds between L3 anions and  $[Ni(H_2O)_6]^{2+}$  cations result in a three-dimensional (3D) supramolecular structure of 1. In compounds 2 and 3, the metal centers are linked by the organic L3 anions to generate 1D infinite chain structures, respectively. The hydrogen bonds between carboxylate oxygen atoms and water molecules lead the structures of 2 and 3 to form 3D supramolecular structures. In 4, the L3 anion is not coordinated to the Ag(I) center, while the L1 ligands bridge adjacent Ag(I) centers to give 1D Ag-L1 chains. The hydrogen bonds among neighboring L3 anions form infinite 2D honeycomb-like layers, in the middle of which there exist large windows. Then, 1D Ag-L1 chains thread in the large windows of the 2D layer network, giving a 3D polythreaded structure. Considering the hydrogen bonds between the water molecules and L3 anions, the structure is further linked into a 3D supramolecular structure. Compounds 5 and 7 were synthesized through their parent compounds 1 and 3, respectively, while 6 and 9 were obtained by their parent compound 2. In 5, the L3 anions and L1 ligands connect the Ni(II) atoms to give a 3D 3-fold interpenetrating dimondoid topology. Compound 6 exhibits a 3D three-fold interpenetrating  $\alpha$ -Po network structure formed by L1 ligands connecting Zn-L3 sheets, while compound 7 shows a 2D (4,4) network topology with the L1 ligands connecting the Cd-L3 double chains. In compound 8, the L1 ligands linked Co-L3 chains into a 2D layer structure. Two mutual 2D layers interpenetrated in an inclined mode to generate a unique 3D architecture of 8. Compounds 9 and 10 display the same 2D layer structures with (4,4) network topologies. The effects of the N-containing ligands and the metal ions on the structures of the complexes 1-10 were discussed. In addition, the luminescent properties of compounds 2-4, 6, 7 and 9 were also investigated.

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# 1. Introduction

Metal–organic frameworks (MOFs) have received considerable interest in coordination chemistry and material science due to their intriguing structural diversities and potential applications in functional materials, nanotechnology, and biological recognition [1]. In this regard, the rational design and assembly of MOFs with intriguing diversities have become a particularly important subject. The construction of the MOFs can be influenced by many factors, such as pH value of solution, temperature, geometric requirements of metal atoms, and the ligands [2]. Particularly, the selection of the ligands for assembling metal ions plays an important role in the formation of the final architectures [3]. Among the N-donor bridging ligands, bis(imidazole) or bis(benz-imidazole) ligands, as an important family of flexible N-containing ligands, have attracted great interest [4]. In our previous work, we have reported a series of fascinating archetypal structures based on 1,1'-(1,4-butanediyl)bis(imidazole) (L1 Scheme 1), 1,1'-(1,5-penta-nedidyl)bis(imidazole), 1,1'-(1,6-hexanediyl)bis(imidazole), 1, 2-bis(imidazol-1-ylmethyl)benzene, 1,3-bis(imidazol-1-ylmethyl)benzene, 2,2'-bis(imidazolyl)ether, 2-(2-pyridyl)imidazole, 1, 1'-(1,4-butanediyl)bis(2-methylbenzimidazole), 1,1'-(1,4-butanediyl)bis(2-benzylbenzimidazole) [5]. On careful inspection of the



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Scheme 1. Two kinds of neutral ligands L1 and L2 involved in this work.



Scheme 2. Structure of the dicarboxylate ligand used in this work.

reported cases, we found that the flexible nature of alkyl  $(-CH_2-)_n$  (n = 2, 4, 5, 6) spacer allows the ligands to bend and rotate freely so as to conform to the coordination geometries of central metal atoms.

On the other hand, multicarboxylates, such as 1,3,5-benzenetricarboxylic acid, 4,4'-oxybis(benzoic acid), 3,3',4,4'-benzophenone tetracarboxylic acid [5c] and 4.4'-oxidiphthalic acid, have been widely investigated for the construction of new coordination frameworks [6]. However, studies on the flexible multicarboxylates are rarely observed. In this work, we synthesize a new flexible dicarboxylate ligand 3,3'-(p-xylylenediamino)bis(benzoic acid) (H<sub>2</sub>L3 Scheme 2). H<sub>2</sub>L3 was chosen as the organic ligand based on the following considerations: (i) The carboxylate group can adopt a variety of coordination modes, for example, chelatingbidentate and bridging-bidentate modes. (ii) Owing to the presence of -CH<sub>2</sub>- and -NH- spacers, H<sub>2</sub>L3 can be used as a flexible ligand to fabricate abundant structural motifs. Herein, we report ten new dicarboxylate coordination frameworks with or without Ncontaining ligand:  $[Ni(H_2O)_6] \cdot (L3)$  (1),  $[Zn(L3)(H_2O)_3]$  (2), [Cd(L3)(H<sub>2</sub>O)<sub>3</sub>]·5.25H<sub>2</sub>O (**3**), [Ag(L1)(H<sub>2</sub>O)]·0.5(L3) (**4**), [Ni(L3)(L1)] (5),  $[Zn(L3)(L1)_{0.5}] \cdot H_2O$  (6),  $[Cd(L3)(L1)_{0.5}(H_2O)]$  (7),  $[CoCl(L3)_{0.5} (L1)_{0.5}$  (8),  $[ZnCl(L3)_{0.5}(L2)_{0.5}]$  (9), and  $[CoCl(L3)_{0.5}(L2)_{0.5}]$  (10). Their structures have been determined by single crystal X-ray diffraction analyses. The crystal structures of these compounds, along with the systematic investigation of the modulated effect of the neutral ligands and the metal ions on the ultimate framework, will be described and discussed in this paper. In addition, the luminescent properties of compounds 2-4, 6, 7 and 9 were also investigated.

#### 2. Experimental

#### 2.1. Materials and physical measurements

All reagents and solvents for syntheses were purchased from commercial sources and used as received. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm<sup>-1</sup> on a Mattson Alpha-Centauri spectrometer. Elemental analyses were carried out with a Perkin–Elmer 240C elemental analyzer. Ligands L1 and L2 were prepared according to the literatures [4f,5d].

# 2.2. Synthesis of 3,3'-(p-xylylenediamino)bis(benzoic acid) (H<sub>2</sub>L3)

A mixture of 1,4-benzendialdehyde (1.34 g, 10 mmol) was dissolved in MeOH (50 mL), and 3-aminobenzoic acid (2.74 g, 20 mmol) in 50 mL MeOH was added dropwise over 30 min. The reaction mixture was stirred for 2 h and the powdery yellow precipitate was obtained. The precipitate was suspended and 1.6 g NaBH<sub>4</sub> was added during a period of 30 min. Then, clear reaction mixture was obtained and filtered. The clear filtrate was diluted with 30 mL water and then acidified with cold dilute HCl solution until the precipitate did not produce when the pH value is about 5. The powdery white precipitate was filtered, washed with water for three times and dried for 24 h under vacuum. Yield: 79%. IR data (KBr, cm<sup>-1</sup>): 3844w, 3757w, 3727w, 3623w, 3426w, 2983w, 2826w, 2600w, 2530w, 1687s, 1605m, 1583w, 1514m, 1423m, 1318s, 1249w, 1113w, 1079m, 1018w, 988w, 933m, 890m, 865w, 827w, 799w, 746s, 675m, 553w, 527w, 422w.

#### 2.3. Syntheses of the metal complexes

#### 2.3.1. Synthesis of $[Ni(H_2O)_6]$ (L3) (1)

A mixture of H<sub>2</sub>L3 (0.076 g, 0.20 mmol) and NaOH (0.016 g, 0.40 mmol) in ethanol/H<sub>2</sub>O (14:1, v/v) (15 mL) was stirred for 10 min at room temperature, then the NiCl<sub>2</sub>·6H<sub>2</sub>O (0.048 g, 0.20 mmol) was added to the solution with constant stirring for 30 min and low blue precipitate was obtained. The precipitate was dissolved by dropwise addition of an aqueous solution of NH<sub>3</sub> (14 M). Green crystals of **1** were obtained by slow evaporation of the solution for several days at room temperature. Yield: 38%. *Anal.* Calc. for C<sub>22</sub>H<sub>30</sub>N<sub>2</sub>NiO<sub>10</sub> ( $M_r$  = 541.17): C, 48.83; H, 5.59; N, 5.18. Found: C, 48.75; H, 5.49; N, 5.24%. IR data (KBr, cm<sup>-1</sup>): 3434 (s), 1628 (w), 1518 (w), 1464 (w), 1396 (s), 1116 (w), 838 (w), 763 (w), 671 (w), 423 (w).

#### 2.3.2. Synthesis of $[Zn(L3)(H_2O)]$ (2)

The preparation of **2** was similar to that of **1** except that  $Zn(NO_3)$ · $GH_2O$  was used instead of NiCl<sub>2</sub>· $GH_2O$ . Colorless crystals of **2** were collected. Yield: 68%. *Anal.* Calc. for  $C_{22}H_{22}N_2O_6Zn$  ( $M_r$  = 475.63): C, 55.53; H, 4.66, N, 5.88. Found: C, 55.01; H, 4.21; N, 5.60%. IR data (KBr, cm<sup>-1</sup>): 3396 (m), 3357 (w), 3309 (w), 3154 (w), 2932 (w), 1605 (m), 1556 (s), 1517 (s), 1417 (w), 1387 (s), 1317 (w), 1258 (m), 1099 (w), 891 (w), 763 (m), 737 (w), 686 (w).

# 2.3.3. Synthesis of [Cd(L3)(H<sub>2</sub>O)<sub>3</sub>]·5.25H<sub>2</sub>O (3)

The preparation of **3** was similar to that of **1** except that  $CdCl_2 \cdot 2.5H_2O$  was used instead of  $NiCl_2 \cdot 6H_2O$ . Colorless crystals of **3** were obtained. Yield: 72%. *Anal.* Calc. for  $C_{22}H_{34.5}CdN_2O_{12.25}$  ( $M_r = 635.42$ ): C, 41.58; H, 5.47; N, 4.41. Found: C, 41.54; H, 5.40; N, 4.36%. IR data (KBr, cm<sup>-1</sup>): 3427 (w), 2465 (m), 2362 (w), 1799 (m), 1676 (w), 1604 (w), 1513 (w), 1392 (w), 852 (s), 717 (s).

#### 2.3.4. Synthesis of $[Ag(L1)(H_2O)] \cdot 0.5(L3)$ (4)

A mixture of H<sub>2</sub>L3 (0.076 g, 0.20 mmol) and Ag<sub>2</sub>CO<sub>3</sub> (0.055 g, 0.20 mmol) in methanol (15 mL) was stirred for 10 min at room temperature, then L1 (0.038 g, 0.20 mmol) was added to the solution with constant stirring for 30 min and the precipitate was obtained. The precipitate was dissolved by dropwise addition of an aqueous solution of NH<sub>3</sub> (14 M). Colorless crystals of **4** were obtained by slow evaporation of the ammoniacal solution at room temperature. Yield: 49%. *Anal.* Calc. for  $C_{21}H_{25}AgN_5O_3$  ( $M_r$  = 503.32): C, 50.11; H, 5.01; N, 13.91. Found: C, 49.95; H, 4.90; N, 13.82%. IR data (KBr, cm<sup>-1</sup>): 3845 (w), 3758 (w), 3723 (w), 3621 (w), 3273 (m), 3123 (m), 3043 (w), 2941 (w), 2898 (w), 2859 (w), 1894 (w), 1820 (w), 1688 (w), 1564 (s), 1520 (m), 1478 (w), 1447 (m), 1380 (s), 1317 (m), 1283 (w), 2087 (w), 823 (w), 759 (w), 730 (w), 652 (m), 626 (w).

#### 2.3.5. Synthesis of [Ni(L3)(L1)] (5)

A mixture containing H<sub>2</sub>L3 (0.076 g, 0.20 mmol), L1 (0.038 g, 0.20 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (0.048 g, 0.20 mmol), and water (10 mL) was sealed in a 15 mL Teflon-lined stainless-steel container. The container was heated to 170 °C for 3 days. The reaction system was then slowly cooled to room temperature at 10 °C h<sup>-1</sup>. Green crystals of **5** suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water, and dried in air at ambient temperature. Yield: 53%. *Anal.* Calc. for  $C_{32}H_{32}N_6NiO_4$  ( $M_r = 623.33$ ): C, 61.66; H, 5.17; N, 13.48. Found: C, 61.52; H, 5.07; N, 13.39%. IR data (KBr, cm<sup>-1</sup>): 2926 (w), 1681 (m), 1600 (w), 1570 (m), 1517 (s), 1416 (s), 1329 (w), 1283 (w), 1108 (w), 812 (w), 760 (m).

#### 2.3.6. Synthesis of $[Zn(L3)(L1)_{0.5}] \cdot H_2O(\mathbf{6})$

A mixture of H<sub>2</sub>L3 (0.076 g, 0.20 mmol), L1 (0.038 g, 0.20 mmol), Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O (0.044 g, 0.20 mmol), and water (10 mL) was sealed in a 15 mL Teflon-lined stainless-steel container. The container was heated to 180 °C for 3 days. The reaction system was then slowly cooled to room temperature at 10 °C h<sup>-1</sup>. Colorless crystals of **6** suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water, and dried in air at ambient temperature. Yield: 64%. *Anal.* Calc. for C<sub>27</sub>H<sub>27</sub>N<sub>4</sub>O<sub>5</sub>Zn ( $M_r$  = 552.94): C, 58.65; H, 4.92; N, 10.13. Found: C, 58.58; H, 4.90; N, 10.02%. IR data (KBr, cm<sup>-1</sup>): 2930 (w), 1562 (m), 1398 (m), 1245 (w), 1104 (w), 764 (m).

#### 2.3.7. Synthesis of [Cd(L3)(L1)<sub>0.5</sub>(H<sub>2</sub>O)] (**7**)

A mixture of H<sub>2</sub>L3 (0.076 g, 0.20 mmol), L1 (0.038 g, 0.20 mmol), Cd(Ac)<sub>2</sub>·2H<sub>2</sub>O (0.053 g, 0.20 mmol), and water (10 mL) was sealed in a 15 mL Teflon-lined stainless-steel container. The container was heated to 180 °C for 3 days. The reaction system was then slowly cooled to room temperature at 10 °C h<sup>-1</sup>. Colorless crystals of **7** suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water, and dried in air at ambient temperature. Yield: 43%. *Anal.* Calc. for C<sub>27</sub>H<sub>27</sub>CdN<sub>4</sub>O<sub>5</sub> ( $M_r$  = 599.94): C, 54.05; H, 4.54; N, 9.34. Found: C, 53.96; H, 4.45; N, 9.28%. IR data (KBr, cm<sup>-1</sup>): 2837 (w), 1542 (s), 1394 (s), 1244 (w), 1087 (w), 938 (w), 857 (w), 814 (w), 760 (m), 681 (w), 652 (w).

# 2.3.8. Synthesis of [CoCl(L3)<sub>0.5</sub>(L1)<sub>0.5</sub>] (8)

A mixture of H<sub>2</sub>L3 (0.076 g, 0.20 mmol), L1 (0.038 g, 0.20 mmol), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.048 g, 0.20 mmol), and ethanol/H<sub>2</sub>O (9:1) (10 mL) was placed in a 15 mL Teflon-lined stainless-steel container. The container was heated to 120 °C for 3 days. The reaction system was then slowly cooled to room temperature at 10 °C h<sup>-1</sup>. Blue crystals of **8** suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water, and dried in air at ambient temperature. Yield: 34%. *Anal.* Calc. for C<sub>16</sub>H<sub>16</sub>ClCo-N<sub>3</sub>O<sub>2</sub> ( $M_r$  = 376.70): C, 51.01; H, 4.28; N, 11.15. Found: C, 50.91; H, 4.32; N, 11.12%. IR data (KBr, cm<sup>-1</sup>): 3025 (w), 1554 (w), 1406 (m), 1095 (w).

# 2.3.9. Synthesis of [ZnCl(L3)<sub>0.5</sub>(L2)<sub>0.5</sub>] (9)

A mixture of H<sub>2</sub>L3 (0.076 g, 0.20 mmol), L2 (0.068 g, 0.20 mmol), ZnCl<sub>2</sub> (0.028 g, 0.20 mmol), and water (10 mL) was sealed in a 15 mL Teflon-lined stainless-steel container. The container was heated to 170 °C for 3 days. The reaction system was then slowly cooled to room temperature at 10 °C h<sup>-1</sup>. Colorless crystals of **9** suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water, and dried in air at ambient temperature. Yield: 62%. *Anal.* Calc. for C<sub>22</sub>H<sub>22</sub>ClN<sub>3</sub>O<sub>2</sub>Zn ( $M_r$  = 461.29):

C, 57.28; H, 4.81; N, 9.11. Found: C, 57.18; H, 4.75; N, 9.08%. IR data (KBr, cm<sup>-1</sup>): 2929 (w), 1564 (m), 1396 (w), 1055 (w).

#### 2.3.10. Synthesis of [CoCl(L3)<sub>0.5</sub>(L2)<sub>0.5</sub>] (**10**)

A mixture of H<sub>2</sub>L3 (0.076 g, 0.20 mmol), L2 (0.068 g, 0.20 mmol), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.048 g, 0.20 mmol), and ethanol/H<sub>2</sub>O (9:1) (10 mL) was placed in a 15 mL Teflon-lined stainless-steel container. The container was heated to 140 °C for 3 days. The reaction system was then slowly cooled to room temperature at 10 °C h<sup>-1</sup>. Blue crystals of **10** suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water, and dried in air at ambient temperature. Yield: 47%. *Anal.* Calc. for C<sub>22</sub>H<sub>22</sub>ClCoN<sub>3</sub>O<sub>2</sub> ( $M_r$  = 454.82): C, 58.10; H, 4.88; N, 9.24. Found: C, 57.94; H, 4.74; N, 9.16%. IR data (KBr, cm<sup>-1</sup>): 2931 (w), 1555 (m), 1431 (s), 1398 (w), 1249 (w), 1064 (w), 748 (m).

#### 2.4. Crystal structure determination

Single-crystal X-ray diffraction data for compound 1-4 were recorded on a Rigaku RAXIS-RAPID single-crystal diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 293 K. Diffraction data for compounds 5 and 7-9 were collected on a Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å), and diffraction data for compounds 6 and 10 were collected on a Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Cu K $\alpha$  radiation ( $\lambda$  = 1.54184 Å) at 293 K. Absorption corrections were applied using multi-scan technique. All the structures were solved by direct method of SHELXS-97 [7] and refined by full-matrix least-squares techniques using the SHELXL-97 program [8] within wingx [9]. Non-hydrogen atoms of the complexes were easily found from the Fourier difference maps and refined with anisotropic atomic displacement parameters. The O8W in compound **3** was refined anisotropically with an occupancy of 0.25. All H atoms bound to carbon were refined using a riding model with d(C-H) = 0.93 Å and  $U_{iso} = 1.2U_{eq}(C)$  for aromatic rings, and d(C-H) = 0.97 Å and  $U_{iso} = 1.5U_{eq}(C)$  for CH<sub>2</sub> groups. The hydrogen atoms bound to nitrogen were located from difference Fourier maps and refined with d(N-H) = 0.75 - 0.86 Å and  $U_{iso} = 1.2U_{eq}(N)$ . H atoms of O8W were not located from difference Fourier maps. Other water H atoms were located from difference Fourier maps and refined with d(O-H) = 0.85 - 0.89 Å,  $U_{iso} = 1.5U_{eq}(O)$  and  $H \cdots H = 1.38 \pm 0.02$  Å. The detailed crystallographic data and structure refinement parameters for compounds 1-10 are summarized in Table 1.

#### 3. Results and discussion

#### 3.1. Description of crystal structures

# 3.1.1. Structure of [Ni(H<sub>2</sub>O)<sub>6</sub>]·(L3) (**1**)

Selected bond distances and angles for compounds **1–10** are listed in Tables S1–S10. The hydrogen-bonding parameters for **1–7** are listed in Table 2. The networks of compounds **5–10** were analyzed by using OLEX program [10]. As shown in Fig. 1a, the Ni(II) center displays an octahedral geometry, and is coordinated to six water molecules to form a cationic complex  $[Ni(H_2O)_6]^{2+}$ . The Ni(II) atom lies on a centre of symmetry. In compound **1**, the carboxylate groups of H<sub>2</sub>L3 ligand are deprotonated, but they did not coordinate to the Ni(II) centers. The intra- and intermolecular hydrogen bonds between L3 anions and water molecules have been observed (Table 2), extending this structure into a three-dimensional supramolecular network (Fig. 1b).

Crystal data and structure refinem	ents for compounds	s 1–10.								
	1	2	3	4	5	9	7	8	6	10
Formula	C <sub>22</sub> H <sub>30</sub> NiN <sub>2</sub> O <sub>10</sub>	$C_{22}H_{24}ZnN_2O_7$	C <sub>22</sub> H <sub>34.5</sub> CdN <sub>2</sub> O <sub>12.25</sub>	$C_{21}H_{25}AgN_5O_3$	$C_{32}H_{32}NiN_6O_4$	$C_{27}H_{27}ZnN_4O_5$	$C_{27}H_{27}CdN_4O_5$	$C_{16}H_{16}C_{0}N_{3}O_{2}CI$	C <sub>22</sub> H <sub>22</sub> ZnN <sub>3</sub> O <sub>2</sub> Cl	C <sub>22</sub> H <sub>22</sub> CoN <sub>3</sub> O <sub>2</sub> CI
Formula weight	541.19	493.63	635.42	503.33	623.35	552.90	599.93	376.70	461.25	454.81
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic	triclinic	triclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	Pna2 <sub>1</sub>	P21/c	$P2_1/n$	$Pna2_1$	$P\bar{1}$	$P\overline{1}$	$P2_1/n$	$P\overline{1}$	PĪ
a (Å)	18.111(6)	31.750(2)	16.4170(16)	12.361(4)	14.4400(4)	8.8050(8)	8.5230(5)	8.9459(5)	9.485(5)	9.4800(18)
$p(\mathbf{A})$	5.763(3)	11.196(4)	22.238(6)	11.295(5)	10.8310(2)	11.3100(11)	10.6230(7)	11.2308(6)	10.847(5)	10.8190(17)
c (Å)	11.677(11)	5.713(1)	7.861(4)	15.751(6)	19.2020(5)	13.7070(13)	14.4820(7)	16.4502(10)	11.297(5)	11.3610(18)
α (°)	06	06	06	06	06	75.317(8)	82.260(5)	06	109.075(5)	109.432(14)
β (°)	91.66(2)	06	102.105(9)	103.848(12)	06	81.625(8)	77.684(5)	101.400(6)	102.112(5)	102.254(14)
γ (°)	06	06	06	06	06	68.513(9)	85.761(5)	06	98.919(5)	98.693(14)
V (Å <sup>3</sup> )	1218.3(14)	2031(4)	2806.1(16)	2135.2(14)	3003.19(13)	1226.5(2)	1267.97(13)	1620.14(16)	1042.1(9)	1042.3(3)
Ζ	2	4	4	4	4	2	2	4	2	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.475	1.615	1.503	1.566	1.379	1.497	1.571	1.544	1.470	1.449
$F(0 \ 0 \ 0)$	568	1024	1304	1028	1304	574	610	772	476	470
Reflections (collected/unique)	11343/2786	19070/4628	27082/6346	20598/4819	11866/5437	12271/4371	8390/4594	7706/2866	7852/4737	10928/3706
Rint	0.0563	0.0970	0.0267	0.0478	0.0441	0.0282	0.0502	0.0723	0.0303	0.0684
Goodness-of-fit (GOF) on $F^2$	1.054	1.046	1.104	1.043	0.817	1.013	0.711	0.770	0.868	0.940
$R_1^{a}[I > 2\sigma(I)]$	0.0491	0.0809	0.0349	0.0458	0.0335	0.0334	0.0362	0.0445	0.0381	0.0447
$wR_2^{b}[I > 2\sigma(I)]$	0.1142	0.2078	0.1037	0.0966	0.0523	0.0833	0.0401	0.0426	0.0680	0.1001
<sup>a</sup> $R_1 = \Sigma  F_0  -  F_c  /\Sigma  F_0 .$ <sup>b</sup> $wR_2 =  \Sigma w( F_0 ^2 -  F_c ^2) /\Sigma  w(F_0 ^2)$	<sup>2</sup> , <sup>2</sup> ) <sup>2</sup>   <sup>1/2</sup> .									

Hydrogen-bonding parameters for compounds 1-7 (Å) and (°).

D–H····A	d(D-H)	$d(H \cdot \cdot \cdot A)$	$d(D \cdot \cdot \cdot A)$	<(DHA)
1				
$O(2W)-H(2A)\cdots O(2)$	0.844(10)	1.901(11)	2.742(3)	174(4)
$O(3W)-H(3A)\cdots O(1)$	0.874(9)	1.890(16)	2.688(4)	151(2)
$O(1W) - H(1A) - O(2W)^{\#1}$	0.860(10)	2.286(12)	3.129(4)	167(3)
$O(1W) - H(1B) - O(3W)^{#2}$	0.856(10)	2.55(2)	3.249(5)	139(3)
$N(1)-H(1N)\cdots O(2)^{\#3}$	0.828(18)	2.54(3)	3.175(4)	135(3)
$O(2W) - H(2B) - O(1)^{#4}$	0.845(10)	1.862(10)	2.706(4)	177(4)
$O(3W)-H(3B)\cdots O(2)^{\#1}$	0.851(10)	2.27(3)	2.806(4)	121(3)
2				
$O(1W)-H(1B)\cdots O(3)^{\#1}$	0.861(19)	2.55(4)	3.338(11)	152(7)
$O(3W) - H(3A) - O(2)^{#2}$	0.89(2)	1.81(7)	2.580(8)	143(9)
$N(1)-H(1N)\cdots O(4)^{\#3}$	0.849(10)	2.58(5)	3.271(8)	139(6)
$O(2W) - H(2B) - O(3)^{#4}$	0.88(2)	2.48(2)	3.310(12)	159(3)
3				
$O(3W) - H(3WB) \cdots O(4W)$	0.844(19)	2.00(2)	2.837(4)	171(5)
O(3W)−H(3WA)···O(4)	0.858(19)	2.03(2)	2.882(4)	171(5)
O(7W)−H(7WB)···O(3W)	0.89(2)	1.91(2)	2.799(5)	171(6)
$O(5W) - H(5WA) + O(1)^{\#1}$	0.854(19)	2.01(2)	2.861(4)	176(5)
$O(5W) - H(5WB) - O(7W)^{#2}$	0.86(2)	1.94(2)	2.784(5)	166(5)
$O(4W) - H(4WB) - O(1)^{#3}$	0.84(2)	2.02(3)	2.807(4)	157(6)
O(6W)−H(6WA)···O(4) <sup>#4</sup>	0.869(19)	1.89(2)	2.750(4)	168(5)
O(6W)−H(6WB)····N(2) <sup>#5</sup>	0.86(2)	2.13(2)	2.951(4)	161(5)
4				
$O(1W) - H(3A) - O(2)^{\#1}$	0.854(18)	1.90(2)	2.723(5)	162(4)
$O(1W) - H(3B) + O(1)^{\#2}$	0.845(18)	1.868(19)	2.706(4)	171(5)
$N(5)-H(5N)\cdots O(1)^{\#3}$	0.852(4)	2.20(4)	2.992(4)	153(4)
5				
$N(2) = H(2N) \cdots O(1)^{\#1}$	0.786(17)	229(2)	2,996(3)	150(3)
(2) H(2H) O(H)	0.700(17)	2.23(2)	2.330(3)	150(5)
$0$ (1)(1) $H(1)(A) = O(2)^{\#1}$	0.802(17)	1 095(19)	2 971(2)	172(2)
O(100)-II(100A)···O(3)	0.092(17)	1.303(10)	2.071(3)	1/3(3)
7				
$O(1W)-H(1WA)\cdots O(3)^{\#1}$	0.831(17)	2.04(2)	2.760(3)	145(3)
$O(1W) - H(1WB) - O(2)^{\#2}$	0.867(17)	2.09(2)	2.909(3)	158(3)

Symmetry codes for 1: #1 = x, y + 1, z; #2 = x, -y + 3/2, z - 1/2; #3 = x, -y + 1/2, z + 1/2; #4 = x, -y + 1/2, z - 1/2. 2: #1 = -x, -y, z - 1/2; #2 = -x + 1/2, y + 1/2, z - 1/2; #3 = -x, -y - 1, z - 1/2; #4 = -x, -y, z - 3/2. 3: #1 = x, -y + 1/2, z + 1/2; #2 = -x + 3, y + 1/2, -z + 5/2; #3 = -x + 3, -y, -z + 2; #4 = -x + 3, y + 1/2, -z + 3/2;#5 = -x + 3, -y + 1, -z + 2. **4**: #1 = -x + 1, -y + 1, -z + 1; #2 = x - 1/2, -y + 1/2, z + 1/2; #3 = -x + 3/2, y - 1/2, -z + 1/2. 5: #1 = x - 1/2, -y + 1/2, z. 6: #1 = x - 1, y + 1, z. 7: #1 = x - 1, y + 1, z; #2 = -x + 1, -y, -z + 1.

# 3.1.2. Structure of $[Zn(L3)(H_2O)_3]$ (2)

As shown in Fig. 2a, the Zn(II) atom is six-coordinated by three carboxylate oxygen atoms (O1, O3<sup>#1</sup> and O4<sup>#1</sup>) from two different L3 anions, and three oxygen atoms (O1W, O2W and O3W) from water molecules in a distorted octahedral geometry. The four oxygen atoms (O1W, O2W, O1 and O4<sup>#1</sup>) occupy the equatorial positions, whereas the other two oxygen atoms (O3W and O3<sup>#1</sup>) occupy the axial positions. The Zn-O bond lengths are in the range of 1.825(11)-2.431(5) Å, and the O-Zn-O angles vary from 57.97(19)° to 162.4(4)°. Notably, the  $Zn-O3^{\#1}$  distance of 2.431(5) Å is slightly longer than ones found in other Zn(II) compounds, but still lies within the normal range [11]. The L3 anions in a *cis*-conformation bridge the adjacent Zn(II) atoms to generate infinite 1D wavelike chains along the crystallographic *c*-axis. The Zn(II)···Zn(II) separation across the L3 anion is 20.091 Å. The  $Zn(II) \cdots Zn(II) \cdots Zn(II)$  angle, defined by the orientation of the two L3 anions in the chain, is 114.24°. The intra- and intermolecular hydrogen bonds between the carboxylate oxygen atoms from L3 anions and water molecules (O1W and O3W) have been observed (Table 2), which extend the structure into a 3D supramolecular architecture (Fig. 2b).

# 3.1.3. Structure of [Cd(L3)(H<sub>2</sub>O)<sub>3</sub>]·5.25H<sub>2</sub>O (3)

As shown in Fig. 3a, the central Cd(II) atom is seven-coordinated by four carboxylate oxygen atoms (O1, O2,  $O3^{\#1}$  and  $O4^{\#1}$ ) from two different L3 anions, and three oxygen atoms (O1W, O2W and

Table



**Fig. 1.** (a) ORTEP diagram showing the coordination environment for Ni<sup>II</sup> atom in **1**. All H atoms are omitted for clarity. (Symmetry codes: #1 = -x, 1 - y, 1 - z; #2 = -x - 1, 1 - y, 2 - z). (b) The 3D hydrogen-bonding structure of **1**.



**Fig. 2.** (a) ORTEP diagram showing the coordination environment for  $Zn^{II}$  atom in **2**. All H atoms are omitted for clarity. (Symmetry codes: #1 = x + 1/2, -y - 1/2, z - 1; #2 = x - 1/2, y - 1, z + 1). (b) The 3D structure of **2** formed by the hydrogen bonds.



**Fig. 3.** (a) ORTEP diagram showing the coordination environment for  $Cd^{II}$  atom in **3.** All H atoms are omitted for clarity. (Symmetry code: #1 = x - 1, y, z - 1). (b) The 3D supramolecular structure of **3** formed through the hydrogen-bonding interactions along *c*-axis.

O9W) from water molecules in a distorted pentagonal bipyramidal geometry. Four chelating carboxylate oxygen atoms (01, 02, 03<sup>#1</sup> and O4<sup>#1</sup>) and one water molecule (O9W) comprise the equatorial plane around the Cd(II), while other two water molecules (O1W and O2W) form the pyramidal apices. The Cd-O bond lengths are in the range of 2.263(3)-2.594(3) Å, and the O-Cd-O angles vary from 52.43(7)° to 178.72(11)°. The L3 anions in a *cis*-conformation bridge the adjacent Cd(II) atoms to form an infinite 1D ripple chain structure along the crystallographic *c*-axis. The Cd(II)...Cd(II) separation is 16.649 Å. The Cd(II) · · · Cd(II) · · · Cd(II) angle, defined by the orientation of the two L3 anions in the chain, is 180°. Furthermore, the hydrogen bonds between the water molecules and the carboxylate oxygen atoms have been observed. The O3W, O4W and O7W act as both hydrogen-bond donors and acceptors, while the O5W only acts as hydrogen-bond donors (Table 2). The hydrogen-bonding interactions linked the 1D ripple chains into a 3D supramolecular framework (Fig. 3b).

# 3.1.4. Structure of $[Ag(L1)H_2O] \cdot 0.5(L3)$ (4)

In order to investigate the influence of the neutral ligand on the complex framework, two related N-containing ligands (L1 and L2) were used and seven new complexes **4–10** were obtained from the reaction systems. There exists one kind of crystallographically unique Ag(I) ion in the structure of **4** (Fig. 4a). The Ag(I) center is coordinated by two nitrogen atoms from two different L1 ligands

 $[Ag(1)-N(1) = 2.109(3) \text{ Å}, Ag(1)-N(4)^{\#1} = 2.121(3) \text{ Å}, N(1)-Ag(1) N(4)^{\#1} = 171.86(12)^{\circ}$  and one water molecule [Ag(1)-O1W =2.716(4) Å] in a distorted T-shape geometry. The Ag-N (L1) bond distances are within the normal range. Although the Ag1-O1W distance of 2.716(4) Å is slightly longer than ones found in other Ag(I) compounds [4h], it still lies within the normal range [12]. The L1 ligands bridge adjacent Ag(I) centers to give a one-dimensional (1D) Ag-L1 chain as illustrated in Fig. 4b. The  $Ag(I) \cdots Ag(I)$  separation is 12.361 Å across the L1 ligands. Notably, the carboxylate oxygen atoms of L3 anions are deprotonated, but the L3 anions are not coordinated to the Ag(I) centers. The hydrogen bonds (N5-H5N···O1<sup>#6</sup>) among neighboring L3 anions linked the L3 anions into infinite 2D honeycomb-like coordination layers, in the middle of which there exist large channels (Fig. 4c). 1D Ag-L1 chains thread in the large window of the 2D layer network, generating a 3D polythreaded structure. If the hydrogen bonds (O3W- $H3A \cdots O2^{#4}$  and  $O3W-H3B \cdots O1^{#5}$ ) are considered (Table 2), the structure is further linked into a 3D supramolecular structure, as shown in Fig. 4d.

# 3.1.5. Structure of [Ni(L3)(L1)] (5)

To study the influence of the N-containing ligand L1 on compound **1**, L1 was added to react with NiCl<sub>2</sub>· $6H_2O$  under different synthetic condition and a new complex **5** was obtained. As shown in Fig. 5a, Ni(II) atom shows a distorted {NiN<sub>2</sub>O<sub>4</sub>} octahedral



(c)



**Fig. 4**. (a) ORTEP diagram showing the coordination environments for  $Ag^l$  atoms in **4**. All H atoms are omitted for clarity. (Symmetry codes: #1 = 1 - x, -y, 1 - z; #2 = x - 1, y, z). (b) An infinite 1D Ag–L1 chain structure of **4**. (c) An infinite 2D anionic supramolecular layer *via* hydrogen-bonding interactions (N5–H5N···O1<sup>#6</sup>). (d) The 3D framework of **4** *via* hydrogen-bonding interactions (O3W–H3A···O2<sup>#4</sup> and O3W–H3B···O1<sup>#5</sup>), sphere packing representation of Ag–L1 chains with threading in the space and all H atoms are omitted for clarity.

coordination geometry with two nitrogen atoms from two different L1 ligands  $[Ni(1)-N(3) = 2.013(2) \text{ Å}, Ni(1)-N(6)^{\#1} = 2.031(2) \text{ Å}]$  and four carboxylate oxygen atoms from two different L3 an-

ions [Ni(1)–O(1) = 2.1106(19) Å, Ni(1)–O(2) = 2.1657(18) Å, Ni(1)–O(3)<sup>#2</sup> = 2.166(2) Å and Ni(1)–O(4)<sup>#2</sup> = 2.090(2) Å]. The four atoms (O1, O3<sup>#2</sup>, O4<sup>#2</sup> and N3) occupy the equatorial positions, whereas



**Fig. 5.** (a) ORTEP diagram showing the coordination environment for Ni<sup>II</sup> atom in **5**. All H atoms are omitted for clarity. (Symmetry codes: #1 = -x, -y, 1 - z; #2 = x - 1/2, 2/3 - y, z). (b) 1D Ni–L1 chains gained by L1 ligands and Ni<sup>II</sup> cations. (c) "U-shaped" 1D sheet formed by L3 anions and Ni<sup>II</sup> cations. (d) The 3D framework of **5** (blue for L1 ligands and orange for L3 anions). (e) Schematic representations of the 3-fold interpenetrating diamond nets of **5**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

other two atoms (O2 and  $N6^{\#1}$ ) locate the apical positions. The L1 ligands connect the Ni(II) ions in a *cis*-conformation to give a

wave-like 1D chain along *c*-axis (Fig. 5b). The Ni–Ni distance is 14.025 Å across the L1 ligands and the dihedral angle between



**Fig. 6.** (a) ORTEP diagram showing the coordination environment for  $Zn^{II}$  atom in **6.** All H atoms are omitted for clarity. (Symmetry codes: #1 = 2 - x, -y, 1 - z; #2 = -x, 1 - y, 1 - z; #3 = 3 - x, -y - 1, -z; #4 = 4 - x, -y, -z; #5 = x + 2, y, z - 1). (b) 2D layer formed by L3 anions and  $Zn^{II}$  cations (blue for L3 anions coordinated to two  $Zn^{II}$  cations). (c) View of a bimetallic [ $Zn_2(CO_2)_2$ ] unit. (d) Schematic representation of 3-fold interpenetrating  $\alpha$ -Po net of **6**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the two imidazole rings of L1 ligands is 61.97°. The L3 anions in a *cis*-conformation bridge the adjacent Ni(II) atoms to generate "U-

shaped" 1D chains with the Ni–Ni distance of 14.632 Å (Fig. 5c). The two types of 1D chains are linked each other by Ni(II) atoms





(c)



(**d**)



**Fig. 7.** (a) The coordination environment of the Cd<sup>II</sup> center in compound **7.** All H atoms are omitted for clarity. (Symmetry codes: #1 = -x - 1, 1 - y, 1 - z; #2 = 2 - x, -y - 1, 1 - z; #3 = -x, -y, 1 - z; #4 = x - 2, 1 + y, z). (b) The 1D two-strand chains formed by L3 and Cd<sup>II</sup> cations. (c) View of the 4<sup>4</sup> network topology. (d) The 2D network structure of **7** (blue for L1 ligands and orange for L3 anions). (e) The parallel relation between the 2D layers of **7**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to form a 3D framework structure of **5** with large channels along the *a*-axis (Fig. 5d). The channels provide the probability for inter-

penetrating array. Herein, the three identical nets are interpenetrated in 3-fold mode [1a].



**Fig. 8.** (a) ORTEP diagram showing the coordination environment for  $Co^{II}$  atom in **8**. All H atoms are omitted for clarity. (Symmetry codes: #1 = 1 - x, -y, 1 - z; #2 = -x - 1, 1 - y, 2 - z; #3 = -x, 1 - y, 1 - z). (b) 2D layer framework of **8** (blue for L1 ligands and orange for L3 anions). (c) Schematic views of the 2D  $\rightarrow$  3D architecture in **8**. (d) 3D supramolecular structure formed through  $\pi$ - $\pi$  stacking interactions. All H atoms and CI atoms are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

From a topological perspective, if the Ni(II) cation is considered as a four-connected node, the framework of compound **5** can be regarded as a diamond network topology. In order to minimize the large void cavity in the diamondoid cage and stabilize the framework, the potential voids formed by a single 3D network show incorporations of another two identical networks, therefore, giving a 3-fold interpenetrating diamond array (Fig. 5e). In addition, the 3D structure of **5** is further stabilized by the hydrogen-bonding interactions (Table 2).

#### 3.1.6. Structure of $[Zn(L3)(L1)_{0.5}] \cdot H_2O(\mathbf{6})$

L1 was used to react with L3 and  $Zn(Ac)_2 \cdot 2H_2O$  under the hydrothermal synthetic condition and a new complex **6** was obtained. As shown in Fig. 6a, the Zn(II) atom is five-coordinated by one nitrogen atom from L1 ligand and four carboxylate oxygen atoms from three different L3 anions in a distorted square pyramidal geometry with a  $\tau$  value of 0.221 [13]. The Zn–O and Zn–N bond lengths are all within the normal ranges [5c,9]. If the L1 ligands are neglected, L3 anions coordinate to neighboring Zn(II) atoms to furnish a 2D polymeric layer (Fig. 6b). Within this layer, two adjacent Zn(II) atoms are bridged by two carboxylate groups to give a binuclear unit [Zn<sub>2</sub>(CO<sub>2</sub>)<sub>2</sub>] (Fig. 6c). It is noteworthy that the L3 anions exhibit two types of coordination modes: one is coordinated to four Zn(II) cations, and the other linked two Zn(II) cations in the 2D layer structure. Furthermore, L1 ligands connect the 2D layers to generate a 3D framework structure.

From the topological view, if the binuclear unit  $[Zn_2(CO_2)_2]$  can be viewed as a six-connected node and the L1 ligand and L3 anion can be viewed as connectors, the overall topology of the 3D framework shows an  $\alpha$ -Po topology [11]. Because of the spacious nature of the single network, it allows other two identical  $\alpha$ -Po nets to interpenetrate it in a normal mode, resulting in a 3-fold interpenetrated  $\alpha$ -Po-related network (Fig. 6d). Among the currently known examples of  $\alpha$ -Po topology, only a few 3-fold interpenetrated network structures have been identified, and this framework adds a new member to them [11]. In addition, there exist the intermolecular hydrogen bonds (Table 2), which consolidate the network of **6**.

# 3.1.7. Structure of [Cd(L3)(L1)<sub>0.5</sub>(H<sub>2</sub>O)] (7)

When Cd(Ac)<sub>2</sub>·2H<sub>2</sub>O was used instead of Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O under similar synthetic conditions, a quite different structure of 7 was obtained. As shown in Fig. 7a, the Cd(II) atom, lying on independent inversion center, shows a distorted {CdNO<sub>5</sub>} octahedral coordination geometry with one nitrogen atom from L1 ligand, four carboxylate oxygen atoms from three different L3 anions and one water molecule. Three carboxylate oxygen atoms and one nitrogen atom (O2, O3<sup>#1</sup>, O4<sup>#1</sup> and N8) occupy the equatorial positions, whereas one carboxylate oxygen atom (O1) and one water molecule (O1W) locate the apical positions with Cd-O distances of 2.392(2) Å and 2.443(3) Å. The L3 anions link neighboring Cd(II) atoms to generate infinite 1D two-strand chains as illustrated in Fig. 7b. The L1 ligands further connected the 1D two-strand chains to generate the 2D layer structures with Cd(II) ··· ·Cd(II) separation of 14.531 Å across the L1 ligands (Fig. 7c). Within this layer, two adjacent Cd(II) atoms are bridged by two carboxylate groups to give a binuclear unit  $[Cd_2(CO_2)_2]$ . From the topological view, if the binuclear unit  $[Cd_2(CO_2)_2]$  can be defined as a four-connected node, the structure of **7** can be classified as a  $4^4$  network topology along the *c*-axis (Fig. 7c) [4d]. Also, the hydrogen bonds (Table 2) involving the water molecules and carboxylate oxygen atoms help to stabilize the structure of 7 (Fig. 7d). The resulting 2D layers are packed in a parallel fashion along the *a*-axis (Fig. 7e).

# 3.1.8. Structure of [CoCl(L3)<sub>0.5</sub>(L1)<sub>0.5</sub>] (8)

In compound **8**, the Co(II) ion is four-coordinated by two carboxylate oxygen atoms from two different L3 anions (Co(1)– O(1) = 1.939(3)Å and Co(1) - O(2) = 1.949(3)Å), one N atom from L1 ligand (Co(1)-N(1) = 1.998(3) Å) and one Cl<sup>-</sup> anion (Co(1)-N(1) = 1.998(3) Å)Cl(1) = 2.2413(12) Å) to furnish a distorted {CoNO<sub>2</sub>Cl} tetrahedral geometry (Fig. 8a). The L3 anions bridge neighboring Co(II) ions to generate infinite 1D chains, which are further linked by the L1 ligands to give the 2D layer structure. Within this 2D layer, two adjacent Co(II) atoms are bridged by two L3 anions to give a binuclear unit  $[Co_2(CO_2)_2]$ . If the  $[Co_2(CO_2)_2]$  unit is considered as a four-connected node, the structure of  $\mathbf{8}$  can be classified as a  $4^4$ network topology. The 2D layer of 8 has rectangular windows with side lengths of 12.065 Å based on the Co(II)...Co(II) distances across the L1 ligands and 20.219 Å across the L3 anions (Fig. 8b). It is well known that the formation of different interpenetrations can be ascribed to the presence of free voids in a single network [14]. In **8**, the 2D (4,4)-layers interpenetrated in an inclined mode, resulting in a new 2D  $\rightarrow$  3D architecture (Fig. 8c) [1a,15]. Notably, there exist  $\pi$ - $\pi$  stacking interactions between the imidazole rings of L1 ligands and the benzene rings of L3 anions (centroid-to-centroid distance of 3.86 Å, face-to-face distance of 3.42 Å, and dihedral angle of 10.9°), which further stabilize the framework of 8 (Fig. 8d).

#### 3.1.9. Structure of $[ZnCl(L3)_{0.5}(L2)_{0.5}]$ (9)

Although compounds **9** and **10** were synthesized under different synthetic conditions, they are isomorphous. Herein, only the structure of **9** is described in detail. The figures for the structure of compound **10** are shown in the Supporting Information (Figs. S1–S3).

As shown in Fig. 9a, each Zn(II) cation is coordinated to two carboxylate O atoms from two different L3 anions (Zn(1)–O(1) = 1.9678(19) Å, Zn(1)–O(2) = 1.9501(19) Å), one N atom from L2 ligand (Zn(1)–N(1) = 2.0081(19) Å) and one Cl<sup>-</sup> anion (Zn(1)–Cl(1) = 2.2251(11) Å) in a distorted {ZnNO<sub>2</sub>Cl} tetrahedral geometry. The L3 anions bridge neighboring Zn(II) ions to generate an infinite 1D chain, which is further linked by L2 ligands to form a 2D sheet with Zn(II)···Zn(II) distance of 12.477 Å across the L2 ligands (Fig. 9b). Within this 2D layer, two adjacent Zn(II) atoms are bridged by two L3 anions to give a binuclear unit [Zn<sub>2</sub>(CO<sub>2</sub>)<sub>2</sub>]. If the [Zn<sub>2</sub>(CO<sub>2</sub>)<sub>2</sub>] unit is considered as a four-connected node, the structure of **9** can be considered as a simple 2D (4,4) grid [1a,16]. The resulting 2D layers are packed in a parallel fashion along the *a*-axis (Fig. 9c).

#### 4. Discussion

#### 4.1. Effect of N-containing ligands

From the structural descriptions above, it can be seen that the N-containing ligands L1 and L2 have a great influence on the construction of the frameworks. Compared with L1, L2 possesses relatively large steric hindrance. Drastic structural changes have taken place in compounds 5-7 and 9 when the N-containing ligands were incorporated in the compounds 1-3. In comparison with 1 and **2**, the introduction of L1 ligands in **5** and **6** not only replaced all coordinated water molecules, but also changed the coordination mode of L3 anions. In 1, the L3 anions did not coordinate to the Ni(II) centers as counteranions. The Ni(II) ions are coordinated by water molecules to form the cationic complex  $[Ni(H_2O)_6]^{2+}$ . When extra L1 ligand was introduced in the reaction system of 1, a structurally different compound 5 was obtained. In 5, the L1 ligands linked the 1D Ni-L3 chains to generate a 3D framework structure with threefold interpenetrating diamond array. In 2, the L3 anions linked the Zn(II) ions to form 1D chain structures. When L1 was introduced in the reaction system of 2, a structurally different compound 6 was obtained. In 6, the L1 ligands extend the Zn–L3 chains

L1 ligands linked 1D Cd–L3 chains into the 2D layer structure. Compared with L1, L2 was a relatively large N-containing ligand. Therefore, the compound **9** (2D structure), containing the L2 ligand, shows a relatively lower dimensional structure than compound **6** (3D structure).

#### 4.2. The effect of metal cations on the framework

From the structures of compounds 1–3 and 5–7, it can be seen that the coordination behaviors of metal ions have a great effect on the structures of the complexes. In compounds 1–3, the metal ions display different coordination numbers. Since the radius of the Cd(II) ion is larger than those of the Zn(II) and Ni(II) ions, the coordination number of the Cd(II) ion (7 in 3) is larger than those of the Zn(II) (6 in 2) and Ni(II) (6 in 1). The compounds 5–7 contain the same carboxylates and N-containing ligands, but they show different structures. The structural differences of **5–7** are mainly caused by the changes of metal ions (Ni(II), Zn(II) and Cd(II)). In 5, there is a six-coordinated Ni(II) ion which is involved in a 3D framework with a 3-fold interpenetrating diamond array. In 6, there exists a five-coordinated Zn(II) ion which is included in a 3D framework structure with a 3-fold interpenetrating  $\alpha$ -Po network topology. When Zn(II) ion is replaced by Cd(II) ion in 7 under similar synthetic conditions, the 2D layered compound 7 was obtained. It should be pointed that although the coordination numbers of the central metals are the same in 5 and 7, their final structures are entirely different.

#### 4.3. Luminescent properties

Luminescent compounds are of great interest due to their various applications in chemical sensors, photochemistry, and electroluminescent (EL) display [17]. The luminescent properties of zinc, cadmium and silver carboxylate compounds have been investigated at room temperature. In this paper, the photoluminescent behaviors of  $H_2L3$ , the N-containing ligands and the compounds **2–4**, **6**, **7** and **9** have been studied in solid state at room temperature. The emission and excitation peaks of **2–4**, **6**, **7** and **9** are shown in Fig. S5.

The photoluminescent spectrum of H<sub>2</sub>L3 ligand shows the main peak at 423 nm ( $\lambda_{ex}$  = 371 nm), which is probably attributable to the  $\pi^* \rightarrow n$  or  $\pi^* \rightarrow \pi$  transition [18]. It should be pointed out that the emissions of compounds 2, 3, 6, 7 and 9 are neither metal-toligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature since the Zn(II) and Cd(II) ions are difficult to oxidize or to reduce because of their d<sup>10</sup> configuration, which are mainly based on the luminescence of ligands [19]. For compounds **2** and **3**, the emission peaks appear at 404 ( $\lambda_{ex} = 362 \text{ nm}$ ) and 412 nm ( $\lambda_{ex}$  = 340 nm), respectively. The emission peaks of compounds 2 and 3, containing only L3 anions and metal ions, exhibit blue-shifts with respect to the band shown by H<sub>2</sub>L3 ligand, which may be attributed to the coordination of L3 anions to metal centers [20]. The compounds 6, 7 and 9 show emissions at around 418  $(\lambda_{ex} = 373 \text{ nm}), 425 (\lambda_{ex} = 375 \text{ nm}) \text{ and } 431 \text{ nm} (\lambda_{ex} = 372 \text{ nm}),$ respectively. They can probably be assigned to the intraligand fluorescent emission of the H<sub>2</sub>L3 ligand because similar emission is observed for the H<sub>2</sub>L3 ligand [21]. The compound 4 exhibits an emission peak at 400 nm ( $\lambda_{ex}$  = 365 nm), showing blue-shift relative to L1 or H<sub>2</sub>L3 ligand. This may be attributed to be the co-action of L1 ligand and H<sub>2</sub>L3 ligand.

#### 5. Conclusion

In summary, ten structurally different coordination frameworks based on a new dicarboxylate ligand have been successfully



into the 3D framework structure. Compared with **3**, L1 ligands in compound **7** partly take place of the coordinated water molecules, resulting in a great change of the framework. In **3**, the organic L3 anions linked Cd(II) ions to form a 1D chain structure. In **7**, the



prepared and characterized by single-crystal X-ray diffraction. These compounds display intriguing and versatile coordination features with 1D. 2D and 3D frameworks. It has been proved that the H<sub>2</sub>L3 is a good candidate for construction of coordination polymers with diverse structures. The influence of L1 and L2 ligands on the structures of the complexes has been investigated. The varieties of the structures also indicate that different metal ions play dominant roles in the final frameworks of these compounds. The photoluminescent emissions show that these complexes may be good candidates for optical materials.

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#### Appendix A. Supplementary data

CCDC 769103, 769104, 769105, 769106, 769107, 769108, 769109, 769110, 769111, and 769112 contains the supplementary crystallographic data for 1-10. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.poly.2010.12.027.

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