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PAPER

Zn(II) and Cd(II) coordination polymers assembled by di(1*H*-imidazol-1-yl) methane and carboxylic acid ligands[†]

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Five new $\operatorname{Zn}^{II}/\operatorname{Cd}^{II}$ coordination polymers constructed from di(1*H*-imidazol-1-yl)methane (L) mixed with different auxiliary carboxylic acid ligands formulated as $[\operatorname{Zn}(L)(\operatorname{H}_2L^1)_2 (\operatorname{H}_2O)_{0.2}]_n$ (1), $\{[\operatorname{Zn}(L)(L^2)] \cdot \operatorname{H}_2O\}_n$ (2), $\{[\operatorname{Cd}_2(L)_2(L^2)_2] \cdot \operatorname{2H}_2O\}_n$ (3), $\{[\operatorname{Cd}(L)(L^3)] \cdot \operatorname{H}_2O\}_n$ (4) and $[\operatorname{Cd}(L)(L^4)]_n$ (5) $(\operatorname{H}_3L^1 = 1,3,5$ -benzenetricarboxylic acid, $\operatorname{H}_2L^2 = 4,4'$ -oxybis(benzoic acid), $\operatorname{H}_2L^3 = m$ -phthalic acid and $\operatorname{H}_2L^4 = p$ -phthalic acid) have been synthesized under hydrothermal conditions and structurally characterized. Four related auxiliary carboxylic acids were chosen to examine the influences on the construction of these coordination frameworks with distinct dimensionality and connectivity. The coordination arrays of 1–5 vary from 1D zigzag chain for 1, 2D (4,4) layer for 2–4, to 2-fold interpenetrated 3D coordination network with the α -Po topology for 5. The thermal and photoluminescence properties of complexes 1–5 in the solid state have also been investigated.

Introduction

Coordination polymers have attracted intensive attention in recent years because of their intriguing structural topologies and tailor-made applications as functional solid materials.¹ However, persistent research has shown that various factors may play important roles in constructing coordination polymers, which result in the complexity and uncertainty of the complexes, and great contributions have been focused on this field to investigate the effects and guide the syntheses.^{2–7} The carboxylate- and pyridine-based ligands, as well as the combination of them have been widely used and providing more variability to construct much more complicated and fantastic topologies with interesting properties. Recently, some studies focused on choosing the Nheterocycles and its derivatives with five-membered rings (imidazole, triazole, tetrazolate, etc.) and multicarboxylate as mixed ligands to construct fantastic structures and topologies.⁸ However, coordination polymers with the flexible di(1H-imidazol-1-yl)methane (L) ligand and carboxylate as the auxiliary ligand are less documented so far.9

To examine the influences of auxiliary carboxylic acids on the construction of coordination frameworks, a series of new coordination polymers, including $[Zn(L)(H_2L^1)_2 \cdot (H_2O)_{0.2}]_n$ (1), {[Zn-(L)(L²)]·H₂O}_n (2), {[Cd₂(L)₂(L²)₂]·2H₂O}_n (3), {[Cd(L)-(L³)]·H₂O}_n (4) and [Cd(L)(L⁴)]_n (5) (H₃L¹ = 1,3,5-benzenetricarboxylic acid, H₂L² = 4,4'-oxybis(benzoic acid), H₂L³ =

m-phthalic acid, and $H_2L^4 = p$ -phthalic acid) have been synthesized with L and four related carboxylate ligands under hydrothermal conditions and structurally characterized. X-ray diffraction analysis of these network solids reveals the remarkable structural transformation from 1D for 1, to 2D for 2–4, and 3D for 5, respectively. The thermal and photoluminescence properties of complexes 1–5 have also been investigated.

Experimental

Materials and synthesis

All the chemicals used for synthesis were of analytical grade and commercially available. L was synthesized according to the literature method.¹⁰ Structures of L and carboxylate ligands used in this work are shown in Scheme 1.

Synthesis of $\{[Zn(L)(H_2L^1)_2] \cdot (H_2O)_{0.2}\}_n$ (1)

1 was hydrothermally synthesized under autogenous pressure. A mixture of $Zn(NO_3)_2$ ·6H₂O (0.5 mmol), L (0.2 mmol), H₃L¹



Scheme 1 The L ligand and carboxylate ligands used in this work.

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(0.2 mmol) and H₂O (12 mL) was sealed in a Teflon-lined autoclave and heated to 140 °C in 12 h. After 48 h, the reaction vessel was cooled to room temperature in 24 h. Colorless crystals were collected with a yield of ~20% based on Zn(NO₃)₂·6H₂O. FT-IR (KBr pellets, cm⁻¹): 3129b, 1701m, 1568m, 1401s, 1098s, 954w, 744s, 680m, 652m, 541w. Anal. Calcd for $C_{25}H_{18.4}N_4O_{12.2}Zn$: C, 47.25; H, 2.92; N, 8.82. Found: C, 46.73; H, 2.99; N, 9.05.

Synthesis of $\{[Zn(L)(L^2)] \cdot H_2O\}_n$ (2)

Single crystals of **2** suitable for X-ray analysis were obtained by the similar method as described for **1**, except H_2L^2 was used instead of H_3L^1 . Yield: ~30%. FT-IR (KBr pellets, cm⁻¹): 3136b, 3137b, 1601m, 1385s, 1283w, 1231s, 1164w, 1082m, 943w, 877m, 780m, 713w, 655w. Anal. Calcd for $C_{21}H_{18}N_4O_6Zn$: C, 51.70; H, 3.72; N, 11.49. Found: C, 50.72; H, 3.68; N, 11.92.

Synthesis of ${[Cd_2(L)_2(L^2)_2] \cdot 2H_2O}_n$ (3)

3 was hydrothermally synthesized under autogenous pressure. A mixture of Cd(NO₃)₂·4H₂O (0.5 mmol), **L** (0.2 mmol), H₂**L**² (0.2 mmol) and H₂O (12 mL) was sealed in a Teflon-lined autoclave and heated to 140 °C in 12 h. After 48 h, the reaction vessel was cooled to room temperature in 24 h. Colorless crystals were collected with a yield of ~20% based on Cd(NO₃)₂·4H₂O. FT-IR (KBr pellets, cm⁻¹): 3415b, 3125b, 1596m, 1541m, 1398s, 1233m, 1162w, 1079w, 965w, 879w, 781w, 615w. Anal. Calcd for C₄₂H₃₄N₈O₁₂Cd₂: C, 47.25; H, 3.21; N, 10.50. Found: C, 47.72; H, 3.48; N, 10.86.

Synthesis of ${[Cd(L)(L^3)] \cdot H_2O}_n$ (4)

Single crystals of **4** suitable for X-ray analysis were obtained by the similar method as described for **3**, except H_2L^3 was used instead of H_2L^2 and two drops of triethylamine were added. Yield: ~35% based on Cd(NO₃)₂·4H₂O. FT-IR (KBr pellets, cm⁻¹): 3119b, 1604m, 1539m, 1387m, 1279w, 1225m, 1091s, 832w, 746m, 661w. Anal. Calcd for C₁₅H₁₄N₄O₅Cd: C, 40.70; H, 3.19; N, 12.66. Found: C, 39.79; H, 3.34; N, 12.33.

Synthesis of $[Cd(L)(L^4)]_n$ (5)

Single crystals of **5** suitable for X-ray analysis were obtained by the similar method as described for **4**, except H_2L^4 was used instead of H_2L^3 . Yield: ~25% based on Cd(NO₃)₂·4H₂O. FT-IR (KBr pellets, cm⁻¹): 3135s, 1583s, 1381s, 1282m, 1082m, 1035w, 927w, 837s, 743s, 652m, 524m. Anal. Calcd for C₁₅H₁₂N₄O₄Cd: C, 42.42; H, 2.85; N, 13.19. Found: C, 42.61; H, 3.12; N, 12.45.

Physical measurements

Elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer. IR spectra were measured on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. The X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectra was carried out by the single-crystal data and diffraction-crystal module of the *Mercury* (Hg) program available free of charge *via* http://www.iucr.org.

X-ray data collection and structure determinations

X-ray single-crystal diffraction data for complexes **1–5** were collected on a Rigaku SCX-mini diffractometer at 293(2) K. The program SAINT¹¹ 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 by full-matrix least-squares methods with SHELXL.¹² Other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2 . The hydrogen atoms of the water molecules in **1**, **2**, and **4** were added by difference Fourier E-maps and refined isotropically. The H atoms of the water molecule were not located in the difference map in **3**. Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths and angles are listed in Tables S1–S6, ESI.† Hydrogenbond parameters are listed in Tables S7–S10, ESI.†

Results and discussion

Crystal structure of the complexes

 $\{[Zn(L)(H_2L^1)_2] \cdot (H_2O)_{0,2}\}_n$ (1). The single crystal X-ray determination reveals that complex 1 crystallizes in the monoclinic space group $P2_1/c$ and features 1D "zigzag" chains. The coordination geometry of the Zn^{II} atom is distorted octahedron considering two weak coordination bonds. The axial positions are occupied by the nitrogen atoms from two different L ligands, and the equatorial plane is defined by four oxygen atoms from two different carboxylate of two separate H_2L^1 ligands in a chelating coordination mode considering weak Zn-O contacts (Fig. 1a). Adjacent Zn^{II} atoms were bridged by the L ligands to afford a 1D infinite zigzag chain along the a axis, as shown in Fig. 1b. It should be noted, the H_3L^1 ligands just partially deprotonate, and abundant hydrogen bonding occurs between the resident carboxylate to form 2D layers in the bc plane (Fig. 1c). The adjacent 2D layers were further linked by the L ligands to afford a 3D supramolecular structure (Fig. 1d).

{[Zn(L)(L²)]·H₂O}_n (2). Complex 2 crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit consists of one Zn^{II} ion, one L ligand, one L² ligand and one lattice water molecule. The Zn^{II} is four-coordinate having an irregular tetrahedral geometry composed of two nitrogen atoms from two L ligands and two oxygen atoms from two L² ligands (Fig. 2a). The adjacent Zn^{II} atoms were connected by L ligands to yield chains with a Zn–Zn distance of 9.103(28) Å, which are further linked by L² ligands to form a 2D layer. The 2D layer can also be considered as an undulated sql net by repeating the [Zn₄(L)₂(L²)₂] unit in the *bc* plane (Fig. 2b). Notably, the [Zn₄(L)₂(L²)₂] unit has a square window with dimensions of 9.103(28)–14.899(33) Å. The free water molecules are located between the adjacent undulating layers, as shown in Fig. 2c.

Table 1 Crystal data and structure refinement parameters for complexes 1-5

Complex reference	1	2	3	4	5
Chemical formula	C ₂₅ H _{18 4} N ₄ O _{12 2} Zn	C ₂₁ H ₁₈ N ₄ O ₆ Zn	C42H34N8O12Cd2	C ₁₅ H ₁₄ N ₄ O ₅ Cd	C15H12N4O4Cd
Formula mass	635.41	487.76	1067.57	442.70	424.69
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
a/Å	10,100(2)	8.8150(18)	18.061(4)	10.234(2)	8.0047(16)
b/Å	22.427(5)	14.859(3)	31.309(6)	9.1507(18)	9.6594(19)
$c/\text{\AA}$	11.398(2)	15.580(3)	15.114(3)	16.895(3)	10.952(2)
α (°)	90.00	90.00	90.00	90.00	101.18(3)
$\beta(\circ)$	101.35(3)	92.25(3)	90.00	103.79(3)	105.39(3)
γ (°)	90.00	90.00	90.00	90.00	105.40(3)
Unit cell volume/Å ³	2531.4(13)	2039.0(7)	8547(3)	1536.6(5)	754.6(3)
Space group	$P2_1/c$	$P2_1/n$	C2221	$P2_1/c$	PĪ
No. of formula units per unit cell, Z	4	4	8	4	2
No. of reflections measured	25 980	17 326	45 281	15 844	8071
No. of independent reflections	5778	3597	9812	3511	3450
R _{int}	0.1156	0.1205	0.0712	0.0548	0.0318
Final R_1 values $(I > 2\sigma(I))$	0.0792	0.0940	0.0555	0.0432	0.0277
Final w $R(F^2)$ values $(I > 2\sigma(I))$	0.1188	0.1622	0.0859	0.0674	0.0528
Final R_1 values (all data)	0.1482	0.1426	0.0787	0.0637	0.0322
Final $wR(F^2)$ values (all data)	0.1363	0.1786	0.0914	0.0719	0.0540

{[$Cd_2(L)_2(L^2)_2$]· $2H_2O$ }_{*n*} (3). The single-crystal X-ray analysis reveals that complex 3 crystallizes in the orthorhombic space group C222₁. There are three independent Cd atoms: Cd1, Cd2 and Cd3 in each asymmetric unit of 3 bearing a similar coordinated configuration. Each Cd^{II} is six coordinated in a distorted octahedral geometry by two nitrogen atoms from two L ligands and four chelate oxygen atoms from two L² ligands (Fig. 3a and 3b). The adjacent Cd^{II} atoms were linked by L ligands along the *a* axis and L² ligands along the *c* axis to afford 2D layers in the *ac* plane. It should be noted, there are two types of 2D layers, in which the L ligand adopts different dihedral angles between the two imidazole rings (*trans* conformation in Fig. 3a, *cis* conformation in Fig. 3b). These 2D layers stack along the *b* axis in an ABAB mode with lattice water molecules between the layers (Fig. 3c).

{[Cd(L)(L³)]·H₂O}_{*n*} (4). Complex 4 crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit consists of one Cd^{II} atom, one L ligand, one L³ ligand and one lattice water molecule. As shown in Fig. 4a, the center Cd1 is hepta-coordinated by two nitrogen atoms from two L ligands and five oxygen atoms from three L³ ligands. Two symmetry related Cd^{II} atoms were linked by one pair of carboxylates of two different L³ ligands in μ_2 - η^2 : η^1 coordination mode forming a [Cd₂] unit. The [Cd₂] units were double-bridged by the other carboxylate of L³ ligands along the *a* axis, and further double-bridged by L ligands along the *b* axis to afford a 2D layer (Fig. 4b). The lattice water molecules filled up in the 2D layer. Considering [Cd₂] units as nodes, the double-bridged ligands as linkers, 4 could be simplified as a (4,4)-connected topological net.

 $[Cd(L)(L^4)]_n$ (5). Complex 5 crystallizes in the triclinic $P\bar{1}$ space group. The asymmetric unit consists of one Cd^{II} atom, one L ligand, and two kinds of half L⁴ ligands. Each Cd^{II} atom is hexa-coordinated in a distorted octahedral geometry by two nitrogen atoms from two L ligands and four oxygen atoms from two different L⁴ ligands (Fig. 5a). One kind of L⁴ ligand adopts a chelating bis-bidentate coordination mode, while the other takes bridging bis-bidentate.¹³ A pair of symmetry related Cd^{II}

atoms are bridged by four bidentate carboxylate groups from two pairs of symmetry related L^4 ligands forming a binuclear unit. The binuclear units were linked by L^4 ligands to afford a 2D layered network in the *ab* plane (Fig. 5b). In addition, the coordination sphere is completed by two nitrogen donors from L ligands. Each binuclear unit was linked to six adjacent ones by two pairs of double-bridged L ligands and four L^4 ligands, affording a 3D double interpenetrating framework (Fig. 5c). Topologically, while the binuclear units are simplified as nodes and the bridging L and L^4 ligands are simplified as the linkers, a 3D 2-fold interpenetrated network with an α -Po topology can be rationalized as shown in Fig. 5d.

Coordination modes and conformations of the ligands in metal complexes

Hydrothermal reactions of Zn/Cd salts and the L ligand with four different aromatic carboxylate ligands give rise to a series of new coordination frameworks. The flexible L ligand can adopt varied conformations to meet the geometric requirement of the metal ions on the construction of the complexes (Chart 1, Table 2). The L ligand adopts a μ_2 bridging coordination mode, but different conformations. The L ligands adopt cis conformation in 1, 2 and 4. trans conformation in 5, and both conformations in 3, respectively. The secondary carboxylate ligands can be fully/partially deprotonated for the balance of charge and mediate the coordination needs of the metal ions to generate interesting frameworks (Chart 2). In complex 1, the L^1 ligands just partially deprotonate adopting a chelating terminal coordination mode and the remaining two carboxylate groups took part in H-bonding interactions. Both 2 and 3 are a 4,4-layer structure with a single-metal as the node by using a flexible V-shaped L^2 ligand; the L² ligand adopts different coordination modes, bisunidentate in 2 and chelating bis-bidentate in 3, respectively. When introducing a much shorter and rigid L^3 ligand in 4, a 4,4layer structure with the M2 unit as the node was afforded and the L³ ligand adopts a chelating bidentate and chelating/bridging bidentate coordination mode. While using a linear and rigid L⁴





(c)

Fig. 2 (a) Coordination environment of the Zn(II) ion. (b) The **sql** net of **2**. (c) Stack of layers containing interlayer water molecules. Symmetry code: A x + 1/2, -y + 5/2, z - 1/2.

Fig. 1 (a) Coordination environment of the Zn(II) ion. (b) 1D chain of **1**. (c) 2D H-bonded layer with H-bonds depicted by the dotted bonds. (d) The L ligands connected adjacent 2D layers to give rise to the 3D supramolecular architecture of **1**. Symmetry code: A x - 1, y, z.

ligand, a two-fold interpenetrating network with α -Po topology based on binuclear units was formed. It should be noted, the L⁴ ligand adopts two kinds of coordination modes: one is the same as the L² ligand in 3, the other is bridging bis-bidentate. The structural differences between 3, 4 and 5 showed that a series of carboxylate ligands with different shape, size, and flexibility are critical factors in the formation of these coordination architectures and the different coordination modes of carboxylate ligands enrich the structural complexity of the Zn/Cd-L-carboxylate system.

XRPD and TGA results

X-ray powder diffraction (XRPD) for certain complexes (1–5) was performed to characterize their purity. The XRPD of the asprepared samples are shown in Fig. S1, ESI.† All diffraction peaks on the curves are in good agreement with the respective single-crystal structures. To examine the thermal stability of the obtained coordination polymers, thermogravimetric analyses (TGA) experiments were carried out (Fig. 6). All five complexes exhibit high thermal stability. The TG curve of 1 shows the first weight loss of 3.4% in the temperature range 25–155 °C, which indicates the exclusion of lattice water molecules and the surface absorption of moisture; then it vigorously decomposed at temperature higher than 370 °C. For 2, the weight loss attributed to the gradual release of water molecules is observed in the range 25–173 °C (obsd, 3.5%; calcd, 3.7%). The decomposition of residual composition occurs at 360 °C, and the final remaining



Fig. 3 (a) The formation of a 2D layer based on the Cd2(II) ions, *trans*-L and L² ligands. (b) The formation of a 2D layer based on the Cd1(II), Cd3(II) ions, *cis*-L and L² ligands. (c) Stacking sequence of the two types of 2D layers in **3** as viewed along the *c* direction. Symmetry code: E *x*, *y*, *z* + 1.

weight of 17.1% corresponds to ZnO (calcd, 16.7%). For 3, an initial weight loss of 4.0% corresponds to the loss of solvent





Fig. 4 (a) Coordination environment of the Cd(II) ion. (b) Doublebridged L and L³ ligands connected the binuclear units to form a 2D layer. Symmetry code: C x, y - 1, z.

water (calcd, 3.4%). Then it could be stable under 330 °C and decomposed at higher temperature. For **4**, the weight loss between 25 and 190 °C corresponds to the release of water molecules (obsd, 3.4%; calcd, 4.1%), then it decomposed upon further heating. Complex **5** is stable under 250 °C, and then it decomposed at higher temperatures. It should be noted that it underwent a weight loss of 17.83% from 250 to 360 °C which may correspond to partial loss of the ligands before it decomposed completely.

Luminescence studies

Luminescent coordination complexes have attracted great attention because of their potential applications as chemical sensors, photochemistry, and electroluminescence displays.¹⁴ The synthesis of metal–organic complexes by conjugated organic spacers and metal centers can be an efficient method for obtaining new luminescence materials, especially for d¹⁰ systems.¹⁵ The luminescence properties of the free ligand L and their





Chart 1 The conformations of the L ligand in complexes 1–5.

Complex	N…N distance (Å)	M…M distance (Å)	Dihedral angle of two imidazole rings (°)
1 2 3	6.423 6.020 5.712 5.715	10.100 9.103 9.045 9.020	95.99 105.16 102.97 91.63
4 5	5.935 6.474	9.151 10.952	107.35 117.30



Chart 2 The coordination modes of the carboxylate ligands in complexes 1–5.



Fig. 6 The TGA diagram for complexes 1-5.

Fig. 5 (a) Coordination environment of the Cd(II) ion. (b) L^4 ligands gat connected the binuclear units to form a 2D layer. (c) View of the 2-fold (37 interpenetrated 3D structure. (d) α -Po topology network of **5**. Symmetry codes: A -x + 1, -y + 1, -z + 1; B x, y, z - 1.

complexes in the solid state at room temperature were investigated. As shown in Fig. 7, there are the main emission bands (374, 334 and 394 nm; $\lambda_{ex} = 310$, 280, 280 nm, respectively) for complexes **1–3**, whereas an intense emission band with wavelength at 354 nm upon excitation at 280 nm for the free ligand **L**, which indicate these emissions may probably be assigned to



Fig. 7 Solid-state photoluminescent spectra of complexes 1-5 and the free ligand L at room temperature.

the intraligand $(\pi - \pi^*)$ transfer of the L ligands. For complexes 4 and 5, the main emission bands (427 and 437 nm; $\lambda_{ex} = 330$, 310 nm) may be assigned to the intraligand $(\pi - \pi^*)$ transfer of the L³ or L⁴ ligands, respectively.¹⁶ The relative intensity of the free ligand compared to the complexes might be assigned to the strong conjugation and intermolecular interaction between the molecule segments of the free ligand.¹⁷

Conclusions

A series of Zn^{II}/Cd^{II} coordination polymers have been prepared under hydrothermal conditions exhibiting a systematic variation of architectures from 1D zigzag chain to 3D double interpenetrating networks by the employment of di(1*H*-imidazol-1-yl) methane and different carboxylic acid ligands. The present study suggests that the variation of auxiliary ligands may play important roles in forming related structures.

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