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Syntheses, structures, and photoluminescence of three cadmium(II) coordination complexes based on pyridine-2,6-dicarboxylic acid and a derivative

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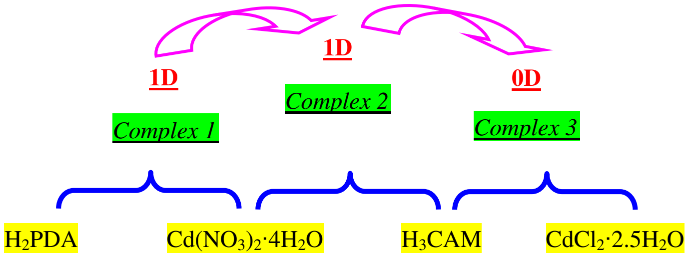

Three Cd(II) coordination complexes (**1**–**3**) have been obtained under hydrothermal conditions and characterized. Compounds **1** and **2** exhibit 1-D chain structures and the structures are further connected by hydrogen bonding interactions to form the 3-D packing structures, while compound **3** shows a discrete Cd_4 structure, which is expanded to a 3-D framework through hydrogen bonds with the CsCl-like eight-connected topology. Fluorescence properties indicate that **1** and **2** yield good luminescence and have potential applications in optical materials.

Three Cd(II) coordination complexes based on two different pyridine dicarboxylic acids (pyridine-2,6-dicarboxylic acid (H_2PDA) and its derivative 4-hydroxypyridine-2,6-dicarboxylic acid (chelidamic acid, H_3CAM)), $[Cd_2(PDA)_2(H_2O)_3]_n$ (**1**), $\{[Cd_2(HCAM)_2(H_2O)_4]\cdot 3H_2O\}_n$ (**2**), and $[Cd_4(HCAM)_4(H_2O)_8]$ (**3**) have been isolated under hydrothermal conditions. Compound **1**, with H_2PDA and $Cd(NO_3)_2\cdot 4H_2O$, exhibits a 1-D chain structure. Compound **2**, obtained by using H_3CAM instead of H_2PDA, contains a different 1-D chain from that of **1**. When using $CdCl_2\cdot 2.5H_2O$ and H_3CAM, a discrete tetranuclear Cd_4 compound (**3**) was obtained, and the isolated molecules are expanded to a eight-connected CsCl-like topology with point symbol $(4^{24}\cdot 6^4)$ through hydrogen bonding interactions. Furthermore, the photoluminescent properties of **1**–**3** were investigated.

Keywords: Cd(II) coordination complexes; Pyridine dicarboxylate acid; 1-D chain; CsCl-like topology; Photoluminescent properties

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1. Introduction

Coordination complexes, as an intersection between synthetic chemistry and materials science, have gained interest for intriguing topologies and applications in functional materials [1–6]. Many efforts have been made to develop coordination complexes with novel topologies, which are organized by coordination bonds and/or other weak interactions (such as hydrogen bonding and π–π interactions) [7–11]. Luminescent complexes have roles in a variety of applications such as molecular light-emitting devices, chemical sensors, and biomaterials [12–14]. Metal ions with d^{10} configurations are good candidates as functional luminescent complexes, such as Cu^+, Ag^+, Zn^{2+}, and Cd^{2+}, because of enhanced emissions arising from π^*–π transitions within a rigid ligand [15–17].

Carboxylate ligands are favorable to build coordination complexes by various binding modes, such as terminal monodentate, chelating to one metal center, bridging bidentate to two metals, and bridging tridentate to three metal centers [18]. Among carboxylate ligands, those combined with rigid groups (such as aromatic molecules and pyridine) exhibit superiority in constructing complexes [19–28]. Pyridine-2,6-dicarboxylic acid (H_2PDA), combining the rigid pyridine ring and carboxyl groups, has been employed in constructing coordination compounds, resulting in many interesting compounds. 4-Hydroxypyridine-2,6-dicarboxylic acid (chelidamic acid, H_3CAM) is a derivative of H_2PDA, in which there is a hydroxyl group at the 4-position of the pyridine ring, and H_3CAM can potentially provide more coordination geometries than H_2PDA [29].

In this contribution, we study the coordination chemistry of H_2PDA and H_3CAM in different d^{10}-Cd(II) complexes. $[Cd_2(PDA)_2(H_2O)_3]_n$ (**1**), $\{[Cd_2(HCAM)_2(H_2O)_4]\cdot 3H_2O\}_n$ (**2**), and $[Cd_4(HCAM)_4(H_2O)_8]$ (**3**) were produced under hydrothermal conditions and characterized by single-crystal X-ray diffraction, IR spectroscopy, and photoluminescent properties.

2. Experimental

2.1. *Materials and physical measurement*

All reagents and solvents were purchased commercially and used without purification. Elemental analyses for C, H, and N were carried out on a Perkin–Elmer analyzer at the Institute of Elemento-Organic Chemistry. FT-IR spectra were recorded as KBr pellets from 400 to 4000 cm^{-1} on a Bio-Rad FTS 135 spectrometer. Fluorescence spectra were recorded at room temperature on an F-7000 FL spectrophotometer.

2.2. *Synthesis*

2.2.1. Preparation of $[Cd_2(PDA)_2(H_2O)_3]_n$ (1). The mixture of 0.2 mM $Cd(NO_3)_2\cdot 4H_2O$ (0.062 g), 0.6 mM H_2PDA (0.100 g), and 8 mL H_2O was placed in a 25 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 72 h, then cooled to room temperature at 5 °C h^{-1}. Colorless block crystals were obtained in 70% yield based on the Cd $(NO_3)_2\cdot 4H_2O$ used. Anal. Calcd for $Cd_2C_{14}H_{12}N_2O_{11}$ (**1**): C, 27.61; H, 1.99; N, 4.60%. Found: C, 27.79; H, 2.06; N, 4.22%. IR (KBr, cm^{-1}): 3454(b,s), 1622.7(vs), 1590.9(s), 1455.8(s), 1286.2(m), 1202.7(m), 1085.2(m), 1025.6(m), 775.6(m), 722.1(s).

2.2.2. Preparation of $\{[Cd_2(HCAM)_2(H_2O)_4]\cdot 3H_2O\}_n$ (2). The mixture of 0.2 mM $Cd(NO_3)_2\cdot 4H_2O$ (0.062 g), 0.6 mM H_3CAM (0.110 g), and 8 mL H_2O was placed in a 25 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 72 h, then cooled to room temperature at 5 °C h^{-1}. Colorless block crystals were obtained in 55% yield based on the $Cd(NO_3)_2\cdot 4H_2O$ used. Anal. Calcd for $Cd_2C_{14}H_{20}N_2O_{17}$ (**2**): C, 23.58; H, 2.83; N, 3.93%. Found: C, 23.02; H, 2.90; N, 3.76%. IR (KBr, cm^{-1}): 3416(b,s), 1598.7(vs), 1418.5(vs), 1350.8(s), 1260.3(m), 1123.9(m), 1026.6(s), 809.7(m), 743.3(s), 588.1(b,s).

2.2.3. Preparation of $[Cd_4(HCAM)_4(H_2O)_8]$ (3). The mixture of 0.2 mM $CdCl_2\cdot 2.5H_2O$ (0.047 g), 0.3 mM H_3CAM (0.055 g), and 8 mL H_2O was placed in a 25 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 72 h, then cooled to room temperature at 5 °C h^{-1}. Colorless block crystals were obtained in 55% yield based on the $CdCl_2\cdot 2.5H_2O$ used. Anal. Calcd for $Cd_4C_{28}H_{28}N_4O_{28}$ (**3**): C, 25.51; H, 2.14; N, 4.25%. Found: C, 25.73; H, 2.00; N, 3.98%. IR (KBr, cm^{-1}): 3448(b,s), 1595.2(vs), 1437.5(s), 1379.4(s), 1242.5(m), 1113.2(m), 1034.1(s), 814.1(m), 730.8(s), 639.5(m).

2.3. *Determination of crystal structure*

Suitable single crystals of **1**–**3** were glued on a glass fiber. Data were collected on a BRUKER SMART 1000 CCD detector with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data were collected at 153 or 293 K. The structures were solved by direct methods using SHELXS-97 [30] and subsequent Fourier difference techniques, and refined anisotropically by full-matrix least-squares on F^2 using SHELXL-97 [31]. The

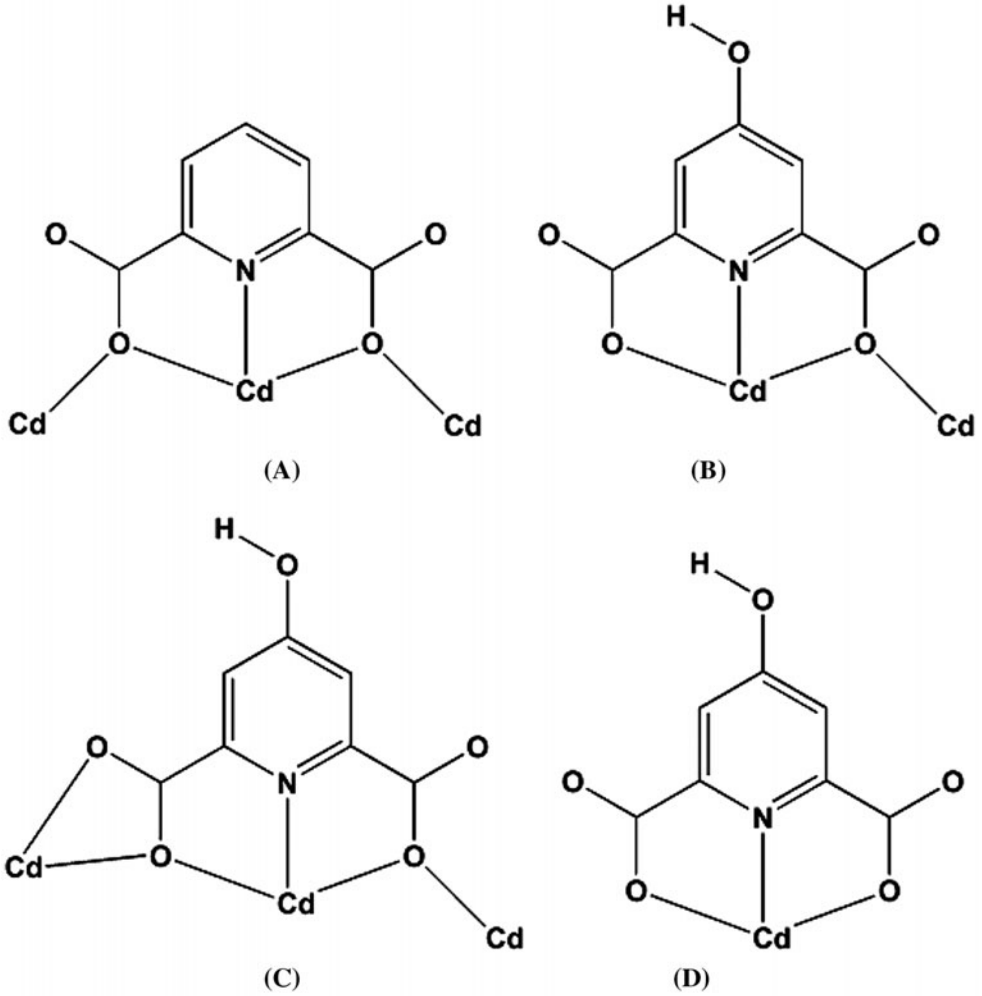
Table 1. Data collection and processing parameters for **1**–**3**.

Compound	**1**	**2**	**3**
Formula	$Cd_2C_{14}H_{12}N_2O_{11}$	$Cd_2C_{14}H_{20}N_2O_{17}$	$Cd_4C_{28}H_{28}N_4O_{28}$
M_r (g M^{-1})	609.06	713.12	1318.14
T (K)	153(2)	293(2)	153(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$C2/c$
a (Å)	27.19(2)	6.6200(13)	17.575(4)
b (Å)	10.193(7)	10.833(2)	12.943(3)
c (Å)	13.996(10)	15.663(3)	16.203(3)
α (°)	90.00	93.96(3)	90.00
β (°)	93.654(9)	100.16(3)	100.64(3)
γ (°)	90.00	104.66(3)	90.00
V (Å^3)	3871(5)	1062.0(4)	3622.4(12)
Z	8	2	4
ρ_{Calcd} (g cm^{-3})	2.090	2.230	2.417
μ (mm^{-1})	2.258	2.095	2.435
$F(0\ 0\ 0)$	2352	700	2560
Crystal size (mm)	0.22 × 0.12 × 0.06	0.15 × 0.12 × 0.10	0.20 × 0.18 × 0.16
θ (°)	1.50–25.01	2.23–25.00	1.97–25.01
Refl. collected/unique [R(int)]	8823/3358 [0.0904]	5536/3714 [0.0197]	15,100/3190 [0.0544]
Data/restraints/parameters	3358/6/262	3714/0/319	3190/0/291
GOF on F^2	1.155	1.050	1.112
R_1, wR_2 [$I > 2\sigma(I)$]	0.0567, 0.1451	0.0280, 0.0692	0.0324, 0.0706
R_1, wR_2 [all data]	0.1059, 0.1697	0.0359, 0.0732	0.0371, 0.0727
Largest diff. peak and hole (e Å^{-3})	2.009 and −1.492	0.542 and −0.760	0.622 and −1.017

hydrogens were set in calculated positions and refined as riding with common fixed isotropic thermal parameters. Detailed information about crystal data and structure refinements is summarized in table 1.

3. Results and discussion

Three compounds (**1**–**3**) were synthesized by hydrothermal reactions of Cd(II) salts ($Cd(NO_3)_2{\cdot}4H_2O$ or $CdCl_2{\cdot}2.5H_2O$) and H_2PDA or H_3CAM. Their structures change from 1-D chains to discrete tetranuclear structure, different from other Cd(II) complexes [32–41]. Compared to the majority of Cd(II) systems, in which Cd(II) ions are connected through –O–C–O– or other longer linkers, in **1**–**3**, as shown in scheme 1, all Cd(II) ions are bridged


(A) (B) (C) (D)

Scheme 1. The coordination modes of PDA and HCAM in **1**–**3**.

by short μ_2-O bridges to form 1-D or 0-D structures. The coordination modes also make structural differences (scheme 1). The oxygens have two kinds of connectivity, one terminal monodentate to one Cd(II) ion, whereas another is a μ_2-bridge to connect two Cd(II) ions.

3.1. *Structural determination of $[Cd_2(PDA)_2(H_2O)_3]_n$ (1)*

Single-crystal X-ray study reveals that **1** crystallizes in the monoclinic system with space group *C*2/*c*. The asymmetric unit, which is shown in figure 1, displays the coordination environments of Cd1 and Cd2, two crystallographically independent Cd(II) ions, two PDA^{2-} anions and three coordinated H_2O molecules. Both Cd1 and Cd2 are seven-coordinate in a distorted pentagonal bipyramidal geometry. Cd1 and Cd2 have similar coordination environments (figure 1), coordinating with one tridentate (–ONO–) PDA^{2-}, two carboxylate O_c from two different PDA^{2-} and two terminal H_2O molecules. Both PDA^{2-} anions show coordination mode **A** to chelate one Cd(II) and bridge another two Cd(II) ions (scheme 1). Two μ_2-O_c atoms (O1 and O5) bridge Cd1 and Cd2 to form a Cd_2O_2 grid, and the distance between Cd1 and Cd2 is 3.990(13) Å. The Cd_2O_2 grids are connected by three bridging μ_2-O atoms (O3A, O7, O10) to construct a 1-D chain (figure 2), and the distance between Cd1 and Cd2A is 3.605(12) Å. The coordinated H_2O molecules provide hydrogen bonding donors, while carboxylates are acceptors, generating intermolecular hydrogen bonds [figure 3(a)]. The O11···O8 distance and angle of O11–H···O8 are 2.856(17) Å and

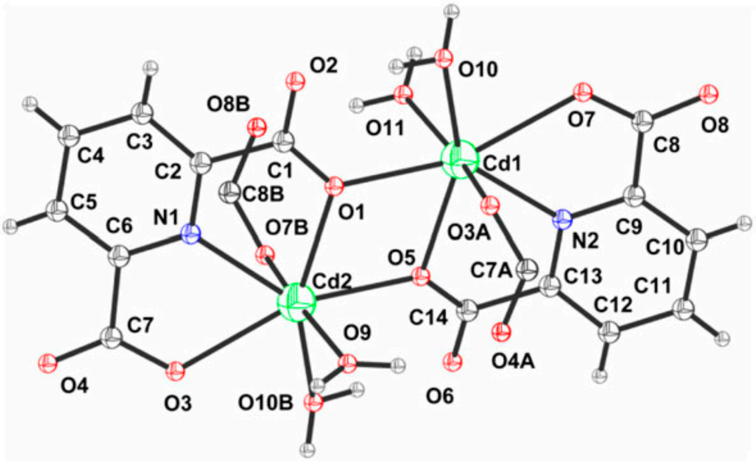


Figure 1. The coordination environments of Cd1 and Cd2 in **1**. Symmetry codes: (A) +*x*, 2 − *y*, −1/2 + *z*; (B) +*x*, 2 − *y*, 1/2 + *z*.

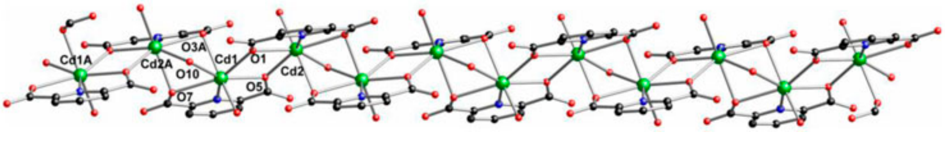


Figure 2. The 1-D chain structure of **1**. Olive, Cd; black, C; blue, N; red, O (see http://dx.doi.org/10.1080/00958972.2015.1011145 for color version).

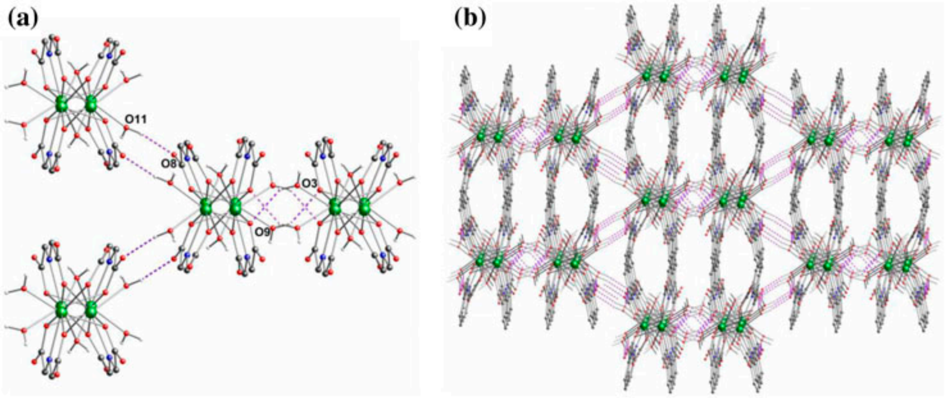


Figure 3. (a) Intermolecular hydrogen bonding interactions in **1**; (b) the 3-D packing structure of **1** showing the hydrogen bonds. Olive, Cd; black, C; blue, N; red, O, purple dot lines, O–H···O hydrogen bonds (see http://dx.doi.org/10.1080/00958972.2015.1011145 for color version).

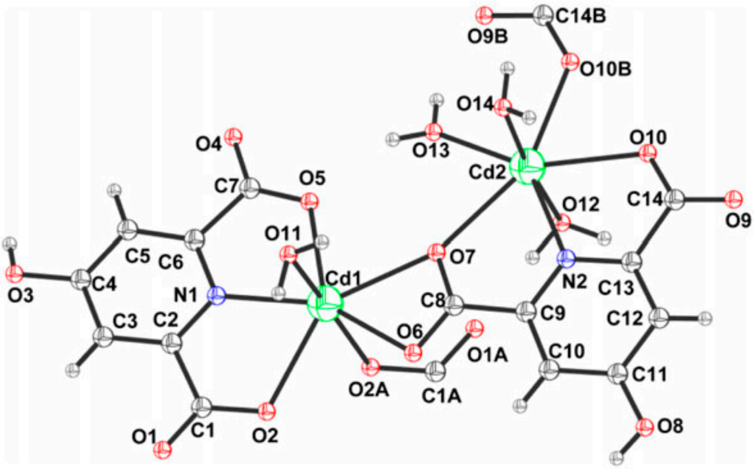


Figure 4. The coordination environments of Cd1 and Cd2 in **2** and solvents are omitted for clarity. Symmetry codes: (A) −*x*, 1 − *y*, 1 − *z*; (B) 1 − *x*, 1 − *y*, 2 − *z*.

165.5(9)°, while those associated with O9–H···O3 are 3.008(13) Å and 140.9(6)°. As a result, each 1-D chain links three other chains through hydrogen bonding interactions to form the 3-D packing structure [figure 3(b)].

3.2. *Structural determination of* $\{[Cd_2(HCAM)_2(H_2O)_4]\cdot 3H_2O\}_n$ *(2)*

When using H_3CAM as ligand, **2** was obtained. Single-crystal X-ray diffraction analysis reveals that **2** possesses a 1-D coordination chain and crystallizes in the triclinic space group *P*-1. There are two crystallographically independent Cd(II) ions, two $HCAM^{2-}$ anions, four coordinated, and three lattice H_2O molecules in the asymmetric unit of **2**. The coordination environments of Cd1 and Cd2 are shown in figure 4. Both Cd1 and Cd2

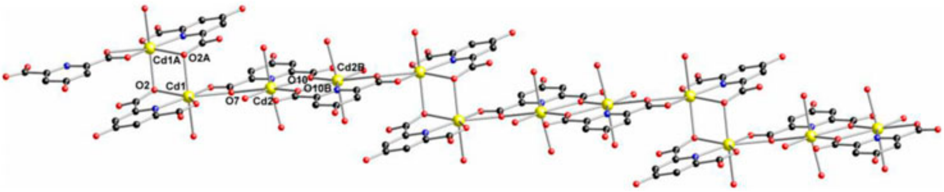


Figure 5. The 1-D structure of **2**. Yellow, Cd; black, C; blue, N; red, O (see http://dx.doi.org/10.1080/00958972.2015.1011145 for color version).

coordinate with seven oxygens, and the coordination geometry is close to a distorted pentagonal bipyramid. The coordination environment of Cd1 is completed by one tridentate $HCAM^{2-}$ anion (O2, N1, O5), one bidentate carboxyl group (O6, O7), one carboxylate O (O2A), and one terminal H_2O (O11), while Cd2 employs two terminal waters instead of the bidentate carboxyl associated with Cd1. All hydroxyl groups are uncoordinated, and the $HCAM^{2-}$ ligands have two types of coordination (**B** and **C**, scheme 1). In mode **B**, the $HCAM^{2-}$ is tridentate on one Cd(II) ion, with one carboxylate O bridging to adjacent Cd(II) ions, while in mode **C**, the ligand chelates to two Cd(II) ions in tridentate and bidentate fashions, and further bridges one Cd(II) through one carboxylate.

Two Cd1 ions are connected by two μ_2-O2 and O2A to form a Cd_2O_2 grid, while a similar Cd_2O_2 grid is constructed by Cd2 ions (Cd2, Cd2B, O10, O10B). Those grids are bridged alternately by μ_2-O_c (O7) to form a 1-D chain structure (figure 5). The hydroxyl groups and coordinated waters provide hydrogen bond donors in sustaining supermolecular packing. Thus, each 1-D chain is surrounded by four other 1-D chains through hydrogen bonds, as shown in figure 6(a), and the O···O distances are 2.565(18) and 2.835(18) Å, respectively, for O8···O4 and O11···O6, while the angles of O–H···O are 173.2(2)° and 154.7(2)°, respectively, for O8–H···O4 and O11–H···O6. As a result, a 3-D packing structure is formed, as shown in figure 6(b).

3.3. *Structural determination of $[Cd_4(HCAM)_4(H_2O)_8]$ (3)*

When using $CdCl_2{\cdot}2.5H_2O$ instead of $Cd(NO_3)_2{\cdot}4H_2O$ in **2**, a tetranuclear Cd_4 compound (**3**) is prepared (figure 7). The single-crystal analysis reveals that **3** crystallizes in the monoclinic space group *C*2/*c* and Cd(II) ions have two types of coordination environments [figure 7(a)]. Cd1 is seven-coordinate with distorted pentagonal bipyramid geometry, whereas Cd2 is six-coordinate with pentagonal pyramid geometry. Cd1 coordinates to one tridentate $HCAM^{2-}$, one $HCAM^{2-}$ anion by using one carboxylate oxygen, and three waters to complete the coordination environment. Cd2 coordinates to one tridentate $HCAM^{2-}$, one bidentate carboxylate from another $HCAM^{2-}$ anion, and one H_2O to form the coordination sphere. Cd1 and Cd1A are bridged by two μ_2-O_c atoms to form a Cd_4 structure [figure 7(b)], and the shortest distance between Cd ions is 3.871(19) (Cd1···Cd1A) and 4.839(19) (Cd1···Cd2) Å. The hydroxyl groups are uncoordinated, and there are two coordination modes of $HCAM^{2-}$ ligands (**C** and **D**, scheme 1). One $HCAM^{2-}$ bridges three Cd(II) ions (**C**), while another is tridentate to one Cd(II) ion (**D**).

The uncoordinated hydroxyl groups and coordinated waters provide hydrogen bonding donors, while the carboxylates are hydrogen bond acceptors. As a result of this connection, each Cd_4 unit connects eight Cd_4 units through hydrogen bonds [figure 8(a)] to form a 3-D

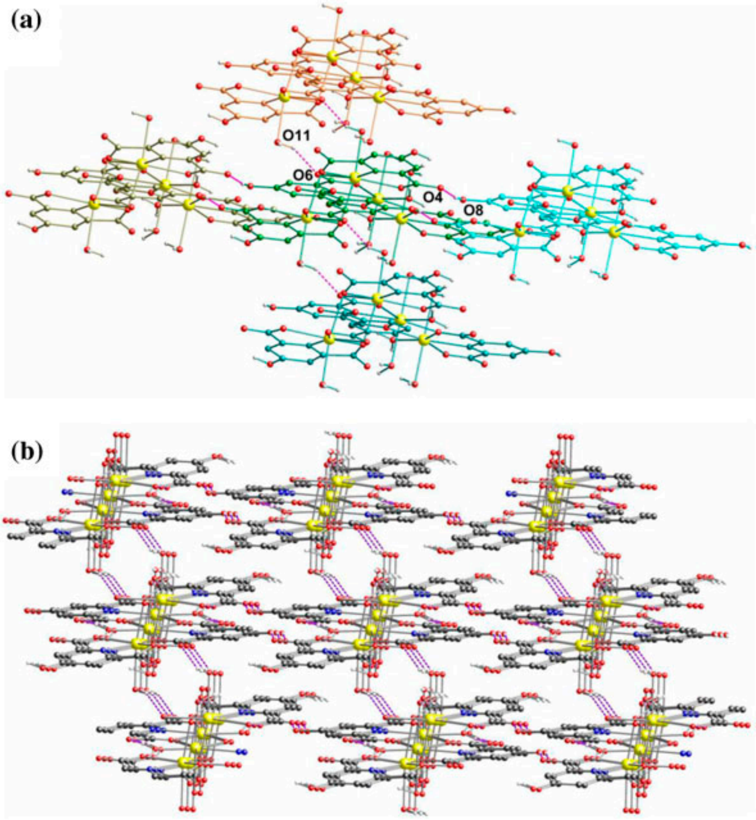


Figure 6. (a) The hydrogen bonding interactions in **2** (different atoms with O in order to highlight the hydrogen bonds); (b) the 3-D packing structure of **2** (right). Yellow, Cd; black, C; blue, N; red, O; purple dot lines, O–H···O hydrogen bonds (see http://dx.doi.org/10.1080/00958972.2015.1011145 for color version).

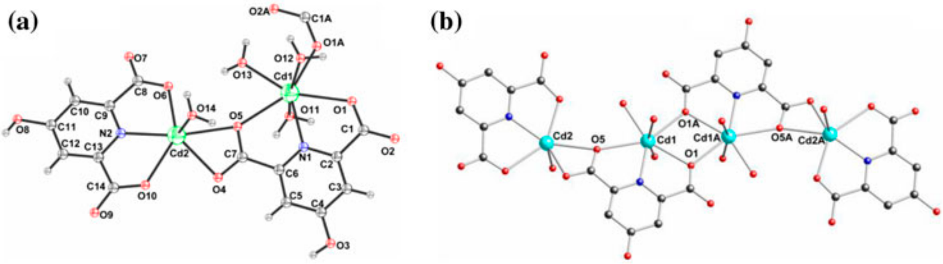


Figure 7. (a) The coordination environments of Cd1 and Cd2 in **3**; (b) the Cd_4 unit of **3**. Symmetry codes: (A) $x + 1$, y, z. Cyan, Cd; gray, C; blue, N; red, O (see http://dx.doi.org/10.1080/00958972.2015.1011145 for color version).

super framework, as shown in figure 8(b). If considering the Cd_4 unit as an eight-connected node [figure 8(a)], the 3-D framework can be considered an eight-connected CsCl-like topology with point symbol $(4^{24}·6^4)$ [figure 8(c)].

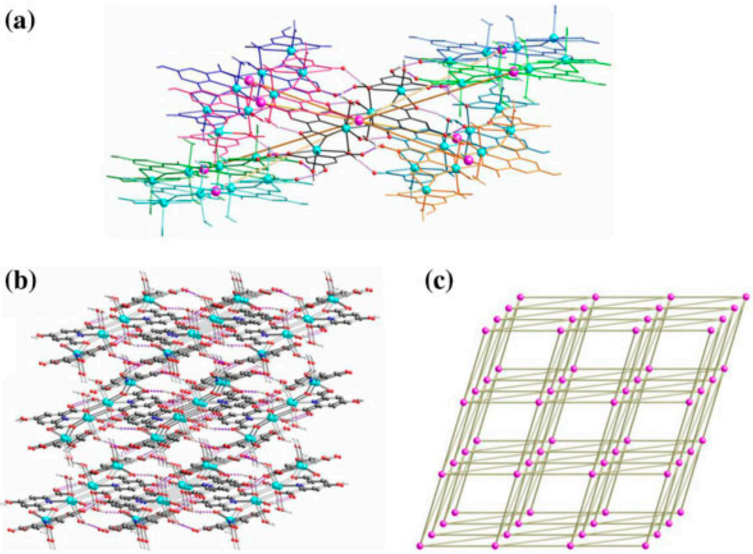


Figure 8. (a) The eight-connected node represented by Cd_4 units in **3** showing the hydrogen bonding interactions; (b) the 3-D framework of **3** constructed by hydrogen bonds; (c) the 8-connected CsCl-like topology based on Cd_4 units. Cyan, Cd; black, C; blue, N; red, O; purple dot lines, O–H···O hydrogen bonds, purple, Cd_4 units (see http://dx.doi.org/10.1080/00958972.2015.1011145 for color version).

3.4. *Structural changes*

Compound **1**, obtained from $Cd(NO_3)_2{\cdot}4H_2O$ and H_2PDA, exhibits a 1-D chain, and the PDA^{2-} is pentadentate with coordination mode **A** to connect three Cd(II) ions. When using H_3CAM instead of H_2PDA, **2** was obtained, showing another type of 1-D chain. Although the hydroxyl group of H_3CAM is uncoordinated, its stereochemical feature provides more coordination modes. In **2**, the $HCAM^{2-}$ ligands have coordination modes **B** and **C**. Using $CdCl_2{\cdot}2.5H_2O$ as the source of Cd(II) ions, a discrete tetranuclear Cd_4 compound (**3**) was obtained. It is clear that the difference between **2** and **3** is the coordination modes of $HCAM^{2-}$ ligands, and modes **C** and **D** are adopted in **3**.

3.5. *IR spectra*

The IR spectra of **1**–**3** show broad peaks at 3600–3000 cm^{-1}, which can be attributed to the existence of the hydrogen bonding interactions between H_2O molecules. The protonated carboxylate exhibits characteristic bands around 1700 cm^{-1}, and in **1**–**3**, those bands are shifted to 1623, 1599, and 1595 cm^{-1}, respectively, indicating deprotonation of carboxylate upon coordination. The coordination modes of carboxylate groups can be distinguished through IR spectra, and the difference $\Delta\nu(\nu_{as} - \nu_s)$ of carboxylate groups is the criterion [42]. The $\nu_{as}(CO_2^{2-})$ and $\nu_s(CO_2^{2-})$ are at 1623, 1591, and 1456 cm^{-1} for **1**, indicating that PDA^{2-} is bidentate. Compared with **1**, $\nu_{as}(CO_2^{2-})$ is at 1599 cm^{-1} and $\nu_s(CO_2^{2-})$ is at 1418 and 1351 cm^{-1} for **2**, while those are at 1595, 1437, and 1379 cm^{-1} for **3**, the $\Delta\nu$ values show that carboxylate groups in **2** and **3** have both monodentate and bidentate coordination.

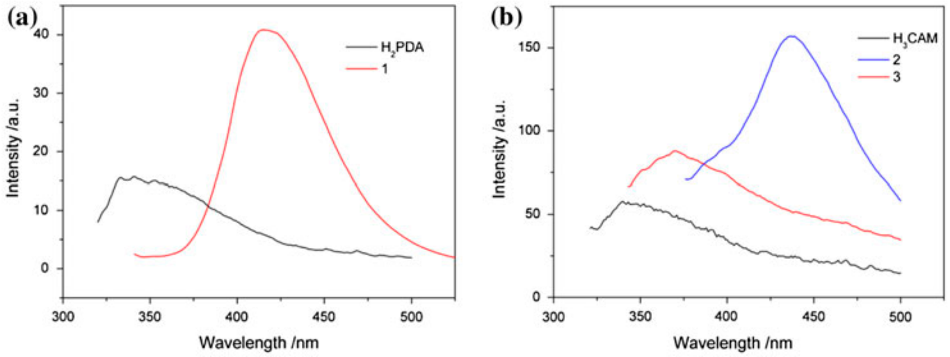


Figure 9. The solid-state emission spectra of **1**–**3** and H_2PDA and H_3CAM at room temperature [(a) for H_2PDA and **1**; (b) for H_3CAM, **2** and **3**].

3.6. *Photoluminescent properties*

Complexes with d^{10}-metal ions have potential applications in chemical sensors, photochemistry, and electroluminescent displays, due to their luminescence properties [43–46]. Thus, solid-state photoluminescence of **1**–**3** as well as free H_2PDA and H_3CAM were measured at room temperature and the emission spectra are shown in figure 9, displaying interesting photoluminescent properties as other Cd(II) complexes [32–38]. Upon excitation at 318 nm, **1** displays an intense UV radiation with λ_{max} at 415 nm, and the free H_2PDA also shows a weak emission at 340 nm [figure 9(a)]. Free H_3CAM shows a broad emission at 340 nm, and **2**, when excited at 316 nm, exhibits a strong emission at 440 nm; **3** displays a broad emission at 370 nm with excitation of 339 nm [figure 9(b)]. Compared with the free H_2PDA and H_3CAM, the enhancement and red-shift in **1**–**3** is probably due to the coordination to Cd(II) increasing the rigidity of ligands. Since Cd(II) is difficult to oxidize or reduce [43, 44], the emissions of **1**–**3** are neither metal-to-ligand or ligand-to-metal charge transfer, and may be assigned to intraligand fluorescent emission.

Compared to other d^{10} complexes [47–49], the luminescence of **1**–**3** based on d^{10}-Cd(II) ion is weak, however, the three compounds display different luminescence due to different coordination modes, which could provide a rational synthetic strategy for design of luminescent materials.

4. Conclusion

Three Cd(II) coordination complexes (**1**–**3**) based on H_2PDA and H_3CAM have been fabricated by using different Cd(II) salts ($Cd(NO_3)_2 \cdot 4H_2O$ or $CdCl_2 \cdot 2.5H_2O$), exhibiting different structural features from other Cd(II) complexes. Both compounds **1** and **2** exhibit 1-D chains, however, the 1-D chains are absolutely different from each other, due to the different ligands. Compound **3**, built from $CdCl_2 \cdot 2.5H_2O$ and H_3CAM, shows a discrete tetranuclear Cd_4 structure, which are expanded to a eight-connected CsCl-like topology through hydrogen bonding interactions. The photoluminescent properties were studied and exhibit that compounds **1** and **2** yield good luminescence and have potential applications in optical materials. The investigation of the difference luminescence in compounds **1**–**3** may provide a rational synthetic strategy for the design of novel luminescent materials.

Supplementary material

The crystallographic data of **1**–**3** has been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC – **1**, 968869; **2**, 968867; **3**, 968868). These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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