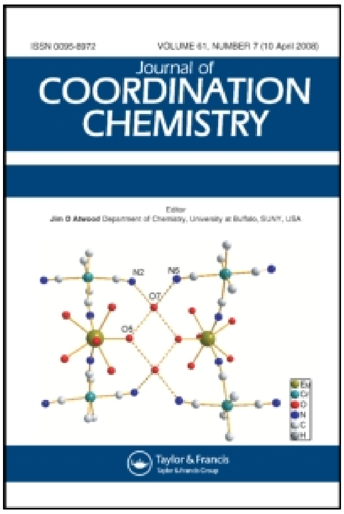

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Two isostructural coordination polymers built by a new bridging chelating ligand: hydrothermal synthesis, crystal structure and photoluminescence

Shu Qiao[a]; Guo-Ping Yong[a]; Yu Xie[a]; Zhi-Yong Wang[a]
[a] Hefei National Laboratory for Physical Science at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, China

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Two isostructural coordination polymers built by a new bridging chelating ligand: hydrothermal synthesis, crystal structure and photoluminescence

SHU QIAO, GUO-PING YONG, YU XIE and ZHI-YONG WANG*

Hefei National Laboratory for Physical Science at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, 230026, China

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Two new isostructural coordination polymers [Cd(Hadab)(H_2O)] (**1**) and [Mn(Hadab)(H_2O)] (**2**) (H_3adab = 3-aminodiacetic benzoic acid) have been synthesized under hydrothermal conditions and characterized by X-ray single crystal analyses, IR spectra and TGA. Compounds **1** and **2** crystallize in the monoclinic space group $C2/c$ and are a 2D network. The 3D pillar-layered networks are constructed by hydrogen bonding interactions between benzoic acid groups. Compound **1** displays intense room temperature photoluminescence in the solid state.

Keywords: 3-Aminodiacetic benzoic acid; Cadmium; Manganese; Coordination polymer; Photoluminescence

1. Introduction

The rational design and synthesis of coordination polymers based on transition metals and multifunctional bridging ligands is of interest due to their interesting topologies and potential applications as functional materials [1, 2]. A synthetic strategy widely used in this area is linking metal ions with polydentate ligands that function as connectors [3]. Polydentate ligands, which provide metal-binding sites, can act as either bridging or chelating ligands, giving network metal-organic coordination polymers [4]. The carboxylate group is one of the most widely used bridging ligands for coordination polymers with interesting photoluminescent properties. The versatility of this group as a ligand is illustrated by the variety of its coordination modes [5]. Extensive work has been carried out using multicarboxylate ligands because of their interesting structural characteristics [6].

Our previous work had shown that the *N*-containing polycarboxylate ligands could be used to construct coordination polymers [4a, 7]. In this article, we report two isostructural metal(II)-aminopolycarboxylate coordination polymers, [M(Hadab)(H_2O)] (M = Cd, **1**; Mn, **2**), (H_3adab = 3-aminodiacetic benzoic acid). The nitrogen of the

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*Corresponding author. Email: qiaoshu@mail.ustc.edu.cn

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aminodiacetic group in Hadab^{2-} is an endodentate site, binding metal(II) ions in conjunction with the other carboxyl groups.

2. Experimental

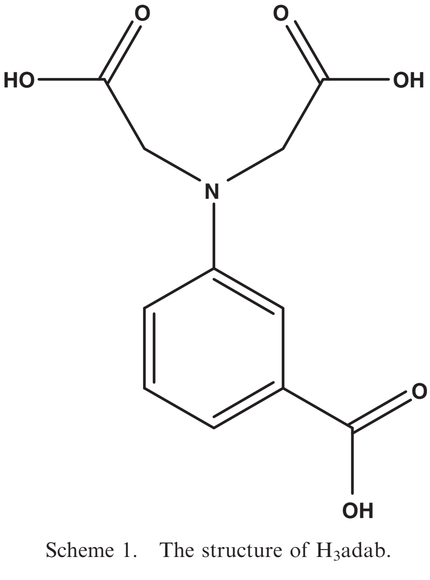
2.1. *Materials and general methods*

All chemicals purchased were of reagent grade and used without further purification, except that *N*,*N*-dimethylformamide (DMF) was distilled. Elemental analyses (C, H and N) were carried out with an Elementar Vario EL III microanalyzer. The FTIR spectra were recorded with a Bruker Vector 22 spectrophotometer in the 4000–400 cm^{-1} region using KBr pellets. ^{1}H NMR spectrum was recorded with a Bruker AV300 spectrometer. The emission spectra for the solid samples were recorded at room temperature on a Fluorolog-3-TAU fluorescence spectrophotometer. Thermogravimetric analyses were performed under air with a heating rate of 10°C min^{-1} with a Shimadzu TGA-50H TG analyzer.

Caution: $Cd(ClO_4)_2 \cdot 6H_2O$ and $Mn(ClO_4)_2 \cdot 6H_2O$ are potentially explosive and should be used with care!!

2.2. *Synthesis of 3-aminodiacetic benzoic acid (H₃adab)*

The ligand, H_3adab, was prepared in a similar method as described for N-(4-carboxyphenyl)iminodiacetic acid (H3cpida) [4a]; scheme 1 shows H_3adab. A solution of KOH (33.6 g, 0.6 mol) in water (100 mL) was added dropwise to a solution of monochloroacetic acid (28.4 g, 0.3 mol) in water (100 mL). 3-Aminobenzoic acid



Scheme 1. The structure of H_3adab.

(13.7 g, 0.1 mol) was slowly added to the resulting alkaline solution, and the mixture was refluxed at 86°C for 30 h. The reaction mixture was then cooled to room temperature and acidified with HCl (6 mol L^{-1}) until the desired acid precipitated as a white solid (pH ≈ 2.5). This precipitate was collected by filtration, washed with water and recrystallized from water. Yield: 57% based on 3-aminobenzoic acid. ^{1}H NMR (300 MHz, D_2O, 25°C): 7.29 (t, $^3J_{H,H} = 7.7$ Hz, 1 H, 5-H), 7.14 (d, $^3J_{H,H} = 7.4$ Hz, 1 H, 6-H), 7.00 (s, 1 H, 2-H), 6.65 (d, $^3J_{H,H} = 7.7$ Hz, 1 H, 4-H), 3.94 (s, 4 H, CH_2). IR data (KBr, cm^{-1}): 3436m, 2924m, 2553w, 1723s, 1680s, 1604m, 1580m, 1494w, 1466m, 1423w, 1367m, 1305m, 1181m, 757s, 672m, 606m.

2.3. *Synthesis of [Cd(Hadab)(H_2O)] (1) and [Mn(Hadab)(H_2O)] (2)*

$Cd(ClO_4)_2 \cdot 6H_2O$ (**1**) or $Mn(ClO_4)_2 \cdot 6H_2O$ (**2**) (0.1 mmol) and H_3adab (0.1 mmol) were placed in a heavy-walled Pyrex tube containing DMF (0.1 mL) and H_2O (0.4 mL). The tube was frozen in liquid N_2, sealed under vacuum, and then heated at 120°C for 12 h. The products were filtered, washed with ethanol, and then dried in air. Air-stable colorless transparent crystals were obtained. **1**: yield 56% (based on Cd). Anal. Calcd for $C_{11}H_{11}CdNO_7$ (%): C, 34.62; H, 2.91; N, 3.67. Found: C, 34.99; H, 2.81; N, 3.74. IR data (KBr, cm^{-1}): 3495w, 2954m, 2919m, 2665w, 1702s, 1585s, 1448s, 1418s, 1341m, 1313m, 1296m, 1264m, 1198m, 1136m, 993m, 971m, 932m, 880m, 809m, 774m, 756m, 721m, 690s, 665m, 641m, 569m, 471m. **2**: yield: 64% (based on Mn). Anal. Calcd for $C_{11}H_{11}MnNO_7$ (%): C, 40.76; H, 3.42; N, 4.32. Found: C, 39.74; H, 3.33; N, 4.33. IR data (KBr, cm^{-1}): 3509w, 2914m, 2665w, 1702s, 1584s, 1494m 1446s, 1421s, 1343m, 1315s, 1294s, 1250m, 1198m, 1140m, 1121m, 994m, 971m, 936m, 881m, 808m, 773m, 757m, 720m, 690s, 640w, 568m, 468w.

2.4. *X-ray crystallographic study*

Crystallographic data for **1** and **2** were collected on a Bruker Smart CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 103 K for **1** and 100 K for **2**. Intensity data were collected by ω scan technique and empirical absorption corrections were applied. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package [8]. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were placed in geometrically calculated positions (H atoms of water molecule not included). Selected crystallographic data and structure refinement for **1** and **2** are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Description of the structures*

Compounds **1** and **2** crystallize in monoclinic $C2/c$ space group and feature a 2D layered network. There are one metal atom (Cd for **1**, Mn for **2**), one $Hadab^{2-}$ ligand,

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

Compound	1	2
Empirical formula	$C_{11}H_{11}CdNO_7$	$C_{11}H_{11}MnNO_7$
Formula weight	381.61	324.15
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a (Å)	30.139(6)	30.133(3)
b (Å)	9.6621(19)	9.5959(8)
c (Å)	8.4106(17)	8.3564(7)
β (°)	94.56(3)	94.889(2)
V (Å^3)	2441.5(8)	2407.5(4)
Z	8	8
F (000)	1504	1320
ρ_{calcd} (g cm^{-3})	2.076	1.789
T(K)	103(2)	100(2)
μ(mm^{-1})	1.882	1.130
Goodness-of-fit on F^2	1.013	0.999
Reflections collected	14091	13329
Independent reflections (R_{int})	3715(0.0214)	3666(0.0295)
Observed reflections	3607	3408
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0168, 0.0415	0.0289, 0.0751
Final R_1, wR_2 [all data]	0.0177, 0.0421	0.0312, 0.0766

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

Compound **1**		Compound **2**	
Cd(1)–O(1)	2.236(10)	Mn(1)–O(1)	2.136(9)
Cd(1)–O(2)#6	2.259(9)	Mn(1)–O(2)#6	2.152(9)
Cd(1)–O(3)	2.273(10)	Mn(1)–O(3)	2.157(9)
Cd(1)–O(4)#4	2.299(10)	Mn(1)–O(4)#4	2.158(9)
Cd(1)–O(1w)	2.308(11)	Mn(1)–O(1w)	2.190(10)
Cd(1)–N(1)	2.553(12)	Mn(1)–N(1)	2.534(11)
O(4)#4–Cd(1)–O(1)	96.97(4)	O(4)#4–Mn(1)–O(1)	95.72(3)
O(4)#4–Cd(1)–O(2)#6	107.89(3)	O(4)#4–Mn(1)–O(2)#6	102.99(3)
O(4)#4–Cd(1)–O(3)	89.26(3)	O(4)#4–Mn(1)–O(3)	91.01(3)
O(4)#4–Cd(1)–O(1w)	104.53(4)	O(4)#4–Mn(1)–O(1w)	101.01(4)
O(4)#4–Cd(1)–N(1)	150.42(3)	O(4)#4–Mn(1)–N(1)	152.90(3)
O(3)–Cd(1)–O(1)	106.11(3)	O(3)–Mn(1)–O(1)	105.10(3)
O(3)–Cd(1)–O(1w)	79.42(3)	O(3)–Mn(1)–O(1w)	81.21(4)
O(3)–Cd(1)–N(1)	71.24(3)	O(3)–Mn(1)–N(1)	72.14(3)
O(2)#6–Cd(1)–O(1)	83.12(4)	O(2)#6–Mn(1)–O(1)	84.93(3)
O(2)#6–Cd(1)–O(3)	159.66(3)	O(2)#6–Mn(1)–O(3)	162.01(4)
O(2)#6–Cd(1)–O(1w)	85.58(4)	O(2)#6–Mn(1)–O(1w)	85.03(4)
O(2)#6–Cd(1)–N(1)	96.35(4)	O(2)#6–Mn(1)–N(1)	98.35(3)
O(1)–Cd(1)–O(1w)	157.94(3)	O(1)–Mn(1)–O(1w)	162.06(4)
O(1)–Cd(1)–N(1)	68.83(4)	O(1)–Mn(1)–N(1)	69.59(3)
O(1w)–Cd(1)–N(1)	93.77(4)	O(1W)–Mn(1)–N(1)	97.27(4)

Symmetry codes: #4 $-x+1/2$, $y+1/2$, $-z+1/2$; #6 x, $-y$, $z-1/2$.

and one coordinated water molecule in the asymmetric unit (figure 1). The metal center (Cd and Mn) is coordinated in a distorted octahedral geometry by one water oxygen atom [Cd1–O1w = 2.3079(11) and Mn1–O1w = 2.1904(10) Å], four carboxylate oxygen atoms [Cd1–O = 2.2362(10)–2.2991(10) and Mn1–O = 2.1359(9)–2.1579(9) Å] and one nitrogen atom [Cd1–N1 = 2.5534(12) and Mn1–N1 = 2.5342(11) Å] from three Hadab^{2-} ligands (figure 1). One water oxygen atom (O1w) and three oxygen atoms (O1, O2A, O3)

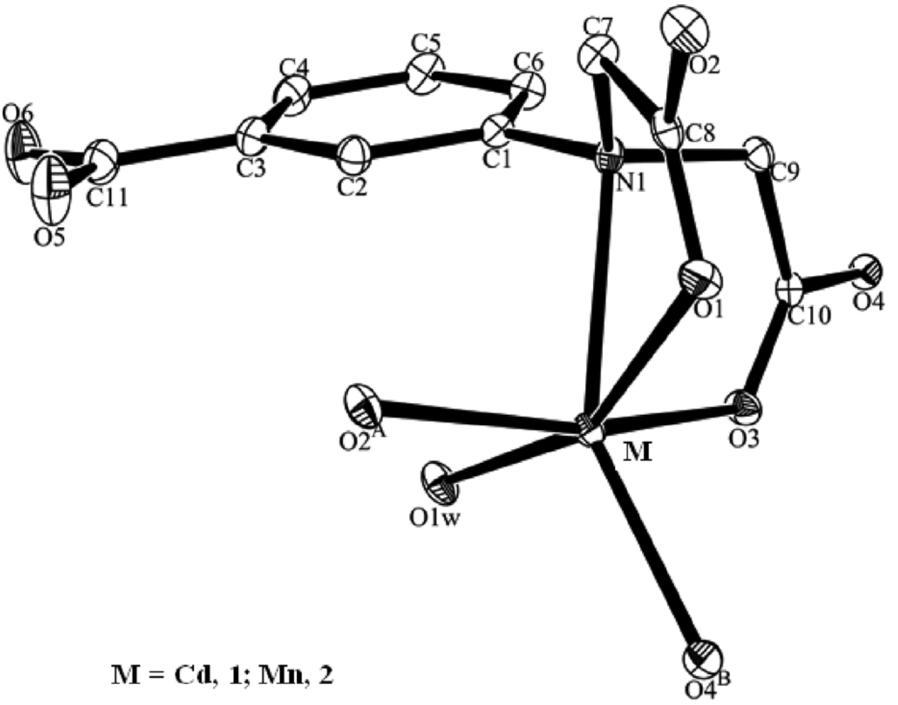
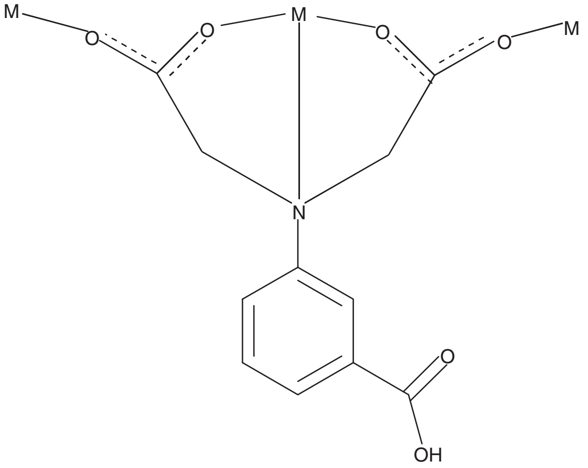


Figure 1. ORTEP drawing at 50% probability level showing the metal(II) coordination environment. Hydrogen atoms are omitted for clarity. Symmetry code: A = $-x+1/2$, $y+1/2$, $-z+1/2$; B = x, $-y$, $z-1/2$.

from aminodiacetic groups form the equatorial plane and one nitrogen atom (N1) and oxygen atom (O4B) occupy the axial positions.

Scheme 2 gives the coordination mode of Hadab^{2-} in **1** and **2** [7b]. One rigid carboxyl group is not deprotonated and remains free, as confirmed by the strong absorption at 1702 cm^{-1} in the IR spectra, indicating the presence of –COOH. The flexible aminodiacetic group adopts a μ_3-bridging-chelating mode to connect three metal atoms forming two MNC$_2$O (M = Cd and Mn) five-member rings. The C–O bond [C11–O6 = 1.3099(17) of **1** and 1.3106(17) Å of **2**] is longer than C–O bond [C11–O5 = 1.2347(17) of **1** and 1.2385(18) Å of **2**] in the rigid carboxyl group, so C11–O5 can be assigned as a double bond and C11–O6 as a single bond. This also confirms that the rigid carboxyl group is not deprotonated.

Each metal center (Cd and Mn) is connected to four adjacent metal centers through the bridging bidentate acetate group of Hadab^{2-} leading to a M$_4$(Hadab)$_4$ unit, which further extends into a 2D network with alternate large and small pseudo-rhombic grid motifs in the *bc* plane (figure 2). In each large pseudo-rhombic grid, the Cd···Cd separations are 5.09 and 5.47 Å and Mn···Mn separations are 5.09 and 5.42 Å, while the Cd···Cd···Cd angles are 56.59° and 123.41° and Mn···Mn···Mn angles are 55.83° and 124.17°. Each acetate of the Hadab^{2-} ligand is bidentate bridging to connect two metal centers. Four metal centers are connected by μ_2-acetato groups to form a 2D grid network. However, according to the flexibility of the aminodiacetic groups, **1** and **2** do not adopt one kind of grid but alternate large and small grid motifs, as shown



Scheme 2. The coordination mode of Hadab^{2-} in 1 and 2.

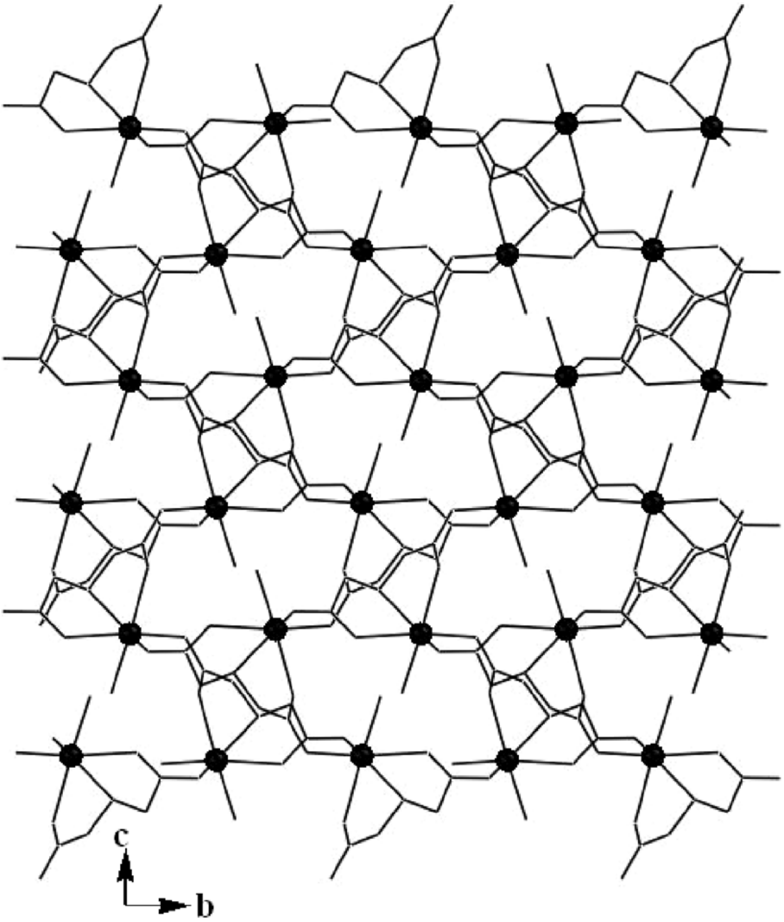


Figure 2. The 2D network of **1** and **2** as viewed down the *a*-axis, showing alternate large and small pseudo-rhombic grids (rigid benzoic acid groups omitted for clarity), the black spheres represent metal nodes.

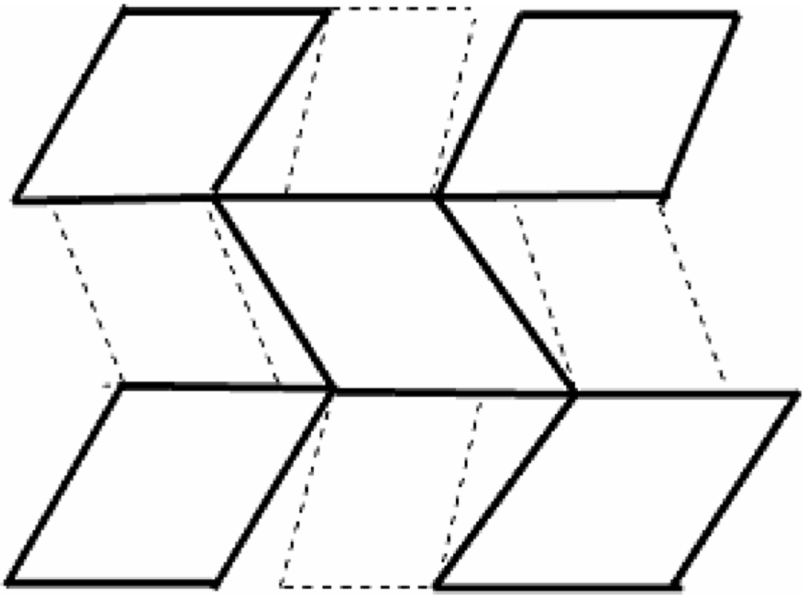


Figure 3. A topological illustration of the alternate large and small grids of **1** and **2**.

in figure 3. It should be noted that there are intralayer hydrogen bonding interactions [O1w $\cdots$ O2 = 2.931 Å, O1w $\cdots$ O4 = 2.695 Å of **1** and 2.975, 2.708 Å of **2**] between coordinated water and carboxyl oxygen atoms.

The 2D layer of **1** and **2** further assemble into a 3D pillar-layered network with benzoic acid groups as pillars (figure 4) through the interlayered hydrogen bonding interactions [O6 $\cdots$ O5 = 2.613 Å] between rigid benzoic acid groups.

3.2. *IR spectra of 1 and 2*

The IR spectrum of **1** shows the characteristic bands of the Hadab^{2-} at 1585 cm^{-1} for the asymmetric stretching vibration and at 1418 cm^{-1} for the symmetric stretching. The separation (Δ) between $\nu_{as}(CO^{2-})$ and $\nu_s(CO^{2-})$ indicates bridging (167 cm^{-1}) coordination modes in **1** [9]. The presence of the protonated rigid carboxyl group in the structure of **1** and **2** is also confirmed by IR spectroscopy, with the characteristic band at 1702 cm^{-1} of the –COOH group. The IR spectrum of **2** is consistent with that of **1**, also demonstrating that **1** and **2** are isostructural.

3.3. *Thermal analyses*

The thermal behaviors of **1** and **2** were examined by thermogravimetric analyses (TGA) under air with a heating rate of 10°C min^{-1}. TG analysis of **1** reveals that the first weight loss appears at ca. 150°C due to loss of one water (Calcd 4.7%; found 4.8%), and the second weight loss starts at ca. 325°C and the decomposition ends above 700°C. Compound **2** shows the first weight loss at ca. 155°C (one water molecule Calcd 5.6%; found 5.9%), and the second weight loss occurs between 310°C and 550°C,

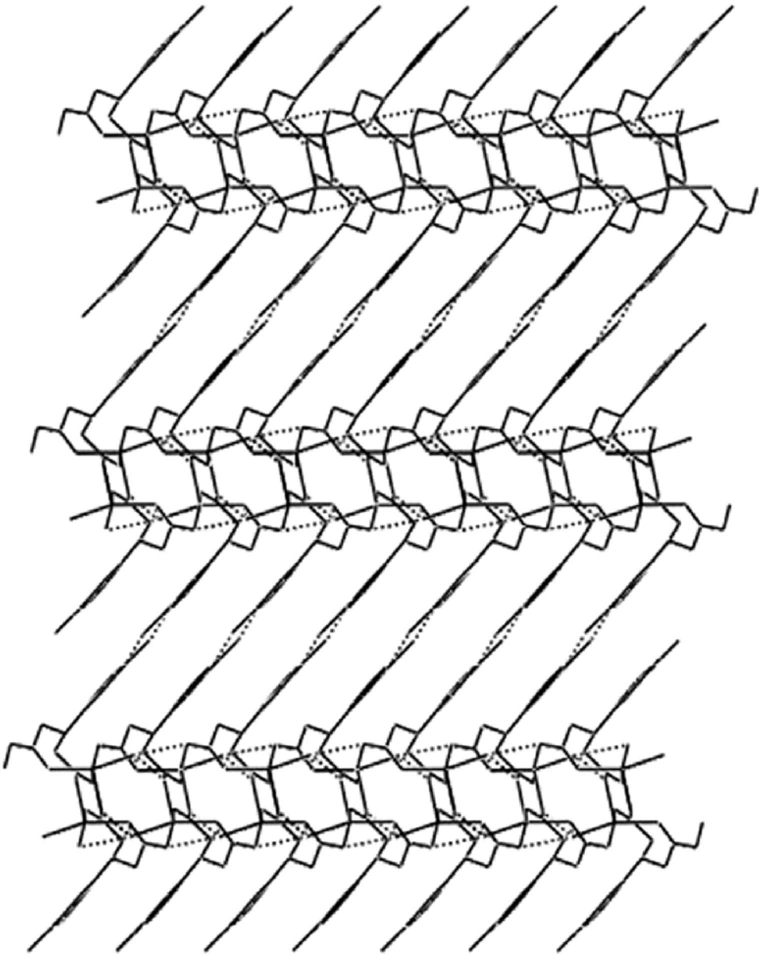


Figure 4. 3D pillar-layered network with benzoic acid groups as pillars of **1** and **2** formed by interlayer O–H · · · O interactions between rigid benzoic acid groups.

characteristic of decomposition of the organic moiety. The remaining weight of 26.92% corresponds to the percentage of MnO_2 (Calcd 26.84%).

3.4. *Photoluminescent properties*

The emission spectra of **1**, **2** and free H_3adab in the solid state at room temperature are depicted in figure 5. H_3adab shows a broad blue-fluorescent emission around 406 nm upon excitation at 300 nm, while **1** and **2** exhibit bathochromic-shifted fluorescent emission around 420 nm upon excitation at 300 nm. Therefore, the emission of **1** and **2** may not be assigned to intraligand fluorescent emission but to ligand-to-metal charge transfer (LMCT) [10]. However, the relative intensities in the emission spectra of H_3adab and **1** and **2** are different (figure 5), indicating that the LMCT have been enhanced or weakened to different extents because of the introduction of metal ions in

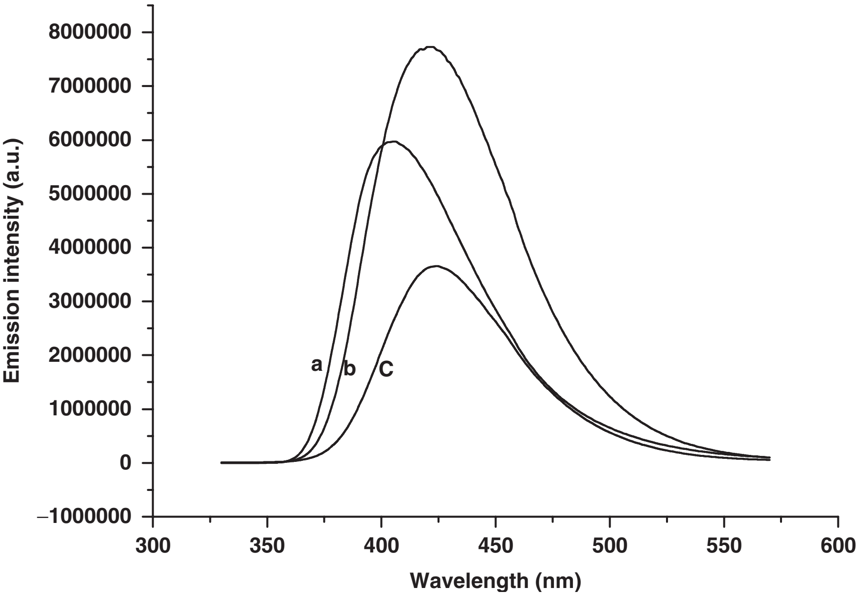


Figure 5. The emission spectra of H_3adab (a), compound **1** (b) and compound **2** (c) in the solid state at room temperature.

the structures. According to the single-crystal X-ray analyses, **1** and **2** are isostructural and their coordination environments and structures are similar; however, the relative intensities of emission peak are distinctly different, indicating that the metal centers play important roles in the LMCT [11]. As a result, **1** and **2**, especially **1**, may be excellent candidates of blue light-emitting materials since these condensed materials are highly thermally stable and insoluble in common polar and nonpolar solvents [12].

4. Conclusions

Two new isostructural 2D coordination polymers, [M(Hadab)(H_2O)] (M = Cd, **1**; Mn, **2**), have been synthesized by the hydrothermal method and structurally characterized by X-ray structural analyses. 2D layered networks of **1** and **2** further assemble into 3D pillar-layered networks through hydrogen bonding interactions. Compound **1** exhibits strong photoluminescence at room temperature.

Supporting information

CCDC 643225 and 643226 contain the supplementary crystallographic data for this article. These data can be obtained free of charge via 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 Email:

deposit@ccdc.cam.ac.uk). The IR spectra and TGA curves of **1** and **2** and the excitation spectra of **1**, **2** and free H_3adab in the solid state at room temperature are provided.

Acknowledgements

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