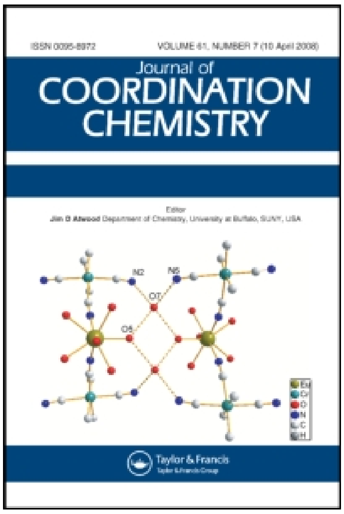

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Syntheses, structures, and optical properties of two cadmium complexes with chelidamic acid

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$[Cd_2(C_7H_3NO_5)_2 \cdot 4(H_2O)]_n \cdot 3nH_2O \cdot 0.5n(CH_3OH)$ (**1**) and $[Cd_3(C_7H_2NO_5)_2 \cdot 10(H_2O)] \cdot 2H_2O \cdot 0.5CH_3OH$ (**2**) were synthesized and characterized by X-ray single-crystal diffraction. The crystal structure of **1** reveals that both Cds are seven-coordinate with pentagonal bipyramid geometries. Coordination polyhedra are interlinked into a 1-D chain, further linked by hydrogen bonds into a 3-D network. Complex **2** is a discrete structure, then independent $[Cd_3(C_7H_2NO_5)_2 \cdot 10(H_2O)]$ are linked by hydrogen bonds into a 3-D network. The optical properties of **1** and **2** were investigated with fluorescent spectra; both exhibit strong green luminescence probably originating from π–π^* transition of the ligand.

Keywords: Cadmium complexes; Coordination polymer; Crystal structure; Luminescence; Syntheses

1. Introduction

Considerable effort has been devoted to the syntheses and characterizations of metal–organic frameworks (MOFs) composed of transition metal ions and bridging organic ligands because of the potential applications in catalysis, electronics, magnetism, and optics, as well as their fascinating framework structures [1–3]. A large number of MOFs with interesting properties have been prepared and characterized [4–6], among which the coordination polymers with good optical properties are of current interest [7–10].

Chelidamic acid (2,6-dicarboxy-4-hydroxypyridine) (hereafter HChel) is a polydentate ligand of use in many areas of science such as coordination chemistry, biochemistry, organic chemistry, medicinal chemistry, and even in HIV investigation [11–15]. A large number of metal complexes containing chelidamic acid ligands have been reported, playing a significant role in extension of the chemistry of chelidamic acid [16–20]. In spite of this large number, the majority of its known complexes are all simple 0-D, such as Cu, Ni, Co, Fe, V, and Cr, etc. [21–27], except Zn, Cu, Sn, Dy, Pr, and Tb complexes [28–34] with a 1-D structure and the Zn, Mn, V, Ag, Cu, Gd, Nd, Dy, and Er complexes [22, 35–40] with a 2-D structure. Herein, we report the syntheses,

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crystal structures, and optical properties of two Cd(II) complexes $[Cd_2(C_7H_3NO_5)_2 \cdot 4(H_2O)]_n \cdot 3nH_2O \cdot 0.5n(CH_3OH)$ (**1**) and $[Cd_3(C_7H_2NO_5)_2 \cdot 10(H_2O)] \cdot 2H_2O \cdot 0.5CH_3OH$ (**2**).

2. Experimental

2.1. *Apparatus*

The elemental analyses (C, H, N, and O) were carried out with a Perkin-Elmer 2400 II elemental analyzer. Photoluminescence analyses were performed on an Edinburgh FLS920 fluorescence spectrometer. IR spectra were recorded on a Magna 750 FT-IR spectrometer as KBr pellets from 4000 to 400 cm^{-1}.

2.2. *Syntheses*

2.2.1. $[Cd_2(C_7H_3NO_5)_2 \cdot 4(H_2O)]_n \cdot 3nH_2O \cdot 0.5n(CH_3OH)$ (1). All the reagents were commercially purchased and used without purification. A mixture of $CdCl_2 \cdot 2.5H_2O$ (0.2 mmol) and chelidamic acid (0.2 mmol) was dissolved in 10 mL water and 2 mL methanol was stirred for 8 h and filtered. The filtrate was allowed to stand at room temperature and light yellow prismatic crystals of **1** that are stable in air were obtained over a period of 10 days. Yield based on chelidamic acid: 76%. Elemental analysis calculated (%) for (**1**): C 23.86, H 3.02, N 3.85. Found (%): C, 23.93; H, 3.08; N, 3.89. IR (KBr, cm^{-1}): 3287 (s), 2970 (w), 2728 (w), 2615 (w), 2491 (w), 1693 (w), 1605 (vs), 1411 (vs), 1348 (s), 1251 (m), 1121 (m), 1025 (s), 932 (w), 894 (m), 806 (s), 773 (m), 722 (s), 585 (w), and 472 (w).

2.2.2. $[Cd_3(C_7H_2NO_5)_2 \cdot 10(H_2O)] \cdot 2H_2O \cdot 0.5CH_3OH$ (2). $CdCl_22.5H_2O$ (0.3 mmol), $CuSO_4$ (0.1 mmol), and chelidamic acid (0.2 mmol) were dissolved in a mixed solution of 10 mL water and 2 mL methanol in an attempt to obtain a new heterometal coordination polymer containing Cu and Cd atoms. After stirring for 8 h, the mixed solution was filtered and the filtrate was allowed to stand at room temperature. Yellow prismatic crystals of **2**, stable in air, were obtained over a period of 10 days. Yield based on chelidamic acid: 58%. Elemental analysis calculated (%) for (**1**): C, 18.72; H, 3.23; N, 3.01. Found (%): C, 18.77; H, 3.26; N, 3.08. IR (KBr, cm^{-1}): 3327 (s), 2965 (w), 2742 (w), 2606 (w), 2496 (w), 1680 (w), 1610 (vs), 1402 (vs), 1339 (s), 1242 (m), 1130 (m), 1013 (s), 938 (w), 898 (m), 810 (s), 762 (m), 712 (s), 576 (w), and 477 (w).

2.3. *Single-crystal X-ray structure determination*

Single crystals of **1** and **2** suitable for X-ray analysis were mounted at the apex of a glass fiber for X-ray diffraction data collection. Data sets of **1** and **2** were collected on Rigaku Mercury CCD and Rigaku AFC7R diffractometers, respectively, using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) from a rotating anode generator at 293(2) K. Intensity data were collected with an ω scan technique and corrected for *LP* factors. The structure was solved by direct methods and difference Fourier synthesis, refined by full-matrix least-squares techniques, and finally refined anisotropically for all non-hydrogen atoms.

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

Complex	**1**	**2**
Empirical formula	$C_{14.5}H_{22}N_2O_{17.5}Cd_2$	$C_{14.5}H_{30}N_2O_{22.5}Cd_3$
Formula weight ($g\,mol^{-1}$)	729.14	929.61
Crystal system	Triclinic	Triclinic
Space group	*P-1*	*P-1*
Unit cell dimensions (Å, °)		
a	9.4698(19)	10.797(2)
b	11.046(2)	11.3480(15)
c	11.225(2)	12.495(3)
α	87.95(3)	107.136(13)
β	74.60(3)	103.266(16)
γ	81.25(3)	101.222(13)
Volume (Å^3), Z	1118.8(4), 2	1366.2(4), 2
Crystal size (mm^3)	0.30 × 0.05 × 0.05	0.25 × 0.20 × 0.08
Calculated density ($g\ cm^{-3}$)	2.164	2.260
Absorption coefficient (mm^{-1})	1.993	2.415
$F(000)$	718	910
θ range for data collection (°)	3.13–25.50	1.96–25.51
Reflections collected	8238	5424
Independent reflection	4160 ($R_{int} = 0.0379$)	5065 ($R_{int} = 0.0749$)
Final R indices [$I > 2\sigma(I)$]	$R_1^a = 0.0331$, $wR_2^b = 0.0824$	$R_1 = 0.0329$, $wR_2 = 0.0927$
R indices (all data)	$R_1 = 0.0412$, $wR_2 = 0.0884$	$R_1 = 0.0403$, $wR_2 = 0.0983$
Goodness-of-fit on F^2	0.987	0.994

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected bond lengths (Å) of **1** and **2**.

Complex **1**			
Cd(1)–O(1W)	2.276(4)	Cd(2)–N(2)^{ii}	2.268(3)
Cd(1)–N(1)^{i}	2.285(3)	Cd(2)–O(2W)	2.269(4)
Cd(1)–O(4)	2.335(3)	Cd(2)–O(9)	2.317(3)
Cd(1)–O(4W)	2.365(3)	Cd(2)–O(7)^{ii}	2.367(3)
Cd(1)–O(1)^{i}	2.410(3)	Cd(2)–O(4W)	2.402(3)
Cd(1)–O(3W)	2.451(3)	Cd(2)–O(3W)	2.454(3)
Cd(1)–O(4)^{i}	2.483(3)	Cd(2)–O(9)^{ii}	2.463(3)
Complex **2**			
Cd(1)–N(1)	2.238(4)	Cd(2)–O(23)^{i}	2.386(3)
Cd(1)–O(1W)	2.291(4)	Cd(2)–O(21)	2.490(3)
Cd(1)–O(21)	2.342(3)	Cd(2)–O(23)	2.496(3)
Cd(1)–O(2W)	2.345(4)	Cd(3)–O(7W)	2.255(4)
Cd(1)–O(13)	2.413(3)	Cd(3)–O(10W)	2.289(4)
Cd(1)–O(11)	2.418(3)	Cd(3)–O(6W)	2.294(4)
Cd(1)–O(22)	2.460(3)	Cd(3)–O(12)	2.379(4)
Cd(2)–O(4W)	2.293(3)	Cd(3)–O(9W)	2.388(4)
Cd(2)–N(2)	2.299(3)	Cd(3)–O(8W)	2.395(4)
Cd(2)–O(3W)	2.310(4)	Cd(3)–O(11)	2.493(3)
Cd(2)–O(5W)	2.347(3)		

Symmetry transformations used to generate equivalent atoms. For **1**: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y, -z+1$. For **2**: (i) $-x+1, -y, -z$.

In **1** and **2**, hydrogens of coordinated and discrete waters (except for O11W and O12W in **2**) and hydroxyl were placed in calculated positions, with O–H distances of 0.85 Å, and refined in riding mode with $U_{iso}(H)$ values of $1.5U_{eq}(O)$. Other hydrogens were allowed to ride on their respective parent atoms with C–H distances of 0.93 Å,

Table 3. Hydrogen bonds of **1** and **2**.

D–H $\cdots$ A	D(D–H) (Å)	d(H $\cdots$ A) (Å)	d(D $\cdots$ A) (Å)	∠(DHA) (°)
Complex **1**				
O(1W)–H(1WA) $\cdots$ O(31)	0.80(5)	1.80(6)	2.586(9)	165(9)
O(1W)–H(1WB) $\cdots$ O(2)^{ii}	0.78(5)	1.93(5)	2.696(5)	168(9)
O(2W)–H(2WA) $\cdots$ O(5W)	0.81(5)	1.95(5)	2.700(6)	154(8)
O(2W)–H(2WB) $\cdots$ O(7W)^{iii}	0.79(5)	1.97(5)	2.757(6)	174(8)
O(3W)–H(3WA) $\cdots$ O(3)	0.79(4)	1.89(4)	2.664(4)	167(5)
O(3W)–H(3WB) $\cdots$ O(10)^{ii}	0.78(4)	2.16(4)	2.887(4)	157(5)
O(4W)–H(4WA) $\cdots$ O(6W)	0.87(4)	1.82(4)	2.686(5)	176(5)
O(4W)–H(4WB) $\cdots$ O(8)	0.82(4)	1.90(4)	2.692(4)	161(5)
O(5W)–H(5WA) $\cdots$ O(7W)^{iv}	0.91(5)	2.30(7)	2.995(9)	134(7)
O(5W)–H(5WB) $\cdots$ O(6W)^{v}	0.94(5)	1.94(5)	2.819(8)	154(8)
O(6W)–H(6WA) $\cdots$ O(5)^{vi}	0.81(5)	2.00(5)	2.811(5)	172(8)
O(6W)–H(6WB) $\cdots$ O(31)^{vii}	0.86(5)	1.99(5)	2.848(10)	173(7)
O(7W)–H(7WA) $\cdots$ O(6)^{i}	0.81(5)	1.94(5)	2.729(5)	163(9)
O(7W)–H(7WB) $\cdots$ O(8)^{ii}	0.89(5)	2.14(7)	2.886(6)	141(9)
O(5)–H(5A) $\cdots$ O(6)^{viii}	0.82	1.77	2.560(4)	162.3
O(10)–H(10A) $\cdots$ O(1)^{ix}	0.82	1.78	2.558(4)	157.4
Complex **2**				
O(1W)–H(1WA) $\cdots$ O(11W)^{ii}	0.83(4)	2.05(4)	2.880(6)	176(7)
O(1W)–H(1WB) $\cdots$ O(15)^{iii}	0.78(4)	1.96(4)	2.741(5)	173(8)
O(2W)–H(2WA) $\cdots$ O(25)^{iv}	0.85(3)	2.02(3)	2.864(5)	171(6)
O(2W)–H(2WB) $\cdots$ O(24)^{v}	0.85(3)	2.23(4)	2.987(5)	150(6)
O(3W)–H(3WA) $\cdots$ O(13)	0.77(4)	2.23(5)	2.893(5)	145(6)
O(3W)–H(3WB) $\cdots$ O(24)^{i}	0.78(4)	1.98(5)	2.697(5)	154(7)
O(4W)–H(4WA) $\cdots$ O(15)^{vi}	0.85(3)	1.86(3)	2.682(5)	164(6)
O(4W)–H(4WB) $\cdots$ O(12W)^{vii}	0.84(3)	1.96(4)	2.727(5)	151(6)
O(5W)–H(5WA) $\cdots$ O(25)^{iv}	0.94(4)	1.72(4)	2.653(5)	169(5)
O(5W)–H(5WB) $\cdots$ O(14)^{viii}	0.78(4)	2.01(4)	2.776(5)	169(6)
O(6W)–H(6WB) $\cdots$ O(31)^{ix}	0.88(4)	1.87(5)	2.643(9)	145(7)
O(7W)–H(7WA) $\cdots$ O(25)^{v}	0.84(3)	1.92(3)	2.726(5)	161(6)
O(7W)–H(7WB) $\cdots$ O(14)^{ix}	0.81(3)	2.00(4)	2.701(5)	144(6)
O(8W)–H(8WA) $\cdots$ O(4W)^{ix}	0.82(3)	2.04(3)	2.859(5)	175(7)
O(9W)–H(9WA) $\cdots$ O(22)	0.83(4)	2.17(5)	2.895(5)	147(6)
O(9W)–H(9WB) $\cdots$ O(24)^{iv}	0.77(4)	2.07(4)	2.824(5)	167(7)
O(10W)–H(10B) $\cdots$ O(15)^{iii}	0.87(3)	1.85(3)	2.722(5)	177(6)
O(10W)–H(10A) $\cdots$ O(12W)^{x}	0.85(3)	2.17(5)	2.910(6)	145(6)

Symmetry transformations used to generate equivalent atoms. For **1**: (i) $-x+1, -y, -z+1$; (ii) $x, y, z-1$; (iii) $-x+2, -y, -z$; (iv) $x, y, z+1$; (v) $-x+2, -y, -z+1$; (vi) $x+1, y, z-1$; (vii) $x+1, y, z$; (viii) $-x, -y, -z+2$; (ix) $-x+1, -y+1, -z+2$. For **2**: (i) $-x+1, -y, -z$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x, -y+1, -z+1$; (iv) $-x+1, -y+1, -z$; (v) $x-1, y, z$; (vi) $x+1, y, z$; (vii) $x, y-1, z$; (viii) $-x, -y, -z$; (ix) $x, y+1, z$; (x) $-x+1, -y+2, -z+1$.

and were included in the refinement with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. All calculations were performed with Siemens SHELXTL$^{\text{TM}}$ Version 5.0 package of crystallographic software [41]. Further details of the X-ray structural analysis are given in table 1. Selected bond lengths are listed in table 2 and hydrogen bonds are listed in table 3.

3. Results and discussion

3.1. *Crystal structure of 1*

As shown in figure 1, the asymmetric unit of **1** consists of two Cds, two chelidamic acid ligands, four coordinated waters, three discrete waters, and half a methanol.

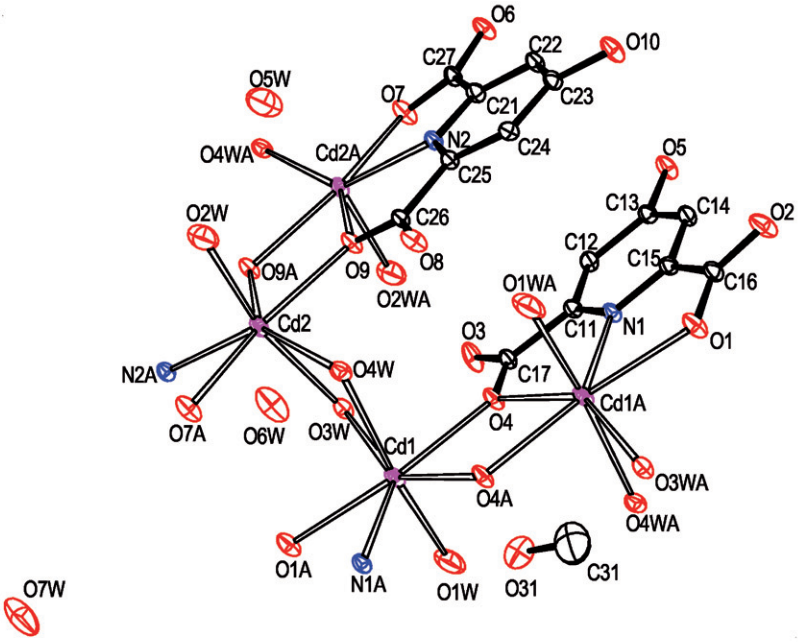

Figure 1. A view of the molecular structure of **1** showing 30% displacement ellipsoids for non-H atoms.

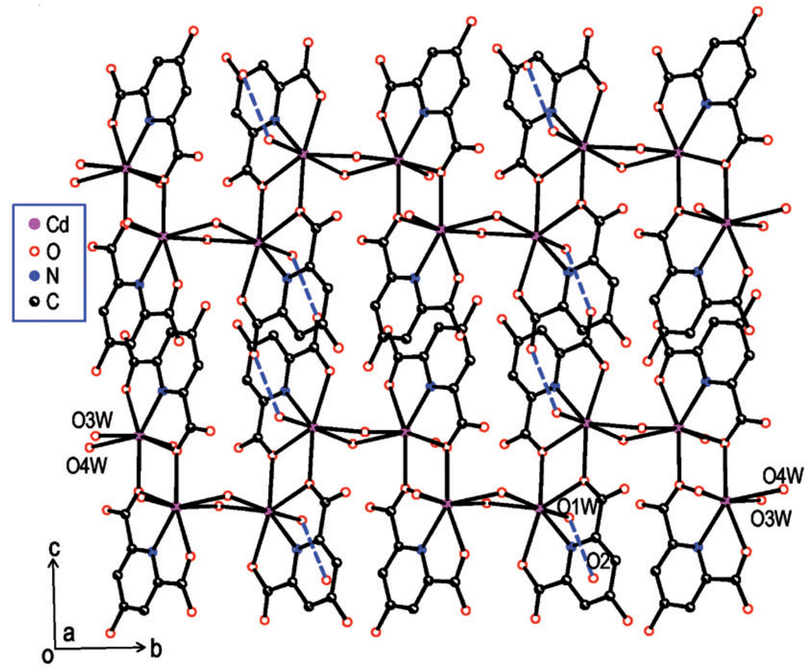

Figure 2. A view of the 2-D layer of **1** in the *bc* plane. Dashed lines represent hydrogen bonds. Hydrogen atoms are omitted for clarity.

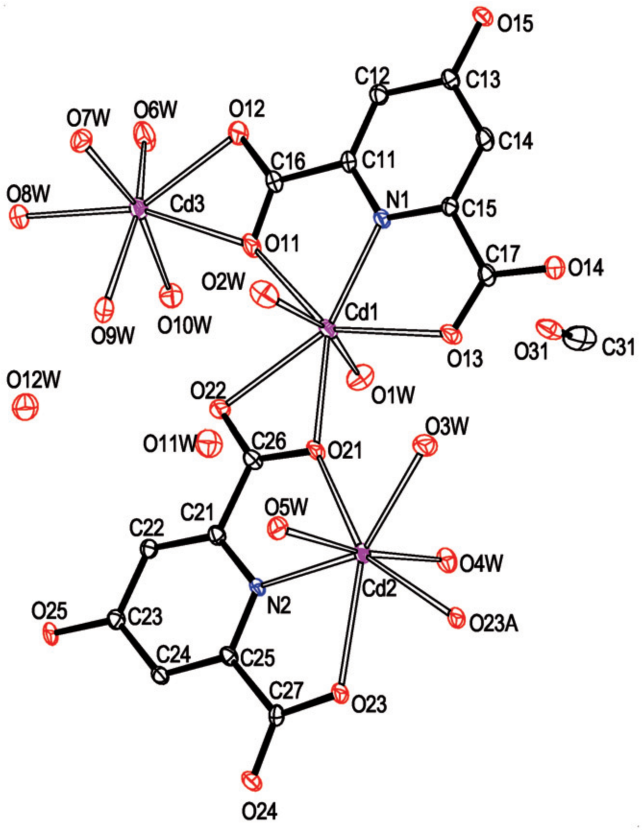

Figure 3. A view of the molecular structure of **2** showing 30% displacement ellipsoids for non-H atoms.

Analogous to Cd complexes reported in the literature [42], in **1** the two cadmiums are seven-coordinate in a distorted pentagonal bipyramid. Cd1 atom is coordinated by one nitrogen and two oxygens from tridentate chelating HChel, one carboxylic oxygen from the symmetry generated HChel, and three coordinated waters. Similar to the coordination environment of Cd1, Cd2 is coordinated by one nitrogen and two oxygens from another tridentate chelating HChel, one carboxylic oxygen from the symmetry generated HChel, and three coordinated waters. Bond distances between Cd and O range from 2.269(4) to 2.483(3) Å, in the normal range [42–46]. The Cd–N bond distances [Cd(1)–N(1)^{i} = 2.285(3) Å, Cd(2)–N(2)^{ii} = 2.268(3) Å ((i) $-x+1$, $-y+1$, $-z+1$; (ii) $-x+1$, $-y$, $-z+1$)] are close to the values reported in cadmium complexes [42–46].

Unlike the majority of the known complexes with chelidamic acid with discrete structures [20–27], **1** forms an infinite chain along the *b* direction through O3W and O4W, as shown in figure 2. Neighboring chains are connected into layers in the *bc* plane through hydrogen bonds between O1W and O2 (figure 2 and table 3). These layers are inter-linked through a very complex hydrogen bonding network involving water molecules and oxygens from chelidamic acid ligands to form a 3-D network (figure S1 and table 3).

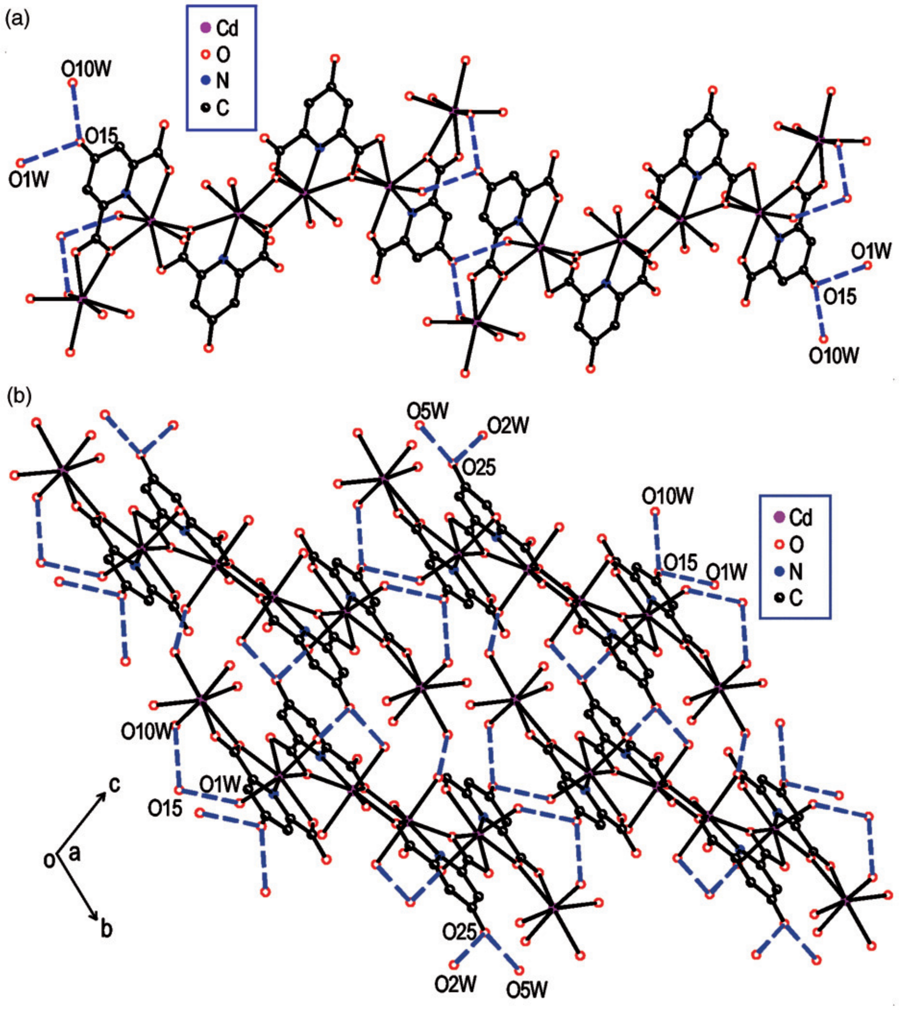

Figure 4. (a) A view of the 1-D chain of **2** extending along the *b* axis; (b) A view of the 2-D layer of **2** in the *bc* plane. Dashed lines represent hydrogen bonds. Hydrogen atoms are omitted for clarity.

3.2. *Crystal structure of 2*

As shown in figure 3, **2** consists of three Cds, two chelidamic acid ligands, ten coordinated waters, two discrete waters, and half a methanol. Similar to **1**, the cadmiums in **2** are seven-coordinate. Cd1 is coordinated by one nitrogen and two oxygens from tridentate chelating HChel, two carboxylic oxygens from the other HChel, and two coordinated waters. Cd2 is coordinated by one nitrogen and two oxygens from another tridentate chelating Hchel, one carboxylic oxygen from the symmetry generated HChel, and three coordinated waters. Cd3 is coordinated by two carboxylic oxygens from the tridentate chelating Hchel and five coordinated waters. The Cd–O bond distances range from 2.255(4) to 2.496(3) Å [42–46] and Cd–N bond distances [Cd(1)–N(1) = 2.238(4) Å, Cd(2)–N(2) = 2.299(3) Å] are close to normal values [42–46].

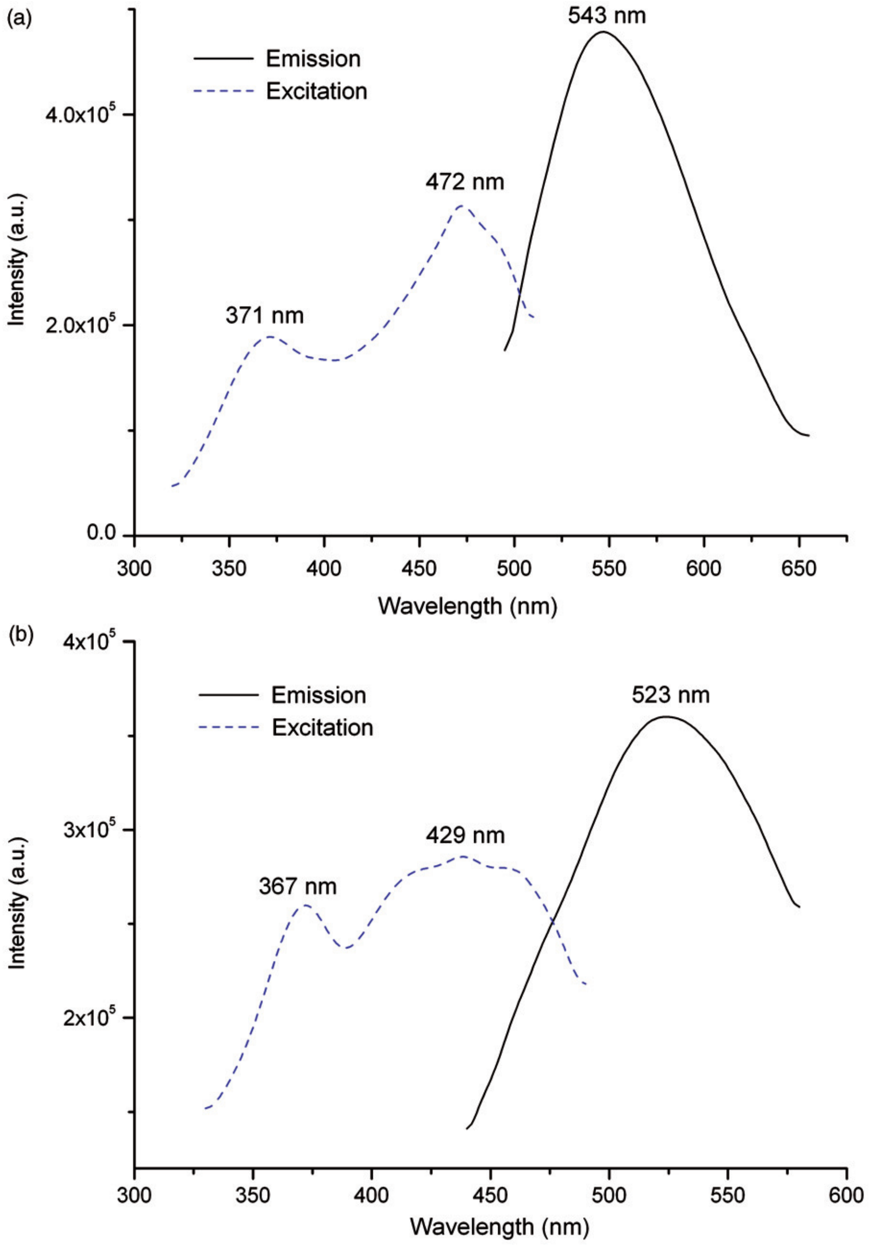

Figure 5. (a) Solid state emission ($\lambda_{em} = 543$ nm) and excitation ($\lambda_{ex} = 371$ or 472 nm) spectra of **1**; (b) Solid state emission ($\lambda_{em} = 523$ nm) and excitation ($\lambda_{ex} = 367$ or 429 nm) spectra of **2**.

Unlike **1** with a 1-D chain structure, **2** has a discrete structure. As shown in figure 4(a), independent molecules of **2**, $[Cd_3(C_7H_2NO_5)_2 \cdot 10(H_2O)]$, are linked by hydrogen bonds between O(1W) and O(15), and O(10W) and O(15) to form a 1-D infinite chain along the *b* direction (table 3). Neighboring chains are connected into a layer in the *bc* plane through hydrogen bonds between O(2W) and O(25), and O5W and O(25), as shown in figure 4(b) and table 3. These layers are inter-linked through a very complex hydrogen bonding network involving water and oxygen from the chelidamic acid ligands to form a 3-D network (figure S2 and table 3).

In summary, compared with the other Cd complexes recently reported in the literature [47–51], the Cd atoms in **1** and **2** have different coordination environments and coordination polyhedra, forming different coordination polymers with different structural types. Complexes **1** and **2** are the first two examples composed of Cd and cheldamic acid. Thus, this report expands the structure types of complexes of chelidamic acid.

3.3. *Optical properties of 1 and 2*

The emission spectra for crystalline samples of **1** and **2** in solid state are shown in figure 5(a) and 5(b), respectively. The maximum emission wavelength of **1** is 543 nm excited with light at $\lambda_{ex} = 371$ or 472 nm. Excitation of **2** with the light at $\lambda_{ex} = 367$ or 429 nm produces green fluorescence with maximum emission wavelength at 523 nm. According to previous work [34], the emission spectrum of the free chelidamic acid ligand features a green fluorescence with the maximum emission at 517 nm with $\lambda_{ex} = 360$ nm. Compared to free chelidamic acid, **1** and **2** have a little blue shift of emission length (26 and 6 nm, respectively), indicating that the emission of **1** and **2** probably originates from π–π^* transition of the ligand [7, 34, 52, 53]. The good luminescent properties indicate the present complexes the candidates for luminescent materials.

4. Conclusions

Cadmium complexes, $[Cd_2(C_7H_3NO_5)_2 \cdot 4(H_2O)]_n \cdot 3nH_2O \cdot 0.5n(CH_3OH)$ (**1**) and $[Cd_3(C_7H_2NO_5)_2 \cdot 10(H_2O)] \cdot 2H_2O$ $0.5CH_3OH$ (**2**), have been synthesized and characterized. Fluorescence spectra of **1** and **2** show strong green luminescent emission. Comparing to the fluorescence spectrum of free chelidamic acid, it can be concluded that emission of **1** and **2** originate from π–π^* transition of the ligand.

Supplementary material

The 3-D network linked through hydrogen bonds of **1** and **2** are available. Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC-728087 and 728088. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +441223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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