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Synthesis, structure, and luminescence of a coordination polymer from fumaropimaric acid and a water cluster

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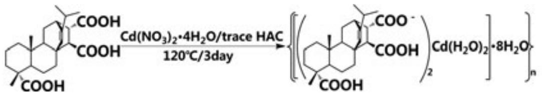

Using fumaropimaric acid (H_3L) as the ligand, a coordination polymer $\{[Cd(H_2L)_2(H_2O)_2]\cdot 8H_2O\}_n$ was synthesized under solvothermal conditions and characterized by elemental analysis, IR, and single-crystal X-ray diffraction. In the complex, Cd(II) is eight-coordinate with a distorted dodecahedral CdO_8 geometry. There is a Cd_2L_2 chelate ring, which forms an infinite 1-D chain structure along the *b* axis. The 1-D chains are further linked by strong O–H···O hydrogen bonding of a water cluster to form a 2-D structure. A dodecamer water cluster consisting of a five-membered ring with envelope conformation is the first reported. The complex is the first example showing three completely different coordination modes of carboxyl groups for Cd(II) complexes. The complex displayed medium fluorescence emission peaks at *ca.* 442 nm.

Keywords: Fumaropimaric acid; Cd(II) Coordination polymer; Water cluster; Envelope conformation; Fluorescence

1. Introduction

Coordination polymers built from transition metal ions and organic bridging ligands have attracted interest due to their structural diversity and promising applications in gas storage, selective gas adsorption and separation, optics, electrics, magnetism, molecular recognition, and catalysis [1]. A large number of coordination polymers have been constructed; some with specific topologies can be designed by wise selection of metal ions and organic ligands [2].

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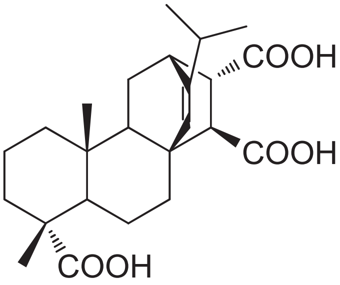
However, precise control of the coordination polymer structure through a self-assembly process is still exceedingly difficult because subtle factors may affect the assembly results. The nature of the ligand, metal ion, the metal–ligand ratio, pH, and other factors can impact the topology of the coordination polymers, leading to unexpected structural diversity. Among all factors, the choice of the ligands is very important because it determines the macrostructures of the final coordination polymers, as does the choice of metal ions. So far, numerous rigid aromatic multicarboxylic acids such as 1,4-benzenedicarboxylic acid (H_2BDC) [3], 1,3,5-benzenetricarboxylic acid (H_3BTC) [4], and 4,4′-biphenyldicarboxylic acid (H_2BPDC) [5] have been adopted as organic linkers. Flexible aliphatic carboxylic acid ligands such as mesoxalic acid [6, 7], glutaric acid [8–11] and fumaric acid [12, 13] have also been reported. However, far less effort has been expended on semi-rigid alkyl carboxylic acids [14, 15]. Ligands that contain semi-rigid carboxylates usually supply variable and abundant coordination modes [16]. In this work, a pine rosin derivative, fumaropimaric acid as a semi-rigid alcyl carboxylic acid (scheme 1), has been used as a linker to synthesize coordination polymers. Notably, rosin is an abundant and renewable material composed of a series of diterpenic resin acids. Its derivatives have been widely used in the production and daily life [17]. This work may expand rosin's applications. The work also reports an interesting coordination polymer with a water cluster. In recent years, research about identification, description, and classification of various water clusters and polymeric water assemblies attracted considerable interest [18–21] because it can help to understand the properties of bulk water in its liquid and solid states, and interpretation of water–water interactions and hydration phenomena in physical and materials chemistry, biochemistry, catalysis and supramolecular chemistry, drug design and pharmacology [18–22]. Here, a water tape formed through five-membered water rings with an envelope conformation has been reported. In addition, it is the first example showing three completely different coordination modes of carboxyl groups within one ligand in a Cd(II) complex.

2. Experimental

2.1. *Materials and methods*

All chemicals purchased were of analytical grade and used as received. Elemental analyses (C, H, and N) were carried out with a Thermo Finnigan Flash 1112A elemental analyzer. IR spectra were recorded from 4000 to 400 cm^{-1} using KBr pellets on a Nicolet 360 FT-IR



Scheme 1. Fumaropimaric acid (H_3L).

spectrophotometer. Powder X-ray diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer with Cu K$_\alpha$ radiation (λ = 1.5406 Å). Fluorescence spectroscopy was recorded on a Perkin-Elmer LS-55 spectrophotometer. H_3L was synthesized via Diels–Alder reaction of levopimaric acid and fumaric acid according to literature [23, 24].

2.2. *Synthesis of* $\{[Cd(H_2L)_2(H_2O)_2]\cdot 8H_2O\}_n$

$\{[Cd(H_2L)_2(H_2O)_2]\cdot 8H_2O\}_n$ was synthesized as follows: a mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.0154 g, 0.05 mM), H_3L (0.0209 g, 0.05 mM), CH_3CN (3 mL), CH_3OH (2 mL), H_2O (6 mL) and three drops of acetic acid (2 M) was heated in a 25 mL capacity stainless steel reactor lined with Teflon at 120 °C for 3 days, and then cooled to room temperature. Colorless needle crystals were obtained. Yield, 32.2% (0.0091 g) based on ligand. IR (cm^{-1}): 3423 (w), 3130 (w), 2954 (s), 1701 (s), 1561 (s), 1394 (s). Anal. Calcd for $C_{48}H_{86}O_{22}Cd$: C, 51.13; H, 7.69. Found: C, 51.01; H, 7.78.

2.3. *X-ray crystallography*

Diffraction data for the complex were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). Empirical absorption corrections were applied by using SADABS. The structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using SHELXTL-97 [25]. All non-hydrogen atoms were refined anisotropically. Hydrogens were placed on calculated positions and assigned isotropic thermal parameters riding on their parent. O5W and O6W are disordered over two sites and fixed at 0.5. Crystallographic data for the complex have been

Table 1. Crystal data and structure refinement details for the complex.

Empirical formula	$C_{48}H_{86}O_{22}Cd$
Formula weight	1127.57
Crystal system	Monoclinic
Space group	*C2*
a (Å)	22.772(2)
b (Å)	7.1655(7)
c (Å)	19.3014(15)
β (°)	117.752(4)
V (Å^3)	2787.2(4)
Z	2
D_c (g cm^{-3})	1.344
μ (mm^{-1})	0.466
Flack parameter	−0.03(2)
F (0 0 0)	1196
T (K)	173(2)
Crystal size (mm^3)	0.11 × 0.12 × 0.13
θ Range (°)	1.19–25.99
Reflections collected	10,384
Independent reflections	4913
Reflections observed [$I > 2\sigma(I)$]	4845 (R_{int} = 0.033)
Data/restraints/parameters	4913/8/330
Goodness-of-fit on F^2	1.143
Final R indices [$I > 2\sigma(I)$]	0.0343/0.0901
R indices (all data)	0.0362/0.1036
Largest difference peak and hole (e Å^{-3})	0.984, −0.412

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Bond lengths			
Cd1–O1W	2.269(3)	Cd1–O5^{i}	2.338(3)
Cd1–O4	2.458(3)	Cd1–O6^{i}	2.602(3)
Cd1···Cd1	7.1655(7)		
Bond angles			
O1W–Cd1–O4	76.12(13)	O5^{i}–Cd1–O5^{iii}	83.21(14)
O1W–Cd1–O5^{i}	133.69(10)	O5^{i}–Cd1–O6^{iii}	81.70(9)
O1W–Cd1–O6^{i}	81.91(10)	O1W^{iv}–Cd1–O5^{i}	83.76(11)
O1W–Cd1–O5^{iii}	83.76(11)	O4^{iv}–Cd1–O5^{i}	152.98(10)
O1W–Cd1–O6^{iii}	122.29(11)	O5^{iii}–Cd1–O6^{i}	81.70(9)
O1W–Cd1–O1W^{iv}	134.19(17)	O6^{i}–Cd1–O6^{iii}	119.27(12)
O1W–Cd1–O4^{iv}	72.92(12)	O1W^{iv}–Cd1–O6^{i}	122.29(11)
O4–Cd1–O5^{i}	97.72(12)	O4^{iv}–Cd1–O6^{i}	154.70(10)
O4–Cd1–O6^{i}	77.82(10)	O5^{iii}–Cd1–O6^{iii}	52.29(9)
O4–Cd1–O5^{iii}	152.98(10)	O1W^{iv}–Cd1–O5^{iii}	133.69(10)
O4–Cd1–O6^{iii}	154.70(10)	O4^{iv}–Cd1–O5^{iii}	97.72(12)
O1W^{iv}–Cd1–O4	72.92(12)	O1W^{iv}–Cd1–O6^{iii}	81.91(10)
O4–Cd1–O4^{iv}	93.44(18)	O4^{iv}–Cd1–O6^{iii}	77.82(10)
O5^{i}–Cd1–O6^{i}	52.29(9)	O1W^{iv}–Cd1–O4^{iv}	76.12(13)

Note: Symmetry codes: (i) *x*, −1 + *y*, *z*; (ii) *x*, 1 + *y*, *z*; (iii) −*x*, −1 + *y*, −*z*; (iv) −*x*, *y*, −*z*.

Table 3. H-bonding network (Å, °) for the complex.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠D–H···A
O1–H1A···O2W^{i}	0.85	6.70	6.390(3)	65
O1W–H1C···O4W^{ii}	0.85	6.51	6.372(3)	77
O2W–H2A···O4W	0.68	2.04	2.673(3)	153
O2W–H2B···O6^{iii}	0.84	10.12	9.844(3)	49
O3–H3B···O6^{iv}	0.85	5.72	5.071(3)	72
O3W–H3C···O5^{v}	0.85	8.22	7.446(3)	64
O3W–H3D···O2W	0.85	2.42	2.878(3)	114
O4W–H4A···O2	0.85	1.94	2.674(3)	145
O4W–H4B···O5W	0.85	2.25	2.769(3)	120
O5W–H5D···O3W^{vi}	0.85	4.83	4.620(3)	71
O6W–H6C···O3W	0.85	1.93	2.779(3)	172
O6W–H6D···O5W	0.85	2.04	2.845(3)	159

Symmetry codes: (i) *x*, 1 + *y*, *z*; (ii) −1/2 + *x*, −1/2 + *y*, *z*; (iii) 1/2 + *x*, −1/2 + *y*, *z*; (iv) *x*, −1 + *y*, *z*; (v) 1/2 − *x*, −1/2 + *y*, −*z*; (vi)1/2 − *x*, 1/2 + *y*, −*z*.

deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 885268. The crystal data and structure refinement of the complex are summarized in table 1. Selected bond lengths and angles of the complex are listed in table 2. The hydrogen-bonding geometry parameters of the complex are listed in table 3.

3. Results and discussion

3.1. *Crystal structure of the complex*

X-ray crystallographic analysis reveals that the complex crystallizes in a chiral space group *C2* with a Flack parameter of −0.03(2) because the ligand contains eight chiral carbons [26]. The asymmetric unit contains half of a Cd(II) ion, one ligand, one coordinated water, and four lattice waters [figure 1(a)]. In the complex, Cd1 is eight-coordinate with a distorted

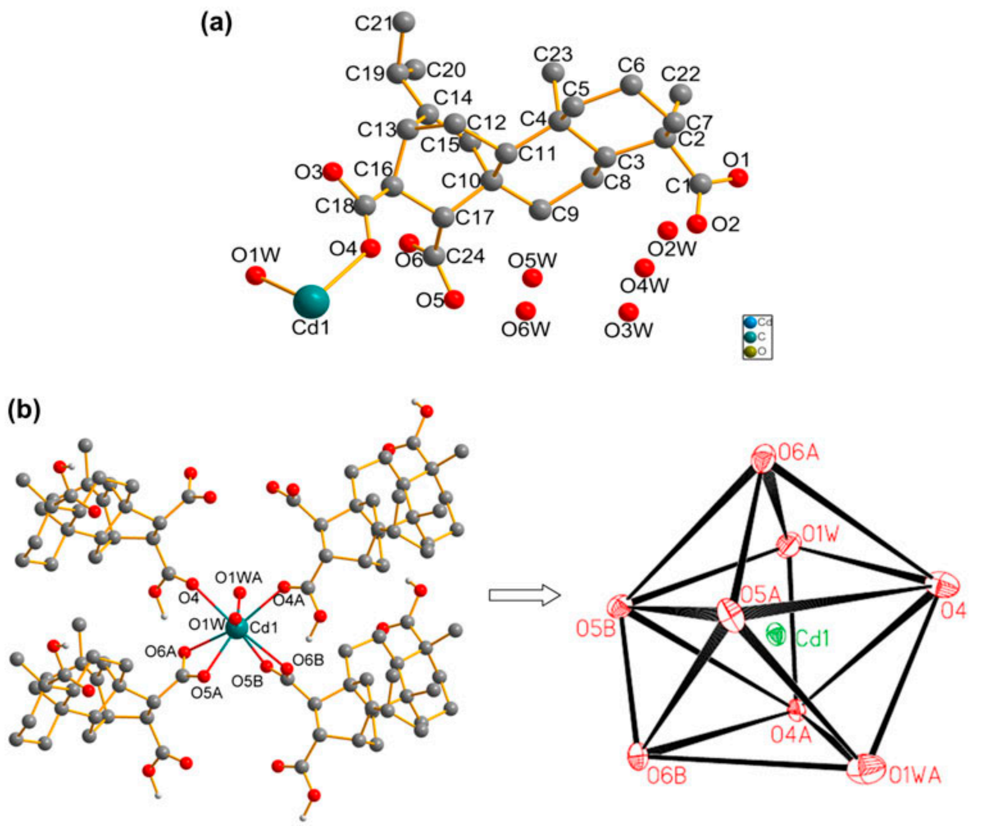


Figure 1. (a) ORTEP drawing (at 30% probability) of the asymmetric unit for the complex. (b) View of the environment of Cd1 ion with distorted dodecahedral CdO_8 geometry in the complex.

Table 4. Comparison of the bond lengths (Å) and angles (°) for the different coordination modes of carboxyl ligands in Cd(II) complexes.

Coordination modes of carboxyl ligand	Complex	Cd–O (Å)	O–Cd–O (°)	References
Not deprotonated, monodentate	$\{[Cd(H_2pza)(H_2O)_2]\cdot 2H_2O\}_n$	2.422(19)		51
	$[Cd(HL)(pybim)]\cdot H_2O$	2.326(2)		16
	$\{[Cd(H_2L)_2(H_2O)_2]\cdot 9H_2O\}_n$	2.458(4)		This work
Deprotonated, chelating bidentate	$[Cd_2(L)(HCOO)(bpy)_2(H_2O)]\cdot H_2O$	2.3553(19; 2.415 (2)	54.72(7)	16
	$[Cd_2(BDC)_2($*p*-bitmb$)_{1.5}(H_2O)_2$	2.399(5); 2.522 (5)	52.77(2)	31
	$\{[Cd(H_2L)_2(H_2O)_2]\cdot 9H_2O\}_n$	2.338(3); 2.602 (3)	52.24(9)	This work

H_4pza = 2,3,5,6-pyrazinetetracarboxylic acid; pybim = 2-(pyridin-2-yl)-1H-benzo[d]imidazole; bpy = 2,2′-bipyridine; H_2BDC = 1,4-benzenedicarboxylic acid; *p*-bitmb = 1,4-bis(1-imidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene; bth = 1,6-bis(1,2,4-triazol-1-yl) hexane; H_2L = (3-carboxyl-phenyl)-(4-(2′-carboxyl-phenyl)-benzyl) ether.

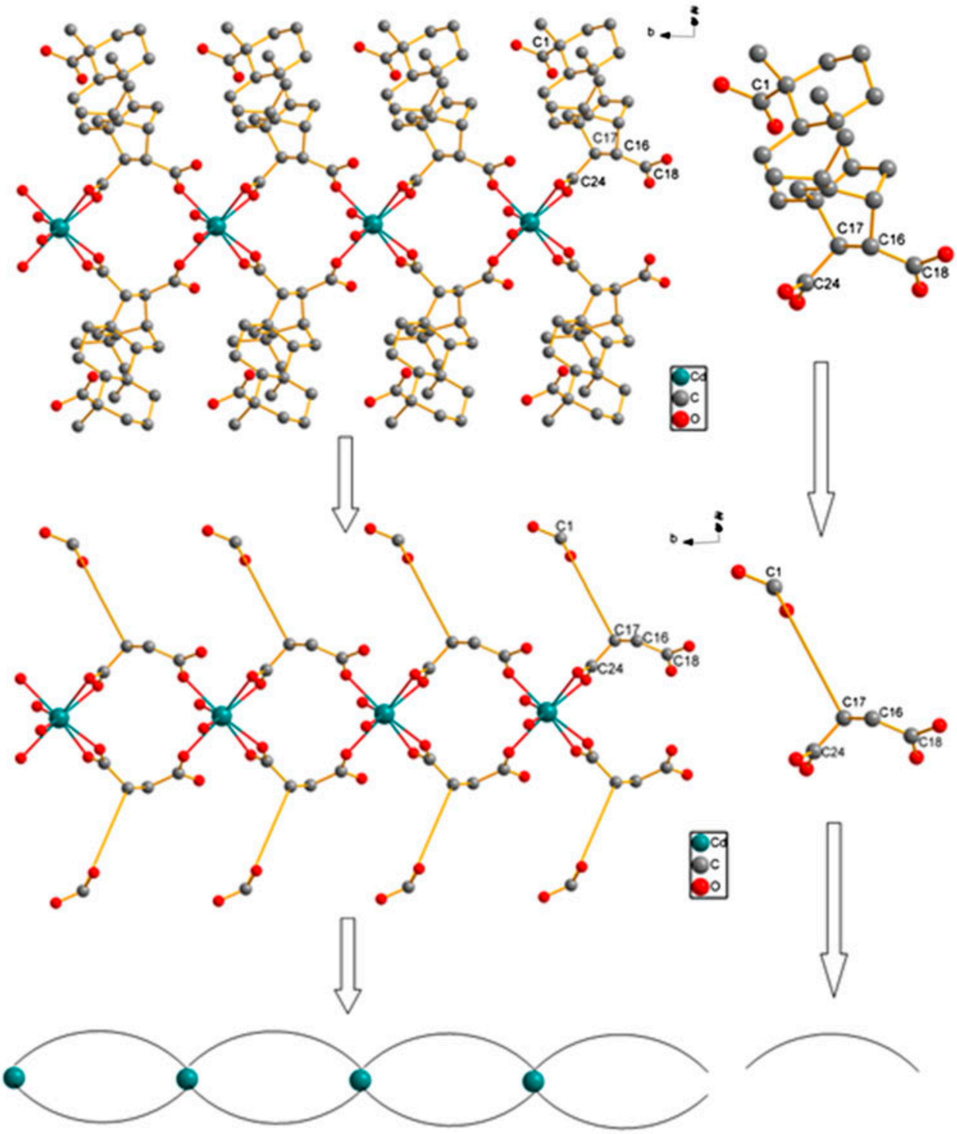


Figure 2. 1-D infinite chain structure along the *b* axis for the complex.

dodecahedral CdO_8 geometry, coordinated by six carboxyl oxygens from four ligands and two oxygens from two water molecules [figure 1(b)]. Six Cd–O bond lengths can be classified as three kinds: $Cd–O_{carboxylate}$ [16, 31], $Cd–O_{carboxy}$ [16, 57], and $Cd–O_w$ (2.269(3) Å), which are comparable to the known values, respectively, as shown in table 4 [16, 31, 57].

Each H_2L^- uses O4, O5, and O6 of its two carboxyls to link two Cd(II) ions and each Cd (II) connects four H_2L^- through carboxyl. So two Cd(II) ions and two H_2L^- ligands form a M_2L_2 chelate ring (SBU) with Cd1···Cd1 distance of 7.1655(7) Å (figure 2). The chelate rings are connected by Cd–O coordination bonds to give an infinite 1-D chain structure

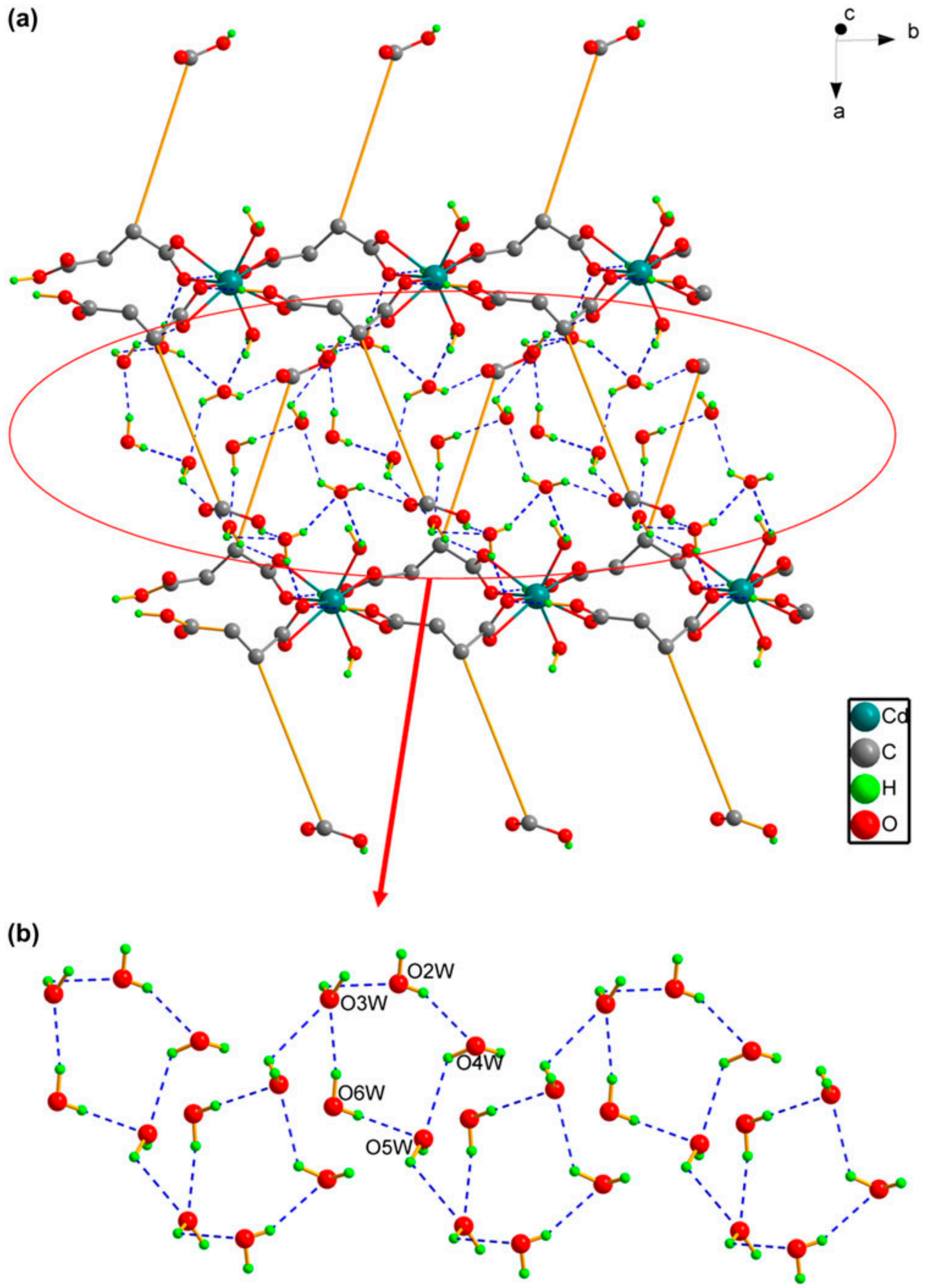
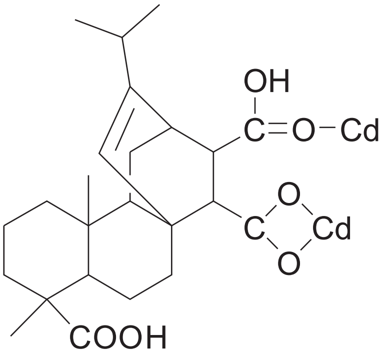


Figure 3. (a) Hydrogen bonding of the water cluster connected to the 2-D structure for the complex. (b) The water tape.

(figure 2). The 1-D chains are further linked by strong O–H···O hydrogen bonds of the water cluster (O1–H1A···O2W, O1W–H1C···O4W, O2W–H2B···O6, O3W–H3C···O5, O4W–H4A···O2) to form a 2-D layer [figure 3(a), table 3].

There are five crystallographically independent water molecules. O1W is from coordinated water and the other four, O2W–O6W (O5W 0.5; O6W 0.5), come from lattice waters. They are self-assembled through hydrogen bonds. As shown in figure 3(b), the five lattice water molecules (O2W–O6W) form a five-membered ring with an envelope conformation where O3W–O6W is almost in a plane, and five-membered rings linked by O5W–H5D···O3W form a water tape along the *b*-axis. The water cluster is stabilized by hydrogen bonds (O1–H1A···O2W, O1W–H1C···O4W, O2W–H2B···O6, O3W–H3C···O5, O4W–H4A···O2). The average O···O distance in the water cluster is 2.79 Å, which is similar to the corresponding values in ice *Ic* (2.75 Å) and *Ih* (2.759 Å) at −130 and −90 °C, respectively [27, 28]. There is a wide variation in the O–O–O angles from 90.43 to 113.19°, which is different from the corresponding value of 109.3° in hexagonal ice [29]. The water cluster in the complex is very interesting. A series of configurations of water clusters such as book, boat, and chair with cyclic conformation [30, 31], as well as ring [32–34], tape [35, 36], folded-chain [37–39], helical chains [40], hanging-ladder [41], cage [42], column [43], chair [44], and prism polyhedral structures have been reported [45–47]. However, five-membered water ring unit with envelope conformation was rarely reported [38]. In BPA·8H_2O (BPA = bis (3-pyrazinylcarbonylaminopropyl) amine) [31], two fused five-membered water rings with envelope conformations appear as a minor unit of the water cluster, where the average O···O distance (2.771 Å) is comparable to that in our complex (2.789 Å), and the O–O–O angles (from 92.28 to 109.05°) are also comparable to that in our complex (from 90.43 to 113.19°).

Organic polycarboxylates have been widely employed to prepare coordination polymers, partly due to their diverse coordination modes [48, 49]. H_3L, fumaropimaric acid, is of particular interest because of potential variable coordination patterns, such as a terminal monodentate, chelating, bridging bidentate, and bridging tridentate, and also because of its ability to act as hydrogen bonding acceptors or donors to assemble supramolecular frameworks. H_3L could be partially or completely deprotonated to L^{3-}, HL^{2-}, or H_2L^- anions, which further enrich the coordination patterns. In the complex, the carboxyl groups of the ligand were partially deprotonated to H_2L^-, as shown in scheme 2. The carboxyl group connected with tertiary carbon was not deprotonated, and not coordinated with Cd(II), just like one of



Scheme 2. Coordination modes of ligand in the complex.

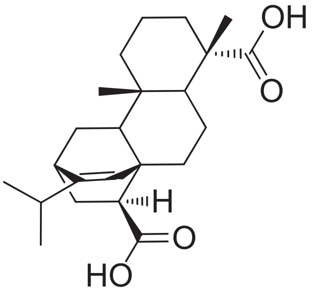
the carboxyl groups in $[Cd(HL)(bth)0.5(H_2O)]\cdot H_2O$ [50]. The hydrogen bonds from this carboxyl and water may prevent the coordination with Cd(II). Another carboxyl group was not deprotonated, but coordinated with Cd(II) by carbonyl oxygen in monodentate coordination, whose distance of Cd–O is in the normal range as shown in table 4. This coordination mode was also rarely observed in the literature [16, 51]. The chelating bidentate coordination is common for carboxylate-based Cd(II) complexes, whose distance of Cd–O and the angle of O–Cd–O is also in normal range as shown in table 4.

Another ligand acrylpimaric acid H_2A [15] (scheme 3), obtained via Diels–Alder reaction of levopimaric acids and acrylic acid, is similar to fumaropimaric acid (H_3L), from levopimaric acids and fumaric acid. They are all semi-rigid alkyl carboxylic acids and from the same precursor. In $[Cd_2A_2(DMF)(H_2O)_{0.5}]\cdot 0.5H_2O$ [15], a 2-D polymer, obtained from acrylpimaric acid and Cd(II), two carboxyl groups are completely deprotonated and coordinated to two Cd(II) ions in tridentate chelate coordination and bridging bidentate coordination, which is quite different from the present complex. The reason may be different pHs. For the present complex, trace acetic acid was added during synthesis so that there was lower pH value (pH 4) in the mixture.

To the best of our knowledge, the present complex is the first example showing three completely different coordination modes of three carboxyl groups in one ligand in coordination with Cd(II).

3.2. *IR spectrum*

IR spectra (figure 4) of the complex displayed the characteristic asymmetric and symmetric stretching vibrations of chelating carboxylate groups with bands at 1561 and 1394 cm^{-1}, respectively. The difference of $\Delta\upsilon(\upsilon_{as}(COO^-) - \upsilon_{sym}(COO^-))$ is often used to determine the bonding of carboxylate complexes [44, 52] with $\Delta\upsilon$ larger than 200 cm^{-1}, indicating monodentate carboxylate, while less than 200 cm^{-1} means bidentate carboxylate [53]. For the complex, the $\upsilon_{as}(COO^-)$ and $\upsilon_{sym}(COO^-)$ vibrations are 1561 and 1394 cm^{-1}, and the difference $\Delta\upsilon(167\ cm^{-1})$ between these frequencies is close to those found in bidentate carboxylate. This observation is consistent with X-ray structural analysis. The absorption at 1701 cm^{-1} is assigned to C=O stretch of monodentate coordinated carboxyl groups. The absorption band at 1704 cm^{-1} is assigned to C=O stretch of non-coordinated carboxyl. The strong band at 3423 cm^{-1} is assigned to O–H stretch, which indicates the presence of water molecules in the complex. The IR spectrum of ice shows the O–H stretch at 3220 cm^{-1}, while that in liquid water appears at 3490 and 3280 cm^{-1} [54, 55]. Thus, the O–H stretch



Scheme 3. Acrylpimaric acid (H_2A).

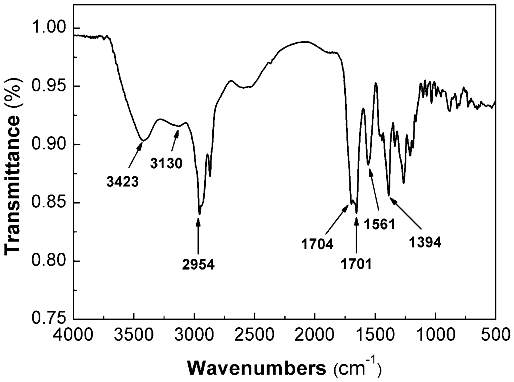


Figure 4. IR of the complex.

in the water cluster of the complex is similar to that of liquid water. The band at 3130 cm^{-1} is assigned to hydroxyl of carboxylate stretching vibration. The IR spectrum of the complex is in agreement with the X-ray crystal structure analysis.

3.3. *P-XRD*

The simulated and experimental P-XRD patterns of the complex are shown in figure 5. The peak positions are in agreement with each other, indicating the phase purity of the bulk products.

3.4. *Luminescence properties*

The solid-state excitation-emission spectra of free H_3L and the complex were measured at room temperature (figure 6). The emission spectrum for H_3L showed a main peak at 440 nm with $\lambda_{ex} = 350$ nm (the maximum excitation wavelength). The emission peak of the complex was found at 442 nm ($\lambda_{ex} = 350$ nm). The emission peak of the complex is

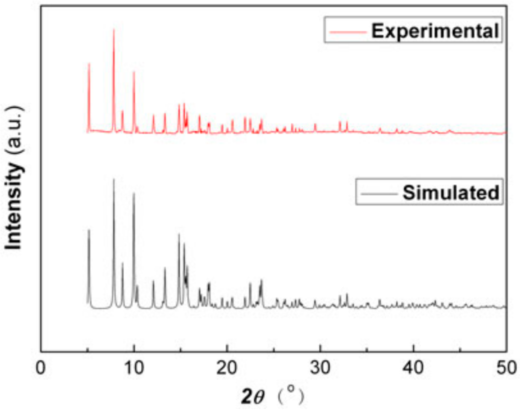


Figure 5. Experimental and simulated X-ray powder diffraction patterns of the complex.

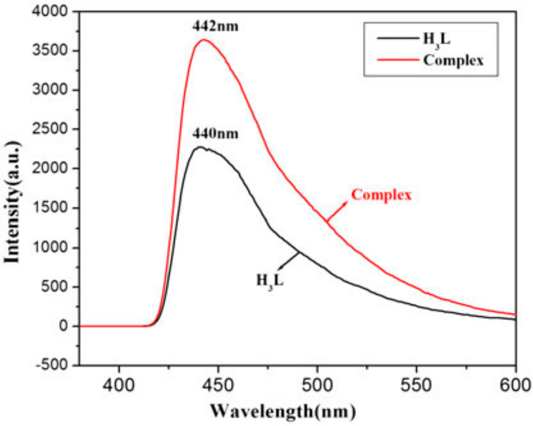


Figure 6. Luminescence emission spectra of the free ligand (H_3L) and the complex in solid state at room temperature.

probably due to π^*–n transitions of the ligand because a similar peak also appears for the free ligand. In contrast to the free ligand, the fluorescence intensity of the complex is significantly enhanced. The rigidity is increased due to coordination of the ligands to metal centers, resulting in enhanced emission [56–58].

4. Conclusion

A new coordination polymer, $\{[Cd(H_2L)_2(H_2O)_2]\cdot 8H_2O\}_n$, from fumaropimaric acid (H_3L) had been synthesized and characterized. Crystallographic studies revealed that Cd(II) is eight-coordinate with a distorted dodecahedron CdO_8 geometry. There is a Cd_2L_2 chelate unit, which forms an infinite 1-D chain structure along the *b* axis. 1-D chains are further linked by strong O–H···O hydrogen bonding of a water cluster to form a 2-D layer. A water tape formed from five-membered water rings with an envelope conformation is reported. The complex may be the first example showing three completely different coordination modes of three carboxyl groups in one ligand for Cd(II). The complex displayed medium fluorescence emission peaks at *ca*. 442 nm.

Supplementary material

CCDC-885268 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the online version.

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