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Synthesis, structure and luminescent properties of Cd(II) and Zn(II) complexes constructed from 3,5-dimethyl-2, 6-pyrazinedicarboxylic acid

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Synthesis, structure and luminescent properties of Cd(II) and Zn(II) complexes constructed from 3,5-dimethyl-2,6-pyrazinedicarboxylic acid

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[Cd₂(phen)₂(DPZDA)₂(H₂O)₂] · 8H₂O (**1**) and [Zn(phen)(DPZDA)(H₂O)] · 2H₂O (**2**) have been synthesized by reaction of Cd(NO₃)₂/Zn(NO₃)₂ with phen and DPZDA (where phen = 1,10-phenanthroline, H₂DPZDA = 3,5-dimethyl-2,6-pyrazinedicarboxylic acid) in aqueous ethanol solution. Elemental analysis, IR spectra, thermal analyses and X-ray single crystal diffraction were carried out to determine the composition and crystal structure of **1** and **2**. In **1**, a 2D supramolecular network containing a novel metal-water decamer were formed by hydrogen bonds. In **2**, a 2D supramolecular structure was constructed from hydrogen bonds and $\pi \cdots \pi$ interactions. Moreover, **1** and **2** displayed photoluminescent properties in the blue range at room temperature.

Keywords: Water cluster; Supramolecular; Self-assembly; Hydrogen bond

1. Introduction

Water is of fundamental importance [1] and study of water clusters is important to obtain a molecular level description of the properties of bulk water. Researchers have investigated different water clusters in different host-guest environments [2]. To understand water clusters, one must have knowledge of the structure of various hydrogen-bonding water networks in diverse environments [3]. Multicarboxylate ligands act as hydrogen-bond acceptors and also hydrogen-bond donors, providing a platform to assemble water molecules into clusters [4]. Small water clusters, including tetramers, hexamers and octamers have been found in different supermolecular complexes with multicarboxylate ligands [5–8]. These water clusters also stabilize the open framework structure. Herein, we report two new complexes, [Cd₂(phen)₂(DPZDA)₂(H₂O)₂] · 4H₂O (**1**) and [Zn(phen)(DPZDA)(H₂O)] · 2H₂O (**2**) (H₂DPZDA = 3,5-dimethyl-2,6-pyrazinedicarboxylic acid, phen = 1,10-phenanthroline). In **1**, we observed water decamers with metal-water coordination interactions

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stabilizing this water cluster. Moreover, **1** and **2** exhibit blue photoluminescence at room temperature.

2. Experimental

2.1. Materials and methods

All chemicals commercially purchased were of reagent grade and used without further purification. Elemental analyses (C, H and N) were carried out with a Finnigan EA 1112 elemental analyzer. IR spectra were recorded on a Nicolet 470 spectrophotometer using KBr pellets in the range 4000–400 cm^{-1} . Thermal analyses were performed on a NETZSCH TG 209 instrument in flowing N₂ with a heating rate of 10°C min⁻¹. Excitation and emission spectra were obtained on a Perkin-Elmer LS55 spectrofluorometer equipped with a 450W xenon lamp as the excitation source.

2.2. Synthesis of **1** and **2**

Complex 1: 0.2 mmol Cd(NO₃)₂ and 3,5-dimethyl-2,6-pyrazinedicarboxylic acid (H₂DPZDA) were dissolved in 50 mL deionized water (solution 1); 0.2 mmol phen was dissolved in 15 mL absolute ethanol (solution 2). Then solution 1 was added to solution 2 dropwise and the pH of the mixture was adjusted to 8 by adding 0.2 mol L⁻¹ KOH. After concentration in a rotary evaporator at 50°C, the concentrated solution was kept at room temperature for 7 d obtaining colorless transparent crystals in 40% yield. Anal. Calcd (%): C, 41.64; H, 4.20; N, 9.71. Found (%): C, 41.23; H, 4.01; N, 9.33. IR (cm⁻¹): 3422(s), 1621(s), 1516(s), 1425(s), 1382(s), 1342(s), 1320(s), 1156(w), 1102(w), 858(s), 728(s).

Complex 2 was prepared by similar method to **1** except for using Zn(NO₃)₂ instead of Cd(NO₃)₂. IR (cm⁻¹): 3379(s), 1632(s), 1515(m), 1424(m), 1402(m), 1376(s), 1336(s), 854(s), 818(m), 727(s) cm⁻¹. Anal. Calcd (%): C, 48.64; H, 4.09; N, 11.35. Found (%): C, 48.40; H, 3.99; N, 11.23.

2.3. X-ray crystallography

Single crystals of **1** and **2** were glued on a glass fiber. Data were collected on a Bruker Smart 1000 CCD diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. Empirical absorption correction was applied. The structures were solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXTL crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. The crystal data and structure refinement of **1** and **2** are summarized in table 1. Selected bond lengths and angles are listed in table 2.

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

Empirical	C ₂₀ H ₂₄ CdN ₄ O ₉	C ₂₀ H ₂₀ ZnN ₄ O ₇
Formula weight	576.83	493.77
Temperature (K)	293	294
Wavelength	0.71073	0.71070
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.1799(19)	7.5717(14)
<i>b</i> (Å)	11.933(3)	9.6481(15)
<i>c</i> (Å)	12.116(3)	15.0542(18)
α (°)	92.281(3)	91.251(7)
β (°)	107.451(3)	103.661(3)
γ (°)	98.790(3)	107.182(7)
Volume (Å ³)	1110.3(4)	1016.0(3)
<i>Z</i>	2	2
<i>P</i> _{calc} (mg m ⁻³)	1.725	1.614
θ range (°)	1.73–25.01	2.22–27.45
Reflections collected	6032	7670
Independent reflections	3858	4580
Data/restraints/parameters	3858/0/309	4580/9/311
Goodness-of-fit on <i>F</i> ²	1.068	1.020
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0383 ωR_2 = 0.1003	<i>R</i> ₁ = 0.0523 ωR_2 = 0.1032
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0476 ωR_2 = 0.1038	<i>R</i> ₁ = 0.0910 ωR_2 = 0.1181

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

Cd(1)–O(5)	2.313(3)	Cd(1)–O(3)#1	2.392(3)
Cd(1)–O(1)	2.363(3)	Cd(1)–N(3)	2.401(3)
Cd(1)–N(4)	2.365(3)	Cd(1)–O(3)	2.436(3)
Cd(1)–N(1)	2.378(3)		
Zn(1)–N(1)	2.087(3)	Zn(1)–N(4)	2.111(3)
Zn(1)–N(3)	2.177(3)	Zn(1)–O(5)	2.105(3)
Zn(1)–O(1)	2.163(2)		
O(5)–Cd(1)–O(1)	93.09(12)	O(5)–Cd(1)–O(3)#1	172.63(10)
O(5)–Cd(1)–N(4)	92.05(12)	O(1)–Cd(1)–O(3)#1	92.91(10)
O(1)–Cd(1)–N(4)	83.93(12)	N(4)–Cd(1)–O(3)#1	84.34(11)
O(5)–Cd(1)–N(1)	82.11(11)	N(1)–Cd(1)–O(3)#1	104.15(10)
O(1)–Cd(1)–N(1)	67.64(11)	O(5)–Cd(1)–N(3)	86.22(12)
N(4)–Cd(1)–N(1)	150.48(12)	O(1)–Cd(1)–N(3)	154.02(11)
N(1)–Zn(1)–O(5)	96.74(12)	N(1)–Zn(1)–N(4)	165.67(11)
O(5)–Zn(1)–N(4)	89.22(13)	N(1)–Zn(1)–O(3)	75.22(10)
O(5)–Zn(1)–O(3)	94.16(10)	N(4)–Zn(1)–O(3)	91.40(10)
N(1)–Zn(1)–O(1)	74.84(10)	O(5)–Zn(1)–O(1)	88.88(11)

Symmetry code, #1: $-x + 2, -y, -z$.

3. Results and discussion

3.1. Descriptions of the structures

The coordination environment of **1** is shown in figure 1. Cd(1) is coordinated with three nitrogen atoms [N(1), N(3) and N(4)] from phen ligands and DPZDA ligands, four oxygen atoms [O(1), O(5), O(3), O(3A)] from carboxylic group of DPZDA ligands and coordinated water. N(1), N(3), N(4), O(1) and O(3) constitute the equatorial plane; the

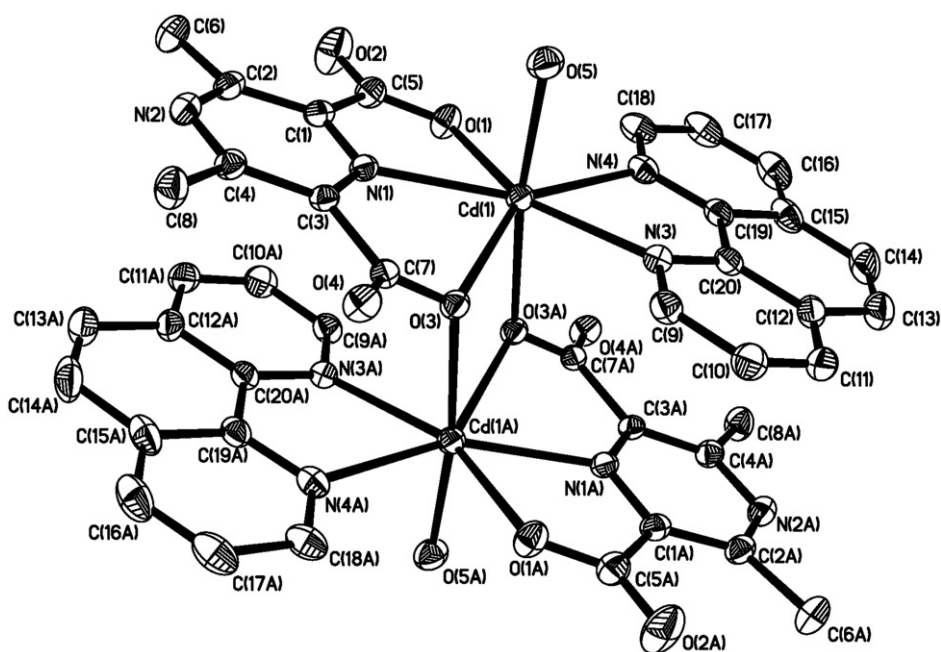


Figure 1. ORTEP representation (30% thermal probability ellipsoids) of **1**.

axial positions are occupied by O(5) and O(3A), so the cadmium(II) is seven-coordinate in a distortion pentagonal bipyramidal configuration. Two Cd(II) centers are linked by carboxylate groups, neighboring complexes are connected to each other via hydrogen bonds along *a* [O(4)⋯O(7) 2.789 Å, O(5)⋯O(7) 2.702 Å and O(1)⋯O(7) 2.853 Å], adjacent chains are linked into a 2D framework via hydrogen bonds with uncoordinated water molecules and oxygen atoms of carboxylic (figure 2). The hydrogen-bonding parameters are reported in table 3. This 2D framework further extends into the final 3D supramolecular structure via π - π stacking interaction of phen rings (edge-to-edge 3.643 Å); the 3D supramolecular structure consists of nanosized channels along *a* axis with dimensions of 12.8 × 8.5 Å (figure 3).

The structurally interesting feature of **1** is that a centrosymmetric water decamer was observed in the crystal, as shown in figure 4. The average O⋯O distance is 2.861 Å, slightly longer than corresponding values in liquid water (2.854 Å) and in ice *I_h* (2.759 Å) [9]. In this decamer, coordinated water and lattice water form a cyclic chair conformation. Atoms O(5) and O(5B) are hydrogen bond donors while O(6), O(6B), O(7), O(7A), O(8), O(8B), O(9) and O(9B) are hydrogen bond donors as well as acceptors. O(5), O(5B), O(7), O(7A), O(9A) and O(9B) show three-coordination, while O(6), O(6B), O(8) and O(8B) show four-coordination; this may be the reason O(6)–O(8) and O(6B)–O(8B) bond lengths are a little longer than the other bonds in this decamer. Theoretical calculations and experiments for decamers [4a, 7a, 10] are fewer than tetramers and hexamers [5, 6]. A recent calculation showed two fused parallel pentamers to be energetically the most stable [10b]. Buck [11] described two decamer structures measured by IR depletion techniques. Atwood *et al.* reported two water decamers (**3**) [10c, 10d]. The structure of the decamer in **1** is different than that in **3**,

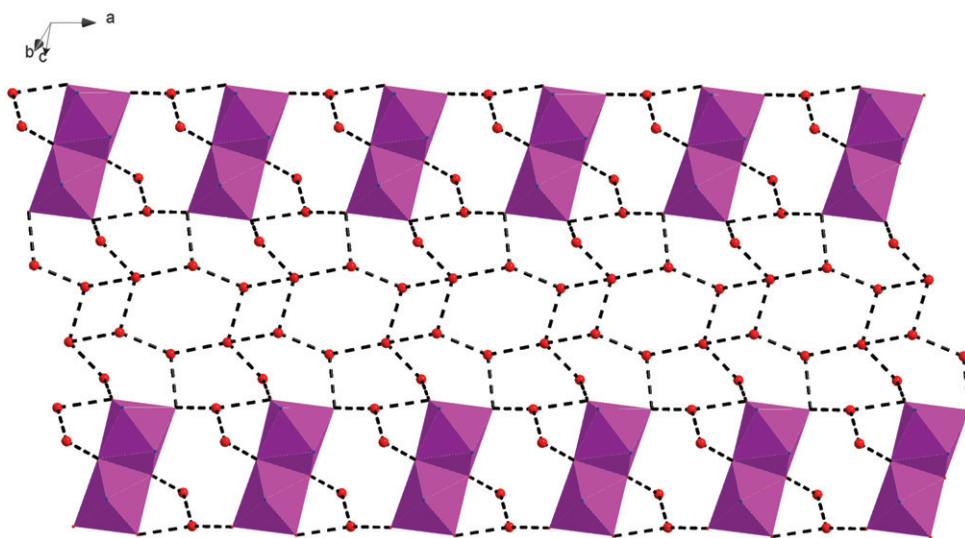


Figure 2. 2-D framework formed by hydrogen-bonding in **1**. (All hydrogen atoms and carbon atoms are omitted for clarity).

Table 3. Hydrogen-bonding parameters in **1**.

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (deg)
O(5)–H(5A)...O(6)	0.850	1.992	157.10	2.795
O(5)–H(5B)...O(7)	0.850	1.858	172.40	2.703
O(6)–H(6D)...O(8)	0.847	2.215	179.50	3.062
O(6)–H(6E)...N(2)#5	0.850	2.157	153.19	2.941
O(7)–H(7A)...O(4)#4	0.850	1.940	176.63	2.789
O(7)–H(7B)...O(1)#3	0.850	2.030	162.52	2.853
O(8)–H(8D)...O(2)#3	0.850	1.999	145.11	2.740
O(8)–H(8E)...O(9)	0.845	2.201	179.59	3.046
O(9)–H(9A)...O(6)#3	0.850	2.026	153.88	2.814
O(9)–H(9B)...O(8)#2	0.851	2.016	178.04	2.866

D = donor atom; A = acceptor atom.

Symmetry code, #1: $-x+2, -y, -z$; #2: $-x+1, -y+1, -z+1$; #3: $x-1, y, z$; #4: $-x+1, -y, -z$; #5: $-x+2, -y+1, -z$.

where $(\text{H}_2\text{O})_{10}$ possesses an adamantane-like structure similar to the smallest subunit of ice I_c . But in **1**, two of the water molecules in the decamer bind to the Cd(II) ions [$\text{Cd}(1)\text{--O}(5)$ 2.313(3) Å], resulting in a novel infinite metal–water chain. Up until now, water clusters containing metal–water chains are very rare [6a, 10d, 10e], such metal–water chains with a binuclear metal seldom reported. The formation of this new conformation should be attributed to the specific surrounding host environment. Complex **1** provides a new crystallographic example of water decamer, and this structure indicated that some water decamers can be stabilized not only by hydrogen bonding but also by coordination interactions.

The coordination environment of metal centers in **2** is shown in figure 4. Zn(II) is coordinated by two nitrogens of phen, two carboxylic oxygen atoms, one nitrogen atom of PDZDA and one oxygen of water as a distorted octahedron. The average Zn–O

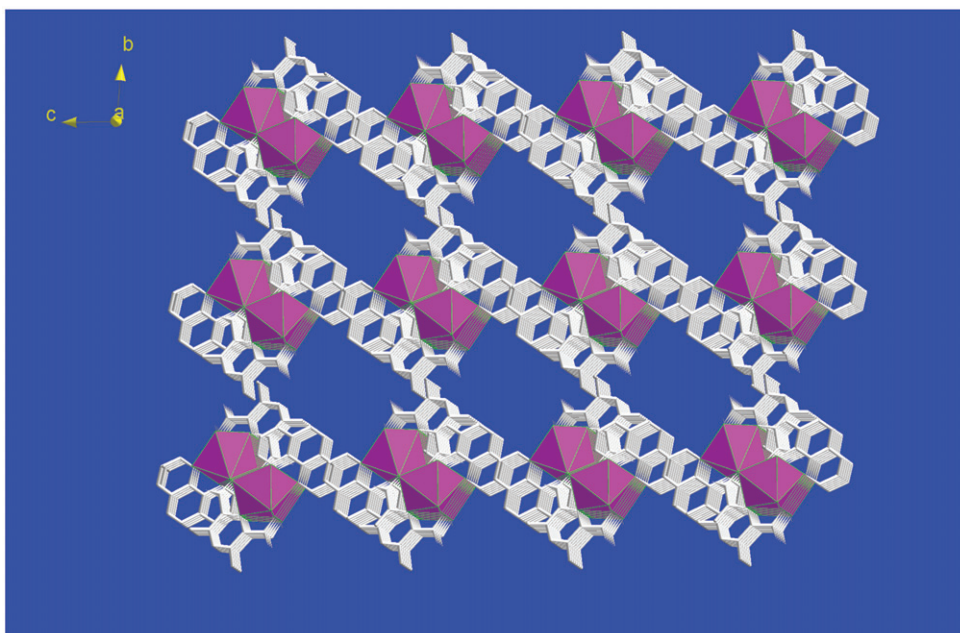


Figure 3. The perspective of 3D structure in **1** with channels (uncoordinated water molecules were omitted for clarity).

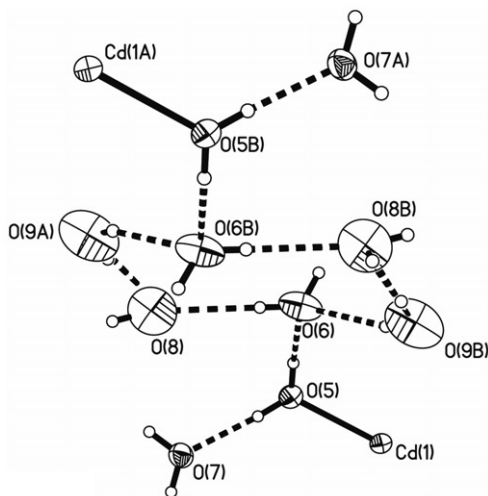


Figure 4. ORTEP plot showing the water decamer and its coordination environment in **1**.

bond length is 2.137 Å and average Zn–N bond distance is 2.125 Å. In the ZnO_3N_3 octahedron N(3), O(1), O(3) and O(5) are equatorial with bond angles as follows: N(1)–Zn(1)–O(1) 74.85°, O(3)–Zn(1)–N(1) 75.22°, O(1)–Zn(1)–N(4) 118.43°, O(3)–Zn(1)–N(4) 91.41°. The sum of these angles is 359.91° (close to 360°), but the bond angle shaped by axial atoms [N(5)–Zn(1)–O(3)] is 163.25°, deviating from 180°.

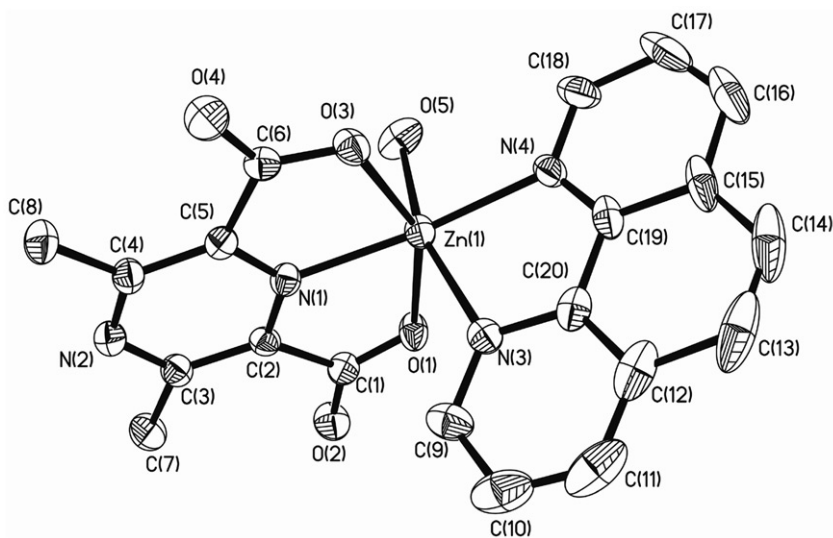


Figure 5. ORTEP representation (30% thermal probability ellipsoids) of **2**.

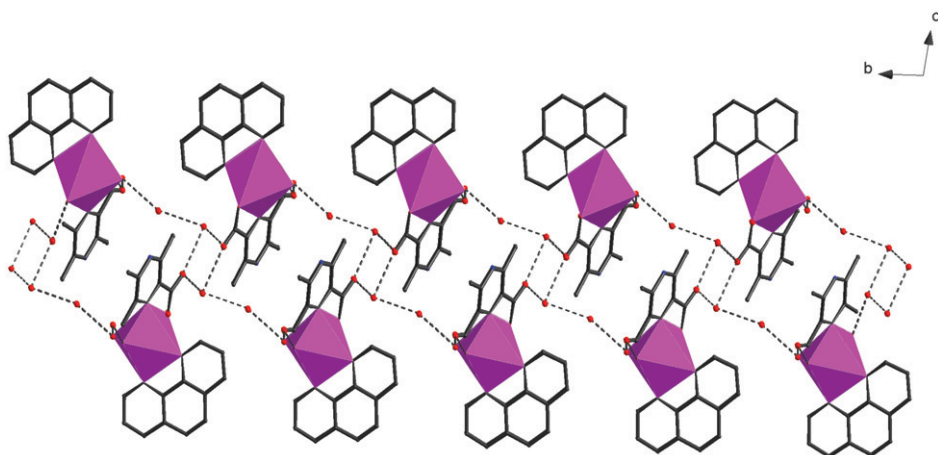


Figure 6. One-dimensional chain constructed by hydrogen bonds in **2**.

Thus, the ZnO_3N_3 octahedron is seriously distorted. The dihedral angle between the least square plane of phen and DPZDA N-hetero ring is 90.9° , indicating that these two planes are perpendicular. The crystalline water molecules locate at one side of the complex and link adjacent complexes via hydrogen bonds [O(5)–O(4) 2.725 Å; O(5)–O(7) 2.685 Å; O(6)–O(7) 2.821 Å; O(6)–O(2) 2.909 Å]. So, a 1D chain could be observed, as shown in figure 6. In addition, O(6) connects with uncoordinated N(2) of PDZDA via weak N–H \cdots O interaction [O(6)–N(2) 2.948 Å; \angle N(2)–H(7) \cdots O(7) is 162.41°] and $\pi\cdots\pi$ stacking interaction between phen rings from adjacent chains could be found with centroid-to-centroid separation of 3.558 Å. The 2D framework

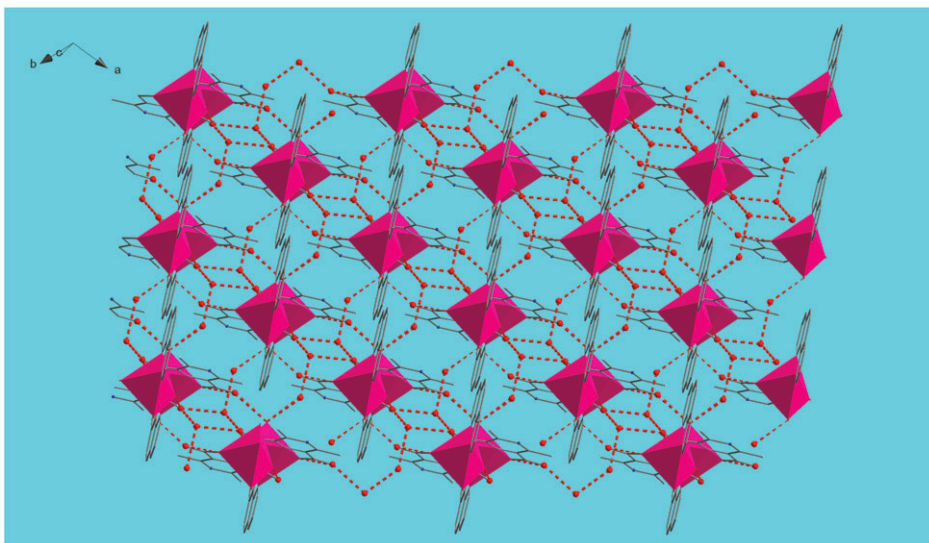


Figure 7. Two-dimensional framework structure based on hydrogen bonds and $\pi \cdots \pi$ stacking interactions in **2**.

structure of **2** is based on hydrogen bonds and $\pi \cdots \pi$ stacking interactions, as revealed in figure 7.

3.2. Thermal analyses

The TG curve of **1** shows that the first weight loss of 15.10% from 90 to 140°C corresponds to the loss of one coordinated water and four uncoordinated water molecules (Calcd: 15.61%). Upon further heating, an obvious weight loss (62.20%) occurs in the temperature range 160–320°C, corresponding to the release of organic ligands (Calcd: 62.13%). After 320°C no further weight loss is observed, indicating complete decomposition of **1**. The residual weight, 21.78% (Calcd: 22.26%), corresponds to CdO. The TG curve of **2** shows the first weight loss of 10.86% from 95 to 130°C, corresponding to loss of coordinated and uncoordinated water molecules (Calcd: 10.94%). An obvious weight loss (72.41%) occurs in the temperature range 130–310°C, corresponding to the release of organic ligands (Calcd: 72.58%). The residual weight, 16.22% (Calcd: 16.48%), corresponds to ZnO.

3.3. Photoluminescent properties

The d^{10} metal compounds have been shown to exhibit interesting photoluminescent properties [12]. The solid-state photoluminescent spectra of **1** and **2** at room temperature are depicted in figure 8. Complexes **1** and **2** exhibit two intense emission maxima at 458 nm and 447 nm in the blue region upon excitation at 353 nm and 362 nm, respectively. In order to understand the photoluminescence of **1** and **2**, we further measured the emission spectrum of the free 3,5-dimethyl-2,6-pyrazinedicarboxylic acid.

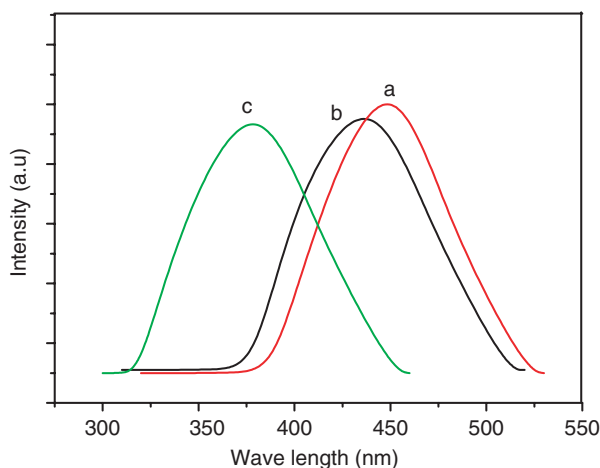


Figure 8. Solid state photoluminescent spectra of **1** (line a), **2** (line b) and free H₂DPZDA (line c) at room temperature.

The 3,5-dimethyl-2,6-pyrazinedicarboxylic acid exhibits a broad emission band maximum at 370 nm upon excitation at 300 nm. According to previous reports [13], emission bands could be assigned to the emission of ligand-to-metal charge transfer (LMCT). This observation indicates that **1** and **2** may be candidates for photoactive materials.

4. Conclusion

In summary, we have synthesized and characterized two new complexes. The solid-state photoluminescent spectra were also studied. Structural analyses reveal that a 2D supramolecular structure was constructed by hydrogen bonds with a metal–water decamer in **1**. This observation could help us understand the formation of water clusters in chemical and biological systems.

Supplementary materials

CCDC: 632418 and 640205 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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