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Hydrothermal Synthesis and Crystal Structure of Three-dimensional Supramolecular Zinc, Manganese Coordination Polymers

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Abstract

Hydrothermal Synthesis and Crystal Structure of Three-dimensional Supramolecular Zinc, Manganese Coordination Polymers

Zhi-Tao Wang · Valentin Valtchev · Qian-Rong Fang · Xiu-Mei Li · Ya-Ru Pan

Two new complexes $[\text{Zn}_2(\text{pzdc})(\text{L})_2(\text{H}_2\text{O})]_{2n} \cdot 2n\text{H}_2\text{O}$ (**1**) and $[\text{Mn}(\mu_2\text{-O})(\text{H}_2\text{O})_2(\text{HL})]_{2n} \cdot 2n\text{NIPH}$ (**2**) (H_2pzdc = pyrazine-2,3-dicarboxylic acid, HL = 3-(2-Pyridyl)pyrazole, H_2NIPH = 5-nitroisophthalic acid) have been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, UV spectrum, TG, fluorescence spectrum and single-crystal X-ray diffraction. Complex **1** shows two-dimensional (2D) network, which was stabilized by O–H···O, C–H···O hydrogen bonding and π - π interactions and extended into 3D supramolecular architecture. Complex **2** is zero-dimensional structure, which was further extended into 3D supramolecular framework through N–H···O, O–H···O, C–H···O hydrogen bonds and π - π interactions.

Keywords hydrothermal synthesis · crystal structure · Zn(II) complex · Mn(II) complex

Introduction

The design and synthesis of metal-organic coordination polymers relied on the selection of ligands and metal ions has become a very attractive research field. This is motivated not only by the intriguing structural diversity but also by the demand of applying functional materials into the fields of catalysis, porosity, magnetism, luminescence and nonlinear optics.^[1-3] In general, grids with various sizes and shapes can be synthesized by choosing suitable single metal ions and organic ligands such as carboxylates and N-donor groups.^[4-6] Self-assembly is a complex process, highly influenced by many factors, such as the coordination geometry of metal ions, the nature of organic ligands, solvent system, temperature, pH value of the solution, the ratio between metal salt and ligand, the templates and the counter anions.^[7-14] Except for these factors, other forces such as hydrogen-bonding, π - π interactions, metal-metal interactions can also greatly influence the supramolecular topology and its dimensionality.^[15-17] Therefore, these considerations made us investigate new coordination structures with pyrazine-2,3-dicarboxylic acid (H₂pzdc), 5-nitroisophthalic acid (H₂NIPH) and chelating ligands. In this manuscript, we reported the syntheses, crystal structures, IR, UV, fluorescence, TG properties of two new complexes, namely, [Zn₂(pzdc)(L)₂(H₂O)]_{2n}·2nH₂O (**1**) and [Mn(μ -O)(H₂O)₂(HL)]_{2n}·2nNIPH (**2**).

Experimental Section

General procedures

All solvents and chemicals were commercial reagents and used without further purification. Elemental analyses (carbon, hydrogen, and nitrogen) were performed with a Vario EL(III) Elemental Analyzer. IR spectrum(4000~400 cm^{-1}) was measured from KBr pellet on a Nicolet 6700 FT-IR spectrometer. TG studies were performed on a Perkin-Elmer TGA7 analyzer. UV spectrum was obtained on a Shimzu UV-250 spectrometer in the 200~400 nm range. The fluorescent studies were carried out on a computer-controlled JY Fluoro-Max-3 spectrometer at room temperature. The crystal structure was determined by a Bruker D8 Venture diffractometer. Power X-ray diffraction (PXRD) patterns were obtained on Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) at room temperature.

Synthesis

$[\text{Zn}_2(\text{pzdc})(\text{L})_2(\text{H}_2\text{O})]_{2n} \cdot 2n\text{H}_2\text{O}$ (**1**): A mixture of H_2pzdc (0.068 g, 0.4 mmol), HL (0.028 g, 0.2 mmol), $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.088 g, 0.4 mmol), and 18 mL H_2O was adjusted to the pH ≈ 6.13 with $0.5 \text{ mol} \cdot \text{L}^{-1}$ NaOH, sealed in a Teflon-lined stainless steel vessel, heated to 160 $^\circ\text{C}$ for five days, and followed by slow cooling (a descent rate of 10 $^\circ\text{C}/\text{h}$) to room temperature. Pale yellow block crystals were obtained. Yield of 32% (based on Zn). Anal. Calcd. For $\text{C}_{44}\text{H}_{32}\text{N}_{16}\text{O}_{11}\text{Zn}_4$: C, 43.23; H, 2.64; N, 18.33. Found C, 42.97; H, 2.15; N, 17.89. IR (cm^{-1}): 3286(w), 2989(w), 1752(m), 1637(m), 1605(m), 1567(w), 1473(w), 1434(w), 1375(m), 1357(m), 1255(w), 1159(w), 1118(w), 1060(w), 1013(m), 890(w), 783(w), 765(w), 636(w), 481(w).

$[\text{Mn}(\mu_2\text{-O})(\text{H}_2\text{O})_2(\text{HL})]_{2n} \cdot 2n\text{NIPH}$ (**2**): A mixture of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.10 g, 0.4 mmol), H_2NIPH (0.084 g, 0.4 mmol), L (0.058 g, 0.4 mmol), and 18 mL H_2O was placed

in a Teflon reactor (30 mL) and the pH value was adjusted to about 7 with 0.5 mol·L⁻¹ NaOH solution. Then the mixture was heated at 140 °C for 7 days. After cooling to room temperature at a rate of 10 °C/h, brown crystals of **1** were collected in 45% yield. Anal. Calcd. for C₃₂H₃₀Mn₂N₈O₁₈ (%):C, 41.57; H, 3.27; N, 12.12. Found (%): 41.36; H, 3.01; N, 11.98. IR (KBr, cm⁻¹): 3413(m), 3102(w), 1630(s), 1606(s), 1583(m), 1533(m), 1495(w), 1443(w), 1334(s), 1101(w), 998(w), 788(w), 720(m), 537(w).

X-ray crystallographic

Single-crystal X-ray diffraction data for **1** and **2** were measured on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 293 K. The structure was solved with the direct method of SHELXS-97 and refined with full-matrix least-squares techniques using the SHELXL-97 program.^{[18,}^{19]} Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were placed at the calculated positions and refined as riding atoms with isotropic displacement parameters. Crystallographic parameters and the data collection statistics for structure **1** and **2** are listed in Table 1. Selected bond lengths and bond angles are shown in Table 2. Further crystallographic parameters have been deposited with the Cambridge Crystallographic Data Centre (no. 1468826 (**1**), 1439401 (**2**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Results and discussion

IR Spectrum

Complex 1: Two bands at 1637 and 1357 cm^{-1} can be attributed to $(\nu(\text{OCO})_{\text{assym}})$ and $(\nu(\text{OCO})_{\text{sym}})$,^[20] respectively. The $\Delta\nu$ ($\nu(\text{OCO})_{\text{assym}} - \nu(\text{OCO})_{\text{sym}}$) is 280 cm^{-1} (>200), exhibiting the presence of monodentate linkage of carboxylates in the dianions. Therefore the carboxylates coordinate to the metal as monodentate ligands via the carboxylate groups.^[21] The absence of the characteristic bands at around 1700 cm^{-1} in complex **1** were owing to the protonated carboxylic group indicates that the complete deprotonation of pzdc ligand upon reaction with Zn ions.^[22] Moreover, X-ray diffraction analysis further attributes the existence of monodentate coordination manners of the carboxylate groups and prence deprotonation of pzdc ligands.

Complex 2: Infrared spectroscopy of complex **2** shows the typical anti-symmetric (1606 cm^{-1}) and symmetric (1334 cm^{-1}) stretching bands of carboxylate groups. The absence of the characteristic band around 1700 cm^{-1} in complex **2** owing to the protonated carboxylic group indicates that the present deprotonation of NIPH ligand. Moreover, the strong and broad band centered at 3413 cm^{-1} for **2** is owing to the H–O–H stretching vibration of water molecule in the light of the known structure.^[23]

Table 1. Crystallographic parameters and summary of data collection for **1** and **2**

Parameter	Complex 1	Complex 2
Empirical formula	C ₄₄ H ₃₂ N ₁₆ O ₁₁ Zn ₄	C ₃₂ H ₃₀ Mn ₂ N ₈ O ₁₈
Fw (g/mol)	1222.34	924.52
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
<i>a</i> [Å]	29.465(2)	7.5193(5)
<i>b</i> [Å]	12.4103(8)	10.7808(6)
<i>c</i> [Å]	14.7059(9)	11.4968(7)
α [°]	90.00	88.3880(10)
β [°]	117.727(2)	86.9260(10)
γ [°]	90.00	85.5920(10)
Volume [Å ³]	4760.1(6)	927.61(10)
Z	8	1
D _c (g/cm ³)	1.706	1.655
GOF	1.014	1.110
Reflns collected/unique	4206/3233	3611/3382
<i>R</i> _{int}	0.0491	0.0100
<i>R</i> 1 [I>2σ(I)]	0.0333	0.0291

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

1			
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Zn(1)-O(1)	2.079(2)	Zn(1)-O(4A)	2.125(2)
Zn(1)-O(5)	1.989(2)	Zn(1)-N(2A)	2.103(2)
Zn(1)-N(8)	2.007(3)	Zn(2)-N(3)	2.180(3)
Zn(2)-N(4)	2.085(3)	Zn(2)-N(5B)	2.063(2)
Zn(2)-N(6)	2.222(3)	Zn(2)-N(7)	2.102(3)
Angle	ω, deg	Angle	ω, deg
O(5)-Zn(1)-N(8)	115.12(12)	O(5)-Zn(1)-O(1)	91.17(9)
N(8)-Zn(1)-O(1)	93.49(10)	O(5)-Zn(1)-N(2A)	137.51(12)
N(8)-Zn(1)-N(2A)	104.72(10)	O(1)-Zn(1)-N(2A)	100.89(9)
O(5)-Zn(1)-O(4A)	84.53(9)	N(8)-Zn(1)-O(4A)	95.62(10)
O(1)-Zn(1)-O(4A)	170.87(10)	N(2A)-Zn(1)-O(4A)	77.25(9)
N(5B)-Zn(2)-N(4)	97.81(10)	N(5B)-Zn(2)-N(7)	92.80(10)
N(4)-Zn(2)-N(7)	169.10(10)	N(5B)-Zn(2)-N(3)	170.90(11)
N(4)-Zn(2)-N(3)	76.88(10)	N(7)-Zn(2)-N(3)	92.91(10)
N(5B)-Zn(2)-N(6)	100.58(11)	N(4)-Zn(2)-N(6)	99.62(10)
N(7)-Zn(2)-N(6)	75.86(11)	N(3)-Zn(2)-N(6)	87.69(10)
2			
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Mn(1)-N(2)	2.2264(14)	Mn(1)-O(8)	2.2376(13)
Mn(1)-N(3)	2.2556(14)	Mn(1)-O(8A)	2.3336(14)
Mn(1)-O(7)	2.1346(14)	Mn(1)-O(9)	2.1469(13)
Angle	ω, deg	Angle	ω, deg
O(7)-Mn(1)-O(9)	89.28(6)	O(7)-Mn(1)-O(8A)	168.77(5)
O(7)-Mn(1)-O(8)	93.40(5)	O(8)-Mn(1)-O(8A)	77.32(5)

O(7)–Mn(1)–N(3)	101.62(6)	O(9)–Mn(1)–N(2)	170.50(6)
O(8)–Mn(1)–N(3)	161.72(5)	N(2)–Mn(1)–O(8)	95.09(5)
N(2)–Mn(1)–O(8A)	94.09(5)	N(2)–Mn(1)–N(3)	73.95(5)
O(7)–Mn(1)–N(2)	93.03(5)	O(9)–Mn(1)–O(8A)	85.12(5)
O(9)–Mn(1)–O(8)	93.97(5)	N(3)–Mn(1)–O(8A)	88.71(5)
O(9)–Mn(1)–N(3)	96.56(5)		

Symmetry codes: **1:** A: $x, 1-y, z-1/2$; B: $-x+3/2, -y+1/2, 1-z$;

2: A: $-x-1, -y+2, -z$.

Description of the Structure

X-ray single-crystal diffraction analysis reveals that **1** crystallizes in the monoclinic system, space group $C2/c$ and features a 2D network structure. The coordination environment of Zn(II) in **1** is displayed in Fig.1. There are two coordination centers, Zn(1) and Zn(2), in the crystal structure. The Zn(1) ion is five-coordinated by two carboxylate oxygen atoms (O(1), O4A)) from two different pzdc ligands, two nitrogen donors (N(2A), N(8)) from pzdc and HL ligands and one coordinated water molecule (O(5)). The Zn(2) ion is also five-coordinated by five nitrogen atoms (N(3), N(4), N(5B), N(6), N(7)). The Zn–O distances fall in the range of 1.989(2)–2.125(2) Å, and Zn–N bond length fall in the 2.007(3)–2.222(3) Å, which are all in the normal ranges and the coordination angles around Zn atom are in the range 75.86(11)–170.90(11)°.

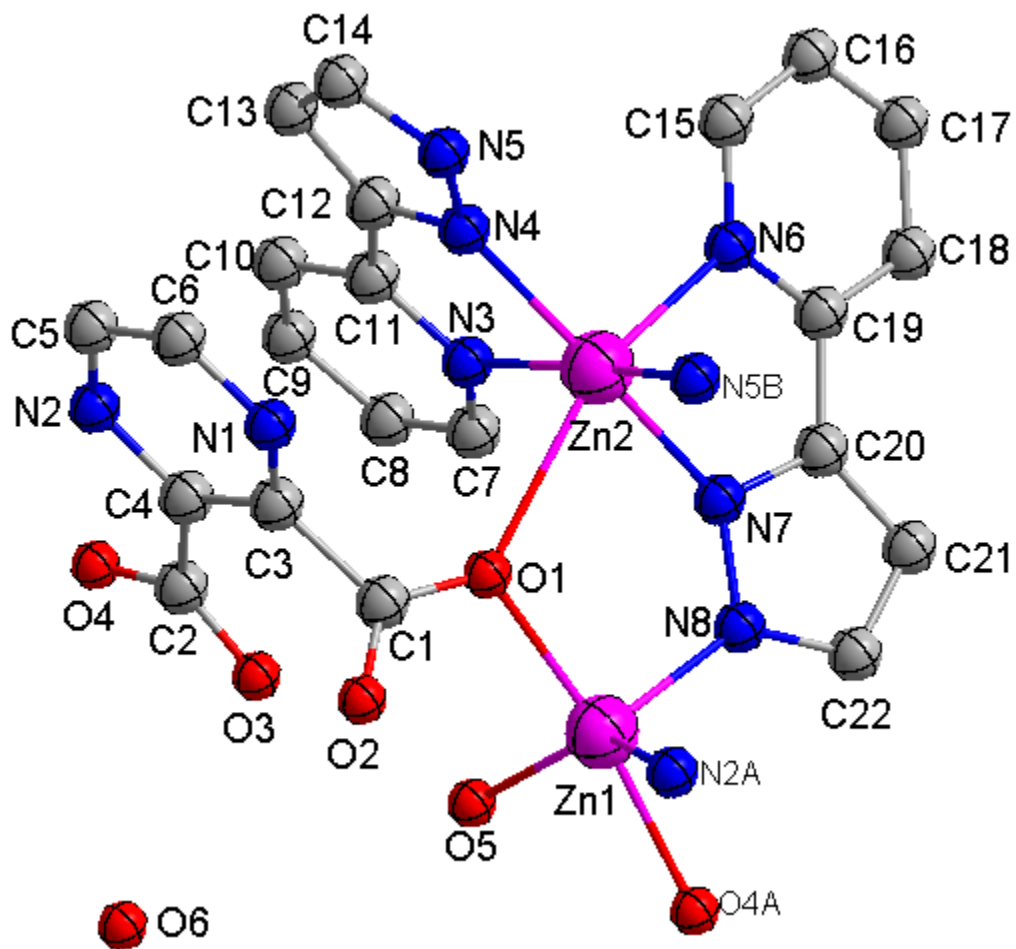


Figure 1. The coordination environment of the Zn(II) center in 1. Symmetry codes: A: $x, 1-y, z-1/2$; B: $-xt3/2, -yt1/2, 1-z$.

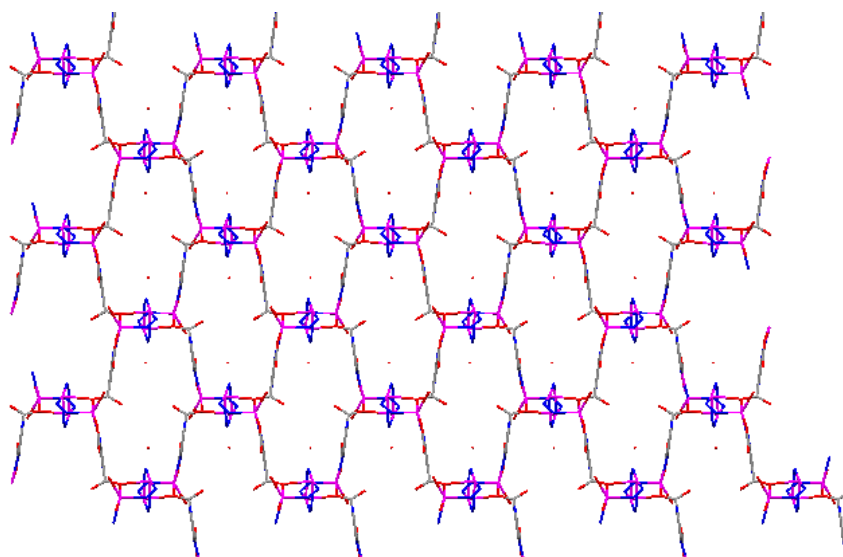


Figure 2. View of the two-dimensional network along a axis (Carbon atoms and one nitrogen atom of HL ligand were omitted for clarity).

In the crystal structure of complex **1**, the HL ligands take μ_3 coordination mode and the completely deprotonated pzdc ligands show one kind of coordination mode, namely, monodentate bridging mode. As a result, two Zn(II) ions are linked by four HL ligand to form dinuclear subunits, which are bridged by pzdc ligands to yield a two-dimensional (2D) network architecture (Fig.2). Each Zn(II) shows a distorted square-pyramidal coordination structure.

It is worth noting that hydrogen bonding interactions are important in the synthesis of supramolecular architecture.^[24] There are existent in O–H···O and C–H···O hydrogen bonding interactions between carboxylate oxygen atom, carbon atoms and coordinated water molecules in complex **1** (Table 3). In addition, there are π - π interactions (Fig.3) in complex **1** between pyrazine ring of pzdc ligand and pyrazole ring of HL ligand. The centroid-to-centroid distance between adjacent ring is 3.456(2) Å for N(4)N(5)C(14)C(13)C(12) and N(1)C(3)C(4)N(2)C(5)C(6) (*x*, *y*, *z*) rings. The perpendicular distance is 3.1530(15) Å for N(4)N(5)C(14)C(13)C(12) and N(1)C(3)C(4)N(2)C(5)C(6) (*x*, *y*, *z*) rings. Thus, the two-dimensional networks are further extended into a three-dimensional supramolecular framework through hydrogen bonds and π - π interactions, which play an important role in stabilizing compound **1**.

Table 3. Hydrogen bonds for complex **1** and **2**

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
1				
O(5)–H(5A)···O(3)	0.85	2.29	2.620(4)	103
O(5)–H(5B)···O(4)	0.85	2.09	2.823(4)	145
C(10)–H(10)···O(2)	0.85(4)	2.42(4)	3.248(5)	164(3)
C(17)–H(17)···O(2)	0.91(5)	2.58(5)	3.317(6)	139(4)
2				
N(1)–H(3)···O(3)	0.98(2)	1.78(2)	2.738(2)	166.6(19)
O(7)–H(4A)···O(4)	0.78(3)	1.91(3)	2.6771(19)	173(2)
O(7)–H(7B)···O(1)	0.84(3)	1.86(3)	2.6920(19)	174(3)
O(8)–H(8A)···O(1)	0.64(2)	1.96(2)	2.5962(18)	173(2)
O(9)–H(9B)···O(2)	0.87 (3)	1.78(3)	2.6418(19)	169(3)
C(1)–H(1A)···O(2)	0.92(2)	2.46(2)	3.372(2)	169.1(19)
C(5)–H(5)···O(5)	1.09(3)	2.35(3)	3.430(3)	171(2)
C(6)–H(6)···O(4)	0.96(3)	2.37(3)	3.324(3)	173(3)
C(7)–H(7)···O(6)	0.91(2)	2.53(2)	3.194(3)	130.9(18)

Complex **2** crystallizes in the triclinic system, space group *P*-1 and features a zero-dimensional structure. The coordination environment of Mn(II) in **2** is displayed in Fig.4. There are two Mn(II) ion, two NIPH ligand, two HL ligand, four coordinated water

molecule and two μ_2 -O atoms in the molecular structure. Each Mn(II) ion is six-coordinated by two coordinated water molecules (O(7), O(9)), two μ_2 -O atoms (O(8), O(8A)) and two nitrogen donors (N(2) and N(3)) from HL ligand to supply a distorted octahedral coordination structure. One coordinated water molecule (O(9)), one μ_2 -O atom (O(8)) and two nitrogen atoms (N(2), N(3)) define an equatorial plane, whereas the axial coordination sites are employed by the other coordinated water molecule (O(7)) and μ_2 -O atom (O(8A)). The Mn–O distances fall in the range of 2.1346(14)~2.3336(14) Å, and Mn–N bond length fall in the 2.2264(14)~2.2556(14) Å, which are all in the normal range and the coordination angles around Mn(II) ion are in the range of 73.95(5)°~168.77(5)°.

In **2**, the HL ligand adopts classic chelating mode, while NIPH ligand was not involved in coordination, which just play a role of balance charge. Two Mn(II) ions are linked by two μ_2 -O atoms to form dinuclear subunits, and exhibits zero-dimensional structure. Further study of the crystal packing of complex **2** suggests that there are three kinds of N–H···O, O–H···O and C–H···O hydrogen bonding interactions between nitrogen atom of HL ligand, carboxylate oxygen atoms of NIPH ligand, coordinated water molecule and carbon atoms of HL and NIPH ligands (Table 3). Moreover, In complex **2**, 5-member ring of HL and 6-member ring of NIPH ligand centroid distances are 3.6879(10) Å for N(1)N(2)C(3)C(2)C(1) and C(9)C(10)C(11)C(12)C(13) C(14) rings (x , y , z), with the vertical distance to be 3.2664(7) Å, indicating the existence of π - π effect, so that the structure is more stable. Therefore, a three-dimensional supramolecular network structure is formed by such hydrogen bonds and π - π stacking (Fig.5).

In order to check the purity of polymer **1** and **2**, powder X-ray diffraction of the as-synthesized sample were measured at room temperature (Fig.S1). The peak positions of experimental patterns are in good agreement with the simulated ones, which clearly indicates good purity of **1** and **2**.^[25, 26]

Thermal analysis

The thermal stability of complex **1** was tested in the range of 50~700 °C under a nitrogen atmosphere at a heating rate of 5 °C·min⁻¹. The TGA curve of complex **1** is shown in Fig.S2. It displays that the first weight loss of 49.5% from 60 to 192 °C corresponds to the release of water molecules and HL ligand (calcd:50.0%). Upon further heating, an obvious weight loss (26.2%) occurs in the temperature range of 192~525 °C, corresponding to the removal of pzdc ligands (calcd: 27.1%). After 525 °C no weight loss is found, which indicates the complete decomposition of **1**.

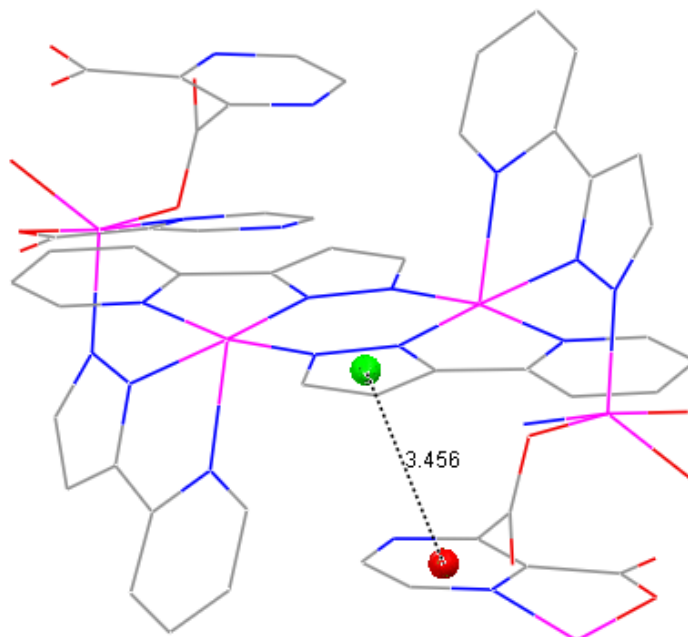


Figure 3. A view of p-p stacking interactions in complex **1**.

Photoluminescent properties

The emission spectrum of complex **1** in the solid state at room temperature is displayed in Fig.6. It can be reviewed that complex **1** shows blue photoluminescence with an emission maximum at *ca.* 460 nm upon excitation at 375 nm. By way of studying the nature of these emission bands, we first investigated the photoluminescence properties of free pyrazine-2,3-dicarboxylic acid, and indicated that it does not emit any luminescence in the range of 400~800 nm. And then we discussed the emission spectrum of HL itself and the result confirmed that it does not emit any luminescence in the range 400~800 nm, which has also been proved previously.^[27] Therefore, on the basis of previous literature,^[28] the emission band could be assigned to the emission of ligand-to-metal charge transfer (LMCT). For possessing strong fluorescent intensity, it appears to be good candidates for novel hybrid inorganic-organic photoactive materials.

UV Spectrum Analysis

The UV spectra for complex **2** (Fig.7), H₂NIPH and HL ligands have been studied in the solid state. For H₂NIPH and HL ligands, there are 277 and 245 nm absorption bands, respectively, while 275 nm for complex **2**, which should be assigned to the $n \rightarrow \pi^*$ ^[29-32] transition of HL ligand in **2**. However, upon ligand coordination to Mn²⁺ ion, the absorption intensity increases.

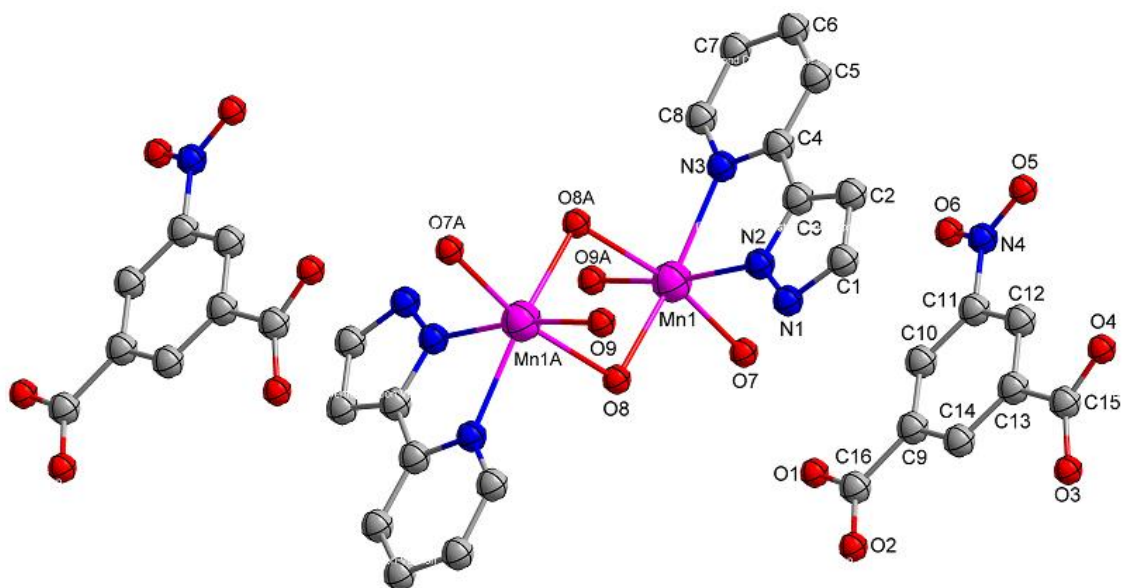


Figure 4. The molecular structure of complex 2. Symmetry codes: A: $-x-1, -y+2, -z$.

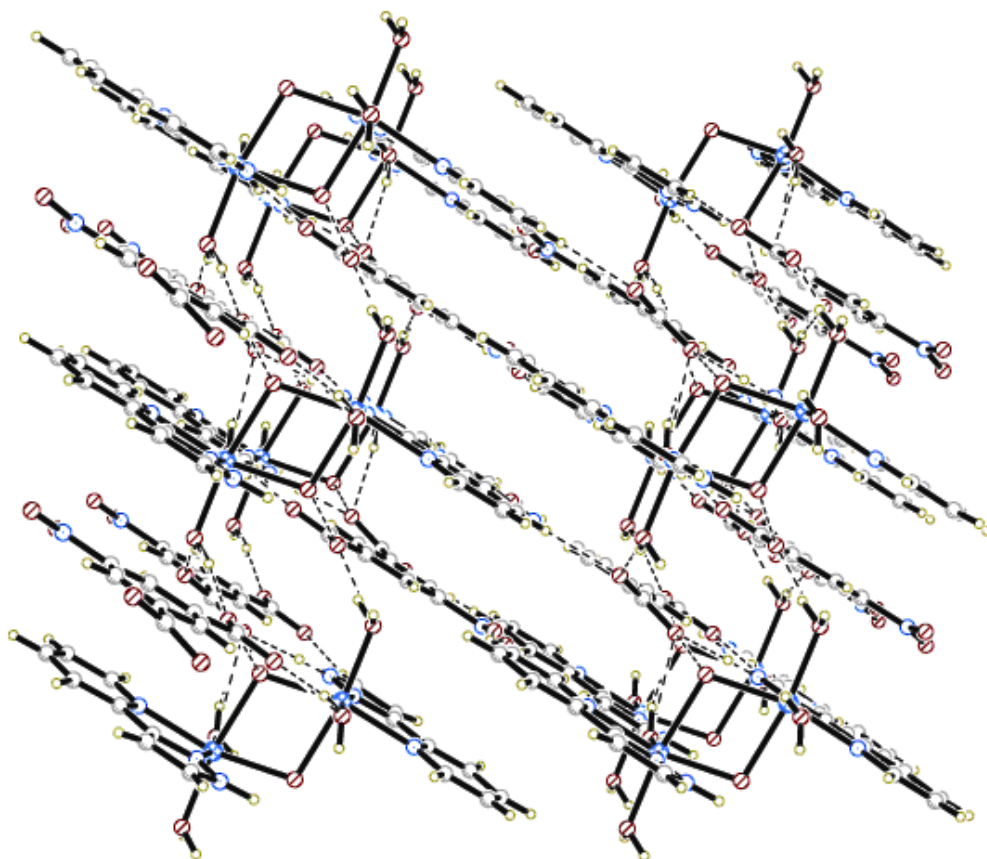


Figure 5. View of the 3D supramolecular architecture of 2 formed by hydrogen-bonding and π - π interactions.

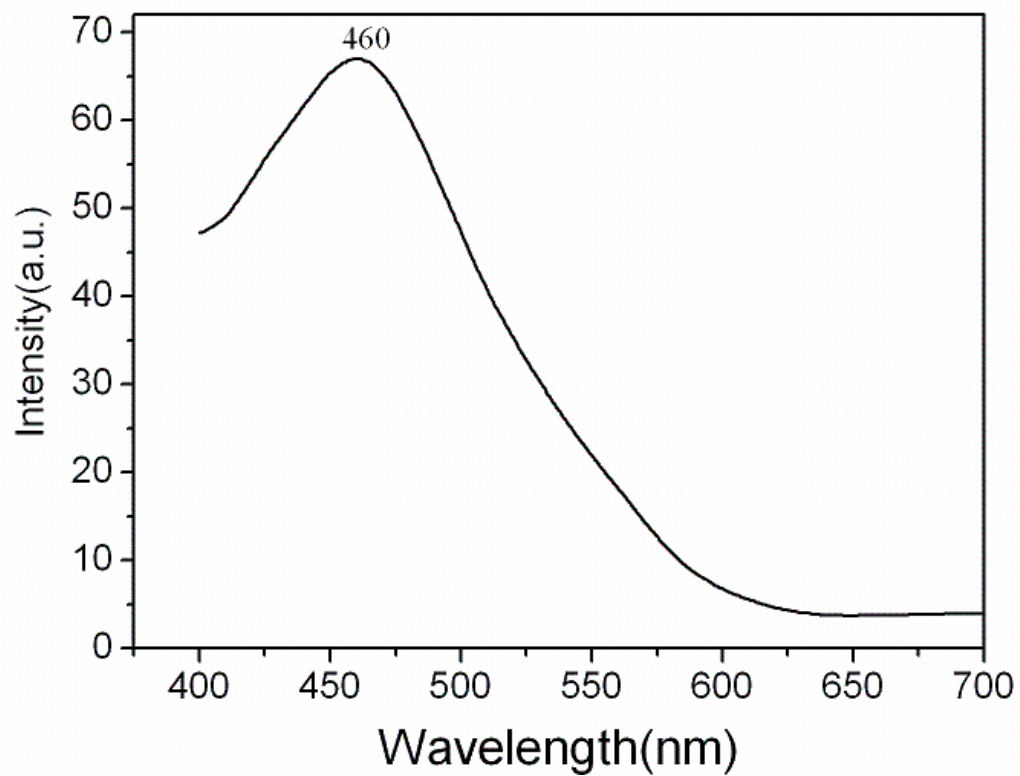


Figure 6. Solid-state emission spectrum of 1 at room temperature.

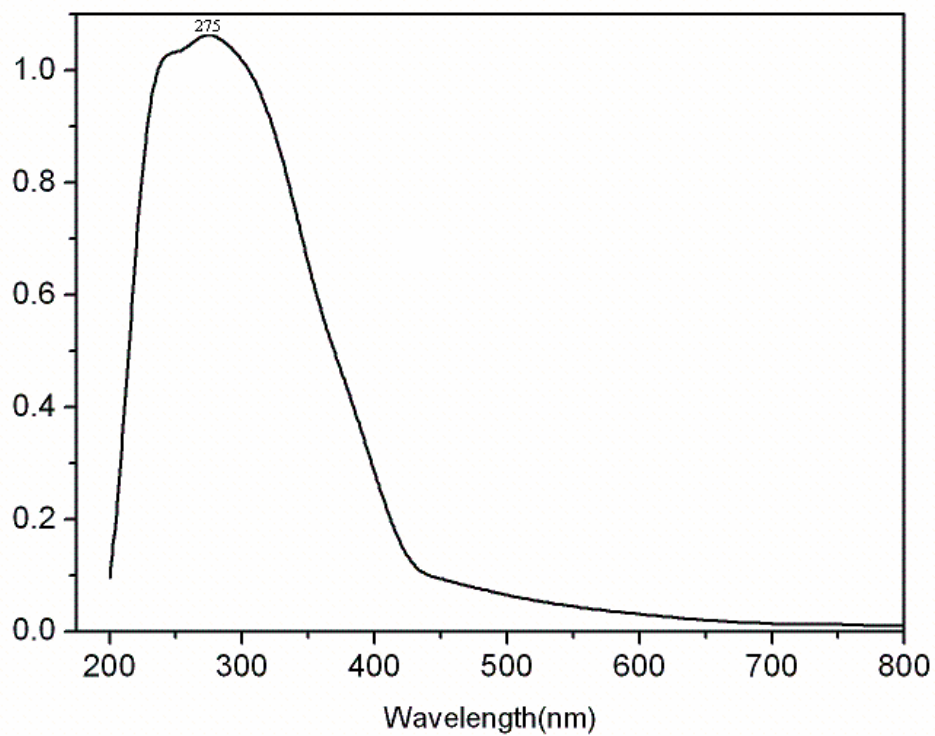


Figure 7. The UV spectrum of 2 at room temperature.

Conclusions

In general, we have described two new supramolecular zinc, manganese coordination polymers. In **1**, the pyrazine-2,3-dicarboxylate ligands function in monodentate bridging coordination mode, the HL ligands take μ_3 coordination mode. As a result, two Zn(II) ions are linked by four HL ligand to yield dinuclear subunits, which are bridged by pzdc ligands to form a two-dimensional network structure. In **2**, the HL ligand takes classic chelating mode, while NIPH ligand was not involved in coordination, which just play a role of balance charge. Two Mn(II) ions are linked by two μ_2 -O atoms to form dinuclear subunits, and exhibits zero-dimensional structure. It is worthy to note that the intermolecular hydrogen bonds and π - π interactions play an important role in the supramolecular structure and extended complex **1** and **2** into 3D supramolecular framework.

Acknowledgments

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Figure captions:

Fig. 1. The coordination environment of the Zn(II) center in **1**. Symmetry codes: A: $x, 1-y, z-1/2$; B: $-x+3/2, -y+1/2, 1-z$.

Fig. 2. View of the two-dimensional network along a axis (Carbon atoms and one nitrogen atom of HL ligand were omitted for clarity).

Fig. 3. A view of π - π stacking interactions in complex **1**

Fig. 4. The molecular structure of complex **2**. Symmetry codes: A: $-x-1, -y+2, -z$.

Fig. 5. View of the 3D supramolecular architecture of **2** formed by hydrogen-bonding and π - π interactions.

Fig. 6. Solid-state emission spectrum of **1** at room temperature

Fig. 7. The UV spectrum of **2** at room temperature

Table 1. Crystallographic parameters and summary of data collection for **1** and **2**

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

Table 3. Hydrogen bonds for complex **1** and **2**

Supporting information:

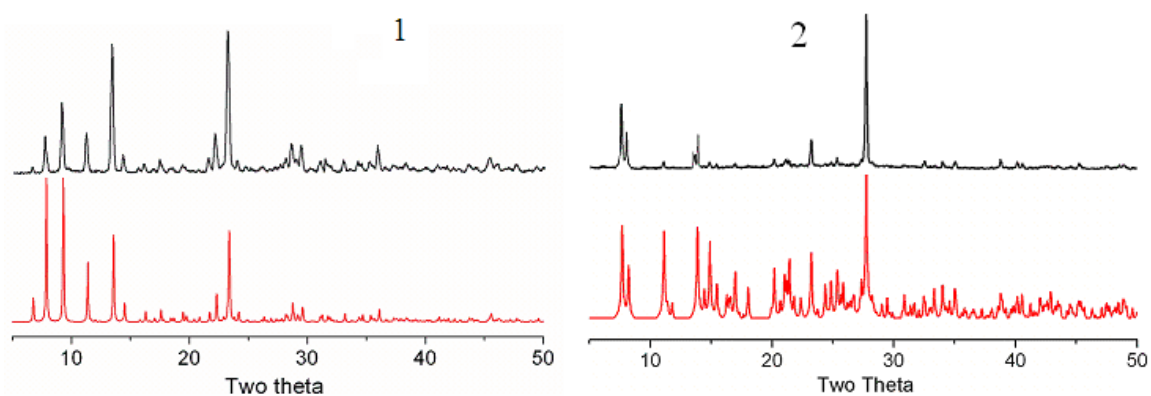


Figure S1. Powder X-ray diffraction of the as-synthesized sample.

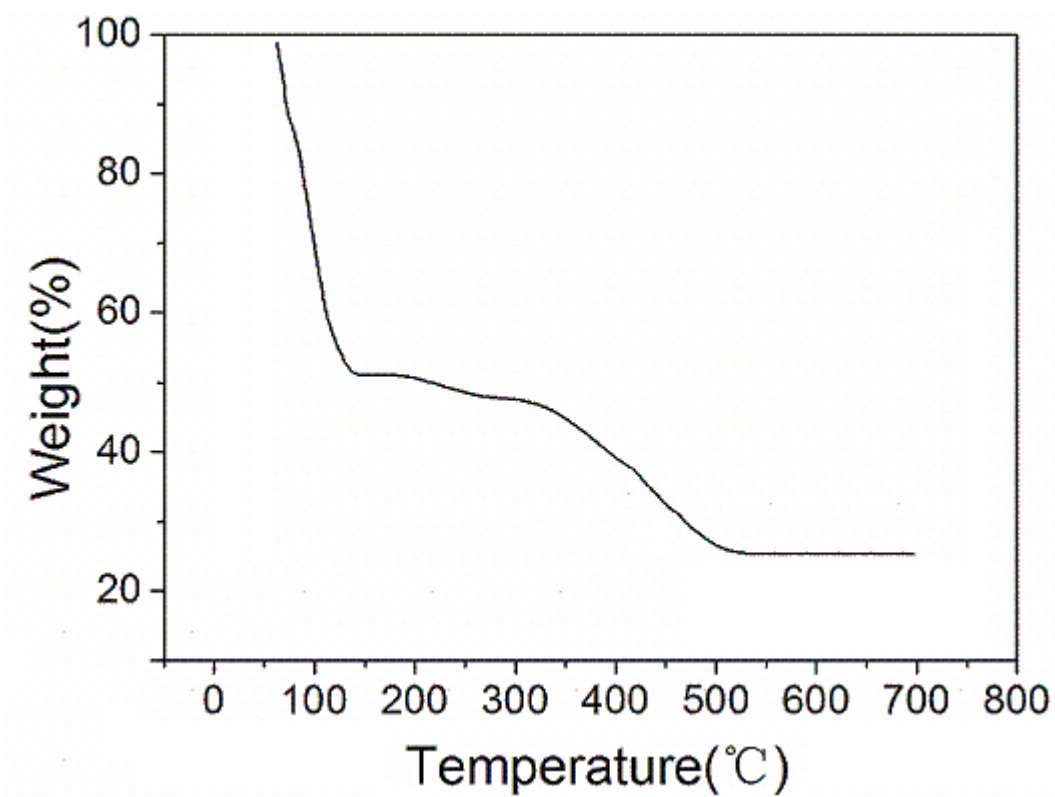


Figure S2. the TGA curve of complex 1.