

## 以 5-甲基-3-吡唑甲酸和菲咯啉为配体的锰和镉的 配合物的合成、晶体结构和荧光性能

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**摘要:** 以 5-甲基-3-吡唑甲酸和菲咯啉为配体, 合成了一个单核锰(II)配合物  $[\text{Mn}(\text{HMPCA})_2(\text{phen})] \cdot 2\text{H}_2\text{O}$  (**1**) 和一个具有双核结构单元的一维镉(II)的配位聚合物  $[\text{Cd}_2(\text{HMPCA})_2(\text{phen})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (**2**) ( $\text{H}_2\text{MPCA}$ =5-甲基-3-吡唑甲酸, phen=菲咯啉), 并用元素分析、红外光谱、X-射线单晶衍射结构分析、热重分析等对其进行了表征。配合物 **1** 属于三斜晶系, 空间群为  $P\bar{1}$ , 配合物 **2** 属于正交晶系, 空间群为  $Pccn$ 。配合物 **1** 中的锰(II)离子位于一个畸变的八面体配位环境中, 独立结构单元间通过分子间氢键作用构成一个三维的超分子结构。而在 **2** 中, 每个镉(II)离子位于一个五角双锥体中, 来自 5-甲基-3-吡唑甲酸根的氧原子桥联 2 个相邻的镉(II)离子, 形成一个一维链; 这些一维链和水分子通过分子间氢键进一步形成一个三维的超分子结构。考察了配合物 **1** 和 **2** 的热稳定性和荧光性能。

**关键词:** 锰; 镉; 5-甲基-3-吡唑甲酸; 菲咯啉; 晶体结构; 荧光

中图分类号: O614.71\*1; O614.24\*2

文献标识码: A

文章编号: 1001-4861(2015)07-1409-08

DOI: 10.11862/CJIC.2015.193

## Syntheses, Crystal Structures and Luminescent Properties of Manganese and Cadmium Complexes Based on 5-Methyl-1*H*-Pyrazole-3-Carboxylic Acid and Phenanthroline Ligands

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**Abstract:** One monomeric complex  $[\text{Mn}(\text{HMPCA})_2(\text{phen})] \cdot 2\text{H}_2\text{O}$  (**1**) and one 1D coordination polymer  $[\text{Cd}_2(\text{HMPCA})_2(\text{phen})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (**2**) with binuclear structural unit ( $\text{H}_2\text{MPCA}$ =5-methyl-1*H*-pyrazole-3-carboxylic acid, phen=phenanthroline) have been synthesized and characterized by elemental analysis, IR spectra, thermogravimetric analysis and single crystal X-ray diffraction. Complex **1** crystallizes in the triclinic system, space group  $P\bar{1}$ , while **2** in the orthorhombic system, space group  $Pccn$ . In **1**, Mn(II) ion located in a distorted octahedral coordination geometry, discrete water molecules and mononucleate units are assembled into a 3D supramolecular network. In **2**, each Cd(II) ion located in a pentagonal bipyramid geometry. Each carboxyl group from HMPA<sup>-</sup> anion bridges two adjacent Cd(II) ions, forming a 1D chain. These chains and water molecules are connected by hydrogen bonds, forming a 3D supramolecular framework. The thermal stability and luminescent properties of them are also investigated. CCDC: 1044243, **1**; 1044244, **2**.

**Key words:** manganese(II); cadmium(II); 5-methyl-1*H*-pyrazole-3-carboxylic acid; crystal structure; photoluminescence

收稿日期: 2015-01-28。收修稿日期: 2015-05-13。

国家自然科学基金(No.20971060, 21101018), 南京大学配位化学国家重点实验室开放课题资助项目。

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The design and synthesis of novel supramolecular frameworks and coordination polymers have received considerable attention due to their topologically diverse structures<sup>[1-2]</sup>, and potential applications in gas storage and separation<sup>[3-6]</sup>, catalysis<sup>[7-8]</sup>, sensors<sup>[9]</sup>, lithium-ion batteries<sup>[10-13]</sup>, magnetic and optical properties, etc<sup>[14-16]</sup>. Synthesis of supramolecular frameworks and coordination polymers through self-assembly is a complicated process, highly influenced by a lot of factors, such as the coordination geometry of metal ions, the nature of organic ligands, the ratio between metal salt and ligand, solvent system, pH value of the solution, temperature, the templates and the counter anions. Without a doubt, among these factors, the rational design and reasonable use of the characteristic ligand occupies the capital, because the slight change of the ligands, such as symmetry, flexibility, and the number of coordinated atoms, may result in dramatic differences in structures and properties<sup>[17]</sup>. The previous work of us and other research groups has indicated that the 5-methyl-1*H*-pyrazole-3-carboxylic acid (H<sub>2</sub>MPCA) ligand has multiple coordination sites, such as Npyrazole and Ocarboxylic acid, and have both bridging and chelating coordination modes to bind metal centers<sup>[18-22]</sup>. Moreover, phenanthroline (phen) is a good candidate for molecular building blocks<sup>[23]</sup>. But, the complexes containing H<sub>2</sub>MPCA and phen have been rarely documented to date<sup>[24]</sup>. As the continuation of our research, and motivated by our interest in functional metal complexes<sup>[25-30]</sup>, we carried out the reactions of H<sub>2</sub>MPCA, phen and corresponding metal salts in different conditions, and isolated two new complexes, namely [Mn(HMPCA)<sub>2</sub>(phen)]·2H<sub>2</sub>O (**1**) with mononuclear structure and a [Cd<sub>2</sub>(HMPCA)<sub>2</sub>(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (**2**) with 1D structure. Herein, we report the syntheses, crystal structures of **1** and **2**. In addition, IR spectra, thermal decomposition and fluorescence property of them will be discussed.

## 1 Experimental

### 1.1 Materials and methods

All chemicals for synthesis were purchased commercially and were used as received unless

otherwise noted. 5-methyl-1*H*-pyrazole-3-carboxylic acid (H<sub>2</sub>MPCA) was synthesized and purified according to the modified literature method<sup>[31]</sup>. The elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 Series II element analyzer. FTIR spectra were recorded on a Nicolet 460 spectrophotometer in the form of KBr pellets. Single-crystal X-ray diffraction measurement of the compounds were carried out with a Bruker Apex II CCD diffractometer. Thermogravimetric analysis (TGA) experiments were carried out on a Dupont thermal analyzer with a heating rate of 10°C·min<sup>-1</sup> under N<sub>2</sub> atmosphere. The luminescent spectra of the solid samples were recorded with a Varian Cary Eclipse spectrometer.

### 1.2 Synthesis

#### 1.2.1 Synthesis of [Mn(HMPCA)<sub>2</sub>(phen)]·2H<sub>2</sub>O (**1**)

To a solution containing H<sub>2</sub>MPCA (0.025 2 g, 0.2 mmol) and imidazole (0.017 0 g, 0.25 mmol) and phen (0.039 6 g, 0.2 mmol) in EtOH (5 mL) was added a solution of Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.049 0 g, 0.2 mmol) in water (5 mL). The resulting solution was stirred for one hour and allowed to stand at room temperature for three months. Yellow block crystals suitable for X-ray diffraction analysis were obtained. Anal. Calcd. for C<sub>22</sub>H<sub>22</sub>MnN<sub>6</sub>O<sub>6</sub>(%): C, 50.63; H, 4.22; N, 16.11. Found (%): C, 50.14; H, 4.55; N, 15.76. IR (KBr, cm<sup>-1</sup>): 3 349 (w), 3 190 (w), 3 129 (w), 3 141 (w), 3 102 (w), 3 060 (m), 2 933 (w), 2 849 (w), 2 602 (w), 1 964 (w), 1 814 (w), 1 679 (s), 1 573 (s), 1 515 (m), 1 493 (m), 1 470 (w), 1 449 (w), 1 419 (s), 1 379 (m), 1 344 (s), 1 330 (m), 1 306 (w), 1 286 (s), 1 220 (w), 1 196 (w), 1 179 (m), 1 144 (w), 1 119 (w), 1 100 (m), 1 091 (w), 1 025 (s), 1 012 (s), 982 (w), 864 (m), 847 (vs), 829 (s), 793 (m), 773 (m), 727 (vs), 684 (m), 651 (w), 639 (m), 544 (m), 508 (w), 474 (w), 439 (m), 420 (m).

#### 1.2.2 Synthesis of [Cd<sub>2</sub>(HMPCA)<sub>2</sub>(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O (**2**)

To a solution containing H<sub>2</sub>MPCA (0.012 6 g, 0.1 mmol) and phen (0.019 8 g, 0.1 mmol) in EtOH (3 mL) was added a solution of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.030 8 g, 0.10 mmol) in water (3 mL). The resulting solution was stirred for 30 minutes and transferred to a Teflon-lined stainless steel vessel for 72 hours with a

temperature of 120 °C. Then the resulting solution was allowed to stand at room temperature for two weeks. Yellow block crystals suitable for X-ray diffraction analysis were obtained. Anal. Calcd. for  $C_{34}H_{32}Cd_2N_8O_8$  (%): C, 45.05; H, 3.53; N, 12.37. Found(%): C, 44.85; H, 3.15; N, 12.46. IR (KBr,  $cm^{-1}$ ): 3 442(s, br), 3 134(s), 1 615(s), 1 613(vs), 1 432(s), 1 431(s), 1 383(s), 1 344(s), 1 031(s), 1 003(m), 748(m).

### 1.3 X-ray crystallography

Single-crystal X-ray diffraction measurements of **1** and **2** were carried out with a Bruker Smart Apex II CCD diffractometer at 293(2) K and 291(2) K. Intensities of reflections were measured using graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073\ nm$ ) with the  $\varphi$ - $\omega$  scans mode in the range of  $1.38^\circ\sim25.50^\circ$  (for **1**) and  $2.34^\circ\sim27.68^\circ$  (for **2**). The structures were solved by direct methods using SHELXS-97<sup>[32]</sup> computer

program and refined by full-matrix least-squares methods on  $F^2$  with the SHELXL-97 program package. Anisotropic thermal factors were assigned to all the non-hydrogen atoms. Hydrogen atoms were included in calculated position and refined with isotropic thermal parameters riding on the parent atoms. H atoms bonded to O or N were located in difference Fourier maps. Crystallographic data parameters for structural analyses are summarized in Table 1.

CCDC: 1044243, **1**; 1044244, **2**.

## 2 Results and discussion

### 2.1 Synthesis and IR spectrum

Complex **1** can be obtained by slow evaporation of a mixed solution of EtOH and deionized water of  $Mn(OAC)_2\cdot4H_2O/H_2MPCA/phen/imidazole$  with molar ratios of 1:1:1:1.25. Imidazole molecule is not included

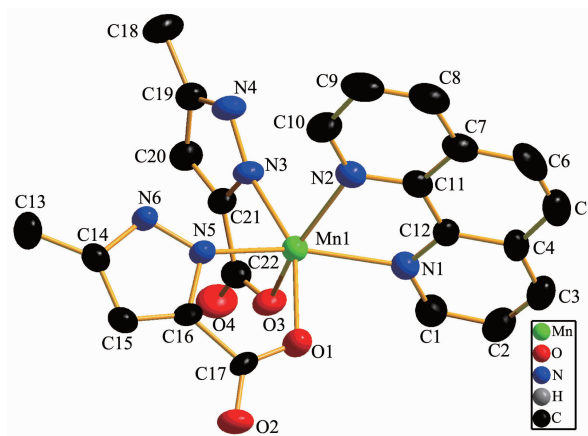
Table 1 Crystal structure parameters of the compounds **1** and **2**

Compound	<b>1</b>	<b>2</b>
Empirical formula	$C_{22}H_{22}MnN_6O_6$	$C_{34}H_{32}Cd_2N_8O_8$
Formula weight	521.4	905.48
Color	Yellow	Yellow
Crystal size / mm	0.26×0.20×0.20	0.28×0.26×0.24
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pccn$
$a$ / nm	0.846 94(14)	2.086 4(8)
$b$ / nm	0.965 61(16)	2.355 8(9)
$c$ / nm	1.512 5(3)	1.635 7(6)
$\alpha$ / (°)	78.229(4)	90
$\beta$ / (°)	80.988(3)	90
$\gamma$ / (°)	74.308(3)	90
$V$ / nm <sup>3</sup>	1.159(4)	8.040(5)
$Z$	2	8
$D_c$ / (g·cm <sup>-3</sup> )	1.494	1.496
$\mu$ / mm <sup>-1</sup>	0.621	1.113
Index ranges ( $h, k, l$ )	-9~10, -10~11, -17~18	-21~25, -22~29, -20~19
$F(000)$	538	3 616
$\theta$ range for data collection / (°)	1.38~25.50	2.34~27.68
Reflections collected	6 517	7 888
Independent reflections ( $R_{int}$ )	4 220 (0.022 8)	5 068 (0.046 9)
Data / restraints / parameters	4 220 / 8 / 319	7 888 / 0 / 486
Goodness-of-fit on $F^2$	1.116	1.041
$R_1, wR_2$ ( $I>2\sigma(I)$ )	0.064 7, 0.237 2	0.055 7, 0.136 4
$R_1, wR_2$ (all data)	0.079 3, 0.269 5	0.075 4, 0.139 9
Largest diff. peak and hole / (e·nm <sup>-3</sup> )	800 and -810	148 and -641

in **1**, indicating it may play a role of base/template. Under same solvent system, when the molar ratio of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}/\text{H}_2\text{MPCA}/\text{phen}$  was 1:1:1, complex **2** was obtained via slow evaporation of the resulting solution obtained by solvothermal reaction. The IR spectra of complexes **1** and **2** reflect the binding patterns of phen and  $\text{H}_2\text{MPCA}$  (see Supplementary materials Fig.S1 and S2). The strong and broad absorption band around  $3\,000\sim3\,600\text{ cm}^{-1}$  region is assigned as characteristic peak of OH vibration, indicating that water molecules exist in the complexes. The absorption peak between  $1\,690\text{ cm}^{-1}$  and  $1\,730\text{ cm}^{-1}$  is not observed, showing all carboxylic groups are deprotonated. The strong peaks at  $1\,679$  (**1**),  $1\,613\text{ cm}^{-1}$  (**2**) and  $1\,379$  (**1**),  $1\,383\text{ cm}^{-1}$  (**2**) are the  $\nu_{\text{as}}(\text{COO}^-)$ , and  $\nu_{\text{s}}(\text{COO}^-)$  stretching mode of the coordinated  $\text{HMPCA}^-$  ligand, respectively. The difference of  $300$  (**1**),  $230\text{ cm}^{-1}$  (**2**) between  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  indicates that  $\text{HMPCA}^-$  ligand adopt monodentate coordination<sup>[33-35]</sup>. While bands assigned to the conjugated  $\text{C}=\text{N}$  stretching vibrations appear at  $1\,573\sim1\,330\text{ cm}^{-1}$ . These assignments are consistent with the X-ray crystal structures of the complexes.

## 2.2 Crystal structures of **1** and **2**

X-ray crystal structure analysis reveals that **1** crystallizes in the triclinic system space group  $P\bar{1}$ . The asymmetric unit of **1** contains one Mn(II) ion, two  $\text{HMPCA}^-$  anions, one phen, two free water molecules. As illustrated in Fig.1, the coordination sphere of Mn(II) is defined by two carboxylic oxygen atoms (O(1), O(3)), two nitrogen atoms (N(1), N(5)) from two  $\text{HMPCA}^-$  anions, and two nitrogen atoms (N(2), N(3)) from one phen ligand, leading to a distorted octahedral geometry. The equatorial position are occupied by N(1), N(3), N(5), and O(1) atoms, O(3) and N(2) atoms are located in the axial positions, and the bond angles of O(3)-Mn(1)-N(2), N(3)-Mn(1)-O(1) are  $157.30(18)^\circ$ , and  $154.00(17)^\circ$  respectively, deviating from  $180^\circ$  (Table 2). The bond distances of Mn(1)-N and Mn(1)-O are in the range of  $0.226\,5(4)\sim0.228\,3(5)\text{ nm}$ , and  $0.213\,4(4)\sim0.218\,0(4)\text{ nm}$ , respectively, which are close to the values observed in other Mn(II) complexes based pyrazole derivative ligands<sup>[24]</sup>.



Hydrogen atoms and solvent molecules were omitted for clarity

Fig.1 Coordination environment of Mn(II) ion in **1** with thermal ellipsoid at 50% probability level

Independent components  $[\text{Mn}(\text{HMPCA})_2(\text{phen})]$  and  $\text{H}_2\text{O}$  are linked by three kinds of hydrogen bonds ( $\text{O}-\text{H}\cdots\text{O}$ ,  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{O}$ ) (Table 3), as shown in Fig.2, resulting in the production of a three dimensional supramolecular framework. It is worth to note that complex **1** has same molecular formula with  $[\text{Mn}(\text{HMPCA})_2(\text{phen})] \cdot 2\text{H}_2\text{O}$  reported by us recently<sup>[24]</sup>, but they have different crystal system, space group, cell parameters and network superstructures et al, so they are two true supramolecular isomers<sup>[36-38]</sup>.

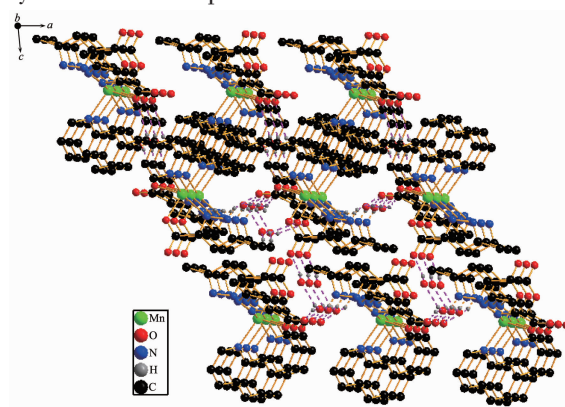


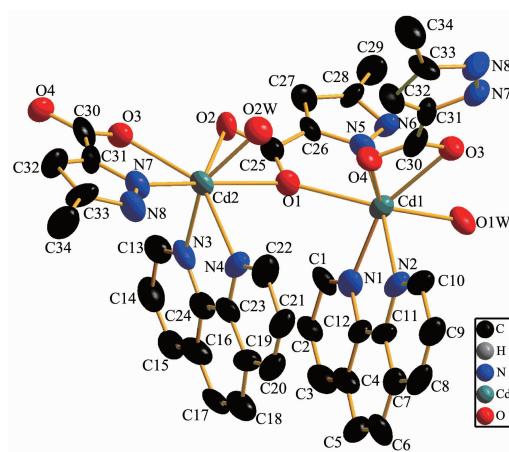
Fig.2 3D framework of **1** (Dash lines: hydrogen bonds)

Coordination polymer **2** crystallizes in the orthorhombic system space group  $Pccn$ . The asymmetric unit of **2** contains one  $[\text{Cd}_2(\text{HMPCA})_2(\text{phen})_2(\text{H}_2\text{O})_2]$  molecule and two free water molecules. As illustrated in Fig.3, the coordination sphere of  $\text{Cd1(II)}$  is defined by three carboxylic oxygen atoms (O(1), O(3), O(4)) and one nitrogen atom N(5) from two  $\text{HMPCA}^-$  anions, two nitrogen atoms (N(1), N(2)) from a phen ligand,

**Table 2** Selected bond lengths (nm) and angles (°) for the compounds **1** and **2**

Complex <b>1</b>					
Mn(1)-O(3)	0.213 5(4)	Mn(1)-N(3)	0.226 5(4)	Mn(1)-N(5)	0.226 9(4)
Mn(1)-O(1)	0.218 0(4)	Mn(1)-N(1)	0.226 6(5)	Mn(1)-N(2)	0.228 4(5)
O(3)-Mn(1)-O(1)	89.22(17)	N(3)-Mn(1)-N(1)	113.98(17)	O(3)-Mn(1)-N(2)	157.33(18)
O(3)-Mn(1)-N(3)	74.32(16)	O(3)-Mn(1)-N(5)	105.55(17)	O(1)-Mn(1)-N(2)	105.68(17)
O(1)-Mn(1)-N(3)	154.03(17)	O(1)-Mn(1)-N(5)	72.79(15)	N(3)-Mn(1)-N(2)	96.47(16)
O(3)-Mn(1)-N(1)	91.59(16)	N(3)-Mn(1)-N(5)	92.10(16)	N(1)-Mn(1)-N(2)	72.99(17)
O(1)-Mn(1)-N(1)	85.87(16)	N(1)-Mn(1)-N(5)	152.10(17)	N(5)-Mn(1)-N(2)	95.29(16)
Complex <b>2</b>					
Cd(1)-O(1W)	0.230 2(4)	Cd(1)-N(1)	0.230 8(5)	Cd(1)-O(4)	0.232 5(4)
Cd(1)-N(5)	0.233 9(5)	Cd(1)-N(2)	0.235 4(5)	Cd(1)-O(1)	0.238 6(4)
Cd(1)-O(3)	0.263 4(4)	Cd(2)-O(2W)	0.227 2(4)	Cd(2)-O(3)	0.240 1(4)
Cd(2)-N(4)	0.240 2(5)	Cd(2)-N(7)	0.2412(5)	Cd(2)-O(2)	0.2440(4)
Cd(2)-O(1)	0.244 7(4)	O(3)-Cd(1)	0.263 4(4)	O(4)-Cd(1)	0.232 5(4)
O(1W)-Cd(1)-N(1)	86.62(15)	O(1W)-Cd(1)-O(4)	126.41(14)	N(1)-Cd(1)-O(4)	141.05(15)
O(1W)-Cd(1)-N(5)	85.19(16)	N(1)-Cd(1)-N(5)	95.82(17)	O(4)-Cd(1)-N(5)	105.94(16)
O(1W)-Cd(1)-N(2)	90.66(15)	N(1)-Cd(1)-N(2)	70.66(19)	O(4)-Cd(1)-N(2)	87.19(16)
N(5)-Cd(1)-N(2)	166.11(18)	O(1W)-Cd(1)-O(1)	151.33(15)	N(1)-Cd(1)-O(1)	83.16(16)
O(4)-Cd(1)-O(1)	75.17(14)	N(5)-Cd(1)-O(1)	69.37(15)	N(2)-Cd(1)-O(1)	110.84(15)
O(1W)-Cd(1)-O(3)	76.49(13)	N(1)-Cd(1)-O(3)	155.98(15)	O(4)-Cd(1)-O(3)	50.16(13)
N(5)-Cd(1)-O(3)	99.59(15)	N(2)-Cd(1)-O(1)	92.29(17)	O(1)-Cd(1)-O(3)	119.53(13)
N(3)-Cd(2)-O(2W)	152.59(17)	N(3)-Cd(2)-O(3)	94.86(17)	N(3)-Cd(2)-N(4)	70.1(2)
O(2W)-Cd(2)-N(4)	91.40(18)	O(3)-Cd(2)-N(4)	144.44(15)	N(3)-Cd(2)-N(7)	107.73(17)
O(2W)-Cd(2)-N(7)	89.87(15)	O(3)-Cd(2)-N(7)	68.81(16)	N(4)-Cd(2)-N(7)	84.90(17)
N(3)-Cd(2)-O(2)	92.39(18)	O(2W)-Cd(2)-O(2)	86.98(15)	O(3)-Cd(2)-O(2)	82.1(2)
N(3)-Cd(2)-N(4)	79.5(2)	O(2W)-Cd(2)-N(4)	77.4(2)	O(3)-Cd(2)-N(4)	82.4(2)
N(3)-Cd(2)-N(7)	91.3(2)	O(2W)-Cd(2)-N(7)	99.5(2)	O(3)-Cd(2)-N(7)	74.86(13)
N(4)-Cd(2)-O(2)	135.54(14)	N(7)-Cd(2)-O(2)	139.47(16)		

and an oxygen atom (O(1W)) from a water molecule, leading to a pentagonal bipyramid geometry with seven coordination. The five atoms (O(3), O(4), O(1W), N(1), O(1)) form the equator plane of the pentagonal bipyramid, while the two axial positions are occupied by two nitrogen atoms (N(5), N(2)). Selected bond lengths and angles are given in Table 2. The bond angles of O(1W)-Cd(1)-N(1), N(1)-Cd(1)-O(1), O(4)-Cd(1)-O(1), O(1W)-Cd(1)-O(3), O(4)-Cd(1)-O(3) are added up to equal to  $375^\circ$ , close to  $360^\circ$ , showing that O(3), O(4), O(1W), N(1) and O(1) atoms are in the equatorial position. Moreover, the bond angle of N(5)-Cd(1)-N(2) is  $166.11^\circ$ , deviates from  $180^\circ$ , again revealing that the coordination polymer **2** has a distorted



Hydrogen atoms and solvent molecules were omitted for clarity

**Fig.3** Coordination environment of Cd(II) ion in **2** with thermal ellipsoid at 50% probability level



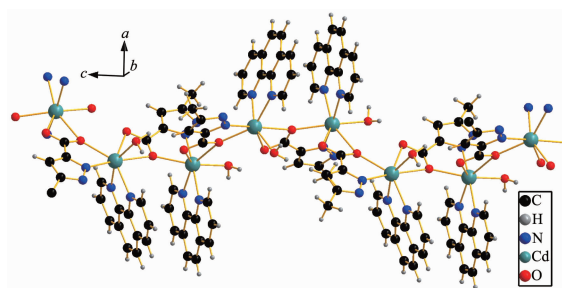
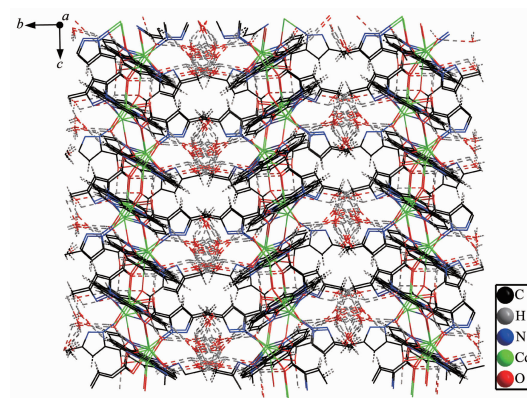
**Table 3** Bond lengths (nm) and angles ( $^{\circ}$ ) of hydrogen bonds for complexes **1** and **2**

D-H $\cdots$ A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle \text{D-H}\cdots\text{A}$
<b>Complex 1</b>				
N(4)-H(4A) $\cdots$ O(2) <sup>i</sup>	0.087	0.201	0.281 1(6)	152
O(5)-H(5X) $\cdots$ O(6) <sup>ii</sup>	0.082	0.235	0.268 7(8)	105
N(6)-H(6A) $\cdots$ O(5)	0.087	0.187	0.273 1(6)	168
O(6)-H(6X) $\cdots$ O(3) <sup>iii</sup>	0.082	0.229	0.303 8(7)	152
O(6)-H(6X) $\cdots$ O(4) <sup>iii</sup>	0.082	0.243	0.305 2(8)	134
O(6)-H(6Y) $\cdots$ O(4)	0.082	0.197	0.277 1(8)	164
C(3)-H(3) $\cdots$ O(1) <sup>iv</sup>	0.093	0.247	0.325 1(9)	142
N(4)-H(4A) $\cdots$ O(2) <sup>i</sup>	0.087	0.201	0.281 1(6)	152
O(5)-H(5X) $\cdots$ O(6) <sup>ii</sup>	0.082	0.235	0.268 7(8)	105
<b>Complex 2</b>				
O(1W)-H1W4 $\cdots$ O(7W) <sup>ii</sup>	0.096	0.234	0.306 8(10)	132
O(1W)-H1W5 $\cdots$ O(2) <sup>i</sup>	0.096	0.203	0.276 1(6)	131
O(2W)-H2W2 $\cdots$ O(4) <sup>i</sup>	0.096	0.227	0.286 0(5)	119
O(2W)-H2W3 $\cdots$ O(3W)	0.096	0.218	0.275 3(10)	117
C(6)-H(6) $\cdots$ O(2) <sup>iii</sup>	0.093	0.253	0.342 3(8)	162
C(29)-H29E $\cdots$ O(7W)	0.096	0.255	0.300 4(12)	109
C(29)-H29F $\cdots$ O(7W)	0.096	0.260	0.300 4(12)	106

Symmetry codes: for **1**: <sup>i</sup> 1+x, y, z; <sup>ii</sup> 1-x, 1-y, 1-z; <sup>iii</sup> -x, 2-y, 1-z; <sup>iv</sup> -x, 2-y, -z; for **2**: <sup>i</sup> 3/2-x, y, -1/2+z; <sup>ii</sup> 3/2-x, 3/2-y, z; <sup>iii</sup> -1/2+x, 1-y, 3/2-z

pentagonal bipyramid geometry. The bond distances of Cd1-O and Cd1-N are in the range of 0.230 2(4)~0.238 6(4) and 0.230 8(5)~0.235 4(5) nm (Table 2), which are close to the values observed in other Cd(II) complexes<sup>[29,39]</sup>. The coordination sphere of Cd2(II) is same with that of Cd1(II), five atoms (O(1), O(2), O(3), N(4), N(7)) form the equator plane of the pentagonal bipyramid, while the two axial positions are occupied by N(3) and O(2W) atoms. The bond angles of O(3)-Cd(2)-O(2), O(3)-Cd(2)-N(7), N(7)-Cd(2)-N(4), and N(3)-Cd(2)-O(2W) are 74.86°, 68.81°, 84.90°, and 152.59° respectively. The Cd1(II) and Cd2(II) ions are connected together by one carboxylic oxygen atom to form a binuclear unit, in which the distance between two Cd(II) ions is 0.463 2 nm. These binuclear units are linked each other to form a 1D chain, as shown in Fig.4. Besides, the separation of 0.348 4 nm between the centroids of the benzene ring from phen ligands, indicates the existence of the significant intramolecular  $\pi$ - $\pi$  interactions. These 1D chains, and the lattice water molecules are interlinked via the interactions of two kinds of intermolecular hydrogen bonds (O-H $\cdots$ O

C-H $\cdots$ O), resulting in the formation of a 3D supermolecular framework, as shown in Fig.5. The

**Fig.4** 1D chain structure of **2****Fig.5** 3D grid-like structure of **2** (Dashed lines: hydrogen bonds)

lengths and angles of the hydrogen bonds are listed in Table 3.

### 2.3 Thermogravimetric analysis

So as to examine the thermal stability of the compounds **1** and **2**, the thermogravimetric analysis were carried out from ambient temperature up to 800 °C (see Supplementary materials, Fig.S2). For **1**, the first weight loss of 7.41% between 126 °C and 199 °C is attributed to the loss of two lattice water molecules (Calcd. 6.90%). The second degradation stage is in the range of 199~434 °C with weight loss of 35.02%, corresponding to the loss of one phen molecule (Calcd. 34.52%). The third degradation stage is in the range of 434~478 °C with weight loss of 24.99%, corresponding to the loss of a HMPCA<sup>-</sup> ligand (Calcd. 23.99%). The remaining material finally degrades to MnO (Calcd. 13.62%, Found 14.79%). For **2**, the first weight loss of 3.53% between 50 °C and 150 °C is attributed to the loss of two lattice water molecules (Calcd. 3.98%). The second degradation stage is in the range of 170~250 °C with weight loss of 4.17%, corresponding to the loss of two coordinated water molecules (Calcd. 3.98%). The third degradation stage is in the range of 250~440 °C with weight loss of 38.65%, corresponding to the loss of two phen molecules (Calcd. 35.80%). Above 440 °C, the remaining material decomposes gradually.

### 2.4 Fluorescence properties

The solid-state fluorescence of two complexes, and free H<sub>2</sub>MPCA ligand were investigated at room temperature. As shown in Fig.6, the strongest emission peaks for free ligand, and complexes **1** and **2** all

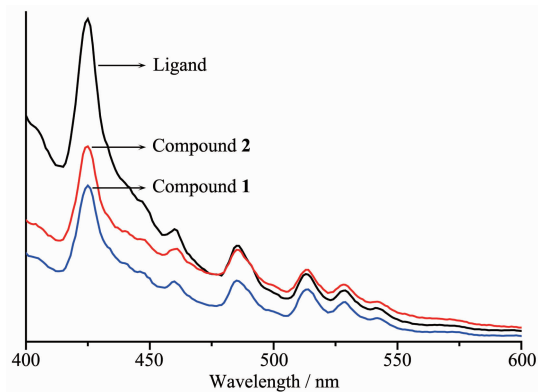


Fig.6 Solid-state fluorescence of compounds **1** and **2**

appear at *ca.* 425 nm ( $\lambda_{\text{ex}}=376$  nm). Therefore the origin of the emission of complexes **1** and **2** may be attributed to the internal charge transfer ( $\pi \rightarrow \pi^*/n \rightarrow \pi^*$  transitions) of the ligand.

## 3 Conclusion

In summary, complexes [Mn(HMPCA)<sub>2</sub>(phen)] · 2H<sub>2</sub>O (**1**) with mononucleate structure and [Cd<sub>2</sub>(HMPCA)<sub>2</sub>(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] · 2H<sub>2</sub>O (**2**) with 1D structure containing binuclear units have been successfully synthesized. The coordination modes of HMPCA<sup>-</sup> anions are different in two complexes. Non-covalent bonds play an important role in the formation of three-dimensional supramolecular architectures of the complexes. Similar to ligand H<sub>2</sub>MPCA, complexes **1** and **2** show blue fluorescence in the solid state at room temperature.

Supporting information is available at <http://www.wjhxsb.cn>

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