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刚性 1,4-二(4-甲基咪唑)苯配体构筑的两个 d^{10} 配位聚合物的合成、结构及荧光性质

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摘要：利用过渡金属镉(锌)盐与 1,4-二(4-甲基咪唑)苯、间苯二甲酸分别采用分层和水热法合成了化合物{[Cd(BMIB)$(H_2O)_2$]$(NO_3)_2$}$_n$(**1**)和{[Zn_2(BMIB)$_{1.5}$(OH)(IP)$_{1.5}$]·H_2O}$_n$(**2**)(BMIB=1,4-二(4-甲基咪唑)苯,IP^{2-}=间苯二甲酸根),并对其进行了元素分析、IR 及 X 射线衍射法表征。晶体结构研究表明:配合物 **1** 属于三斜晶系,$P\bar{1}$ 空间群。晶胞参数:a=0.382 08(3) nm,b=0.904 72(7) nm, c=1.378 29(10) nm,α=98.581(4)°, β=97.020(3)°,γ=94.398(3)°。配合物 **2** 属于单斜晶系,$C2/c$ 空间群。晶胞参数:a=3.764 07(9) nm,b=1.017 18(5) nm, c=2.015 31(11) nm, β=120.860(2)°。配合物 **1** 是由配体 BMIB 连接镉离子形成一维链状结构,由氢键连接成二维层结构。而配合物 **2** 是由配体 IP^{2-}连接锌离子形成一维梯状结构,该一维梯通过羟基和 BMIB 连接成三维网络结构。此外,配合物 **1** 和 **2** 具有较好的荧光性能。

关键词：1,4-二(4-甲基咪唑)苯；晶体结构；荧光

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Syntheses, Crystal Structures and Fluorescence Properties of Two Complexes Constructed from Rigid 1,4-bis(4-methyl-imidazolyl)Benzene

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Abstract: The reaction of $M(NO_3)_2·6H_2O$ (M=Cd, Zn), isophthalic acid(H_2IP) as well as 1,4-bis(4-methyl-imidazolyl) benzene(BMIB) results in formation of a 1D complex {[Cd(BMIB)$(H_2O)_2$]$(NO_3)_2$}$_n$ (**1**) and 3D complex {[Zn_2(BMIB)$_{1.5}$(OH)(IP)$_{1.5}$]·H_2O}$_n$ (**2**). X-ray diffraction crystal structure analysis shows that **1** crystallizes in triclinic system, space group $P\bar{1}$ with a=0.3820 8(3) nm, b=0.904 72(7) nm, c=1.378 29(10) nm, α=98.581(4)°, β=97.020(3)°, γ=94.398(3)°. In **1**, BMIB links all the Cd atoms into a 1D chain, which forms 2D bilayer through the H-bond interactions. The complex **2** crystallizes in monoclinic system, space group $C2/c$ with a=3.764 07(9) nm, b=1.017 18(5) nm, c=2.015 31(11) nm, β=120.860(2)°. On the other hand, in **2**, the carboxylate group of ligand IP^{2-} with μ_2-η^1:η^1 coordination mode links metal atoms to give a 1D double-chain structure, which forms 3D network through Zn-N and Zn-OH interactions. In addition, the fluorescence property of complexes **1** and **2** have been investigated, which exhibit good fluorescence in the solid state at room temperature. CCDC:1511866, **1**; 1511867, **2**.

Keywords: 1,4-bis(4-methyl-imidazolyl)benzene; crystal structure; fluorescence

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0 Introduction

Recently, metal-organic frameworks (MOFs) based on multidentate N-heterocyclic ligands such as imidazole, triazole, tetrazole, benzimidazole or pyridinehave attracted unparalleled attention owing to their intriguing molecular topologies and potential applications in ion exchange, gas sorption and storage, catalysis, optics and so on[1-8]. On the other hand, the use of auxiliary ligands is also an effective method for the framework formation of coordination polymers owing to the fact that they can satisfy and even adjust the coordination needs of the metal center and generate more meaningful architectures. However, systematic investigation of the role of auxiliary ligands in the formation of coordination frameworks is not well documented so far. From another point of view, MOFs containing metal ions with a d^{10} configuration, such as Zn(Ⅱ), Cd(Ⅱ) and Hg(Ⅱ), are potential materials for optical applications, such as fluorescence probes and nonlinear optical materials [9-13]. In order to further investigate the influence of organic ligands with different metal ions on the coordination architectures and related properties, in this contribution, isophthalic acid (H_2IP) and 1,4-bis (4-methyl-imidazolyl)benzene (BMIB) were employed to synthesize two new coordination polymer, namely $\{[Cd(BMIB)(H_2O)_2](NO_3)_2\}_n$ (**1**) and $\{[Zn_2(BMIB)_{1.5}(OH)(IP)_{1.5}]\cdot H_2O\}_n$ (**2**).

1 Experimental

1.1 Materials and instruments

The regents were used as commercial sources without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were recorded on Bruker Vector22 FTIR spectrophotometer using KBr discs. Thermogravimetric analyses (TGA) were performed on a TGA V5.1A Dupont 2100 instrument heating from room temperature to 700 ℃ under N_2 with a heating rate of 20 ℃·min^{-1}. Powder X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with Cu $K\alpha$ (λ =0.154 18 nm) radiation at room temperature, using an operating tube voltage of 40 kV and tube current of 30 mA in the 2θ range between 5° and 50°. Fluorescence measurements were performed using an F-7000 Fluorescence Spectrophotometer at room temperature in the solid state.

1.2 Syntheses of the complexes 1 and 2

The complex **1** was prepared by a layering method. An aqueous solution (5 mL) of H_2IP (17.0 mg, 0.1 mmol) was carefully adjusted to pH 6 by NaOH solution and placed at the bottom of a test tube. Then a buffer layer of a solution (5 mL) of methanol+H_2O (1∶1, *V*/*V*) was layered over it, and afterward, a solution of $Cd(NO_3)_2\cdot 6H_2O$ (30.8 mg, 0.1 mmol) in methanol (5 mL) was layered over the buffer layer. Colorless block crystals of **1** were collected in 50% yield after several days. Anal. Calcd. for $C_{14}H_{18}CdN_6O_8$ (%): C 32.89, H 3.52, N 16.45; Found (%): C 32.82, H 3.49, N 16.49. IR (KBr pellet, cm^{-1}): 3 448(s), 1 615(m), 1 523(m), 1 384(s), 1 342(m), 1 285(w), 1 230(m), 1 107(m), 1 088(m), 1 031(m), 934 (m), 829(w), 739(m), 658(m).

The starting materials for preparation of **2** are similar to those of **1** except that $Zn(NO_3)_2\cdot 6H_2O$ (29.7 mg, 0.1 mmol) was used instead of $Cd(NO_3)_2\cdot 6H_2O$. By the hydrothermal method (heated at 140 ℃ for 3 days), complex **2** was gained. Colorless single crystals of **2** were collected by filtration and washed by water and ethanol for several times with a yield of 26%. Anal. Calcd. for $C_{33}H_{30}Zn_2N_6O_8$(%): C 51.47, H 3.90, N 10.92; Found (%): C 51.52, H 3.86, N 10.98. IR (KBr pellet, cm^{-1}): 3 418(s), 1 665(s), 1 563(s), 1 429(m), 1 397(m), 1 356(s), 1 287(m), 1 241(w), 1 107(m), 956 (w), 847(w), 781(m), 728(m), 664(w), 592(w).

1.3 X-ray crystallography

The X-ray diffraction measurements for **1** (Dimension: 0.28 mm ×0.24 mm ×0.22 mm) and **2** (Dimensions: 0.26 mm×0.22 mm×0.20 mm) were carried out on a Bruker Smart Apex Ⅱ CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm). The data were integrated by using the SAINT program [14], which also did the intensity corrections for Lorentz and polarization effect. An empirical absorption correction was applied using the SADABS program[15]. The structures were

solved by direct methods using the program SHELXS-97 and all the non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package[16-17]. Crystal data and structure refinement parameters are listed in Table 1. The selected bond lengths are given in Table 2.

CCDC:1511866, **1**; 1511867, **2**.

Table 1 Crystal Data and Structure Parameters for the Title Complexes

Complex	**1**	**2**
Empirical formula	$C_{14}H_{18}CdN_6O_8$	$C_{33}H_{30}Zn_2N_6O_8$
Formula weight	510.74	769.37
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a / nm	0.382 08(3)	3.764 07(9)
b / nm	0.904 72(7)	1.017 18(5)
c / nm	1.378 29(10)	2.015 31(11)
V / nm^3	0.465 38(6)	6.623 7(5)
Z	1	8
Absorption coefficient / mm^{-1}	1.231	1.509
F(000)	256	3152
Reflections collected, unique	7 172,1 832 (R_{int}=0.055 3)	19 553,7 498 (R_{int}=0.008 7)
Data, restraints, parameters	1 832, 0, 134	7 498, 0, 447
Final R indices ($I>2\sigma(I)$)	R_1=0.050 0, wR_2=0.126 3	R_1=0.056 2, wR_2=0.142 4
largest diff. peak and hole / (e·nm^{-3})	664 and −501	576 and −582

Table 2 Selected bond lengths (nm) for complexes 1 and 2

			1		
Cd(1)-N(1)	0.225 7(4)	Cd(1)-O(1W)	0.240 4(4)	Cd(1)-N(1A)	0.225 7(4)
Cd(1)-O(1WA)	0.240 4(4)				
			2		
Zn(1)-N(5)	0.203 0(3)	Zn(2)-N(1)	0.203 8(2)	Zn(1)-O(1)	0.199 1(2)
Zn(2)-N(3)	0.202 4(2)	Zn(1)-O(1W)	0.192 2(2)	Zn(2)-O(5)	0.250 7(3)
Zn(1)-O(4A)	0.196 5(2)	Zn(2)-O(1W)	0.191 0(2)		

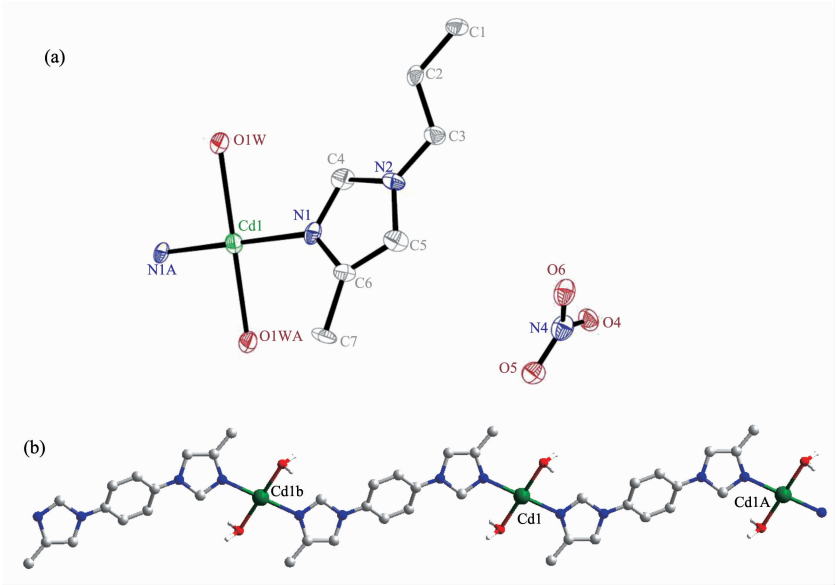
Symmetry codes: A: $-x$, $2-y$, $-z$ for **1**; A: x, $-1+y$, z for **2**

2 Results and discussion

2.1 Structure description

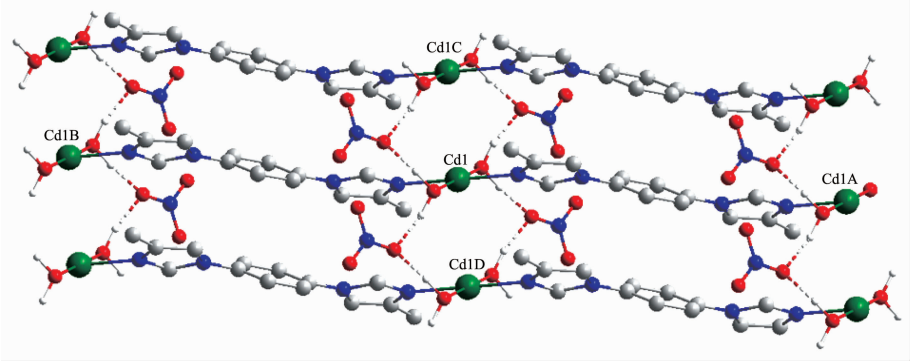
The results of structural analysis revealed that complex **1** has a 1D chain structure. The asymmetric unit of **1** contains half of Cd(Ⅱ) cation, one NO_3^- anion, one coordinated water molecule and half of 1,4-bis(4-methyl-imidazolyl)benzene ligand. As shown in Fig.1a, the metal Cd^{2+} ion center locates in a slightly distorted square coordination geometry environment: two O atoms from two water and two N atom from two BMIB ligands. Firstly, an infinite chain built up by Cd(Ⅱ) ions and BIMB through the μ_1-η^1:η^1 coordination modes of 4-methy-imidazolyl groups (Fig.1b). Then, the adjacent chains are interlinked by the H-bonding interactions (O1W-H1X···O5 and O1W-H1Y···O5) to form a 2D bilayer structure, as shown in Fig.2. Finally, the 2D layers of **1** connect together through the C-H···O non-classic hydrogen bonding interactions to give the 3D supramolecular structure.

When the reaction of ligand H_2IP and BMIB with $Zn(NO_3)_2\cdot 6H_2O$ was carried out by hydrothermal reaction, instead of layering method used for preparation of **1**, a new complex **2** was obtained. The



All H atoms have been omitted for clarity; Symmetry codes: A:−*x*, 2−*y*, −*z* in (a); A:1+*x*, *y*, 1+*z*; B:−1+*x*, *y*, −1+*z* in (b)

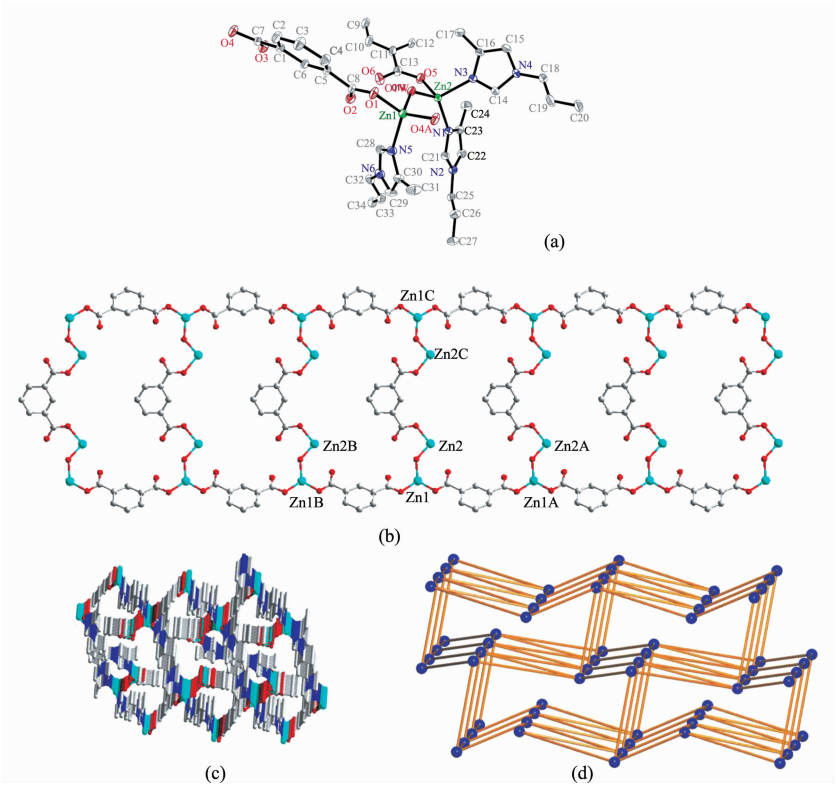
Fig.1 Coordination environment of the Cd(Ⅱ) ion in 1 showing 30% probability displacement ellipsoids; (b) 1D chain structure of **1**



Symmetry codes: A:1+*x*, *y*, 1+*z*; B:−1+*x*, *y*, −1+*z*; C:−1+*x*, −1+*y*, *z*; D: 1+*x*, −1+*y*, *z*

Fig.2 2D layer structure of **1** linked by H-bonding

crystallographic data showed that complex **2** crystallizes in monoclinic with *C*2/*c* space group. There are two Zn(Ⅱ), one hydroxyl, one and half of IP^{2-} ligands, one and half of BMIB ligands and one free water molecule in the asymmetric unit of **1**. Each Zn (Ⅱ) atom has a distorted tetrahedral coordination geometry with a different O_3N and O_2N_2 donor set as illustrated in Fig.3a. The Zn1 atom is coordinated by two O atoms (O1, and O4A) from two IP^{2-} anions, one hydroxyl O atom and one N atom (N5) from a BMIB molecule. Zn2 has a similar coordination environment to that of Zn1 except that only two O atoms (O5 and O1W) from one IP^{2-} anions coordinate to Zn2 and the additional N atoms (N1, N3) are from the BMIB molecules. It is note that all IP^{2-} ligands exhibit the same coordination mode, namely each ligand coordinate to two Zn(Ⅱ) atoms using its two carboxylate groups in μ_2-η^1:η^1-bismonodentate, then the double-chain is formed by the coordination mode (Fig.3b). Such 1D double-chains are further connected together via the Zn-N coordination between the imidazole groups and Zn(Ⅱ) to generate a complicated 3D framework as illustrated in Fig.3c. Topological analysis was carried out to get the insight of the structure of **2** (Fig.3d). As discussed above, each IP^{2-} ligand and BMIB is neighbored by two Zn (Ⅱ) atoms, and thus can be considered as a 2-connector. On the other hand, each binuclear [Zn_2] unit links six ligands, which can be



Lattice water molecule and hydrogen atoms are omitted for clarity; Symmetry codes: A: x, $-1+y$, z in (a); A: x, $-1+y$, z; B: x, $1+y$, z; C: $2-x$, y, $3/2-z$ in (b)

Fig.3 (a) ORTEP drawing of **2** with 30% thermal ellipsoids; (b) 1D double-chain of **2** constructed by Zn(Ⅱ) and IP^{2-} ligands; (c) View of the 3D framework of **2**; (d) Topological representation of the 3D structure of **2**

regarded as a 6-connectors. The resulting structure of **2** is 6-c net with net point (Schläfli) symbol ($3^3 \cdot 4^6 \cdot 5^5 \cdot 6$) (Fig.3d) calculated by TOPOS [18], which is different from the common reported pcu topology.

2.2 Thermal gravimetric analyses and PXRD study

Thermal gravimetric analyses (TGA) were performed to verify the thermal stability of the complexes. The results indicated that a weight loss of 7.15% was observed in the temperature range of 25~170 ℃ for **1**, which corresponds to the release of all coordinated water molecules (Calcd. 7.05%). After the loss of water molecules, a plateau region was observed from 170 to 320 ℃, and then a rapid weight loss was detected, which is attributed to the decomposition of the complex (Fig.4a). The TG curve of **2** shows the first weight loss of 2.52% from 25 to 120 ℃, which corresponds to the loss of one lattice water molecule

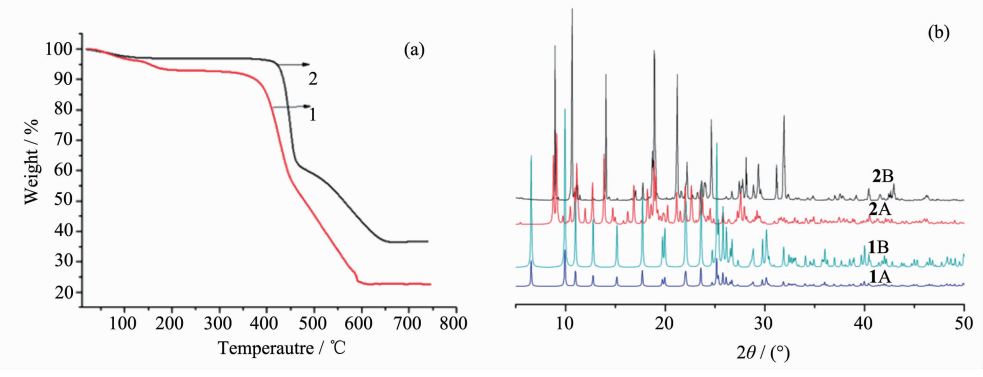


Fig.4 TG curves of complexes **1** and **2** (a) and powder X-ray diffraction patterns of **1** and **2** (b) (A: simulated; B: as-synthesized)

(Calcd. 2.34%). After the loss of water molecules, a plateau region is observed from 120 to 395 ℃, and the 3D framework of complex **3** may still stand. A rapid weight loss can be detected from 395 to 420 ℃, which is attributed to the decomposition of the IP^{2-} and BMIB ligand. It can be concluded that the two complexes have high thermal stability in the class of MOFs.

Therefore, the result indicates that complexes **1** and **2** has high stability. The purity of complex **1** and **2** were confirmed by powder X-ray diffraction (PXRD) study, and the results showed that the experimental PXRD pattern for them are consistent well with the corresponding stimulated one obtained from the single crystal structure (Fig.4b).

2.3 Photoluminescence property

Metal-organic frameworks have been reported to have ability to adjust the emission wavelength of organic materials through incorporation of metal centers, especial for the d^{10} metal elements [19]. So it gives us an impetus to make an investigation on the luminescence properties of them in view of potential applications as light-emitting diodes (LEDs). The emission spectra of complexes **1** and **2**, together with the BMIB ligand, were studied in the solid state at room temperature and depicted in Fig.5. It shows that there are emission bands at 410 nm (λ_{ex}=370 nm) for **1**. Such fluorescent emissions may be assigned to intra-ligand π-π* transitions, since the free BMIB ligand exhibited a similar broad emission at 411 nm upon excitation at 360 nm. It is noteworthy that intense fluorescent emissions at 428nm (λ_{ex}=370 nm) for **2** was observed under the same conditions. The emission bands of complex **2** has red-shift of 17 nm compared with the BMIB ligand, which attribute to the coordination interactions between the metal ion and the BIMB and H_2IP ligands. And such emission bands may be tentatively assigned to ligand-to-metal charge transfer (LMCT)[20]. The results suggest that the complexes **1** and **2** may be good candidate for potential blue-fluorescent materials, since they are highly thermally stable and insoluble in common solvents.

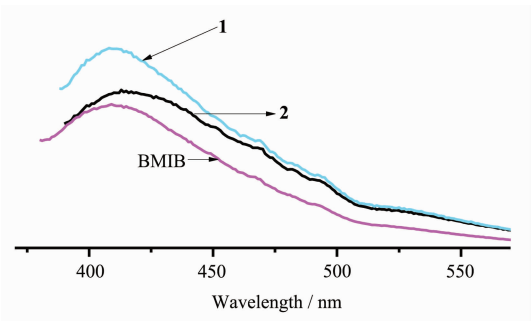


Fig.5 Emission spectra of **1**, **2** and ligand(BMIB) in the solid state at room temperature

3 Conclusions

In summary, two new coordination polymers with different framework structures have been successfully constructed based on the connectivity co-effect between the rigid BMIB ligand and carboxylates together with metal salts under hydrothermal/layering conditions. The results suggest that the structural diversification of coordination polymers may result from the different synthetic method and metal ions. Moreover, complexes **1** and **2** both exhibit photoluminescence property, which appear to be potential hybrid inorganic-organic photoactive materials.

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