

柔性 1,5-二(2-乙基咪唑)戊烷配体构筑的两个 d^{10} 金属配合物的合成、结构及性质

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摘要: 利用过渡金属镉(锌)盐与 1,5-二(2-乙基咪唑)戊烷(BEIP)、5-羟基间苯二甲酸(5-OHH₂IP)在水热条件下合成了配合物[Cd(BEIP)(Cl)₂]_n(**1**)和[Zn(BEIP)(5-OHIP)]_n(**2**), 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** 属于正交晶系, $Pca2_1$ 空间群。配合物 **2** 属于单斜晶系, $P2_1/n$ 空间群, $\beta=100.542(4)^\circ$ 。配合物 **1** 是由配体 1,5-二(2-乙基咪唑)戊烷连接镉离子形成一维链状结构。而配合物 **2** 是由配体间苯二甲酸连接锌离子形成一维链状结构, 该一维链通过 1,5-二(2-乙基咪唑)戊烷连接成二维网络结构, 进而通过氢键连接成三维超分子结构。此外, 配合物 **1** 和 **2** 具有较高的稳定性和较好的荧光性能, 配合物 **2** 对甲基橙染料有一定的降解作用。

关键词: 1,5-二(2-乙基咪唑)戊烷; 晶体结构; 荧光

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Syntheses, Crystal Structures and Properties of Two d^{10} Metal Complexes Constructed from 1,5-bis(2-ethyl-imidazolyl)pentane

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Abstract: Reaction of CdCl₂ or ZnCl₂·4H₂O, 5-hydroxyisophthalic acid (5-OHH₂IP) as well as 1,5-bis(2-ethyl-imidazolyl)pentane(BEIP) results in formation of a 1D [Cd(BEIP)(Cl)₂]_n (**1**) and 2D [Zn(BEIP)(5-OHIP)]_n (**2**). X-ray diffraction crystal structure analysis shows that **1** crystallizes in orthorhombic system, space group $Pca2_1$, while **2** is of monoclinic, space group $P2_1/n$ with $\beta=100.542(4)^\circ$. In **1**, the 1,5-bis (2-ethyl-imidazolyl)pentane links all the Cd atoms into a 1D chain. In **2**, the carboxylate group with $\mu_2\text{-}\eta^1\text{:}\eta^1$ coordination mode links metal atoms to give a 1D zigzag chain structure, which forming the 2D layer through Zn-N interactions by BEIP ligands. Finally the 2D layers are further assembled into 3D framework by the H-bond interaction. In addition, the properties of complexes **1** and **2** have been investigated, which exhibit good fluorescence in the solid state at room temperature. And complex **2** shows good photocatalytic activity for the degradation of methyl orange solution. CCDC:1523229, **1**; 1523230, **2**.

Keywords: 1,5-bis(2-ethyl-imidazolyl)pentane; crystal structure; fluorescence

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0 Introduction

In recent years, coordination polymers (CPs) based on multidentate N-heterocyclic ligands attracted an upsurge of research interest owing to their intriguing molecular topologies and potential applications in gas sorption and storage, catalysis, luminescence, and so on^[1-8]. On the other hand, the use of auxiliary ligands is also an effective method for the framework construction of coordination polymers attributing to the fact that they can satisfy and even adjust the coordination needs of the metal center and generate more meaningful architectures. Especially, bis(imidazole) with $-\text{CH}_2-$ spacers are good N-donor bridging ligands, and the flexible nature of $-\text{CH}_2-$ spacers allows the ligands to bend and rotate freely when coordinating to metal centers to conform to the coordination geometries of different metal ions^[9-10]. Furthermore, 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, CPs 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^[11-15]. In order to further investigate the influence of organic ligands with different metal ions on the coordination architectures and related properties, in this article, 5-hydroxyisophthalic acid(5-OHH₂IP) and 1,5-bis(2-ethyl-imidazolyl)pentane(BEIP) were employed to synthesize two new coordination polymers, namely $[\text{Cd}(\text{BEIP})(\text{Cl})_2]_n$ (**1**) and $2\text{D} [\text{Zn}(\text{BEIP})(5\text{-OHIP})]_n$ (**2**). Moreover, the luminescent property and photocatalytic activity for the degradation of methyl orange have also been investigated.

1 Experimental

1.1 Materials and instruments

The reagents 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 °C under N_2 with a heating rate of 20 °C \cdot min⁻¹. Fluorescence measurements were performed using an F-7000 Fluorescence Spectrophotometer at room temperature in the solid state. UV-Vis absorption spectra were measured with a Hitachi U-3010 UV-Vis spectrophotometer.

1.2 Syntheses of the complexes **1** and **2**

A mixture of CdCl_2 (18.3 mg, 0.1 mmol), 5-OHIP (18.2 mg, 1 mmol), BEIP (31.5 mg, 0.1 mmol), NaOH (0.008 g, 0.2 mmol), and deionized water (10 mL) was sealed in a 20 mL Teflon-lined stainless steel vessel and heated at 140 °C for 96 h. After cooling to room temperature, colorless block crystals were obtained and washed with alcohol several times (Yield: 40% based on Cd). Anal. Calcd. for $\text{C}_{15}\text{H}_{24}\text{CdN}_4\text{Cl}_2$ (%): C 40.57; H 5.41; N 12.62; Found (%): C 40.52; H 5.49; N 12.57. The preparation of **2** is similar to that of **1** except that $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ (20.9 mg, 0.1 mmol) was used instead of CdCl_2 . Colorless single crystals of **2** were collected by filtration and washed by water and ethanol for several times with a yield of 33%. Anal. Calcd. for $\text{C}_{23}\text{H}_{28}\text{ZnN}_4\text{O}_5$ (%): C 54.56; H 5.54; N 11.07; Found (%): C 54.52; H 5.61; N 10.99. IR (KBr pellet, cm^{-1}): 1 672(m), 1 563(s), 1 429(m), 1 397(m), 1 356(s), 1 275(m), 1 241(w), 1 107(m), 956(w), 847(w), 781(m), 733(m), 664(w), 592(w), 433(m) for **1**. 3 128(s), 1 599(s), 1 555(m), 1 435(s), 1 362(s), 1 271(w), 1 157(m), 1 113(m), 997(m), 929(m), 829(w), 736(s), 669(m), 428(m) for **2**.

1.3 X-ray crystallography

The data of two single crystals with dimensions of 0.30 mm \times 0.28 mm \times 0.24 mm for **1** and 0.20 mm \times 0.15 mm \times 0.10 mm for **2**, respectively, were carried out on a Bruker Smart Apex II CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). The data were integrated by using the SAINT program^[16], which also did the intensity corrections for Lorentz and polarization effect. An empirical absorption correction was applied using the SADABS program^[17]. 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^[18-19], all the hydrogen atoms were positioned geometrically and refined using a riding model. Atoms C12, C13, C14, and C12, C13, C14 in

1 were disordered with the site occupancy factors of 0.637(18) and 0.363(18), respectively. Crystal data and structure refinement parameters are listed in Table 1. The selected bond lengths are given in Table 2. CCDC:1523229, **1**; 1523230, **2**.

Table 1 Crystal data and structure parameters for the title complexes

Complex	1	2
Empirical formula	C ₁₅ H ₂₄ CdN ₄ Cl ₂	C ₂₃ H ₂₈ ZnN ₄ O ₅
Formula weight	443.68	505.86
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pca</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / nm	1.328 15(11)	0.980 90(5)
<i>b</i> / nm	0.872 77(7)	1.909 63(10)
<i>c</i> / nm	1.599 22(13)	1.211 67(6)
<i>V</i> / nm ³	1.853 8(3)	2.231 35(19)
<i>Z</i>	4	4
Absorption coefficient / mm ⁻¹	1.468	1.144
<i>F</i> (000)	896	1 056
Reflection collected, unique	8 022, 4 055(<i>R</i> _{int} =0.082 9)	9 873, 4 377 (<i>R</i> _{int} =0.042 5)
Data, restraint, parameter	1 832, 2, 230	4 377, 0, 301
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ =0.033 7, <i>wR</i> ₂ =0.091 8	<i>R</i> ₁ =0.048 2, <i>wR</i> ₂ =0.122 1
Largest diff. peak and hole / (e·nm ⁻³)	539 and -693	982 and -618

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

1					
Cd(1)-N(1)	0.224 8(4)	Cd(1)-Cl(1)	0.244 26(14)	Cd(1)-N(3)	0.222 4(4)
Cd(1)-Cl(2)	0.241 13(16)				
2					
Zn(1)-N(4A)	0.201 3(2)	Zn(1)-N(1)	0.200 3(2)	Zn(1)-O(1)	0.198 92(19)
Zn(1)-O(3B)	0.194 1(2)				

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

1.4 Photocatalytic activity

In the process of photocatalysis, 40 mg complex **2** was suspended in 1.5 × 10⁻⁵ mol · L⁻¹ MO aqueous solution (100 mL), then magnetically stirred in the dark for about 30 min to ensure the establishment of an adsorption-desorption equilibrium. After that, the mixture was stirred and continuously exposed to UV irradiation from a 300 W high pressure mercury vapor lamp equipped with cool water circulating. The MO concentration was determined by measuring the maximum absorbance at 465 nm, and all the tests were

carried out three times to ensure the reproducibility.

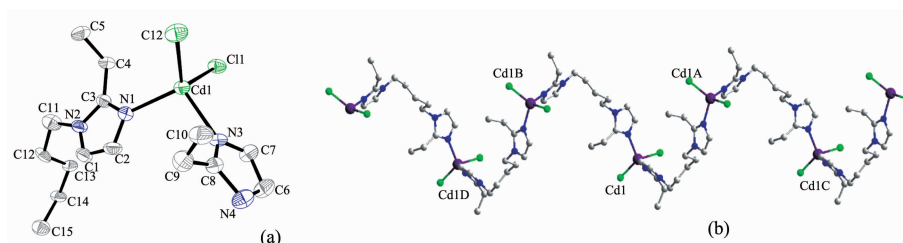
2 Results and discussion

2.1 Structure description

The results of structural analysis revealed that complex **1** contains one Cd(II) cation, one 1, 5-bis(2-ethyl-imidazolyl)pentane ligand and two coordinated Cl⁻. As shown in Fig.1a, the metal Cd²⁺ ion center is located in a slightly distorted tetrahedral coordination geometry environment with two Cl atoms and two N atom from two different BEIP ligands. Then, an

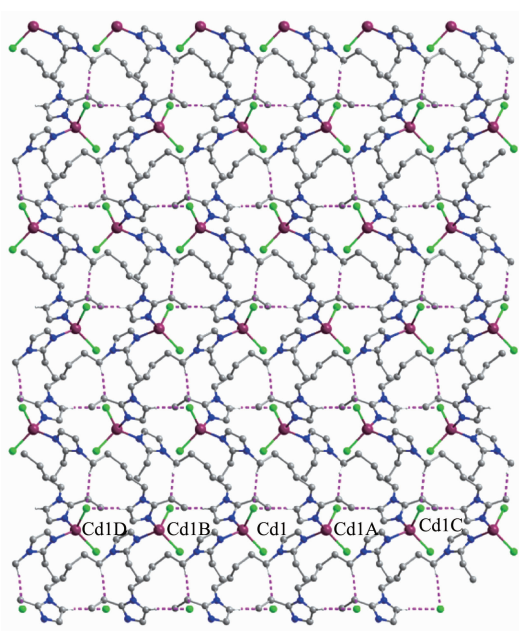
infinite chain built up by Cd(II) ions and BEIP through the $\mu_1\text{-}\eta^1\text{:}\eta^1$ coordination modes of 2-ethylimidazolyl groups (Fig.1b). Finally, the 1D chains of **1**

connect together through the C-H \cdots Cl non-classic hydrogen bonding interactions to give the 2D supramolecular structure (Fig.2).



All H atoms have been omitted for clarity; Symmetry codes: A: $1-x, 1-y, -1/2+z$; B: $1-x, 1-y, 1/2+z$; C: $x, y, -1+z$; D: $x, y, 1+z$

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

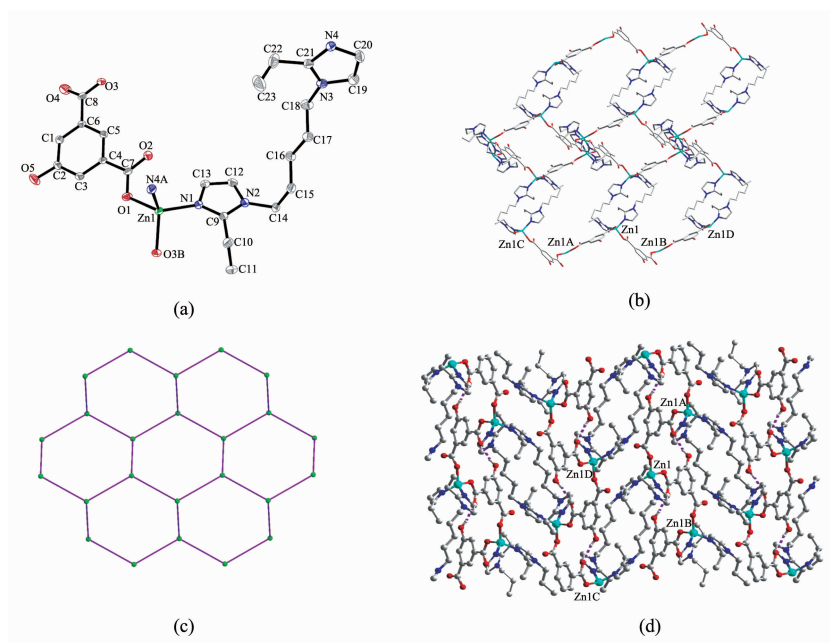


Symmetry: A: $1-x, 1-y, -1/2+z$; B: $1-x, 1-y, 1/2+z$; C: $x, y, -1+z$; D: $x, y, 1+z$

Fig.2 2D layer structure linked by C-H \cdots Cl H-bonding

Complex **2** was synthesized in a similar procedure as complex **1**, but here $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ was used instead of CdCl_2 . The crystallographic data showed that complex **2** crystallizes in monoclinic with $P2_1/n$ space group. There are one Zn(II), one 5-OHIP $^{2-}$ ligand, one BEIP ligand in the asymmetric unit of **1**. Each Zn^{2+} ion is four-coordinated in a distorted tetrahedral geometry by two nitrogen atoms from two BEIP ligands and two oxygen atoms from two 5-OHIP $^{2-}$ ligands. The bond angles around the Zn^{2+} ion are in the range of $100.00(9)^\circ \sim 122.19(9)^\circ$. The bond lengths of Zn-O are $0.194\ 1(2) \sim 0.198\ 92(19)$ nm and Zn-N are $0.200\ 3(2), 0.201\ 3(2)$ nm, respectively. In

2, each 5-OHIP $^{2-}$ anion serves as a μ_2 -bridge linking two adjacent Zn^{2+} ions in the bimonodentate mode to give rise to a 1D zigzag chain, while such 1D chains are further double-bridged by BEIP ligands into a 2D layer (Fig.3b). It is note that each flexible BEIP is ligated to two Zn^{2+} ions with two terminal imidazole groups assuming the anti-gauche conformation and a pair of oppositely arranged μ_2 -BEIP ligands bind two Zn^{2+} ions from adjacent chains to form a $[\text{Zn}_2(\text{BEIP})_2]$ 24-membered metallomacrocyclic ring. From the viewpoint of network topology^[20], if the Zn^{2+} ions are considered as 3-connected nodes, 5-OHIP $^{2-}$ and BEIP ligands as linear connectors, the whole structure can



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

Fig.3 (a) ORTEP drawing of **2** with 30% thermal ellipsoids; (b) 2D layer constructed by Zn(II) and 5-OHIP²⁻ and BEIP ligands; (c) Topological representation of the 2D structure of **2**; (d) View of the 3D framework of **2** with the H-bond interaction

be simplified to a 3-connected 6^3 topological net (Fig. 3c). The 2D layers are further assembled by intermolecular hydrogen bonds with a H(5)⋯O(2) distance of 0.190 nm and the angle of 160° (O(5)-H(5)⋯O(2)), leading to formation of a 3D framework (Fig.3d).

2.2 Thermal gravimetric analyses and photoluminescence property

Thermal gravimetric analyses (TGA) were performed to verify the thermal stability of the coordination polymers. Since there are not any solvent molecules in the two complexes, the results indicated that they exhibit excellent thermal stability as no weight loss step occurs below 310 and 380 °C for **1** and **2**, respectively. When the temperature rises up, the whole framework begins to collapse (Fig.4).

On the other hand, CPs with d^{10} metal centers have been investigated for their photoluminescent properties and potential applications in chemical sensors and photochemistry [21-22]. The solid-state luminescent properties of **1**, **2** and ligand BEIP were investigated at room temperature and the solid-state

emission spectra are shown in Fig.5. It shows that there are emission bands at 463 nm (λ_{ex} =370 nm) for **1**, 468 nm (λ_{ex} =370 nm) for **2**. Such fluorescent emissions may be assigned to intra-ligand π - π^* transitions, since the free BEIP ligand exhibited a similar broad emission at 448 nm upon excitation at 360 nm. It is noteworthy that the emission bands of both complexes is 15 nm and 20 nm red-shifted compared with the free BEIP ligand. The results suggest that complexes **1** and **2** may be good candidate of potential fluorescent materials.

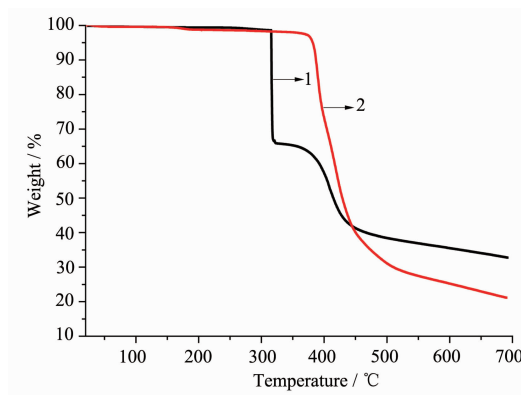


Fig.4 TG curves of complexes **1** and **2**

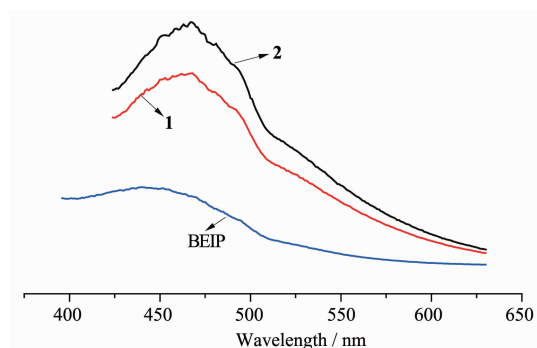


Fig.5 Emission spectra of **1**~**2** and ligand (BEIP) in the solid state at room temperature

2.3 Photocatalytic activity

Methyl orange (MO) is a model of dye pollutant, which can be used to evaluate the effectiveness of photocatalysts in the wastewater^[23-26]. And the diffuse reflection spectra of complex **2** was explored. In Fig.

6a, the newly appeared absorption at 352 nm should be assigned to LMCT and the value of the band gap was calculated as 2.95 eV, which indicated complex **2** might be a photocatalyst for MO.

Thus, the photocatalytic activity of as-prepared **2** was tested by the degradation of MO solution under 365 nm ultraviolet (UV) light irradiation. As illustrated in Fig.6b and 6c, the change in the concentration of MO solution is obvious with the use of complex **2** as photocatalyst. It can be seen that approximately 79.8% of MO has been decomposed after 3.0 h of irradiation rather than the blank experiment. The result indicates that complex **2** is active for the decomposition of MO under UV light irradiation.

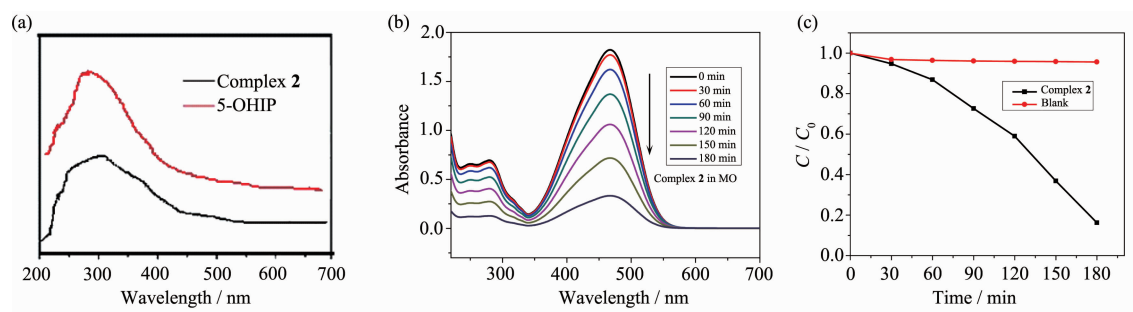


Fig.6 UV-Vis spectra of complex **2** and ligand 5-OHIP (a), absorption spectra of the MO solution during the decomposition reaction with the use of complex **2** (b) and degradation of MO with complex **2** (c)

3 Conclusions

In summary, two new CPs with different framework structures have been successfully constructed based on the connectivity co-effect between the flexible BEIP ligand and carboxylates together with metal salts under hydrothermal conditions. The results suggest that the structural diversification of CPs may result from the different metal ions. Moreover, complexes **1** and **2** both exhibit photoluminescence property, which appear to be potential hybrid inorganic-organic photoactive materials. And complex **2** exhibits photocatalytic activity for the degradation of MO solution under ultraviolet light irradiation.

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