

以 4-(1-咪唑基)苯甲酸和桥联氯构筑的一维梯状结构的镉配位聚合物的晶体结构和荧光性质

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摘要: 水热条件下以 CdCl_2 和 4-(1-咪唑基)苯甲酸(Himbz)为反应物合成出一个新的具有一维梯子型链状结构的配位聚合物 $[\text{Cd}(\text{imbz})(\text{Cl})(\text{H}_2\text{O})]_n$ (**1**), 并分别用元素分析, 红外谱图, 差热分析和 X-射线单晶衍射表征该结构。晶体结构分析结果表明: 4-(1-咪唑基)苯甲酸离子(imbz)将 $\text{Cd}(\text{II})$ 离子连接成一维 Z 字链, 进而通过桥联氯原子被连接成一维梯状链结构, 荧光谱图表明常温固态下配合物 **1** 发射蓝色荧光, 荧光寿命为 2.21 ns。

关键词: 镉配位聚合物; 晶体结构; 4-(1-咪唑基)苯甲酸; 荧光性质

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A New 1D Ladder-Like Cadmium(II) Coordination Polymer Based on 4-(1*H*-Imidazol-1-yl)benzoate and Chloro Ligands: Crystal Structure and Luminescence

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Abstract: The self-assembly of 4-(1*H*-Imidazol-1-yl)benzoic acid and CdCl_2 under hydrothermal condition gave a new 1D cadmium coordination polymer, $[\text{Cd}(\text{imbz})(\text{Cl})(\text{H}_2\text{O})]_n$ (**1**) (imbz=4-(1*H*-Imidazol-1-yl)benzoate), which has been characterized by elemental analysis, IR, TGA and single-crystal X-ray diffraction. The imbz ligands link the $\text{Cd}(\text{II})$ ions to form an infinite 1D zigzag chain, which the neighboring zigzag chains are further connected into a ladder chain through $\mu_2\text{-Cl}$ ligands. The photoluminescence and lifetime of complex **1** in the solid state at room temperature have been studied. CCDC: 890931.

Key words: cadmium(II) coordination polymer; crystal structure; 4-(1*H*-Imidazol-1-yl)benzoate; luminescent

0 Introduction

The rational design and construction of coordination polymers have garnered much attention due to their fascinating topology and potential application in catalysis, separation, sorption, luminescence, biological chemistry etc.^[1-6]. Recently, with the development of crystal engineering of

coordination polymers, judicious choice of metal centers and felicitous organic linkers has been proven to be an efficient way to design and synthesize compounds with novel architecture and interesting properties. It is widely recognized that the N-heterocyclic aromatic carboxylate ligands are excellent candidates for constructing novel structures. In the structural investigation of 4-(1*H*-Imidazol-1-yl)

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benzoate complexes, it has been found that the 4-(1*H*-Imidazol-1-yl)benzoic acid (Himbz) functions as a multidentate ligand, with versatile binding and coordination modes. For example, Gao et al.^[7] have successfully synthesized two 1D Cd(II) coordination polymers with phenylformic acid-imidazole ditopic ligand. Zhang et al.^[8] obtained a novel 2D square grid cobalt complex based on Himbz ligand. Herein, we report a new cadmium coordination polymer, [Cd(imbz)(Cl)(H₂O)]_n (imbz=4-(1*H*-Imidazol-1-yl)benzoate) (**1**), that features one-dimensional ladder-like chain structure. Complex **1** has been characterized by IR spectroscopy, elemental analysis, single-crystal X-ray diffraction, TGA, and by photoluminescence.

1 Experimental

1.1 Materials and measurements

All chemicals purchased were of reagent grade and used without further purification. All syntheses were carried out in 23 mL Teflon-lined autoclaves under autogenous pressure. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. Infrared spectra were recorded (4 000~400 cm⁻¹) as KBr disks on a Shimadzu IR-440 spectrometer. Luminescence spectra and lifetime for crystal solid samples were recorded at room temperature on an Edinburgh FLS920 phosphorimeter. Thermogravimetry analyses (TGA) were performed on a automatic simultaneous thermal analyzer (DTG-60, Shimadzu) under a flow of N₂ at a heating rate of 10 °C·min⁻¹ between ambient temperature and 800 °C.

1.2 Synthesis of [Cd(imbz)(Cl)(H₂O)]_n (**1**)

Complex **1** was prepared by the addition of stoichiometric amounts of CdCl₂ (0.091 g, 0.5 mmol) and NaOH (0.01 g, 0.25 mmol) to a hot aqueous solution (15 mL) of Himbz (0.094 g, 0.5 mmol). The mixture was stirred for 0.5 h at room temperature. Then was sealed in a 23 mL Teflon reactor and kept under autogenous pressure at 150 °C for 72 h. The mixture was cooled to room temperature as a rate of 5 °C·h⁻¹ and colorless block crystals were obtained in a yield of 48% based on the imbz. Anal. Calcd. for C₁₀H₉CdClN₂O₃ (%): C, 33.99; H, 2.55; N, 7.93. Found

(%): C, 34.03; H, 2.51; N, 7.89. IR (KBr pellet) (cm⁻¹): 3 503(vs), 2 138 (m), 1 606(s), 1 541(s), 1 519 (s), 1 456(w), 1 395(s), 1 304(m), 1 264(w), 1 231(w), 1 187(w), 1 122(m), 1 060(s), 1 016(m), 965(m), 929 (m), 849(m), 827(w), 780(s), 740(w), 700(w), 660(w).

1.3 Crystal structure determination

A single crystal with dimensions of 0.32 mm×0.27 mm×0.19 mm was mounted on a glass fiber for data collection which was performed on a Bruker APEXII area-detector diffractometer operating at 50 kV and 30 mA using a Mo *K*α radiation (λ=0.071 073 nm) at 296(2) K by using a ω scan mode. In the range of 2.10°<θ<27.55°, a total of 6065 reflections were collected, of which 2 609 were unique (*R*_{int}=0.018 8) and 2 324 observed ones (*I*>2σ(*I*)) were used in the succeeding structure calculations. Data collection and reduction were performed using the APEX II software^[9]. Multi-scan absorption corrections were applied using the SADABS^[9]. The structure was solved by direct methods and refined on F² by full-matrix least squares technique using the SHELX-97 program package^[10]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Water H atoms were tentatively located in difference Fourier maps and were refined with distance restraints of O-H 0.090 nm and H...H 0.148 nm, with a standard deviation of 0.001 nm, and with *U*_{iso} (H)=1.5 *U*_{eq} (O). The final *R*=0.020 6 and *wR*=0.063 4 (*w*=1/[σ² (*F*_o²)+(0.042 5*P*)²+0.783 3*P*], where *P*=(*F*_o²+2*F*_c²)/3) for 2 324 observed reflections with *I*>2σ(*I*). *S*=1.052, (Δ/σ)_{max}=0.000, (Δρ)_{max}=425 e·nm⁻³ and (Δρ)_{min}=-445 e·nm⁻³. Crystal parameters and details of the data collection and refinement are given in Table 1. Selected bond lengths and angles are given in Table 2. H-bonding parameters for **1** are given in Table 3.

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2 Results and discussion

2.1 IR spectra

The IR spectra of complex **1** shows broad bands in the 3 503 cm⁻¹, which may be assigned to the

Table 1 Crystal data and structure refinements of the complex 1

Empirical formula	C ₁₀ H ₉ CdClN ₂ O ₃	<i>Z</i>	8
Formula weight	353.04	μ / mm ⁻¹	2.128
Size / mm	0.32×0.27×0.19	<i>D_c</i> / (g·cm ⁻³)	2.040
θ range for data collection / (°)	2.10 to 27.55	<i>F</i> (000)	1 376
Crystal system	Monoclinic	Reflections collected	7 259
space group	<i>C2/c</i>	Independent reflections(<i>R_{int}</i>)	2 609(0.018 8)
<i>a</i> / nm	1.947 5(3)	Goodness of fit on <i>F</i> ²	1.052
<i>b</i> / nm	0.920 38(14)	<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> >2 σ (<i>I</i>))	0.020 6, 0.063 4
<i>c</i> / nm	1.285 2(2)	<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.024 2, 0.066 2
<i>V</i> / nm ³	2.299 3(6)	($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} / (e·nm ⁻³)	425, -445

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

Cd1-O1	0.235 93 (17)	Cd2-N1	0.22350(19)	Cd1-O2	0.235 56 (16)
Cd2-O3	0.239 27(17)	Cd1-Cl1	0.25518(6)	Cd1-Cl1	0.268 28(7)
O2-Cd1-O1	55.31(6)	N1 ⁱⁱ -Cd2-N1 ⁱⁱⁱ	164.04(12)	O2 ⁱ -Cd1-O1	119.82(7)
N1 ⁱⁱⁱ -Cd2-O3	85.38(7)	O1-Cd1-O1 ⁱ	173.95(10)	N1 ⁱⁱ -Cd2-Cl1 ⁱ	99.55(6)
O2-Cd1-Cl1	147.96(4)	N1-Cd2-O3	84.90(7)	O1-Cd1-Cl1	93.96(5)
O3-Cd2-Cl1 ⁱ	83.55(5)	Cl1-Cd1-Cl1 ⁱ	94.32(3)	Cl1 ⁱ -Cd2-Cl1	88.44(3)

Symmetry codes i: -x, y, 5/2-z; ii: 1/2-x, 1/2-y, 2-z; iii: -1/2+x, 1/2-y, 1/2+z

Table 3 Hydrogen bond lengths and angles for the complex 1

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H-A) / nm	<i>d</i> (D-A)/ nm	\angle DHA / (°)
O(3)-H(3C)...O(2) ^v	0.090	0.187	0.2757(2)	170

Symmetry codes: v: x, 1+y, z

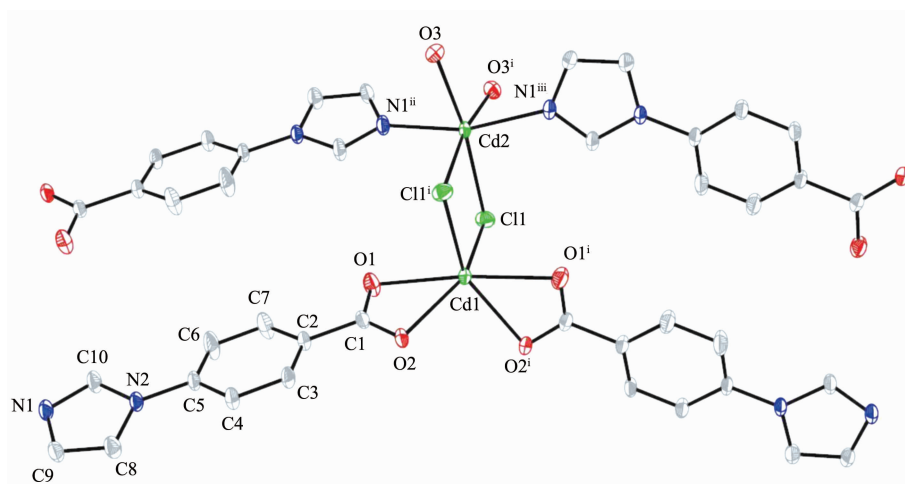
ν (O-H) stretching vibrations of the coordinated water molecules. The features at about 1606 and 1519 cm⁻¹ are associated with the asymmetric (COO) and symmetric (COO) stretching vibrations. The $\Delta\nu$ (ν_{as} (COO⁻)- ν_s (COO⁻)) values are 87 cm⁻¹ (less than 105 cm⁻¹), indicating the coordination of carboxylate with Cd(II) in chelating mode [11], which is well consistent with X-ray diffraction structural analysis.

2.2 Structure description

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in monoclinic space group *C2/c* and displays a 1D ladder-like chain, which built by imbz ligands and μ_2 -Cl ligands. Coordination environment of Cd(II) atoms of complex **1** are shown in Fig.1. Ion Cd1 is six-coordinated by four oxygen atoms from two imbz ligands and two μ_2 -Cl ligands and displays a distorted octahedral coordination geometry.

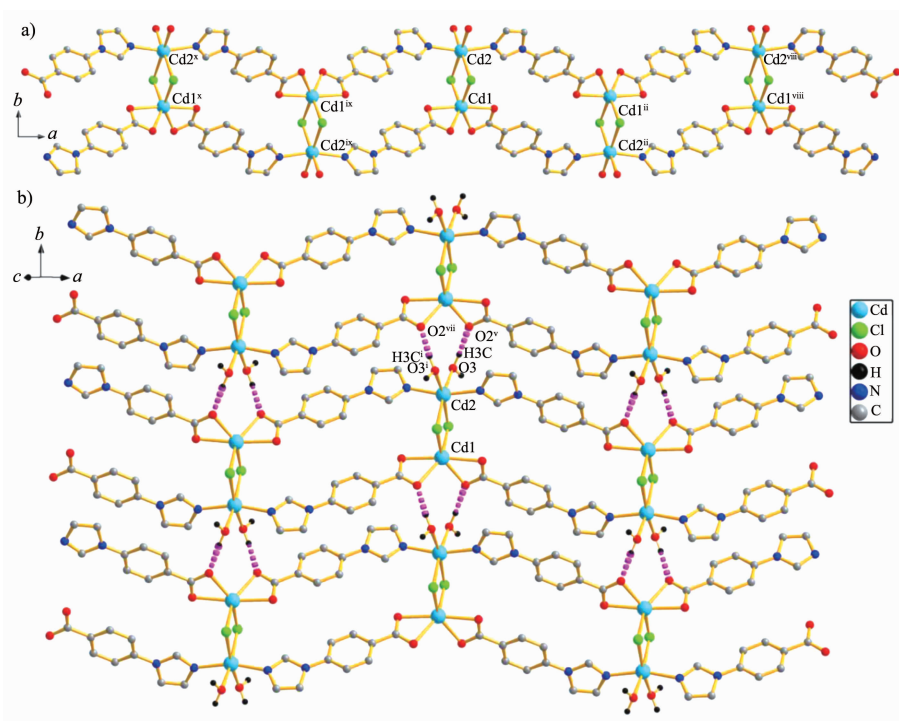
Ion Cd2 is also surrounded by distorted octahedral environment defined by two nitrogen atoms from two imbz ligands, two μ_2 -Cl ligands and two water molecules. The Cd-O, Cd-N, Cd-Cl bond lengths and O-Cd-O, O-Cd-N, O-Cd-Cl, N-Cd-Cl bond angles, all of which are within the range of those observed for other analogical Cd(II) complexes^[12-13], are ranging from 0.223 50 (19) to 0.268 28 (7) nm and 55.31 (6) to 173.95(10)°, respectively.

In the complicated polymeric structure of complex **1**, the imbz ligands exhibit μ_2 bridging to link two Cd(II) ions. On the basis of these connections of μ_2 linear bridging imbz ligands and μ_2 -Cl ligands, Cd(II) centers were connected together to form a ladder-like chain in the *c* axis direction (Fig.2a), with the adjacent separation of Cd(II) ions are 0.365 (8) and 1.235 (9) nm, respectively. These ladder chains are



All hydrogen atoms are omitted for clarity; Symmetry codes: i: $-x, y, 5/2-z$; ii: $1/2-x, 1/2-y, 2-z$; iii: $-1/2+x, 1/2-y, 1/2+z$.

Fig.1 Coordination environment of Cd(II) atoms in complex **1** drawn with 30% probability displacement ellipsoids



Symmetry codes i: $-x, y, 5/2-z$; ii: $1/2-x, 1/2-y, 2-z$; v: $x, 1+y, z$; vii: $x, -1+y, z$; viii: $1+x, y, -1+z$; ix: $-1/2-x, 1/2-y, 3-z$; x: $-1+x, y, 1+z$

Fig.2 (a) 1D ladder-like chain of **1** in the c axis; (b) View of the 2D layered network of complex **1** formed by hydrogen bonds parallel to the c axis

further connected into a 2D layered network through O3-H3C...O2 hydrogen bonding interactions parallel to the c -axis (Table 3, Fig.2b).

2.3 Thermal analysis

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stability of complex **1**. The samples were heated up in flowing N_2 with a heating

rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The TG and DTA curves are depicted in Fig.3, which shows that a gradual weight-loss step of 15.7% ($180\sim 220\text{ }^{\circ}\text{C}$), corresponding to the escape of the one coordinated water molecule and one chlorine atom (Calcd. 15.1%). The weight-loss step that occurs above $390\text{ }^{\circ}\text{C}$ corresponds to the decomposition of the framework. The final product may be

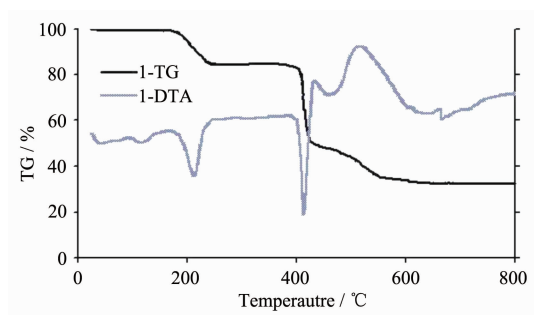


Fig.3 Thermogravimetric curves (DTA and TG) for complex **1**

the CdO with total loss of 63.89wt% (Calcd. 63.63%).

2.4 Luminescent properties

Due to the excellent luminescent properties of Cd (II) ions, the photoluminescence of complex **1** was investigated. The Himbz ligand with its extended aromaticity, which is thus regarded to be a good candidate for enhance emissive properties. The emission spectrum of compound **1** and the free Himbz ligand in the solid state at room temperature is shown in Fig.4. It can be observed that one intense maximum emission is located at 423 nm upon excitation 339 nm, while the free Himbz ligand exhibits fluorescent emission band at 330 nm upon excitation at 299 nm. Compared with the free Himbz, complex **1** has a large red-shift, which may be caused by ligand-to-metal charge transfer (LMCT) transition, as indicated by previous publication^[14]. The luminescent lifetime of solid complex **1** using an Edinburgh FLS920 phosphorimeter with 450 W xenon lamp as excitation source show lifetime for complex **1** of 2.21 ns (Fig.5), which could be used for light-emitting luminescent materials.

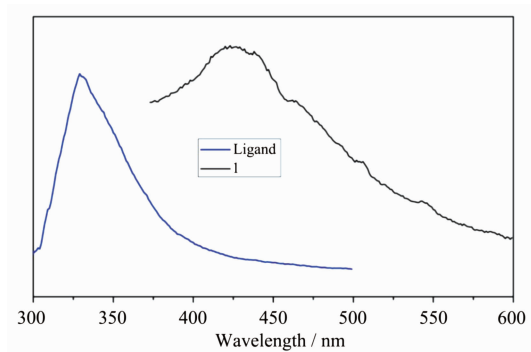


Fig.4 Solid-state emission spectrum of Himbz ligand and complex **1** at room temperature

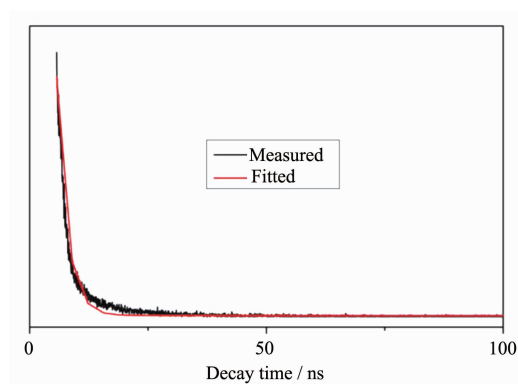


Fig.5 Luminescent lifetime of complex **1** in the solid state at room temperature

2.5 UV-Vis absorption spectra

Fig.6 illustrates the UV-Vis absorption spectra of **1** in solid state. In the exploited wavelength domain from 200~800 nm, the B band of imbz ligand which is attributed to the $\pi-\pi^*$ transition is observed with a second-most intense of absorption around 233 nm. The most intense absorption at 264 nm corresponds to the K band of the $L \rightarrow M$ (charge transfer) transition between imbz ligands and Cd^{2+} ions^[15].

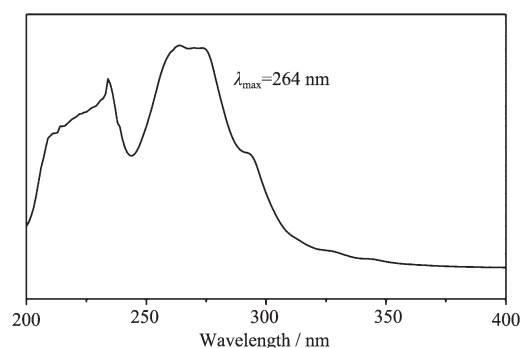


Fig.6 UV-Vis absorption spectroscopy of complex **1** in solid state

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