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5-4-(1*H*-四唑基)苯氧基-间苯二甲酸构筑的镉配位聚合物的合成、晶体结构及荧光性质

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摘要: 以柔性配体为原料,在水热条件下合成了 1 个新的三维镉配位聚合物{[$Cd_2L(OH)(H_2O)$]·$2H_2O$}$_n$(**1**)(H_3L=5-4-(1*H*-四唑基)苯氧基-间苯二甲酸),并对其进行了元素分析、红外、热重、荧光以及单晶 X-衍射表征及研究。单晶衍射结果表明,配合物结晶于三斜晶系 $P\bar{1}$ 空间群。配合物中,相邻的 Cd(1)和 Cd(2)原子通过 μ_3-桥联的羟基形成 1 个四核镉簇单元。相邻的四核簇二级构筑单元通过 5-4-(1*H*-四唑基)苯氧基-间苯二甲酸连接形成三维结构。配合物 **1** 的荧光测试表明该化合物是 1 个潜在的蓝色发光材料。

关键词: Cd(Ⅱ); 配位聚合物; 晶体结构; 荧光性质
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A Cd(Ⅱ) Coordination Polymer Constructed by 5-(4-(1*H*-tetrazol-5-yl)phenoxy)isophthalic Acid: Synthesis, Crystal Structure and Luminescent Properties

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Abstract: A new complex {[$Cd_2L(OH)(H_2O)$]·$2H_2O$}$_n$ (**1**) (H_3L=5-(4-(1*H*-tetrazol-5-yl)phenoxy) isophthalic acid) with a flexible ligand has been synthesized under hydrothermal conditions, and characterized by elemental analysis, infrared spectroscopy (IR), thermogravimetry analysis (TG), fluorescent spectra, powder and single-crystal X-ray diffractions. Single crystal structural analysis reveals complex crystallizes in triclinic space group of $P\bar{1}$. In complex, adjacent Cd (1) and Cd (2) atoms were connected by μ_3-bridging hydroxide anion to form a tetranuclear Cd cluster. These tetranuclear Cd(Ⅱ) secondary building units were further interconnected by the L^{3-} ligand to form a three-dimensional (3D) structure. The fluorescent characterization of **1** indicates that the compound s may be a candidate for blue fluorescent materials. CCDC: 919803.

Key words: Cd(Ⅱ); coordination polymer; crystal structure; luminescent property

0 Introduction

In decades, metal-organic frameworks (MOFs) have attracted intense attention due to their aesthetic topological structure and promising applications in the fields of gas separation/adsorption [1], ion exchange [2], catalysis [3], magnetism [4], and optical properties [5]. Recently, polycarboxylate and polypyridine ligands are reported as building blocks in self-assembling of MOFs with novel topologic structure and charming properties. [6-7] A flexible ligand with both polycarboxylate and polypyridine groups may be a

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good candidate for constructing such materials. Herein, we report a new Cd(Ⅱ) complex {[$Cd_2L(OH)(H_2O)$]·$2H_2O$}$_n$ with the use of such a flexible ligands, 5-(4-(1*H*-tetrazol-5-yl) phenoxy)isophthalic acid (H_3L). The thermal stability and luminescent properties of the complex are investigated in the solid state.

1 Experimental

1.1 Reagents and physical measurements

All reagents were obtained from commercial sources and used as received. Infrared spectra were obtained in KBr disks on a Nicolet Avatar 360 FTIR spectrometer in the range of 400~4 000 cm^{-1}. Solid state fluorescent measurements were carried out with a Perkin-Elmer LS 55 spectrofluorimeter. Thermogravimetric analysis was performed on a TA Instruments TGA 2050 Thermogravimetric Analyzer with a heating rate of 10 ℃·min^{-1} up to 800 ℃

1.2 Synthesis of {[$Cd_2L(OH)(H_2O)$]·$2H_2O$}$_n$

A mixture of $CdCl_2·2H_2O$ (0.1 mmol, 21.9 mg), H_3L (0.05 mmol, 16.3 mg), NaOH (0.2 mmol, 8 mg) and 10 mL water was placed in a 25 mL Teflon-lined stainless steel container, heated at 200 ℃ for 72 h and cooled to room temperature. Colorless crystals of **1** were selected, washed with distilled water and dried in air. Yield: 23.4% (based on $CdCl_2·2H_2O$). Anal. Calcd. for $C_{15}H_{14}Cd_2N_4O_9$ (%): C 29.10, H 2.28, N 9.05; Found (%): C 29.08, H 2.30, N 9.07. IR (KBr, cm^{-1}): 3 436(s), 3 137(s), 1 625(s), 1 565(s), 1 444(s), 1 410(s), 1 255(m), 1 162(m), 1 103(m), 976(m), 863(m), 770(m), 727(m), 623(m), 520(m), 445(m).

1.3 Structure determinations

Single-crystal X-ray diffraction measurement for complex **1** was carried out using a Bruker SMART APEX CCD diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) operating at T=296 (2) K. The data was integrated by the SAINT program. Absorption corrections were applied with SADABS. The structure was solved by direct methods (SHELXS 97) and refined by full-matrix least squares on F^2 using SHELXTL 97[8]. Hydrogen atoms bonded to the carbon atoms were generated geometrically and refined isotropically with the riding mode. Details of the crystal parameters, data collection, and refinements for **1** are summarized in Table 1.

CCDC: 919803.

Table 1 Crysta1 data of the title complex

Empirical formula	$C_{15}H_{14}Cd_2N_4O_9$	Volume / nm^3	0.919 3(7)
Formula weight	619.1	D_c / (g·cm^{-3})	2.236 4
Temperature / K	296(2)	Absorption coefficient / mm^{-1}	2.374
Crystal system	triclinic	F(000)	600
Space group	$P\bar{1}$	Crystal size/ mm	0.30×0.20×0.20
a / nm	0.915 3(1)	θ / (°)	2.23 to 28.50
b / nm	0.948 7(1)	Limiting indices	$-10\leqslant h\leqslant 10$, $-11\leqslant k\leqslant 11$, $-13\leqslant l\leqslant 13$
c / nm	1.115 3(2)	Reflections collected / unique	6 908 / 3 266(R_{int}=0.016 6)
α / (°)	90.929(2)	Data / restraints / parameters	3 266/10/293
β / (°)	99.746(2)	Goodness-of-fit on F^2	1.062
γ / (°)	105.174(2)	Final R indices [$I>2\sigma(I)$]	R_1=0.0188, wR_2=0.0477
Z	2	Largest diff. peak and hole / (e·nm^{-3})	440 and −520

2 Results and discussion

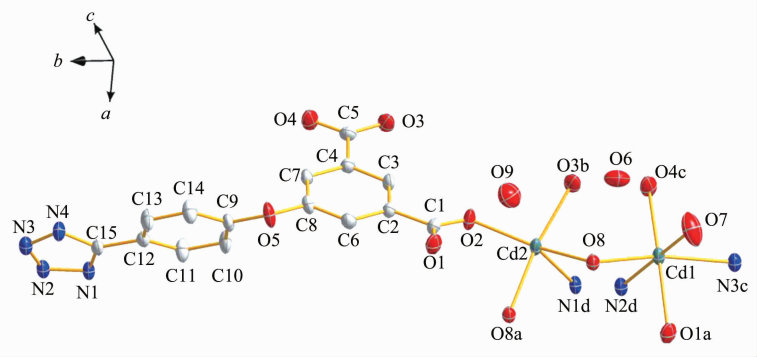
2.1 IR spectrum

The IR Spectrum shows that a strong peak at 3 436 cm^{-1} is the O-H stretching vibration of the coordination water. The stretching vibration of the aromatic rings can be found at 3 137 cm^{-1}. The asymmetric and symmetric stretching of carboxylate anion appear at 1 625 cm^{-1} ($\nu(OCO)_{assym}$) and 1 444 cm^{-1} ($\nu(OCO)_{sym}$), respectively. The $\Delta\nu(\nu(OCO)_{assym}-\nu(OCO)_{sym})$

is 181 cm^{-1} (<200) which shows the carboxylates bind to Cd ions as bidentate ligands.[9] The peak at 1 565 cm^{-1} can be contributed to the stretching vibration of C-N. The stretching peak of tetrazole of the ligand appears at 1 103 cm^{-1}. In addition, the X-ray diffraction analysis further reveals the existence of bridging coordination manners of the carboxylate groups.

2.2 Description of structure

X-ray crystallography study reveals that complex **1** crystallizes in triclinic space group of $P\bar{1}$. The asymmetric unit of **1** contains two Cd centers, one L^{3-} ligand, one μ_3-bridging OH^- anion, one coordinated water molecule and two lattice water molecules. As illustrated in Fig.1, each Cd center is six-coordinated forming distorted octahedral geometry with different coordination situations. Cd (1) atom is coordinated to two carboxylate oxygen atoms and two tetrazolyl nitrogen atoms from four distinct L^{3-} ligands, one OH^- anion and one water molecule. Cd (2) atom is surrounded by two OH^- anions, two carboxylate oxygen atoms and one tetrazolyl nitrogen atom from three distinct L^{3-} ligand, and one water molecule. The average Cd-O distance is 0.227 4 nm shorter than the typical average Cd-O distance 0.236 0 nm[10]. The Cd-N distance is 0.237 6 nm, which are comparable to the value of the reported Cd (Ⅱ) complex [11]. The nearest Cd-Cd distance is 0.339 2(1) nm.

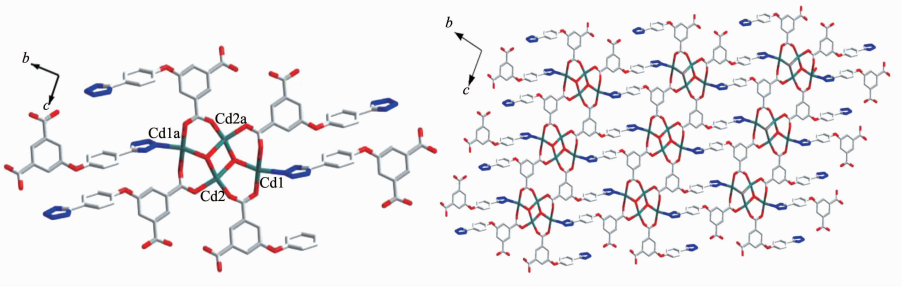


Hydrogen atoms are omitted for clarity. Symmetry codes: a: −*x*+1, −*y*+1, −*z*+1; b: −*x*+1, −*y*+1, −*z*+2; c: *x*−1, *y*−2, *z*−1; d: −*x*+2, −*y*+2, −*z*+2

Fig.1　Coordination environment of the Cd(Ⅱ) atom in the title complex with ellipsoids at 50% probability

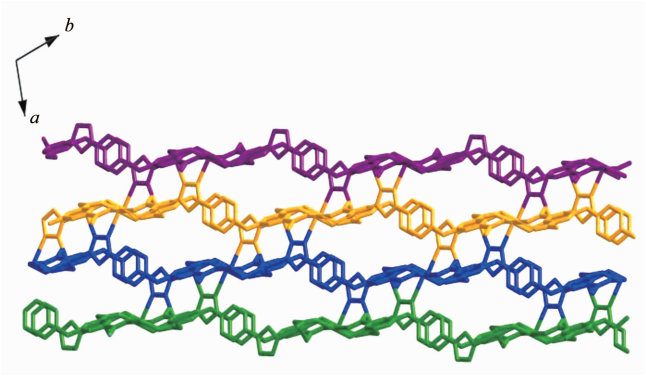
As shown in Fig.2a, four adjacent Cd atoms are joined together by two μ_3-bridging OH^- anions to give an unique $[Cd_4(OH)_2]$ tetranuclear cluster. In the cluster, four Cd atoms are almost coplanar. Furthermore, the Cd clusters were interconnected by carboxylate oxygen atoms and N(3) atoms of tetrazolyl group from six distinct L^{3-} ligands to form a 2D layer in bc plane (Fig.2b).

As shown in Fig.3, the 2D layers are further connected by the rest N(1) and N(2) atoms of tetrazolyl group from distinct L^{3-} ligands to form a three-dimensional framework with 1D channels. The 1D channels are partly occupied by lattice water molecules. There are abundant of hydrogen-bonding



Symmetry codes: a: −*x*+1, −*y*+1, −*z*+1

Fig.2　Tetranuclear Cd cluster (a) and the 2D framework (b) viewed along the *a* axis



Hydrogen atoms and lattice water molecules are omitted for clarity

Fig.3 3D framework viewed along *c* axis

Table 2 Hydrogen bonding geometry parameters for the title complex

D-H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠DHA / (°)
O6-H6A···N4e	0.085 2	0.218 9	0.3026	167.10
O6-H6B···O9	0.084 9	0.259 5	0.329 6	140.52
O7-H7A···N4c	0.084 5	0.239 9	0.294 9	123.33
O7-H7B···O6	0.087 0	0.196 2	0.275 1	150.25
O9-H9A···O6f	0.085 9	0.208 5	0.291 3	161.52
O9-H9B···O1	0.086 3	0.197 2	0.282 0	167.27
O9-H9B···O2	0.086 3	0.263 4	0.314 0	118.57
O8-H8···O6	0.075 1	0.228 6	0.299 8	158.69

Symmetry codes: c: $x-1, y-2, z-1$; e: $-x+1, -y+2, -z+2$; f: $-x, -y+1, -z+1$

interactions among OH^- anions, lattice water molecules and the L^{3-} ligands. The *d*(D···A) distances and D-H···A angles of hydrogen bonds arrange from 0.275 1 to 0.329 6 nm and 118.57° to 167.27°, respectively (Table 2). Undoubtedly, the hydrogen bonds are of favourable to the stabilization of the complex.

2.3 PXRD and TG analysis

To confirm the phase purity of compound **1**, the as-synthesized samples were characterized by Powder X-ray diffraction pattern (PXRD) at room temperature. The PXRD of **1** is in agreement with the simulated one from the single-crystal X-ray data (Fig.4a and 4b). It indicates that the crystal structure is truly representative of the bulk material. To determine the thermal stability of **1**, the TG measurement was carried out in the range of 20~800 ℃ (Fig.5). The TG plot of **1** shows a weight loss of 8.54% from room temperature to 125 ℃, corresponding to the removal of the lattice and coordinated H_2O molecules (Calcd. 8.72%). Then no weight loss was observed until the complex start to decompose after 400 ℃. The residues (39.20%) may be CdO (Calcd. 41.48%).

Rescently, the dehydration/rehydration of MOFs have drawn considerable attention because of their

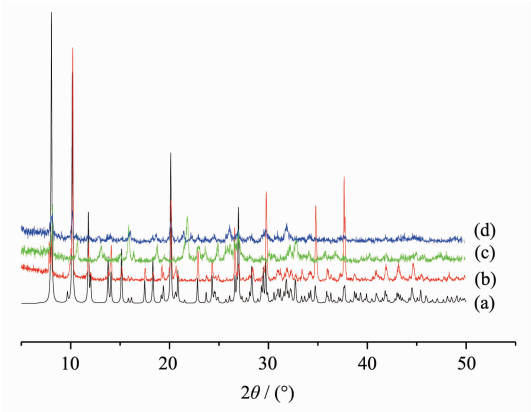


Fig.4 PXRD spectra of **1**: experimental (a), simulated (b), (c) after heated under 140 ℃ for 12 h, (d) after rehydrated under room temperature in water for 24 h

intriguing adsorption properties[12]. The TG plot reveals that complex **1** may be stable after the removal of the lattice and coordinated water molecules until 400 ℃. Hence, it may undergo a crystal-to-crystal phase transition upon guest and coordinated water molecules release. The PXRD of **1** show that the diffraction pattern of dehydrated sample deviates from the simulated one from the single-crystal X-ray data indicating a new crystal phase (Fig.4c).

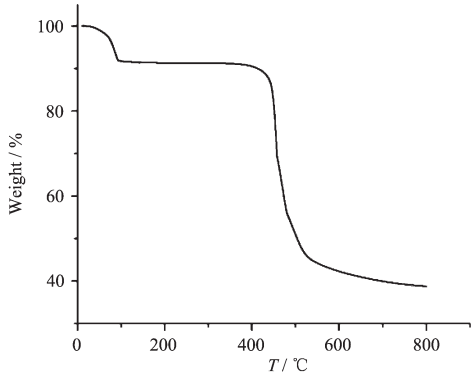


Fig.5　TG curve of complex **1**

After dipped in water for 24 h, the PXRD of rehydrated sample is recovered with the simulated one again suggesting the reversibility of the H_2O sorption process of **1** (Fig.4d). Therefore, the dehydration and rehydration of water molecules in complex is a reversible process.

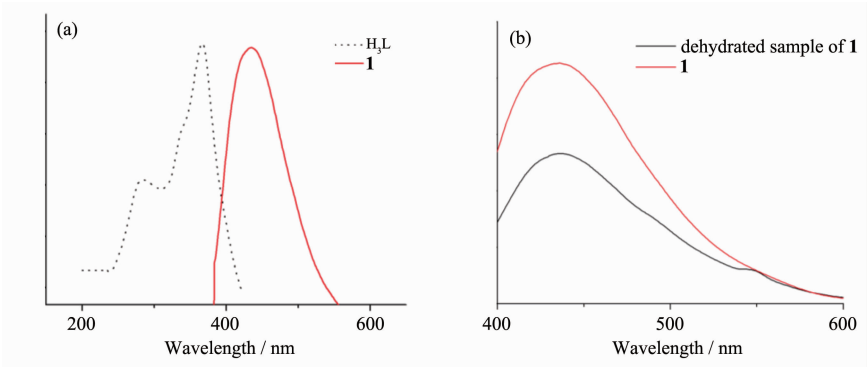


Fig.6　(a) Fluorescent emission spectra of free ligand and **1** in the solid state at room temperature; (b) The fluorescent emission spectra of **1** and its dehydrated sample

2.4　Luminescent properties

The luminescent spectra of free ligand (H_3L) and **1** were investigated in solid state at room temperature. As shown in Fig.6a, the free ligand exhibits an broad emission band with the maximum intensity at 367 nm (λ_{ex}=331 nm). While the complex **1** exhibits an intense emission band with the maximum intensity at 435 nm upon excitation at 365 nm. It is red-shifted 68 nm compared to the emission wavelength of the free ligand. The blue luminescence of **1** may result from ligand-to-metal charge transfer (LMCT)[13]. Correspondingly, the fluorescent emission spectrum of dehydrated smaple was also recorded in solid state at room temperature. As shown in Fig.6b, the fluorescent emission spectra of dehydrated sample exhibits similar intense emission band at 435 nm, but a new emission band at about 540 nm. The new emission band in the fluorescent emission spectra of **1** suggests that a new crystal phase was formed during the dehydration process.

3　Conclusion

A new cadmium complex, $\{[Cd_2L(OH)(H_2O)]\cdot 2H_2O\}_n$, was successfully synthesized under hydrothermal conditions and characterized. The fluorescent spectrum of compound indicates that it is a candidate for blue fluorescent material. The PXRD and TG analysis show that the dehydration and rehydration of water molecules in complex **1** is a reversible process.

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