

一个吡啶二甲酸镉配位聚合物的合成、晶体结构及荧光性质

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摘要: 通过水热方法,采用 H₃CAM(H₃CAM=4-hydroxy-pyridine-2,6-dicarboxylic acid)与 Cd(NO₃)₂·4H₂O 反应,合成了 1 个镉配位聚合物[Cd₄(HCAM)₄(H₂O)₈]_n (**1**),并对其结构和荧光性质进行了研究。结构分析结果表明该配合物属于单斜晶系,C2/c 空间群。四个 HCAM²⁻配体桥联 4 个镉离子形成了 1 个四核镉单元。这些孤立的单元通过氢键作用形成了 1 个三维配位框架。研究表明,该配合物在室温下能发出蓝色荧光。

关键词: 镉配合物; 4-羟基吡啶-2,6-二甲酸; 荧光

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Synthesis, Crystal Structure and Luminescent Properties of One Cadmium(II) Coordination Polymer Based on Pyridinedicarboxylic Acid Ligand

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Abstract: A cadmium(II) complex of [Cd₄(HCAM)₄(H₂O)₈]_n (H₃CAM=4-hydroxy-pyridine-2,6-dicarboxylic acid) (**1**) has been synthesized under hydrothermal condition and characterized by elemental analysis, IR spectroscopy, TG analysis, and luminescent analysis. Single-crystal X-ray diffraction analyses reveal that complex **1** has a tetranuclear unit with four cadmium ions bridged by four HCAM²⁻ ligands. The Cd(II) complex belongs to monoclinic system, with space group C2/c, *a*=1.754 77(4) nm, *b*=1.293 47(4) nm, *c*=1.652 25(4) nm, *β*=100.714(2)°, *V*=3.684 81(17) nm³, *Z*=4, *R*₁=0.024 4, *wR*₂=0.058 1. The discrete tetranuclear units are further assembled into a 3D supramolecular framework through H-bond interactions. In the solid state, complex **1** shows blue emission at room temperature. CCDC: 794674.

Key words: cadmium complex; 4-hydroxy-pyridine-2,6-dicarboxylic acid; luminescent properties

The design and synthesis of coordination polymers and discrete complexes have achieved great progress over the past decades^[1-2]. These complexes have shown not only their versatile architectures^[3-5] but also their desirable properties as luminescent, magnetic, catalytic, and gas absorption and separation properties^[1,6-12].

Especially, high-nuclearity and poly-nuclearity transition metal cluster have been intensively pursued in order to develop their physical properties^[13-17]. In view of the most common synthetic route, the crucial factor is to choose the appropriate ligand and metal ion for controlling the high-nuclearity structures^[18]. Many

multi-carboxylate or heterocyclic carboxylic acids are used for this purpose^[1,3,4,12-17]. In the designed synthesis of the complexes, 4-hydroxy-pyridine-2,6-dicarboxylic acid (H₃CAM) is an excellent pyridine dicarboxylate ligand^[19-20], which can afford at most one nitrogen atom and five O coordination sites. In order to extend the investigation in this field, we designed and synthesized complex [Cd₄(HCAM)₄(H₂O)₈]_n (**1**). Herein, we report the synthesis, crystal structure, and luminescent properties of the complex.

1 Experimental

1.1 Reagents and physical measurements

All chemicals and solvents were of A.R. grade and used without further purification. Carbon, hydrogen and nitrogen were determined using an Elementar Vario EL elemental analyzer. IR spectra were recorded using KBr pellets and a Nicolet FT-170SX instrument. Fluorescence measurements were made on an Edinburgh FLS920 Instrument. Thermogravimetric analysis (TGA) data were collected on a Netzsch TG-209 instrument with a heating rate of 10 °C · min⁻¹.

1.2 Synthesis of [Cd₄(HCAM)₄(H₂O)₈]_n (**1**)

A mixture of Cd(NO₃)₂ · 4H₂O (0.092 5 g, 0.3 mmol), H₃CAM (0.060 3 g, 0.3 mmol), a drop of triethylamine, and water (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 d, followed by cooling to room temperature at a rate of 10 °C · h⁻¹. Pale

yellow prismatic crystals of complex **1** were isolated manually, and washed with distilled water (yield 0.091 g, 80%). Elemental anal. calcd. for C₂₈H₂₈Cd₄N₄O₂₈(%): C, 25.5; H, 2.14; N, 4.25. Found (%): C, 25.8; H, 2.08; N, 4.22. IR spectrum (KBr, cm⁻¹): 3 448m, 3 067m, 1 567vs, 1 422s, 1 347s, 1 123w, 1 032m, 805m, 744m, 633w and 591w.

1.3 Structure determinations

Single-crystal data for complex **1** was collected at 296(2) K on a Bruker Smart Apex 1000 CCD diffractometer with Mo K α radiation (λ =0.071 073 nm). A total of 10 006 reflections were collected in the range of 1.97° < θ < 26.00° with 3 616 independent ones (R_{int} = 0.027 5). The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms (except for the ones bound to water molecules) were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. The hydrogen atoms of water molecules were located by difference maps and constrained to ride on their parent O atoms. All calculations were performed using the SHELXTL-97 system^[21]. The crystallographic data is summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

CCDC: 794674.

Table 1 Crystallographic data collection and structure refinement for complex **1**

Empirical formula	C ₂₈ H ₂₈ Cd ₄ N ₄ O ₂₈	<i>F</i> (000)	2 560
Formula weight	1 318.14	Crystal size / mm	0.38×0.32×0.29
Temperature / K	296(2)	θ range / (°)	1.97–26.00
Wavelength / nm	0.071 073	Index ranges	−21 ≤ <i>h</i> ≤ 21, −15 ≤ <i>k</i> ≤ 13, −18 ≤ <i>l</i> ≤ 20
Crystal system	Monoclinic	Reflections collected / unique (R_{int})	10 006 / 3 616 (0.027 5)
Space group	<i>C</i> 2/ <i>c</i>	Completeness to θ =26.99° / %	99.70
<i>a</i> / nm	1.754 77(4)	Independent reflections (R_{int})	3 990 (0.027 8)
<i>b</i> / nm	1.293 47(4)	Reflections observed ($I > 2\sigma(I)$)	3 653
<i>c</i> / nm	1.652 25(4)	Max. and min. transmission	0.5436 and 0.4632
β / (°)	100.714(2)	Data / restraints / parameters	3 616 / 7 / 297
Volume / nm ³	3.684 81(17)	Goodness-of-fit on F^2	0.964
<i>Z</i>	4	R_1, wR_2 ($I > 2\sigma(I)$)	0.021 9, 0.056 6
D_c / (g · cm ⁻³)	2.376	R_1, wR_2 (all data)	0.024 4, 0.058 1
Absorption coefficient / mm	2.393	Largest diff. peak and hole / (e · nm ⁻³)	391 and −414

Table 2 Selected bond lengths (nm) and angles (°)

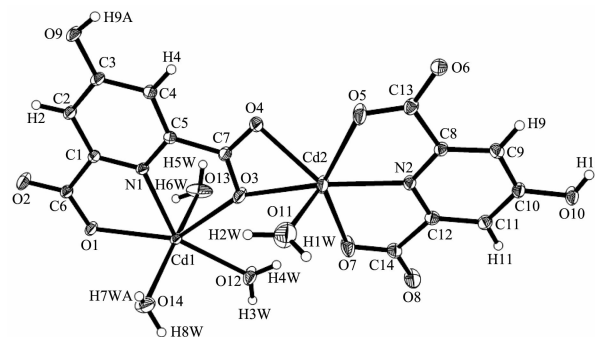
Cd(1)-O(12)	0.226 4(2)	Cd(1)-N(1)	0.228 6(2)	Cd(1)-O(14)	0.233 7(2)
Cd(1)-O(1)A	0.234 55(18)	Cd(1)-O(13)	0.237 5(2)	Cd(1)-O(1)	0.240 70(19)
Cd(1)-O(3)	0.250 86(19)	Cd(2)-N(2)	0.220 4(2)	Cd(2)-O(11)	0.219 3(3)
Cd(2)-O(4)	0.226 41(19)	Cd(2)-O(7)	0.230 6(2)	Cd(2)-O(3)	0.246 68(19)
Cd(2)-O(5)	0.247 6(2)				
O(12)-Cd(1)-N(1)	138.05(8)	O(4)-Cd(2)-O(7)	133.69(8)	O(7)-Cd(2)-O(5)	141.94(7)
O(12)-Cd(1)-O(14)	91.02(9)	N(2)-Cd(2)-O(3)	149.65(8)	O(3)-Cd(2)-O(5)	133.68(6)
N(1)-Cd(1)-O(14)	101.31(8)	O(11)-Cd(2)-O(3)	84.88(10)	Cd(1)A-O(1)-Cd(1)	108.69(7)
O(12)-Cd(1)-O(1)A	81.49(9)	O(4)-Cd(2)-O(3)	55.04(6)	Cd(2)-O(3)-Cd(1)	157.41(10)
N(1)-Cd(1)-O(1)A	81.60(8)	O(7)-Cd(2)-O(3)	82.75(7)	O(12)-Cd(1)-O(1)	152.80(9)
O(14)-Cd(1)-O(1)A	81.58(9)	N(2)-Cd(2)-O(5)	69.44(7)	N(1)-Cd(1)-O(1)	68.88(7)
O(12)-Cd(1)-O(13)	88.05(10)	N(1)-Cd(1)-O(3)	67.94(8)	O(14)-Cd(1)-O(1)	84.31(8)
N(1)-Cd(1)-O(13)	89.02(8)	O(14)-Cd(1)-O(3)	101.47(9)	O(1)A-Cd(1)-O(1)	71.31(7)
O(14)-Cd(1)-O(13)	165.35(8)	O(1)A-Cd(1)-O(3)	151.74(7)	O(13)-Cd(1)-O(1)	89.87(9)
O(1)A-Cd(1)-O(13)	83.99(9)	O(13)-Cd(1)-O(3)	91.70(9)	O(12)-Cd(1)-O(3)	70.42(9)
O(11)-Cd(2)-O(4)	94.22(9)	O(1)-Cd(1)-O(3)	136.77(7)	N(2)-Cd(2)-O(4)	136.68(8)
N(2)-Cd(2)-O(7)	72.55(8)	N(2)-Cd(2)-O(11)	116.62(11)	O(11)-Cd(2)-O(7)	100.79(11)

Symmetry transformations used to generate equivalent atoms: A: $-x+1, -y+1, -z$.

2 Results and discussion

2.1 Structure description

As shown in Fig.1, the asymmetric unit of complex **1** contains two crystallographically independent Cd(II) centres. The Cd1 is seven-coordinated by one nitrogen atom and three oxygen atoms from two different HCAM²⁻ ligands, and the other three oxygen atoms coming from three water ligands, respectively, resulting in a distorted pentagonal bipyramid coordination geometry. One N atom (N1), three O atoms (O1, O1A, O3 and O12) from two different HCAM²⁻ ligands and one O atom from water ligand locate in the equatorial plane, while two O (O13 and O14) atoms from water ligands occupy the axial positions. Unlike the coordination geometry of Cd1, Cd2 is six-coordinated ligated by one nitrogen and four oxygen atoms from two independent HCAM²⁻ ligands, and one oxygen atom coming from water ligand, completing its highly distorted octahedron configuration with the equatorial plane defined by one N atom (N2) and four O atoms from two different HCAM²⁻ ligands (O4, O5 and O7) and one water ligand (O11). The axial positions are taken by O3 and N2 from two different HCAM²⁻ ligands.



Thermal ellipsoids are drawn at the 30% level; Symmetry code: A: $-x+1, -y+1, -z$

Fig.1 ORTEP drawing of the asymmetric unit of complex **1**

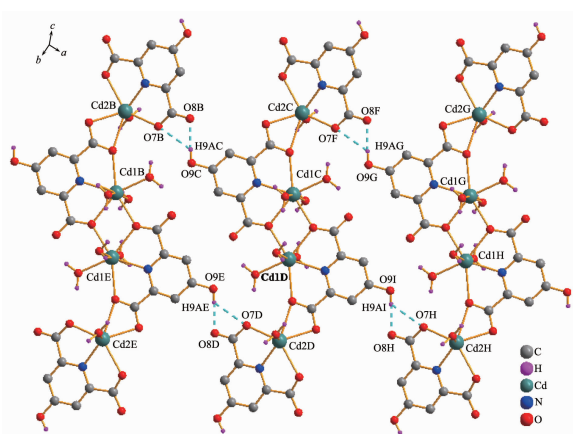
The Cd-O bond distances are in the range of 0.226 4(2)~0.250 8(2) nm for Cd-O_{carboxyl} and 0.221 0(3)~0.246 7(2) nm for Cd-O_{water}, which are well comparable to those reported for other oxygen donor compounds^[22-23]. The bond distances of Cd1-O10, Cd1-N1 and Cd1-N2 are 0.228 7(2) and 0.220 5(2) nm, respectively. Four cadmium ions are bridged by four HCAM²⁻ ligands to form a unit. Each HCAM²⁻ ligand adopts a μ_3 -pentadentate coordination mode (Fig.1). As shown in Fig.2, these units are formed 2D sheet structure through hydrogen bonding along a axis. Then the 2D network formed among parallel layers through hydrogen bonding

Table 3 Hydrogen bond lengths and bond angles for complex 1

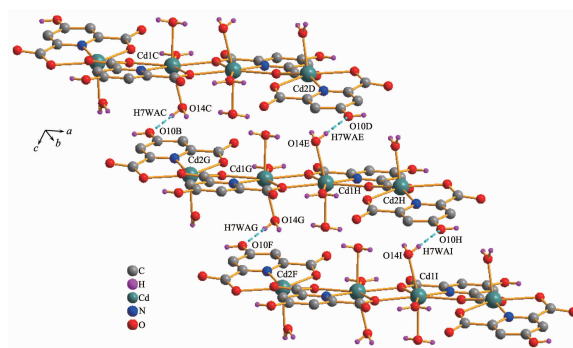
D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
O(9)-H(9A)...O(8)C	0.082	0.183	0.264 9(3)	177.0
O(9)-H(9A)...O(7)C	0.082	0.258	0.212 4(3)	124.8
O(10)-H(10)...O(5)D	0.082	0.192	0.272 9(3)	170.5
O(11)-H(1W)...O(12)E	0.089	0.236	0.288 8(4)	118.3
O(11)-H(1W)...O(9)D	0.089	0.240	0.318 1(4)	147.8
O(11)-H(1W)...O(7)E	0.089	0.265	0.332 0(4)	133.6
O(11)-H(2W)...O(6)F	0.090	0.288	0.274 3(4)	158.6
O(12)-H(3W)...O(2)B	0.090	0.183	0.262 4(3)	145.2
O(14)-H(7WA)...O(14)E	0.07	0.232	0.293 9(5)	148.1
O(14)-H(8W)...O(6)G	0.084	0.192	0.275 2(3)	172.8
O(13)-H(5W)...O(4)H	0.082 4(19)	0.207(2)	0.289 0(4)	171(6)

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

G: $x+1/2, y-1/2, z$; H: $-x+1/2, -y+3/2, -z$.



Dashed lines represent the hydrogen bonds; Symmetry code: B: $-0.5+x, 1.5-y, 0.5+z$; C: $x, 1-y, 0.5+z$; D: $1-x, y, 0.5-z$; E: $0.5-x, 0.5+y, 0.5-z$; F: $x, 1-y, 0.5+z$; G: $0.5+x, 0.5-y, 0.5+z$; H: $1.5-x, -0.5+y, 0.5-z$; I: $1-x, y, 0.5-y$

Fig.2 View of 1D chain of complex 1 in the bc plane

Symmetry code: B: $x, 1-y, -0.5+z$; C: $x, -y, -0.5+z$; D: $1-x, -1+y, -0.5-z$; E: $1-x, y, -0.5-z$; F: $x, 2-y, -0.5+z$; G: $x, 1-y, -0.5+z$; H: $1-x, y, -0.5-z$; I: $1-x, 1+y, -0.5-z$

Fig.3 2D sheet formed through hydrogen bonding interactions between adjacent sheets along b axis

interactions (Fig.3a). The layers are further arranged to construct a 3D H-bonding zigzag structure due to different stretching directions of the 2D sheets. This indicates that the hydrogen bonds play an important role in stabilizing the framework of complex 1.

2.2 Thermal analysis

In order to examine the thermal stability of the complex 1, thermal gravimetric (TG) analyses was carried out in the range of 20~800 $^\circ\text{C}$ under nitrogen atmosphere. The TG curve of the complex 1 (Fig.4) reveals that the initial weight loss of 10.90% (calcd. 10.89%) occurs from 160 to 258 $^\circ\text{C}$ corresponding to the loss of eight water ligands. Above 320 $^\circ\text{C}$ the complex 1 is destroyed gradually.

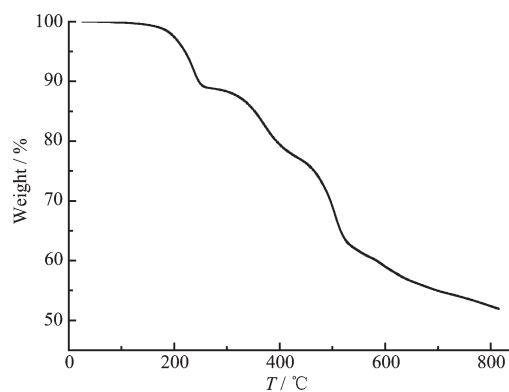


Fig.4 TGA curve for complex 1

2.3 Luminescent properties

Previous studies have shown that the complex containing cadmium exhibits photoluminescent properties^[24]. The solid-state luminescent properties of

free H₃CAM ligand and complex **1** were investigated at room temperature, as shown in Fig.5. Complex **1** exhibits a blue fluorescent emission band at 527 nm upon excitation (ex) at 468 nm which is 2 nm red-shifted emission compared to the free ligand. It is observed that the fluorescent intensities of complex **1** is weaker than those of the free H₃CAM ligand. The reason of fluorescence quenching is under investigation.

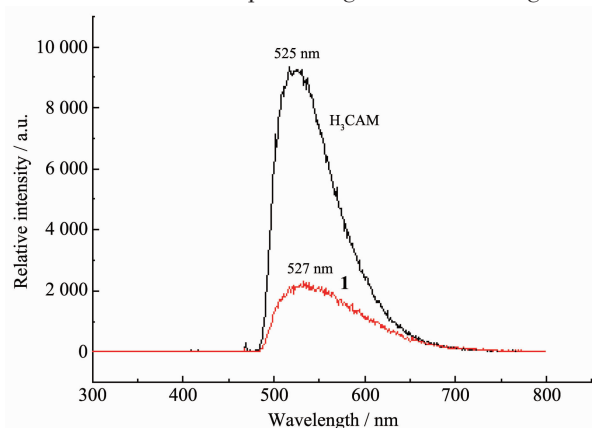


Fig.5 Photoluminescent emission spectra of complex **1** and H₃CAM ligand in the solid state at room temperature

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