

三维混配型三核镉(II)配合物的合成及荧光性质

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摘要: 水热合成法合成了新颖的三核超分子配合物 $[\text{Cd}_3(\text{PDA})_3(2,2'\text{-bipy})_3(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**1**) (H_2PDA =pyridine-2,6-dicarboxylic acid), 并进行了元素分析、红外、热重、荧光及单晶衍射测试。该化合物属单斜晶系, $P2_1/n$ 空间群, 晶胞参数分别为: $a=2.122\ 81(14)\ \text{nm}$, $b=1.006\ 09(7)\ \text{nm}$, $c=2.830\ 64(19)\ \text{nm}$, $\beta=108.937\ 0(10)^\circ$ 。中心原子配位数为 7, 羧基以双齿形式将 Cd1、Cd2、Cd3 桥联组成三核配合物。分子间氢键与 π - π 堆积构筑成三维超分子结构。荧光分析表明该配合物在室温下发出强烈的蓝色荧光, 具有潜在的应用价值。

关键词: 镉配合物; π - π 堆积; 三维结构; 荧光

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3D Framework and Intense Photoluminescence of a Novel Trinuclear Cadmium(II) Complex with Mixed Ligands

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Abstract: A novel trinuclear cadmium(II) supramolecular complex $[\text{Cd}_3(\text{PDA})_3(2,2'\text{-bipy})_3(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**1**) (H_2PDA =pyridine-2,6-dicarboxylic acid) has been prepared under hydrothermal condition and characterized by elemental analysis, IR, TG, fluorescence spectrum and single-crystal X-ray diffraction. The complex crystallizes in monoclinic system, space group $P2_1/n$ with $a=2.122\ 81(14)\ \text{nm}$, $b=1.006\ 09(7)\ \text{nm}$, $c=2.830\ 64(19)\ \text{nm}$, $\beta=108.937\ 0(10)^\circ$. The structure of the complex consists of trinuclear units with all metal centers being seven-coordinated. Cd1, Cd2 and Cd3 atoms are bridged by three carboxylate groups in dimonodentate fashion to give a trinuclear molecular building block $[\text{Cd}_3\text{N}_9(\text{CO}_2\text{R})_6]$. Intermolecular hydrogen-bond interactions and face-to-face π - π stacking interactions lead the complex to a 3D supramolecular architecture. Fluorescent analyses show that the complex exhibits intense blue photoluminescence at room temperature and may be potential candidate for photoactive material. CCDC: 712746.

Key words: cadmium complex; π - π stacking interactions; 3D structure; photoluminescence

0 Introduction

Over the last years much attention has been paid to polynuclear transition-metal complexes because such complexes possess promising perspectives toward new

functional materials^[1-3]. For example, these compounds have potential applications in the areas of catalysis^[4], conductivity^[5], magnetism^[6], and optical materials. It is known that molecular self-assembly to polynuclear complexes structures is the basis for the construction of

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new products^[7]. In principle, some control over molecular architecture can be gained by judicious selection of the factors which affect the crystal structure of the compound, such as the chemical structure of the organic spacers (ligands), the coordination geometry preference of the metal, the inorganic counter ions, and the metal-to-ligand ratio^[8-12]. Amongst those factors, ligand design is often a useful way of manipulating the overall structure^[13]. pyridine-2,6-dicarboxylic acid (H_2PDA) is a very important carboxylate derivative, which has a rigid 120° angle between the central pyridine ring and two carboxylate groups and therefore could potentially provide various coordination motifs to form both discrete and consecutive metal complex under appropriate synthesis condition^[14-16]. A systematic study of coordination complexes based on H_2PDA has been undertaken, which gives rich coordination motifs for PDA ^[17-21]. Herein, we have synthesized a new trinuclear cadmium(II) supramolecular complex introducing another organic bidentate ligand 2,2'-bipy. Otherwise polynuclear d^{10} metal-organic complexes have been found to exhibit interesting photoluminescent properties^[22-23]. The photoluminescent emission peaks have also been studied in this work, defining a little difference compared with others. The photoluminescent emission makes the title compound apotentially useful photoactive solid-state material.

1 Experimental

1.1 Materials and physical measurement

All materials and organic solvents were of analytical grade and used without further purification. Distilled, deionized water was used throughout. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 elemental analyzer. The infrared spectrum was recorded as a KBr pellet on a Nicolet 170SXFTIR spectrometer in the $4\,000\sim400\text{ cm}^{-1}$ range. The electronic absorption spectra were taken on a Shimadzu UV-240 spectrophotometer. TG measurement

was carried out on a Perkin-Elmer7 thermal analysis system in air with a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Fluorescent analyses were performed on an Edinburgh Instruments FL920 analyzer.

1.2 Synthesis of $[Cd_3(PDA)_3(2,2'\text{-bipy})_3(H_2O)_2]\cdot 2H_2O$ (**1**)

A mixture of $Cd(CH_3COO)_2\cdot 2H_2O$ (0.133 7 g), H_2PDA (0.083 9 g), 2,2'-bipy (0.078 8 g) and H_2O (10 mL) was stirred for half an hour in air, with adding KOH ($0.5\text{ mol}\cdot\text{L}^{-1}$) solution until $pH=4.8$. The mixture was transferred to a Teflon-lined stainless steel autoclave (25 mL) and kept at $170\text{ }^\circ\text{C}$ for 4 d, and cooled the autoclave to room temperature, then crystals were recovered. The crystals were washed with distilled water twice and dried under vacuum. The yield was 25% based on Cd. Anal. Calcd. for $Cd_3C_{52}H_{52}N_9O_{21}(\%)$: C, 44.57; H, 2.99; N, 9.18. Found(%): C, 43.93; H, 3.03; N, 9.06.

1.3 X-ray crystallography

Single-crystal X-ray crystallographic analysis of **1** with approximate dimensions $0.22\text{ mm}\times0.24\text{ mm}\times0.28\text{ mm}$ was performed at $291(2)\text{ K}$ on a Bruker SMART APEX CCD diffractometer with graphite monochromated $Mo\ K\alpha$ ($\lambda=0.071\,073\text{ nm}$) radiation. Data collection, indexing, and initial cell refinements were carried out using SMART software^[24]. Frame integration and final cell refinements were carried out using SAINT software^[25]. Absorption corrections for each data set were applied using SADABS^[26]. The single Crystal structure of title compound was solved by direct methods using the SHELXS^[27], and refined on F^2 by the full-matrix least-squares methods using the SHELXL program^[27]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were located at their ideal positions as a riding mode. The crystallographic data and structure determination parameters for the complex are summarized in Table 1. Selected bond distances and angles are given in Table 2.

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Table 1 Crystallographic parameters of the title compound

Empirical formula	$Cd_3C_{51}H_{41}N_9O_{16}$	Absorption coefficient / mm^{-1}	1.191
Formula weight	1 373.13	$F(000)$	2728
T / K	291(2)	Crystal size / mm	$0.22\times0.24\times0.28$

Continued Table 1

Wavelength / nm	0.071 073	θ range / (°)	2.10~26.00
Crystal system	Monoclinic	Index ranges	$-22 \leq h \leq 26, -12 \leq k \leq 11, -34 \leq l \leq 34$
Space group	$P2_1/n$	Reflections collected	30 222
V / nm^3	5.718 3(7)	Unique reflections	11 117
a / nm	2.122 81(14)	Data / restraints / parameters	11 117 / 1.02 / 739
b / nm	1.006 09(7)	Final R indices ($I > 2\sigma(I)$)	$R_1=0.068\ 3, wR_2=0.104\ 2$
c / nm	2.830 64(19)	R indices (all data)	$R_1=0.046\ 2, wR_2=0.099\ 5$
$\beta / (^\circ)$	108.937 0(10)	Goodness-of-fit on F^2	1.025
Z	4		

(a) $R_1 = \sum \|F_o| - |F_c|\| / \sum |F_o|$; (b) $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; (c) $w^{-1} = \sigma^2(F_o)^2 + (0.05P)^2 + 1.99P$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2 Selected bond lengths (nm) and bond angles (°) of the title compound

Cd1-N1	0.227 5(4)	Cd1-O3	0.245 4(3)	Cd1-N4	0.234 3(4)
Cd1-O5	0.254 9(3)	Cd1-N5	0.234 9(4)	Cd1-O6	0.232 5(3)
Cd1-O2	0.236 3(4)	Cd2-N2	0.234 5(4)	Cd2-N6	0.239 1(4)
Cd2-N7	0.233 8(4)	Cd2-O6	0.249 6(4)	Cd2-O7	0.237 0(3)
Cd2-O10	0.233 8(3)	Cd2-O2w	0.227 8(3)	Cd3-N3	0.232 9(4)
Cd3-N8	0.234 1(4)	Cd3-N9	0.238 6(4)	Cd3-O7	0.240 8(3)
Cd3-O10	0.245 9(3)	Cd3-O12	0.239 7(3)	Cd3-O1w	0.226 1(3)
N1-Cd1-O2	70.00(13)	N1-Cd1-O3	68.48(13)	O6-Cd1-O5	52.81(11)
N4-Cd1-N5	69.33(15)	O6-Cd1-O3	75.46(12)	N5-Cd1-O5	97.81(15)
N1-Cd1-N4	97.63(15)	N6-Cd2-O6	82.69(12)	N2-Cd2-O7	91.85(14)
O10-Cd2-O7	69.17(11)	N7-Cd2-N6	69.08(14)	O2w-Cd2-O10	83.27(11)
O2w-Cd2-O7	114.81(11)	O2w-Cd2-N2	94.37(12)	O2w-Cd2-O6	76.88(11)
O2w-Cd2-N6	93.80(12)	O2w-Cd2-N7	156.56(13)	N3-Cd3-O12	68.73(13)
N3-Cd3-O10	67.00(13)	O7-Cd3-O10	66.61(10)	N8-Cd3-N9	69.30(14)
O1w-Cd3-N9	94.39(12)	O1w-Cd3-O7	78.93(11)	O1w-Cd3-O12	85.59(11)
O1w-Cd3-N3	94.95(12)	O1w-Cd3-N8	163.63(13)	O1w-Cd3-O10	109.43(11)

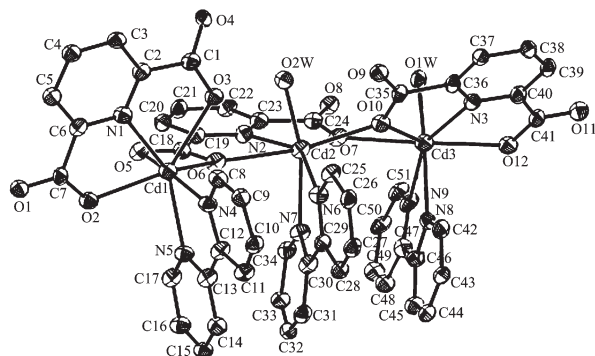
2 Results and discussion

2.1 Crystal structure

Single crystal X-ray diffraction analysis reveals that each asymmetric unit contains three Cd^{2+} ions, three PDA ligands, three 2,2'-bipy ligands, two coordinated water molecules and two crystal water molecules (Fig.1). Cd1, Cd2, Cd3 are all seven-coordinated with a distorted pentagonal bipyramidal geometry. The Cd1 atom is coordinated by four oxygen atoms and three nitrogen atoms from two PDA ligands and one 2,2'-bipy ligand to form a coordination sphere (Cd-O 0.226 1(3)~0.254 9(3) nm, Cd-N 0.227 5(4)~0.234 9(4) nm). The Cd2 is ligated by three carboxylic oxygen atoms (Cd-O 0.233 8(3)~0.249 6(4) nm) from

two PDA ligands, one oxygen atom from water molecule (Cd-O 0.227 8(3) nm) and three nitrogen atoms from PDA and 2,2'-bipy ligands (Cd-N 0.234 4(4)~0.238 2(4) nm). The Cd3 atom is coordinated by four oxygen atoms and three nitrogen atoms from two PDA ligands, one 2,2'-bipy ligand and one water molecule to furnish the coordination geometry. The Cd-O bond lengths vary from 0.226 1(3) to 0.245 9(3) nm, the Cd-N bond lengths are in the range of 0.232 9(4)~0.238 6(4) nm, all of which are comparable to those reported for other cadmium-oxygen and cadmium-nitrogen donor complexes^[28-29]. Cd1, Cd2 and Cd3 atoms are bridged by three carboxylate groups in dimonodentate fashion to give a trinuclear molecular building block $[\text{Cd}_3\text{N}_9(\text{CO}_2\text{R})_6]$ with shorter separation of $\text{Cd}\cdots\text{Cd}$ (0.387 3 and 0.456 6 nm).

Cd2 and Cd3 atom have the same coordination environments, which are different from Cd1 atom. It is rare that the same metal ions have different coordination environments in one molecular building block in one compound^[30-32]. The dihedral angles between the two pyridine rings in the same 2,2'-bipyridine are 2.31°, 6.24° and 11.62°, respectively. Three crystallographically independent PDA molecules show two distinct coordination motifs B, E and I which are found in other coordination complexes^[33].



Crystal water molecular and hydrogen atoms being omitted for clarity

Fig.1 Molecular structure of compound **1** with thermal ellipse at the 30% probability level

Another important interaction is the face-to-face stacking interaction. The shortest $\pi \cdots \pi$ centroid-to-centroid distance between the offset face-to-face (the interior alternate angle is 87.19°) aromatic rings intramolecular is 0.371 2 nm (Fig.2). The shortest $\pi \cdots \pi$ centroid-to-centroid distances between the offset face-to-face aromatic rings (Cg(*n*) with N(*n*)) intermole-

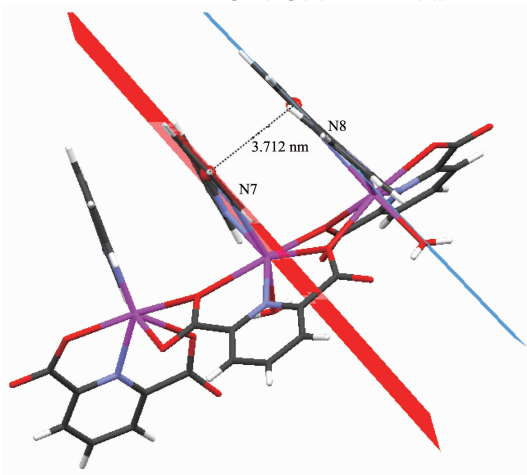


Fig.2 Intramolecular face-to-face π - π stacking interactions of the compound **1**

cular are 0.356 9 nm (Cg(2)→Cg(3), symmetry codes: 1/2-*x*, -1/2+*y*, 1/2-*z*;), 0.373 1 nm (Cg(4)→Cg(5), symmetry codes: -*x*, 1-*y*, 1-*z*), 0.374 1 nm (Cg(9)→Cg(9), 1-*x*, -*y*, 1-*z*), respectively. The extensive $\pi \cdots \pi$ stacking interaction increases the stability of the structure. Meanwhile, the structure is extended into a 3D supramolecular framework via the face-to-face π - π stacking interactions between the pyridine rings of 2,2'-bipy ligands.

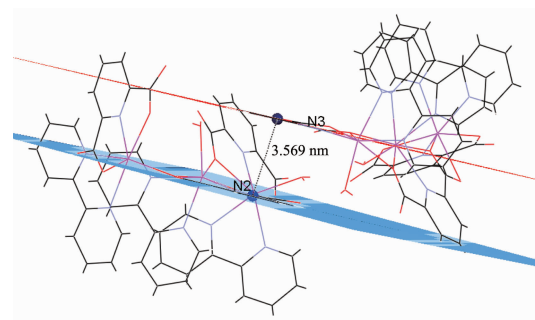


Fig.3 Intermolecular face-to-face π - π stacking interactions of the compound **1**

2.2 IR spectrum

The FTIR spectrum of the complex is very much consistent with the structural data. Characteristic bands for the dicarboxylate groups at 1 614 and 1 578 cm^{-1} due to the asymmetric stretching, and at 1 362 and 1 317 cm^{-1} due to the symmetric stretching are observed. The strong band at the 3 400 cm^{-1} (O-H stretching vibration) indicates the presence of uncoordinated methanol and water molecules. In addition to these peaks, the peaks at 1 437 and 1 475 cm^{-1} are assigned to the absorption of C=N and C=C group of PDA and 2, 2'-bipy.

2.3 TG analyses

The TGA data of the complex indicate three obvious weight losses shown in Fig.4. The first weight loss starts at ca. 50~150 °C to give a total weight loss of 11.23% (calcd. 5.24%), corresponding to the loss of water molecules. And then at ca. 215~378 °C to give a total loss of 31.51% (calcd. 30.03%) corresponding to the loss of 2,2'-bipy ligands. And then the third step was attributed to the removal of PDA ligands from 378 to 482 °C with the lost weight of 37.7% (calcd. 36.49%).

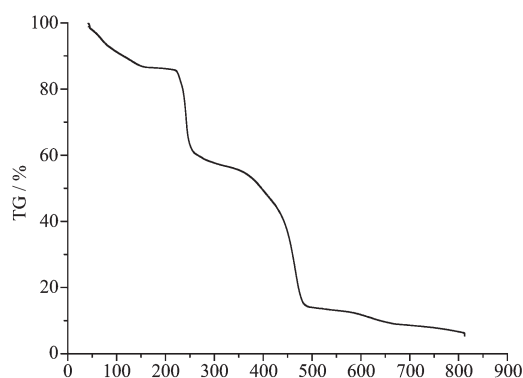


Fig.4 TG curve of the compound 1

2.4 Luminescent property

The solid state emission spectra of title complexes at room temperature are depicted in Fig.5. Complex exhibits intense blue emissions maximum at 460 nm, when excited at 325 nm. Comparably, the H₂PDA ligand shows emission at 366 nm with excitation at 325 nm, which is attributable to the $\pi^* \rightarrow n$ transition^[34]. The luminescence of the complex is tentatively assigned to the intraligand fluorescent emission and the red-shift in the complex is probably due to the coordination of H₂PDA to the Cd(II) centers^[35]. The thermal stability as well as the photoluminescent emission makes the complex a potentially useful photoactive solid-state material.

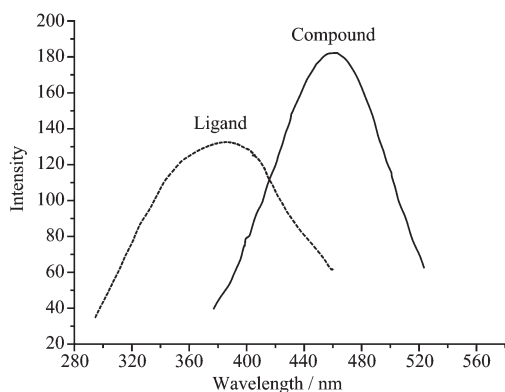


Fig.5 Emission spectrum of the complex in the solid state at room temperature

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