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4-羟基吡啶-2,6-二羧酸配体构筑的环状四核镉配合物的水热合成、晶体结构及性质研究

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摘要: 在水热条件下合成了一个金属镉配合物$[Cd_4(cam)_4(phen)_4]\cdot 4H_2O$($H_2cam$=4-羟基吡啶-2,6-二羧酸,phen=1,10-邻菲咯啉),并用元素分析、红外光谱、X-射线单晶衍射、热重分析和荧光分析对其进行了表征。晶体结构表明:该配合物属于单斜晶系,$P2_1/c$空间群,晶胞参数为:a=1.421 61(10) nm,b=1.946 42(13) nm,c=1.439 66(10) nm,β=115.385 0(10)°。每个 $Cd^{Ⅱ}$离子七配位呈变形五角双锥几何构型,两对 $Cd^{Ⅱ}$离子与 4 个$(cam)^{2-}$离子相连形成了环状四核结构。相邻的四核单元通过氢键的识别作用形成二维超分子网;氢键和 $\pi\cdots\pi$ 堆积作用进一步将其扩展为三维超分子结构。

关键词: 镉配合物; 晶体结构; 水热合成; 荧光
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Hydrothermally Synthesis, Crystal Structure and Properties of a Cyclic Tetranuclear Cadmium Complex Based on 4-Hydroxypyridine-2,6-dicarboxylic Acid

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Abstract: A cadmium complex $[Cd_4(cam)_4(phen)_4]\cdot 4H_2O$ (H_2cam=4-hydroxypyridine-2,6-dicarboxylic acid hydrate, phen =1,10-phenanthroline) has been hydrothermal synthesized and structurally characterized by elemental analyses, thermal stability analysis, IR and single-crystal X-ray diffraction analyses. Crystal structural analysis reveals that it crystallizes in monoclinic system, space group $P2_1/c$, a=1.421 61(10) nm, b=1.946 42(13) nm, c=1.439 66(10) nm, β=115.385 0(10)°. The $Cd^{Ⅱ}$ ion is seven-coordinate with a slightly distorted pentagonal bipyramid geometry. Two pairs $Cd^{Ⅱ}$ ions joined with four $(cam)^{2-}$ ions to form a cyclic tetranuclear structure. The neighboring tetranuclear units are linked into 2D supramolecular network through hydrogen bonding interaction. Hydrogen bonding and $\pi\cdots\pi$ stacking interactions contact the 2D network to form 3D supramolecular structures. CCDC: 820965.

Key words: cadmium complex; crystal structure; hydrothermal synthesis; luminescence

The self-assembled construction of supramolecular structure is of current interest because controlling the molecular organization in the solid state can lead to materials with structure and promising properties[1-7]. One of the efficient routs to complexes is to employ a multifunction ligand to link metal ions give an infinite framework. Recently, increasing investigations have been focused on the

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constructions of complexes using heterocyclic carboxylic acids such as pyridine-[8-11], pyrazole-[12-13], and imidazole-carboxylic acids[14-16] as building blocks. These building blocks contain multi-oxygen and nitrogen atoms and can coordinate with metal ions in different ways, resulting in the formations of various metal-organic frameworks (MOFs) with specific topologies and useful properties. In this aspect, 4-hydroxypyridine-2,6-dicarboxylic acid hydrate (H_2cam) has six potential donor atoms, which can yield the formation of MOF through multiple bonding interactions and adopt different conformations and coordination modes and provide abundant structural motifs. Furthermore, they can act not only as hydrogen bond donors but as acceptors, which make them a wonderful candidate for the construction of supramolecular networks depending upon the number of deprotonated carboxylate groups. However, to the best of our knowledge, cam-metal complex have been documented very little to date[17-19]. We also notice that the introduction of N-containing auxiliary ligands, such as phen into the system may lead to new structural evolution and fine-tuning the structural motif of the complexes. With the aim of understanding the coordination chemistry of them and studying the influence on the framework structure of the complexes, we have recently engaged in the research of this kind of complex. Fortunately, we have now isolated a novel complex, $[Cd_4(cam)_4(phen)_4]\cdot 4H_2O$. Herein we reported the synthesis, structure, thermal stability and photoluminescence of the title complex.

1 Experimental

1.1 Reagents and physical measurements

All chemicals and reagents were used as received from commercial sources without further purification. All reactions were carried out under hydrothermal conditions. Elemental analyses (C, H, N) were determined with a Elementar Vario EL Ⅲ elemental analyzer. IR spectra were recorded as KBr pellets on a Bruker EQUINOX55 spectrophotometer in the 4 000~400 cm^{-1} region. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Thermogravimetric analyses (TGA) were performed under nitrogen with a heating rate of 10 ℃·min^{-1} using a Universal V2.6 DTA Instruments.

1.2 Synthesis of $[Cd_4(cam)_4(phen)_4]\cdot 4H_2O$ (1)

A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.1 mmol, 0.030 8 g), cam (0.1 mmol, 0.018 3 g), phen (0.1 mmol, 0.019 8 g) in molar ratio 1:1:1 and water (10 mL) was stirred and adjusted to pH 6.5 with 0.5 mol·L^{-1} NaOH solution, then sealed in a 25 mL Telfon-lined stainless steel container, which was heated to 160 ℃ for 72 h, then cooling to room temperature at a rate of 5 ℃·h^{-1}. Pale-yellow block crystals were obtained. Yield: 48%. Anal. Calcd. for $C_{76}H_{52}N_{12}O_{24}Cd_4$ (%): C, 46.22; H, 2.66; N, 8.49; Found (%): C, 46.25; H, 2.64; N, 8.52. FIIR (KBr, cm^{-1}) for 1: 3 078 (w), 1 707 (m), 1 617(s), 1 526(s), 1 440(s), 1 270(m), 1 231(m), 1 073(m), 855(w), 814(m), 733(m).

1.3 X-ray crystallography

Intensity data were collected on a Bruker Smart APEX Ⅱ CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm) at room temperature. Empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by the full-matrix least-squares based on F^2 using SHELXTL-97 program[20]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. The water hydrogen atoms were located from difference Fourier syntheses. Crystal data and structural refinement parameters for **1** are summarized in Table 1. Selected bond distances and bond angles are listed in Table 2.

CCDC: 820965.

Table 1 Crystal data and structural refinement parameters for the title complex

Empirical formula	$C_{76}H_{52}N_{12}O_{24}Cd_4$	Z	2
Formula weight	1 966.90	D_c / (g·cm^{-3})	1.815

Continued Table 1

Crystal system	Monoclinic	μ / mm^{-1}	1.258
Space group	$P2_1/c$	F(000)	1 952
a / nm	1.421 61(10)	λ (Mo $K\alpha$) / nm	0.071 073
b / nm	1.946 42(13)	Reflections collected	17906
c / nm	1.439 66(10)	S on F^2	1.030
β / (°)	115.385 0(10)	R_1,wR_2 (I>2σ(I))	0.031 3, 0.064 6
V / nm^3	3.599 0(4)	R_1,wR_2 (all data)	0.038 2, 0.067 5

Table 2 Selected bond distances (nm) and bond angles (°) for the title complex

Cd(1)-O(1)	0.241 7(3)	Cd(1)-O(10A)	0.225 7(2)	Cd(2)-O(9)	0.242 8(2)
Cd(1)-O(4)	0.254 4(2)	Cd(2)-O(6)	0.256 6(2)	Cd(2)-O(5)	0.242 4(2)
Cd(1)-N(1)	0.230 2(3)	Cd(2)-N(6)	0.229 2(2)	Cd(2)-O(4)	0.243 8(2)
Cd(1)-N(3)	0.228 2(2)	Cd(2)-N(4)	0.238 9(3)	Cd(2)-N(5)	0.233 0(3)
Cd(1)-N(2)	0.236 0(3)				
O(10A)-Cd(1)-N(3)	90.27(8)	O(10A)-Cd(1)-N(1)	154.19(9)	N(3)-Cd(1)-N(1)	109.66(9)
O(10A)-Cd(1)-N(2)	100.98(10)	N(3)-Cd(1)-N(2)	145.82(10)	N(1)-Cd(1)-N(2)	71.89(10)
O(10A)-Cd(1)-O(1)	95.97(9)	N(3)-Cd(1)-O(1)	69.64(9)	N(1)-Cd(1)-O(1)	106.10(9)
N(2)-Cd(1)-O(1)	77.10(9)	O(10A)-Cd(1)-O(4)	90.23(9)	N(3)-Cd(1)-O(4)	68.13(8)
N(1)-Cd(1)-O(4)	82.63(8)	N(2)-Cd(1)-O(4)	142.83(8)	O(1)-Cd(1)-O(4)	137.31(7)
N(6)-Cd(2)-N(5)	108.19(10)	N(6)-Cd(2)-N(4)	144.99(9)	N(5)-Cd(2)-N(4)	70.60(10)
N(6)-Cd(2)-O(5)	135.22(8)	N(5)-Cd(2)-O(5)	89.77(9)	N(4)-Cd(2)-O(5)	79.37(8)
N(6)-Cd(2)-O(9)	69.98(7)	N(5)-Cd(2)-O(9)	99.56(9)	N(4)-Cd(2)-O(9)	75.69(8)
O(5)-Cd(2)-O(9)	148.56(8)	N(6)-Cd(2)-O(4)	106.35(8)	N(5)-Cd(2)-O(4)	142.14(9)
N(4)-Cd(2)-O(4)	89.53(8)	O(5)-Cd(2)-O(4)	54.21(7)	O(9)-Cd(2)-O(4)	106.44(8)
N(6)-Cd(2)-O(6)	66.32(7)	N(5)-Cd(2)-O(6)	95.89(9)	N(4)-Cd(2)-O(6)	147.89(8)
O(5)-Cd(2)-O(6)	71.38(7)	O(9)-Cd(2)-O(6)	136.24(7)	O(4)-Cd(2)-O(6)	84.08(7)

Symmetry code A: 1–x, 1–y, 1–z.

2 Results and discussion

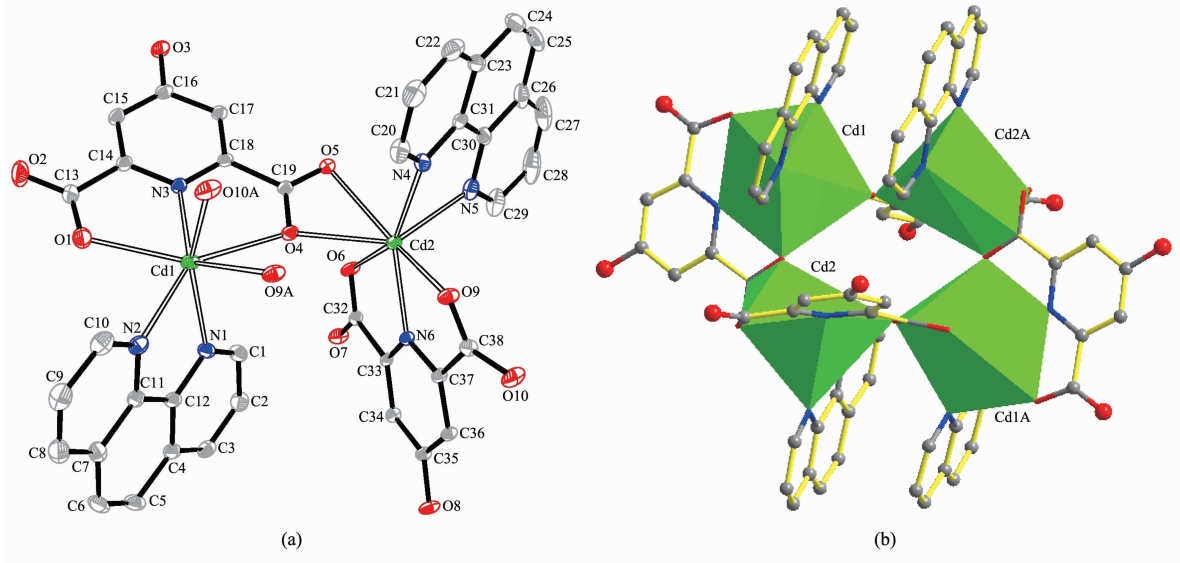
2.1 Structure of $[Cd_4(cam)_4(phen)_4]\cdot 4H_2O$

The asymmetric unit consists of two Cd Ⅱ ions, two completely deprotonated cam^{2-} ions, two phen ligands and two lattice water molecules. As illustrated in Fig. 1a, each Cd1 atom is coordinated by two nitrogen atoms (Cd1-N1 0.230 2(3); Cd1-N2 0.236 0(3) nm) from one chelating phen ligand, one nitrogen atom from a cam^{2-} ion (Cd1-N3 0.228 2(2) nm), two oxygen atoms (O1, O4) (Cd1-O1 0.241 7(3); Cd1-O4 0.254 4(2) nm) from two carboxylate groups of one (cam)$^{2-}$ anion, the other oxygen atom from one carboxylate group of another (cam)$^{2-}$ anion (Cd1-O10A 0.225 7(2) nm). However, the distance of 0.270 1(3) nm between Cd1-O9A suggests a nonnegligible interaction between them. Thus, the Cd1 atom can be regarded as a distorted pentagonal bipyramid. Five atoms O1, O4, O9A, N2 and N3 comprise the equatorial plane, while another two atoms N1, O10A occupy the axial positions. The coordination geometry in Cd2 is similar to that in Cd1 except for the slight difference in bond lengths and angles. Cd2 atom is seven-coordinated (N3O4) and with the five atoms O4, O6, N4, N5 and N6 in the equatorial plane and two atoms O5 and O9A in the axial positions. The Cd2-O bond lengths are in the range of 0.242 4(2)~0.256 6(2) nm, in good agreement with previous studies[21].

It worth to noting that the cam^{2-} ligand adopts a pentadentate chelating and bridging coordination mode (Fig.1a); one carboxylate group connects with one Cd Ⅱ ion monodentately, one carboxylate group

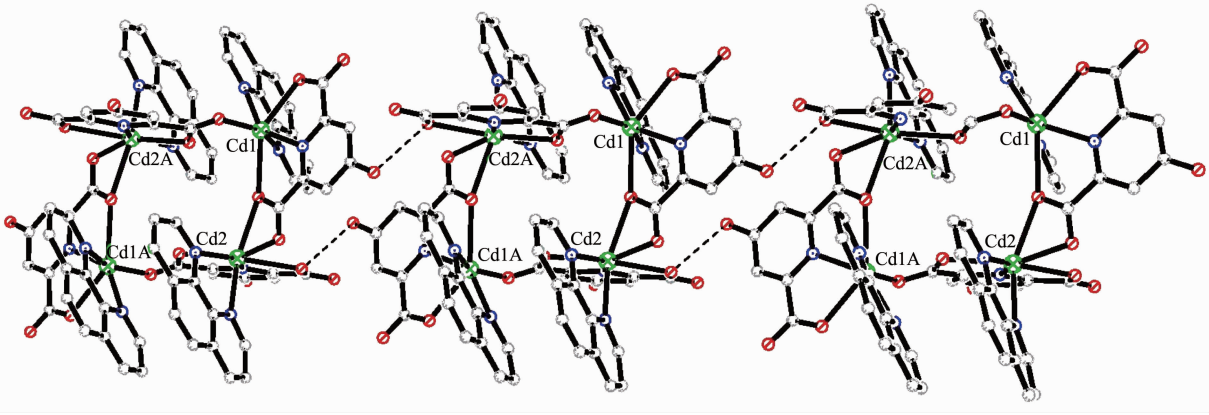
adopts a chelate/bridge tridentate coordination mode connecting two $Cd^{Ⅱ}$ ions; whereas the nitrogen atom adopts a monodentate coordination mode connecting one $Cd^{Ⅱ}$ ion. This coordination mode has never been observed in other metal-cam complexes[17-19].

Based on the connection mode, two pairs of $Cd^{Ⅱ}$ centers are bridged by four cam^{2-} anions to form a tetranuclear cadmium structure in an conner-sharing mode, which containing a type of micropore with size of *ca.* 0.771 6 nm×0.613 1 nm (based on the distances of Cd1⋯Cd1A and Cd2⋯Cd2A; symmetry code: A: 1−*x*, 1−*y*, 1−*z*). (Fig.1b). The cyclic tetranuclear structure is decorated with four phen ligands at the four directions. Interestingly, the adjacent tetranuclear molecular recognize each other to generate a 1D supramolecular chain via hydrogen bonding interaction between the coordinated carboxylate oxygen atom (O6) and hydroxyl oxygen atom (O3) (O3B−H3B⋯O6C, 0.268 4(3) nm; symmetry codes: B: 1+*x*, *y*, *z*; C: 2−*x*, 1−*y*, 2−*z*) (Fig.2). The neighboring supramolecular chains further linked into 2D supramolecular network through hydrogen bonding interaction between hydroxyl oxygen atom (O8) and the carboxylate group oxygen atom (O7) of $(cam)^{2-}$ anion (O8A−H8A⋯O7D, 0.264 0 (3) nm; symmetry codes: A: 1−*x*, 1−*y*, 1−*z*; D: 1−*x*, −0.5+*y*, 1.5−*z*) (Fig. 3). While the $\pi\cdots\pi$ stacking interactions are observed in supramolecular chains between coordinated cam^{2-}



Symmetry code: A: 1−*x*, 1−*y*, 1−*z*; Ellipsoid probability was drawn at 30%, all H atoms are omitted for clarity

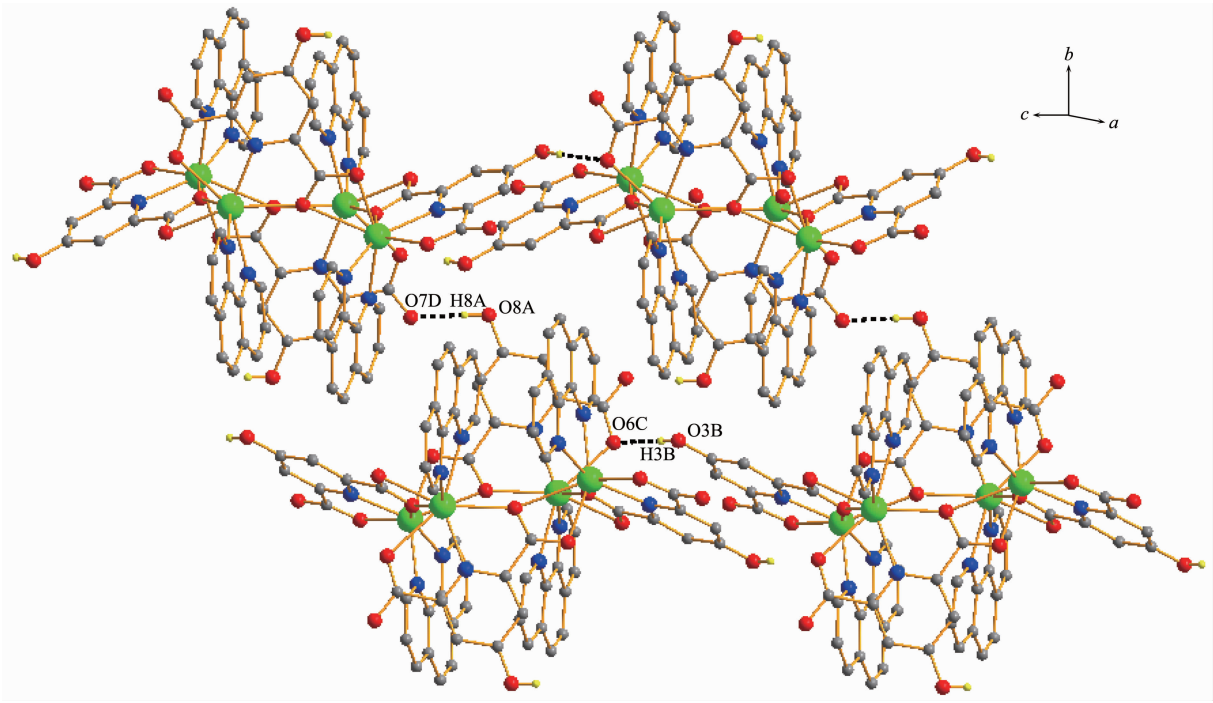
Fig.1 (a) ORTEP view of the asymmetric unit in the title complex; (b) View of the tetranuclear cadmium unit



Symmetry code: A: 1−*x*, 1−*y*, 1−*z*

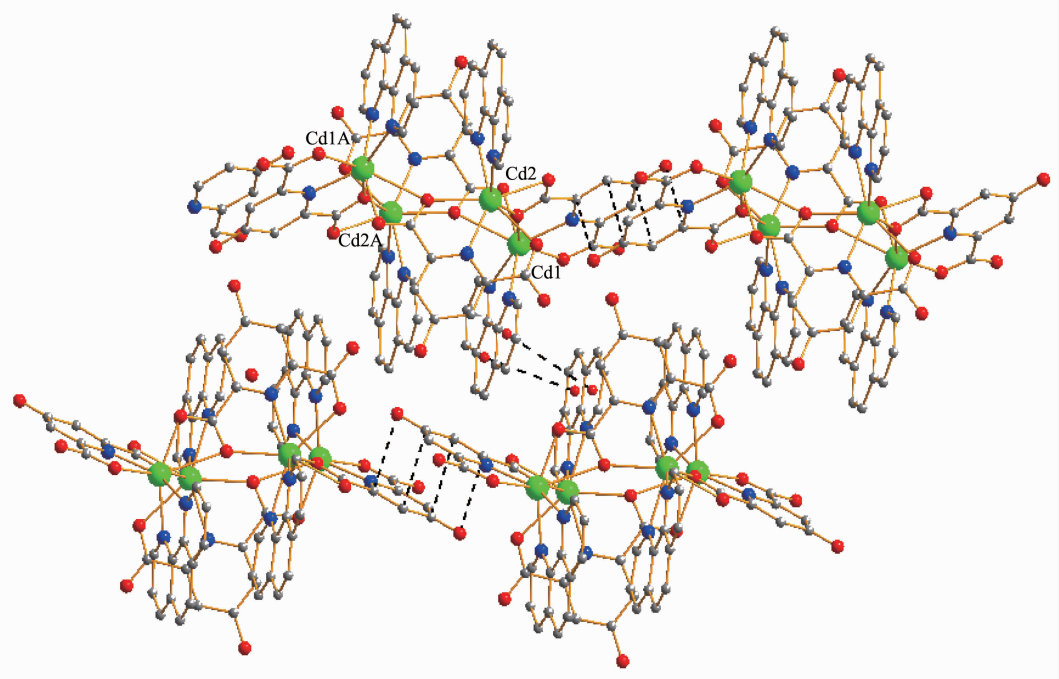
Fig.2 Perspective view of the 1D supramolecular chain

anion with edge-to-edge distances of 0.320 2 and 0.324 1 nm. Interestingly, the adjacent 1D supramolecular chains are also linked by the slipped $\pi\cdots\pi$ interactions between the offset face-to-face phenyl rings of adjacent phen ligands due to its centroid-centroid distance of 0.356 1 and 0.382 2 nm, which make the crystals more stable (Fig.4). More remarkably, the neighboring 2D supramolecular networks are arranged in a [ABAB…] alternation to form 3D supramolecular structure through hydrogen



Symmetry codes: A: 1−*x*, 1−*y*, 1−*z*; B: 1+*x*, *y*, *z*; C: 2−*x*, 1−*y*, 2−*z*; D: 1−*x*, −0.5+*y*, 1.5−*z*

Fig.3　View of 2D supramolecular networks based on hydrogen bond interactions



Symmetry code: A: 1−*x*, 1−*y*, 1−*z*

Fig.4　$\pi\cdots\pi$ stacking interactions (black) between the neighboring complexes

bonding interaction between lattice water and the carboxylate group oxygen atom of cam^{2-} anion (O11–H11···O2B, 0.270 8(3); O12–H12···O1B, 0.291 2(3) nm) and C–H···O interactions (C27C–H27C···O7, 0.262 0(3) nm); symmetry codes: B: 1+*x*, *y*, *z*; C: 1–*x*, 1–*y*, 2–*z*.

2.2 IR Spectra

The title complex exhibit a broad band in the 3 000~3 300 cm^{-1} region, which may be ascribed to hydrogen-bonded ν(O-H) and ν(N-H), and may also include ν(C-H) vibrations. In infrared spectra, no band was observed in the region 3 600~3 300 cm^{-1}. This indicated the absence of O-H stretching vibrations of carboxylic acids and suggests the complete deprotonation of cam ligand, which is consistent with the X-ray structural analysis. The characteristic absorptions for the asymmetric and symmetric vibrations of the carboxylate groups of the cam ligand are observed at 1 526 and 1 440 cm^{-1}, respectively. The separation $\Delta\nu$ (COO) between the ν_{as}(COO) and ν_s (COO) band is 86 cm^{-1}, which is smaller than 200 cm^{-1}, indicating that the carboxyl groups are coordinated in bridging mode[22].

2.3 Luminescent properties

Taking into account the excellent luminescent properties of d^{10} metal complexes, the luminescence of the title complex and free H_2cam ligand were investigated. The free ligand exhibits one weak emission band at 372 nm upon excitation at 289 nm. It was found that the title complex exhibit a emission peak at *ca.* 395 nm upon excitation at 310 nm (Fig.6), which means a red shift of *ca.* 23 nm relative to that of the free ligand. According to the literature[23-25], it may be tentatively assigned to ligand to metal charge transfer (LMCT). By comparing the emission spectra of the title complex and free ligand, we can conclude that the enhancement of luminescence of the title complex may be attributed to the ligation of ligand to the metal center, which effectively increases the rigidity and reduces the loss of energy by radiationless decay[25-26].

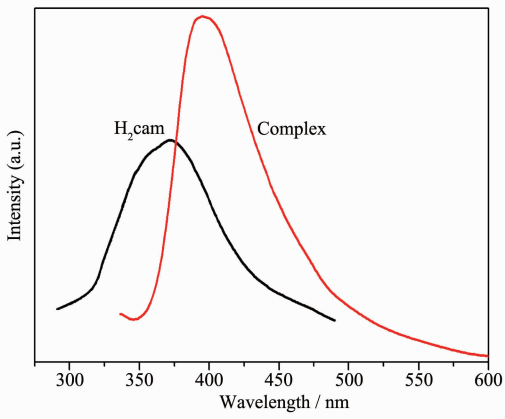


Fig.6 Emission spectra of free ligand H_2cam and the title complex in the solid state at room temperature

2.4 Thermogravimetric analyses

To characterize the thermal stability of the complex, thermal gravimetric analyses (TGA) were carried out. The TGA curve of the complex shows the first weight loss of 4.03% over the temperature range 85~125 ℃, corresponding to the loss of four free water molecular (Calcd. 3.65%). Then the complex was relatively stable up to 220 ℃, followed by two-step weight loss in the range of 220~630 ℃, the second weight loss is 38.56% from 220 to 450 ℃, corresponding to consecutive loss of phen ligands (Calcd. 40.3%). The third weight loss step is 36.28% from 450 to 605 ℃, assigned to the decomposition cam^{2-} ligands (Calcd. 37.12%). The remaining weight of 25.55% is in accordance with the mass of CdO residue (Calcd. 25.96%).

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