

由苯并咪唑-5-羧酸构筑的 Cd(II)配合物的水热合成、 晶体结构和荧光性质

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摘要: 通过水热合成的方法得到 1 个由苯并咪唑-5-羧酸(HL)配体构筑的 Cd(II)配合物 $[\text{Cd}(\text{L})_2(\text{H}_2\text{O})]_n$ 。在配合物中, 镉中心为变形的八面体配位构型。每个配体连接着 2 个镉原子, 每个镉原子通过 4 个配体相互连接, 在 *bc* 面上形成以平行四边形为基本结构单元的二维层状结构, 层与层之间通过 $\text{N}-\text{H}\cdots\text{O}$ 和 $\text{O}-\text{H}\cdots\text{O}$ 氢键连接形成三维超分子网络结构。此外, 我们还研究和讨论了配合物的固态荧光性质。

关键词: 镉的配合物; 苯并咪唑-5-羧酸; 水热合成; 荧光性质

中图分类号: O614.24² 文献标识码: A 文章编号: 1001-4861(2009)08-1402-06

Synthesis, Crystal Structure and Luminescence Property of A Cd(II) Complex with Benzimidazole-5-carboxylic Acid

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Abstract: A Cd(II) complex, $[\text{Cd}(\text{L})_2(\text{H}_2\text{O})]_n$ (**1**), based on benzimidazole-5-carboxylic acid (HL) ligand has been hydrothermally synthesized. The Cd(II) atoms have a distorted octahedron coordination geometry. Each L ligand links two Cd(II) atoms and each Cd(II) atom attaches to four L ligands to form a two-dimensional (2D) layer structure along *bc* plane, which consists of regular parallelograms, then yield a three-dimensional (3D) supramolecular network by $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. The TGA and luminescence property in solid state of complex **1** have been further studied and discussed in this paper. CCDC: 722775.

Key words: Cd(II) complex; benzimidazole-5-carboxylic acid; hydrothermally synthesis; luminescence property

Molecular self-assembly has emerged as an attractive approach to the fabrication of new materials. In a spontaneous molecular self-assembly process, the structural information stored in both the organic ligand and the metal ion is read out by the coordination through their coordination geometry^[1]. So the selection of appropriate metal ions and organic ligands is the key in the construction of complexes. Research in the area of coordination polymers built from transitional metal ions

and rigid aromatic carboxylates continues to be interesting due to their intriguing structural topologies^[2] and potential properties^[3,4] for eventual application as functional materials. As known, transitional metal ions, for their lower coordination numbers and stable coordination geometry, have been widely used in the architecture of complexes. The multiple coordination sites of ligands can form the structures of higher dimensions^[5-8]. Benzimidazole-5-carboxylic acid, as a

收稿日期: 2009-03-23。收修改稿日期: 2009-06-08。

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member of them, has been less studied up to now. The linear, rigid ligand benzimidazole-5-carboxylic acid, which possesses one imidazole ring and one rigid carboxyl group, is of great important and widely employed to ligate metal ions as building blocks to construct coordination polymers. It is well known that supramolecular architectures having different topologies and functions is one of the important targets in crystal engineering^[9~11]. Our strategy lies in the recognition that the benzimidazole-5-carboxylic acid ligand with an imidazole ring and a carboxylate group can serve as a strong N-H...O hydrogen bonding donor-acceptor site, and generate secondary net-to-net interaction^[12]. With the aim of understanding the coordination chemistry of benzimidazole-5-carboxylic acid and preparing new materials with interesting structural topology and physical properties, we recently began studies on the assembly reactions of benzimidazole-5-carboxylic acid with metal ions via solution or hydrothermal synthetic methods. Herein, we wish to report the hydrothermal synthesis and crystal structure of a first three-dimensional cadmium complex $[\text{Cd}(\text{L})_2(\text{H}_2\text{O})]_n$ (**1**).

1 Experimental

1.1 Materials and measurements

All starting materials and solvents for syntheses were obtained commercially and used without further purification. IR spectra were recorded on an FTIR-8700 spectrometer with KBr pellets in the range of 4 000~400 cm^{-1} . Elemental analysis was performed on a PE-2400(II) element analysis instrument. The crystal data collections were carried out on a Bruker SMART APEX-II CCD diffractometer. Thermogravimetric analysis was determined on a Mettler-Toledo TGA/SDTA 851° under oxygen atmosphere. Luminescence spectra were recorded using on a FluoroMax-4 Fluorescence Spectrometer in solid state at room temperature.

1.2 Synthesis of the complex

A mixture of benzimidazole-5-carboxylic acid (0.087 3 g, 0.6 mmol), $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.114 2 g, 0.5 mmol) and H_2O -ethanol (1:1, 16 mL) was sealed in a 25 mL stainl-ess-steel reactor with a Teflon liner and was heated at 433 K for 3 d. After cooling to room temperature at a rate of 2 °C per hour, the red crystals suitable for X-ray analysis were obtained in 45% yield. Elemental Anal. Found (%): C, 42.47; H, 2.63; N, 12.40. Calcd. for $\text{C}_{16}\text{H}_{12}\text{CdN}_4\text{O}_5$ (%): C, 42.45; H, 2.67; N, 12.38; IR (KBr, cm^{-1}): 3 406(w), 3 168(s), 3 130(s), 2 922(w), 1 597(m), 1 541(s), 1 469(m), 1 380(s), 1 288(w), 786(s).

1.3 X-ray crystal structure analysis

A crystal of **1** with dimensions of 0.54 mm×0.36 mm×0.16 mm was selected for structure determination. Data collection was performed on a Bruker SMART APEX-II CCD diffractometer using a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 296(2) K. The data was collected up to 2θ maximum of 55.14° using the ω -scan technique. A total of 13 425 reflections were collected with 3 597 unique ones ($R_{\text{int}}=0.024\ 1$), of which 3 149 reflections with $I>2\sigma(I)$ were considered as observed and used in the subsequent structure determination and full-matrix leastsquare refinements. Data intensities were corrected for Lorentz-polarization factors and empirical absorption. The structure was solved by direct methods and expanded with Fourier techniques. Anisotropic displacement parameters were applied to all non-hydrogen atoms in full-matrix least-squares refinements based on F^2 . The hydrogen atoms were assigned with isotropic displacement factors and included in the final refinement cycles by the use of geometrical restraints. All calculations were performed with SHELX-97 package^[13]. All pertinent crystallographic data for **1** is summarized in Table 1. The select bond distances and bond angles are listed in Table 2.

Table 1 Crystallographic data for complex **1**

Empirical formula	$\text{C}_{16}\text{H}_{12}\text{CdN}_4\text{O}_5$	μ / mm^{-1}	1.439
Formula weight	452.7	F(000)	1 792
Crystal color and habit	Red, block	Crystal size / mm	0.54×0.36×0.16
Temperature / K	296(2)	θ range for data collection / (°)	1.76~27.57
Wavelength / nm	0.071 073	Limiting indices	$-31 \leq h \leq 28, -10 \leq k \leq 11, -18 \leq l \leq 19$

Continued Table 1

Crystal system	Monoclinic	Reflections collected	13 425
Space group	$C2/c$	Reflections unique (R_{int})	3 597 (0.024 1)
a / nm	2.424 68(10)	Refinement method	Full-matrix least-squares on F^2
b / nm	0.890 30(4)	Data / restraints / parameters	3 597 / 3 / 241
c / nm	1.516 30(6)	Goodness-of-fit on F^2	1.016
β / ($^\circ$)	107.623(2)	Final R indices [$I > 2\sigma(I)$]	$R_1=0.023$ 2, $wR_2=0.057$ 3
V / nm ³	3.119 6(2)	R indices (all data)	$R_1=0.028$ 5, $wR_2=0.059$ 9
Z	8	Largest diff. peak and hole / ($e \cdot \text{nm}^{-3}$)	545 and -356
D_c / ($\text{g} \cdot \text{cm}^{-3}$)	1.928		

Table 2 Selected bond distances (nm) and bond angles ($^\circ$) for **1**

Cd(1)-O(1) ⁱ	0.222 19(16)	Cd(1)-O(1W)	0.235 91(15)	Cd(1)-N(1)	0.227 90(17)
Cd(1)-O(4)	0.238 57(14)	Cd(1)-N(3) ⁱⁱ	0.228 18(17)	Cd(1)-O(3)	0.251 08(15)
O(1) ⁱ -Cd(1)-N(1)	83.17(6)	N(3) ⁱⁱ -Cd(1)-O(4)	94.14(6)	O(1) ⁱ -Cd(1)-N(3) ⁱⁱ	109.10(7)
O(1W)-Cd(1)-O(4)	89.44(6)	N(1)-Cd(1)-N(3) ⁱⁱ	110.97(7)	O(1) ⁱ -Cd(1)-O(3)	102.58(6)
O(1) ⁱ -Cd(1)-O(1W)	84.50(6)	N(1)-Cd(1)-O(3)	83.88(6)	N(1)-Cd(1)-O(1W)	157.90(6)
N(3) ⁱⁱ -Cd(1)-O(3)	146.18(6)	N(3) ⁱⁱ -Cd(1)-O(1W)	90.39(6)	O(1W)-Cd(1)-O(3)	81.00(5)
O(1) ⁱ -Cd(1)-O(4)	155.97(7)	O(4)-Cd(1)-O(3)	53.44(5)	N(1)-Cd(1)-O(4)	94.43(6)

Symmetry transformations used to generate equivalent atoms: ⁱ $x, y-1, z$; ⁱⁱ $x, -y+1, z-1/2$.

CCDC: 722775.

2 Results and discussion

2.1 IR Spectrum

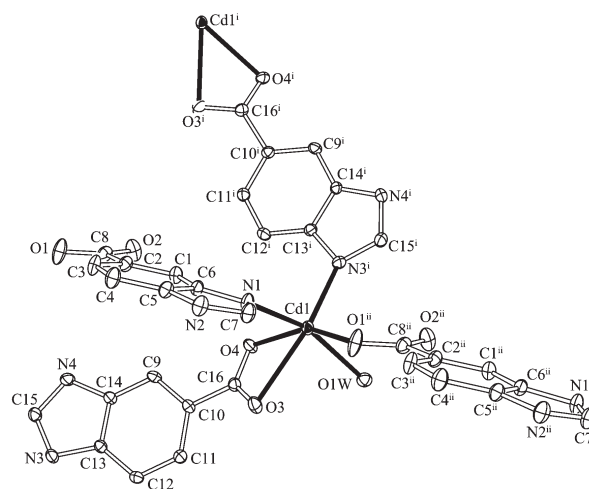
Complex **1** was synthesized by the hydrothermal method at 160 $^\circ\text{C}$. The strong peaks from 3 406 to 2 922 cm^{-1} of complex **1** are assigned to the N-H stretching vibrations and the O-H stretching vibrations. The conspicuous carboxylate stretching at 1 597, 1 541, 1 469, 1 380 cm^{-1} represent two groups of the antisymmetric $\nu_{as}(\text{COO}^-)$ and symmetric stretching frequency $\nu_s(\text{COO}^-)$. The strong band appearing at the 706 cm^{-1} in **1** is ascribed to the asymmetric stretching vibration of the aromatic ring. These data clearly show the formation of the complex.

2.2 Crystal structure of complex **1**

The X-ray diffraction study shows that the asymmetric unit of **1** is composed of one Cd atom, two benzimidazole-5-carboxylic acid ligands and one coordinated water molecule.

As shown in Fig.1, each Cd(II) center displays a distorted CdO_4N_2 octahedral coordination geometry, which is formed from three carboxylate oxygen atoms of

two L ligands, two nitrogen atoms of two L ligands and one coordinated water molecule. Four atoms O3-O1ⁱ-N3ⁱ-O4 form a relatively normal equatorial plane of the octahedron, with the torsion angle of $3.726(44)^\circ$, and the Cd1 atom is slightly deviated from the plane (-0.014 46 nm), while atoms N1 and O1W occupy the axial positions, with O1W-Cd1-N1 angle of 157.899° .



Symmetry codes: ⁱ $x, 1-y, -0.5+z$; ⁱⁱ $x, -1+y, z$

Displayment ellipsoids are plotted at the 30% probability level, hydrogen atoms are omitted for clarity

Fig.1 Coordination environment of the Cd(II) atom in **1**

The Cd1-N1, Cd1-N3ⁱ bond lengths are 0.227 90(17) and 0.228 18(17) nm, respectively, which are both in the normal range. The Cd-O_{carboxyl} [0.222 19(16)~0.251 08(15) nm] and Cd-O_{water} [0.235 91(15) nm] distances are also in the normal range. The dihedral angle between benzimidazole rings where N3ⁱ and N1 resides is 68.687(47)°.

For the L ligand, the carboxylic groups in **1** are all deprotonated, two coordination modes of the carboxylic groups have been found in complex **1**: one kind of carboxylic groups act as chelating coordination mode to

one Cd(II) atom, while the other kind of carboxylic groups exhibit as monodentate coordination mode. So the whole L ligand links two Cd(II) atoms (Fig.1) by carboxylic group and N atom.

Each L ligand links two Cd(II) atoms and each Cd(II) atom attaches to four L ligands to form a new 2D layer structure (Fig.2a) along *bc* plane. By representing the L ligands as the lines, complex **1** consists of regular parallelograms (Fig.2b) with the diagonal distance of 1.689 74(7) nm×0.804 96(4) nm.

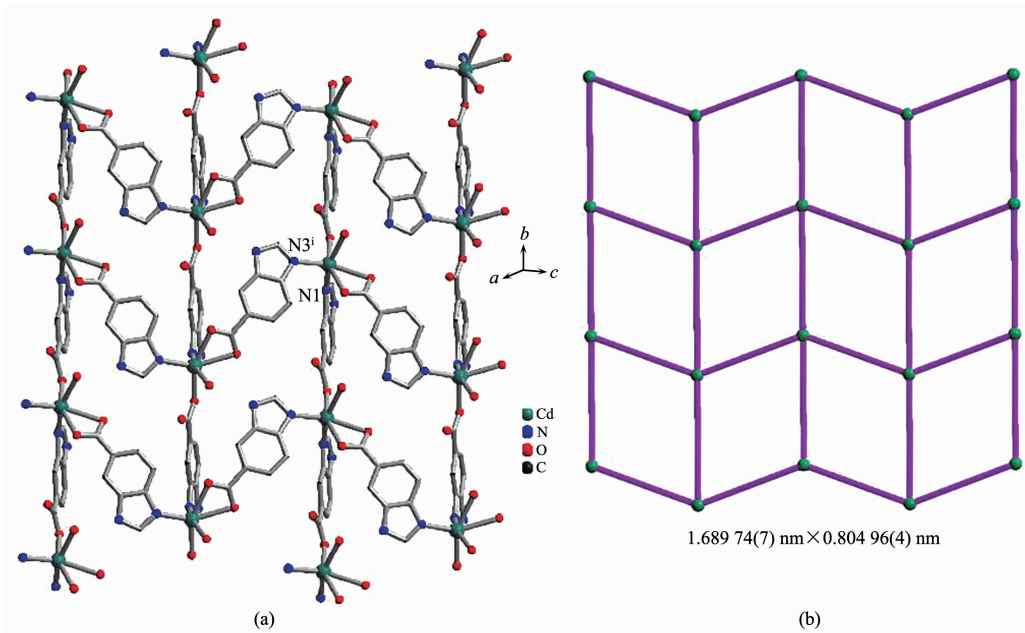


Fig.2 (a) A view of the two-dimensional layered structure of **1**; (b) Schematic representation for the two-dimensional layer of **1**

Viewing the structure along *b* axis, we can find the Cd(II) centers are linked via the carboxylic groups and N atoms of the L ligands to generate one-dimensional chains with the Cd···Cd separation of 0.890 30(4) nm. The L ligands have opposite connection orientations between adjacent chains. The benzimidazole rings stand on the same side of the chains. The dihedral angle between the two adjacent benzimidazole rings of two adjacent chains is 0.253(41)° and the distance between their centroids is 0.759 73(3) nm. Viewing the structure along *c* axis, we find each L ligand links two Cd(II) atoms to form similar wave-like chains with the Cd···Cd separation of 0.979 26(4) nm. The dihedral angle between the two adjacent benzimidazole rings of the two adjacent chains is 0.000(57)° and the distance between their centroids is 0.890 30(4) nm, which means

that the two planes are parallel. The dihedral angle between benzimidazole rings where N3ⁱ and N1 resides is 68.687(47)°, which means that the two planes are inclined to perpendicularity.

Hydrogen-bonding interactions are usually important in the synthesis of supermolecular architecture^[14]. It should be noted that one of the strong hydrogen bonds in the structure, that involving N2 as a donor and O3 as an acceptor with N2···O3 bond length of 0.291 7(2) nm, links two individual layers to form a double 2D layers structure, which consists of two kinds of rings: (1) the ring where centroids A and B reside is a 10-membered ring with Cd···Cd separation of 0.780 01(3) nm. The dihedral angle between the two benzimidazole rings where centroids A and B reside respectively, is 0.299(39)° with A···B separation of 0.395 00(2) nm; (2)

the ring where centroids B, C, E and D reside is a 23-membered ring with Cd \cdots Cd separation of 0.923 49(3) nm. The dihedral angle between the two benzimidazole rings where centroids B and E reside respectively, is 0.000(46) $^\circ$ with B \cdots E separation of 0.375 44(1) nm and the distance between the two planes is 0.365 77 nm. The dihedral angle between the two benzimidazole rings where centroids C and D reside respectively, is 0.000 49 $^\circ$ and the distance between centroids C and D is 0.992 09(3) nm. The benzimidazole rings which stand in the inner of the double 2D layers are mutually occlusal. These double 2D layers are further linked by O1W-H2 \cdots O4ⁱⁱⁱ (symmetry code: ⁱⁱⁱ $-x+1/2, -y+1/2, -z$) hydrogen bonds to yield an intriguing 3D supramolecular network (Fig.3). These supramolecular interactions together with the coordinate-covalent interactions between metal ions and organic ligands strengthen the stability of the network structure.

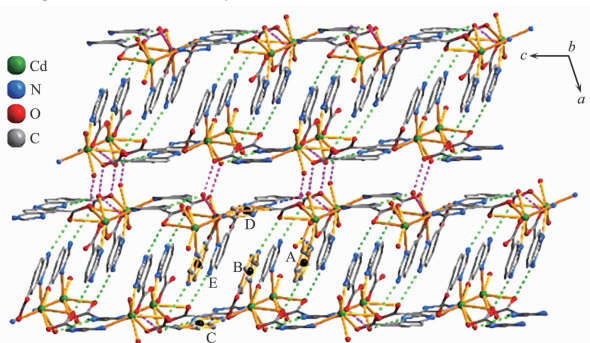


Fig.3 3D supramolecular network of **1** formed by hydrogen bonds (the green dash lines represent the N-H \cdots O hydrogen bonds and the red dash lines represent the O-H \cdots O hydrogen bonds; A, B, C, D and E are the centroids of the benzimidazole rings)

2.3 Thermal analysis

The thermal analysis experiment was performed on samples consisting of numerous single crystals of complex **1** under O₂ atmosphere. The sample of the complex **1** was heated from 40 to 800 $^\circ\text{C}$ (Fig.4). The first weight loss of 3.92% (calcd 3.98%) between 105 and 158 $^\circ\text{C}$ corresponds to the loss of coordinated water molecule in complex **1**. The further decomposition occurred in the range 322 ~648 $^\circ\text{C}$, which may be attributed to the elimination of the L ligands. The remaining products may be CdO (obsd. 28.44%, calcd. 28.36%).

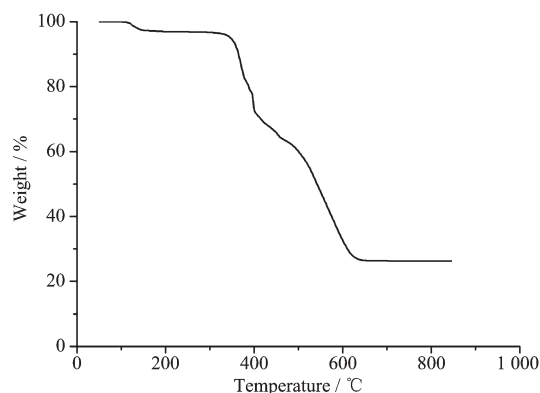


Fig.4 Thermal analysis curve of complex **1**

2.4 Luminescence property

The solid state luminescence spectrum of the ligand reveals a fluorescent emission maximum at approximately 343 nm (excited at 304 nm), while a violet-fluorescent emission band is observed at 376 nm (excited at 293 nm) for complex **1** (Fig.5). It is clear that the red-shift of emission occurs in complex **1**. As we know, many aromatic ligands cannot exhibit visible emissive on their own, but when they coordinated to Cd(II)^[15], these complexes can show much visible luminescence. These changes are perhaps attributed to the coordination of those ligands to Cd(II), which increases the conformational rigidity of the ligand, thus reduces the loss of energy through a radiationless pathway^[16]. These results indicate that complex **1** maybe have potential applications as photoactive material.

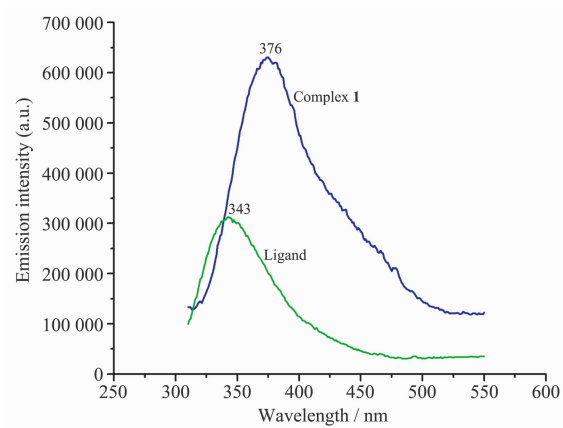


Fig.5 Fluorescence emission spectrum of **1** in the solid state at room temperature

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