



研究简报

一个镉配位聚合物[Cd(Pyphen)(1,4-BDC)(H₂O)]·0.5Pyphen 的合成、结构和荧光性质研究

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关键词: 配位聚合物; 晶体结构; 荧光; 对苯二甲酸

中图分类号: O614.24²

文献标识码: A

文章编号: 1001-4861(2008)05-0835-04

Synthesis, Structure and Photoluminescence of a Cd(II) Coordination Polymer: [Cd(Pyphen)(1,4-BDC)(H₂O)]·0.5Pyphen

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Abstract: The title complex, [Cd(Pyphen)(1,4-BDC)(H₂O)]·0.5Pyphen (**1**) (Pyphen=pyrazino[2,3-*f*][1,10]phenanthroline and 1,4-H₂BDC=1,4-benzenedicarboxylic acid) has been obtained by using hydrothermal synthesis and characterized by elemental analysis, IR, fluorescence spectrum and single-crystal X-ray diffraction. It crystallizes in orthorhombic, space group *Pbcn* with *a*=2.489 2(5) nm, *b*=0.967 88(19) nm, *c*=2.057 0(4) nm, *V*=4.955 9(17) nm³, *Z*=8, CdC₂₉H₁₈N₆O₄, *M_r*=642.89, *D_c*=1.723 g·cm⁻³, *F*(000)=2 576, *μ*(Mo *Kα*)=0.937 mm⁻¹, *R*=0.039 6 and *wR*=0.102 6. The compound **1** exhibits one-dimensional chain structures, which are further stacked through *π-π* interactions to form supramolecular layers. Solid-state luminescent spectrum of the complex **1** indicates intense fluorescent emission. CCDC: 679004.

Key words: coordination polymer; crystal structure; photoluminescence; 1,4-benzenedicarboxylic acid

0 Introduction

The metal-organic coordination architectures formed with transition metal ions and organic ligands have been a promising topic for many years due to their intriguing structures and potential applications in catal-

ysis, separation, gas storage, molecular recognition, magnetic devices and non-linear optical materials^[1-6]. So far, several rational synthetic strategies have been proposed to achieve the metal-organic supramolecular arrays, and one of the most effective approaches is to employ appropriate bridging building blocks capable of

收稿日期: 2007-10-22。收修改稿日期: 2007-12-26。

吉林省自然科学基金项目(No.20060516);吉林师范大学博士基金项目(No.2006006);四平市科学技术局基金项目(No.2005016)和吉林师范大学学科与基础建设基金项目(No.2006041)。

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binding metal centers through direct dative bonds^[7-9]. In this regards, the aromatic multicarboxylate ligands, such as 1,4-benzenedicarboxylic acid (1,4-H₂BDC), is widely used to construct the metal-organic frameworks with diverse topology and interesting properties^[10-13]. The rod-like 1,4-H₂BDC molecule possesses interesting features that are conducive to formation of versatile coordination structures. In addition, Zn(II), Cd(II) and Ag(I) d¹⁰ metal complexes including 1,4-BDC give interesting photoluminescent phenomena. Also, the complexes based on dicarboxylate ligand and the new chelating ligand pyrazino [2,3-f] [1,10]phenanthroline (Pyphen) have rarely been reported^[14-16]. Consequently, we choose the 1,4-H₂BDC as the bridging ligand, Pyphen as the secondary chelating ligand and divalent cadmium ion as the metal center, generating a new coordination polymer, [Cd (Pyphen) (1,4-BDC) (H₂O)] · 0.5Pyphen (**1**).

1 Experimental

1.1 Generals

The pyphen ligand was synthesized according to the reported method^[17] and all other materials were analytical reagent grade and used as received without further purification. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer; IR spectra were obtained on a Perkin-Elmer 2400LSII spectrometer; the visible luminescent properties of compound **1** and 1,4-H₂BDC ligand were measured on a Perkin-Elmer LS55 spectrometer.

1.2 Synthesis and crystal growth

A mixture of CdCl₂ · 2H₂O (0.081 g, 0.5 mmol), 1,4-H₂BDC (0.083 g, 0.5 mmol), Pyphen (0.120 g, 0.5 mmol), NaOH (0.008 g, 0.2 mmol) and deionized water (12 mL) was heated to 180 °C for five days in a 25 mL Teflon-lined stainless steel vessel under autogenous pressure. Subsequently, it was cooled to room temperature at a rate of 10 °C · h⁻¹. Pale yellow crystals of **1** was isolated by filtration and washed with water and dried at ambient temperature. IR (KBr, cm⁻¹): 3 347m, 3 119m, 1 684s, 1 619w, 1 557m, 1 523s, 1 422m, 1 390m, 1 371m, 1 281s, 1 015m, 849m, 833m, 778s, 732w, 700m, 622w. Anal. Calcd. For CdC₂₉H₁₈N₆O₄ (%): C 54.13; H

2.80; N 13.07. Found (%): C 54.23; H 2.72; N 13.19.

1.3 Crystal structure determination

A single crystal with dimensions of 0.31 mm × 0.30 mm × 0.19 mm was selected and mounted on a Rigaku RAXIS-RAPID single crystal diffractometer equipped with a narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated Mo K α radiation, λ = 0.071 073 nm) at a temperature of 20 ± 2 °C. The data processing was accomplished with the PROCESS-AUTO program. Out of the total 42 450 reflections collected in the 3.00° ≤ θ ≤ 27.47° range, 5 673 were independent with R_{int} = 0.045 8, of which 4 230 with $I > 2\sigma(I)$ were considered as observed and used in the succeeding refinement. The structure was solved by Direct Method with SHELXS-97 program^[18] and refined with SHELXL-97^[19] by full-matrix least-squares techniques on F^2 . All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The H atoms of water molecule were located from difference Fourier map and refined with distance restraints of O ... H = 0.085 nm. The final R = 0.039 6 and wR = 0.102 6 ($w = 1/[\sigma^2(F_o^2) + (0.037 7P)^2 + 0.28P]$, where $P = (F_o^2 + 2F_c^2)/3$). S = 1.101, ($\Delta\rho$)_{max} = 805, ($\Delta\rho$)_{min} = -656 e · nm⁻³ and (Δ/σ)_{max} = 0.001.

CCDC: 679004.

2 Results and discussion

2.1 Description of crystal structure

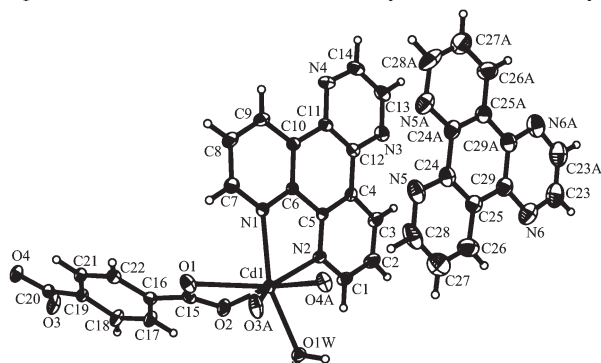
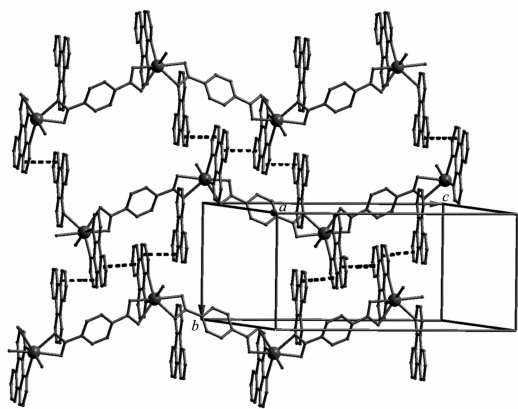
The selected bond distances and angles are listed in Table 1. The asymmetric unit of **1** consists of one Cd(II) atom, one Pyphen molecule, one 1,4-BDC ligand, and one coordinated water molecule. As shown in Fig.1, each Cd(II) atom is seven-coordinated by two nitrogen atoms (Cd1-N1 = 0.236 9(3) and Cd1-N1 = 0.239 3(3) nm) from one Pyphen molecule, and five oxygen atoms (Cd1-O1 = 0.248 5(3), Cd1-O2 = 0.234 7(3), Cd1-O3A = 0.237 2(2), Cd1-O4A = 0.240 9(3) and Cd1-O1W = 0.22 7(3) nm) from two different 1,4-BDC anions and one water molecule in a distorted monocapped octahedral coordination geometry^[20]. The two neighboring Cd(II) atoms are bridged by the 1,4-BDC ligands to form a zigzag chain structure with the long Cd-Cd distance of 1.121 1 nm (Fig.2). The Pyphen ligands are attached on

Table 1 Selected bond distances (nm) and angles (°)

| | | | | | |
|--------------------------------|------------|--------------------------------|------------|--|------------|
| Cd(1)-N(1) | 0.236 9(3) | Cd(1)-N(2) | 0.239 3(3) | Cd(1)-O(1) | 0.248 5(3) |
| Cd(1)-O(2) | 0.234 7(3) | Cd(1)-O(3) ^{#1} | 0.237 2(2) | Cd(1)-O(4) ^{#1} | 0.240 9(3) |
| Cd(1)-O(1W) | 0.229 7(3) | | | | |
| O(1W)-Cd(1)-O(2) | 83.05(9) | O(1W)-Cd(1)-O(3) ^{#1} | 89.35(11) | O(1W)-Cd(1)-N(2) | 89.86(9) |
| O(3) ^{#1} -Cd(1)-N(2) | 143.90(9) | N(1)-Cd(1)-O(4) ^{#1} | 91.49(9) | O(1W)-Cd(1)-O(1) | 115.62(9) |
| O(3) ^{#1} -Cd(1)-O(1) | 80.00(8) | O(1W)-Cd(1)-N(1) | 159.06(10) | O(2)-Cd(1)-O(3) ^{#1} | 122.32(10) |
| O(2)-Cd(1)-N(2) | 93.36(10) | O(1W)-Cd(1)-O(4) ^{#1} | 83.89(9) | O(3) ^{#1} -Cd(1)-O(4) ^{#1} | 53.94(8) |
| O(2)-Cd(1)-O(1) | 53.81(9) | N(2)-Cd(1)-O(1) | 131.76(9) | O(2)-Cd(1)-N(1) | 101.97(10) |
| N(1)-Cd(1)-O(3) ^{#1} | 104.43(11) | N(1)-Cd(1)-N(2) | 69.68(9) | O(2)-Cd(1)-O(4) ^{#1} | 166.48(10) |
| N(2)-Cd(1)-O(4) ^{#1} | 90.11(9) | N(1)-Cd(1)-O(1) | 82.76(9) | O(4) ^{#1} -Cd(1)-O(1) | 130.56(8) |

Symmetry codes: ^{#1} $x, -y, z+1/2$.

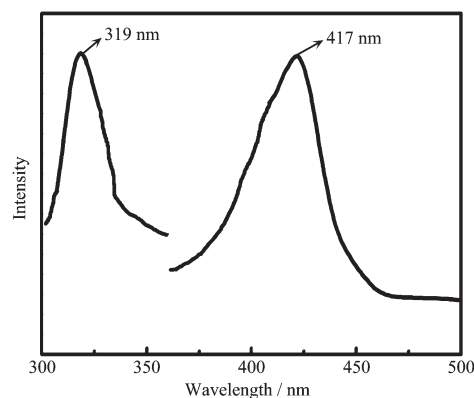
the sides of the chain as a bidentate chelating ligand. Furthermore, the chains are interconnected by the aromatic π - π interactions between two Pyphen ligands (face-to-face distance *ca.* 0.347 nm), resulting in a supramolecular layer (Fig.2). Also, hydrogen bond interactions are usually important in the synthesis of supramolecular architecture. Finally, the O-H \cdots O hy-

Fig.1 Coordination environment of Cd(II) atom in complex **1** (displacement ellipsoids at the 30% probability level)Fig.2 Supramolecular layer structure of **1** constructed through interchain π - π interactions

drogen bonds that involved in the coordinated water molecule and carboxylate oxygen atoms stabilize the structure of **1**.

2.2 Photoluminescent properties

Because compound **1** is insoluble in common polar and non-polar solvents, solid-state excitation and emission spectrum was used for photoluminescent measurements. Solid-state **1** exhibits strong photoluminescence at room temperature. The free 1,4-H₂BDC ligand shows an emission band at 407 nm (λ_{ex} =345 nm). The emission band for the free ligand is attributable to the π^* - n transitions^[21]. The fluorescence emission spectrum of compound **1** in the solid state at room temperature is depicted in Fig.3. The emission spectrum of compound **1** exhibits a main peak at 417 nm (λ_{ex} =319 nm), which is similar to other Cd-organic complexes^[21]. Thus, according to the previous literature, the emission band could be assigned to the emission of ligand to-metal charge transfer (LMCT)^[21].

Fig.3 Luminescent spectrum of the compound **1** in the solid state at room temperature

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