第 29 卷第 12 期 无 机 化 学 学 报 Vol.29 No.12
2013 年 12 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 2704-2708

# 3,5-二硝基苯甲酸镉配合物的合成、晶体结构、热稳定性和荧光性质

聂 雪* 陈满生* 庾江喜
(衡阳师范学院化学与材料科学系,衡阳 421008)

**摘要**:以 3,5-二硝基苯甲酸,咪唑为配体,合成了新化合物[Cd($H_2O$)$_2$(DNBA)(Im)$_2$](DNBA)·$H_2O$,(DNBA=3,5-二硝基苯甲酸阴离子)。该配合物属正交晶系,空间群为 *Ccc*2,晶胞参数:*a*=1.324 99(4) nm,*b*=1.516 01(5) nm,*c*=2.789 22(8) nm;*V*=5.602 7(3) nm$^3$,$D_c$=1.719 g·cm$^{-3}$,*Z*=8,$\mu$=0.866 mm$^{-1}$,*F*(000)=2 912,最终偏离因子 $R_1$=0.058 3,$wR_2$=0.146 4。该配合物中包含两个单核镉(Ⅱ)配合物,且配合物中还包含未配位的 3,5-二硝基苯甲酸,金属中心均是六配位变形八面体结构。并测定和研究了标题化合物的热重和荧光性能。

**关键词**:镉(Ⅱ)配合物;晶体结构;热稳定和荧光性能
**中图分类号**:O **文献标识码**:A **文章编号**:1001-4861(2013)12-2704-05
**DOI**:10.3969/j.issn.1001-4861.2013.00.395

## Synthesis, Crystal Structure, Thermal Stability and Luminescent Properties of Cd(Ⅱ) Complex Constructed from 3,5-Dinitrobenzoic Acid

NIE Xue* CHEN Man-Sheng* YU Jiang-Xi
(*Department of Chemistry and Materials Science, Hengyang Normal University, Hengyang, Hunan* 421008, *China*)

**Abstract:** A new complex [Cd($H_2O$)$_2$(DNBA)(Im)$_2$](DNBA)·$H_2O$ has been synthesized by $H_2$DNBA and Im with Cd(Ⅱ), where $H_2$DNBA =3,5-dinitrobenzoic acid, Im=imidazole. The crystal belongs to orthorhombic system, space group *Ccc*2. The cell parameters are: *a*=1.324 99(4) nm, *b*=1.516 01(5) nm, *c*=2.789 22(8) nm; *V*=5.602 7(3) nm$^3$, $D_c$=1.719 g·cm$^{-3}$, *Z*=8, $\mu$=0.866 mm$^{-1}$, *F*(000)=2 912, final discrepancy factors $R_1$=0.058 3, $wR_2$=0.146 4. There are two mononuclear Cd(Ⅱ) complexes in the asymmetric unit of the compound, and where the two Cd(Ⅱ) ions are in the same coordination number. In addition, the luminescent property of **1** is also discussed in the liquid state at room temperature. CCDC: 952035.

**Key words:** cadmium(Ⅱ) complex; crystal structure; thermal stability and fluorescent property

## 0 Introduction

Coordination polymers using carboxylic acids as ligands have been widely studied in recent years [1-3] because of carboxylates′ diverse coordination styles as well as the carboxylic acids based coordination polymers′ rigid structures. Different coordination patterns of carboxylates lead to various coordination polymers with rigid crystal structures[4-9]. Furthermore, the rational design and synthesis of metal-organic frameworks (MOFs) constructed from metal salts and bridging ligands have attracted great attention, not only because of their intriguing variety of architectures and topologies[9-13], but also because of their potential applications in ion-exchange, nonlinear optics, molecular sieves, gas storage, catalysis,

收稿日期:2013-03-27。收修改稿日期:2013-05-26。
湖南省自然科学基金(No.13JJ6069)和湖南省教育厅一般项目(No.13C082)资助项目。
*通讯联系人。E-mail:xuehuanie@126.com,cmsniu@163.com;会员登记号:S06N7223M1009。

magnetism, and molecular sensing. In the obtained coordination polymers, carboxylates often act as either mono-dentate, bidentate or chelate ligands. In this paper, 3,5-nitrobenzoic acid was served as the starting material to obtain the dinuclear complex of Cd(Ⅱ) in which carboxylates adopt chelate fashions. DSC and TG thermal analyses and luminescent were conducted in order to deeply investigate the properties of the complex.

## 1 Experimental

### 1.1 Materials and instruments

The regents were used as commercial sources without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were recorded on Bruker Vector22 FT-IR spectrophotometer using KBr discs. Thermogravimetric analyses (TG) were performed on a PERKINELMER TG/DTA6300 instrument heating from room temperature to 1 000 ℃ under $N_2$ with a heating rate of 10 ℃·min$^{-1}$. Luminescence spectra were recorded at room temperature with a WGY-10 fluorescence spectrophotometer.

### 1.2 Synthesis of the title compound

A ethanol/water solution (10 mL) of $Cd(NO_3)_2 \cdot 6H_2O$ (1.0 mmol) was mixed under stirring with the solution (10 mL) of 3,5-nitrobenzoic acid ligand (1 mmol) in the same solvent, and the solution was adjusted to pH=6 or so with 0.2 mol·L$^{-1}$ sodium hydroxide solution. (2.0 mmol) imidazole was added and stirred for several 6 hours. Then, the resulting clear solution was allowed to evaporate slowly at room temperature for three weeks, affording colorless crystals. The product was collected by filtration, washed with ethanol and then dried in air, Yields based on Cd: 40.5%. Molecular formula is $C_{20}H_{20}N_6CdO_{15}$. Elemental analysis(%) C, 33.11; H, 2.76; N, 11.59. Found(%): C, 33.15; H, 2.71; N, 11.58. Main IR bands (cm$^{-1}$): 3 273 s, 1 624s, 1 604s, 1 533s, 1 450ms, 1 306ms, 1 244s, 1 066s, 846ms, 723m, 624w.

### 1.3 Crystal structure determinations

A crystal with the dimensions of 0.20 mm×0.16 mm×0.10 mm was put on a Bruker SMART APEX-Ⅱ CCD diffractometer, which was equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda$=0.071 073 nm) by using $\omega$-$\varphi$ scan mode at 291(2) K. Of the total 9 701 reflections collected in the range of $2.04° \leqslant \theta \leqslant 26.00°$, 5 234 were independent with $R_{int}$=0.010 4; 4 284 were considered to be observed ($I>2\sigma(I)$) and used in the succeeding refinement. The crystal structure was solved with a direct method by using SHELXS-97 program[14]. The final refinements including hydrogen atoms converged to $R_1$=0.058 3, $wR_2$=0.146 4; $w=1/[\sigma^2(F_o^2)+(0.08P)^2+1.22P]$, where $P=(F_o^2+2F_c^2)/3$, $(\Delta/\sigma)_{max}$=0.000, $S$=1.049. Crystallographic data of complex **1** are shown in Table 1.

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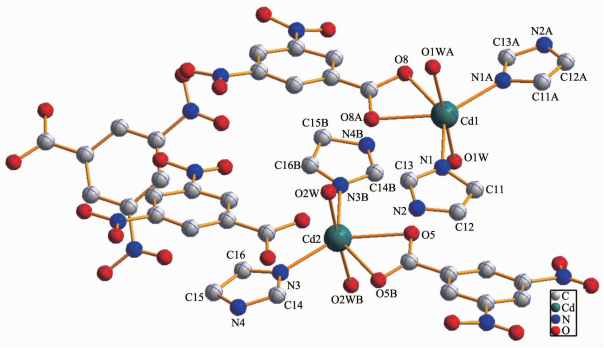
## 2 Results and discussions

### 2.1 Crystal structure analysis

The crystal structure of **1** is revealed in Fig.1. Selected bond lengths and bond angles are shown in Table 2. As shown in Fig.1, the title complex consists of two $Cd(H_2O)_2(DNBA)(Im)_2$ complexes, two DNBA

**Table 1　Crystallographic data of the title complex 1**

| | | | |
|---|---|---|---|
| Empirical formula | $C_{20}H_{20}N_6CdO_{15}$ | $V$ / nm$^3$ | 5.602 7(3) |
| Formula weight | 724.84 | $D$ / (g·cm$^{-3}$) | 1.719 |
| Size / mm | 0.20×0.16×0.10 | $F$(000) | 2912 |
| $\theta$ range for data collection / (°) | 2.04 to 26.00 | $\mu$ (Mo $K\alpha$) / mm$^{-1}$ | 0.866 |
| Crystal system | Orthorhombic | Reflections collected | 9 701 |
| Space group | $Ccc2$ | Independent reflections | 5 234 ($R_{int}$=0.010 4) |
| $a$ / nm | 1.324 99(4) | Final GooF | 1.049 |
| $b$ / nm | 1.51601(5) | $R_1$, $wR_2$ ($I>2\sigma(I)$) | 0.058 3, 0.146 4 |
| $c$ / nm | 2.789 22(8) | $R_1$, $wR_2$ (all data) | 0.060 7, 0.147 1 |
| $Z$ | 8 | Largest diff. peak and hole / (e·nm$^{-3}$) | 875, −622 |

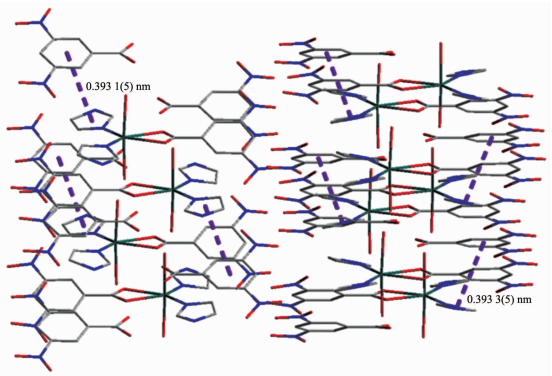



All water molecules are omitted for clarity; Symmetry code: A: 2–*x*, –*y*, *z*; B: 3/2–*x*, 1/2–*y*, *z*

Fig.1 Molecular structure of the title complex with thermal ellipsoids at 30% probability level

anions and two lattice water molecules, which is entirely different from the reported $Cd_2(dnba)_4(pyridine)_4$[15]. The Cd(Ⅱ) ions are six-coordinated by two nitrogen atoms from two Ims, two oxygen atoms from two DNBA anions and the other two oxygen atoms from two water molecules, giving a distorted octahedral coordination geometry. In **1**, both Cd(1) and Cd(2) have the same coordinated environment, therefore, Cd (1) is described representatively here. In **1**, the bond length of Cd(1)-O(1W) is 0.229 9(5) nm, which is shorter than that of Cd(1)-O(8) (0.240 2(7) nm), indicating that the water molecule has a stronger coordination capability with the Cd (II) ion than the oxygen atom of DNBA anion. On the other hand, in complex **1**, O(5), N(3), N(5) and N(6) locate at the equator plane, O(1) and O(1W) occupy the axial positions. The bond angles of O(8)-Cd(1)-N(1)A, N(1)A-Cd(1)-N(1), N(1)-Cd(1)-O(8)A and O(8)A-Cd(1)-O(8) are 90.9(3)°, 124.3(4) °, 90.9(3)° and 53.9(3)°, respectively; and the sum of the above angles is 360.0°.

An interesting feature of the structure is that the weak $\pi$-$\pi$ interaction link two mononuclear Cd complexes into 1D chain structure. That is to say, in the neighboring asymmetric units, there was a offset face-to-face overlap between the Im (N(1)-C(11)-C(12)-N(2)-C(13)) and benzene rings of uncoordinated DNBA anions (C(22)-C(23)-C(24)-C(25)-C(24C)-C(23C)). The dihedral angle of these two planes of 15.15°, the vertical interval of 0.370 6 nm, and the shortest centroid-to-centroid distance of 0.393 3(5) nm. And there was another offset face-to-face overlap between the Im (N(3)-C(14)-N(4)-C(15)-C(16)) and benzene rings of another uncoordinated DNBA anions (C(17)-C(18)-C(19)-C(17D)-C(18D)-C(21)). The dihedral angle of these two planes of 16.14°, the vertical interval of 0.370 6 nm, and the shortest centroid-to-centroid distance of 0.393 1(5) nm (Fig.2). Furthermore, the chains are bridged through the hydrogen-bonding interactions between the water molecules and the




$\pi$-$\pi$ interaction are shown as dotted lines

Fig.2 Molecular $\pi$-$\pi$ packing interactions in the complex **1**

**Table 2 Selected bond lengths (nm) and bond angles (°) of complex 1**

| | | | | | |
|---|---|---|---|---|---|
| Cd(1)-N(1) | 0.226 8(7) | Cd(1)-O(8) | 0.240 2(7) | Cd(1)-O(1W) | 0.229 9(5) |
| Cd(2)-N(3) | 0.224 4(8) | Cd(2)-O(5) | 0.242 6(7) | Cd(2)-O(2W) | 0.230 4(5) |
| | | | | | |
| N(1)-Cd(1)-N(1)A | 124.3(4) | N(1)-Cd(1)-O(1W) | 89.6(3) | N(1)A-Cd(1)-O(1W) | 91.5(3) |
| N(1)-Cd(1)-O(8)A | 90.9(3) | N(1)-Cd(1)-O(8) | 144.8(2) | O(1W)-Cd(1)-O(1W)A | 177.8(7) |
| O(1W)-Cd(1)-O(8) | 88.5(3) | O(8)A-Cd(1)-O(8) | 53.9(3) | O(1W)-Cd(1)-O(8)A | 89.5(3) |
| N(3)-Cd(2)-N(3)B | 124.6(4) | N(3)-Cd(2)-O(2W) | 91.8(3) | N(3)-Cd(2)-O(2W)B | 90.0(3) |
| O(2W)-Cd(2)-O(5) | 88.5(3) | O(5)B-Cd(2)-O(5) | 53.3(3) | O(2W)-Cd(2)-O(2W)B | 176.2(6) |
| N(3)-Cd(2)-O(5)B | 91.1(3) | N(3)-Cd(2)-O(5) | 144.3(2) | O(2W)-Cd(2)-O(5)B | 88.1(3) |

Symmetry transformations used to generate equivalent atoms: A: 2–*x*, –*y*, *z*; B: 3/2–*x*, 1/2–*y*, *z*.

**Table 3　Selected hydrogen bond lengths and bond angles of complex 1**

| D–H···A | *d*(D-H) / nm | *d*(H-A) / nm | *d*(D···A) / nm | ∠DHA / (°) |
|---|---|---|---|---|
| O(2W)–H(2Y)···O(8)A | 0.096 | 0.190 | 0.276 5(9) | 148 |
| O(1W)–H(1X)···O(11)C | 0.096 | 0.182 | 0.271 9(10) | 154 |
| N(2)–H(2A)···O(3W)D | 0.086 | 0.219 | 0.296 2(12) | 149 |
| O(2W)–H(2X)···O(14) | 0.096 | 0.175 | 0.264 7(9) | 154 |
| O(1W)–H(1Y)···O(11) | 0.096 | 0.186 | 0.272 8(9) | 149 |
| O(3W)–H(3Y)···O(14) | 0.085 | 0.213 | 0.297 6(13) | 173 |
| O(3W)–H(3Y)···O(14)D | 0.085 | 0.245 | 0.307 0(12) | 130 |

Symmetry transformations used to generate equivalent atoms: A: 2–*x*, –*y*, *z*; C: 2–*x*, 1+*y*, –1/2+*z*; D: 1–*x*, –*y*, *z*.

carboxylate O atoms and imidazole N atoms to form an overall two-dimensional supramolecular structure. There are other C–H···O hydrogen bonds within the 2D network, which further consolidate the structure (Table 2).

## 2.2　IR spectra characteristics and thermal analyses

The IR spectrum of the complex exhibits a medium broad band centered at *ca.* 3 273 $cm^{-1}$, due to the $\nu$(O-H) absorptions of water molecules. The strong absorption at 1 624 $cm^{-1}$ is attributable to the $\nu$(C=N) vibration of the ligand, and no strong IR band from -COOH appeared at 1 701 $cm^{-1}$, so all the 3,5-dinitrobenzoic acid ligand should be complete deprotonated. These IR results are coincident with the crystallographic structural analyses. To study its stability, DSC and TG analyses of compound 1 was performed (Fig.3). In the DSC curve there are mainly three continuous exothermic processes with the peak temperatures at 400, 580 and 626 K, respectively. The TG curve of compound **1** shows the first weight loss of 7.52% from 20 to 120 ℃, which corresponds to the loss of two coordinated water molecules and two free water molecules (Calcd. 7.45%). After the loss of water molecules, a plateau region is observed from 120 to 287 ℃ that the framework of complex **1** may still stand. A rapid weight loss of 24.93% can be detected from 287 to 345 ℃, which is assigned as the removal of four nitro groups from four 3,5-dinitrobenzoates (24.81%). After the loss of the above molecules, the framework is stable up to 400 ℃, followed by further weight loss at high temperature. The end product of decomposition of complex **1** is CdO with weight percentage 18.00% (Calcd. 17.31%).

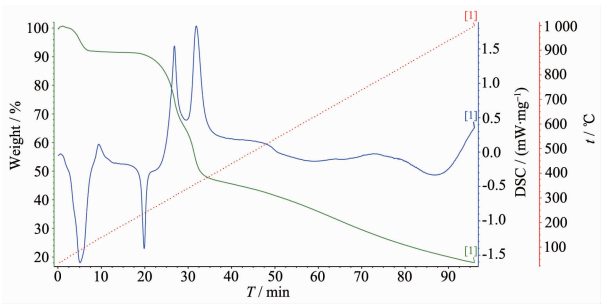



Fig.3　Thermal analysis curves of the title complex

## 2.3　Fluorescence property

The fluorescence property of **1** was measured in the liquid state at room temperature in the range of 290~400 nm. The optimized excitation wavelength is 285 nm, and the emission spectrum is shown in Fig.4. Complex **1** exhibits one broad emission band around 318 nm. Comparably, under the same conditions, we measured the fluorescence property of the ligands $H_2$DNBA and Im, and the results show that the Im gives off fluorescent emission at about 307, while $H_2$DNBA displays the emission band at about 320 nm.

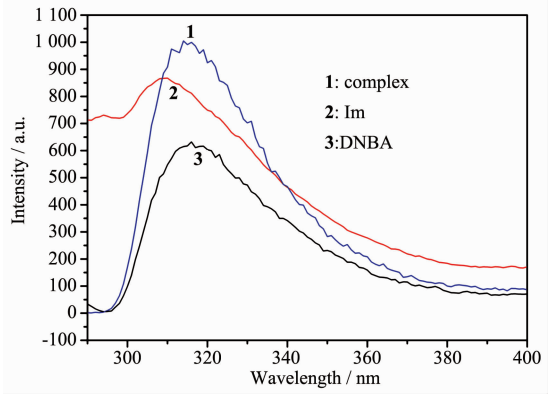



Fig.4　Emission spectra of complex **1** and the ligands in the liquid state at room temperature

The emission band of **1** is similar to that of $H_2$DNBA, indicating that intraligand excitation is responsible for the emission of **1**. In addition, the fluorescence intensity of **1** is stronger than that of $H_2$DNBA, which is probably due to the increased rigidity of ligands coordinated with Cd(Ⅱ) ions.

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