

3,5-二氨基苯甲酸构筑的 Zn(II)、Cd(II)两种配合物的合成及晶体结构

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摘要: 利用 3,5-二氨基苯甲酸配体合成了 2 种新的配合物 $[\text{Cd}(\text{diaba})(\text{phen})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ (**1**) 和 $[\text{Zn}(\text{diaba})(2,2'\text{-bipy})_2](\text{H}_2\text{diaba}=3,5\text{-diaminobenzoic acid; phen}=1,10\text{-phenanthroline, } 2,2'\text{-bipy}=2,2'\text{-bipyridine})$, 并对其进行了元素分析、红外光谱和 X 射线单晶衍射测定。配合物 **1** 属于正交晶系, 空间群为 $Fddd$, $a=1.425\ 81(7)\text{ nm}$, $b=2.564\ 62(13)\text{ nm}$, $c=3.092\ 47(17)\text{ nm}$ 。配合物 **2** 属于单斜晶系, 空间群为 $C2/c$, $a=1.273\ 62\text{ nm}$, $b=1.592\ 78\text{ nm}$, $c=1.519\ 35\text{ nm}$, $\beta=107.334^\circ$ 。配合物 **1** 和 **2** 都为单核晶体。配合物 **1** 的结构单元由 1 个 Cd^{II} 、1 个 3,5-二氨基苯甲酸和 2 个 phen 构成。配合物 **2** 的结构单元由 1 个 Zn^{II} 、1 个 3,5-二氨基苯甲酸和 2 个 2,2'-bipy 构成。两种配合物再通过氢键或 $\pi\text{-}\pi$ 堆积形成三维超分子网络。研究了配合物的热稳定性和荧光性质。

关键词: 配合物; 合成; 晶体结构

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Synthesis and Crystal Structure of Zn(II)、Cd(II) Two Complexes Constructed from 3,5-Diaminobenzoic Acid Ligand

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Abstract: The title complexes, $[\text{Cd}(\text{diaba})(\text{phen})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Zn}(\text{diaba})(2,2'\text{-bipy})_2]$ (**2**) ($\text{diaba}=3,5\text{-diaminobenzoic acid; phen}=1,10\text{-phenanthroline, } 2,2'\text{-bipy}=2,2'\text{-bipyridine}$), has been synthesized by hydrothermal reactions and characterized by IR, TG, fluorescent spectrum and single-crystal X-ray diffraction techniques. The structure indicates that the complex **1** crystallizes in orthorhombic, space group $Fddd$ with $a=1.425\ 81(7)\text{ nm}$, $b=2.564\ 62(13)\text{ nm}$, $c=3.092\ 47(17)\text{ nm}$. The structure indicates that the complex **2** crystallizes in monoclinic, space group $C2/c$ with $a=1.273\ 62\text{ nm}$, $b=1.592\ 78\text{ nm}$, $c=1.519\ 35\text{ nm}$, $\beta=107.334^\circ$. The crystal structure of complex **1** consists of one Cd^{II} , one 3,5-diaminobenzoic acid ligand and two phen ligands. The crystal structure of complex **2** consists of one Zn^{II} , one 3,5-diaminobenzoic acid ligand and two 2,2'-bipy ligands. In two complexes, the adjacent mononuclear molecular recognize each other to generate a 3D supramolecular structure via the hydrogen bonding or the $\pi\text{-}\pi$ stacking interaction. In additional, thermal stability and photoluminescence properties of two complexes have also been studied. CCDC: 936420, **1**; 936421, **2**.

Key words: complex; synthesis; crystal structure

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Recently, the chemistry of Zn (II) and Cd (II) complexes has attracted interest for a number of reasons. The Zn (II) and Cd (II) are d^{10} electronic configuration and can adopt different coordination numbers from 4 to 6. Moreover, the Zn and Cd complexes offer not only the fascinating structure, but only a wide range of potential application in many aspects, such as optical, electrical conductivity, catalysis and even photoluminescent materials^[1-4]. Up to now, a large numbers of complexes formed by Zn (II), Cd (II) and various N-donor, aromatic/heterocyclic multicarboxylate ligands have been successfully synthesized and characterized^[5-10]. However, the complex based on 3, 5-diaminobenzoic acid with Zn(II), Cd(II) have never been reported before.

Inspired by our previous works^[11], we employed 3,5-diaminobenzoic acid and Zn(II), Cd(II) to synthesize two novel complexes, namely, $[\text{Cd}(\text{diaba})(\text{phen})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Zn}(\text{diaba})(2,2'\text{-bipy})_2]$ (**2**) (diaba=3,5-diaminobenzoic acid; phen=1,10-phenanthroline, 2,2'-bipy=2,2'-bipyridine), which provides the first example of complex based on 3,5-diaminobenzoic acid-Zn(II), Cd(II).

1 Experimental

1.1 Materials and methods

The reagents and solvents employed were commercially available and used as received without further purification. Elemental analyses for carbon, hydrogen, and nitrogen were performed with a Vario EL III elemental analyzer. The FTIR spectra were recorded from KBr pellets in the range 4 000~400 cm^{-1} on a Bruker EQUINOX-55 spectrometer. 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 $^{\circ}\text{C} \cdot \text{min}^{-1}$

using a NETZSCH STA 449C thermogravimetric analyzer.

1.2 Syntheses of title complex

Single-crystal samples of complex **2** were obtained by the similar method as described for **1**.

$[\text{Cd}(\text{diaba})(\text{phen})_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ (**1**). **1** was synthesized hydrothermally in a 23-mL teonlined autoclave by heating a mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 mmol), daba (1.0 mmol), phen (0.5 mmol), and H_2O (8 mL) at 160 $^{\circ}\text{C}$ for 4 days. After the reactive mixture was slowly cooled to room temperature, colorless block crystals of **1** were obtained (Yield: 41%, based on Cd). Anal. Calcd. for $\text{C}_{31}\text{H}_{27}\text{O}_6\text{N}_7\text{Cd}(\%)$: C, 52.74; H, 3.85; N, 13.89. Found(%): C, 52.45; H, 3.53; N, 13.31. IR (cm^{-1}): 3 327(br), 1 618(w), 1 558 (s), 1 411 (s), 1 375 (w), 1 184 (w), 999 (w), 854 (s), 777(s).

$[\text{Zn}(\text{diaba})(2,2'\text{-bipy})_2]$ (**2**). Yield: 38% (based on Zn). Anal. Calcd. for $\text{C}_{27}\text{H}_{23}\text{N}_6\text{O}_2\text{Zn}(\%)$: C, 61.32; H, 4.38; N, 15.89. Found (%): C, 61.26; H, 4.54; N, 15.96. IR (cm^{-1}): 3 464 (br), 1 602 (s), 1 537 (s), 1 438 (s), 1 354 (s), 1 195 (w), 1 026 (s), 862 (w), 788 (m).

1.3 Crystal structure determination

Diffraction intensities for the complexes **1** and **2** were collected at 293 K on a Bruker SMART 1000 CCD diffractometer employing graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\text{nm}$). A semiempirical absorption correction was applied using the SADABS program^[12]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS 97 and SHELXL 97 programs, respectively^[13-14]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions. The crystallographic data for complex **1** are listed in Table 1, and selected bond lengths and angles are listed in Table 2.

CCDC: 936420, **1**; 936421, **2**.

Table 1 Crystallographic data for compounds **1** and **2**

Compound	1	2
Empirical formula	$\text{C}_{31}\text{H}_{27}\text{O}_6\text{N}_7\text{Cd}$	$\text{C}_{27}\text{H}_{23}\text{N}_6\text{O}_2\text{Zn}$
Formula weight	706.00	528.88
Crystal dimensions / mm	0.32×0.21×0.10	0.42×0.30×0.11

Continued Table 1

Crystal system	Orthorhombic	Monoclinic
Space group	<i>Fddd</i>	<i>C2/c</i>
<i>a</i> / nm	1.425 81(7)	1.273 62(13)
<i>b</i> / nm	2.564 62(13)	1.592 78(15)
<i>c</i> / nm	3.092 47(17)	1.519 35(16)
β / (°)	90	107.334(10)
<i>V</i> / nm ³	11.308 1(10)	2.942 2(5)
<i>Z</i>	8	4
<i>D_c</i> / (g·cm ⁻³)	1.659	1.194
Absorption coefficient / mm ⁻¹	0.833	0.866
<i>F</i> (000)	5 728	1 092
<i>T</i> / K	273(2)	273(2)
Reflections collected	17 808	2 656
Reflections unique	3 505	2 656
Observed data(<i>I</i> >2σ(<i>I</i>))	2 073	2 130
<i>R_{int}</i>	0.027 1	0.027 1
Parameters	208	165
Goodness-of-fit on <i>F</i> ²	1.076	1.092
<i>R_i</i> (<i>I</i> >2σ(<i>I</i>))	0.030 2	0.030 1
<i>wR₂</i>	0.079 4	0.080 9

Table 2 Selected bond length (nm) and angles (°) for compounds 1 and 2

1					
Cd(1)-O(1)	0.233 2(2)	Cd(1)-N(1)	0.234 36(18)	Cd(1)-N(2)	0.233 67(19)
O(1)-Cd(1)-O(1)A	55.41(11)	O(1)-Cd(1)-N(2)	134.08(7)	O(1)A-Cd(1)-N(2)	102.44(7)
N(2)A-Cd(1)-N(2)	118.06(10)	O(1)-Cd(1)-N(1)	83.07(7)	N(2)A-Cd(1)-N(1)	97.55(7)
N(2)-Cd(1)-N(1)	71.60(6)	O(1)-Cd(1)-N(1)A	115.94(7)	N(1)-Cd(1)-N(1)A	159.39(10)
2					
Zn(1)-N(1)	0.210 82(16)	Zn(1)-N(2)	0.212 01(16)	Zn(1)-O(1)	0.221 43(15)
N(1)-Zn(1)-N(1)A	102.34(9)	N(1)-Zn(1)-N(2)	77.88(6)	N(1)-Zn(1)-N(2)A	100.26(6)
N(2)-Zn(1)-N(2)A	177.09(9)	N(1)-Zn(1)-O(1)	156.84(6)	N(1)-Zn(1)-O(1)A	99.77(5)
N(2)-Zn(1)-O(1)	91.52(6)	N(2)-Zn(1)-O(1) A	91.00(6)	O(1)-Zn(1)-O(1)A	59.44(7)

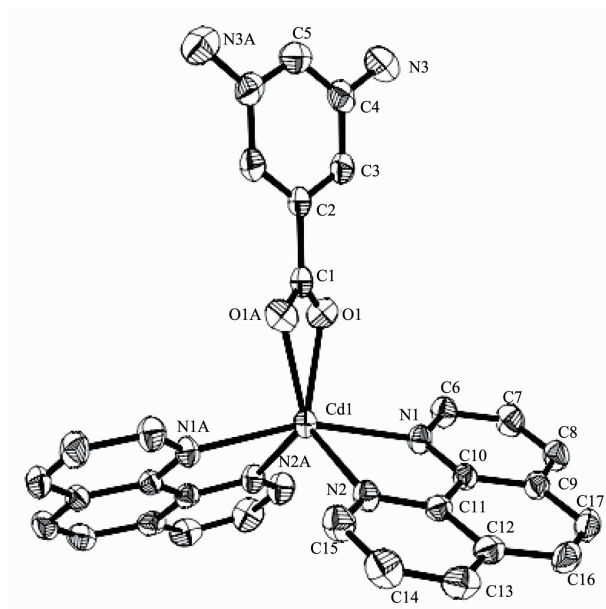
Symmetry operations: **1**: A $-x+1/4, y, -z+1/4$; **2**: A $-x, y, -z+1/2$

2 Result and discussion

2.1 Crystal structure of [Cd(diaba)(phen)₂] \cdot H₂O(1)

The structures of the two complexes were determined by single-crystal X-ray diffraction analyses. Complex **1** belongs to orthorhombic, space group *Fddd*. While complex **2** belongs to monoclinic with *C2/c* space group.

The crystal structure of **1** consists of one crystallographic independent Cd^{II} cation, one diaba ligand and two phen ligands. Each Cd^{II} cation is surrounded by four nitrogen atoms from two 1,10-phen ligands, and two oxygen atoms from one diaba ligand, composing a distorted octahedron pyramidal geometry (Fig.1). The Cd-N bond lengths are 0.233 67 (19), 0.234 36 (18) nm, respectively, and the Cd-O bond lengths are 0.233 2(2) nm, which drop into the normal



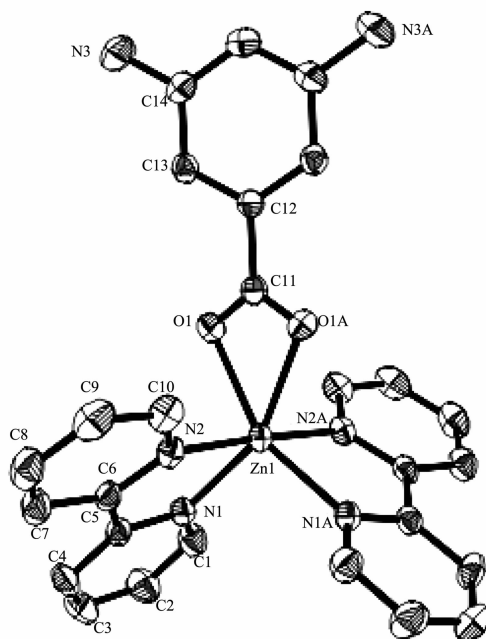
All hydrogen atoms are omitted for clarity; 50% thermal ellipsoids. Symmetry code: A: $-x+1/4, y, -z+1/4$

Fig.1 Coordination environments of Cd atom in complex **1**

scope of Cd-N and Cd-O bond lengths ^[15]. The details are depicted in Table 2. The deproton NO_3^- ions do not coordinate with the central atoms, acting as free ions in the crystal lattice to charge balance. At last the Cd octahedrons, crystal waters and NO_3^- ions construct the new 3D supramolecular network by

intricate hydrogen bonds and weak $\pi \cdots \pi$ stacking interaction.

The structure of complex **2** is the same as complex **1**, they are mononuclear structure. Each Zn^{II} ion is six-coordinated to four nitrogen atoms of two 2,2'-bipy ligands and two oxygen atoms of one diaba



All hydrogen atoms are omitted for clarity; 50% thermal ellipsoids. Symmetry code: A: $-x, y, -z+1/2$

Fig.2 Coordination environments of Zn atom in complex **2**

ligand, fabricating a distorted octahedron pyramidal geometry (Fig.2). The Zn-N bond lengths are 0.210 82(16), 0.212 01(16) nm, respectively, and the Zn-O bond lengths are 0.221 43 (15) nm, which drop into the normal scope of Zn-N and Zn-O bond lengths [16]. The 3D supramolecular network is also constructed via intricate hydrogen bonds and weak $\pi \cdots \pi$ stacking interaction.

2.2 Thermogravimetric analyses

Thermogravimetric analyses have been performed in air for **1** and **2** between 20 and 800 °C (Fig.3, Fig. 4). TGA curve of complex **1** illustrates that weight loss was observed for lattice water and NO_3^- ion up to 300 °C; after this, significant weight loss occurred and ended at ca. 700 °C, indicating the complete decomposition of the complex to form CdO. This conclusion has been also supported by the percentage of the residues (18.03%), which is in accordance with the expected value (18.13%). For **2**, there are not lattice and coordination water molecules and thus decomposition of the organic components occurs at

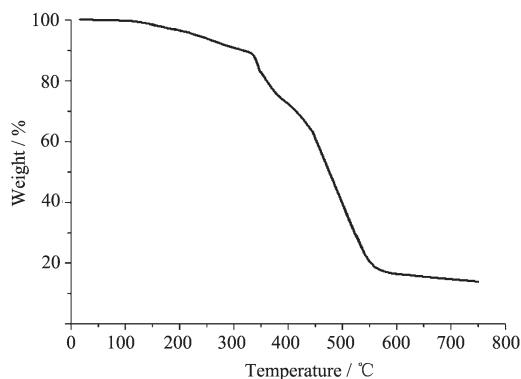


Fig.3 TGA curve for complex **1**

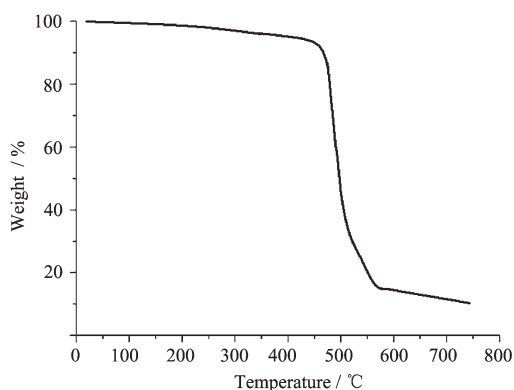


Fig.4 TGA curve for complex **2**

430 °C, indicating the complete decomposition of the complex to form ZnO (Obsd: 14.7% and Calcd: 15.3%).

2.3 Fluorescent properties

Solid-state Luminescent emission spectra of complexes **1** and **2** are depicted in Fig.5. The intense broad photoluminescence emissions are found at 399 nm ($\lambda_{\text{ex}}=335$ nm) for **1**, at 395 nm ($\lambda_{\text{ex}}=325$ nm) for **2**. In order to understand the nature of the emission band, the photoluminescence property of free diaba ligand was measured with the observation of one weak emission at 367 nm ($\lambda_{\text{ex}}=300$ nm). In comparison to the free ligand, most of the emission maxima of complexes **1** and **2** are changed, which are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature, since the Zn^{II} and Cd^{II} ions are difficult to oxidize or reduce. Thus, they may be assigned to intraligand ($\pi-\pi^*$) fluorescent emission [17]. Many aromatic ligands that are not strongly emissive themselves display significant luminescence when coordinated to Zn^{II} or Cd^{II} [18]. The enhancement of luminescence is perhaps a result of the coordination effect of those ligands to the metal center, which effectively increases the rigidity of ligands, thereby reducing the non-radiative decay of the intraligand ($\pi-\pi^*$) excited state [19].

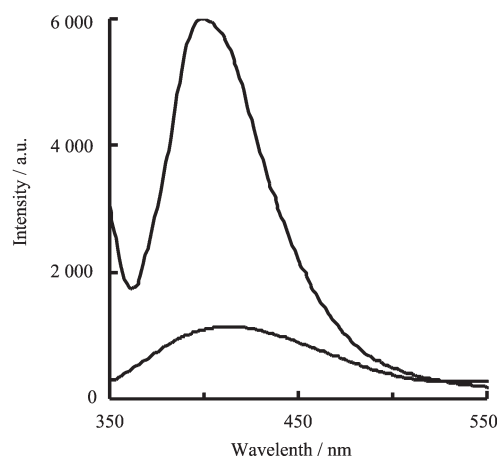


Fig.5 Solid-state emission spectra of **1**(low curve), **2** (tall curve) at room temperature

References:

- [1] Allendorf M D, Bauer C A, Bhaktaa R K, et al. *Chem. Soc. Rev.*, **2009**,**38**:1330-1352

- [2] Rocha J, Carlos L D, Paza F A A, et al. *Chem. Soc. Rev.*, **2011**,**40**:926-940
- [3] Karabach Y Y, Silva M F C G, Kopylovich M N, et al. *Inorg. Chem.*, **2010**,**49**:11096-11105
- [4] XUE Ming (薛 铭), CHEN Si-Ru (陈思如), GUO Li-Jia (郭莉佳), et al. *Chem. J. Chinese Universities* (高等学校化学学报), **2012**,**33**(9):1889-1894
- [5] Ma L F, Wang L Y, Wang Y Y, et al. *Inorg. Chem.*, **2009**,**48**(3):915-924
- [6] Ma L M, Li B, Sun X Y, et al. *Anorg. Allg. Chem.*, **2010**,**636**:1606-1611
- [7] Xu C Y, Li L K, Wang Y P, et al. *Cryst. Growth Des.*, **2011**,**5**:1869-1879
- [8] Sun D, Yan Z H, Blatov V A, et al. *Cryst. Growth Des.*, **2013**,**13**(3):1277-1289
- [9] Zhang Z H, Chen S C, He M Y, et al. *Cryst. Growth Des.*, **2013**,**13**(3):996-1001
- [10] HU Jing-Song(胡劲松), LIU Xi-Hui(刘希慧), SHI Jian-Jun (石建军), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2013**,**29**(3):444-448
- [11] Zhang M L, Li D S, Wang J J, et al. *Dalton Trans.*, **2009**,**11**: 5355-5364
- [12] Sheldrick G M. *SADABS, A Program for Empirical Absorption Correction of Area detector Data*, University of Gttingen, Germany, **1997**.
- [13] Sheldrick G M. *SHELXS 97, Program for Crystal Structure Solution*, University of Gttingen, Germany, **1997**.
- [14] Sheldrick G M. *SHELXL 97, Program for Crystal Structure Refinement*, University of Gttingen, Germany, **1997**
- [15] Tian D, Pang Y, Zhou Y H, et al. *CrystEngComm*, **2011**,**13**: 957-966
- [16] Liu B, Yang G P, Wang Y Y, et al. *Inorg. Chim. Acta*, **2011**,**367**:127-134
- [17] Wen L L, Dang D B, Duan C Y, et al. *Inorg. Chem.*, **2005**,**44**:7161-7170
- [18] Bai H Y, Ma J F, Yang J, et al. *Cryst. Growth Des.*, **2010**,**10**:1946-1959
- [19] Chang Z, Zhang A S, Hu T L, et al. *Cryst. Growth Des.*, **2009**,**9**:4840-4846