1,3-二(4-吡啶基)丙烷 Cd(Ⅱ)配合物的合成、晶体结构及发光性质研究

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摘要：以 1, 3-二(4-吡啶基)丙烷(L)为配体,合成了一种新的 Cd(Ⅱ)配合物$\{[CdL_2(H_2O)_2]\cdot 2(C_7H_6N_5)\}_n$($C_7H_6N_5$=5-(3-氨基苯基)四唑离子)。X 射线单晶衍射结构分析表明该配合物为一维链状结构,Cd(Ⅱ)分别与 4 个 1, 3-二(4-吡啶基)丙烷配体的 4 个氮原子,2 个配位水分子的氧原子形成了六配位的扭曲八面体几何构型,1, 3-二(4-吡啶基)丙烷配体桥梁相邻的 Cd(Ⅱ)离子形成了一维的无限延伸的链状结构,分子间通过 O-H…N、N-H…N 氢键作用构筑成三维超分子网络结构。

关键词: 1, 3-二(4-吡啶基)丙烷;Cd(Ⅱ)配合物;晶体结构;荧光性质
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Synthesis, Crystal Structure and Luminescent Properties of a Cd(Ⅱ) Complex with 1, 3-Di(4-pyridy)propane

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Abstract: A new Cd(Ⅱ) complex $\{[CdL_2(H_2O)_2]\cdot 2(C_7H_6N_5)\}_n$ ($C_7H_6N_5$=5-(3-aminophenyl)tetrazole ion) based on a ligand L (L=1,3-di(4-pyridy)propane) has been synthesized and structurally characterized by X-ray single crystal diffraction analysis. Structural analysis reveals that the complex is a one-dimensional complex. The Cd(Ⅱ) ion adopts a distorted octahedral coordinated geometry formed by four N atoms and two O atoms, of which four N atoms from different L ligands, two O atoms from different H_2O. In the crystal, adjacent Cd(Ⅱ) centers are bridged by L ligands to generate a one-dimensional chain structure. The one-dimensional chains are further connected into a three-dimensional supramolecular network by O-H … N, N-H … N hydrogen bonding contacts. CCDC: 908806.

Key words: 1, 3-di(4-pyridy)propane; Cd(Ⅱ) complex; crystal structure; fluorescence

0 Introduction

In the field of supramolecular chemistry, great interest has recently been focused on the crystal engineering of coordination frameworks due to their new topologies, intriguing architectures, intertwining phenomena, and potential applications in microelectronics, nonlinear optics, molecular selection, ion exchange, and catalysis [1-3]. What is particularly attractive is the novel types of structural motifs observed in these species. Supramolecular chemistry has advanced to a stage at which it is possible to select molecular building blocks that will assemble into structures with specific and desired network topologies,

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so that a rational design of frameworks with potentially interesting properties is possible [4-7]. Flexible ligands were used often to obtain new frameworks such as 1, 3-di (4-pyridy)propane (L), which is an important highly flexible N-donor bridging ligand. The ligands exhibit a special ability to form compounds and play an important role in bridging metal cations. The frameworks constructed from metals and 1, 3-di (4-pyridy)propane ligands have been widely reported[8-10]. In this paper, we report the synthesis and crystal structure of a new Cd(Ⅱ) complex with 1,3-di (4-pyridy)propane and 5-(3-aminophenyl)tetrazole, the complex is prepared in the solvothermal condition.

1 Experimental

1.1 Materials and measurement

All commercially available chemicals are of reagent grade and were used as received without further purification. The FTIR spectra were recorded from KBr pellets in the range of 4 000~400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. All fluorescence measurements were carried out on a LS 50B Luminescence Spectrometer (Perkin-Elmer, Inc., USA). Thermogravimetric analyses (TGA) were carried out in an N_2 atmosphere with a heating rate of 10 ℃·min^{-1} on a TG/ DTA7300 integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Focus X-ray diffractometer using Cu *Kα* radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data.

1.2 Synthesis of the complex

A mixture of 5-(3-aminophenyl)tetrazole (0.02 mmol, 3 mg), $Cd(NO_3)_2·4H_2O$ (0.04 mmol, 12.3 mg) and 1, 3-di (4-pyridy)propane (0.04 mmol, 7.9 mg) were placed in a small vial including H_2O (0.5 mL), DMF (0.5 mL) and ethanol (0.5 mL). The vial was sealed and heated at 332 K for two days, then allowed to cool to room temperature. Colorless block-like crystals suitable for X-ray diffraction were collected and dried in air. Yield: 75% (based on Cd). Anal. Calcd. (%) for $C_{40}H_{44}N_{14}O_2Cd$: C, 55.52; H, 5.12; N, 22.7; Found (%): C, 56.24; H, 5.25; N, 22.9.

1.3 Crystal structure determination

A suitable crystal with dimension of 0.34 mm×0.28 mm×0.16 mm for the complex was carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyanoacrylate adhesive. X-ray single-crystal diffraction data for Cd(Ⅱ) complexe were collected on a BRUKER SMART APEX II CCD diffractometer equipped with a graphite-monochromatic Mo *Ka* radiation (λ=0.071 073 nm) using an ω scan mode at 173 (2) K. Empirical absorption corrections were applied using SADABS program [11]. The structure was solved by direct methods and refined with a full-matrix least-squares technique using SHELXTL-97 program package [12]. All hydrogen atoms were placed geometrically and were subsequently refined in a

Table 1　Crystal data and structure refinement for the title complex

Empirical formula	$C_{40}H_{44}CdN_{14}O_2$	Absorption coefficient / mm^{-1}	0.601
Formula weight	865.29	F(000)	1 784
Temperature / K	173(2)	Crystal size / mm	0.34×0.28×0.16
Wavelength / nm	0.071 073	Theta range for data collection / (°)	2.06 to 25.49
Crystal system	Monoclinic	Limiting indices h, k, l	−14~14, −17~20, −17~23
space group	$C2/c$	Reflections collected / unique	8550 / 3720, R_{int}=0.0384
a / nm	1.236 6(3)	Completeness / %	99.8 (θ=25.49°)
b / nm	1.715 0(3)	Refinement method	Full-matrix least-squares on F^2
c / nm	1.920 6(4)	Data/restraints/parameters	3720/0/267
β / (°)	100.99(3)	Goodness-of-fit on F^2	0.962
Volume / nm^3	3.998 4(15)	Final R indices (I>2σ(I))	R_1=0.0328, wR_2=0.0463
Z	4	R indices (all data)	R_1=0.0414, wR_2=0.0629
Calculated density / (g·cm^{-3})	1.437	Largest diff. peak and hole / (e·nm^{-3})	449 and −321

riding-model approximation. The crystallographic data as well as details of the data collection and refinement for the complex are listed in Table 1. Selected bond lengths and angles are given in Table 2.

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

Cd1-O2	0.2301(3)	Cd1-O1	0.2309(3)	Cd1-N1^{i}	0.23483(19)
Cd1-N1	0.23483(19)	Cd1-N2^{ii}	0.2371(2)	Cd1-N2^{iii}	0.2371(2)
O2-Cd1-O1	180.0	O2-Cd1-N1^{i}	91.82(5)	O1-Cd1-N1^{i}	88.18(5)
O2-Cd1-N1	91.82(5)	O1-Cd1-N1	88.18(5)	N1^{i}-Cd1-N1	176.36(10)
O2-Cd1-N2^{ii}	89.15(6)	O1-Cd1-N2^{ii}	90.85(6)	N1^{i}-Cd1-N2^{ii}	83.47(7)
N1-Cd1-N2^{ii}	96.58(7)	O2-Cd1-N2^{iii}	89.15(6)	O1-Cd1-N2^{iii}	90.85(6)
N1^{i}-Cd1-N2^{iii}	96.58(7)	N1-Cd1-N2^{iii}	83.47(7)	N2^{ii}-Cd1-N2^{iii}	178.30(11)

Symmetry codes: ^{i} $-x$, y, $-z+1/2$; ^{ii} $x-1/2$, $-y+1/2$, $z+1/2$; ^{iii} $x+1/2$, $-y+1/2$, $-z$

Table 3 Hydrogen bond lengths and bond angles for the title complex

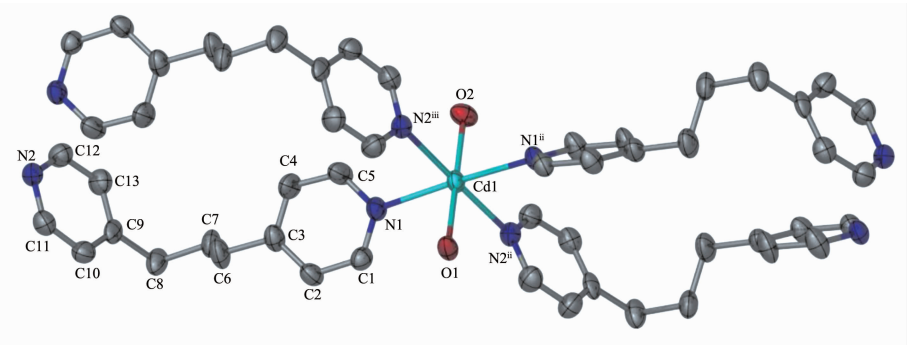
D-H…A	d(D-H) / nm	d(H···A) / nm	d(D···A) / nm	∠DHA(°)
O1-H1A…N4^{iv}	0.082(2)	0.201(2)	0.2811(3)	169.2
N3-H3A…N5^{v}	0.08800	0.25493	0.3378(4)	157.23
N3-H3B…N5^{vi}	0.08791	0.24399	0.3275(3)	158.72

Symmetry codes: ^{iv} $1-x$, $y-1$, z; ^{v} $2-x$, y,$1/2-z$; ^{vi} x, $2-y$, $z-1/2$

2 Results and discussion

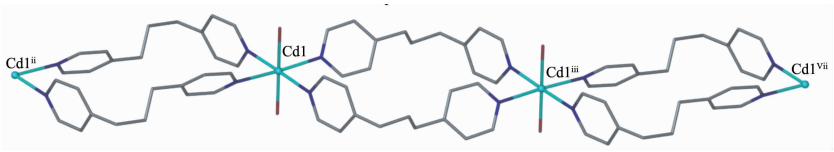
2.1 Crystal structure of $\{[CdL_2(H_2O)_2]\cdot 2(C_7H_6N_5)\}_n$

Single-Crystal X-ray diffraction analysis reveals that the complex crystallizes in monoclinic system with *C*2/*c* space group. The asymmetry unit of the complex consists of one Cd(Ⅱ) ion together with two L molecules, two coordinate water molecules and two free 5-(3-aminophenyl)tetrazole ions ($C_7H_6N_5$). The Cd(Ⅱ) complex is a one-dimensional coordination polymer, the Cd(Ⅱ) ion is six-coordinated by four nitrogen and two oxygen atoms, of which four nitrogen atoms from four different L molecules (N1, N1^{i}, N2^{ii}, N2^{iii}), two oxygen atoms from coordinate water molecules (O1, O2), as shown in Fig.1. The bond angles around Cd atom range from 83.47(7) to 180.0°, the bond angle of O-Cd-O is 180.0° indicating the three atoms are in a line. The Cd-O bond distances are almost similar (Cd1-O1 0.2309(3) nm and Cd1-O2 0.2301 (3) nm). The Cd-N bond distances are 0.234 83 (19) and 0.237 1 (2) nm. In the crystal, adjacent Cd(Ⅱ)



Symmetry codes: ^{i} $-x$, y, $1/2-z$; ^{ii} $x-1/2$, $1/2-y$, $z+1/2$; ^{iii} $1/2-x$, $1/2-y$, $-z$; Hydrogen atoms and free $C_7H_6N_5$ ion were omitted for clarity

Fig.1 Coordination environment of Cd(Ⅱ) in the title complex with 30% probability displacement ellipsoids



Symmetry codes: ii $x-1/2, 1/2-y, 1/2+z$; iii $-x+1/2, -y+1/2, -z$, vii $1-x, y, -z-1/2$

Fig.2　A view of 1D chain structure of the Cd(Ⅱ) complex

centers are bridged by L molecules to generate a infinite one-dimensional chain structure (Fig.2).

It is successfully leads to the assembly of the one-dimensional units by intermolecular hydrogen bonds because of the introducing 5-(3-aminophenyl)tetrazole molecular in the complex, the units are linked by intermolecular hydrogen bonding (N3-H3A⋯N5^{v}; N3-H3B⋯N5^{vi}) (Table 3) to generate a one-dimensional chain. The chains are further assembled into a three-dimensional supramolecular framework by the other intermolecular hydrogen bonding (O1-H1A⋯N4^{iv}) (Fig. 3).

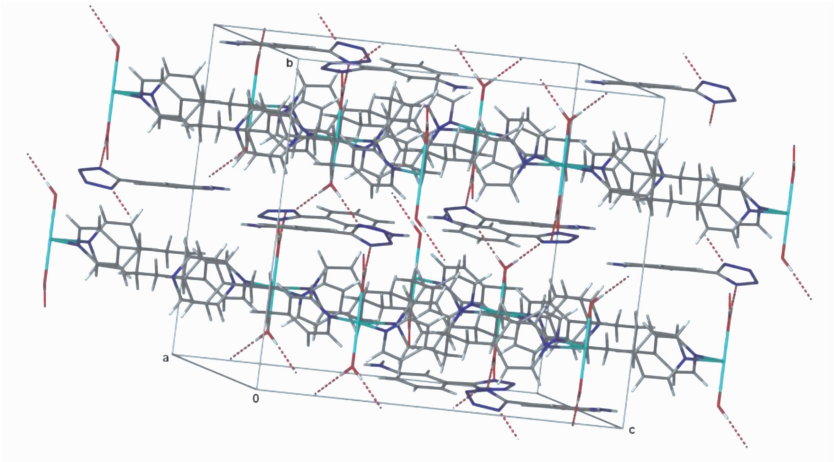


Fig.3　Packing diagram of the Cd(Ⅱ) complex

2.2　Power X-ray diffraction analysis

In an attempt to confirm the homogeneity of the material synthesized under the hydrothermal condition, we have analyzed the PXRD pattern of the complex and correlated the result with the simulated powder pattern obtained from the single crystal data. As depicted in Fig.4, the basic features of the PXRD patterns resemble the simulated from single crystal data for the complex, indicating that the bulk products obtained are homogenous in nature.

2.3　IR spectrum

In the IR spectra, the complex exhibits characteristic N-H stretching bands at 3 338 and 3 226 cm^{-1} because of the stretching vibration coupling of the two N-H, which 3 338 cm^{-1} for an asymmetric stretching and 3 226 cm^{-1} for a symmetric stretching. The very strong absorption bands of 1 614 cm^{-1} were attributed to C =N stretching contributions, the strong absorption bands at 1 473 and 1 429 cm^{-1} and the bands in the rang 3 100~3 000 cm^{-1} stretching vibration of benzene ring were assigned to pyridine ring stretching vibration. The strong bands at ca. 3 431 cm^{-1} are corresponding to the vibration of the coordinate water molecules in the complex.

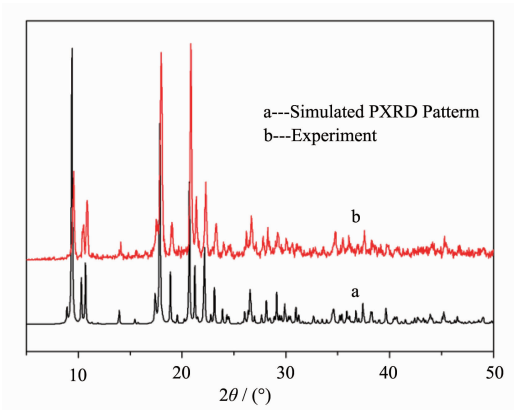


Fig.4　Experimental and simulated powder XRD patterns of the Cd(Ⅱ) complex

2.4 Thermogravimetric analyses

Thermogravimetric analyses (TGA) experiments were conducted to determine the thermal stability of the title complexes, which is an important aspect for metal-organic frameworks [13-14]. TGA was performed on crystalline samples of the complex under an N_2 atmosphere from 30 to 800 °C. In the complex, the first weight loss of 64.36% (Calcd. 64.10%), corresponding to an endothermic peak, which implying removal of two guest 5-(3-aminophenyl)tetrazole ions ($C_7H_6N_5$), two coordinate water molecules and one L molecule per formula unit $\{[CdL_2(H_2O)_2]\cdot 2(C_7H_6N_5)\}_n$ from 105 to 340.3 ℃. Then a drop of weigh is observed after 444 ℃, indicating the decomposition of the framework of the complex (Fig.5).

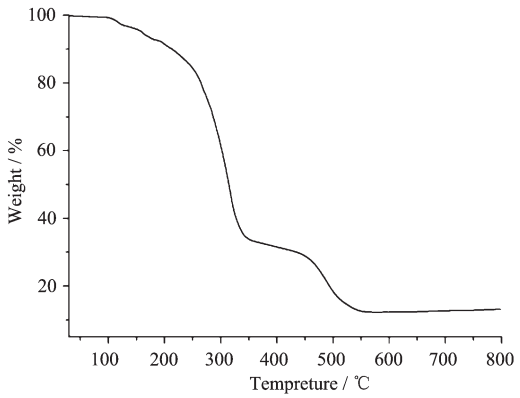


Fig.5 TGA curve of the Cd(Ⅱ) complex

2.5 Fluorescent emission

Previous studies have shown that compounds containing cadmium could exhibit fine photoluminescent properties [15-17]. Hence, we also investigated the photoluminescent properties of the Cd (Ⅱ) complex (Fig.6). In the solid state, strong photoluminescence emission bands at 358 nm is observed for the complex, respectively, upon photoexcitation at 335 nm. Since L molecules and the free 5-(3-aminophenyl)tetrazole molecules exhibit weak photoluminescence emission at 384 and 390 nm, which may originate from the ligand-to-ligand π_L-π_L* charge transfer (LLCT) transition emission. The position blue-shift (comparing with L molecules and 5-(3-aminophenyl)tetrazole molecules) of the strong emission peak (358 nm) and the fluorescent enhancement of the complex, may be assigned to the effect of ligand-to-metal or metal-to-ligand charge transfer (LMCT or MLCT) transition emission similar to previous reports.

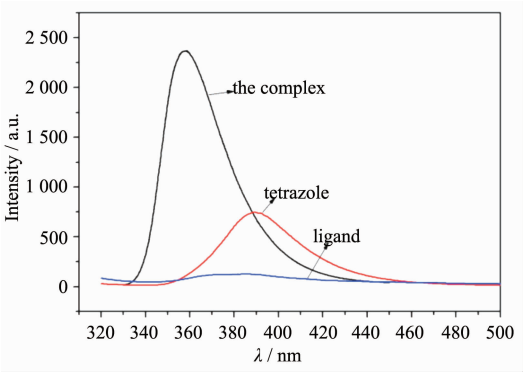


Fig.6 Solid-state emission spectra of the title complex at room temperature

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