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柔性双三氮唑配体构筑的二维镉(Ⅱ)配合物的合成、结构和荧光性质

郝金明 李欢欢 李光跃 崔广华*
(河北联合大学化学工程学院,唐山 063009)

摘要: 水热条件下,合成了 1 个镉的配位聚合物{[Cd(L)(HBTC)(H_2O)]·H_2O}$_n$(L=1,2-二(1,2,4-三氮唑-1-亚甲基)苯,H_3BTC=1,3,5-均苯三酸)并对其进行了元素分析,红外光谱,热重以及 X 射线单晶衍射分析。结构分析表明,镉中心为六配位八面体结构,赤道平面上,4 个配位 O 原子分别来自 2 个 $HBTC^{2-}$二价阴离子和配位水,轴向上的 2 个配位 N 原子来自 2 个不同的 L 配体。该配合物是 1 个二维(4,4)网络结构,并进一步被分子间的 O–H…O 氢键作用构筑成三维超分子结构。同时研究了配合物的荧光性质。

关键词: 镉(Ⅱ)配合物; 晶体结构; 荧光特性; (4,4)网络
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Two Dimensional Cadmium (Ⅱ) Coordination Polymer Constructed from Flexible Bis(triazole) Ligand: Synthesis, Structure and Fluorescence Property

HAO Jin-Ming LI Huan-Huan LI Guang-Yue CUI Guang-Hua*
(*College of Chemical Engineering, Hebei United University, Tangshan, Hebei* 063009, *China*)

Abstract: The new coordination polymer named, {[Cd(L)(HBTC)(H_2O)]·H_2O}$_n$ (L=1,2-bis(1,2,4-triazol-1-ylmethyl) benzene, H_3BTC =1,3,5-benzenetricarboxylic acid) has been synthesized hydrothermally and characterized by elemental analysis, IR spectroscopy, thermogravimetric (TG) analysis and single-crystal X-ray diffraction analysis. The cadmium center is six coordinated with three O_{COO-} atoms from two different $HBTC^{2-}$ dianions and one water molecule locate in the equatorial positions, while apical sites are occupied by two N atoms from two distinct L ligands in a distorted octahedral geometry. The structural analysis shows that the complex possesses a two-dimensional 2D (4,4) layer structure, and displays a three-dimensional (3D) supramolecular structure via multiple intermolecular O–H…O hydrogen bonds. The fluorescence property of the complex also has been studied. CCDC: 917952.

Key words: cadmium(Ⅱ) complex; crystal structure; fluorescence property; (4,4) network

0 Introduction

The design and construction of metal-organic coordination polymers (MOCPs) is of current interest in the field of crystal engineering, not only stemming from their tremendous potential applications in gas storage, luminescence, magnetism, conductivity and catalysis, but also from their intriguing variety of architectures and topologies[1-5]. In recent years, the self-assembly of MOCPs based on the nitrogen-donor and polycarboxylates mixed ligands is an effective strategy widely adopted in this field[6-7]. The ligands

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*通讯联系人。E-mail:tscghua@126.com

triazole and its derivatives have received a great attention because of their marvelous structures and unique properties[8-10]. Specifically, 1,2,4-triazole-based ligands have been used so far to prepare polymeric coordination networks due to the 1,2,4-triazole ring can bridge metal ions through a variety of coordination modes. All these bridging coordination types provide infinite possibilities for the design and preparation of hybrid inorganic/organic architectures.

The flexible bis (triazole) ligands such as 1,4-bis (1,2,4-triazol-1-ylmethyl)benzene, 1,2-bis(1,2,4-triazol-1-yl)ethane and 1,3-bis (1,2,4-triazol-1-ylmethyl) benzene have been widely used to build fascinating structures because of their excellent coordinating ability and variable conformationsdue [11-13]. However, the exploration of Cd(Ⅱ) complexes based on flexible 1,2-bis(1,2,4-triazol-1-ylmethyl)benzene and auxiliary polycarboxylates mixed-ligands is rarely reported. In order to explore the coordination properties of bis (triazole) ligands and construct novel networks, we have hydrothermally synthesized the complex, $[Cd(L)(HBTC)(H_2O)]\cdot H_2O\}_n$ (L =1,2-bis (1,2,4-triazol-1-ylmethyl)benzene) ligand and (H_3BTC =1,3,5-benzenetricarboxylic acid). H_3BTC is chosen as auxiliary ligand because the multicarboxylic groups of the molecule may be completely or partially deprotonated, and those anions may act as bridging ligands in various coordination modes[14-15].

1 Experimental

1.1 Materials and general methods

All regents and solvents for synthesis were obtained from commercial sources and used as received. The ligand L was prepared according to literature method[16]. Elemental analyses were obtained on a Perkin-Elmer automatic analyzer. IR spectra were recorded on a Nicolet FTIR Avatar 360 spectrophotometer in the 4 000~400 cm^{-1} region using KBr pellets. The TG-DTA measurements were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800 ℃ under N_2 atmosphere at a heating rate of 10 ℃·min^{-1}. The fluorescence spectra were performed with a Hitachi F-7000 spectrophotometer at room temperature.

1.2 Synthesis of the complex $\{[Cd(L)(HBTC)(H_2O)]\cdot H_2O\}_n$

A mixture of $Cd(OAc)_2\cdot 2H_2O$ (266.5 mg, 1 mmol), L ligand (238 mg, 1 mmol), 1,3,5-benzenetricarboxylic acid (210 mg, 1mmol), NaOH (40.0 mg, 1 mmol), and H_2O (15 mL) was placed in a teflon-lined stainless vessel and heated to 140 ℃ for 3 d under autogenous pressure, and then cooled to room temperature at a rate of 10 ℃·h^{-1}. The resulting white block crystals of the complex were obtained by filtration, washed with distilled water, and dried at ambient temperature (yield: 68%). Elemental Anal. Calcd. for $C_{21}H_{20}CdN_6O_8$ (%): C, 42.26; H, 3.38 N, 14.08. Found(%): C, 42.13; H, 3.35; N, 14.20. IR (KBr, cm^{-1}): 3 420(m), 3 244(m), 3 147(m), 1 683(m), 1 612(m), 1 556(s), 1 436(m), 1 367(s), 1 275(m), 1 134(w), 979(w), 880(w), 736(m), 645(w).

1.3 X-ray crystallography

Single crystal X-ray diffraction measurements were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. The determination of unit cell parameters and data collections were performed with Mo $K\alpha$ radiation (λ=0.071 073 nm). The structure was solved by direct method and refinements on F^2 were performed by full-matrix least-squares methods using the SHELXTL-97 program package[17]. The hydrogen atoms of organic ligands were generated theoretically onto the specific atoms and refined isotropically. The hydrogen atoms of water molecule were added by difference Fourier maps, and refined using a riding model. The crystal data and structure refinement details for the complex are given in Table 1. Table 2 lists the data of relevant bond distances and angles.

CCDC: 917952.

2 Results and discussion

2.1 Synthesis and IR spectroscopy

The complex was obtained by hydrothermal reaction of cadmium acetate dihydrate, L ligand, H_3BTC and sodium hydroxide at a molar ratio of 1∶1∶1. This coordination polymer is stable in the air and

Table 1 Crystallographic data and structural refinement of the complex

Empirical formula	$C_{21}H_{20}CdN_6O_8$	Z	2
Formula weight	596.84	Calculated density / ($g\cdot cm^{-3}$)	1.661
Temperature / K	293(2)	Absorption coefficient / mm^{-1}	0.974
Wavelength / nm	0.071 073	$F(000)$	600
Crystal system	Triclinic	Crystal size / mm	0.18×0.17×0.15
Space group	$P\bar{1}$	θ range for data collection / (°)	2.39 to 25.00
a / nm	1.021 28(9)	Reflections collected / unique	9 130 / 4 176 (R_{int}=0.028 0)
b / nm	1.097 54(8)	Completeness to θ=25.00° / %	99.60
c / nm	1.161 10(9)	Data / restraints / parameters	4 176 / 2 / 329
α / (°)	76.853(1)	Goodness-of-fit on F^2	0.889
β / (°)	86.122(1)	Final R indices ($I>2\sigma(I)$)	R_1=0.035 3, wR_2=0.109 8
γ / (°)	70.333(1)	R indices (all data)	R_1=0.039 8, wR_2=0.116 2
V / nm^3	1.193 37(2)	Largest diff. peak and hole / ($e\cdot nm^{-3}$)	1 213 and −674

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

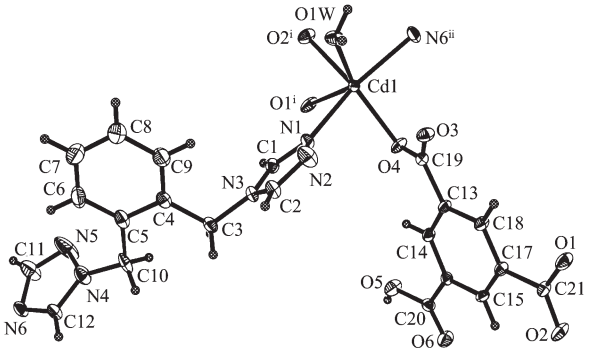
Cd1-O4	0.224 7(3)	Cd1-N1	0.229 6(3)	Cd1-N6^{ii}	0.231 4(3)
Cd1-O2^{i}	0.233 0(3)	Cd1-O1^{i}	0.246 0(3)	Cd1-O1W	0.237 0(3)
O4-Cd1-N1	86.65(11)	O4-Cd1-N6^{ii}	90.03(12)	N1-Cd1-N6^{ii}	160.23(13)
O4-Cd1-O2^{i}	136.05(10)	N1-Cd1-O2^{i}	107.46(12)	N6^{i}-Cd1-O2^{i}	88.34(12)
O4-Cd1-O1W	139.13(10)	N1-Cd1-O1W	81.65(11)	N6^{ii}-Cd1-O1W	88.24(12)
O2^{i}-Cd1-O1W	84.72(10)	O4-Cd1-O1^{i}	87.36(10)	N1-Cd1-O1^{i}	84.49(12)
N6^{ii}-Cd1-O1^{i}	114.84(12)	O2^{i}-Cd1-O1^{i}	54.32(10)	O1W-Cd1-O1^{i}	129.78(10)

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

insoluble in common solvents such as water, ethanol, methanol and acetone. For the IR spectrum of the complex, the $\nu_{C=N}$ breathing vibrations of triazole ring of the L ligand is 1 556 cm^{-1}. A band at about 3420 cm^{-1} may be assigned to the stretching vibrations (ν_{OH}) of water molecules, and the broad peak of this band illustrates the existence of hydrogen bonds. It should be noted that the medium peak at 1 683 cm^{-1} arises from the vibrations of the undeprotonated carboxylate group for the complex, indicating the incomplete deprotonation of the H_3BTC ligand. The IR spectrum of complex also shows characteristic bands of the carboxyl group at 1 612 cm^{-1} for the antisymmetric stretching and 1 436 cm^{-1}, 1 367 cm^{-1} for symmetric stretching. The separations ($\Delta\nu$) between ν_{asym} (COO^-) and ν_{sym} (COO^-) indicate the presence of chelating and monodentate (176 cm^{-1} and 245 cm^{-1}) coordination modes of carboxyl group[18].

2.2 Description of crystal structure

The complex crystallizes in the triclinic system, space group $P\bar{1}$, and the asymmetric unit consists of one Cd atom, one L ligand, one $HBTC^{2-}$ dianions, one coordinated and one lattice water molecules. As shown in Fig.1, each Cd(Ⅱ) is six coordinated with three O_{COO-} atoms (O1^{i}, O2^{i} , O4, ^{i} $x-1, y, z$) from two different $HBTC^{2-}$ dianions and one O atom (O1W) from coordinated water molecule locate in the equatorial positions, while apical sites are occupied by two N



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

Fig.1 Coordination environment around the Cd(Ⅱ) ion in the complex at 30% probability thermal ellipsoids

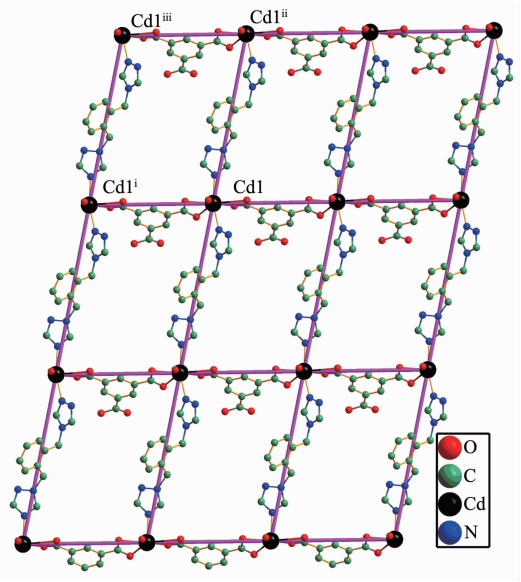
Table 3　Classical hydrogen bond lengths and angles for the complex

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠DHA / (°)
O1W–H1WA···O6^{iv}	0.085 0	0.186	0.271 0	178
O1W–H1WB···O3^{v}	0.085 0	0.192	0.271 9	157
O2W–H2WB···O2^{vi}	0.085 0	0.187	0.270 4	166
O2W–H2WA···O1W^{vii}	0.085 0	0.210	0.293 8	167
O5–H5···O2W^{viii}	0.085 0	0.176	0.255 8	157

Symmetry codes: ^{iv} $x-1, y+1, z$; ^{v} $-x+1, -y+2, -z$; ^{vi} $x, y-1, z+1$; ^{vii} $-x+1, -y+1, -z+1$; ^{viii} $x, y, z-1$.

atoms (N1, N6^{ii}, ^{ii} $x, y+1, z-1$) from two distinct L ligands in a distorted octahedral geometry. The Cd-O bond lengths vary from 0.225 (2) to 0.246 (3) nm, the Cd-N bond lengths vary from 0.230(3) to 0.231(3) nm and the O-Cd-O angles range from 49.96(1)° to 169.27(1)°, the N-Cd-N angles being 160.23(1)°, which is within the extent expected for such species[19].

In the structure of the complex, each L ligand shows a bis-monodentate mode and bridges two Cd(Ⅱ) atoms forming a 1D linear infinite cation chain. These chains are further linked by $HBTC^{2-}$ dianions adopting chelating and monodentate bridging coordination modes to form a 2D (4, 4) rectangle-grids (Fig.2), which contains a 70-member ring parallelogram with Cd(II) atoms at each corner, L at each long edges and $HBTC^{2-}$ at each short edges. The length of the edges are defined by Cd1···Cd1^{i} and Cd1···Cd1^{ii} distance of 1.021(1) and 1.405(9) nm, respectively. The ligands L adopt *cis* conformation, the dihedral angles between the mean planes of the two triazole rings is 30.75(1)°. Additionally, there exists strong intermolecular O–H···O hydrogen bonding interactions between the lattice water molecules and carboxylate oxygen atoms which extend the 2D layer to a 3D supramolecular network. The d (D ··· A) distances and D–H ··· A angles of hydrogen bonds arrange from 0.255 8 to 0.293 8 nm and 157° to 178°, respectively. The classical hydrogen bond lengths and angles are listed in Table 3.



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

Fig.2　2D (4,4) network of the complex

2.3　Thermal property

Thermogravimetric analysis to measure the thermal stability of the complex was carried out by heating complex to 800 ℃ at 10 ℃·min^{-1} under N_2 and TG curve is shown in Fig.3. As it is revealed there are two main steps of weight losses. The first one is about 6.5% (Calcd. 6.0%), which starts at about 60 and ends at 180 ℃, implying the removal of one coordinated and one lattice water molecules, and then the second one between 320 and 660 ℃ corresponding to the release of all ligands. After 660 ℃, no weight loss is observed, indicating the complete decomposition of the complex. The residual weight 21.54% (Calcd.

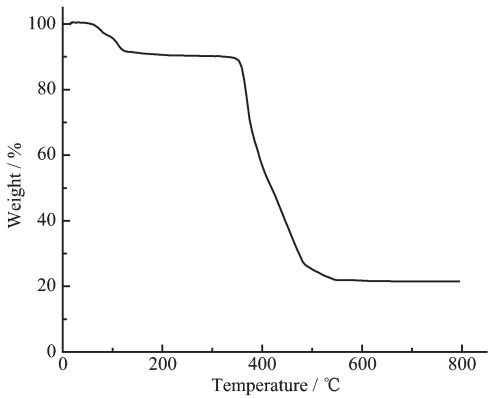


Fig.3　TG curve of the complex

21.45%) corresponds to CdO.

2.4 Fluorescence property

The emission spectra of the complex and free L ligand in the solid state are investigated at room temperature. It exhibits light purple emission with maximum at 403 nm upon excitation at 306 nm as depicted in Fig.4. Furthermore, it can be seen that the free L ligand shows a sharp peak with a maximum emission at 428 nm (under 267 nm excitation). Compared with its corresponding free ligand, the emission peak is blue-shifted 25 nm for the complex, the emission of the complex may be ascribed to the ligand-centered $n \rightarrow \pi$ or $\pi \rightarrow \pi^*$ orbital transitions within the aromatic ring of the L ligand, since the Cd^{2+} ion is difficult to oxidize or reduce due to its d^{10} configuration[20].

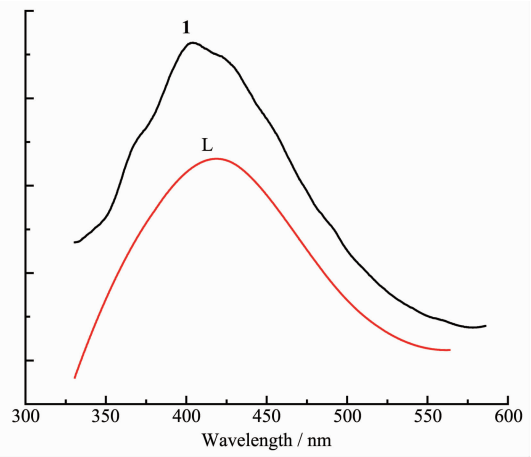


Fig.4 A solid-state photoluminescent spectra of the complex and free L ligand

3 Conclusions

A new cadmium(Ⅱ) complex with two-dimensional (2D) (4,4) square-planar layer structure has been synthesised by hydrothermal method. The 3D supramolecular network is further constructed by hydrogen bonding interactions. On the basis of this work, further syntheses and structural studies of related coordination polymers with flexible bis (triazole) ligands are also under way in our laboratory.

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