两个基于四氮唑衍生物的配位聚合物的合成

黄登登　陈立庄*

(江苏科技大学环境与化学工程学院, 镇江　212003)

摘要： 在水热条件下，5-(4-吡啶基)四氮唑(4-PTZ)分别与氯化锌和氯化镉反应，得到 2 个基于此配体的配位聚合物，它们的分子式分别为 $\{[Zn(4-PTZ)_2Cl_2]\cdot 4H_2O\}_n$ (**1**)和 $\{[Cd_3(4-PTZ)_2(H_2O)_2Cl_6]\cdot 3H_2O\}_n$ (**2**)，且表现出不同的配位模式。这 2 个化合物均结晶在单斜晶系，化合物 **1** 的晶胞参数分别为：a=0.691 75(8) nm；b=2.668 8(3) nm；c=1.122 66(12) nm；β=93.535 0(10)°；V=2.068 7(4) nm³；Z=4；R_1=0.031 8($I>2\sigma(I)$)；wR_2=0.082 9；空间群为 $P2_1/n$。化合物 **2** 的晶胞参数分别为：a=1.897 13(13) nm；b=1.055 79(7) nm；c=1.446 49(10) nm；β=102.489 0(10)°；V=2.828 7(3) nm³；Z=4；R_1=0.026 2($I>2\sigma(I)$)；wR_2=0.134 3；空间群为 $C2/c$。通过元素分析、红外光谱分析和热重分析对该化合物进行了表征，另外荧光测定结果显示化合物 **1** 和 **2** 的固态粉末在室温下均表现出较强的紫外荧光发射特性。

关键词： 配位聚合物；一维链；水热反应；四唑；荧光

Assembly of Two Coordination Polymers Based on Tetrazole Derivatives

HUANG Deng-Deng　CHEN Li-Zhuang*

(*School of Environmental and Chemical Engineering, Jiangsu University of Science
and Technology, Zhenjiang, Jiangsu* 212003, *China*)

Abstract: Two mixed metal-organic coordination polymers, namely $\{[Zn(4-PTZ)_2Cl_2]\cdot 4H_2O\}_n$ (**1**) and $\{[Cd_3(4-PTZ)_2(H_2O)_2Cl_6]\cdot 3H_2O\}_n$ (**2**), were synthesized under hydrothermal condition using 5-(4-pyridyl)tetrazolate (4-PTZ), which exhibited diverse coordination modes in two complexes. The two compounds are both crystallized in a monoclinic system. Compound **1**: a=0.691 75(8) nm; b=2.668 8(3) nm; c=1.122 66(12) nm; β=93.535 0(10)°; V=2.068 7(4) nm³; Z=4; R_1=0.031 8 for $I>2\sigma(I)$; wR_2=0.082 9; space group $P2_1/n$. Compound **2**: a=1.897 13(13) nm; b=1.055 79(7) nm; c=1.446 49(10) nm; β=102.489 0(10)°; V=2.828 7(3) nm³; Z=4; R_1=0.026 2 for $I>2\sigma(I)$; wR_2=0.134 3; space group $C2/c$. They are characterized by elemental analysis, IR spectroscopy and TGA. In addition, **1** and **2** have ultraviolet fluorescence emissions in the solid state at room temperature. CCDC: 984430, **1**; 984429, **2**.

Key words: coordination polymer; 1D chain; hydrothermal reaction; tetrazole; fluorescence

0　Introduction

In recent years, great deal of efforts have been invested in the rational design and synthesis of metal-organic coordination polymers in the field of crystal engineering with the driving force of various structural characteristics and high versatility such as ion exchange, photoluminescent, sensing of target

molecules, magnetism, nonlinear optics, catalysis, etc[1-8]. Extensive investigations have demonstrated that the metal ions, the geometries, and the coordination sites of organic ligands play significant roles in directing the final structures that are formed via self-assembly processes[9-11]. Without a doubt, among these factors, the rational design and reasonable use of the characteristic ligands occupies the capital, because changes in the flexibility, length, and symmetry of the organic ligands can result in a remarkable class of coordination polymers bearing diverse architectures and functions[12-13]. Among various organic ligands, the tetrazolyl functional group has found a wide range of applications in coordination chemistry as ligands because of the multiple N-donor atoms of tetrazole group. Ligands containing tetrazole groups could serve as excellent multidentate or bridging building blocks for the construction of polymeric structures[14-17]. The combination of nitrogen donor ligands and pyridine ring as connecting ligands is widely used for the construction of coordination polymers, among which a series of cadmium and zinc coordination polymers containing 5-(4-pyridyl)tetrazolate (4-PTZ) ligands have been reported[18-20]. Taking all these into consideration, as a continuation of our systematic studies of tetrazolyl ligands[21-22], we choose 5-(4-pyridyl)tetrazolate as an organic building block in an attempt to construct metal-organic polymers with various structural features. Herein, we report the synthesis, crystal structures and luminescent properties of two coordination polymers based on 5-(4-pyridyl)tetrazolate, namely $\{[Zn(4-PTZ)_2Cl_2] \cdot 4H_2O\}_n$ (**1**) and $\{[Cd_3(4-PTZ)_2(H_2O)_2 Cl_6] \cdot 3H_2O\}_n$ (**2**).

1 Experimental

1.1 Materials and methods

All the materials except the 5-(4-pyridyl) tetrazolate ligand are of analytical reagent grade and used as received without further purification. The ligand 5-(4-pyridyl)tetrazolate was prepared by the method reported in the literature[23]. Infrared spectra are recorded on a SHIMADZU IRprestige-21 FTIR-8400S spectrometer in the spectral range of 4 000 ~

500 cm^{-1}. The solid-state fluorescence spectra were recorded on a SHIMADZU RF-5301PC. Elemental analyses were taken on a Perkin-Elmer 240C elemental analyzer. Thermo gravimetric analyses (TGA) were conducted on a Netszch TGA 209 F3 thermo gravimeter with a heating rate of 10 K·min^{-1} in an N$_2$ atmosphere.

1.2 Synthesis of the compounds

$\{[Zn(4-PTZ)_2Cl_2] \cdot 4H_2O\}_n$ (**1**): A mixture of ZnCl$_2$ (13.6 mg, 0.1 mmol), 5-(4-pyridyl)tetrazolate) (14.7 mg, 0.1 mmol) and 14 mL H$_2$O was placed in a 25 mL Teflon-lined stainless steel vessel, and heated to 140 ℃ for 3 days, then cooled to room temperature at a rate of 5 ℃·h^{-1}. Colorless rod-like crystals of **1** were obtained. The yield of complex **1** was 52%. IR (KBr pellet, cm^{-1}): 3 481 (m), 3 092 (m), 2 670(m), 2 119 (w), 1 645 (vs), 1 530 (vs), 1 434 (vs), 1 386(w), 1 232 (m), 835 (vs), 750(vs), 710 (w), 522(w). Anal. Calcd. for C$_{12}$H$_{18}$Cl$_2$N$_{10}$O$_4$Zn(%): C, 28.68; H, 3.61; N, 27.87; Found: C, 28.71; H, 3.55; N, 27.92.

$\{[Cd_3(4-PTZ)_2(H_2O)_2Cl_6] \cdot 3H_2O\}_n$ (**2**): The same synthetic procedure as for **1** was used except that ZnCl$_2$ was replaced by CdCl$_2$·2.5H$_2$O. Colorless block crystals were obtained in 48% yield (based on Cd). IR data (KBr pellet, cm^{-1}): 3 472(m), 3 236(s), 3 154(s), 3 095(s), 1 637(vs), 1 595(s), 1 511(s), 1 443(w), 1 380 (m), 1 240(m), 1 197(w), 1 130(w), 1 088(w), 1 054 (w), 1 012(w), 942(m), 891(m), 846(m), 793(s), 733(vs), 699(m), 526(w). Anal. Calcd. for C$_{12}$H$_{20}$Cd$_3$Cl$_6$N$_{10}$O$_5$(%): C, 15.43; H, 2.16; N, 14.99; Found: C, 15.39; H, 2.12; N, 14.93.

1.2 X-ray crystallography

Single crystals of complexes **1** and **2** with appropriate dimensions were chosen under an optical microscope, data of them were collected on a Bruker SMART-APEX II CCD with Mo $K\alpha$ radiation (λ = 0.071 073 nm) at 296 K. The structures were solved by direct methods and refined with full-matrix least-squares technique using SHELXTL-97 software package[24-25]. All non-hydrogen atoms were refined with independent anisotropic displacement parameters, and hydrogen atoms were located and included at their geometrically idealized positions. Hydrogen atoms of

water molecules were located in difference Fourier maps and rened using a riding model, with $U_{iso}(H)=1.2U_{eq}$ (C, N, O). Data collection and structure refinement parameters and crystallographic data for complexes **1** and **2** were given in Table 1. Selected coordination bond lengths and bond angles of **1** and **2** are summarized in Table 2 and 3, respectively.

CCDC: 984430, **1**; 984429, **2**.

Table 1　Crystal data collection and parameters for 1 and 2

	1	2
Empirical formula	$C_{12}H_{18}Cl_2N_{10}O_4Zn$	$C_{12}H_{20}Cd_3Cl_6N_{10}O_5$
Formula weight	502.63	934.28
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a / nm	0.691 75(8)	1.897 13(13)
b / nm	2.668 8(3)	1.055 79(7)
c / nm	1.122 66(12)	1.446 49(10)
β / (°)	93.535 0(10)	102.489 0(10)
V / nm³	2.068 7(4)	2.828 7(3)
Z	4	4
D_c / (g·cm⁻³)	1.614	2.194
μ / mm⁻¹	1.487	2.845
$F(000)$	1 024	1 792
θ range / (°)	1.53 to 27.83	2.20 to 27.54
Collected reflections	17 867	11 891
Unique reflections	4 740	3 183
R_1, wR_2 ($I>2\sigma(I)$)	0.031 8, 0.076 0	0.026 2, 0.119 0
R_1, wR_2 (all data)	0.045 5, 0.082 9	0.035 5, 0.134 3
GOF	1.022	1.029
Largest peak and hole / (e·nm⁻³)	0.299 and −0.328	2.244 and −2.275

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

Zn(1)-N(6)	0.201 79(17)	Zn(1)-N(2)	0.202 92(18)	Zn(1)-Cl(2)	0.222 24(6)
Zn(1)-Cl(3)	0.222 96(7)				
N(6)-Zn(1)-N(2)	105.13(7)	N(6)-Zn(1)-Cl(2)	109.77(5)	N(2)-Zn(1)-Cl(2)	112.37(6)
N(6)-Zn(1)-Cl(3)	108.28(6)	N(2)-Zn(1)-Cl(3)	108.85(6)	Cl(2)-Zn(1)-Cl(3)	112.13(3)

Table 3　Selected bond lengths (nm) and bond angles (°) of 2

Cd(1)-O(1)	0.230 4(3)	Cd(1)-N(3)	0.244 6(3)	Cd(1)-Cl(2)	0.257 71(8)
Cd(1)-Cl(1)	0.259 40(8)	Cd(1)-Cl(2)ⁱ	0.260 31(9)	Cd(1)-Cl(3)	0.263 71(9)
Cd(2)-N(4)	0.234 6(3)	Cd(2)-N(4)ⁱⁱ	0.234 6(3)	Cd(2)-Cl(1)ⁱⁱ	0.262 08(8)
Cd(2)-Cl(3)ⁱⁱ	0.264 56(9)	Cd(2)-Cl(3)	0.264 56(9)	Cl(2)-Cd(1)ⁱ	0.260 31(9)
O(1)-Cd(1)-N(3)	178.35(9)	O(1)-Cd(1)-Cl(2)	89.04(8)	N(3)-Cd(1)-Cl(2)	90.24(7)
O(1)-Cd(1)-Cl(1)	95.34(8)	N(3)-Cd(1)-Cl(1)	86.22(6)	Cl(2)-Cd(1)-Cl(1)	97.26(3)
O(1)-Cd(1)-Cl(2)ⁱ	89.55(8)	N(3)-Cd(1)-Cl(2)ⁱ	88.93(7)	Cl(2)-Cd(1)-Cl(2)ⁱ	87.09(3)
Cl(1)-Cd(1)-Cl(2)ⁱ	173.48(3)	O(1)-Cd(1)-Cl(3)	96.76(8)	N(3)-Cd(1)-Cl(3)	83.86(6)
Cl(2)-Cd(1)-Cl(3)	173.07(3)	Cl(1)-Cd(1)-Cl(3)	86.01(3)	Cl(2)ⁱ-Cd(1)-Cl(3)	89.16(3)
N(4)-Cd(2)-N(4)ⁱⁱ	180.000(1)	N(4)-Cd(2)-Cl(1)ⁱⁱ	92.49(7)	N(4)ⁱⁱ-Cd(2)-Cl(1)ⁱⁱ	87.51(7)

Continued Table 2

N(4)-Cd(2)-Cl(3)^{ii}	94.53(7)	N(4)^{ii}-Cd(2)-Cl(3)^{ii}	85.47(7)	Cl(1)^{ii}-Cd(2)-Cl(3)^{ii}	85.29(3)
N(4)-Cd(2)-Cl(3)	85.47(7)	N(4)^{ii}-Cd(2)-Cl(3)	94.53(7)	Cl(1)^{ii}-Cd(2)-Cl(3)	94.71(3)
Cl(3)^{ii}-Cd(2)-Cl(3)	180.0				

Symmetry codes: ^{i} −x+1/2, −y+3/2, −z+2; ^{ii} −x+1/2, −y+1/2, −z+2

2　Results and discussion

2.1　Single-crystal structures of complexes 1 and 2

　　X-ray single crystal structure determination of **1** shows that complex **1** is packing with a discrete Zn(II) molecule with the formula $C_{12}H_{10}Cl_2N_{10}Zn$ and four uncoordinated water molecules. It also reveals that complex **1** crystallized in the monoclinic, space group $P2_1/n$. The Zn(II) atom has a distorted tetrahedral coordination environment, coordinated by two Cl atoms and two N atoms of the tetrazole group (Fig.1). The metal-ligand bond distance in complex **1** provides a direct comparison of the variation of metal to chlorine and metal to tetrazole bonding to those similar coordination polymers based on Zinc[26-27]. The metal-chlorine bond distance is relatively constant in the complex. The largest difference in this bond length is 0.000 72 nm. In comparison with the Zn(1)-N(2) bond distance of 0.202 92(18) nm, the Zn(1)-N(6) bond distance of 0.201 79(17) nm is slightly shorter than that in complex **1**. Furthermore, the bond angles of Cl(2)-Zn(1)-N(2) and Cl(2)-Zn(1)-N(6) are 112.37(6)° and 109.77(5)° respectively. Comparably, the bond angles of Cl(3)-Zn(1)-N(2) and Cl(3)-Zn(1)-N(6) are 108.85(6)° and 108.28(6)°, which are a little smaller. Moreover, the bond angle of Cl(2)-Zn(1)-Cl(3) is 112.13(3)°. The two dihedral angles between the least-squares pyridine ring and the least-squares plane of the tetrazole ring in complex **1** are 2.952(82)° and 1.665(74)° respectively. The molecular packing of **1** is further stabilized by intermolecular H-bond between N atoms of tetrazole ligands and Cl atoms of the neighboring molecule and the lattice water molecules. Moreover, weak hydrogen bonding interactions also exist in **1**, which are C(4)−H(4)⋯Cl(2)^{vii} (0.359 0(2) nm), C(5)−H(5)⋯Cl(3)^{iii} (0.347 3(3) nm), C(9)−H(9)⋯Cl(2)^{ix} (0.340 8(3) nm) and C(5)−H(5)⋯O(4) (0.324 7(4) nm) respectively. These hydrogen bonding interactions

help to stabilize the crystal structure of **1** and form a 2D supramolecular structure (Table 4 and Fig.2).
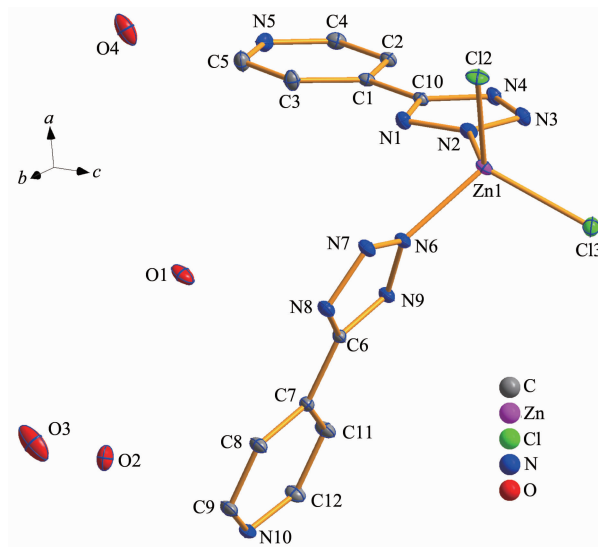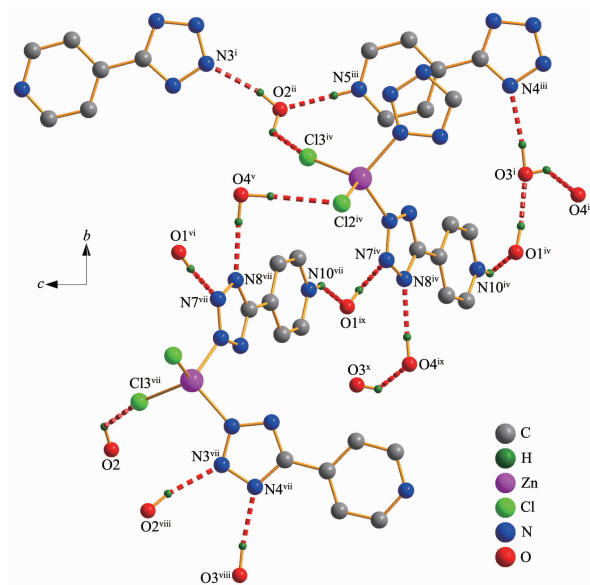

Fig.1　View of the coordination environment of Zn(II) in complex **1** with displacement ellipsoids drawn at the 15% probability level

Symmetry codes: ^{i} 5/2−x, 3/2+y, 3/2−z; ^{ii} 5/2−x, 1/2+y, 3/2−z; ^{iii} 5/2−x, 3/2+y, 1/2−z; ^{iv} 3/2+x, 3/2−y, −1/2+z; ^{v} 1/2+x, 3/2−y, 1/2+z; ^{vi} 3/2+x, 3/2−y, 1/2+z; ^{vii} 2+x, 1+y, z; ^{viii} 1+x, y, z; ^{ix}1+x, 1+y, z; ^{x} 2−x, 2−y, 1−z; ^{xi} 5/2−x, 1/2+y, 1/2−z; ^{xii} 1/2+x, 3/2−y, −1/2+z

Fig.2　Perspective views of the 2D network of **1** through H-bonding along the a axis

Table 4　Hydrogen bond lengths (nm) and bond angles (°) of 1

D–H⋯A	d(D-H)	d(H⋯A)	d(D⋯A)	∠DHA
O(1)–H(1WB)⋯N(7)[x]	0.086	0.220	0.303 7(3)	166
O(1)–H(1WA)⋯O(3)[v]	0.091	0.189	0.278 8(3)	168
O(2)–H(2WA)⋯N(3)[iv]	0.090	0.204	0.292 4(3)	167
O(2)–H(2WB)⋯Cl(3)[vi]	0.089	0.266	0.322 9(2)	122
O(3)–H(3WA)⋯O(4)[viii]	0.072	0.242	0.273 9(4)	109
N(5)–H(5A)⋯O(2)[ii]	0.086	0.188	0.274 0(3)	179
O(3)–H(3WB)⋯N(4)[iv]	0.099	0.203	0.298 9(3)	164
O(4)–H(4WB)⋯N(8)[xi]	0.091	0.195	0.286 1(3)	178
O(4)–H(4WA)⋯Cl(2)[iii]	0.099	0.241	0.338 5(2)	171
N(10)–H(10)⋯O(1)[i]	0.086	0.192	0.270 1(3)	150
C(4)–H(4)⋯Cl(2)[vii]	0.093	0.282	0.359 0(2)	141
C(5)–H(5)⋯O(4)	0.093	0.258	0.324 7(4)	130
C(5)–H(5)⋯Cl(3)[iii]	0.093	0.276	0.347 3(3)	134
C(9)–H(9)⋯Cl(2)[ix]	0.093	0.270	0.340 8(3)	133

Symmetry codes: [i] −1+x, y, z; [ii] x, −1+y, −1+z; [iii] x, y, −1+z; [iv] x, 1+y, z; [v] 1−x, 1−y, 1−z; [vi] 1−x, 1−y, 2−z; [vii] 2−x, −y, 1−z; [viii] 2−x, 1−y, 1−z; [ix] −3/2+x, 1/2−y, −1/2+z; [x] −1/2+x, 1/2−y, −1/2+z; [xi] 1/2+x, 1/2−y, −1/2+z

The single crystallographic analysis reveals that the title compound $\{[Cd_3(4\text{-}PTZ)_2(H_2O)_2Cl_6]·3H_2O\}_n$ (**2**) crystallizes in the monoclinic system, space group $C2/c$. Complex **2** exhibits a zigzag 1D chain, the chain can be considered as constructed by the basic unit, which is composed of linear trinuclear cadmium cations, μ_2-Cl atom bridges and water molecules. In the fundamental unit, neighboring Cd(Ⅱ) ions of the trinuclear species are linked by one bridged tetrazole ligand and two chloride atoms. The neighboring Cd²⁺ centers are connected by two ways to generate Cd⋯Cd interactions: (i) The μ_2-Cl⁻ adopts asymmetry mode to bind two neighboring Cd²⁺ centers with different bond lengths of Cd(2)-Cl(1) and Cd(2)-Cl(3). With the linkage of μ_2-Cl⁻, an inorganic skeleton chain $[CdCl_2]_n$ formed; (ii) tetrazole ligands bind neighboring Cd²⁺ with its 2- and 3- positioned nitrogen atoms anchoring on the both sides of the inorganic skeleton like wing (Fig.3). Four chloride atoms are coordinated to the central cadmium atom and form a square plane, with the octahedron of the central ion compressed along the N(4)-Cd(2)-N(4)[i] axis. The distances of Cd(2)-N(4) (0.234 6(3) nm), Cd(2)-Cl(1) (0.262 08(8) nm), and Cd(2)-Cl(3) (0.264 56(9) nm) are consistent with the bond length that has the similar coordination mode in

Cd(Ⅱ) compound[28]. Two chloride anions and one water molecule complete the octahedral coordination sphere of the terminal Cd(Ⅱ) ions in the unit, and the Cd(1)-Cl(2) distances of 0.257 71(8) nm and 0.260 31(9) nm
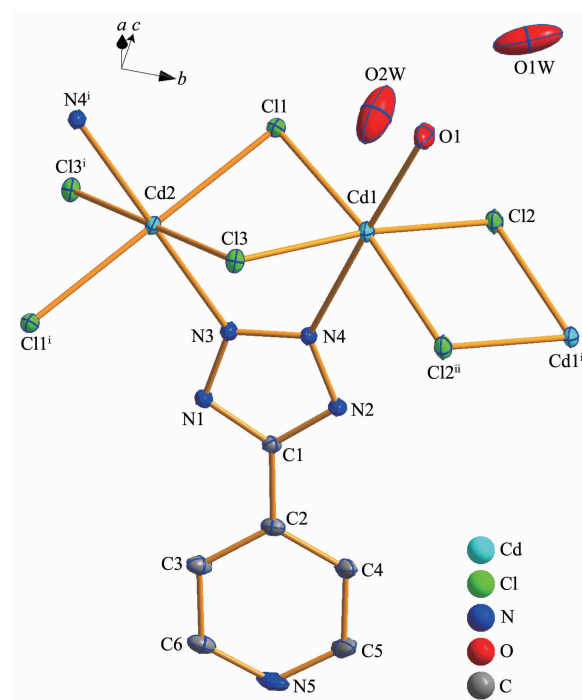
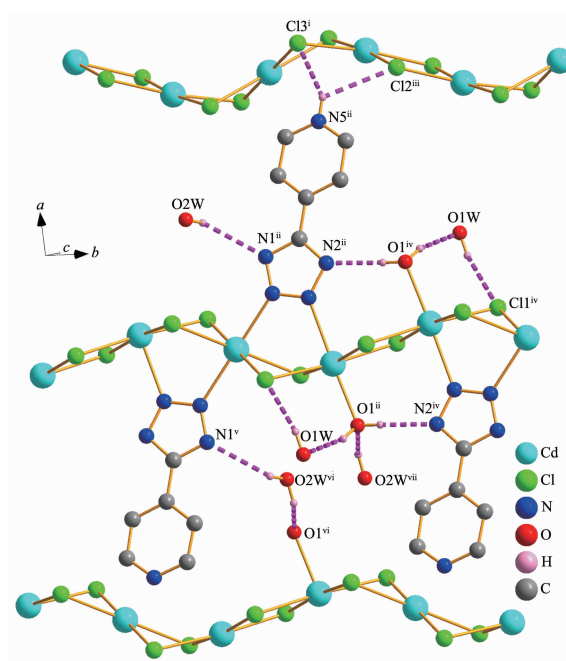Symmetry codes: [i] 1/2−x, 1/2−y, 2−z; [ii] 1/2−x, 3/2−y, 2−z

Fig.3　Coordination environment of cadmium-chloride and cadmium-tetrazole in **2** with displacement ellipsoids drawn at the 15% probability level

respectively, are essentially different from the Cd(1)-N (tetrazole) and Cd(1)-Cl distances ($d_{Cd(1)-N(3)}$=0.244 60(3) nm, $d_{Cd(1)-Cl(1)}$=0.259 40(8) nm, and $d_{Cd(1)-Cl(3)}$=0.263 71(9) nm). In addition, the bridging angles of Cd(1)-Cl(1)-Cd(2) and Cd(1)-Cl(3)-Cd(2) are 86.294° and 84.920° respectively, and the Cd⋯Cd distance in the trinuclear unit is 0.356 63(3) nm. These distances and angles are indicative of a distorted octahedron around Cd(1). The terminal chloride atoms in the fundamental unit adopt a double bridging mode to connect with other units. On the basis of this connection mode, all trinuclear Cd clusters giving rise to infinite one-dimensional chains along b axis as shown in Fig.4. Furthermore, the adjacent chains are connected together through hydrogen bonding interactions, which occur among the lattice water molecules, the chloride atoms, and the -NH groups of the 5-(4-pyridyl) tetrazolate molecules. Thus, a 3D supramolecular network is formed via both coordinating and hydrogen-bond interaction (Fig.5 and Table 5).
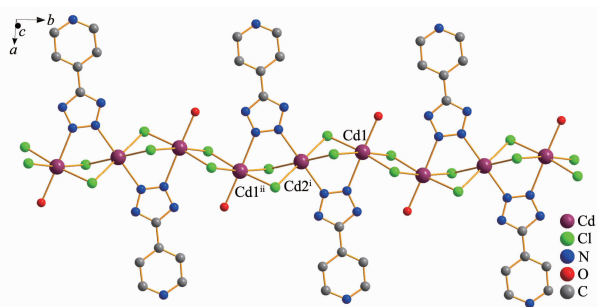
Symmetry codes: i 1/2−x, 1/2+y, 3/2−z; ii x, 1−y, −1/2+z

Fig.4　Coordination 1D chain along the b axis in 2

Symmetry codes: i 1+x, y, z; ii 1−x, y, 3/2−z; iii 3/2−x, 3/2−y, 2−z; iv 1/2+x, 3/2−y, −1/2+z; v 1/2+x, 1/2−y, −1/2+z; vi x, 1−y, −1/2+z; vii 1−x, y, 3/2−z

Fig.5　Hydrogen-bonded network of the supramolecular structure in 2

2.2　Fluorescence

Aromatic organic molecules, organic polymers, and mixed inorganic-organic hybrid coordination polymers have been applied as fluorescence-emitting materials[29]. Organic materials affect emission wavelengths, so it is of great significance to select proper organic spacers and metal centers (Zn, Cd, Pb, Ca, B, etc.) for the syntheses of inorganic-organic coordination polymers[30-32]. The solid-state fluorescence spectra

Table 5　Hydrogen bond lengths (nm) and bond angles (°) of 2

D–H⋯A	d(D-H)	d(H⋯A)	d(D⋯A)	∠DHA
O2W–H2WB⋯N1iv	0.085	0.258	0.303 9(7)	115
O1–H1A⋯O1Wvii	0.086	0.255	0.336 3(13)	158
O1–H1B⋯N2v	0.084	0.207	0.291 2(4)	177
O2W–H2WA⋯O1	0.085	0.231	0.279 1(8)	117
O1W–H1WA⋯Cl1viii	0.085	0.267	0.344 2(13)	152
O1W–H1WB⋯O1W	0.085	0.260	0.323 3	132
N5–H5A⋯Cl3iii	0.086	0.268	0.337 2(3)	139
N5–H5A⋯Cl2vi	0.086	0.281	0.335 6(4)	123

Symmetry codes: iii −x, y, 3/2−z; iv 1/2+x, 1/2+y, z; v 1/2−x, 3/2−y, 2−z; vi −1/2+x, 3/2−y, −1/2+z; vii −1/2+x, 3/2−y, 1/2+z; viii 1/2+x, 3/2−y, −1/2+z

of powdered **1** at room temperature (Fig.6) show maximal emission peaks at 360 nm (with λ_{ex}=320 nm), suggesting that **1** may be a good ultraviolet-light-emitting material. Similarly, as evidenced by the maximal emission peaks at 375 nm (with λ_{ex}=350 nm) of solid-state **2** at room temperature (Fig.7), **2** may also be an eligible ultraviolet-light-emitting material. The photoluminescent mechanism is tentatively attributed to ligand-to-ligand transitions, being in reasonable agreement with this class of metal complexes reported previously[33-34].
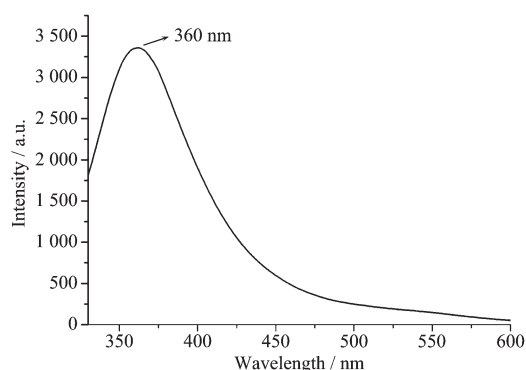

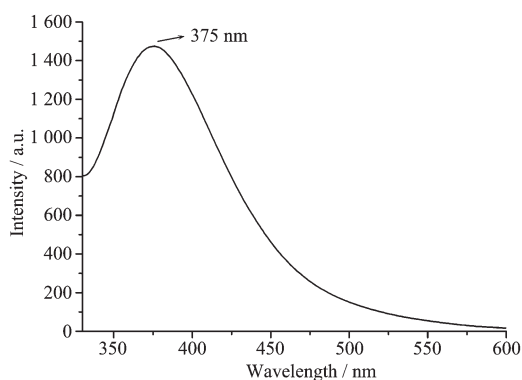Fig.6　Fluorescent emission spectrum of **1** in the solid state at room temperature

Fig.7　Fluorescent emission spectrum of **2** in the solid state at room temperature

2.3　TGA

To study the thermal stability of **1** and **2** and to further confirm their molecular formula, thermogravimetric (TG) analysis was performed in N_2 atmosphere on samples of complexes **1** and **2** (Fig.8). The TGA curves of **1** and **2** both show two identifiable weight loss steps respectively. For **1**, the first weight loss from 60 to 280 ℃ is attributed to the loss of four lattice water molecules (Obsd. 15.2%, Calcd. 14.3%).

The second weight loss of **1** between 300 and 630 ℃ perhaps correspond to the release of Cl atoms (Obsd. 15.5%, Calcd. 14.1%). Upon temperature increase, the structure of **1** begins to collapse. For **2**, the first weight loss in the temperature range of 50~200 ℃ is consistent with the removal of the uncoordinated water molecules (Obsd. 6.4%, Calcd. 5.8%). The second weight loss of **2** between 240 and 540℃, corresponds to the release of Cl atoms and the coordinated water molecules(Obsd. 27.5%, Calcd. 26.7%). Upon temperature increase, the structure of **2** begins to collapse.
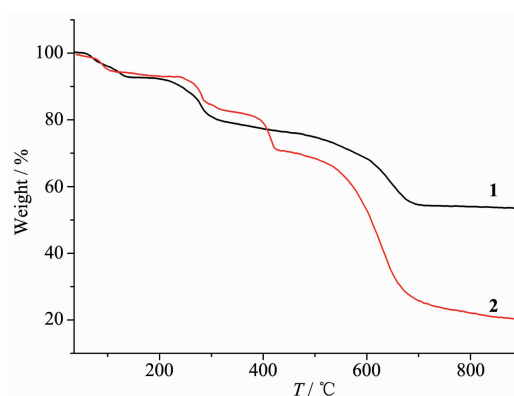

Fig.8　TGA curves of compounds **1** and **2**

3　Conclusions

In summary, two coordination polymers **1** and **2** based on 5-(4-pyridyl)tetrazolate ligands have been synthesized under hydrothermal conditions and structurally characterized. It′s worth mentioning complex **2** is a polymer chain constructed via the trinuclear metal cation units, which are bridged by tetrazolyl ligands. In addition, **1** and **2** display strong ultraviolet fluorescence emissions in the solid state at room temperature, suggesting that they may be good ultraviolet-light-emitting materials. Furthermore, this work may provide a useful approach for the design and construction of other structural crystalline materials, which further helps us to understand the relationships between structures and properties.

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