

5-[N-乙酸根(4-吡啶基)]四唑为桥联配体的铜(II)、镉(II)配聚合物

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摘要: 以 5-[N-乙酸根(4-吡啶基)]四唑为桥联配体, 分别与 $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ 和 CdCl_2 的水溶液反应, 获得配聚合物 $[\text{Cu}(\text{a4-ptz})_2 \cdot 2\text{H}_2\text{O}]_n$ (**1**) 和 $[\{\text{Cd}(\text{a4-ptz}) \cdot (\text{H}_2\text{O})_2\text{Cl}\} \cdot \text{H}_2\text{O}]_n$ (**2**), 2 个化合物通过元素分析、IR、TGA 等表征, 并测定了它的晶体结构。结果表明: 化合物 **1** 是一个二维四方格子结构的配位聚合物, 化合物 **2** 含有四元环(Cd_2Cl_2)的一维 Z-型聚合链。化合物 **2** 在 280 °C 以下热稳定性好, 并且不溶于一般溶剂, 因此可成为潜在的荧光材料。

关键词: 铜(II); 镉(II); 四唑; 配聚合物; 晶体结构; 发光

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New Cu(II) and Cd(II) Coordination Polymers Employing 5-[N-acetato(4-pyridyl)] Tetrazolate as a Bridging Ligand

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Abstract: Two coordination polymers $[\text{Cu}(\text{a4-ptz})_2 \cdot 2\text{H}_2\text{O}]_n$ (**1**) and $[\{\text{Cd}(\text{a4-ptz}) \cdot (\text{H}_2\text{O})_2\text{Cl}\} \cdot \text{H}_2\text{O}]_n$ (**2**) were synthesized and characterized by elemental analysis, IR spectroscopy, thermal analysis, and X-ray crystal structure analysis. Complex **1** exhibits a 2D square grid polymeric structure with dimensions of 1.220 0 nm \times 1.220 0 nm. Complex **2** possesses a 1D Z-type polymeric chain, which contains four-membered ring (Cd_2Cl_2). The thermal stability of complex **2** up to about 280 °C (TGA measurement) and their insolubility in common solvents make it a good candidate for potential fluorescent materials. CCDC: 658850, **1**; 658851, **2**.

Key words: copper(II); cadmium(II); tetrazole; coordination polymer; crystal structure; luminescence

0 Introduction

The tetrazole is able to participate in at least seven distinct types of coordination modes with metal ions in the construction of novel metal-organic frameworks th-

ough the four nitrogen electron-donating atoms^[1-9]. Thus the tetrazole functional group has found a wide range of applications in coordination chemistry as ligands, in medicinal chemistry and materials science, including special explosives^[1,2]. The study of some metal-organic

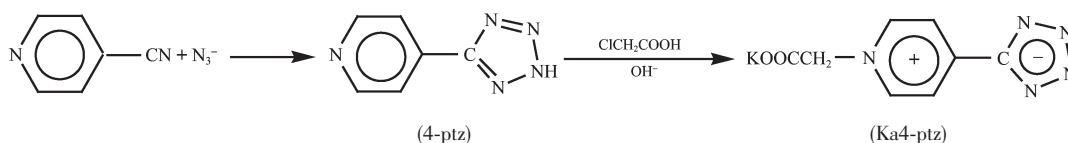
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coordination complexes containing tetrazole groups ligands has received increasing attention over recent years, example of 5-(4-pyridyl)tetrazole (4-H-ptz)^[1,3,5a], 5-(2-pyridyl)tetrazole (2-H-ptz)^[5b], (4,5-ditetrazoyl)-imidazole(4,5-dtim)^[5c], 1,4-bis(1H-tetrazol-5-yl)benzene (H₂btb), 4-(1H-tetrazol-5-yl)benzotrile (4-Htbn)^[4], tetrazole-1-acetic acid (Htza)^[6], 5,5'-(1,4-phenylene) bis (1H-tetrazole) (2H-pbtz)^[7], and 5-methyltetrazole (Hmtta)^[5d,8,9]. Inspired by Sharpless' s and Xiong' s pioneering work^[5,10], we have recently studied [2+3] cycloaddition reactions of nitriles 4-cyanopyridine (4-



Scheme 1

1 Experimental section

1.1 Materials

The 4-ptz was prepared from NaN₃ and 4-cyanopyridine according to a reported procedure^[1,3]. Copper perchlorate hexahydrate was prepared by the reaction of copper oxide with perchloric acid. Other chemicals and reagents were obtained from commercial sources and used as received. All solvents were predried over activated molecular sieves and refluxed over the appropriate drying agents under argon.

1.2 Physical measurements

The IR spectra were recorded on a Nicolet MagNa-IR 550 as KBr disk (4 000~400 cm⁻¹). ¹H NMR spectra were performed on Bruker 600 MHz Ultrashield spectrometer and are reported as parts per million (ppm) from TMS (δ). The elemental analysis (C, H, and N) were performed on a Carlo-Erba EA1110 CHNO-S microanalyzer. Thermogravimetric analysis (TGA) were performed with a SDT 2960 thermoanalyzer under N₂ (25~800 °C range) at a heating rate of 5 °C · min⁻¹. The photoluminescent spectra were performed on a Perkin-Elmer LS55 spectrofluorometer.

1.3 Synthesis of a4-ptz potassium salt ligand

The a4-ptz potassium salt ligand was prepared according to the literature method^[11]. Chloroacetic acid (4.37 g, 0.05 mol), 4-ptz (7.36 g, 0.05 mol), and

cnpy) to NaN₃ in the presence of ZnCl₂ as Lewis acid in aqueous solution. A novel ligand 5-[N-acetato (4-pyridyl)] tetrazolate (designated as a4-ptz anion) was obtained in the reaction of 5-(4-pyridyl)tetrazole (4-ptz) with chloroacetic acid in methanolic potassium hydroxide solution (Scheme 1). To our surprise, in the reactions of a4-ptz with Cu(ClO₄)₂ · 6H₂O and CdCl₂, two unprecedented coordination polymers, [Cu (a4-ptz)₂ · 2H₂O]_n (**1**) and [{Cd (a4-ptz) · (H₂O)₂Cl} · H₂O]_n (**2**) were formed. The present report is the synthesis, crystal structures and luminescent properties.

potassium hydroxide (5.62 g, 0.10 mol) in 300 mL of methyl alcohol was refluxed 24 h, cooled to room temperature. The precipitate was then filtered, washed with 2×30 mL methanol, and dried to give 7.25 g of 4-ptz potassium salt as a white powder, 58.8% yield, m.p. > 280 °C. ¹H NMR (600 MHz, in DMSO-d₆) δ (ppm) 7.6~8.2 (4H), 5.5 (2H); Anal. Calcd. (%): C₈H₆N₅O₂K, C, 39.50; H, 2.49; N, 28.79. Found(%): C, 39.61; H, 2.58; N, 28.64. IR data: 3 440(s), 1 639(s), 1 618(s), 1 543(s), 1 477(s), 1 377(s), 1 311(s), 1 217(m), 1 201(m), 1 118(m), 1 020(m), 848(s), 732(m) cm⁻¹.

1.4 Synthesis of [Cu(a4-ptz)₂ · (H₂O)₂]_n (**1**)

A mixture of a4-ptz potassium salt (0.048 6 g, 0.2 mmol) and Cu(ClO₄)₂ · 6H₂O (0.037 1 g, 0.1 mmol) was dissolved in distilled water (5 mL). The solution was heated at 100 °C for 8 h with stirring, then cooled to the room temperature and filtered. Slow evaporation of the filtrate in air gave blue block crystals of [Cu(a4-ptz)₂ · (H₂O)₂]_n (**1**). The yield of **1** was about 55% based on Cu²⁺ consumed. Anal. Calcd. (%): C₁₆H₁₆N₁₀O₆Cu: C, 37.84; H, 3.18; N, 27.58. Found (%): C, 37.61; H, 3.21; N, 27.44. IR data: 3 440 (s), 1 648 (s), 1 618 (s), 1 572(s), 1 474(s), 1 382(s), 1 294(s), 1 196(m), 1 183(m), 1 124(m), 1 020(m), 847(s), 735(m) cm⁻¹.

1.5 Synthesis of [{Cd(a4-ptz) · (H₂O)₂Cl} · H₂O]_n (**2**)

The similar reaction of a4-ptz potassium salt

(0.048 6 g, 0.2 mmol) with CdCl_2 (0.018 3 g, 0.1 mmol) in H_2O (5 mL) was carried out and followed by treatment similar to the preparation of **1**. The colorless crystals of $[\{\text{Cd}(\text{a4-ptz}) \cdot (\text{H}_2\text{O})_2\text{Cl}\} \cdot \text{H}_2\text{O}]_n$ (**2**) was obtained. Yield: 48% based on CdCl_2 . Anal. Calcd. (%): $\text{C}_8\text{H}_{12}\text{N}_5\text{O}_5\text{ClCd}$: C, 23.66; H, 2.98; N, 17.25. Found (%): C, 23.48; H, 3.09; N, 17.37. IR data: 3 440(s), 1 642(s), 1 618(s), 1 568(m), 1 474(s), 1 383(s), 1 310(s), 1 219(m), 1 196(m), 1 167(m), 1 018(m), 872(m), 727(m), 660(m) cm^{-1} .

1.6 Crystal structure determination

All measurements were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromatized $\text{Mo K}\alpha$ ($\lambda = 0.07107$ nm). A blue crystal of **1** with dimensions of 0.42 mm \times 0.33 mm \times 0.20 mm and a colorless block crystal of **2** with dimensions of 0.28 mm \times 0.20 mm \times 0.10 mm were in turn mounted on the glass fibers, cooled at 193 K in

liquid nitrogen stream. The diffraction data were collected at ω mode with a detector-to-crystal distance of 35 mm. The collected data were reduced by using the program CrystalClear (Rigaku and MSC, Ver.1.3, 2001), and an absorption correction (multiscan) was applied, which resulted in transmission factors ranging from 0.581 to 0.798 for **1** and from 0.563 to 0.823 for **2**. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of **1** and **2** were solved by direct methods, and refined on F^2 by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms. The final refinement was based on 3 360 (**1**) and 2 105 (**2**) reflections with $I > 2.00\sigma(I)$, and 315 (**1**) and 206 (**2**) variable parameters. A summary of the key crystallographic information for **1** and **2** is tabulated in Table 1.

CCDC: 658850, **1**; 658851, **2**.

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

Compound	1	2
Empirical formula	$\text{C}_{16}\text{H}_{16}\text{N}_{10}\text{O}_6\text{Cu}$	$\text{C}_8\text{H}_{12}\text{N}_5\text{O}_5\text{ClCd}$
Formula weight	507.93	406.08
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a / nm	1.700 1(3)	0.762 09(10)
b / nm	0.875 62(12)	0.904 09(9)
c / nm	1.421 3(2)	1.089 27(17)
α / ($^\circ$)		71.050(9)
β / ($^\circ$)	104.981(3)	88.271(12)
γ / ($^\circ$)		65.352(9)
V / nm^3	2.044 0(5)	0.640 15(15)
Z	4	2
T / K	193(2)	193(2)
$D_{\text{calc}} / (\text{g} \cdot \text{cm}^{-3})$	1.651	2.107
μ / mm^{-1}	1.128	1.943
$F(000)$	1 036	400
Unique reflections (R_{int})	3 738 (0.046 6)	2 303 (0.025 6)
No. observations ($I > 2.00\sigma(I)$)	3 360	2 105
No. variables	315	206
$R^{\text{[a]}}$, $wR^{\text{[b]}}$	0.046 6, 0.113 4	0.025 6, 0.056 7
GOF $^{\text{[c]}}$	1.140	1.138
$\Delta\rho_{\text{max}} / (\text{e} \cdot \text{nm}^{-3})$	808	755
$\Delta\rho_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	-395	-545

^[a] $R = \sum |F_o| - |F_c| / \sum |F_o|$, ^[b] $wR = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}$, ^[c] $\text{GOF} = \{ \sum w(F_o^2 - F_c^2)^2 / (n-p) \}^{1/2}$, where n is number of reflections and p is total numbers of parameters refined.

2 Results and discussion

2.1 Crystal structure description

Complex **1** crystallizes in the monoclinic space group $P2/c$ and the asymmetric unit contains one $[\text{Cu}_{0.5}(\text{a4-ptz}) \cdot \text{H}_2\text{O}]$ molecule, while complex **2** crystallizes in the triclinic space group $P\bar{1}$ and the asymmetric unit consists of a $[\text{Cd}(\text{a4-ptz}) \cdot (\text{H}_2\text{O})_2\text{Cl}] \cdot 0.5\text{H}_2\text{O}$ molecule. The perspective view of **1** and **2** are shown in Fig.1 and 2, their selected bond lengths and bond angles are

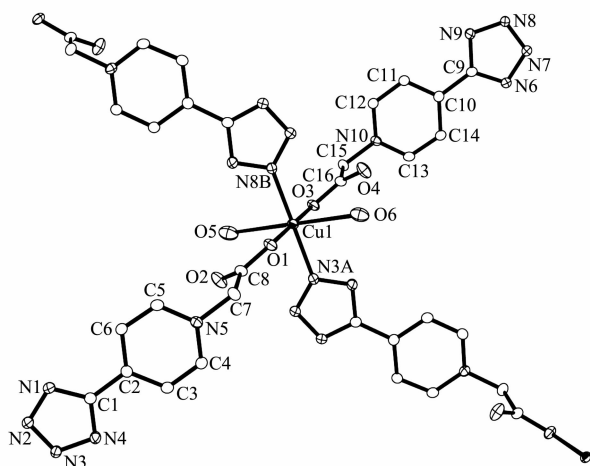


Fig.1 Structure of the complex **1**

listed in Tables 2 and 3, respectively.

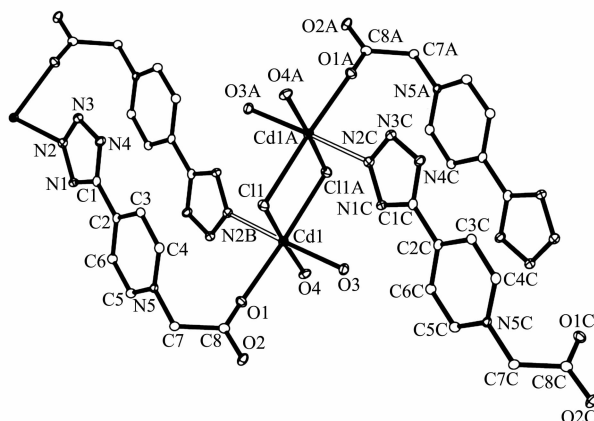


Fig.2 Structure of the complex **2**

The X-ray diffraction single crystal structure analysis revealed that the structures of **1** consist of a 4+2 elongated octahedrally coordinated metal centers, where four a4-ptz units act as bidentate ligands via their carboxylate-O and tetrazolate-N atoms [Cu(1)-O(1) 0.196 9(2) nm; Cu(1)-O(3) 0.197 1(2) nm; Cu(1)-N(8B) 0.200 2(2) nm; Cu(1)-N(3A) 0.200 9(2) nm]. The two axial positions are weakly ligated by two water molecules [Cu(1)-O(5) 0.262 6(4) nm; Cu(1)-O(6) 0.255 8(3)

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$) for **1** and **2**

1					
Cu(1)-O(1)	0.1969(2)	Cu(1)-O(3)	0.1971(2)	Cu(1)-N(8B)	0.2002(2)
Cu(1)-N(3A)	0.2009(2)	Cu(1)-O(6)	0.2558(3)	Cu(1)-O(5)	0.2626(4)
O(1)-Cu(1)-O(3)	179.34(8)	O(1)-Cu(1)-N(8B)	90.42(9)	O(3)-Cu(1)-N(8B)	89.92(9)
O(1)-Cu(1)-N(3A)	90.03(9)	O(3)-Cu(1)-N(3A)	89.63(9)	N(8B)-Cu(1)-N(3A)	179.30(9)
O(1)-Cu(1)-O(6)	85.63(9)	O(3)-Cu(1)-O(6)	94.91(9)	N(8B)-Cu(1)-O(6)	95.73(9)
N(3A)-Cu(1)-O(6)	84.85(9)	O(1)-Cu(1)-O(5)	94.58(9)	O(3)-Cu(1)-O(5)	84.89(9)
N(8B)-Cu(1)-O(5)	84.38(10)	N(3A)-Cu(1)-O(5)	95.05(10)	O(6)-Cu(1)-O(5)	179.77(8)
2					
Cd(1)-O(4)	0.2264(2)	Cd(1)-O(1)	0.2308(2)	Cd(1)-N(2B)	0.2330(3)
N(2C)-Cd(1A)	0.2330(3)	Cd(1)-O(3)	0.2341(2)	Cd(1)-Cl(1)	0.25755(9)
Cd(1A)-Cl(1)	0.26470(10)	Cl(1A)-Cd(1)	0.26470(10)		
O(4)-Cd(1)-O(1)	85.88(9)	O(4)-Cd(1)-N(2B)	89.13(9)	O(1)-Cd(1)-N(2B)	87.70(9)
O(4)-Cd(1)-O(3)	89.68(9)	O(1)-Cd(1)-O(3)	94.48(8)	N(2B)-Cd(1)-O(3)	177.44(9)
O(4)-Cd(1)-Cl(1)	174.17(6)	O(1)-Cd(1)-Cl(1)	93.95(6)	N(2B)-Cd(1)-Cl(1)	96.69(7)
O(3)-Cd(1)-Cl(1)	84.52(7)	O(4)-Cd(1)-Cl(1A)	91.29(7)	O(1)-Cd(1)-Cl(1A)	174.27(6)
N(2B)-Cd(1)-Cl(1A)	87.27(7)	O(3)-Cd(1)-Cl(1A)	90.48(7)	Cl(1)-Cd(1)-Cl(1A)	89.37(3)
Cd(1)-Cl1-Cd(1A)	90.63(3)				

Symmetry codes: (1) A: $1-x, -1-y, -z$; B: $-x, 1-y, -z$; (2) A: $-x, 1-y, -z$; B: $-x, 1-y, 1-z$; C: $-x, 1-y, 1-z$.

Table 3 Selected hydrogen bond lengths (nm) and angles ($^{\circ}$) for **1** and **2**

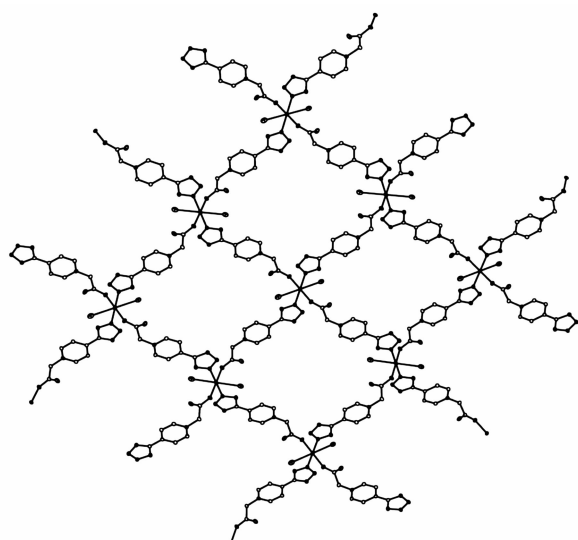
D-H \cdots A	D-H / nm	H \cdots A / nm	D \cdots A / nm	D-H \cdots A / ($^{\circ}$)
1				
O(5)-H(5B) \cdots N(9)#1	0.083(3)	0.215(4)	0.289 0(4)	148(4)
O(6)-H(6A) \cdots O(4)	0.082(4)	0.189(4)	0.267 0(4)	159(4)
O(6)-H(6B) \cdots N(4)#2	0.082(4)	0.224(4)	0.286 2(4)	133(5)
C(3)-H(3) \cdots O(2)#3	0.095	0.252	0.315 8(4)	124
C(4)-H(4) \cdots N(2)#4	0.095	0.241	0.335 0(4)	168
C(5)-H(5) \cdots O(3)#5	0.095	0.242	0.325 3(4)	146
C(7)-H(7A) \cdots N(1)#4	0.099	0.261	0.354 4(4)	157
C(7)-H(7B) \cdots O(5)#5	0.099	0.221	0.316 6(4)	161
C(11)-H(11) \cdots O(4)#6	0.095	0.251	0.313 2(4)	123
C(12)-H(12) \cdots N(7)#7	0.095	0.241	0.334 1(4)	167
C(13)-H(13) \cdots O(1)#8	0.095	0.251	0.327 9(4)	138
C(15)-H(15A) \cdots O(6)#8	0.099	0.221	0.314 6(4)	157
C(15)-H(15B) \cdots N(6)#7	0.099	0.258	0.351 4(4)	158
2				
O(3)-H(3A) \cdots N(1)#1	0.082(2)	0.202(2)	0.283 7(4)	175(3)
O(3)-H(3B) \cdots O(2)#2	0.082(4)	0.193(4)	0.272 8(4)	167(4)
O(4)-H(4A) \cdots O(5)#3	0.082(4)	0.185(4)	0.263 3(4)	174(4)
O(4)-H(4B) \cdots O(2)#4	0.082(4)	0.196(4)	0.277 5(4)	176(7)
O(5)-H(5A) \cdots O(3)#5	0.082(4)	0.281(5)	0.336 3(3)	127(4)
O(5)-H(5B) \cdots Cl(1)	0.081(4)	0.228(3)	0.294 8(4)	140(5)
C(4)-H(4) \cdots O(5)	0.095	0.244	0.308 9(4)	125
C(5)-H(5) \cdots N(3)#6	0.095	0.245	0.333 8(5)	155
C(7)-H(7A) \cdots N(3)#6	0.099	0.255	0.343 4(5)	148
C(7)-H(7A) \cdots N(4)#6	0.099	0.256	0.346 8(5)	152

Symmetry codes: (**1**) (#1) $-x, 1+y, 1/2-z$; (#2) $1-x, -1+y, 1/2-z$; (#3) $1-x, y, 1/2-z$; (#4) $x, -1+y, z$; (#5) $x, 1-y, -1/2+z$; (#6) $-x, y, 1/2-z$; (#7) $x, 1+y, z$; (#8) $x, -y, 1/2+z$; (**2**) (#1) $x, y, -1+z$; (#2) $1-x, -y, -z$; (#3) $x, -1+y, z$; (#4) $-1+x, y, z$; (#5) $1-x, 1-y, -z$; (#6) $1+x, -1+y, z$.

nm]. The O(N)-Cu-N(O) bridging angles are $84.38(10)^{\circ}$ ~ $95.73(9)^{\circ}$. Three axial bond-angles are close to 180° [O(1)-Cu(1)-O(3) $179.34(8)^{\circ}$; O(6)-Cu(1)-O(5) $179.77(8)^{\circ}$ and N(8B)-Cu(1)-N(3A) $179.30(9)^{\circ}$]. Each μ -a4-ptz ligand acting in end-to-end bridging mode coordinated via carboxylate-O and tetrazolate-N to Cu center, forming a 2D square grid network polymeric structure with dimensions of 1.2200×1.2200 nm (Fig.3) extended along the bc plane. Again, there are one intramolecular hydrogen bond [O(6)-H(6A) \cdots O(4) $0.267 0(4)$ nm] and two intermolecular hydrogen bond [O(5)-H(5B) \cdots N(9) $0.289 0(4)$, $-x, 1+y, 1/2-z$; O(6)-H(6B) \cdots N(4) $0.286 2(4)$ nm, $1-x, -1+y, 1/2-z$] within the 2D plane, and a complicated hydrogen bond system (Table 3, #3~#8 for **1**) connects the adjacent 2D planes to form a 3D

network structure, among carboxylate-O, O', tetrazolate-N, ligand water molecules, pyridine-CH and methylene group (Fig.4).

The solid-state structure of **2** (Fig.2) has a slightly distorted octahedral coordination environment. Each Cd(II) ion center is coordinated by three O atoms [Cd(1)-O(1) $0.230 8(2)$; Cd(1)-O(3) $0.234 1(2)$; Cd(1)-O(4) $0.226 4(2)$ nm] from one carboxylate-O of μ -a4-ptz and two aqua ligands, one N atom [Cd-N $0.233 0(3)$ nm] from tetrazolate-N of μ -a4-ptz ligands and two μ -Cl $^{-}$. Each Cl $^{-}$ coordinates to two Cd [Cd(1)-Cl(1) $0.257 55(9)$ nm, Cd(1A)-Cl(1) $0.264 70(10)$ nm] in a bidentate bridged fashion with the Cl-Cd-Cl bridging angle of $89.37(3)^{\circ}$ and Cd-Cl-Cd bridging angle of $90.63(3)^{\circ}$. The adjacent Cd \cdots Cd and Cl \cdots Cl distance is $0.371 3$



Hydrogen atoms are omitted for clarity

Fig. 3 Perspective view of a section of the 2D polymeric plane of complex **1** extended along the *bc* plane

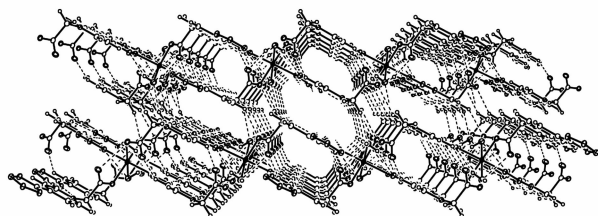


Fig. 4 3D network structure of complex **1** extended along the *a* axis by intermolecular hydrogen bond

nm and 0.367 3 nm, respectively. Hence each a four-membered ring (2Cd 2Cl) is connected by a pair μ -a4-ptz ligands acting in end-to-end bridging mode via their carboxylate-O and tetrazolate-N atoms forming a 1D Z-type polymeric chain of **2** extended along the *a* axis (Fig. 5). There existed π - π interactions (0.347 3 nm) between the pyridyl and tetrazolate groups from neighbouring a4-ptz ligands, which can be regarded as a stabilizing factor for the 1D structure. In addition, two intramolecular hydrogen bond are formed among the lattice water, pyridine-CH and Cl within this chain [O(5)-H(5B)···Cl(1) 0.294 8(4) nm; C(4)-H(4)···O(5) 0.308 9(4) nm], eight intermolecular hydrogen bonds are formed among carboxylate groups, ligand water molecules, tetrazolate-N (1,3,4), pyridine-CH and methylene group (Table 3: #1~#6 for **2**) to link adjacent chains. Therefore complex **2** takes a 3D network structure through these hydrogen bonding interactions (Fig. 6).

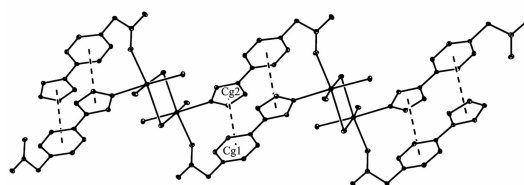


Fig. 5 1D Z-type polymeric chain of complex **2** extended along the *a* axis, the π - π interactions are indicated by dashed lines

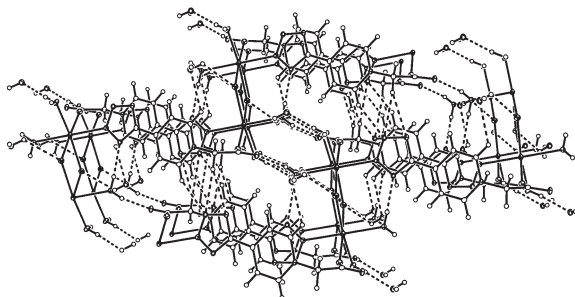


Fig. 6 3D network structure of complex **2** extended along the *a* axis by eight intermolecular hydrogen bond (#1~#6)

The six-membered pyridine ring and the five-membered tetrazolate ring of the a4-ptz ligands are almost planar (the mean deviation from two planes are smaller than 0.000 5 nm) and their mean planes have acute angles of 4.1° and 2.0°, for **1** and **2**, respectively. The pyridine ring-tetrazolate ring distance [C(1)-C(2) bond. length] are 0.146 7(4) nm and 0.146 4(4) nm for **1** and **2**, respectively. N-N and N-C bond distance of tetrazolate ring anion are 0.130 9~0.134 6 nm. These are close to the distances reported for 4-ptz (0.146 3(4), 0.131 9~0.134 5 nm)^[1].

2.2 Thermal analysis

The thermogravimetric analysis (TGA) of the polycrystalline sample **1** showed one continued mass loss of 6.82% in the temperature range of ~35~175 °C (Fig. 7), corresponding to the removal of two H₂O molecules per formula unit (calculated 7.09%). Beyond 200 °C, the decomposition of the network apparently occurred. The final residue of 12.68% (calculated 12.51%) at 750 °C corresponds to the percentage of Cu in **1**. On the other hand, the TGA curve of sample **2** showed also one continued mass loss of 14.20% in the temperature range of ~35~250 °C, corresponds roughly to the loss of the H₂O molecules (calculated 13.30%).

Up to about 280 °C, the decomposition of the one-dimensional polymeric chain of complex **2** apparently occurred.

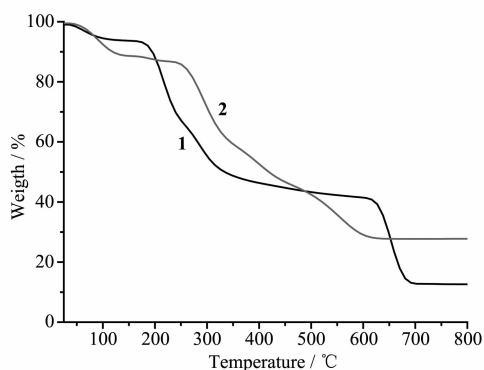


Fig.7 Plot of TGA curves for **1** and **2** under N₂ at a heating rate of 5 °C·min⁻¹

2.3 Luminescent properties

Aromatic organic molecules, all organic polymers, and mixed inorganic-organic hybrid coordination polymers have been investigated for fluorescence properties and for potential applications as fluorescence-emitted materials. Owing to the ability of organic materials to affect wavelength emissions, synthesis of inorganic-organic coordination polymers by the judicious choice of organic spacers and metal centers (such as Zn, Cd, Pb, Ca, B, etc.) can be an efficient method to obtain new types of luminescent materials. The luminescent properties of complex **1**, **2**, and a4-ptz potassium salt ligand were investigated in the solid state. Upon excitation at 345 nm, complex **2** shows a strong emission peak at 373 nm (Fig.8). The emission of complex **2** is neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) in

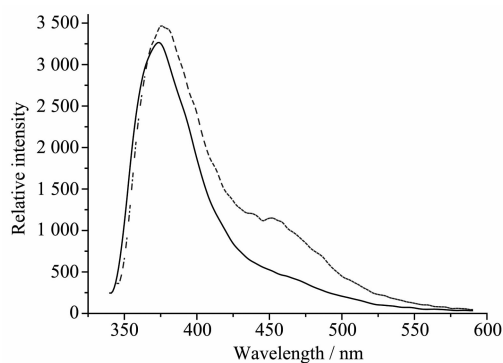


Fig.8 Emission spectra of complex **2** (solid line) and free a4-ptz potassium salt (dashed line) (excited at 345 nm) in the solid state at ambient temperature

nature, and can probably be assigned to intraligand (π - π^*) fluorescent emission since a similar emission ($\lambda_{\text{max}} = 376 \text{ nm}$) is also observed for free a4-ptz potassium salt. The thermal stability of complex **2** up to about 280 °C (TGA measurement) and their insolubility in common solvents make it a good candidate for potential fluorescent materials. The solid state luminescent emission of complex **1** were not found under the same conditions, which means that **1** reveals fluorescence quenching effect.

3 Conclusion

Two coordination polymers [Cu(a4-ptz)₂·(H₂O)₂]_n (**1**) and [Cd(a4-ptz)·(H₂O)₂Cl]·H₂O]_n (**2**) were readily prepared via reactions of Cu(ClO₄)₂·6H₂O and CdCl₂ with a4-ptz as ligand. Both complexes were characterized by elemental analysis, IR spectrometry, thermal analysis, and X-ray crystal structure analysis. The complexes **1** and **2** have distorted octahedrally coordinated metal centers. Each μ -a4-ptz ligand acting in end-to-end bridging mode is coordinated to the metal center via its carboxylate-O and tetrazolate-N atoms, A 2D square grid polymeric structure and a 1D Z-type polymeric chain are constructed for complex **1** and **2**, respectively. Furthermore, **1** and **2** form 3D structure through hydrogen bonding. Complex **2** exhibit strong luminescent properties at room temperature in the solid state.

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