



新型一维 Cd(II)配位聚合物的合成、晶体结构和光致发光性质

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Synthesis, Crystal Structure and Photoluminescence of a New 1D Cd(II) Coordination Polymer

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Abstract: A new 1D chain coordination polymer $[\text{Cd}(\text{dpq})(\text{ox})_{0.5}\text{Cl}]_n$ (**1**) (dpq=dipyrido[3,2-d:2',3'-f]quinoxaline and ox=oxalate) has been hydrothermally synthesized and structurally characterized by elemental analysis, IR and single crystal X-ray diffraction analysis. Compound **1** ($\text{CdClC}_{15}\text{H}_8\text{N}_4\text{O}_2$): monoclinic, space group $P2_1/c$, $a=0.854\ 04(5)$ nm, $b=2.094\ 90(13)$ nm, $c=0.839\ 22(5)$ nm, $Z=4$, $V=1.438(15)$ nm³, $M_r=424.11$, $D_c=1.959$ g·cm⁻³, $F(000)=828.0$, $\mu=1.719$ mm⁻¹, $S=1.028$, the final $R=0.025\ 8$ and $wR=0.057\ 5$. The crystal structure analysis indicates that the cadmium ion is coordinated by two oxygen atoms from a oxalate, two chelating nitrogen atoms from a dpq molecule and two Cl⁻ anions. The adjacent Cd(II) ions are linked by Cl⁻ anions and oxalate ligands in alternate sequence to form a 1D chain coordination polymer and the adjacent chains are further connected by π - π stacking interactions to form a 2D supramolecular network. Moreover, the title compound exhibits blue emission in the solid state at room temperature. CCDC: 680748.

Key words: oxalic acid; crystal structure; cadmium(II) complex; photoluminescence property

0 Introduction

The design and synthesis of extended supramolecular architectures has been a particularly active field of chemical research in recent years due to their intriguing structural topologies and potential applications in host-guest chemistry, luminescence, and magnetism^[1-3]. Weak intermolecular forces, such as π - π

stacking interactions and hydrogen bonds, play an important role in construction of complicated supramolecular arrays through self-assembly of molecules in the field of supramolecular chemistry^[4-7]. Dipyrido[3,2-d:2',3'-f]quinoxaline (dpq) with large conjugated systems for π - π stacking interactions as a terminal ligand has been widely used in construction of various complicated complexes by Chen^[8], Che^[9] and our group^[10-12]. On

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the other hand, many d^{10} metal halide complexes have attracted extensive interest in recent years for the fact that they not only exhibit appealing structures but also possess photoluminescent properties^[13-15]. However, to our knowledge, there is no report on cadmium (II) complex with Cl^- anions and oxalate ligands in alternate sequence in 1D chain coordination polymer. In this work, a new 1D chain coordination polymer $[\text{Cd}(\text{dpq})(\text{ox})_{0.5}\text{Cl}]_n$ (ox=oxalate) has been prepared.

1 Experimental

1.1 General procedures

All chemicals purchased were of reagent grade and used without further purification. dpq was synthesized by the methods of the literature^[16] and characterized by ^1H NMR spectrometer analyses and FTIR spectra. ^1H NMR analyses were performed on a Varian Mercury Vx300 spectrometer analyzer and FTIR spectra were taken on a Magna FTIR 560 spectrometer ($500\sim 4\,000\text{ cm}^{-1}$) with KBr pellets. Fluorescence spectra were performed on an F-4500 fluorescence/phosphorescence spectrophotometer at room temperature and elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C analyzer.

1.2 Synthesis of $[\text{Cd}(\text{dpq})(\text{ox})_{0.5}\text{Cl}]_n$

A mixture of CdCl_2 (0.1 mmol), dpq (0.1 mmol), oxalic acid (0.1 mmol), NaOH (0.2 mmol), H_2O (8 mL), stirred for 20 minutes, was sealed to a Teflon-lined stainless steel autoclave (25 mL) and kept at $170\text{ }^\circ\text{C}$ for 4 days. After the mixture was slowly cooled to room temperature, yellow block crystals suitable for X-ray

diffraction of **1** were obtained in 25% yield (based on Cd). Anal. Calcd. for $\text{CdClC}_{15}\text{H}_8\text{N}_4\text{O}_2$ (%): C, 42.44; H, 1.89; N, 13.20; Found(%): C, 42.48; H, 1.98; N, 13.24. IR (KBr, cm^{-1}): 1 624s, 1 579m, 1 560m, 1 541w, 1 527w, 1 508w, 1 487m, 1 390s, 1 340w, 1 313m, 1 267w, 1 244w, 1 211w, 1 120w, 1 082m, 879w, 823s, 794s, 738s, 704m, 638m.

1.3 X-ray crystallography

A yellow single crystal with dimensions of $0.22\text{ mm}\times 0.36\text{ mm}\times 0.43\text{ mm}$ was selected for X-ray structure analysis. Data were collected on a Bruker Smart Apex II CCD diffractometer with Mo $K\alpha$ ($\lambda=0.071\,073\text{ nm}$) at 293 K ($-10\leq h\leq 9$, $-23\leq k\leq 26$, $-10\leq l\leq 10$) in the range of $1.94^\circ\leq\theta\leq 27.0^\circ$ by using an ω - 2θ scan mode. A total of 8 484 reflections were collected, of which 3 132 were independent ($R_{\text{int}}=0.025\,1$) and 2 514 reflections were used in the succeeding refinement. The structures were solved by the direct method and refined by the Full-matrix least-squares on F^2 using the SHELXL-97 software^[17-18]. All the non-hydrogen atoms were refined anisotropically. All H atoms were positioned geometrically ($\text{C-H}=0.093\text{ nm}$) and refined as riding mode. The final $R=0.025\,8$ and $wR=0.057\,5$ ($w=1/[\sigma^2(F_o^2)+(0.025\,4P)^2+0.028\,0P]$, where $P=(F_o^2+2F_c^2)/3$, $S=1.028$. The highest peak and deepest hole in the final difference Fourier map are 313 and $-301\text{ e}\cdot\text{nm}^{-3}$. The crystal data and structure refinement details for **1** are given in Table 1. Selected bond lengths and angles are listed in Table 2.

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Table 1 Crystal data and structure refinement for **1**

Empirical formula	$\text{CdClC}_{15}\text{H}_8\text{N}_4\text{O}_2$	$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.959
Crystal size / mm	$0.43\times 0.36\times 0.22$	μ / mm^{-1}	1.719
Formula weight	424.11	$F(000)$	828
Crystal system	Monoclinic	θ range / ($^\circ$)	$1.94\sim 27$
Space group	$P2_1/c$	Reflections collected	8 484
a / nm	$0.854\,04(5)$	Unique reflections / R_{int}	3 132 / 0.025 1
b / nm	$2.094\,9(13)$	Data / restraints / parameters	3 132 / 0 / 208
c / nm	$0.839\,22(5)$	Goodness-of-fit on F^2	1.028
$\beta / (^\circ)$	$106.719(10)$	Final R indices [$I>2\sigma(I)$]	$R_1=0.025\,8$, $wR_2=0.054\,2$
V / nm^3	$1.438(15)$	R indices (all data)	$R_1=0.036\,7$, $wR_2=0.057\,5$
Z	4	Largest diff. peak and hole / ($\text{e}\cdot\text{nm}^{-3}$)	313 / -301

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

Cd-N(1)	0.239 3(2)	Cd-Cl	0.263 07(7)	Cd-O(2) ⁱⁱ	0.226 26(17)
Cd-N(2)	0.235 1(2)	Cd-Cl ⁱ	0.255 54(7)	Cd-O(1)	0.228 68(18)
O(2) ⁱⁱ -Cd-O(1)	73.62(6)	O(1)-Cd-N(1)	87.35(7)	N(2)-Cd-Cl ⁱ	101.92(5)
O(2) ⁱⁱ -Cd-N(2)	94.10(7)	N(2)-Cd-N(1)	70.19(7)	N(1)-Cd-Cl ⁱ	92.08(5)
O(1)-Cd-N(2)	152.53(7)	O(2) ⁱⁱ -Cd-Cl ⁱ	162.75(5)	O(2) ⁱⁱ -Cd-Cl	84.78(5)
O(2) ⁱⁱ -Cd-N(1)	99.41(7)	O(1)-Cd-Cl ⁱ	94.27(5)	O(1)-Cd-Cl	107.95(5)
Cd ⁱ -Cl-Cd	92.52(2)	N(1)-Cd-Cl	164.69(5)	N(2)-Cd-Cl	94.92(5)

*Symmetry codes: ⁱ 1-x, 1-y, 1-z; ⁱⁱ 1-x, 1-y, 2-z.

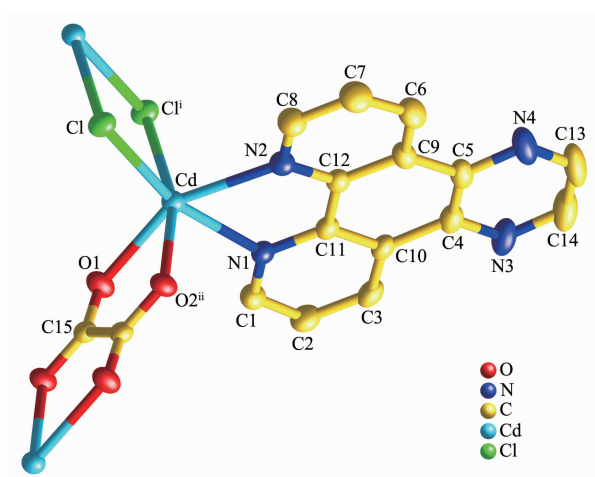
2 Results and discussion

2.1 Description of the structure

Single-crystal X-ray analysis reveals that each Cd(II) in **1** is coordinated by two nitrogen atoms from a chelating dpq ligand, two Cl⁻, and two oxygen atoms from an oxalate to form an octahedron coordination sphere, as shown in Fig.1. The pyrazine nitrogen atoms of dpq ligands do not coordinate to the Cd(II). In the coordination octahedron, the bond angles around Cd(II) vary from 70.19(7) $^{\circ}$ (O-Cd-O) to 164.69(5) $^{\circ}$ (N-Cd-Cl), indicating the octahedron is slightly distorted, which may be induced by the steric effect. The angle of Cd-Cl-Cd is 92.52 (2) $^{\circ}$, which is slightly smaller than that in [Ph₄P][Cd(TP)_{0.5}Cl₂]·H₂O (Cd-Cl-Cd is 93.09(5) $^{\circ}$)^[14]. The Cd-Cl [0.255 54(7) nm for Cd-Clⁱ (1-x, 1-y, 1-z) and 0.263 07 (7) nm for Cd-Cl] are also similar to the complex found in the related cadmium-chlorate^[14]. The bond distances of Cd-N [0.235 1(2) nm for Cd-N(2),

0.239 3(2) nm for Cd-N(1)], Cd-O [0.226 26(17) nm for Cd-O (2)ⁱⁱ (1-x, 1-y, 2-z) and 0.228 68 (18) nm for Cd-O(1)] are similar to those found in the related complexes^[8-12].

In compound **1**, Cd(II) are linked by Cl⁻ and oxalate in alternate sequence to form a 1D chain coordination polymer (Fig.2). The Cd···Cd (1-x, 1-y, 1-z) distance linked by two Cl⁻ is 0.374 75(3) nm, which is slightly longer than that in [Ph₄P][Cd(TP)_{0.5}Cl₂]·H₂O (0.372 nm)^[14]. The Cd···Cd (1-x, 1-y, 2-z) distance linked by oxalate is 0.584 73 (4) nm. The adjacent chains are further linked through intermolecular π - π stacking interactions between pyridyl rings [Cg1 is the center of ring N(1)/C(1)/C(2)/C(3)/C(10)/C(11)] and the central rings of dpq ligands [Cg2 is the center of ring C(4)/C(5)/C(9)/C(10)/C(11)/C(12)] to form



Symmetry codes: ⁱ 1-x, 1-y, 1-z; ⁱⁱ 1-x, 1-y, 2-z

Fig.1 Coordination environment in **1** with 30% probability thermal ellipsoids

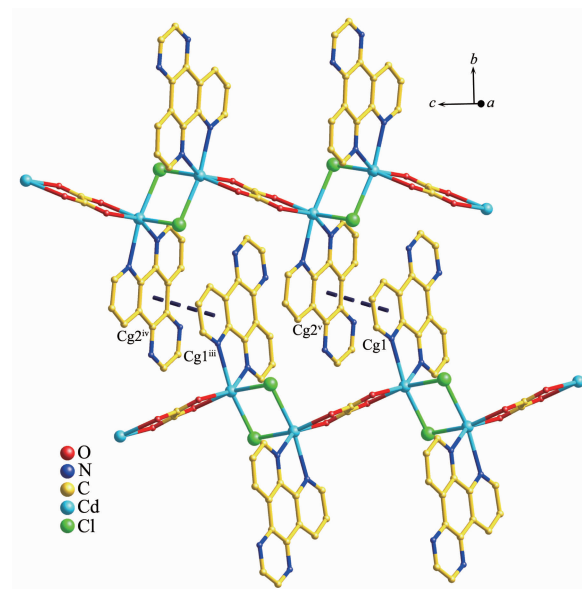


Fig.2 A view of 2D supramolecular network formed by 1D zigzag coordination polymers through intermolecular π - π stacking interactions

a 2D supramolecular layer, as shown in Fig.2. The distance of center to center, Cg1...Cg2, is 0.368 34(16) nm and the perpendicular distance of Cg1...Cg2 from face to face is 0.349 7 nm. The dihedral angle is 7.28°. Up to now, only one 1D chain coordination polymer linked by carboxylate and Cl⁻ in alternate sequence has been prepared by Wu^[14]. In that report, Cd(II) was five coordinated and there were no chelating ligands coordinated to the metal cations, which is structurally different from that of **1**.

2.2 IR spectra and photoluminescence emission

The main features in the IR spectra of the title compound mainly concern the carboxylate groups and the dpq ligands. The absorptions at 1 579 and 1 390 cm⁻¹ are attributed to the asymmetric stretching vibration $\nu_{\text{asym}}(\text{COO}^-)$ and the symmetric $\nu_{\text{sym}}(\text{COO}^-)$, respectively^[12]. The absorptions at 794 and 738 cm⁻¹ are assigned to the dpq ligands^[8-12]. The photoluminescence spectrum of **1** in solid state at room temperature is shown in Fig.3. The free dpq ligand displays two photoluminescence emission peaks at 436 nm (main peak) and 562 nm (shoulder peak) upon excitation at 360 nm^[11-12]. Compound **1** exhibits blue photoluminescence with an emission maximum at *ca.* 451 nm upon excitation at 410 nm. The red-shift main peak compared with that of dpq can be mainly assigned to $\pi^* \rightarrow \pi$ transition of the coordinated dpq ligands. The blue-shift shoulder peak at 530 nm, compared with that of dpq, may be attributed to the chelating of the dpq ligand to the metal ion (LMCT)^[19-20]. Therefore, the title complex may be good candidate for blue photoactive material because it

is stable in air at ambient temperature and insoluble in the common solvents such as water, alcohol, toluene, and acetone.

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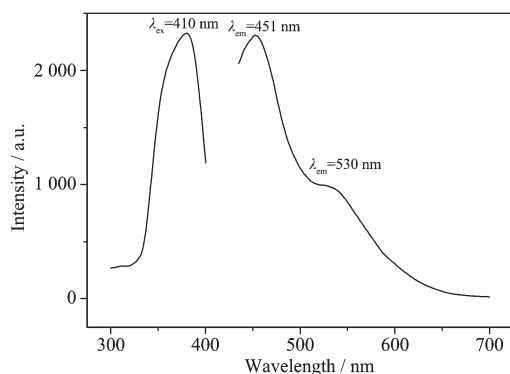


Fig.3 Solid-state emission spectrum of compound **1** at room temperature