

两个基于2-甲基-5-(2-吡啶基)-1,3,4-噁二唑的镉(II) 配位聚合物的合成、晶体结构及表征

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摘要: 以2-甲基-5-(2-吡啶基)-1,3,4-噁二唑(L)为配体合成了2个镉(II)配位聚合物: $[\text{Cd}_2(\text{L})_2(\mu\text{-SCN})_4]_n$ (**1**)和 $[\text{Cd}_2(\text{L})_2(\mu\text{-Cl})_4]_n$ (**2**), 测定了它们的单晶结构,并用紫外光谱、荧光光谱及热重分析进行了表征。配合物**1**和**2**分别属于三斜和单斜晶系,空间群分别为 $P\bar{1}$ 和 $P2_1/n$ 。配合物**1**是通过2个硫氰酸根负离子桥联形成的双桥镉(II)配位聚合物,中心Cd(II)原子具有畸变的八面体构型 $[\text{CdN}_4\text{S}_2]$ 。配合物**2**是通过2个氯离子桥联形成的双桥镉(II)配位聚合物,中心镉(II)原子具有畸变的八面体构型 $[\text{CdCl}_4\text{N}_2]$ 。配合物**1**和**2**都具有荧光性质。

关键词: 1,3,4-噁二唑; 合成; 晶体结构; 镉(II)配合物; 荧光

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Syntheses, Crystal Structures and Characterization of Two Polymeric Cadmium(II) Complexes Based on 2-Methyl-5-(2-pyridyl)-1,3,4-oxadiazole

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Abstract: Two polymeric cadmium(II) complexes derived from 2-methyl-5-(2-pyridyl)-1,3,4-oxadiazole (L), $[\text{Cd}_2(\text{L})_2(\mu\text{-SCN})_4]_n$ (**1**) and $[\text{Cd}_2(\text{L})_2(\mu\text{-Cl})_4]_n$ (**2**), were synthesized and characterized by single crystal X-ray diffraction, UV-visible spectra, fluorescence and thermogravimetric analysis (TGA). Complexes **1** and **2** crystallize in triclinic and monoclinic system, respectively. The space groups of complexes **1** and **2** are $P\bar{1}$ and $P2_1/n$, respectively. Complex **1** is a double-bridged cadmium(II) polymer bridged by two thiocyanate anions, and the central Cd(II) ions have distorted octahedral geometries $[\text{CdN}_4\text{S}_2]$. Complex **2** is a double-bridged cadmium(II) polymer bridged by two chloride anions, and the central cadmium(II) ions have distorted octahedral geometries $[\text{CdCl}_4\text{N}_2]$. Both complexes **1** and **2** have fluorescence properties. CCDC: 1945282, **1**; 1945285, **2**.

Keywords: 1,3,4-oxadiazole; synthesis; crystal structure; cadmium(II) complex; fluorescence

0 Introduction

1,3,4-Oxadiazole and its derivatives are important heterocyclic complexes, which play a significant role in the fields of medicine, pesticides and chemistry due to

their extensive biological activities. Some 1,3,4-oxadiazole derivatives have important physiological activities, such as antibacterial^[1], antiinflammatory^[2], anticonvulsive^[3], hypoglycemic^[4], analgesic^[5], anticancer^[6], anti-depressant^[7], anti-tumor^[8], insecticidal^[9], antioxidant^[10],

antiviral^[11] and anesthetic^[12]. The 1,3,4-oxadiazole ring can be introduced into organic complexes to synthesize special materials, such as electron transporting materials^[13], corrosion inhibitors of metals^[14-16] and stabilizers for polymer^[17].

1,3,4-Oxadiazole ring possesses a planar structure and has aromatic properties. The nitrogen atoms on the 1, 3, 4-oxadiazole ring have strong electron-donating capacities, which can coordinate to transition metal ions and form stable complexes^[18-21]. Some metal complexes of 1,3,4-oxadiazole derivatives exhibit good biological activities^[22-24]. Khler and Rentschler reported^[25] the first 1,3,4-oxadiazole based dinuclear iron(II) complex which shows spin crossover behavior in 2016. Although metal complexes with 1,3,4-oxadiazole derivatives have been reported, few transition metal complexes with pyridine-substituted 1,3,4-oxadiazole complex have been reported so far. To continue our work^[26], we reported here two polymeric cadmium(II) complexes, bis(2-methyl-5-(2-pyridyl)-1,3,4-oxadiazole- κ^2N,N')tetra(μ -thiocyanato- κ^2N,S)biscadmium(II) polymer, $[Cd_2(L)_2(\mu-SCN)_4]_n$ (**1**), and bis(2-methyl-5-(2-pyridyl)-1,3,4-oxadiazole- κ^2N,N')tetra(μ -chloro)biscadmium(II) polymer, $[Cd_2(L)_2(\mu-Cl)_4]_n$ (**2**), where L=2-methyl-5-(2-pyridyl)-1, 3, 4-oxadiazole. Their crystal structures, spectral properties and thermal stabilities were studied.

1 Experimental

1.1 Materials and measurements

2-Methyl-5-(2-pyridyl)-1,3,4-oxadiazole (L) was synthesized according to the literature method^[26]. All other chemicals were analytical grade and used without further purification. The UV-Vis spectra were recorded on UV-3900 UV spectrophotometer. Fluorescence spectral data were obtained on F-2500 fluorescence spectrometer. Single crystal data were collected on a Bruker Smart APEX II CCD single crystal X-ray diffractometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH TG209C thermal analyzer in nitrogen atmosphere at a heating rate of 10 K·min⁻¹.

1.2 Synthesis of complex 1

Ligand L (0.097 g, 0.6 mmol) was dissolved in 20 mL warm distilled water, then 0.093 g Cd(NO₃)₂·4H₂O

(0.3 mmol) and 0.058 g KSCN (0.6 mmol) were added to the warm solution with stirring, and a white precipitate formed. The solution became clear after 14 mL distilled water was added, then it was filtered, and the filtrate was left to stand at room temperature for slowly evaporating. Several days later white crystals were collected (0.084 g, yield: 71.8%). A single crystals suitable for X-ray diffraction was picked. Anal. Calcd. for C₁₀H₇CdN₅OS₂(%): C 30.82, H 1.81, N 17.97; Found (%): C 30.71, H 1.76, N 17.84. UV-Vis (thin acetonitrile, λ /nm): 235.66 ($\epsilon_{\max}=3.084\times10^3$ L·mol⁻¹·cm⁻¹), 276.30 ($\epsilon_{\max}=1.682\times10^4$ L·mol⁻¹·cm⁻¹).

1.3 Synthesis of complex 2

Ligand L (0.161 g, 1 mmol) was dissolved in 30 mL warm acetonitrile, then 0.114 g CdCl₂·2.5H₂O (0.5 mmol) dissolved in 5.0 mL distilled water was added with stirring, and the solution became turbid. The solution became clear after 12 mL distilled water was added, then it was filtered, and the filtrate was left to stand at room temperature for slowly evaporating. Several days later, white crystals were obtained (0.120 g, yield: 69.8%). A single crystal suitable for X-ray diffraction was picked. Anal. Calcd. for C₈H₇CdCl₂N₃O(%): C 27.89, H 2.05, N 12.20; Found(%): C 27.70, H 1.89, N 12.06. UV-Vis (thin acetonitrile, λ /nm): 238.68 ($\epsilon_{\max}=1.970\times10^3$ L·mol⁻¹·cm⁻¹), 275.74 ($\epsilon_{\max}=1.343\times10^3$ L·mol⁻¹·cm⁻¹).

1.4 Crystal structure determination

Selected single crystals of **1** and **2** were mounted on a Bruker SMART APEX II CCD X-ray diffractometer with a detector distance of 5 cm and frame exposure time of 10 s using graphite-monochromated Mo K α ($\lambda=0.071\ 073$ nm) radiation at 293(2) K. The structures were solved by direct methods and refined on F^2 by full-matrix least squares procedures using SHELXTL-2014 software^[27]. All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms on carbon atoms were generated geometrically on the parent atoms, but not refined. Crystal data and structure refinements for complex **1** and **2** are listed in Table 1. Selected bond lengths and angles for **1** and **2** are listed in Table 2.

CCDC: 1945282, **1**; 1945285, **2**.

Table 1 Crystal data and structure refinement for 1 and 2

Complex	1	2
Formula	C ₁₀ H ₇ CdN ₅ OS ₂	C ₈ H ₇ CdCl ₂ N ₃ O
Formula weight	389.73	344.47
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
<i>a</i> / nm	0.839 53(2)	0.720 0(2)
<i>b</i> / nm	0.947 64(2)	0.937 3(3)
<i>c</i> / nm	1.043 47(2)	1.585 5(5)
α / (°)	77.257(2)	
β / (°)	67.457(2)	95.834(3)
γ / (°)	64.440(2)	
<i>V</i> / nm ³	0.690 17(3)	1.064 4(6)
<i>Z</i>	2	4
<i>D_c</i> / (g·cm ⁻³)	1.875	2.150
μ / mm ⁻¹	1.882	2.527
<i>h, k, l</i>	-11~11, -12~12, -13~13	-8~8, -11~11, -19~18
θ range / (°)	2.388~27.998	2.528~25.989
<i>F</i> (000)	380	664
<i>R_{int}</i>	0.019 3	0.042 2
Reflection collected	10 268	7 848
Independent reflection	3 314	2 069
Observed reflection	3 075	1 840
Data, restrain, parameter	3 314, 0, 174	2 069, 0, 138
Goodness-of-fit on <i>F</i> ²	1.057	1.083
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.019 2, 0.044 7	0.023 1, 0.044 5
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.021 3, 0.045 4	0.026 3, 0.045 8
(Δρ) _{max} , (Δρ) _{min} / (e·nm ⁻³)	415, -379	383, -453

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

1					
Cd1-N4 ⁱ	0.230 31(16)	C9-S1	0.165 05(19)	C10-N5	0.114 4(2)
Cd1-N5 ⁱⁱ	0.227 43(17)	Cd1-N3	0.244 83(15)	C10-S2	0.163 76(19)
Cd1-N2	0.239 65(15)	Cd1-S1	0.262 22(5)		
C9-N4	0.114 7(2)	Cd1-S2	0.275 95(5)		
N5 ⁱⁱ -Cd1-N4 ⁱ	91.78(6)	N2-Cd1-N3	69.82(5)	N5 ⁱⁱ -Cd1-S2	96.17(4)
N5 ⁱⁱ -Cd1-N2	156.88(7)	N5 ⁱⁱ -Cd1-S1	100.68(6)	N4 ⁱ -Cd1-S2	170.79(5)
N4 ⁱ -Cd1-N2	84.19(6)	N4 ⁱ -Cd1-S1	96.26(4)	N2-Cd1-S2	86.67(4)
N5 ⁱⁱ -Cd1-N3	87.49(7)	N2-Cd1-S1	102.39(4)	N3-Cd1-S2	85.41(4)
N4 ⁱ -Cd1-N3	90.31(5)	N3-Cd1-S1	169.31(4)	S1-Cd1-S2	86.850(16)
2					
Cd1-N2	0.240 4(2)	Cd1-Cl1	0.253 84(8)	Cd1-Cl1 ⁱ	0.268 51(9)
Cd1-N3	0.245 41(19)	Cd1-Cl2	0.254 39(7)	Cd1-Cl2 ⁱⁱ	0.269 59(9)
N2-Cd1-N3	69.59(7)	Cl1-Cd1-Cl2	105.90(3)	N2-Cd1-Cl2 ⁱⁱ	83.12(5)
N2-Cd1-Cl1	95.15(5)	N2-Cd1-Cl1 ⁱ	93.76(5)	N3-Cd1-Cl2 ⁱⁱ	89.96(5)

Continued Table 2

N3-Cd1-Cl1	160.61(5)	N3-Cd1-Cl1 ⁱ	83.87(5)	Cl1-Cd1-Cl2 ⁱⁱ	100.29(3)
N2-Cd1-Cl2	157.11(5)	Cl1-Cd1-Cl1 ⁱ	85.34(3)	Cl2-Cd1-Cl2 ⁱⁱ	84.34(3)
N3-Cd1-Cl2	91.36(5)	Cl2-Cd1-Cl1 ⁱ	96.76(3)	Cl1i-Cd1-Cl2 ⁱⁱ	173.756(18)

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

2 Results and discussion

2.1 Crystal structural analyses

2.1.1 Crystal structure of **1**

Complex **1** crystallizes in triclinic system with

space group $P\bar{1}$ (Fig.1a). It is a polymeric cadmium(II) complex bridged by two thiocyanate anions (Fig.1c). The distances between the adjacent cadmium ions Cd1ⁱ and Cd1-Cd1ⁱⁱ are 0.579 24(2) and 0.572 98(2)

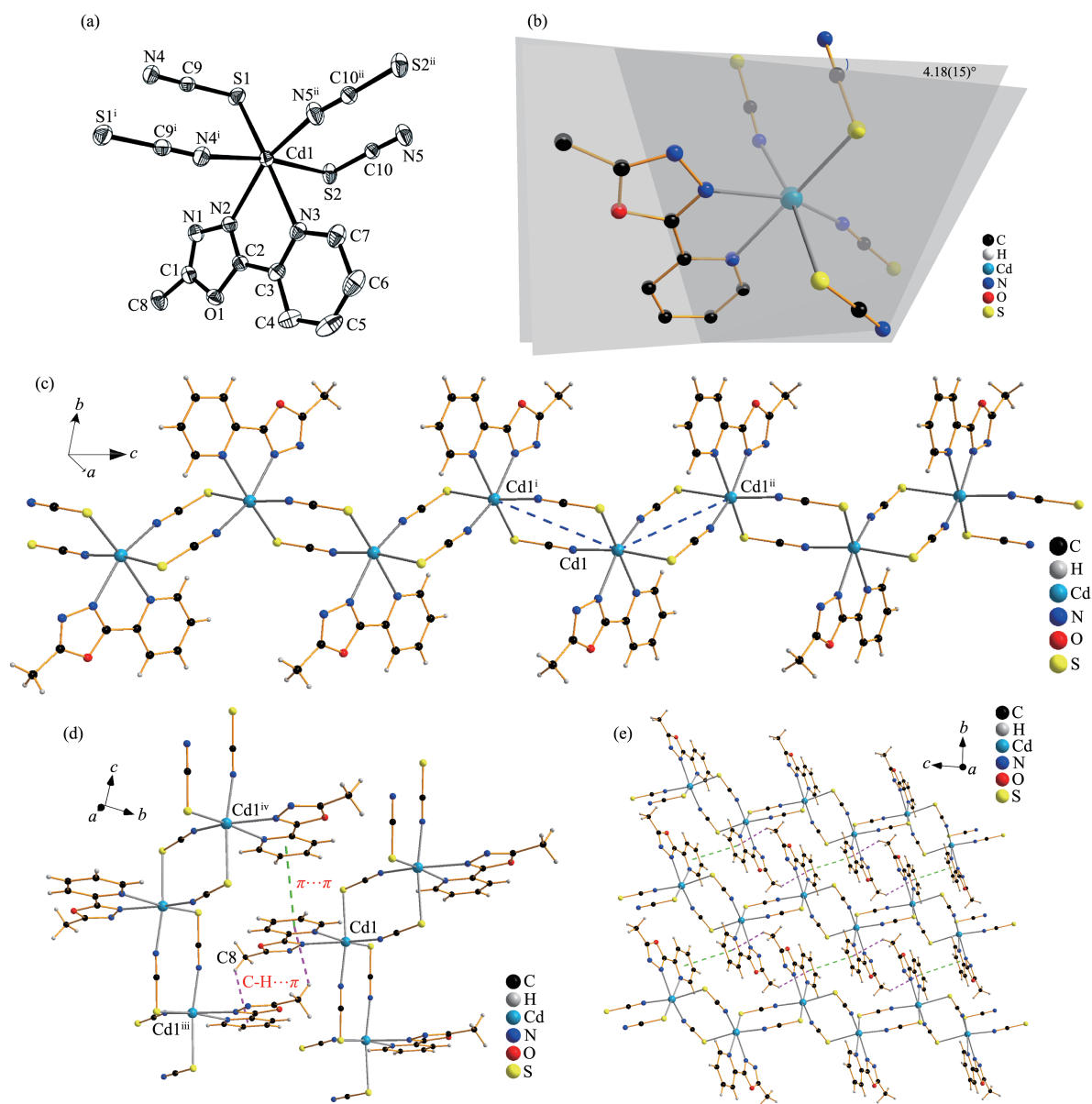


Fig.1 (a) Structure of **1** with ellipsoids at 30% level and the hydrogen atoms omitted for clarity, symmetry codes: ⁱ 1-x, 1-y, -z; ⁱⁱ 1-x, 1-y, 1-z; (b) Diagram of **1** showing the dihedral angle between the oxadiazole and pyridine rings; (c) Segment of polymeric chain of **1**; (d) Non-covalent interactions in **1**, symmetry codes: ⁱⁱⁱ 2-x, -y, -z; ^{iv} 2-x, -y, 1-z; (e) 2D structure of **1** linked through $\pi \cdots \pi$ and C-H $\cdots\pi$ interactions

nm, respectively. In complex **1**, the central Cd1(II) ions are coordinated by four thiocyanate ions through nitrogen or sulfur atoms (N4ⁱ, N5ⁱⁱ, S1 and S2). The central Cd1(II) ions are also coordinated by two nitrogen atoms from L (N2 and N3), and every central Cd1(II) ion possesses a distorted octahedral geometry [CdN₄S₂]. The bond lengths of Cd1-S1, Cd1-S2, Cd1-N4ⁱ and Cd1-N5ⁱⁱ are 0.262 22(5), 0.275 95(5), 0.230 31(16) and 0.227 43(17) nm, respectively. The bond lengths of Cd1-N2 and Cd1-N3 are 0.239 65(15) and 0.244 83(15) nm, respectively.

In complex **1**, the 1,3,4-oxadiazole ring and pyridine ring are coplanar with a dihedral angle of 4.18(15)° (Fig.1b). There is a weak face-to-face $\pi \cdots \pi$ interaction (Cg3ⁱⁱⁱ...Cg3^{iv}) between pyridine rings with a centroid-centroid distance of 0.389 39(12) nm. In addition, the pyridine ring involves an edge-to-face C-H \cdots π interaction (C8-H8B \cdots Cg3ⁱⁱⁱ). The polymeric chains of **1** are linked together through $\pi \cdots \pi$ and C-H \cdots π interactions to form a two-dimensional network structure^[28] (Fig.1d and 1e, Table 3).

Table 3 C-H \cdots π and $\pi \cdots \pi$ interactions for **1**

D-H \cdots A	<i>d</i> (D-H) / nm	<i>d</i> (H \cdots A) / nm	<i>d</i> (D \cdots A) / nm	\angle DHA / (°)
C8-H8B \cdots Cg3 ⁱⁱⁱ	0.096 00	0.288 91	0.356 5(2)	128.36
$\pi \cdots \pi$			<i>d</i> (Cg \cdots Cg) / nm	Dihedral angle / (°)
Cg3 ⁱⁱⁱ ...Cg3 ^{iv}			0.389 39(12)	0.04

Symmetry codes: ⁱⁱⁱ 2-x, -y, -z; ^{iv} 2-x, -y, 1-z; Cg3: N3, C3, C4, C5, C6, C7.

2.1.2 Crystal structure of **2**

Complex **2** crystallizes in monoclinic system with space group *P*2₁/*n*. It is a polymeric cadmium(II) complex bridged by two chloride anions (Fig. 2a, 2b and 2c). The distances between the adjacent cadmium ions Cd1 - Cd1ⁱ and Cd1 - Cd1ⁱⁱ are 0.384 19(10) and 0.388 5(1) nm, respectively. The Cd1(II) ions are coordinated by four bridged chlorine atoms (Cl1, Cl1ⁱ, Cl2 and Cl2ⁱⁱ) and two nitrogen atoms (N2 and N3) from the ligand of L, and the central Cd1(II) ions have distorted octahedral geometries [CdCl₄N₂]. The bond lengths of Cd1-Cl1, Cd1-Cl1ⁱ, Cd1-Cl2 and Cd1-Cl2ⁱⁱ are 0.253 84 (8), 0.268 51(9), 0.254 39(7) and 0.269 59(9) nm, respectively. The bond lengths of Cd1-N2 and Cd1-N3 are 0.240 4(2) and 0.245 41(19) nm, respectively.

In complex **2**, the 1,3,4-oxadiazole ring and pyridine ring are coplanar with a dihedral angle of 5.33(11)° (Fig.2b). One non-classical hydrogen bond of C4-H4 \cdots Cl2ⁱⁱⁱ (Symmetry code: *x*, -1+y, *z*) exists between the C4 and Cl2 atoms (Table 4 and Fig.2d). There is also a weak face-to-face $\pi \cdots \pi$ interaction (Cg4 \cdots Cg5^v) between the 1,3,4-oxadiazole ring and pyridine ring with a centroid - centroid distance of 0.378 18(18) nm. In addition, an edge-to-face C-H \cdots π interaction involving the pyridine ring, C8-H8C \cdots Cg5^{iv} (Symmetry code: 1-x, 1-y, -z). The polymeric chains of **2** are linked together through hydrogen-bonding, $\pi \cdots \pi$ and C-H \cdots π interactions to form a two-dimensional network structure^[28] (Fig.2e).

Table 4 Hydrogen bonds, C-H \cdots π and $\pi \cdots \pi$ interactions for **2**

D-H \cdots A	<i>d</i> (D-H) / nm	<i>d</i> (H \cdots A) / nm	<i>d</i> (D \cdots A) / nm	\angle DHA / (°)
C4-H4 \cdots Cl2 ⁱⁱⁱ	0.093	0.279	0.352 9(2)	138
C8-H8C \cdots Cg5 ^{iv}	0.096	0.261	0.346 5(3)	149
$\pi \cdots \pi$			<i>d</i> (Cg \cdots Cg) / nm	Dihedral angle / (°)
Cg4 \cdots Cg5 ^v			0.378 18(18)	5.34(12)

Symmetry codes: ⁱⁱⁱ *x*, -1+y, *z*; ^{iv} 1-x, 1-y, -z; ^v -x, 1-y, -z; Cg4: O1, C1, N1, N2, C2; Cg5: N3, C3, C4, C5, C6, C7.

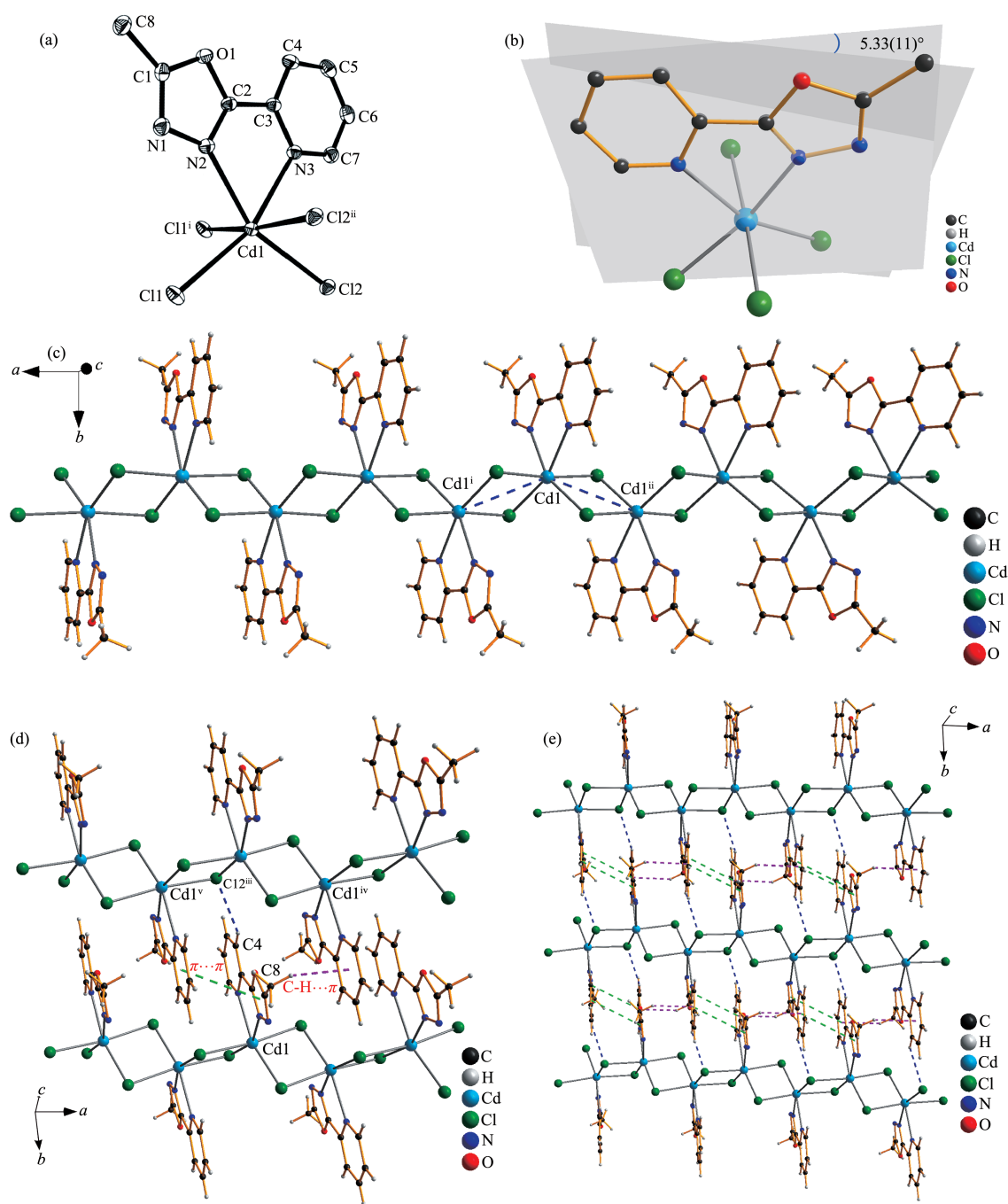


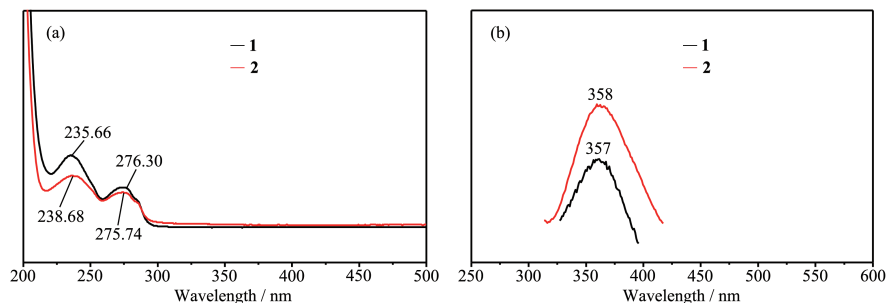
Fig.2 (a) Structure of **2** with ellipsoids at 30% level and the hydrogen atoms are omitted for clarity, symmetry codes: ⁱ 1-x, 2-y, -z; ⁱⁱ -x, 2-y, -z; (b) Diagram of **2** showing the dihedral angle between oxadiazole and pyridine rings; (c) Segment of the polymeric chain; (d) Non-covalent interactions in **2**, symmetry codes: ⁱⁱⁱ x, -1+y, z; ^{iv} 1-x, 1-y, -z; ^v -x, 1-y, -z; (e) 2D structure of **2** linked through H-bonding, $\pi \cdots \pi$ and C-H $\cdots \pi$ interactions

2.2 Spectral characterizations

The UV-Vis spectra of **1** and **2** in acetonitrile solution are shown in Fig. 3a. The maximum absorption peaks of complex **1** appeared at 235.66 nm ($\epsilon_{\max}=3.084 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and 276.30 nm ($\epsilon_{\max}=1.682 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), and those for **2** appeared at 238.68

nm ($\epsilon_{\max}=1.970 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and 275.74 nm ($\epsilon_{\max}=1.343 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). All these are attributed to the π - π^* transition of ligand L.

The fluorescence properties of **1** and **2** were investigated in acetonitrile solution at room temperature (Fig. 3b). The maximum emission wavelength of com-

Fig.3 UV-Vis (a) and fluorescence (b) spectra for **1** and **2** in acetonitrile solution

plexes **1** and **2** were 357 nm ($\lambda_{\text{max,ex}}=274.5$ nm) and 358 nm ($\lambda_{\text{max,ex}}=274$ nm) with the fluorescence quantum yields of 0.22 and 0.54, respectively. All these are attributed to the π - π^* transitions of ligand L. The fluorescence quantum yields of **1** and **2** were calculated using 2-amino-pyridine ($\Phi=0.60$ in H_2SO_4 , $0.05 \text{ mol}\cdot\text{L}^{-1}$) as the standard according to the following equation:

$$\Phi_{\text{sample}} = \Phi_{\text{std}} \left(\frac{I_{\text{sample}}}{I_{\text{std}}} \right) \left(\frac{A_{\text{std}}}{A_{\text{sample}}} \right) \left(\frac{n_{\text{sample}}}{n_{\text{std}}} \right)^2$$

The sample and std represent the sample and reference sample of 2-amino-pyridine, respectively; I represents the fluorescence integral strength; A represents the absorbance; n represents refractive index of the solvent.

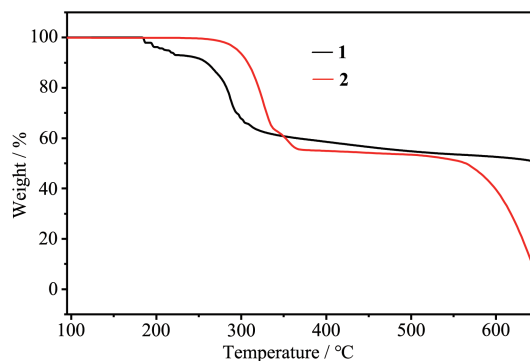
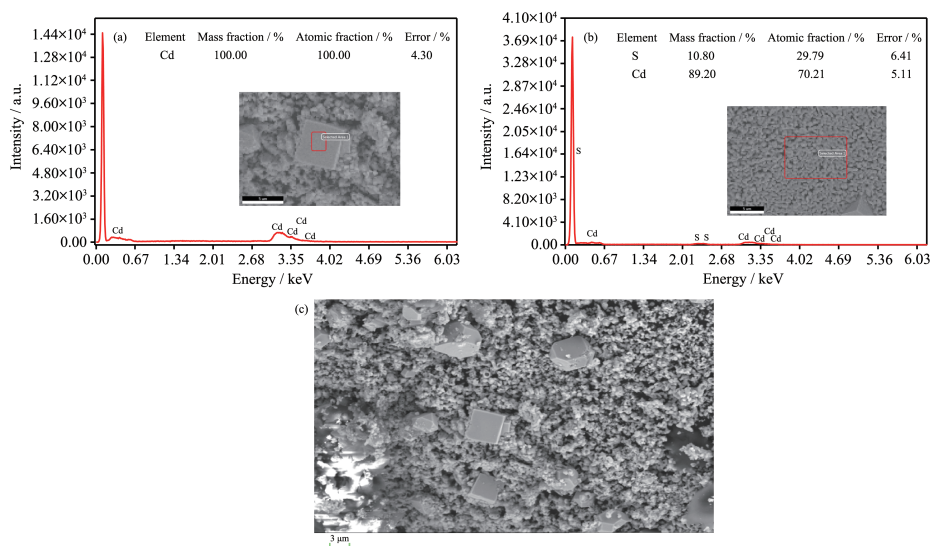
2.3 Thermal gravimetric analyses

Thermalgravimetric analyses (TGA) of complexes **1** and **2** were performed on a NETZSCH TG209C thermal analyzer in nitrogen atmosphere with a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$. The final residues of complex **1** and **2**

were determined by X-ray energy dispersive spectroscopy (EDS) analyses on EDAX ELEMENT.

The TGA curves of complexes **1** and **2** are presented in Fig.4. Complex **1** was stable below 150°C and decomposed sharply between 220 and 320°C . Total weight loss is equal to 49.52% at 650°C . EDS analyses show that the residues are Cd (Fig.5a) and Cd_2S (Fig.5b).

Complex **2** was stable below 270°C and decom-

Fig.4 TGA curves for complexes **1** and **2**Fig.5 Scanning electron microscopy (SEM) images and EDS spectra of the residues of **1**

posed sharply between 280 and 360 °C. When the temperature was 500 °C, the total weight loss was equal to 46.57%. EDS analyses show that the residues at 500 °C are CdCl₂ with a little CdO (Fig.6). When the temperature continued to rise, almost no residue was left and observed at 650 °C (the total weight loss was close to 98.05%).

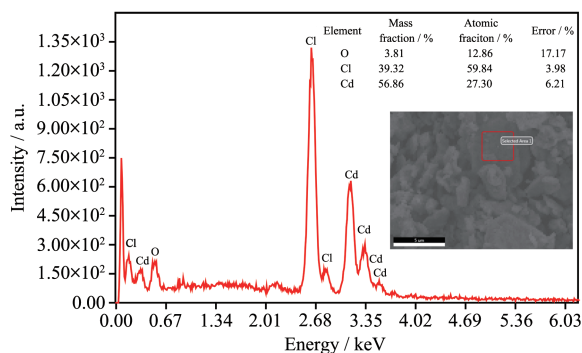


Fig.6 SEM image and EDS spectrum of the residue of **2**

3 Conclusions

Two polymeric cadmium(II) complexes of [Cd₂L₂(μ-SCN)₄]_n (**1**) and [Cd₂L₂(μ-Cl)₄]_n (**2**) were synthesized and characterized. Complex **1** is a double-bridged cadmium(II) complex through two thiocyanate anions, and the central cadmium(II) ions have distorted octahedral geometries [CdN₄S₂]. Complex **2** is a double-bridged cadmium(II) complex through two chloride anions, and the central cadmium(II) ions have distorted octahedral geometries [CdCl₄N₂]. Both complexes of **1** and **2** have fluorescence properties.

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