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2-甲基-5-(2-吡啶基)-1,3,4-噁二唑 Cu(Ⅱ),Cd(Ⅱ)配合物的合成,晶体结构和表征

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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$[Cu_2L_2(\mu\text{-}Cl)_2Cl_2]$ (**1**)和$[CdL_2(NO_3)_2]$ (**2**),测定了 X 射线单晶结构,用红外光谱、紫外光谱、荧光及热重分析进行了表征。配体 L 和配合物 **2** 属于单斜晶系,配合物 **1** 属于三斜晶系。L,**1** 和 **2** 的空间群分别为 $P2_1/c$,$P\bar{1}$ 和 $C2/c$。配合物 **1** 是通过 2 个氯原子(Cl1,Cl1^i)桥联形成的双桥双核 Cu(Ⅱ)配合物,具有畸变四方锥构型$[CuCl_3N_2]$。配合物 **2** 具有畸变八面体构型$[CdN_4O_2]$。

关键词:晶体结构;1,3,4-噁二唑;合成;Cu(Ⅱ)配合物;Cd(Ⅱ)配合物
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Syntheses, Crystal Structures and Spectral Properties of Cu(Ⅱ), Cd(Ⅱ) Complexes with 2-Methyl-5-(2-pyridyl)-1,3,4-oxadiazole

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Abstract: 2-Methyl-5-(2-pyridyl)-1,3,4-oxadiazole(L), $[Cu_2L_2(\mu\text{-}Cl)_2Cl_2]$ (**1**) and $[CdL_2(NO_3)_2]$ (**2**) were synthesized and characterized by single crystal X-ray diffraction, IR, UV-Vis, fluorescence and TGA. Ligand L and complex **2** crystallize in monoclinic system. Complex **1** crystallizes in triclinic system. The space groups of compound L, complexes **1** and **2** are $P2_1/c$, $P\bar{1}$ and $C2/c$, respectively. Complex **1** is a binuclear Cu(Ⅱ) complex bridged by two Cl atoms (Cl1, Cl1^i) and has a distorted tetragonal pyramidal geometry with $[CuCl_3N_2]$. Complex **2** has a distorted octahedral geometry with $[CdN_4O_2]$. CCDC: 1851091, L; 1851090, **1**; 1851089, **2**.

Keywords: crystal structure; 1,3,4-oxadiazole; synthesis; Cu(Ⅱ), Cd(Ⅱ) complexes

0 Introduction

1,3,4-Oxadiazole and its derivatives are important compounds, which have gained considerable attentions in recent years. 1,3,4-Oxadiazole compounds play a significant role in medicine and pesticides. Some 1,3,4-oxadiazole derivatives have important physiological activities[1-5], such as analgesic[6], antibacterial[7], anticancer[8], anti-inflammatory[9] and insecticides[10]. The 1,3,4-oxadiazole ring can be introduced into organic compounds to synthesize special materials, such as electron transporting materials[11], corrosion inhibitors of metals[12-14] and stabilizers for polymer[15].

1,3,4-Oxadiazole rings have π-electron conjugated planar structures. The nitrogen and oxygen atoms on the oxadiazole rings have strong electron donation capacities, which can coordinate to transition metal ions and form stable complexes[16-19]. Some metal

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complexes of 1,3,4-oxadiazole derivatives exhibit good biological activities[20-22]. Khler and Rentschler reported the first 1,3,4-oxadiazole based dinuclear iron (Ⅱ) complex showing spin crossover behavior in 2016[23]. Although some metal complexes with substituted l,3,4-oxadiazole have been reported, the metal complexes with 2-methyl-5-(2-pyridyl)-1,3,4-oxadiazole have not been reported so far. Here we reported two metal complexes $[Cu_2L_2(\mu\text{-}Cl)_2Cl_2]$ (**1**) and $[CdL_2(NO_3)_2]$ (**2**), where L=2-methyl-5-(2-pyridyl)-1,3,4-oxadiazole. The crystal structure, spectral properties and thermal stability are studied.

1 Experimental

1.1 Materials and measurements

All chemicals were analytical grade and used without further purification. The C, H, N elemental analyses were performed on a Perkin-Elmer240. Melting points were determined on an X4 digital microscopic melting point apparatus and uncorrected. The UV-Vis spectra were recorded on an UV-6000PC UV-Vis absorption spectrophotometer. The IR spectra were recorded from 400 to 4 000 cm^{-1} using KBr pellets on an IR prestige-21 Shimadzu infrared spectrophotometer. Fluorescence spectral data were obtained on a F-2700FL spectrophotometer. ^1H NMR spectra were recorded on a Bruker Avance300 spectrometer at ambient temperature in $CDCl_3$ using TMS as an internal standard. 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 STA49F3 thermal analyzer in nitrogen atmosphere at the heating rate of 10 $K\cdot min^{-1}$.

1.2 Synthesis of 2-methyl-5-(2-pyridyl)-1,3,4-oxadiazole (L)[24]

The 2,5-disubstituted 1,3,4-oxadiazole are prepared from diacylhydrazines using *p*-toluenesulfonyl chloride or benzenesulfonyl chloride as dehydrating reagents. *N*-acetyl-*N*′-(2-picolinoyl)hydrazine (5.37 g, 30 mmol), *p*-toluenesulfonyl chloride (8.6 g, 45 mmol) and triethylamine (12.5 mL, 60 mmol) were added to acetonitrile (150 mL). The mixture was stirred for 5 h at room temperature, and then refluxed for 10 h at 90℃. Then the solvent was evaporated. The residue was dissolved in 10% NaOH solution (100 mL) and extracted with $CHCl_3$ (3×80 mL). The organic phase was dried over $MgSO_4$ and concentrated. Recrystallization from ethyl acetate gave a colorless crystals (4.13 g, Yield: 85.6%), m.p. 96~97 ℃. Anal. Calcd. For $C_8H_7N_3O$(%): C 59.62, H 4.38, N 26.07; Found(%): C 59.45, H 4.27, N 25.93. ^1H NMR ($CDCl_3$): δ 2.704 (s, 3H), 7.470~8.792 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 164.729, 164.023, 150.127, 143.462, 137.307, 125.754, 122.869, 11.168. IR (KBr, cm^{-1}): 3 062, 3 000, 2 930, 1 578, 1 553, 1 454, 1 358, 1 254, 1 152, 1 103, 1 047, 1 034, 971, 955, 798, 749, 709. UV-Vis (λ_{max}/nm): 240, 276.

1.3 Synthesis of complex 1

0.170 Grams of $CuCl_2\cdot 2H_2O$ (1 mmol) was added to a warm solution of L (0.322 g, 2 mmol) in 30 mL acetonitrile. The solution turned green and a precipitation formed. The solution gradually became clear after 4 mL of distilled water was added, filtered, and the filtrate was left to stand at room temperature for slowly evaporating. Several days later green crystals were collected (0.236 g, Yield: 48.0%), and a single crystal suitable for X-ray was picked. Anal. Calcd. For $C_{16}H_{14}Cl_4Cu_2N_6O_2$(%): C 32.50, H 2.39, N 14.22; Found(%): C 32.38, H 2.33, N14.07. IR (KBr, cm^{-1}): 3 074, 3 019, 2 965, 1 600, 1 575, 1 560, 1 488, 1 411, 1 248, 1 161, 1 097, 1 057, 1 046, 1 027, 940, 922, 788, 757, 740, 707. UV-Vis (λ_{max}/nm): 240, 275.

1.4 Synthesis of complex 2

0.231 g of $Cd(NO_3)_2\cdot 4H_2O$ (0.75 mmol) was added to a warm solution of L (0.242 g, 1.5 mmol) in 20 mL acetonitrile. A colorless mixture was formed and filtered. The filtrate was left to stand at room temperature for slowly evaporating. Several days later colorless crystals were obtained (0.199 g, Yield: 42.0%). A single crystal suitable for X-ray was picked. Anal. Calcd. for $C_{16}H_{14}CdN_8O_8$(%): C 34.39, H 2.53, N 20.05; Found (%): C 34.27, H 2.44, N 19.87. IR (KBr, cm^{-1}): 3 072, 2 940, 1 583, 1 567, 1 555, 1 492, 1 433, 1 421, 1 398, 1 378, 1 289, 1 160, 1 135, 1 098, 1 047, 1 034, 1 011, 948, 920, 818, 803, 754, 735, 707. UV-Vis (λ/nm): 240, 276.

1.5 Crystal structure determination

Well-shaped single crystals of L, **1** and **2** were picked for X-ray diffraction studies. The data were collected at 296(2) K on a Bruker SMART APEX Ⅱ CCD X-ray diffractometer with a detector distance of 5 cm and frame exposure time of 10s using graphite-monochromated Mo $K\alpha$ (λ=0.071 073 nm) radiation. The structures were solved by direct methods and refined on F^2 by full-matrix least squares procedures using SHELXTL software[25]. All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms on carbon atoms were generated geometrically and allowed to ride on the parent atoms, but not refined. Crystal data and structure refinement for L, **1** and **2** are listed in Table 1. Selected bond lengths and angles for L, **1** and **2** are listed in Table 2. The molecular graphics were prepared by using the DIAMOND 3.1 program.

CCDC: 1851091, L; 1851090, **1**; 1851089, **2**.

Table 1　Crystal data and structure refinement for L, 1 and 2

Compound	L	**1**	**2**
Formula	$C_8H_7N_3O$	$C_8H_7Cl_2CuN_3O$	$C_8H_7Cd_{0.5}N_4O_4$
Formula weight	161.17	295.61	279.38
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$
a / nm	0.786 3(8)	0.826 4(5)	1.090 0(3)
b / nm	1.069 6(11)	0.851 7(5)	1.384 4(4)
c / nm	0.938 9(10)	0.901 1(8)	1.362 3(4)
α / (°)		109.627(8)	
β / (°)	99.344(13)	113.387(8)	99.090(4)
γ / (°)		99.513(6)	
V / nm^3	0.779 1(14)	0.514 6(6)	2.029 9(11)
Z	4	2	8
D_c / (g·cm^{-3})	1.374	1.908	1.828
θ range / (°)	2.63~26.00	2.71~25.50	2.40~25.79
μ / mm^{-1}	0.096	2.613	1.141
F(000)	336	294	1112
R_{int}	0.027 9	0.021 9	0.033 3
Reflection collected	5 584	3 752	7 223
Independent reflection	1 506	1 881	1 933
Observed reflection	1 188	1 771	1 682
Data, restrain, parameter	1 506, 0, 111	1 881, 0, 138	1 933, 2, 151
Goodness-of-fit on F^2	1.050	1.091	1.108
R_1, wR_2 [$I>2\sigma(I)$]	0.038 2, 0.100 4	0.023 0, 0.062 5	0.028 0, 0.060 8
R_1, wR_2 (all data)	0.049 3, 0.107 1	0.024 5, 0.063 1	0.034 6, 0.062 6
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	183, −107	337, −313	361, −320

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

L					
C2-N1	0.128 26(19)	C3-O1	0.135 68(18)	N1-N2	0.140 7(2)
C2-O1	0.136 59(17)	C3-N2	0.128 9(2)		
N1-C2-O1	112.36(14)	C3-O1-C2	102.77(11)	C3-N2-N1	106.30(10)
N2-C3-O1	112.32(11)	C2-N1-N2	106.25(12)		

Continued Table 1

			1		
Cu1-Cl1	0.272 52(13)	Cu1-Cl2	0.223 29(16)	Cu1-N3	0.210 2(3)
Cu1-Cl1^{i}	0.226 86(10)	Cu1-N2	0.202 5(2)		
N2-Cu1-N3	79.18(10)	N3-Cu1-Cl2	166.14(6)	Cl2-Cu1-Cl1	101.89(4)
N2-Cu1-Cl2	93.43(9)	N3-Cu1-Cl1^{i}	91.19(8)	Cl1-Cu1-Cl1^{i}	90.89(5)
N2-Cu1-Cl1^{i}	168.72(6)	N3-Cu1-Cl1	90.50(6)		
N2-Cu1-Cl1	95.00(7)	Cl2-Cu1-Cl1^{i}	94.76(7)		
			2		
Cd1-N2	0.248 9(2)	Cd1-O2	0.245 4(2)	Cd1-O3	0.247 9(2)
Cd1-N3	0.238 9(2)				
N3i-Cd1-N3	113.98(12)	N3-Cd1-N2	68.93(8)	O2^{i}-Cd1-N2^{i}	154.16(7)
N3-Cd1-O2^{i}	104.18(8)	N2^{i}-Cd1-N2	130.77(11)	O2^{i}-Cd1-O2	80.72(10)
N3-Cd1-O2	125.82(7)	O2-Cd1-N2^{i}	74.61(7)		
N3-Cd1-N2^{i}	84.59(8)	O2-Cd1-N2	154.16(8)		

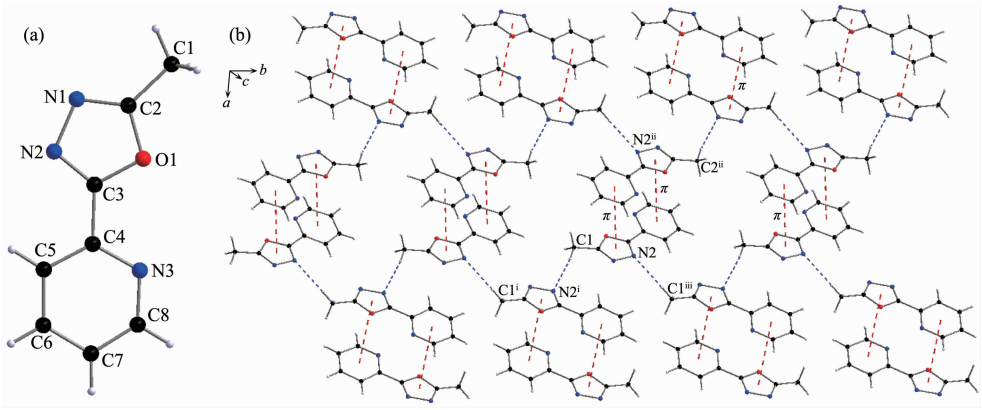
Symmetry codes: ^{i} 2–x, 1–y, 1–z for **1**; ^{i} 2–x, y, 3/2–z for **2**.

2 Results and discussion

2.1 Crystal structural analyses

2.1.1 Crystal structure of L

X-ray diffraction structure analysis reveals that L crystallizes in monoclinic system with space group $P2_1/c$. The oxadiazole ring and pyridyl ring of L are close to coplanar. The dihedral angle between them is 10.66° . In the crystals there is a non-classical hydrogen bond interactions of C1–H1A⋯N2^{i}, and a weak face-to-face $\pi\cdots\pi$ interaction exists between the 1,3,4-oxadiazole ring and pyridyl ring (Table 3 and Fig.1). All these interactions link the L molecules into a two-dimensional network structure.



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

Fig.1 (a) Structure of L with atomic labeling; (b) 2D structure of L linked by hydrogen bond and $\pi\cdots\pi$ interactions

Table 3 Hydrogen bond and $\pi\cdots\pi$ interactions for L

D–H⋯A	d(D-H) / nm	d(H⋯A) / nm	d(D⋯A) / nm	∠DHA/(°)
C1–H1A⋯N2^{i}	0.095 94	0.255 21	0.349 7(4)	168.40
			d(Cg-Cg) / nm	Dihedral angle / (°)
Cg1⋯Cg2^{ii}			3.891(4)	10.66

Cg1: O1, C2, N1, N2, C3; Cg2: N3, C4, C5, C6, C7, C8; Symmetry codes: ^{i} 2–x, –1/2+y, 1/2–z; ^{ii} 1–x, 2–y, –z.

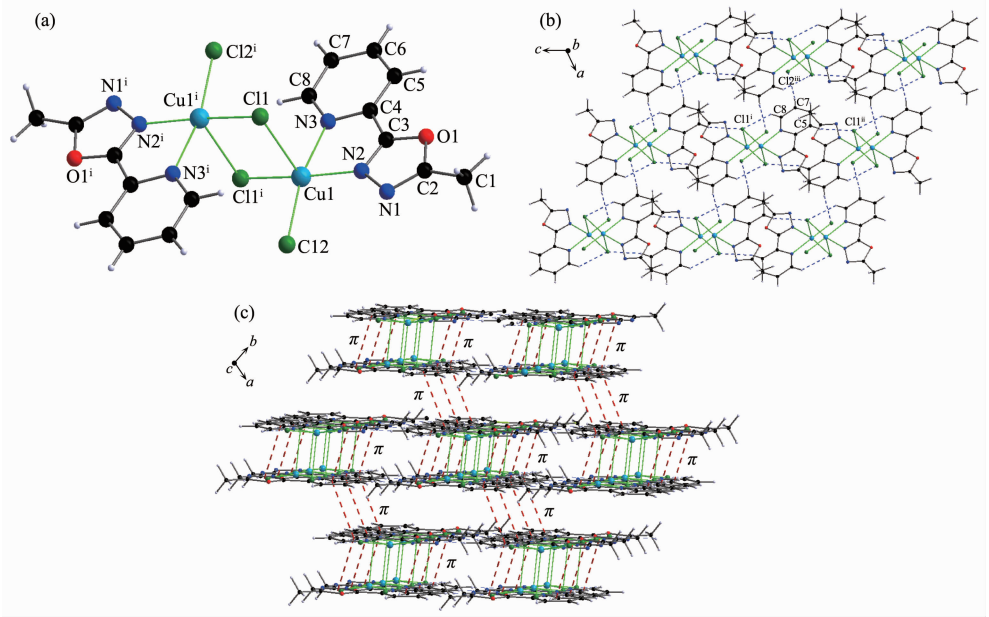
2.1.2　Crystal structure of **1**

Complex **1** is a double-bridged binuclear Cu(Ⅱ) complex (Fig.2) crystallizing in triclinic system with space group $P\bar{1}$. Two copper(Ⅱ) ions are bridged by two Cl atoms (Cl1 and Cl1^{i}). The N2, N3, Cl1^{i} and Cl2 atoms are close to coplanar around the Cu1(Ⅱ) ion. The Cl1 atom sits at the side of the plane making the center Cu1(Ⅱ) ion form a distorted tetragonal geometry [$CuCl_3N_2$]. The bond lengths of Cu1-N2, Cu1-N3, Cu1-Cl1 and Cu1-Cl2 are 0.202 5(2), 0.210 2(3), 0.272 52(13) and 0.223 29(16) nm, respectively. The bond lengths of Cu-N are within the normal ranges observed for distorted tetragonal Cu(Ⅱ) complex or trigonal bipyramid Cu(Ⅱ) complexes[26].

In complex **1**, there are three non-classical intermolecular hydrogen bonding interactions: C5–H5⋯Cl1^{i}, C7–H7⋯Cl2^{iii} and C8–H8⋯Cl1^{ii}. All these intermolecular hydrogen bonding interactions link complex **1** molecules into a two-dimensional network structure (Table 4 and Fig.2). A face-to-face $\pi\cdots\pi$ interaction exists between the 1,3,4-oxadiazole and pyridyl rings with a centroid-centroid distance of 0.387 4(4) nm (Table 4). Another face-to-face $\pi\cdots\pi$ interaction is found between the pyridyl rings with a centroid-centroid distance of 0.362 9(4) nm. Complex **1** molecules are linked into a layered three-dimensional networks through these $\pi\cdots\pi$ interactions (Fig.2).

2.1.3　Crystal structure of **2**

Complex **2** crystallizes in monoclinic system with space group $C2/c$. The center Cd1(Ⅱ) ion are



Symmetry codes: ^{i} 2–x, 1–y, 1–z; ^{ii} 2–x, 1–y, –z; ^{iii} –1+x, –1+y, –1+z

Fig.2　(a) Structure of **1** with atomic labeling; (b) 2D structure of **1** through the hydrogen bond interactions; (c) 3D structure of **1** linked by hydrogen bond and $\pi\cdots\pi$ interactions

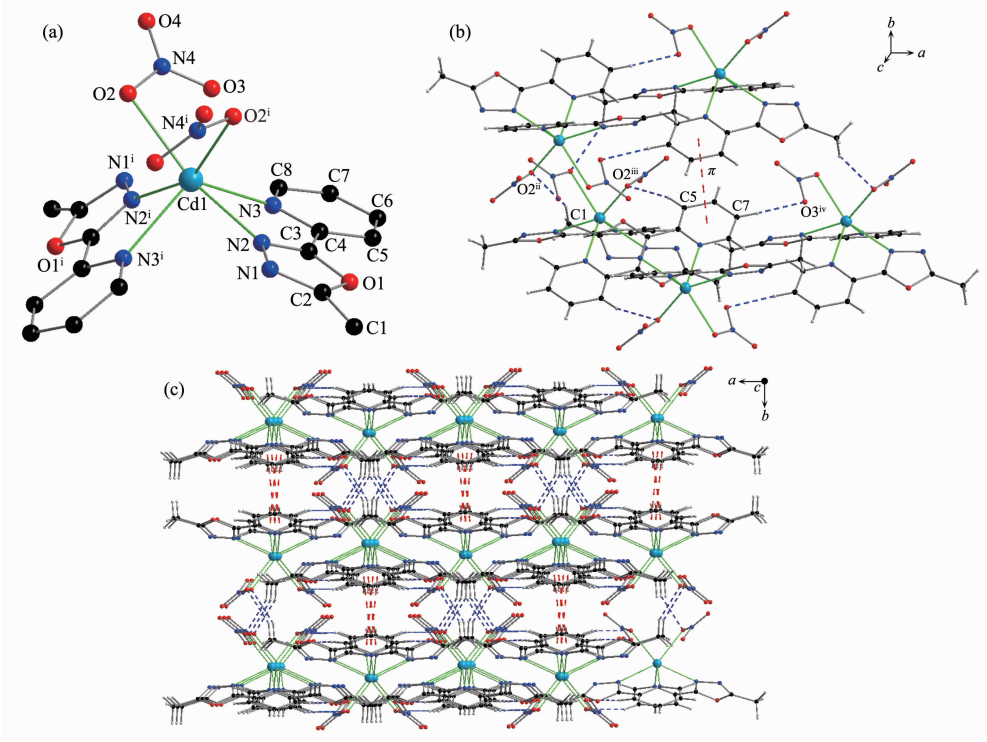
Table 4　Hydrogen bond and $\pi\cdots\pi$ interactions for 1

D–H⋯A	d(D-H) / nm	d(H⋯A) / nm	d(D⋯A) / nm	∠DHA / (°)
C8–H8⋯Cl1^{i}	0.093 05	0.268 37	0.324 2(4)	119.30
C5–H5⋯Cl1^{ii}	0.092 97	0.270 21	0.352 8(4)	148.46
C7–H7⋯Cl2^{iii}	0.092 95	0.273 53	0.365 5(5)	170.21
			d(Cg-Cg) / nm	Dihedral angle / (°)
Cg3⋯Cg4^{ii}			0.3874(4)	2.41
Cg4⋯Cg4^{iv}			0.3629(4)	0.00

Cg3: O1, C2, N1, N2, C3; Cg4: N3, C4, C5, C6, C7, C8; Symmetry codes: ^{i} 2–x, 1–y, 1–z; ^{ii} 2–x, 1–y, –z; ^{iii} –1+x, –1+y, –1+z; ^{iv} 1–x, 1–y, –z.

coordinated by two molecules of L and two nitrate ions. Four coordinated nitrogen atoms (N2, N2^{i}, N3, N3^{i}) and two oxygen atoms (O2, O2^{i}) make the center Cd1(Ⅱ) ion form a distorted octahedral geometry [CdN_4O_2] (Fig.3). The bond lengths of Cd1-N2, Cd1-N3 and Cd1-O2 are 0.248 9(2), 0.238 9(2) and 0.245 4(2), respectively. The Cd-N bond lengths are within the normal ranges observed for the 1,3,4-oxadiazole based Cd(Ⅱ) complex[17].

In complex **2**, there are three non-classical intermolecular hydrogen bonding interactions: C1–H1C⋯O2^{ii}, C5–H5⋯O2^{iii} and C7–H7⋯O3^{iv} (Table 5 and Fig.3). In addition, the pyridyl rings involve a face-to-face $\pi\cdots\pi$ interaction with a centroid-centroid distance of 0.391 01(19) nm. All these interactions link the complex **2** molecules into a three-dimensional network structure.



Symmetry codes: ^{i} 2–x, y, 3/2–z; ^{ii} 3/2–x, 1/2+y, 3/2–z; ^{iii} –1/2+x, 1/2–y, –1/2+z; ^{iv} 5/2–x, 1/2–y, 1–z

Fig.3 (a) Structure of **2** with atomic labeling; (b) Hydrogen bond and $\pi\cdots\pi$ interactions in **2**; (c) 3D structure of **2**

Table 5 Hydrogen bond and $\pi\cdots\pi$ interactions for 2

D–H⋯A	*d*(D-H) / nm	*d*(H⋯A) / nm	*d*(D⋯A) / nm	∠DHA/(°)
C1–H1C⋯O2^{ii}	0.096 05	0.255 58	0.342 2(5)	150.02
C5–H5⋯O2^{iii}	0.093 07	0.241 18	0.330 8(4)	161.60
C7–H7⋯O3^{iv}	0.092 97	0.250 81	0.339 8(4)	160.46
			d(Cg-Cg) / nm	Dihedral angle / (°)
Cg2⋯Cg2^{v}			0.391 1(2)	0.02

Cg2: N3, C4, C5, C6, C7, C8; Symmetry codes: ^{ii} 3/2–x, 1/2+y, 3/2–z; ^{iii} –1/2+x, 1/2–y, –1/2+z; ^{iv} 5/2–x, 1/2–y, 1–z; ^{v} 2–x, 1–y, 1–z.

2.2 Spectral characterization

In the IR spectrum of L (Fig.4), the bands of 1 578, 1 553 and 1 454 cm^{-1} are attributed to the aromatic rings stretching vibrations of pyridine and 1,3,4-oxadiazole. As the nitrogen atoms coordinate to the central Cu(Ⅱ) or Cd(Ⅱ) ions in complexes **1** and **2**, the corresponding absorption bands are blue-shifted. In the spectra of **1** and **2**, absorption bands at 1 600 cm^{-1} (or 1 583 cm^{-1}), 1 575 cm^{-1} (or 1 567 cm^{-1}) and 1 488 cm^{-1} (or 1 492 cm^{-1}) are observed, which are

assigned to the aromatic rings stretching vibrations. This indicates that the Cu1(Ⅱ) and Cd1(Ⅱ) ions are coordinated by nitrogen atoms from oxadiazole and pyridine rings. In complex **2**, the bands of 1 289 cm^{-1} are attributed to NO_3^-.

The UV-Vis spectra of L is given in Fig.5(a). Maximum absorption peak appears at 240 and 276 nm, which are attributed to the π-π^* and n-π^* transitions, respectively. The fluorescence property of L has been examined in ethanol solution at room temperature. The fluorescence spectrum is shown in Fig.5(b), which shows L is fluorescent. Maximum emission peak and excitation wavelength is 403 and 250 nm, respectively, which is attributed to π-π^* electronic transition[27].

In the UV-Vis spectra of **1** and **2**, the maximum absorption peak of **1** appears at 240.04 nm and 275.09 nm, and those for **2** appear at 240.13 nm and 276.05 nm. This is attributed to π-π^* and n-π^* transitions. The fluorescence properties of complexes **1** and **2** have been examined in methanol solution at room temperature, but no fluorescence properties were observed.

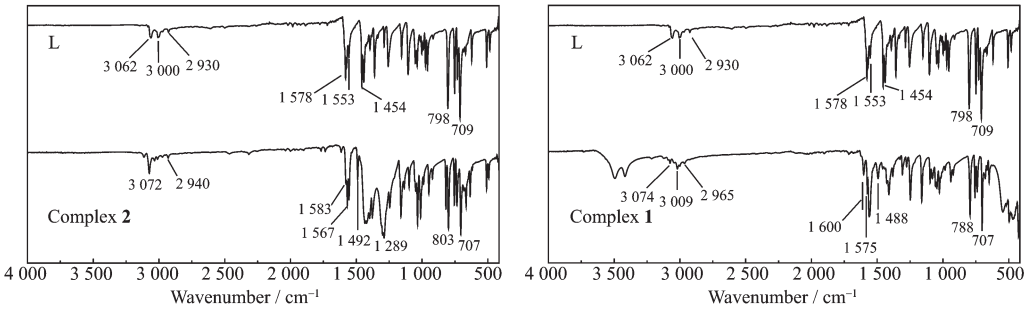


Fig.4　IR spectra of L, **1** and **2**

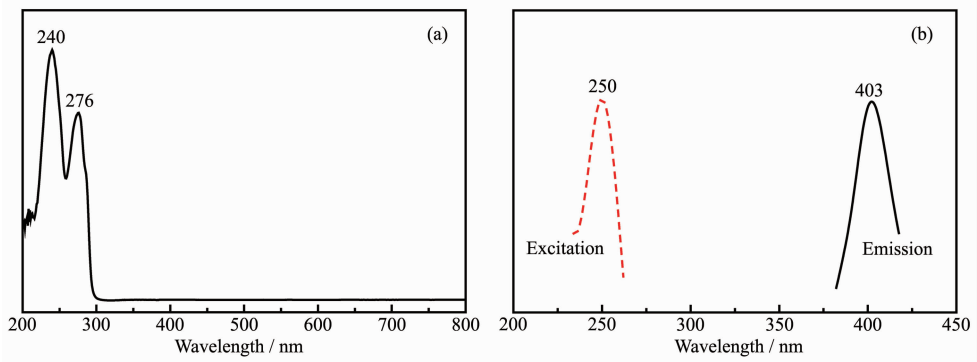


Fig.5　IR, UV-Vis and fluorescence spectra of L

2.3　Thermal gravimetric analysis

Thermal gravimetric analyses (TGA) of complexes **1** and **2** were accomplished in nitrogen atmosphere with the heating rate of 10 K·min^{-1}. The TGA curves of complexes **1** and **2** are presented in Fig.6. When the temperature is below 95 ℃, complex **1** is stable. Complex **1** decomposed gradually with the temperature raised between 95 and 800 ℃. Total weight loss was close to 71.00% at 800 ℃. The final residue is CuO (Calcd. 26.9%). Complex **2** is stable below 150 ℃. Complex **2** decomposed sharply with the temperature raised between 200 and 300 ℃. When the temperature reached to 650 ℃, total weight loss is close to 80.97% (Calcd. 77.02%).

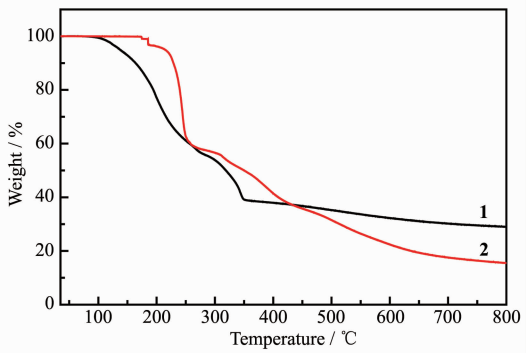


Fig.6　TGA curves for complexes **1** and **2**

3 Conclusions

Ligand L, complexes **1** and **2** were synthesized and characterized. The free ligand L exhibits fluorescence. Complex **1** is a double-bridged binuclear Cu(Ⅱ) complex. Two copper(Ⅱ) ions are bridged by two Cl atoms, and the central copper(Ⅱ) ions have distorted tetragonal geometries $[CuCl_3N_2]$. In complex **2**, the central Cd(Ⅱ) ion have a distorted octahedral geometry $[CdN_4O_2]$.

Supporting information is available at http://www.wjhxxb.cn

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