

2-吡啶肼啶缩 2-乙酰吡啶铜, 锌和镉配合物的晶体结构及荧光性质

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摘要: 合成并通过单晶衍射、元素分析、红外光谱表征了配合物 $[(\text{Cu})(\text{L})(\text{Cl})_2](\mathbf{1})$, $[(\text{Zn})(\text{L})(\text{Cl})_2](\mathbf{2})$ 和 $\{[(\text{Cd})_2(\text{L})(\text{I})_4]\}_n(\mathbf{3})$ 的结构(L 为 2-吡啶肼啶缩 2-乙酰吡啶)。单晶衍射结果表明, 配合物 **1** 和 **2** 同构, 中心金属分别与来自配体的 NNN 电子供体以及 2 个氯离子配位形成一个扭曲的三角双锥结构。在配合物 **3** 中, 相邻的 2 个五配位的 Cd(II) 离子通过 2 个 $\mu_2\text{-I}^-$ 阴离子桥连形成沿 *c* 轴方向的一维链。此外还研究了配合物 **1~3** 的荧光及热性质。

关键词: 吡啶肼啶; 配合物; 荧光; 晶体结构; 热稳定性

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Cu(II), Zn(II) and Cd(II) Complexes with Picolinamide Azine Derived from 2-Acetyl Pyridine and 2-Picolinamide Hydrazone: Crystal Structures and Fluorescence Properties

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Abstract: Three complexes $[(\text{Cu})(\text{L})(\text{Cl})_2](\mathbf{1})$, $[(\text{Zn})(\text{L})(\text{Cl})_2](\mathbf{2})$ and $\{[(\text{Cd})_2(\text{L})(\text{I})_4]\}_n(\mathbf{3})$ (L is derived from 2-acetyl pyridine and picolinamide hydrazone) have been synthesized and characterized by single-crystal X-ray diffraction, elemental analysis and IR spectroscopy. X-ray diffraction analysis results show that complexes **1** and **2** are isostructural. The coordination geometry of the metal ion in each complex is a distorted trigonal bipyramid with three nitrogen atoms from the ligand L and two chloride anions. However, in complex **3**, two adjacent five-coordinated Cd(II) ion are connected by two bridged $\mu_2\text{-I}^-$ anions, resulting in the formation of one-dimensional chain along *c* axis. In addition, the thermal stability and luminescent properties of the complexes are also studied in detail. CCDC: 1412923, **1**; 1412924, **2**; 1412925, **3**.

Key words: picolinamide azine; complex; fluorescence; crystal structure; thermostability

Schiff bases as an important class of ligands play a crucial role in coordination chemistry and have been widely applied in different fields^[1-5]. In recent years, there are many reports about the Schiff bases of acylhydrazone and their metal complexes because of their high biological and pharmaceutical activities^[6-8]. However, the investigations on the metal complexes of Schiff bases derived from picolinamide hydrazone are

relatively few.

It is well known that Zn(II) and Cd(II) ions are closely related to biochemistry, clinical diagnostics as well as environmental pollution^[9-13] due to their fluorescence properties. Therefore, in this paper, Cu(II), Zn(II) and Cd(II) complexes with a Schiff base ligand derived from 2-acetyl pyridine and picolinamide hydrazone have been synthesized and structural

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determined by single-crystal X-ray diffraction. In addition, the thermal stability and luminescent properties of the complexes are also investigated.

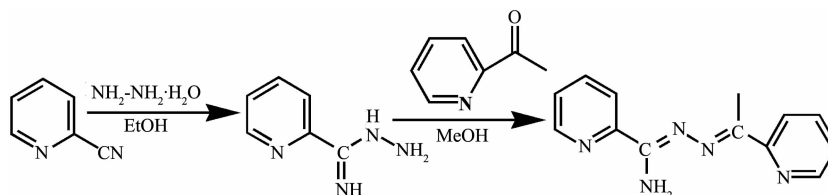
1 Experimental

1.1 Materials and measurements

Solvents and starting materials for synthesis were purchased commercially and used as received. Elemental analysis was carried out on an Elemental Vario EL analyzer. The IR spectra ($\lambda=4\,000\sim400\text{ cm}^{-1}$) were determined by the KBr pressed disc method on a Bruker V70 FTIR spectrophotometer. ^1H NMR spectra of L was acquired with Bruker AV400 NMR instrument in d_6 -DMSO solution with TMS as internal standard. The UV spectra were recorded on a Purkinje General TU-1800 spectrophotometer. Fluorescence spectra were determined on an Edinburgh FLS980 spectrophotometer.

1.2 Preparations of the ligand and complexes 1~3

As shown in scheme 1, the intermediate product picolinamide hydrazone was prepared via the literature method^[14]. The ligand L was produced by condensation of 2-acetyl pyridine (3.63 g, 0.03 mol) and picolinamide hydrazone (4.05 g, 0.03 mol) in anhydrous methanol solution (150 mL) with continuous stirring at room temperature for 3 h. The yellow solid was filtered and washed three times by methanol. Yield: 4.87 g (68%). m.p.: 105~107 °C. Elemental analysis Calcd. for $\text{C}_{13}\text{H}_{13}\text{N}_5$ (%): C: 65.25; H: 5.48; N: 29.27; Found (%): C: 65.27; H: 5.44; N: 29.29. FTIR (cm^{-1}): $\nu(\text{NH}_2)$ 3 316, $\nu(\text{N}=\text{C}-\text{NH}_2)$ 1 613, $\nu(\text{N}=\text{C}-\text{CH}_3)$ 1 561, $\nu(\text{N}=\text{C}-\text{C}-\text{NH}_2)$ pyridine ring) 1 514, $\nu(\text{N}=\text{C}-\text{C}-\text{CH}_3)$ pyridine ring) 1 465, ^1H NMR (400 MHz, d_6 -DMSO) δ : 7.34~7.38(1H), 7.70~7.78 (1H), 8.22~8.24 (2H), 8.40~8.42 (2H), 8.58~8.63 (2H) for pyridine-H, 6.38 (2H, s, $-\text{NH}_2$), 2.63~2.64(3H, s, $-\text{CH}_3$).



Scheme 1 reaction scheme for the synthesis of L

The complexes **1~3** were generated by reaction of the ligand L (5 mmol) with equimolar of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, $\text{ZnCl}_2\cdot 6\text{H}_2\text{O}$ and CdI_2 in methanol solution (10 mL), respectively. Crystals suitable for X-ray diffraction analysis were obtained by evaporating the corresponding reaction solutions at room temperature.

1: green blocks. Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{Cl}_2\text{N}_5\text{Cu}$ (%): C: 41.78; H: 3.51; N: 18.74. Found (%): C: 41.77; H: 3.48; N: 18.74. FTIR (cm^{-1}): $\nu(\text{NH}_2)$ 3 305, $\nu(\text{N}=\text{C}-\text{NH}_2)$ 1 637, $\nu(\text{N}=\text{C}-\text{CH}_3)$ 1 561, $\nu(\text{N}=\text{C}-\text{C}-\text{NH}_2)$ pyridine ring) 1 536, $\nu(\text{N}=\text{C}-\text{C}-\text{CH}_3)$ pyridine ring) 1 476.

2: colorless blocks. Anal. Calcd. For $\text{C}_{13}\text{H}_{13}\text{Cl}_2\text{N}_5\text{Zn}$ (%): C: 41.57; H: 3.49; N: 18.65. Found (%): C: 41.60; H: 3.47; N: 18.67. FTIR (cm^{-1}): $\nu(\text{NH}_2)$ 3 268, $\nu(\text{N}=\text{C}-\text{NH}_2)$ 1 624, $\nu(\text{N}=\text{C}-\text{CH}_3)$ 1 561, $\nu(\text{N}=\text{C}-\text{C}-\text{NH}_2)$ pyridine ring) 1 520, $\nu(\text{N}=\text{C}-\text{C}-\text{CH}_3)$ pyridine ring) 1 479.

3: colorless blocks. Anal. Calcd. For $\text{C}_{13}\text{H}_{13}\text{I}_4\text{N}_5\text{Cd}_2$ (%): C:16.07; H: 1.35; N: 7.21. Found (%): C: 16.13; H: 1.37; N: 7.16. FTIR (cm^{-1}): $\nu(\text{NH}_2)$ 3 302, $\nu(\text{N}=\text{C}-\text{NH}_2)$ 1 636, $\nu(\text{N}=\text{C}-\text{CH}_3)$ 1 584, $\nu(\text{N}=\text{C}-\text{C}-\text{NH}_2)$ pyridine ring) 1 475, $\nu(\text{N}=\text{C}-\text{C}-\text{CH}_3)$ pyridine ring) 1 432.

1.3.1 X-ray crystallography

The X-ray diffraction measurement for complexes **1~3** was performed on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) by using φ - ω scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program^[15]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-97 program^[16]. All non-hydrogen atoms were refined anisotropically. All the H

atoms were positioned geometrically and refined using a riding model. Details of the crystal parameters, data collection and refinements for complexes **1**~**3** are

summarized in Table 1. Selected bond distances and angles of three compounds are listed in Table 2.

CCDC: 1412923, **1**; 1412924, **2**; 1412925, **3**.

Table 1 Crystal data and structure refinement for complexes **1**~**3**

	1	2	3
Empirical formula	C ₁₃ H ₁₃ Cl ₂ N ₅ Cu	C ₁₃ H ₁₃ Cl ₂ N ₅ Zn	C ₁₃ H ₁₃ I ₄ N ₅ Cd ₂
Formula weight	373.72	375.55	971.68
<i>T</i> / K	296(2)	296(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> / nm	0.831 03(15)	0.845 94(7)	2.161 9(2)
<i>b</i> / nm	1.675 8(3)	1.686 78(13)	0.763 56(7)
<i>c</i> / nm	1.061 12(19)	1.070 57(8)	1.365 69(13)
β / (°)	98.148(3)	98.556 0(10)	101.578(2)
<i>V</i> / nm ³	1.462 8(5)	1.510 6(2)	2.208 5(4)
<i>Z</i>	4	4	4
<i>D_c</i> / (g·cm ⁻³)	1.697	1.651	2.922
Absorption coefficient / mm ⁻¹	1.857	1.978	7.523
<i>F</i> (000)	756	760	1 736
Reflections collected	7 272	7 590	5 363
Unique (<i>R_{int}</i>)	2 568(0.041 3)	2 653(0.025 2)	1 937(0.027 6)
Data/restraints / parameters	2 568 / 0 / 190	2 653 / 0 / 190	1 937 / 0 / 111
Goodness-of-fit (GOF) on <i>F</i> ²	1.023	1.021	1.047
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ =0.065 8, <i>wR</i> ₂ =0.189 5	<i>R</i> ₁ =0.041 0, <i>wR</i> ₂ =0.110 7	<i>R</i> ₁ =0.028 7, <i>wR</i> ₂ =0.057 9
<i>R</i> indices (all data)	<i>R</i> ₁ =0.083 2, <i>wR</i> ₂ =0.200 6	<i>R</i> ₁ =0.052 0, <i>wR</i> ₂ =0.117 8	<i>R</i> ₁ =0.038 1, <i>wR</i> ₂ =0.061 0
Largest peak and hole / (e ⁻ ·nm ⁻³)	831 and -573	840 and -318	745 and -755

Table 2 Selected bond lengths (nm) and angles (°) in complexes **1**~**3**

1					
Cu1-N3	0.197 0(6)	Cu1-N1	0.199 2(6)	Cu1-N5	0.201 8(6)
Cu1-Cl2	0.234 2(2)	Cu1-Cl1	0.245 9(2)		
Cl2-Cu1-Cl1	107.64(8)	N3-Cu1-N1	91.2(3)	N3-Cu1-N5	79.4(2)
N1-Cu1-N5	170.5(2)	N3-Cu1-Cl2	134.1(2)	N1-Cu1-Cl2	94.99(18)
N5-Cu1-Cl2	91.36(19)	N3-Cu1-Cl1	117.2(2)	N1-Cu1-Cl1	94.14(18)
N5-Cu1-Cl1	90.59(18)				
2					
Zn1-N3	0.205 8(3)	Zn1-N1	0.214 3(3)	Zn1-N5	0.216 9(4)
Zn1-Cl2	0.229 58(12)	Zn1-Cl1	0.231 01(12)		
N3-Zn1-N1	85.99(14)	N3-Zn1-N5	75.97(14)	N1-Zn1-N5	161.63(13)
N3-Zn1-Cl2	127.43(11)	N1-Zn1-Cl2	95.76(10)	N5-Zn1-Cl2	92.55(10)

Continued Table 2

N3-Zn1-Cl1	116.86(11)	N1-Zn1-Cl1	96.96(10)	N5-Zn1-Cl1	94.30(10)
Cl2-Zn1-Cl1	115.04(5)				
3					
Cd1-N2	0.232 6(5)	Cd1-N1	0.238 3(5)	Cd1-I2	0.273 96(7)
Cd1-I1	0.282 58(7)	Cd1-I1 ⁱⁱ	0.300 89(7)		
I1-Cd1-I1 ⁱⁱ	90.176(18)	N2-Cd1-I2	128.55(12)	N1-Cd1-I2	93.27(13)
N2-Cd1-N1	68.71(18)	N1-Cd1-I1	95.83(13)	I2-Cd1-I1	121.20(2)
N2-Cd1-I1	108.69(12)	N1-Cd1-I1 ⁱⁱ	159.83(13)	I2-Cd1-I1 ⁱⁱ	100.05(2)
N2-Cd1-I1 ⁱⁱ	91.12(12)				

Symmetry code: ⁱⁱ $-x, -y+1, -z+1$

2 Results and discussion

2.1 Crystal structures description

Complex **1** and **2** are isostructural, thus complex **1** is discussed for example. As shown in Fig.1a, the

central Cu(II) ion in complex **1** is coordinated to one ligand L with NNN donor sets and two additional chloride anions. The maximal two angles between the coordinated atoms and Cu(II) ion are $170.5(2)^\circ$ and $134.1(2)^\circ$, respectively. According to the Addison rule^[17],

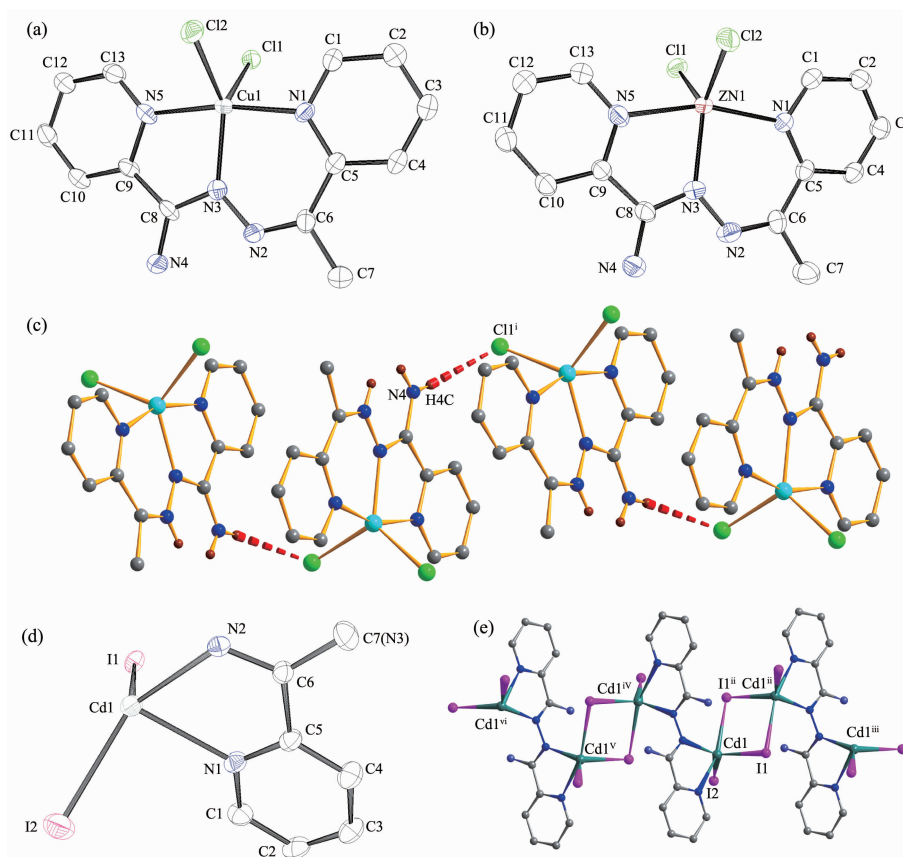
Symmetry codes: ⁱ $x-1/2, -y+1/2, z-1/2$; ⁱⁱ $-x, 1-y, 1-z$; ⁱⁱⁱ $x, 1-y, 0.5+z$; ^{iv} $-x, y, 0.5-z$; ^v $x, 1-y, -0.5+z$; ^{vi} $-x, 1-y, -z$

Fig.1 ORTEP drawing of **1** (a), **2** (b) with 30% thermal ellipsoids; (c) Chain-like structure formed by hydrogen bonds (shown in dashed line) in complexes **1** (H atoms of C-H bonds are omitted for clarity); (d) ORTEP drawing of the asymmetric unit of complex **3** with 30% thermal ellipsoids; (e) chain-like structure along *c* axis in complex **3**

the geometric index τ is 0.606 7, indicating that the coordination geometry of Cu(II) ion in **1** is best described as a distorted trigonal bipyramid rather than tetragonal pyramid. The equatorial plane of the trigonal bipyramid is made up of Cl1, Cl2 and N3 atoms, N1 and N5 atoms occupy the axial positions in trans manner. In the crystal of **1**, intermolecular N-H \cdots Cl hydrogen bonds (N4-H4C \cdots Cl1ⁱ, with D \cdots A distance being 0.324 1(7) nm, D-H \cdots A angle being 154.9°, Symmetry code ⁱ $x-1/2, -y+1/2, z-1/2$) link the complexes into chain-like structure (Fig.1c). Similar hydrogen bonds are observed in the crystal of **2**, with D \cdots A distance being 0.333 7(4) nm, D-H \cdots A angle being 154.3°.

As shown in Fig.1d, the asymmetric unit of complex **3** contains a half of the molecule with a pseudosymmetry twofold rotational axis. The distances of C6-C7(N3) (0.140 1(8) nm) are intermediate between C-C and C-N single bond^[2-3], indicating that C7 and N3 occupy the same position and the occupy value of each atom is 0.5. Each Cd(II) ion is coordinated with two nitrogen atoms provided by the ligand L and three iodide anions. The maximal two angles between the coordinated atoms and Cd(II) ion are 159.83(13)° and 128.55(12)°, respectively. The coordination geometry of five-coordinated Cd(II) ion is best described as a distorted trigonal bipyramid, since the geometric index τ is 0.521 3^[17]. Moreover, two adjacent trigonal bipyramid units are connected by two bridged μ_2 -I⁻ anions, resulting in the formation of one-dimensional chain along c axis (Fig.1e). It should be noted that the imine C=N double bond adopts Z configuration in complexes **1** and **2**, while E configuration in the complex **3**.

2.2 IR spectra

The IR spectra for the complexes are more or less similar due to the similarity in coordination modes of the ligand with the metal centre. The (N=C-NH₂) characteristic stretching vibration absorption of the free ligand is at 1 611 cm⁻¹, it shifts to 1 637, 1624 and 1 636 cm⁻¹ in complexes **1~3**, respectively, showing the N=C-NH₂ bonds participate in the coordination in each complex. Vibration of ν (N=C-CH₃) in free ligand L, complexes **1** and **2** is at about

1 561 cm⁻¹, while it shifts to 1 584 cm⁻¹ in complex **3**, indicating that the N=C-CH₃ bonds in complex **3** take part in the coordination. The ν (N=C) of two pyridine rings in the free ligand L are at 1 514 and 1 465 cm⁻¹. However, the peaks appear at 1 536 and 1 476, 1 520 and 1 479, 1 475 and 1 432 cm⁻¹ in complexes **1~3**, respectively, inferring that the nitrogen atoms of both pyridine rings in the ligand L coordinate with the metal centre. The ν (N-H) vibrations of the free ligand L and complexes **1~3** are at 3 316, 3 305, 3 268 and 3 302 cm⁻¹, respectively.

2.3 Thermal decomposition process of compounds 1~3

For detecting the thermal stabilities of complexes **1~3**, thermal gravimetric (TG) analyses were carried out from the room temperature to 800 °C with the linear heating rate of 10 °C · min⁻¹ under argon atmosphere (Fig.2).

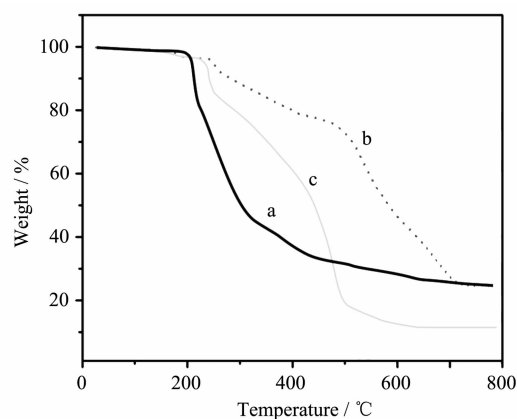


Fig.2 TG curves for **1**(a), **2**(b) and **3**(c)

The thermal decomposition processes of three complexes are quite similar. All of them are thermally stable up to about 200 °C and prove no solvent molecules in the complexes. Only one main process of weight loss below 800 °C could be considered as the decomposition of the organic ligand and two haloride anions. The remainders of the complexes **1~3** might be the metal oxides because the residue weights (23.79%, 23.67% and 14.34%) are agreement with the calculated values of 21.3%, 21.67% and 13.21%, respectively.

2.4 UV spectra

The UV spectra of L and complexes **1~3** in

CH₃OH solution (concentration: $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) were measured at room temperature (Fig.3). The spectra of L features two main bands located around 205 ($\epsilon = 18\,154 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and 327 nm ($\epsilon = 17\,744 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), respectively. The bands could be assigned to characteristic- h^* transitions centered on pyridine rings and imine unit, respectively^[18]. Similar bands are observed at 220 ($\epsilon = 28\,443 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and 322 nm ($\epsilon = 13\,123 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) in the complex **3**. However, there are three bands in both spectra of **1** (222 ($\epsilon = 11\,960 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 262 ($\epsilon = 10\,076 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 355 nm ($\epsilon = 2\,408 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)) and **2** (239 ($\epsilon = 14\,385 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 274 ($\epsilon = 12\,484 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 334 nm ($\epsilon = 14\,795 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)). This phenomenon is probably due to the different configuration of C=N bond in the complexes **1** and **2** (Z configuration) from that in the free ligand L and complex **3** (E configuration).

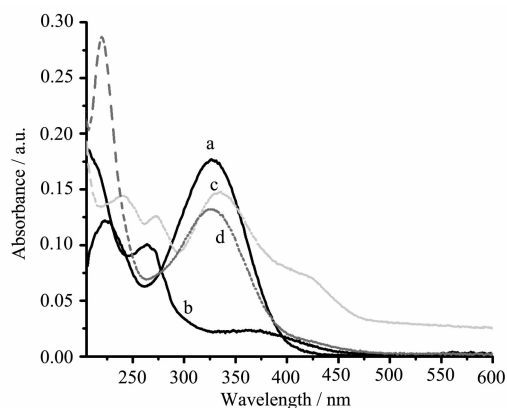


Fig.3 UV spectra of the ligand L (a), **1** (b), **2** (c) and **3** (d) in CH₃OH solution at room temperature

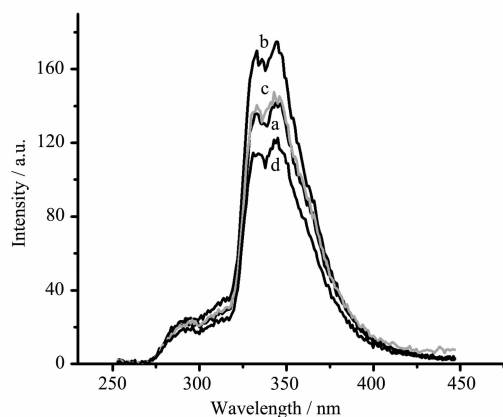


Fig.4 Fluorescence emission spectra of the ligand L (a), **1** (b), **2** (c) and **3** (d) in CH₃OH solution at room temperature

2.4 Fluorescence spectra

The fluorescence spectra of the ligand L and complexes **1~3** have been studied in CH₃OH solution (concentration: $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) at room temperature. The results show that the emission spectra of the three complexes exhibit two peaks at 332 and 344 nm when excited at 233 nm, which is similar as that of the ligand (Fig.4). It is obvious that complexes **1~3** are photoluminescent with the emission peaks corresponding to $\pi \rightarrow \pi^*$ transition of metal-perturbed intraligand^[19].

References:

- [1] HUANG Chao (黄超), WU Juan (吴娟), CHEN Dong-Mei (陈冬梅), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2015**, *31*:109-113
- [2] CHEN Yan-Min (陈延民), XIE Qing-Fan (解庆范), LIU Jin-Hua (刘金花), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2015**, *31*:74-80
- [3] CHEN Yan-Min (陈延民), CHU Zhao-Hua (储召华), HAO Gui-Xia (郝桂霞), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2015**, *31*:317-322
- [4] CHEN Xiao-Hua (陈小华), WU Qiong-Jie (吴琼洁), LÜ Wei (吕玮), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2013**, *29*:1521-1526
- [5] LI Shi-Xiong (李石雄), LIAO Bei-Ling (廖蓓玲), LUO Pei (罗培), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2015**, *31*:291-296
- [6] Yang Z Y, Yang R D, Li F S, et al. *Polyhedron*, **2000**, *19*: 2599-2604
- [7] Yang Z Y, Wang B D, Li Y H, *J. Organomet. Chem.*, **2006**, *691*:4159-4166
- [8] Wang Y, Yang Z Y. *Transition Met. Chem.*, **2005**, *30*:902-906
- [9] Zhou X Y, Li P X, Shi Z H, et al. *Inorg. Chem.*, **2012**, *51*: 9226-9231
- [10] Wu Z K, Chen Q Q, Yang G Q, et al. *Sens. Actuators B*, **2004**, *99*:511-515
- [11] Zhang G Q, Yang G Q, Zhu L N, et al. *Sens. Actuators B*, **2006**, *114*:995-1000
- [12] Sali S, Grabchev I, Chovelon J M, et al. *Spectrochim. Acta A*, **2006**, *65*:591-597
- [13] Kulatililke C P, Silva S A, Eliav Y. *Polyhedron*, **2006**, *25*: 2593-2596
- [14] Xu Z Q, Laurence K, Thompson, et al. *Inorg. Chem.*, **1997**, *36*:3985-3995

- [15]Sheldrick G M. *SADABS*, University of Göttingen, Germany, **1996**.
- [16]Sheldrick G M. *SHELX-97, Program for the Solution and the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.
- [17]Addison A W, Rao T N. *J. Chem. Soc. Dalton Trans.*, **1984**,**5**:1349-1356
- [18]Song X Q, Zang Z P, Liu W S, et al. *J. Solid State Chem.*, **2009**,**182**:841-848
- [19]ZHUO Xin (卓馨), PAN Zhao-Rui (潘兆瑞), WANG Zuo-Wei (王作为), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2006**,**22**:1847-1851