

## 基于 3-乙基-2-乙酰吡嗪缩胍基甲酸甲酯的铜和锌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 X 射线衍射、元素分析及红外光谱表征了配合物  $[\text{Cu}(\text{HL})\text{Cl}_2] \cdot \text{H}_2\text{O}$  (**1**) 和  $[\text{ZnL}_2]$  (**2**) 的结构 (HL 为 3-乙基-2-乙酰吡嗪缩胍基甲酸甲酯)。单晶衍射结果表明, 在配合物 **1** 中,  $\text{Cu}(\text{II})$  离子拥有四方锥配位构型, 与一个中性配体 HL 和 2 个氯离子配位。配合物 **2** 中,  $\text{Zn}(\text{II})$  离子与来自 2 个阴离子配体 L 的  $\text{N}_2\text{O}$  电子供体配位, 配位构型为扭曲的八面体。此外还研究了配合物 **1** 和 **2** 的固体荧光性质。

**关键词:** 胍基甲酸甲酯; 吡嗪; 荧光; 晶体结构

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### Cu(II) and Zn(II) Complexes Based on Methyl (1-(3-Ethylpyrazin-2-yl)ethylidene)carbazate: Crystal Structures and Fluorescence Properties

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**Abstract:** Two complexes, namely  $[\text{Cu}(\text{HL})\text{Cl}_2] \cdot \text{H}_2\text{O}$  (**1**) and  $[\text{ZnL}_2]$  (**2**) (HL=methyl (1-(3-ethylpyrazin-2-yl)ethylidene)carbazate) have been synthesized and characterized by single-crystal X-ray diffraction, elemental analysis and IR spectroscopy. X-ray diffraction analysis results show that in complex **1**, the  $\text{Cu}(\text{II})$  ion with a distorted square pyramid coordination geometry is coordinated with one neutral ligand HL and two chloride anions. However, the central  $\text{Zn}(\text{II})$  ion in complex **2** is surrounded by two independent anionic ligands with  $\text{N}_2\text{O}$  donor set, thus possesses a distorted octahedral coordination geometry. The luminescent properties of the complexes were also studied in detail. CCDC: 1544291,  $(\text{H}_2\text{L})\text{NO}_3$ ; 1544292, **1**; 1544293, **2**.

**Keywords:** methyl hydrazinocarboxylate; pyrazine; fluorescence; crystal structure

Transition metal complexes have become of increasing importance in synthetic chemistry, coordination chemistry, homogenous catalysis and biological chemistry<sup>[1]</sup>. Among the various types of ligands, Schiff bases,

including acylhydrazones<sup>[2-4]</sup>, thiosemicarbazones<sup>[5-6]</sup> and semicarbazones<sup>[7-8]</sup>, and their transition metal complexes have been widely investigated due to the high biological and pharmaceutical activities. However, as

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their structurally analogous, carbazates (R-O-CO-NH-NH<sub>2</sub>) have been paid much less attention<sup>[9]</sup>.

On the other hand, Cu<sup>2+</sup> and Zn<sup>2+</sup> are crucial to the life because they are present as important cofactors of various enzymes and numerous proteins<sup>[10]</sup>. Furthermore, pyrazines are an important class of nitrogen heterocyclic compounds with a variety of biological activities and are used as key structural motifs for the synthesis of various pharmaceutical agents<sup>[11-12]</sup>. Our previous work has shown that the semicarbazone, namely, methyl (pyrazin-2-yl)ethylidene)carbazate could coordinate with Ni(II) and Cd(II) ions<sup>[9]</sup>. As the continuation of our work on Schiff base metal complexes, we report here the crystal structures of Cu(II) and Zn(II) complexes with methyl (1-(3-ethylpyrazin-2-yl)ethylidene)carbazate (HL). In addition, the luminescent properties of the complexes in solid state were 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 ( $\nu=4\ 000\sim400\text{ cm}^{-1}$ ) were determined by the KBr pressed disc method on a Bruker V70 FT-IR spectrophotometer. <sup>1</sup>H NMR spectra of L was acquired with Bruker AV400 NMR instrument in DMSO-d<sub>6</sub> solution with TMS as internal standard. The UV spectra were recorded on a Purkinje General TU-1800 spectrophotometer. Fluorescence spectra were determined on a Varian CARY Eclipse spectrophotometer.

### 1.2 Preparation of the ligand, complexes 1 and 2

As shown in Scheme 1, the ligand HL was produced by condensation of 3-ethyl-2-acetyl pyrazine (1.51 g, 0.01 mol) and methyl hydrazinocarboxylate (0.90 g, 0.01 mol) in anhydrous methanol solution (30

mL) with continuous stirring at room temperature for 3 h. The white solid was filtered and washed three times by cold methanol. Yield: 1.44 g (65%). m.p. 111.9~112.5 °C. Elemental analysis Calcd. for C<sub>10</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>(%): C: 54.04; H: 6.35; N: 25.21; Found(%): C: 54.22; H: 6.26; N: 25.15. FT-IR (cm<sup>-1</sup>):  $\nu(\text{C=O})$  1 727,  $\nu(\text{C=N})$  1 605,  $\nu(\text{C=N})_{\text{pyrazine}}$  1 560. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  10.44(1H, s, NH), 8.48~8.53 (2H, dd, pyrazine-H), 3.73 (3H, s, CH<sub>3</sub>), 3.01~3.06 (2H, q, CH<sub>2</sub>), 2.26 (3H, s, CH<sub>3</sub>), 1.21~1.25 (3H, t, CH<sub>3</sub>).

Crystals of (H<sub>2</sub>L)NO<sub>3</sub>, complexes **1** and **2** suitable for X-ray diffraction analysis were obtained by slow evaporating the methanol solution (10 mL) of the ligand HL (5 mmol) with equimolar of Ga(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O at room temperature, respectively.

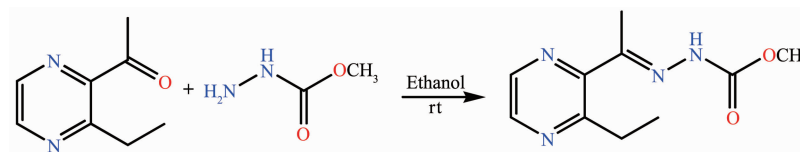
(H<sub>2</sub>L)NO<sub>3</sub>: colorless rods.

**1**: green plates. Anal. Calcd. for C<sub>10</sub>H<sub>16</sub>N<sub>4</sub>O<sub>3</sub>Cl<sub>2</sub>Cu (%): C: 32.05; H: 4.30; N: 14.95. Found(%): C: 32.12; H: 4.15; N: 15.02. FT-IR(cm<sup>-1</sup>):  $\nu(\text{C=O})$  1 720,  $\nu(\text{C=N})$  1 566,  $\nu(\text{C=N})_{\text{pyrazine}}$  1 508.

**2**: yellow plates. Anal. Calcd. for C<sub>20</sub>H<sub>26</sub>N<sub>8</sub>O<sub>4</sub>Zn (%): C: 47.30; H: 5.16; N: 22.06. Found(%): C: 47.22; H: 5.12; N: 22.15. FT-IR (cm<sup>-1</sup>):  $\nu(\text{N=C-O})$  1 644,  $\nu(\text{C=N})$  1 562,  $\nu(\text{C=N})_{\text{pyrazine}}$  1 510.

### 1.3 X-ray crystallography

The single crystal X-ray diffraction data for (H<sub>2</sub>L)NO<sub>3</sub>, complexes **1** and **2** were 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  $\varphi$ - $\omega$  scan mode at 296(2) K. Semi-empirical absorption correction was applied to the intensity data using the SADABS program<sup>[13]</sup>. The structures were solved by direct methods and refined by full matrix least-square on  $F^2$  using the SHELXTL-97 program<sup>[14]</sup>. All non-hydrogen atoms were refined anisotropically. All the H atoms were positioned geometrically and refined using a riding model. The



Scheme 1 Synthesis route of HL

**Table 1** Crystal data and structure refinement for (H<sub>2</sub>L)NO<sub>3</sub>, complexes **1** and **2**

	(H <sub>2</sub> L)NO <sub>3</sub>	<b>1</b>	<b>2</b>
Empirical formula	C <sub>10</sub> H <sub>13</sub> N <sub>5</sub> O <sub>5</sub>	C <sub>10</sub> H <sub>16</sub> N <sub>4</sub> O <sub>3</sub> Cl <sub>2</sub> Cu	C <sub>20</sub> H <sub>26</sub> N <sub>8</sub> O <sub>4</sub> Zn
Formula weight	285.27	374.71	507.86
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> / nm	0.739 8(11)	0.984 6(2)	0.959 0(9)
<i>b</i> / nm	1.991(3)	1.976 4(5)	1.931 1(16)
<i>c</i> / nm	1.807(3)	0.845 53(19)	1.498 0(10)
$\beta$ / (°)	102.15(3)	114.560(3)	127.38(4)
<i>V</i> / nm <sup>3</sup>	2.602(7)	1.496 4(6)	2.204(3)
<i>Z</i>	8	4	4
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.456	1.663	1.530
Unique	4 584	2 632	3 879
<i>R</i> <sub>int</sub>	0.047 7	0.025 1	0.135 8
GOF	1.028	1.028	1.010
<i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.060 8, <i>wR</i> <sub>2</sub> =0.162 6	<i>R</i> <sub>1</sub> =0.031 4, <i>wR</i> <sub>2</sub> =0.080 6	<i>R</i> <sub>1</sub> =0.096 2, <i>wR</i> <sub>2</sub> =0.248 5
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.114 1, <i>wR</i> <sub>2</sub> =0.196 2	<i>R</i> <sub>1</sub> =0.038 3, <i>wR</i> <sub>2</sub> =0.084 6	<i>R</i> <sub>1</sub> =0.149 0, <i>wR</i> <sub>2</sub> =0.280 2

O5 and O6 atoms of the nitrate anion in (H<sub>2</sub>L)NO<sub>3</sub> occupied two positions, with the occupancy value of OV<sub>05(06)</sub>/OV<sub>05A(06A)</sub> being 0.723/0.277. Details of the crystal parameters, data collection and refinements for (H<sub>2</sub>L)NO<sub>3</sub>, complexes **1** and **2** are summarized in Table 1.

CCDC: 1544291, (H<sub>2</sub>L)NO<sub>3</sub>; 1544292, **1**; 1544293, **2**.

## 2 Results and discussion

### 2.1 Crystal structure description

Selected bond distances and angles, hydrogen bonds information for (H<sub>2</sub>L)NO<sub>3</sub>, complexes **1** and **2** are listed in Table 2 and 3, respectively. The reaction of the

**Table 2** Selected bond lengths (nm) and angles (°) in (H<sub>2</sub>L)NO<sub>3</sub>, complexes **1** and **2**

(H <sub>2</sub> L)NO <sub>3</sub>					
O1-C9	0.118 2(4)	N4-C9	0.135 0(4)	N3-C7	0.125 8(4)
C19-O3	0.117 0(4)	C19-N8	0.135 3(4)	C17-N7	0.124 6(4)
<b>1</b>					
Cu1-O1	0.208 5(2)	Cu1-N1	0.201 6(2)	Cu1-N3	0.196 4(2)
Cu1-Cl1	0.243 89(9)	Cu1-Cl2	0.219 94(9)		
Cl2-Cu1-Cl1	104.18(4)	N3-Cu1-N1	77.76(9)	N3-Cu1-Cl2	161.27(7)
N3-Cu1-Cl1	94.45(7)	N3-Cu1-O1	78.35(9)	N1-Cu1-Cl2	99.61(7)
N1-Cu1-Cl1	102.52(7)	N1-Cu1-O1	152.38(9)	O1-Cu1-Cl2	98.55(6)
O1-Cu1-Cl1	92.95(6)				
<b>2</b>					
Zn1-O1	0.212 0(5)	Zn1-N1	0.214 4(7)	Zn1-N3	0.207 2(6)
Zn1-O3	0.210 9(6)	Zn1-N5	0.214 0(6)	Zn1-N7	0.206 6(7)
N7-Zn1-N3	176.9(2)	O3-Zn1-O1	94.9(2)	N7-Zn1-N1	108.2(2)
N7-Zn1-O3	75.0(2)	N7-Zn1-N5	74.2(2)	N3-Zn1-N1	74.3(2)
N3-Zn1-O3	106.8(2)	N3-Zn1-N5	104.0(2)	O3-Zn1-N1	93.7(3)
N7-Zn1-O1	102.2(2)	O3-Zn1-N5	149.1(2)	O1-Zn1-N1	149.6(2)
N3-Zn1-O1	75.4(2)	O1-Zn1-N5	93.1(2)	N5-Zn1-N1	94.2(3)

ligand HL with  $\text{Ga}(\text{NO}_3)_3$  generates crystals of  $(\text{H}_2\text{L})\text{NO}_3$ , establishing the hydrolysis of the metal salt. The asymmetric unit of  $(\text{H}_2\text{L})\text{NO}_3$  contains two counter nitrate anions and two independent protonated (N2 and N6 atoms of pyrazines) organic ligands. Bond lengths of carbonyl C9-O1 (0.118 2(4) nm) and C19-O3 (0.117 0(4) nm) are shorter than those of some

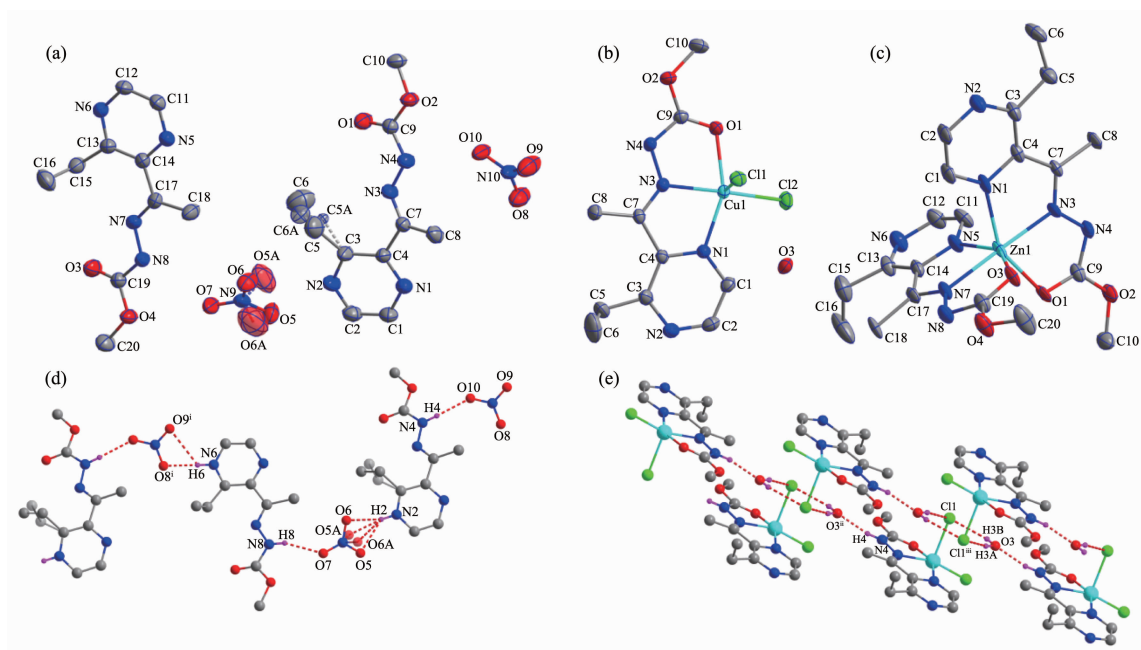
reported neutral semicarbazones<sup>[15]</sup>. In the crystal,  $\text{H}_2\text{L}$  molecules are linked by nitrate anions into one-dimensional chains (Fig.1d) via intermolecular N-H...O hydrogen bonds.

As shown in Fig.1b, complex **1** contains one crystal water molecule and one discrete Cu(II) complex, in which the ratio of the ligand HL and metal is 1:1 and

Table 3 Hydrogen bonds information for  $(\text{H}_2\text{L})\text{NO}_3$  and complex **1**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{D-H}\cdots\text{A} / (^\circ)$
$(\text{H}_2\text{L})\text{NO}_3$				
N2-H2...O5A	0.86	0.194	0.276 3(15)	160.1
N2-H2...O6A	0.86	0.234	0.304(2)	138.8
N2-H2...O5	0.86	0.211	0.281 6(6)	138.9
N2-H2...O6	0.86	0.213	0.292 5(7)	154
N4-H4...O10	0.86	0.207	0.287 7(5)	155.3
N8-H8...O7	0.86	0.213	0.294 9(5)	158.7
N6-H6...O8 <sup>i</sup>	0.86	0.183	0.269 2(5)	177
N6-H6...O9 <sup>i</sup>	0.86	0.244	0.302 2(5)	125.4
<b>1</b>				
N4-H4...O3 <sup>ii</sup>	0.86	0.188	0.272 2(3)	166.6
O3-H3A...Cl1 <sup>iii</sup>	0.85	0.228	0.312 5(3)	170.4
O3-H3B...Cl1	0.85	0.239	0.317 6(2)	153.6

Symmetry codes: <sup>i</sup>  $x-1, y, z-1$ ; <sup>ii</sup>  $x, y, z-1$ ; <sup>iii</sup>  $-x+1, -y+1, -z+1$



H atoms are omitted for clarity in (a)~(c); H atoms of C-H bonds are omitted for clarity in (d) and (e);

Symmetry codes: <sup>i</sup>  $x-1, y, z-1$ ; <sup>ii</sup>  $x, y, z-1$ ; <sup>iii</sup>  $-x+1, -y+1, -z+1$

Fig.1 Diamond drawing of  $(\text{H}_2\text{L})\text{NO}_3$  (a), complexes **1** (b) and **2** (c) with 30% thermal ellipsoids; Extended chain-like supramolecular structure in  $(\text{H}_2\text{L})\text{NO}_3$  (d) and complex **1** (e)

the ligand is neutral tridentate with carbonyl C=O bond length being 0.122 5(3) nm. The Cu(II) ion is also coordinated with two chloride anions, giving a distorted square pyramid coordination geometry ( $\tau=0.148$ )<sup>[16]</sup>. In the solid state, crystal water molecules link the complexes into a one-dimensional chain along *c* axis (Fig.1e) through intermolecular N-H $\cdots$ O and O-H $\cdots$ Cl hydrogen bonds.

By contrast, the central Zn(II) ion in complex **2** is surrounded by two independent anionic ligands with N<sub>2</sub>O donor set, thus possesses a distorted octahedral coordination geometry. The enolization of C=O bond of the ligand can be confirmed by the bond lengths of C-O being 0.125 3(9) and 0.124 7(10) nm<sup>[9,16]</sup>. The distances of Zn-N/O bonds were in the range of 0.206 6(7)~0.214 4(7) nm, comparable with those in some reported complexes with similar donor set<sup>[16]</sup>. As expected, there exist none classic hydrogen bonds in the crystal of **2**.

## 2.2 IR spectra

The  $\nu(\text{C=O})$  of the free ligand HL is at 1 727 cm<sup>-1</sup>, and it shifts to lower frequency value in complex **1**, confirming the coordination of the carbonyl group<sup>[9]</sup>. However, such absorption band is disappeared in complex **2**, meanwhile, new (N=C-O) stretching vibration absorption is observed at 1 644 cm<sup>-1</sup>, revealing that the C=O in O=C-N moiety has enolized and the oxygen atom coordinates to the Zn(II) ion<sup>[16]</sup>. The  $\nu(\text{C=N})$  bands of the imine group and pyrazine ring in the ligand HL shift to lower frequency values in both complexes, indicating that the N atoms of both units take part in the coordination<sup>[16]</sup>, which is in accordance with the crystal structure study.

## 2.3 UV spectra

The UV spectra of HL, complexes **1** and **2** in CH<sub>3</sub>OH solution ( $1 \times 10^{-5}$  mol·L<sup>-1</sup>) were measured at room temperature (Fig.2). The spectra of HL features only one main band located around 285 nm ( $\epsilon=6$  389 L·mol<sup>-1</sup>·cm<sup>-1</sup>), which could be assigned to characteristic  $\pi$ - $\pi^*$  transition of pyrazine unit<sup>[9]</sup>. Similar bands are observed at 284 nm ( $\epsilon=5$  143 L·mol<sup>-1</sup>·cm<sup>-1</sup>) in that of complex **2**. However, there are three bands in spectra of **1** at 257 nm ( $\epsilon=9$  334 L·mol<sup>-1</sup>·cm<sup>-1</sup>), 291

nm ( $\epsilon=10$  444 L·mol<sup>-1</sup>·cm<sup>-1</sup>) and 385 nm ( $\epsilon=6$  864 L·mol<sup>-1</sup>·cm<sup>-1</sup>). The former two could be contributed to the characteristic  $\pi$ - $\pi^*$  transition of pyrazine and imine unit, respectively, while the final one is probably due to the ligand-to-metal charge transfer (LMCT)<sup>[16]</sup>.

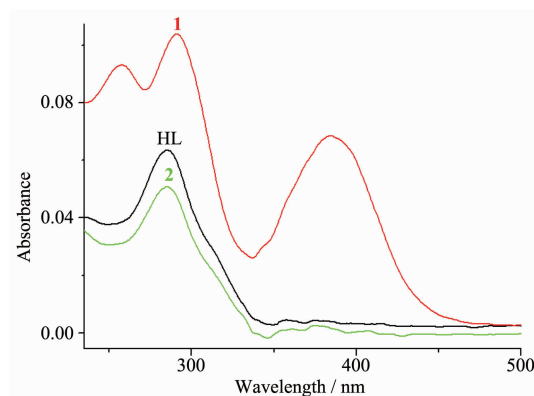


Fig.2 UV spectra of the ligand HL, complexes **1** and **2** in CH<sub>3</sub>OH solution at room temperature

## 2.4 Fluorescence spectra

Fig.3 shows the emission spectra of the ligand HL, complexes **1** and **2** in solid state. When excited at 330 nm, the ligand shows single emission band at 400 nm, while complex **2** exhibits two broad emissions at 400 and 490 nm, which is probably due to the energy transferring from the ligand to the Zn(II) ion<sup>[17]</sup>. The behavior of Zn<sup>2+</sup> coordinated to the ligand is regarded as that of emissive species resulting in a CHEF effect (chelation enhancement of the fluorescence emission)<sup>[18]</sup>. By contrast, the center Cu(II) ion induces obvious fluorescence quenching of HL in complex **1**.

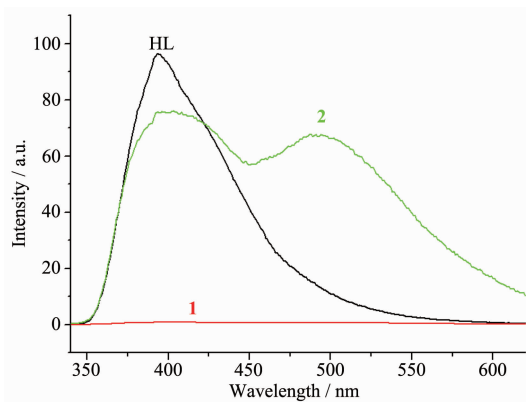


Fig.3 Fluorescence emission spectra of the ligand HL, complexes **1** and **2** in solid state at room temperature

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