

3-乙基-2-乙酰吡嗪缩 4-苯基氨基脲铜/锌配合物的晶体结构及荧光性质

毛献杰¹ 周利华² 伏思连² 尹 航² 赵晓雷^{*1} 吴伟娜^{*1} 王 元¹

(¹河南理工大学化学化工学院,焦作 454000)

(²河南理工大学材料科学与工程学院,焦作 454000)

摘要: 合成了配合物[Cu(HL)(H₂O)(NO₃)]NO₃ (**1**)和[Zn(HL)Cl₂] (**2**) (HL 为 3-乙基-2-乙酰吡嗪缩 4-苯基氨基脲),并通过单晶 X 射线衍射、元素分析及红外光谱表征了结构。单晶衍射结果表明,配合物 **1** 中,中心 Cu(II)离子与 1 个中性三齿缩氨基脲配体,1 个水分子和 1 个硝酸根配位,配位构型为扭曲的四方锥。配合物 **2** 中 Zn(II)离子周围的配位原子为 N₂OCl₂,其配位构型与配合物 **1** 中 Cu(II)离子的相同。甲醇溶液中,配合物 **2** 的荧光发射峰与配体 HL 相似。而配合物 **1** 由于配体和金属离子之间的能量转移,最大荧光发射峰略有红移。

关键词: 缩氨基脲; 铜配合物; 锌配合物; 吡嗪; 荧光

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Crystal Structures and Fluorescence Property of Cu(II)/Zn(II) Complexes of 1-(3-Ethylpyrazin-2-yl)ethylidene-4-phenylsemicarbazide

MAO Xian-Jie¹ ZHOU Li-Hua² FU Si-Lian² YIN Hang² ZHAO Xiao-Lei^{*1} WU Wei-Na^{*1} WANG Yuan¹

(¹College of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo, Henan 454000, China)

(²School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo, Henan 454000, China)

Abstract: Two complexes, namely [Cu(HL)(H₂O)(NO₃)]NO₃ (**1**) and [Zn(HL)Cl₂] (**2**) (where HL is 1-(3-ethylpyrazin-2-yl)ethylidene-4-phenylsemicarbazide) 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 center Cu(II) ion is penta-coordinated by one neutral tridentate semicarbazone, one coordinated water molecule and one monodentate nitrate, thus giving a distorted square pyramid coordination geometry. The coordination geometry of the Zn(II) ion in complex **2** is same as that of the Cu(II) ion in complex **1**, while with N₂OCl₂ donor set. In methanol solution, the fluorescence spectra of the ligand HL and complex **2** are quite similar, whilst the emission peak of complex **1** has slightly red-shift, primarily due to the charge transfer between the ligand and metal ion. CCDC: 1497370, **1**; 1497371, **2**.

Keywords: semicarbazone; Cu(II) complex; Zn(II) complex; pyrazine; fluorescence

It is well known that Schiff bases are an important class of ligands in coordination chemistry and have been found extensive application in different fields^[1-2]. As one of the most promising systems, a

sizable number of transition metal complexes with acylhydrazones and thiosemicarbazones derived from acetyl-pyridine/pyrazine have been extensively investigated as potential anticancer agents^[4-11]. However,

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*通信联系人。E-mail:zhaoxiaolei@hpu.edu.cn, wuwn08@hpu.edu.cn; 会员登记号: S06N6704M1112。

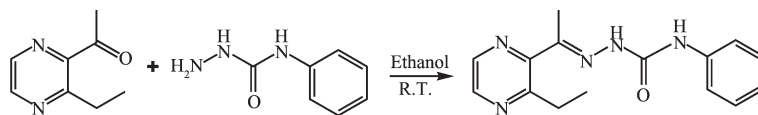
semicarbazones, as their structurally analogous, have been paid much less attention^[12].

Generally, both Cu(II) and Zn(II) ions are closely related to biochemistry, clinical diagnostics as well as environmental pollution^[1,11]. Furthermore, a large amount of Zn(II) complexes with Schiff bases have been reported for their fluorescence properties^[7]. Therefore, in this paper, Cu(II) and Zn(II) complexes with a semicarbazone ligand derived from 2-acetyl-3-ethylpyrazine and 4-phenylsemicarbazide have been synthesized and structural determined by single-crystal X-ray diffraction. In addition, the fluorescence properties of three compounds in methanol solution 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 ($\nu=4\ 000\sim 400\ \text{cm}^{-1}$) were determined by the KBr pressed disc method on a Bruker V70 FTIR spectrophotometer. ¹H NMR spectra of HL was acquired with Bruker AV400



Scheme 1 Synthesis route of HL

The complexes **1** and **2** were generated by reaction of the ligand HL (5 mmol) with equimolar of Cu(NO₃)₂ and ZnCl₂ 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 C₁₅H₁₉N₇O₈Cu (%): C: 36.85; H: 3.92; N: 20.05. Found(%): C: 36.75; H: 4.02; N: 19.94. FTIR(cm⁻¹): $\nu(\text{C}=\text{O})$ 1 687, $\nu(\text{C}=\text{N})$ 1 582, $\nu(\text{C}=\text{N})_{\text{pyrazine}}$ 1 550, $\nu_1(\text{NO}_3)$ 1 494, $\nu_4(\text{NO}_3)$ 1 384 and 1 301.

2: Colorless needles. Anal. Calcd. for C₁₅H₁₇Cl₂N₅OZn (%): C: 42.93; H: 4.08; N: 16.69. Found (%): C: 42.76; H: 4.22; N: 16.78. FTIR (cm⁻¹):

NMR instrument in DMSO-d₆ 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 and in the measurements of emission and excitation spectra the pass width is 5 nm.

1.2 Preparations of the ligand HL, complexes **1** and **2**

As shown in Scheme 1, the ligand HL was produced by condensation of 2-acetyl-3-ethylpyrazine (1.50 g, 0.01 mol) and 4-phenylsemicarbazide (1.51 g, 0.01 mol) in ethanol solution (30 mL) with continuous stirring at room temperature for 5 h. The white solid was filtered and washed three times by cold ethanol. Yield: 2.15 g (76%). m.p. 121~124 °C. Elemental analysis Calcd. for C₁₅H₁₇N₅O (%): C: 63.59; H: 6.05; N: 24.72. Found(%): C: 63.46; H: 6.18; N: 24.57. FTIR (cm⁻¹): $\nu(\text{C}=\text{O})$ 1 705, $\nu(\text{C}=\text{N})$ 1 609, $\nu(\text{C}=\text{N})_{\text{pyrazine}}$ 1 595. ¹H NMR (400 MHz, DMSO-d₆): 10.00 (1H, s, NH), 8.71 (1H, s, NH), 8.46~8.51 (2H, m, pyrazine-H), 7.47~7.56 (2H, m, phenyl-H), 7.25~7.27 (2H, m, phenyl-H), 6.95~6.98 (1H, m, phenyl-H), 3.04~3.10 (2H, d, CH₂), 2.28 (3H, s, CH₃), 1.21~1.25 (3H, s, CH₃).

(C=O) 1 694, (C=N) 1578, (C=N)_{pyrazine} 1 550.

1.3.1 X-ray crystallography

The X-ray diffraction measurement for complexes **1** and **2** were performed on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatized Mo K α radiation ($\lambda=0.071\ 073\ \text{nm}$) by using φ - ω ichscan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program^[13]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-97 program^[14]. 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** and **2** are summarized in Table 1. CCDC: 1497370, **1**; 1497371, **2**.

Table 1 Crystal data and structure refinement for complexes **1** and **2**

	1	2
Empirical formula	C ₁₃ H ₁₉ N ₇ O ₈ Cu	C ₁₃ H ₁₇ Cl ₂ N ₅ OZn
Formula weight	488.91	419.61
<i>T</i> / K	296(2)	296(2)
Size / mm	0.20×0.18×0.06	0.20×0.08×0.08
Crystal system	Orthorhombic	Triclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> $\bar{1}$
<i>a</i> / nm	0.985 9(2)	0.751 2(3)
<i>b</i> / nm	0.857 78(16)	1.068 1(4)
<i>c</i> / nm	2.328 4(4)	1.118 1(5)
α / (°)	90	87.704(7)
β / (°)	90	81.163(7)
γ / (°)	90	80.412(7)
<i>V</i> / nm ³	1.587 3(5)	0.874 0(6)
Flack parameter	0.013(16)	—
<i>Z</i>	4	2
<i>D</i> _c / (g·cm ⁻³)	1.583	1.594
Unique	3 618	3 056
<i>R</i> _{int}	0.039 1	0.021 5
GOF	1.012	1.035
<i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ =0.036 9, <i>wR</i> ₂ =0.073 5	<i>R</i> ₁ =0.038 6, <i>wR</i> ₂ =0.086 7
<i>R</i> indices (all data)	<i>R</i> ₁ =0.051 0, <i>wR</i> ₂ =0.079 3	<i>R</i> ₁ =0.054 0, <i>wR</i> ₂ =0.094 0

2 Results and discussion

2.1 Crystal structures description

A diamond drawing of complexes **1** and **2** is shown in Fig.1. Selected bond distances and angles are listed in Table 2. As shown in Fig.1a, complex **1** contains one discrete cationic Cu (II) complex and one free nitrate as counter anion in the unit cell. The center Cu(II) ion is penta-coordinated by one neutral semicarbazone with N₂O donor set, one coordinated water molecule and one monodentate nitrate, thus giving a distorted square pyramid coordination geometry ($\tau=0.318$)^[15].

However, most bond angles are highly deviated from those of the ideal geometry. The basal plane of the square-pyramid is made up of N1, N3, O1 and O2. The bond lengths from Cu (II) center to these

atoms are in the range of 0.192 2(3)~0.201 3(3) nm. The fifth coordination site is occupied by O5 atom located axially at 0.221 2(3) nm. In addition, the second O atom (O3) of the coordinated nitrate group occupied a sixth-coordinate position at a distance greater than 0.26 nm, namely 0.261 6 nm, to give the (4+1+1*) type coordination^[11]. In the solid state, the complexes were linked into a one-dimensional chain along a axis (Fig.1b) by intermolecular N-HO and O-HO hydrogen bonds (Table 3).

Similarly, the semicarbazone HL acts as a neutral tridentate ligand in complex **2** (Fig.1c). Coordinated by two additional chloride anions, the Zn(II) ion adopts a distorted square pyramid coordination geometry ($\tau=0.169$)^[15]. In the crystal, two pairs of intermolecular N-HCl hydrogen bonds link two complex molecules into a centrosymmetric dimer (Fig.1d).

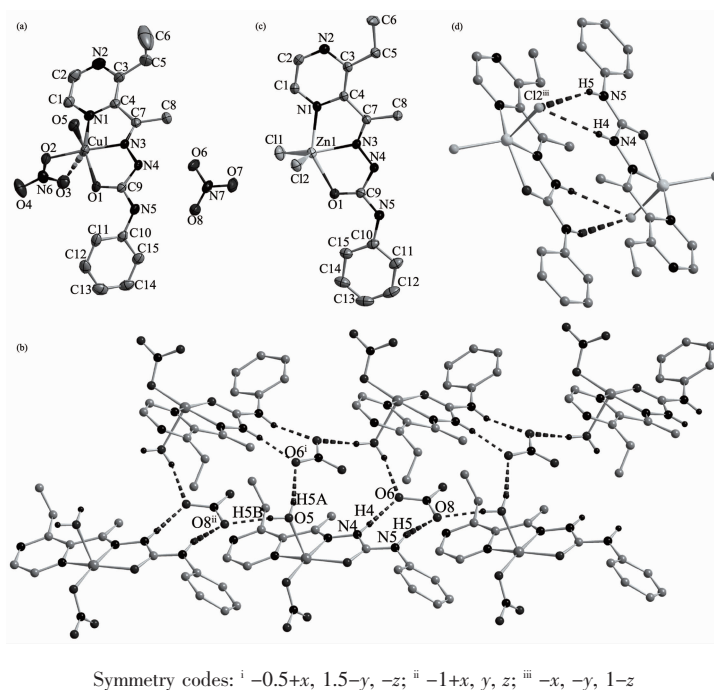


Fig.1 Diamond drawing of **1** (a) and **2** (c) with 30% thermal ellipsoids and H atoms being omitted for clarity; Extend chain-like structure along *a* axis in complex **1**(b) and the centrosymmetric dimer in complex **2** (d)

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

1					
Cu1-O1	0.199 0(2)	Cu1-O2	0.192 2(3)	Cu1-O5	0.221 2(3)
Cu1-N1	0.201 3(3)	Cu1-N3	0.192 7(3)	N1-Cu1-O5	91.54(11)
O2-Cu1-N3	175.13(12)	O2-Cu1-N1	102.27(12)	O2-Cu1-O5	89.02(12)
O2-Cu1-O1	96.99(11)	N3-Cu1-N1	78.89(13)	N3-Cu1-O5	95.69(12)
N3-Cu1-O1	80.78(12)	O1-Cu1-N1	156.05(11)	O1-Cu1-O5	102.98(11)
2					
Zn1-O1	0.223 7(2)	Zn1-N1	0.218 4(3)	Zn1-N3	0.211 5(3)
Zn1-Cl1	0.222 33(12)	Zn1-Cl2	0.225 44(13)	N1-Zn1-O1	144.35(10)
N3-Zn1-N1	72.01(10)	N3-Zn1-O1	73.68(10)	N3-Zn1-Cl2	107.47(8)
N3-Zn1-Cl1	134.24(9)	O1-Zn1-Cl2	99.45(8)	N1-Zn1-Cl2	99.73(8)
N1-Zn1-Cl1	100.05(8)	Cl1-Zn1-O1	96.87(8)	Cl1-Zn1-Cl2	118.27(5)

Table 3 Hydrogen bonds information in complexes **1** and **2**

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
1				
N(4)-H(4)...O(6)	0.086	0.197	0.281 6(4)	169.8
N(5)-H(5)...O(8)	0.086	0.208	0.291 4(4)	161.6
O(5)-H(5A)...O(6) ⁱ	0.084 6(10)	0.203 0(17)	0.286 0(5)	167(4)
O(5)-H(5B)...O(8) ⁱⁱⁱ	0.084 7(10)	0.205 7(16)	0.289 0(4)	168(5)
2				
N(4)-H(4)...Cl(2) ⁱⁱⁱ	0.086	0.262	0.334 5(3)	143.1
N(5)-H(5)...Cl(2) ⁱⁱⁱ	0.086	0.25	0.327 7(3)	150.6

Symmetry codes: ⁱ $-0.5+x, 1.5-y, -z$; ⁱⁱ $-1+x, y, z$; ⁱⁱⁱ $-x, -y, 1-z$

2.2 IR spectra

The FTIR spectral region for both complexes is more or less similar due to the similar coordination modes of the ligands. The $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{N})_{\text{pyridine}}$ bands are at 1 705, 1 609 and 1 595 cm^{-1} , respectively. They shift to lower frequency values in the spectra of complexes, indicating that the carbonyl O, imine N and pyridine N atoms take part in the coordination^[12]. In addition, the intense absorption bands in the spectra of complex **1** associated with the asymmetric stretching appear at 1 384 and 1 301 cm^{-1} (ν_4) as well as 1 494 cm^{-1} (ν_1), clearly establishing the existence of monodentate and bidentate NO_3^- ligands, respectively^[12,15]. It is in accordance with the crystal structure study.

2.3 UV spectra

The UV spectra of the ligand HL, complexes **1** and **2** in methanol solution ($c=1\times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) were measured at room temperature (Fig.2). The spectra of HL features one main band located around 275 nm ($\epsilon=6\ 929 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and a shoulder at 282 nm ($\epsilon=6\ 567 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), which could be assigned to characteristic $\pi-\pi^*$ transition of benzene and pyridine units, respectively^[12]. Both bands have no shift while with hyperchromic effect in the spectra of **2** (275 nm, $\epsilon=8\ 863 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ and 282 nm, $\epsilon=8\ 331 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). The new absorbance band at 411 nm ($\epsilon=1\ 101 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) of **2** may be from the $n\rightarrow\pi^*$ transition of the intra-ligand^[12]. By contrast, complex **1** exhibits two bands at 310 nm ($\epsilon=8\ 863 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and 432 nm ($\epsilon=6\ 173 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), which should be assigned

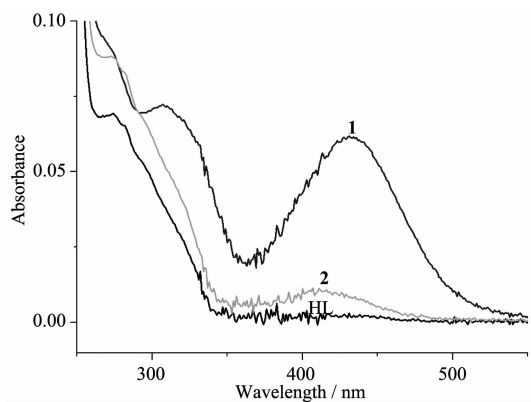


Fig.2 UV spectra of the ligand HL, complexes **1** and **2** in the methanol solution at room temperature

to $\pi\rightarrow\pi^*$ transition of imine bond and the ligand-to-metal charge transfer (LMCT), respectively^[12,16].

2.4 Fluorescence spectra

The fluorescence spectra of the ligand HL, complexes **1** and **2** have been studied in methanol solution ($c=1\times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) at room temperature. As shown in Fig.3, the emission spectra of the ligand HL and complex **2** are quite similar, each of them exhibits two indistinct peaks at 311 and 328 nm when excited at 285 nm. The emissions may be assigned to $\pi^*\rightarrow\pi$ or $\pi^*\rightarrow n$ transition of the intra-ligand^[12,16]. However, complex **1** shows a remarkable peak at about 333 nm under the same tested condition. Compared with the emission of free ligand HL, a red-shift of 5 nm was observed for complex **1**, primarily due to the metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT)^[16].

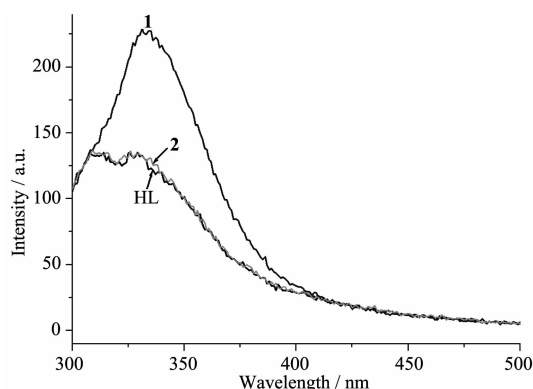


Fig.3 Fluorescence emission spectra of the ligand HL, complexes **1** and **2** in the methanol solution at room temperature

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