

吡嗪缩氨基脲配体铜/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 $[\text{Cu}_2(\text{L})_2\text{Br}_2] \cdot \text{CH}_3\text{OH}$ (**1**) 和 $[\text{Zn}_2(\text{L})_2(\text{CH}_3\text{COO})_2] \cdot 2\text{CH}_3\text{OH}$ (**2**) 的结构 (HL 为 3-乙基-2-乙酰吡嗪缩 4-苯基氨基脲)。单晶衍射结果表明, 配合物 **1** 中, 中心 Cu(II) 离子与来自 1 个三齿缩氨基脲配体阴离子和 2 个 μ^2 -桥联的溴离子配位, 拥有扭曲的四方锥配位构型。配合物 **2** 中 Zn(II) 离子配位构型与配合物 **1** 中 Cu(II) 离子的相同, 周围的供体原子为 N_2O_3 。配合物 **2** 中的 2 个醋酸根的配位模式不尽相同, 其中一个为 $\mu\text{-OCO}$ 双齿桥联, 另外一个为 $\mu\text{-O}$ 单齿桥联。甲醇溶液中, 配合物 **1** 和 **2** 的荧光发射峰与配体 HL 相似。

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 Properties of Cu(II)/Zn(II) Complexes with a Semicarbazone Ligand Bearing Pyrazine Unit

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Abstract: Two complexes, namely, $[\text{Cu}_2(\text{L})_2\text{Br}_2] \cdot \text{CH}_3\text{OH}$ (**1**) and $[\text{Zn}_2(\text{L})_2(\text{CH}_3\text{COO})_2] \cdot 2\text{CH}_3\text{OH}$ (**2**) (HL = 1-(3-ethylpyrazin-2-yl)ethylidene-4-phenylsemicarbazide) have been synthesized and characterized by single crystal X-ray diffraction, elemental analysis and IR spectroscopy. In complex **1**, the center Cu(II) ion with a distorted square pyramid coordination geometry is coordinated by one tridentate deprotonated semicarbazone with N_2O donor set and two μ^2 -bridged bromide anions. 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 N_2O_3 donor set. In addition, two acetate anions in complex **2** exhibit different coordination modes, one of which is bidentate bridge ($\mu\text{-OCO}$), while the other one is oxygen bridge ($\mu\text{-O}$). In the methanol solution, both complexes exhibit the intra-ligand emission. CCDC: 1516162, **1**; 1516163, **2**.

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

Schiff bases are an important class of ligands in coordination chemistry and have been paid much attention due to their extensive application in different fields^[1-3]. Among them, thiosemicarbazones derived from acetyl-pyridine/pyrazine and their transition metal complexes have been extensively investigated as

potential anticancer agents^[3-12]. However, the study on the complexes of semicarbazones bearing pyrazine unit is relatively few^[13-14].

On the other hand, both Cu(II) and Zn(II) ions are closely related to biochemistry, clinical diagnostics as well as environmental pollution^[2,14]. Our previous work

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has shown that the semicarbazone, namely, 1-(3-ethylpyrazin-2-yl)ethylidene-4-phenylsemicarbazide (HL) could act as a neutral ligand to form stable mononuclear complexes with $\text{Cu}(\text{NO}_3)_2$ and ZnCl_2 , respectively^[14]. In addition, it has been demonstrated that the type of the metal salts could influence the structures of complexes efficiently^[14]. Moreover, the polynuclear metal complexes are highly desired, because they usually possess higher anticancer activities than the mononuclear ones^[2,15]. Therefore, as a continuation of our work, two binuclear complexes, $[\text{Cu}_2(\text{L})_2\text{Br}_2] \cdot \text{CH}_3\text{OH}$ (**1**) and $[\text{Zn}_2(\text{L})_2(\text{CH}_3\text{COO})_2] \cdot 2\text{CH}_3\text{OH}$ (**2**) have been synthesized and structural determined by single-crystal X-ray diffraction. The fluorescence properties of both complexes in methanol solution were also investigated.

1 Experimental

1.1 Materials and measurements

Solvents and starting materials for synthesis were purchased commercially and used as received. The ligand HL was prepared according to the literature method^[14]. 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. The UV spectra were recorded on a Purkinje General TU-1800 spectrophotometer. Fluorescence spectra were determined on a Varian CARY Eclipse spectrophotometer, in the measurements of emission and excitation spectra the pass width is 5 nm.

1.2 Preparations of complexes **1** and **2**

The complexes **1** and **2** were generated by

reaction of the ligand HL (5 mmol) with equimolar of CuBr_2 and $\text{Zn}(\text{OAc})_2$ 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: Black blocks. Anal. Calcd. for $\text{C}_{31}\text{H}_{36}\text{N}_{10}\text{O}_3\text{Br}_2\text{Cu}_2$ (%): C: 42.14; H: 4.11; N: 15.85. Found (%): C: 41.95; H: 4.22; N: 15.77. FTIR (cm^{-1}): $\nu(\text{N}=\text{C}-\text{O})$ 1625, $\nu(\text{C}=\text{N})$ 1 580, $\nu(\text{C}=\text{N})_{\text{pyrazine}}$ 1 548.

2: Yellow blocks. Anal. Calcd. For $\text{C}_{36}\text{H}_{46}\text{N}_{10}\text{O}_8\text{Zn}_2$ (%): C: 49.27; H: 5.28; N: 15.96. Found (%): C: 49.33; H: 5.38; N: 16.00. FTIR (cm^{-1}): $\nu(\text{N}=\text{C}-\text{O})$ 1 618, $\nu(\text{C}=\text{N})$ 1 579, $\nu(\text{C}=\text{N})_{\text{pyrazine}}$ 1 552, $\nu_{\text{as}}(\text{COO}^-)$ 1 569, $\nu_{\text{s}}(\text{COO}^-)$ 1 436 and 1 413.

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 $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) by using $\varphi-\omega$ scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program^[16]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-97 program^[17]. All non-hydrogen atoms were refined anisotropically. The H atoms of the disordered methanol molecule in **1** are not added. All the other 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: 1516162, **1**; 1516163, **2**.

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

	1	2
Empirical formula	$\text{C}_{31}\text{H}_{36}\text{N}_{10}\text{O}_3\text{Br}_2\text{Cu}_2$	$\text{C}_{36}\text{H}_{46}\text{N}_{10}\text{O}_8\text{Zn}_2$
Formula weight	883.60	877.57
T/K	296(2)	296(2)
Size / mm	0.22×0.20×0.20	0.20×0.18×0.15
Crystal system	Orthorhombic	Triclinic
Space group	$Pbcn$	$P\bar{1}$
a/nm	2.198 4(3)	0.974 0(8)
b/nm	0.751 69(11)	1.448 6(12)

Continued Table 1

c / nm	2.047 6(3)	1.492 0(12)
$\alpha / (^{\circ})$		110.694(11)
$\beta / (^{\circ})$		98.243(12)
$\gamma / (^{\circ})$		93.619(14)
V / nm^3	3.383 8(9)	1.934(3)
Z	4	2
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.734	1.507
Unique reflection	2 970	6 721
R_{int}	0.051 1	0.015 7
GOF	1.022	1.06 2
R indices [$I > 2\sigma(I)$]	$R_1=0.032\ 8$ $wR_2=0.077\ 1$	$R_1=0.045\ 9$ $wR_2=0.128\ 7$
R indices (all data)	$R_1=0.048\ 1$ $wR_2=0.083\ 4$	$R_1=0.060\ 9$ $wR_2=0.139\ 3$

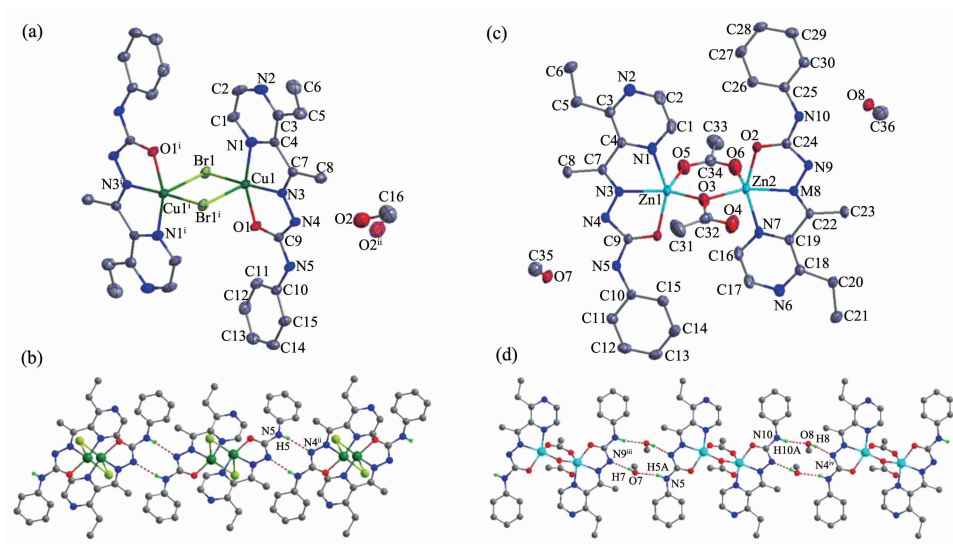
2 Results and discussion

2.1 Crystal structures description

The diamond drawing of complexes **1** and **2** is shown in Fig.1. Selected bond distances and angles are listed in Table 2. The lengths of C-O bond of the semicarbazone moiety are 0.125 8(4) nm (complex **1**) or 0.125 6(4) and 0.125 3(4) nm (complex **2**), which are longer than those of the reported neutral hydrazone or semicarbazones^[13-14], indicating that the

ligand HL has enolized and deprotonated in both complexes. On the contrary, it acts as a neutral ligand in the literature complexes $[\text{Cu}(\text{HL})(\text{H}_2\text{O})(\text{NO}_3)]\text{NO}_3$ and $[\text{Zn}(\text{HL})\text{Cl}_2]$ ^[14].

As shown in Fig.1a, complex **1** contains one centrosymmetric dimeric Cu(II) molecule and one disordered methanol in the asymmetric unit. Two Cu atoms of the dimer were separated by 0.350 6 nm and doubly bridged by two bromide anions to form an ideal planar four-membered Cu_2Br_2 core. Each Cu(II)



H atoms are omitted for clarity in (a) and (b); Disordered methanol are omitted in (c); Symmetry codes: ⁱ $-x+1, -y, -z+2$; ⁱⁱ $-x+1, y, -z+3/2$; ⁱⁱⁱ $x, y+1, z$; ^{iv} $x, y-1, z$

Fig.1 Diamond drawing of **1** (a) and **2** (b) with 30% thermal ellipsoids, extend chain-like structures along c axis in complex **1**(c) and along b axis in complex **2** (d)

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

1					
Br1-Cu1	0.235 90(6)	Cu1-N1	0.200 4(3)	Cu1-N3	0.192 4(3)
Cu1-O1	0.194 9(2)	Cu1-Br1 ⁱ	0.284 52(7)		
Br1-Cu1-Br1 ⁱ	95.85(2)	N3-Cu1-O1	80.22(11)	N3-Cu1-Br1	170.89(9)
N3-Cu1-Br1 ⁱ	93.04(9)	N3-Cu1-N1	79.87(12)	O1-Cu1-Br1	96.85(7)
O1-Cu1-Br1 ⁱ	95.90(8)	O1-Cu1-N1	158.90(12)	N1-Cu1-Br1	101.75(9)
N1-Cu1-Br1 ⁱ	92.05(9)				
2					
Zn1-O1	0.206 9(3)	Zn1-O3	0.196 3(3)	Zn1-O5	0.198 6(3)
Zn1-N1	0.215 5(3)	Zn1-N3	0.202 7(3)	Zn2-O2	0.205 1(3)
Zn2-O3	0.196 9(3)	Zn2-O6	0.200 2(3)	Zn2-N6	0.213 7(3)
Zn2-N8	0.203 0(3)				
O5-Zn1-N3	109.51(12)	N3-Zn1-O1	76.72(11)	O3-Zn1-O5	105.72(13)
O3-Zn1-O1	99.83(11)	O3-Zn1-N1	96.62(12)	O3-Zn1-N3	144.25(12)
O5-Zn1-O1	105.33(13)	O5-Zn1-N1	94.19(15)	N3-Zn1-N1	75.16(11)
O1-Zn1-N1	149.84(11)	O3-Zn2-O6	102.38(12)	O3-Zn2-N8	148.00(12)
O6-Zn2-O2	93.54(13)	O6-Zn2-N6	94.82(15)	O6-Zn2-N8	109.51(12)
N8-Zn2-O2	76.82(11)	N8-Zn2-N6	75.32(11)	O3-Zn2-O2	104.09(11)
O3-Zn2-N6	100.00(11)	O2-Zn2-N6	152.12(10)		

Symmetry codes: ⁱ $-x+1, -y, -z+2$ **Table 3** Hydrogen bonds information in complexes **1** and **2**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
1				
N5-H5...N4 ⁱⁱ	0.086	0.217	0.300 2(4)	161.4
2				
O7-H7...N9 ⁱⁱⁱ	0.082	0.202	0.282 3(4)	167.8
O8-H8...N4 ^{iv}	0.082	0.205	0.286 5(4)	173.3
N5-H5A...O7	0.086	0.216	0.294 4(4)	151.8
N10-H10A...O8	0.086	0.22	0.298 2(4)	151.9

Symmetry codes: ⁱⁱ $-x+1, y, -z+3/2$; ⁱⁱⁱ $x, y+1, z$; ^{iv} $x, y-1, z$

ion is also coordinated by one L^- anion with N_2O donor set, giving a distorted square pyramid coordination geometry ($\tau=0.200$)^[13]. The basal plane of the square-pyramid is made up of N1, N3, O1 and Br1. The bond lengths from Cu(II) center to these atoms are in the range of 0.192 4(3)~0.235 90(6) nm. The fifth coordination site is occupied by Br1ⁱ atom (Symmetry codes: ⁱ $-x+1, -y, -z+2$) located axially at 0.284 52(7) nm. In the solid state, the dimers were linked into a one-dimensional chain along c axis (Fig. 1b) by pairs of intermolecular N-H...N hydrogen

bonds (Table 3).

Similarly, a discrete dimeric Zn(II) molecule with Zn...Zn distance being 0.335 8 nm could also be observed in complex **2** (Fig.1c). Each Zn(II) ion adopts a distorted square pyramid coordination geometry ($\tau=0.093, 0.069$ for Zn1 and Zn2, respectively)^[13], and is surrounded by one L^- and two acetate anions, one of which is bidentate bridge ($\mu\text{-OCO}$), while the other one is oxygen bridge ($\mu\text{-O}$). In the crystal, methanol molecules link the dimers into a one-dimensional chain along b axis (Fig.1d) via intermolecular N-H...O

and O-H...N hydrogen bonds.

2.2 IR spectra

The FTIR spectral region for both complexes is more or less similar due to the similar coordination modes of the ligand. The $\nu(\text{C}=\text{O})$ of the free ligand at $1\,705\text{ cm}^{-1}$ disappears in both complexes, meanwhile, new $\text{N}=\text{C}-\text{O}$ stretching vibration absorption is observed at $1\,625$ and $1\,618\text{ cm}^{-1}$ in complexes **1** and **2**, respectively, revealing that the $\text{C}=\text{O}$ in $\text{O}=\text{C}-\text{N}$ moiety has enolized and the oxygen atom coordinates to the metal ions in both complexes^[13-14]. The $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{N})_{\text{pyrazine}}$ bands of the free ligand are at $1\,609$ and $1\,595\text{ cm}^{-1}$, respectively. They shift to lower frequency values in the complexes, indicating that the imine N and pyrazine N atoms take part in the coordination^[14]. In addition, the general pattern the IR spectroscopy of complex **1** supports the normal coordination of the $\mu\text{-OCO}$ and $\mu\text{-O}$ bridged acetate anions^[18]. It is in accordance with the crystal structure study.

2.3 UV spectra

The UV spectra of complexes **1** and **2** in methanol solution (concentration: $1 \times 10^{-5}\text{ mol} \cdot \text{L}^{-1}$) were measured at room temperature (Fig.2). As our previous work shown, 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 $\pi\text{-}\pi^*$ transition of benzene and pyrazine units, respectively^[14]. In complexes **1** and **2**, the shoulder is absent and a combined band at 272 nm ($\epsilon=11\,323\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and

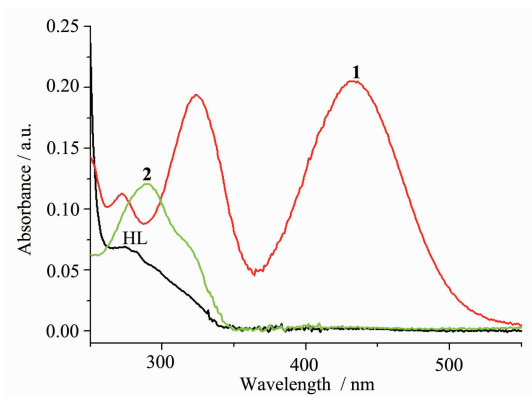


Fig.2 UV spectra of the ligand HL, complexes **1** and **2** in the methanol solution at room temperature

291 nm ($\epsilon=12\,132\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) could be observed, respectively. The band at about 320 nm of complexes **1** ($\epsilon=19\,557\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and **2** ($\epsilon=7\,432\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, as shoulder) should be assigned to $\pi \rightarrow \pi^*$ transition of imine bond^[14,18]. In addition, complex **1** exhibits another band at 434 nm ($\epsilon=20\,511\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), corresponding to the ligand-to-metal charge transfer (LMCT)^[19].

2.4 Fluorescence spectra

The fluorescence spectra of the ligand HL, complexes **1** and **2** have been studied in methanol solution (concentration: $1 \times 10^{-5}\text{ mol} \cdot \text{L}^{-1}$) at room temperature. As shown in Fig.3, the emission spectra of three compounds are quite similar, and each of them exhibits two indistinct peaks at 311 and 325 nm when excited at 285 nm . The emissions may be assigned to $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ transition of the intra-ligand^[14,19]. By contrast, the emission of the literature complex $[\text{Cu}(\text{HL})(\text{H}_2\text{O})(\text{NO}_3)]\text{NO}_3$ has slightly red-shift (5 nm) when compared with that of HL^[14]. Therefore, it may be roughly concluded that the type of the anions may influence not only the structure, but also the property of the complexes.

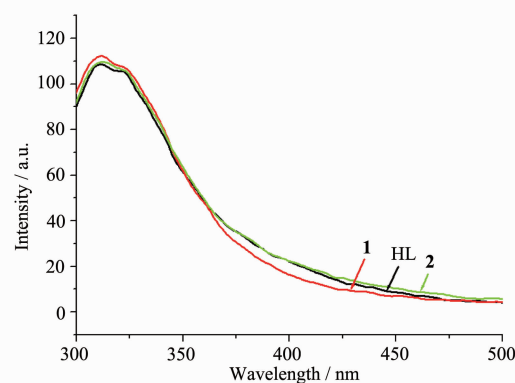


Fig.3 Fluorescence emission spectra of the ligand HL, complexes **1** and **2** in the methanol solution at room temperature

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