2-乙酰吡嗪苯甲酰腙钴、锌和铜配合物的晶体结构及荧光性质

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摘要: 合成了配合物[Co(L)$_2$] (**1**),[Zn(L)$_2$] (**2**)和[Cu$_2$(L)$_2$Cl$_2$] (**3**)(HL 为 2-乙酰吡嗪苯甲酰腙),并通过单晶衍射、元素分析及红外光谱表征了它们的结构。单晶衍射结果表明,配合物 **1** 和 **2** 同构,配体和金属的比例为 2:1。每个配合物中,中心金属离子与来自 2 个阴离子配体 L$^-$的 N_2O 电子供体配位,形成扭曲的八面体配位构型。在双核配合物 **3** 中,Cu(Ⅱ)离子与 1 个阴离子三齿酰腙配体、2 个 μ_2 桥联的氯离子配位,拥有扭曲的四方锥配位构型。此外还研究了配合物的荧光性质。

关键词: 酰腙; 配合物; 吡嗪; 晶体结构; 荧光
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Co(Ⅱ)/Zn(Ⅱ)/Cu(Ⅱ) Complexes Containing Hydrazone Ligand Bearing Pyrazine Unit: Syntheses, Crystal Structures and Fluorescence Properties

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Abstract: Three complexes, namely, [Co (L)$_2$] (**1**), [Zn (L)$_2$] (**2**) and [Cu$_2$ (L)$_2$Cl$_2$] (**3**) based on HL (HL =2-acetylpyrazine benzoylhydrazone) were synthesized and characterized by X-ray diffraction analyses. The results show that complexes **1** and **2** are isostructural, in which the molar ratio between the metal and the ligand is 1:2. The metal ion in each complex is surrounded by two enolizated ligands L$^-$ with N_2O donor set, thus giving a distorted octahedral geometry. However, in the bi-nuclear complex **3**, each Cu(Ⅱ) ion is coordinated with one monoanionic tridentate hydrazone ligand and two μ_2-chloride anions, as [CuN_2OCl_2], indicating the coordination geometry is a distorted tetragonal pyramid. In addition, the luminescent properties of the complexes are discussed in detail. CCDC: 1552007, **1**; 1552008, **2**; 1552009, **3**.

Keywords: acylhydrazone; complex; pyrazine; crystal structure; fluorescence

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Acylhydrazones have attracted much more attention mainly due to their variable bonding modes towards transition metal ions and wide range of biological properties, such as antioxidant, anti-inflammatory, antibacterial and antitumor activities[1]. Up to now, a number of acylhydrazone transition metals bearing pyridine heterocycle scaffold, possess potent anticancer activity[2-5]. In fact, 2-acetylpyrazine thiosemicarbazones have been reported to exhibit remarkable biological activity *in vitro* against K562 leukemia cell lines through the work of Li and co-workers[6-8]. However, the investigation on the 2-acetylpyrazine acylhydrazone complexes is relatively scarce[9]. Here, the structures of three transition metal complexes based on 2-acetylpyrazine benzoylhydrazone are described. In addition, the fluorescent properties of the ligand and the complexes were studied in detail.

1 Experimental section

1.1 Materials and measurement

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 (ν=4 000~400 cm^{-1}) were determined by the KBr pressed disc method on a Bruker V70 FT-IR spectrophotometer. ^1H NMR spectra of HL was acquired with Bruker AV400 NMR instrument in DMSO-d_6 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, in the measurements of emission and excitation spectra the pass width is 10 nm.

1.2 Preparations of the ligand and complexes 1~3

As shown in Scheme 1, the ligand HL was produced by condension of 2-acetylpyrazine (1.22 g, 0.01 mol) and benzohydrazide (1.36 g, 0.01 mol) in anhydrous ethanol solution (30 mL) with continuous stirring at room temperature for 3 h. The white solid was filtered and washed three times by cold ethanol. Yield: 1.92 g (80%). m.p. 183~184 ℃. Elemental analysis Calcd. for $C_{13}H_{12}N_4O$ (%): C: 64.99; H: 5.03; N: 23.32. Found(%): C: 65.18; H: 4.94; N: 23.23. FT-IR (cm^{-1}): ν(C=O) 1 687, ν(C=N) 1 579, $\nu(C=N)_{pyrazine}$ 1 532. ^1H NMR (400 MHz, DMSO-d_6): δ 11.07 (1H, s, NH), 9.27 (1H) and 8.65~8.67 (2H) for pyrazine-H, 7.90 (2H) and 7.52~7.63 (3H) for phenyl-H, 2.46 (3H, s, CH_3).

The complexes **1~3** were generated by reaction of the ligand HL (5 mmol) with equimolar of $Co(NO_3)_2$, $Zn(OAc)_2$ and $CuCl_2$ in ethanol solution (10 mL), respectively. Crystals suitable for X-ray diffraction analysis were obtained by evaporating the corresponding reaction solutions at room temperature.

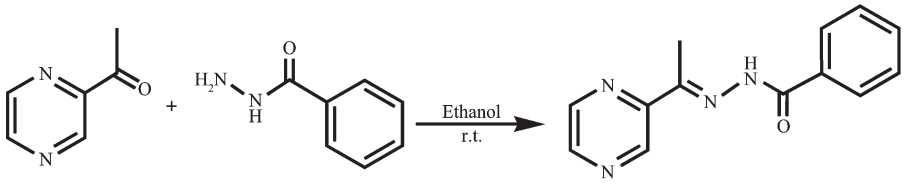
1: brown blocks. Anal. Calcd. for $C_{26}H_{22}N_8O_2Co$ (%): C: 58.10; H: 4.13; N: 20.85. Found(%): C: 58.15; H: 4.00; N: 20.63. FT-IR (cm^{-1}): ν(N=C-O) 1 638, ν(C=N) 1 572, $\nu(C=N)_{pyrazine}$ 1 527.

2: brown blocks. Anal. Calcd. for ($C_{26}H_{22}N_8O_2Zn$) (%): C: 57.42; H: 4.08; N: 20.60. Found(%): C: 57.32; H: 3.92; N: 20.39. FT-IR (cm^{-1}): ν(N=C-O) 1 639, ν(C=N) 1 573, $\nu(C=N)_{pyrazine}$ 1 526.

3: green blocks. Anal. Calcd. For ($C_{13}H_{11}N_4OClCu$)(%): C: 46.16; H: 3.28; N: 16.56. Found(%): C: 46.22; H: 3.16; N: 16.37. FT-IR (cm^{-1}): ν(N=C-O) 1 634, ν(C=N) 1 565, $\nu(C=N)_{pyrazine}$ 1 525.

1.3 X-ray crystallography

The X-ray diffraction measurement for complexes **1~3** (size: 0.15 mm×0.14 mm×0.12 mm, 0.25 mm×0.22 mm×0.20 mm, and 0.14 mm×0.12 mm×0.08 mm, respectively) were performed on a Bruker SMART APEX Ⅱ CCD diffractometer equipped with a graphite monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm)



Scheme 1 Synthesis route of HL

by using φ-ω scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program[10]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-97 program[11]. 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.

CCDC: 1552007, **1**; 1552008, **2**; 1552009, **3**.

Table 1　Selected crystallographic data for complexes 1~3

Complex	1	2	3
Empirical formula	$C_{26}H_{22}N_8O_2Co$	$C_{26}H_{22}N_8O_2Zn$	$C_{13}H_{11}N_4OClCu$
Formula weight	537.45	543.89	338.25
T / K	296(2)	296(2)	296(2)
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	$Aba2$	$Aba2$	$P\bar{1}$
a / nm	1.235 6(10)	1.244 7(5)	0.760 5(5)
b / nm	1.932 7(16)	1.936 4(11)	0.77 42(5)
c / nm	0.980 3(8)	0.984 5(4)	1.252 8(8)
α / (°)			89.770(10)
β / (°)			89.192(12)
γ / (°)			64.630(10)
V / nm^3	2.341(3)	2.372 9(19)	0.666 4(7)
Z	4	4	2
D_c / (g·cm^{-3})	1.525	1.522	1.686
Unique reflection	2 646	2 062	2 331
R_{int}	0.092 3	0.044 0	0.019 7
GOF	1.022	1.029	1.018
Final R indices [$I>2\sigma(I)$]	R_1=0.053 3, wR_2=0.078 9	R_1=0.081 1, wR_2=0.259 5	R_1=0.035 3, wR_2=0.08 26
R indices (all data)	R_1=0.104 5, wR_2=0.09 22	R_1=0.083 5, wR_2=0.261 8	R_1=0.046 5, wR_2=0.088 6

2　Results and discussion

2.1　Crystal structure description

Selected bond distances and angles for complexes **1~3** are listed in Table 2. In each complex, C=O bond of the ligand HL is enolized, which could be confirmed by the bond lengths of C-O being 0.127 8(6), 0.126 6(8) and 0.128 8(4) nm in complexes **1~3**, respectively. The results are in excellent agreement with previously known acylhydrazone complexes in the literature[5].

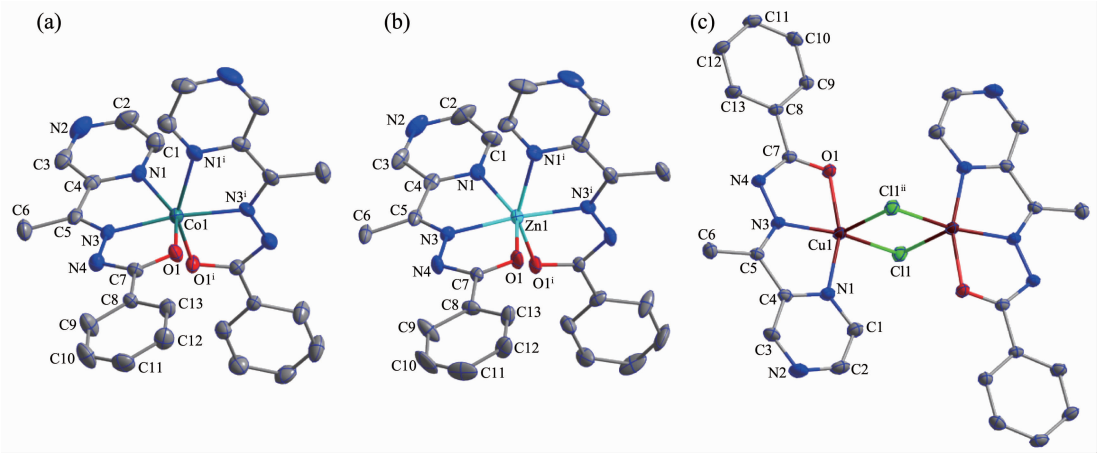
Complexes **1** and **2** are isostructural and crystallize in the orthorhombic, space group $Aba2$. Thus, the complex **1** is discussed in detail for an example. As shown in Fig.1a, the central Co(Ⅱ) ion in complex **1**, which is situated on the two fold rational axis, is surrounded by two independent anionic ligands with N_2O donor set, thus possessing a distorted octahedral coordination geometry. The distances of Co-N/O bonds were in the range of 0.204 4(4)~0.212 8(5) nm, which are shorter than those of the corresponding Zn-N/O bonds in complex **2**, since the radius of the Zn(Ⅱ) ion is greater than that of Co(Ⅱ) ion.

By contrast, complex **3** contains one discrete dimeric Cu(Ⅱ) molecule in the unit cell. Two Cu atoms of the dimer were separated by 0.338 1 nm and doubly bridged by two chloride anions to form an ideal planar four-membered Cu_2Cl_2 core. Each of the Cu(Ⅱ) ions is penta-coordinated by one tridentate anionic ligand and two chloride anions (one of which acts as a μ_2-bridge), thus giving a distorted square pyramid coordination geometry (τ=0.047)[9]. As expected, there exist no

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

1					
Co1-N3	0.204 4(4)	Co1-O1	0.208 0(4)	Co1-N1	0.212 8(5)
N3^{i}-Co1-N3	171.6(3)	N3^{i}-Co1-O1	100.25(18)	N3-Co1-O1	74.58(17)
O1^{i}-Co1-O1	106.3(2)	N3^{i}-Co1-N1	110.5(2)	N3-Co1-N1	75.9(2)
O1-Co1-N1	147.82(16)	N1-Co1-N1^{i}	87.5(3)	O1-Co1-N1^{i}	91.11(18)
2					
Zn1-N3	0.207 2(8)	Zn1-O1	0.209 2(8)	Zn1-N1	0.224 9(8)
N3-Zn1-N3^{i}	173.8(5)	N3^{i}-Zn1-O1	101.5(3)	N3-Zn1-O1	74.5(3)
O1-Zn1-O1^{i}	101.0(5)	N3^{i}-Zn1-N1	108.4(3)	N3-Zn1-N1	76.1(3)
O1-Zn1-N1	149.7(3)	N1-Zn1-N1^{i}	90.1(4)	O1-Zn1-N1^{i}	92.0(3)
3					
Cu1-N3	0.194 7(3)	Cu1-O1	0.197 8(2)	Cu1-N1	0.204 4(3)
Cu1-Cl1	0.226 26(14)	Cu1-Cl1^{ii}	0.264 91(16)		
Cl1-Cu1-Cl1^{ii}	93.36(6)	N3-Cu1-O1	79.63(10)	N3-Cu1-N1	79.92(10)
O1-Cu1-N1	159.55(10)	N3-Cu1-Cl1	162.37(9)	O1-Cu1-Cl1	99.98(7)
N1-Cu1-Cl1	99.39(8)	N3-Cu1-Cl1^{ii}	104.24(9)	O1-Cu1-Cl1^{ii}	95.42(8)
N1-Cu1-Cl1^{ii}	89.93(9)				

Symmetry codes: ^{i} $-x+1, -y, z$; ^{ii} $-x+1, -y, -z+1$



H atoms are omitted for clarity; Symmetry codes: ^{i} $-x+1, -y, z$; ^{ii} $-x+1, -y, -z+1$

Fig.1 Diamond drawing of **1~3** (a~c, respectively) with 30% thermal ellipsoids

classical hydrogen bonds in all three complexes.

2.2 IR spectra

The ν(C=O) of the free ligand is 1 687 cm^{-1}, which is disappeared in complexes **1~3**, meanwhile, new (N=C-O) stretching vibration absorption is observed at 1 634~1 639 cm^{-1}, revealing that the C=O in O=C-N moiety has enolizated and the oxygen atom coordinates to each metal ion[12]. The ν(C=N) bands of the imine group and pyrazine ring in the ligand HL shift to lower frequency values in the complexes, indicating that the N atoms of both units take part in the coordination[4]. It is in accordance with the crystal structure study.

2.3 UV spectra

The UV spectra of HL, complexes **1** and **2** in CH_3OH solution (concentration: 2×10^{-5} mol·L^{-1}) were

measured at room temperature (Fig.3). The spectra of HL features two bands located at 231 (ε=3 889 L·mol^{-1}·cm^{-1}) and 297 nm (ε=10 473 L·mol^{-1}·cm^{-1}), which could be assigned to characteristic π-π* transition of benzene and pyrazine units[12]. Similar bands are observed at 257 (ε=5 770 L·mol^{-1}·cm^{-1}) and 288 nm (ε=5 562 L·mol^{-1}·cm^{-1}); 254 (ε=4 464 L·mol^{-1}·cm^{-1}) and 303 nm (ε=5 090 L·mol^{-1}·cm^{-1}) in the complexes **1** and **2**, respectively. However, such two bands combined at 268 (ε=8 775 L·mol^{-1}·cm^{-1}) in the spectra of **3**. In addition, complexes **1**~**3** exhibit new absorbance bands at 374 (ε=7 390 L·mol^{-1}·cm^{-1}), 386 (ε=7 650 L·mol^{-1}·cm^{-1}) and 403 nm (ε=7 496 L·mol^{-1}·cm^{-1}), respectively, probably due to the ligand-to-metal charge transfer (LMCT)[13]. This indicates that an extended conjugation is formed after complexation in complexes **1**~**3**.

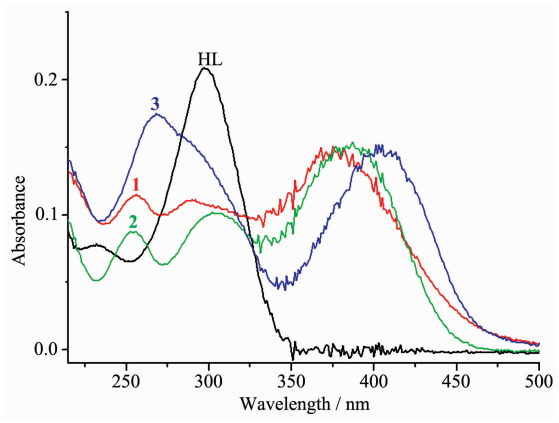


Fig.2　UV spectra of the ligand HL and complexes **1**~**3** in CH_3OH solution at room temperature

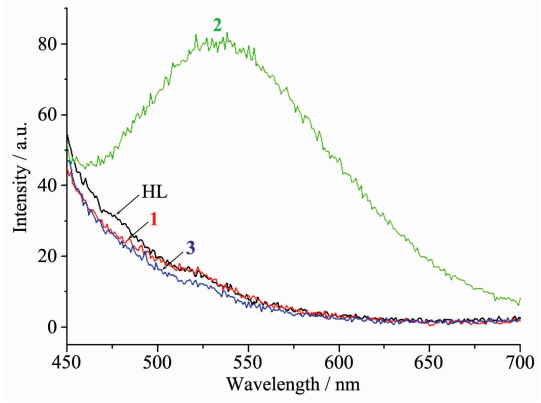


Fig.3　Fluorescence emission spectra of ligand HL and complexes **1**~**3** in CH_3OH solution at room temperature

2.4　Fluorescence spectra

The fluorescence spectra of the ligand HL, complexes **1**~**3** have been studied in CH_3OH solution (concentration: 2×10^{-5} mol·L^{-1}) at room temperature. The results show that complex **2** shows significant emission peak at 535 nm when excited at 380 nm, while HL, complexes **1** and **3** are free of fluorescence under same conditions. The ligand HL exhibits no fluorescence primarily due to C=N isomerization. Binding with Zn^{2+} inhibits the isomerization of C=N, thereby increasing the fluorescence intensity through the CHEF mechanism[14].

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