

三个包含酰胺型配体铜/锌配合物的合成、结构及荧光性质

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摘要: 合成并通过单晶衍射表征了 3 个配合物 $[\text{CuLCl}_2] \cdot \text{CH}_3\text{CN}$ (**1**), $[\text{CuLBr}_2] \cdot \text{CH}_3\text{CN}$ (**2**) 和 $[\text{ZnL}(\text{NO}_3)_2] \cdot \text{CH}_3\text{CN}$ (**3**) (L=2-(5-氯-8-喹啉氧基)-1-(吡咯烷-1-基)乙酮)。在配合物 **1** 和 **2** 中, 五配位的铜离子采取扭曲的四方锥配位构型, 与来自配体 L 的 2 个氧原子和 1 个氮原子及 2 个卤离子配位。而在配合物 **3** 中, 锌离子与 1 个三齿配位的配体 L, 1 个单齿配位的硝酸根和 1 个双齿配位的硝酸根配位, 配位构型为扭曲的八面体。乙腈溶液中, 配合物 **1** 和 **2** 在 410 nm 处的最大荧光发射峰与配体 L 的相似, 强度有所降低。而配合物 **3** 由于配体到锌离子之间的能量转移, 最大荧光发射峰红移至 430 nm。

关键词: 铜配合物; 锌配合物; 酰胺型配体; 晶体结构; 荧光

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Syntheses, Crystal Structures and Fluorescence Properties of Three Cu(II)/Zn(II) Complexes with an Amide Type Ligand

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Abstract: Three complexes, $[\text{CuLCl}_2] \cdot \text{CH}_3\text{CN}$ (**1**), $[\text{CuLBr}_2] \cdot \text{CH}_3\text{CN}$ (**2**) and $[\text{ZnL}(\text{NO}_3)_2] \cdot \text{CH}_3\text{CN}$ (**3**) (L=2-(5-chloroquinolin-8-yloxy)-1-(pyrrolidin-1-yl)ethanone), were synthesized and characterized by X-ray diffraction. In each of complexes **1** and **2**, the five-coordinated Cu(II) ion is in a distorted tetragonal pyramid with a NO_2 donor set from one ligand L and two halide anions. However, the Zn(II) ion in complex **3** is surrounded by one tridentate ligand L and two nitrate anions, one of which is monodentate and the other is bidentate, thus giving distorted octahedral coordination geometry. In CH_3CN solution, complexes **1** and **2** exhibit similar peak at 410 nm as that of the ligand L, while with a decrease of the fluorescence intensity. However, the emission band of complex **3** red-shifts to 430 nm because of energy transferring from the ligand L to the Zn(II) ion. CCDC: 1474712, **1**; 1474713, **2**; 1474714, **3**.

Keywords: Cu(II) complex; Zn(II) complex; amide type ligand; crystal structure; fluorescence

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It is well known that the amide type ligands, which are effective chelating agents for lanthanide(III) ions and have terminal-group effects, will shield the encapsulated ions from interaction with the surroundings effectively to achieve strong characteristic fluorescent emission of the centre metal ions^[1-6]. Besides, some acetamide ligands bearing quinolinyloxy unit have also been used for the recognition of important transition metal ions, such as Zn(II), Cd(II) or Hg(II), due to the metal-induced fluorescence emission enhancement^[7-8]. Our previous work shows that this kind of ligands could coordinate to Cu(II)/Zn(II) ions to form stable complexes^[9-10]. Thus, in this paper, three Cu(II)/Zn(II) complexes containing an amide type ligand were synthesized and characterized by X-ray diffraction. In addition, the fluorescence properties of all compounds are investigated in detail.

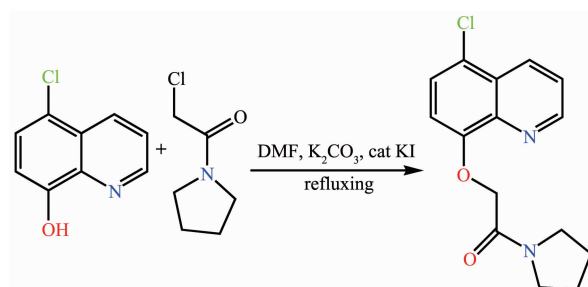
1 Experimental

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. ^1H NMR spectra of the ligand L 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.

1.2 Preparations of the complexes

The ligand L (Scheme 1) was prepared according to literature methods^[5], while using 2-chloro-1-(pyrrolidin-1-yl)ethanone instead of 2-chloro-*N*-phenylacetamide. Yield: 69%; m.p. 89~92 °C. Elemental analysis for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_2\text{Cl}$ (%): Calcd: C: 65.29; H: 4.19; N: 8.96; Found: C: 65.18; H: 4.33; N: 8.88. ^1H NMR (400 MHz, CDCl_3): δ 8.97~8.98 (1H, dd, Ar-H), 8.50~8.53 (1H, dd, Ar-H), 7.72~7.75 (1H, q, Ar-H), 7.67~7.69 (1H, d, Ar-H), 7.13~7.17 (1H, d, Ar-H), 4.99 (2H, s, CH_2), 3.53~3.56 (2H, t, CH_2), 3.33~3.37 (2H, t, CH_2),



Scheme 1 Synthetic scheme for ligand L

1.87~1.92 (2H, m, CH_2), 1.77~1.82 (2H, m, CH_2). FT-IR (cm^{-1}): $\nu(\text{C}=\text{O})$ 1 682, $\nu(\text{C}=\text{N})$ 1 598, $\nu(\text{Ar}-\text{O}-\text{C})$ 1 254.

The ligand L (0.1 mmol) and $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.1 mmol) were dissolved in an acetonitrile solution (4 mL). After stirred for about 1 h, the mixture was filtered and set aside to crystallize at room temperature. The crystals suitable for single crystal X-ray analyses are obtained after few days. The synthesis of **2** and **3** is similar to that of **1**, while using CuBr_2 and $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ instead of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, respectively.

1: orange rods. Yield: 59% (based on L). Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_3\text{O}_2\text{Cl}_3\text{Cu}$ (%): C, 43.79; H, 3.89; N, 9.01. Found(%): C, 43.62; H, 4.01; N, 8.98. IR (KBr, cm^{-1}): $\nu(\text{C}\equiv\text{N})$, 2 249, $\nu(\text{C}=\text{O})$ 1 624, $\nu(\text{C}=\text{N})$ 1 588, $\nu(\text{Ar}-\text{O}-\text{C})$ 1 242.

2: orange rods. Yield 68% (based on L). Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_3\text{O}_2\text{ClBr}_2\text{Cu}$ (%): C, 36.78; H, 3.27; N, 7.57. Found (%): C, 36.67; H, 3.19; N, 7.52. IR (KBr, cm^{-1}): $\nu(\text{C}\equiv\text{N})$, 2 248, $\nu(\text{C}=\text{O})$ 1 622, $\nu(\text{C}=\text{N})$ 1 589, $\nu(\text{Ar}-\text{O}-\text{C})$ 1 238.

3: colorless rods. Yield 68% (based on L). Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_5\text{O}_8\text{ClZn}$ (%): C, 39.18; H, 3.48; N, 13.44. Found(%): C, 39.07; H, 3.39; N, 13.52. IR (KBr, cm^{-1}): $\nu(\text{C}\equiv\text{N})$, 2 247, $\nu(\text{C}=\text{O})$ 1 634, $\nu(\text{C}=\text{N})$ 1 588, $\nu(\text{Ar}-\text{O}-\text{C})$ 1 244, $\nu_1(\text{NO}_3)$ 1 485, $\nu_4(\text{NO}_3)$ 1 385 and 1 302.

1.3 X-ray crystallography

The X-ray diffraction measurement for complexes **1**~**3** 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 φ - ω scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program^[11]. The structures were solved by

Table 1 Selected crystallographic data for complexes 1~3

	1	2	3
Empirical formula	C ₁₇ H ₁₈ N ₃ O ₂ Cl ₃ Cu	C ₁₇ H ₁₈ N ₃ O ₂ ClBr ₂ Cu	C ₁₇ H ₁₈ N ₃ O ₈ ClZn
Formula weight	466.23	555.15	521.18
<i>T</i> / K	296(2)	296(2)	296(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>Pbcn</i>	<i>Pbcn</i>	<i>P2₁/c</i>
<i>a</i> / nm	1.475 9(13)	1.491 0(9)	0.868 9(10)
<i>b</i> / nm	1.193 2(11)	1.201 3(7)	2.278(2)
<i>c</i> / nm	2.203(2)	2.287 2(14)	1.089 7(12)
β / (°)			91.49(2)
<i>V</i> / nm ³	3.880(6)	4.097(4)	2.156(4)
<i>Z</i>	8	8	4
<i>D_c</i> / (g·cm ⁻³)	1.596	1.800	1.606
Unique reflections	3 421	3 614	3 780
<i>R</i> _{int}	0.106 8	0.050 4	0.064 8
Goodness of fit (on <i>F</i> ²)	1.054	1.030	1.022
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ =0.058 2, <i>wR</i> ₂ =0.119 1	<i>R</i> ₁ =0.035 6, <i>wR</i> ₂ =0.074 8	<i>R</i> ₁ =0.058 2, <i>wR</i> ₂ =0.121 9
<i>R</i> indices (all data)	<i>R</i> ₁ =0.088 4, <i>wR</i> ₂ =0.133 0	<i>R</i> ₁ =0.064 5, <i>wR</i> ₂ =0.084 5	<i>R</i> ₁ =0.118 4, <i>wR</i> ₂ =0.148 3
Largest peak and hole / (e·nm ⁻³)	473 and -543	401 and -480	329 and -424

direct methods and refined by fullmatrixleast-square on F^2 using the SHELX-97 program^[12]. All non-hydrogen atoms were refined anisotropically. The H atoms for water molecules are located from difference Fourier map and refined with restraints in bond length and thermal parameters. 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 1~3 are summarized in Table 1.

CCDC: 1474712, 1; 1474713, 2; 1474714, 3.

2 Results and discussion

2.1 Crystal structures of the complexes

Complexes 1 and 2 are isostructural and crystallize in the orthorhombic, space group *Pbcn*. As shown in Fig.1, in each complex, the Cu(II) ion is five-coordinated by one amide ligand with NO₂ donor set and two halide anions (chloride for 1 and bromide for 2). Selected bond lengths and angles are summarized in Table 2. According to the Addison rule^[9], the geometric index τ is 0.285 5 and 0.396 1 for Cu(II)

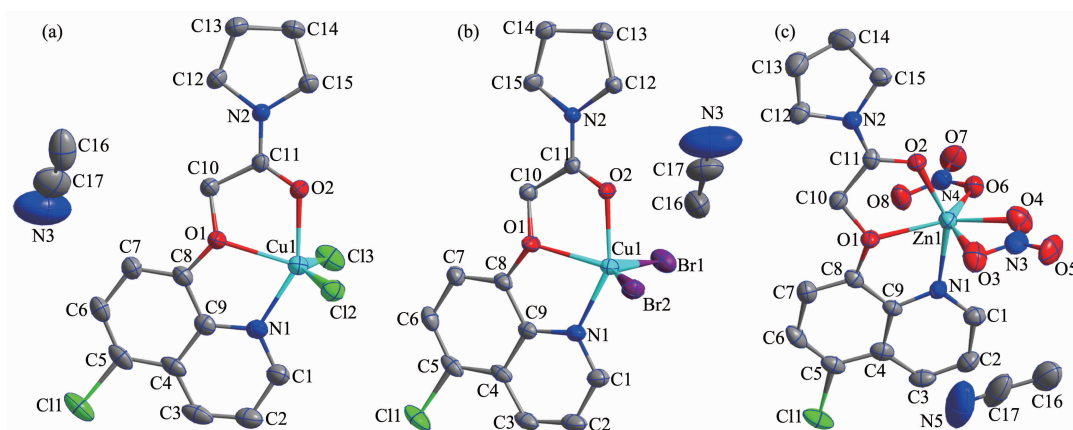


Fig.1 Molecular structures of complexes 1~3 (a~c) shown with 30% probability displacement ellipsoids

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

1					
Cu1-N1	0.200 4(5)	Cu1-O1	0.222 0(4)	Cu1-O2	0.201 1(4)
Cu1-Cl2	0.222 0(2)	Cu1-Cl3	0.221 8(2)		
Cl2-Cu1-O1	114.75(13)	N1-Cu1-O2	148.83(17)	N1-Cu1-Cl2	96.65(15)
N1-Cu1-O1	75.54(16)	N1-Cu1-Cl3	96.95(15)	O2-Cu1-Cl2	97.09(13)
O2-Cu1-O1	73.31(14)	O2-Cu1-Cl3	94.53(14)	Cl3-Cu1-Cl2	131.70(9)
Cl3-Cu1-O1	113.50(12)				
2					
Cu1-N1	0.202 1(3)	Cu1-O1	0.219 8(3)	Cu1-O2	0.201 7(3)
Cu1-Br1	0.240 12(12)	Br2-Cu1	0.238 21(11)		
Br2-Cu1-Br1	127.62(4)	O2-Cu1-N1	151.39(13)	O2-Cu1-Br2	96.47(9)
O2-Cu1-Br1	94.58(9)	O2-Cu1-O1	74.69(10)	N1-Cu1-Br2	97.66(11)
N1-Cu1-Br1	96.27(11)	N1-Cu1-O1	76.70(12)	O1-Cu1-Br2	120.76(9)
O1-Cu1-Br1	111.55(8)				
3					
Zn1-N1	0.205 8(5)	Zn1-O1	0.222 2(4)	Zn1-O2	0.202 1(4)
Zn1-O3	0.237 1(6)	Zn1-O4	0.208 2(5)	Zn1-O6	0.201 4(5)
O6-Zn1-O2	99.22(16)	N1-Zn1-O4	103.9(2)	O6-Zn1-O3	140.71(19)
O6-Zn1-N1	100.05(18)	O6-Zn1-O1	124.96(16)	O2-Zn1-O3	94.69(18)
O2-Zn1-N1	146.61(17)	O2-Zn1-O1	73.08(15)	N1-Zn1-O3	87.33(19)
O6-Zn1-O4	85.4(2)	N1-Zn1-O1	73.54(16)	O4-Zn1-O3	55.5(2)
O2-Zn1-O4	104.6(2)	O4-Zn1-O1	149.7(2)	O1-Zn1-O3	94.22(19)

ion in complexes **1** and **2**, respectively, indicating that the coordination geometry of Cu(II) ion in each complex is a distorted tetragonal pyramid. It is worth noting that the coordination behavior of the ligand **L** in both complexes is quite different to those in $[\text{CuL}^1_2\text{Cl}_2] \cdot \text{DMF}$ and $[\text{CuL}^2_2\text{Cl}_2]$, ($\text{L}^1 = N$ -(4-chlorophenyl)-2-(quinolin-8-yloxy)acetamide, $\text{L}^2 = N,N$ -diphenyl-2-(quinolin-8-yloxy)acetamide)^[10]. In the literature complexes, the carbonyl oxygen atom of the amide type ligands did not take part in coordination to center Cu(II) ion.

By contrast, the Zn(II) ion in complex **3** (Fig.1c) is surrounded by one tridentate ligand **L** and two nitrate anions, one of which is monodentate and the other is bidentate, thus giving distorted octahedral coordination geometry. Its structure is different from that of $[\text{ZnL}^3(\text{NO}_3)_2] \cdot \text{CH}_3\text{CN}$ ($\text{L}^3 = N$ -(naphthalen-1-yl)-2-(quinolin-8-yloxy)acetamide), in which the ligand L^3 is also tridentate while two nitrate anions are both monodentate^[9]. As expected, there are no classic hyd-

rogen bonds in the structures of all three complexes.

2.2 IR spectra

The IR spectra of free ligand **L** show strong band at 1 682 cm^{-1} , which is attributable to stretch vibrations of the carbonyl group ($\nu(\text{C}=\text{O})$). The peak at 1 598 cm^{-1} should be assigned to the $\nu(\text{C}=\text{N})$, and the peak at 1 254 cm^{-1} to $\nu(\text{Ar}-\text{O}-\text{C})$, respectively. In three complexes, the $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N}-\text{N})$ and $\nu(\text{quinoline C}=\text{N})$ shifts to lower wavenumber in three complexes, indicating that carbonyl oxygen, ethereal oxygen and quinoline nitrogen atoms take part in coordination^[9]. In addition, the intense absorption bands in the spectra of complex **3** associated with the asymmetric stretching appear at 1 385, 1 302 cm^{-1} (ν_4) and 1 485 cm^{-1} (ν_1), clearly establishing that two NO_3^- groups are monodentate and bidentate ligands, respectively^[13]. The $\nu(\text{C} \equiv \text{N})$ bands in complexes **1~3** appear at around 2 250 cm^{-1} , clearly showing the existence of CH_3CN molecules. It is in accordance with the result

of the crystal structure study.

2.3 UV spectra

The UV spectra of L, and complexes **1**~**3** in CH₃CN solution (concentration: 1×10^{-5} mol·L⁻¹) were measured at room temperature (Fig.2). The spectra of L features two main bands located at 244 ($\epsilon=156\ 000$ L·mol⁻¹·cm⁻¹) and 316 nm ($\epsilon=19\ 500$ L·mol⁻¹·cm⁻¹), which should be assigned to characteristic π - π^* transitions centered on quinoline ring and the acetamide unit, respectively^[9-10]. Similar bands at 243 ($\epsilon=224\ 000$ L·mol⁻¹·cm⁻¹) and 318 ($\epsilon=42\ 900$ L·mol⁻¹·cm⁻¹) nm, 243 ($\epsilon=198\ 000$ L·mol⁻¹·cm⁻¹) and 322 ($\epsilon=40\ 000$ L·mol⁻¹·cm⁻¹) nm, 245 ($\epsilon=90\ 000$ L·mol⁻¹·cm⁻¹) and 319 ($\epsilon=10\ 800$ L·mol⁻¹·cm⁻¹) nm in complex **1**~**3**, respectively. The spectra variations indicated that the ligand L takes part in the coordination in three complexes.

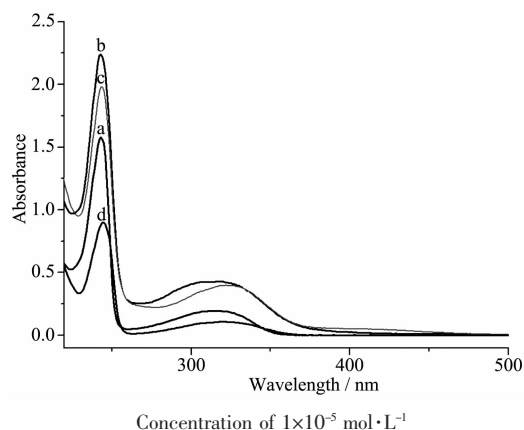


Fig.2 UV spectra of L (a), **1** (b), **2** (c) and **3** (d) in CH₃CN solution at room temperature

2.5 Fluorescence spectra

The fluorescence spectra of the ligand L and complexes **1**~**3** have been studied in CH₃CN solution (concentration: 1×10^{-5} mol·L⁻¹) at room temperature. The results show that the emission spectra of complexes **1** and **2** exhibit only one main peak at 410 nm when excited at 320 nm, which is similar as that of the ligand L (Fig.3). Compared with that of the ligand L, the fluorescence intensity of complexes **1** and **2** decreased dramatically, probably due to the inherent magnetic property of Cu²⁺ ions^[14]. However, the emission band of complex **3** red-shifts to 430 nm (excited at 320 nm), indicating the energy transferring

from the ligand L to the Zn(II) ion^[9,13].

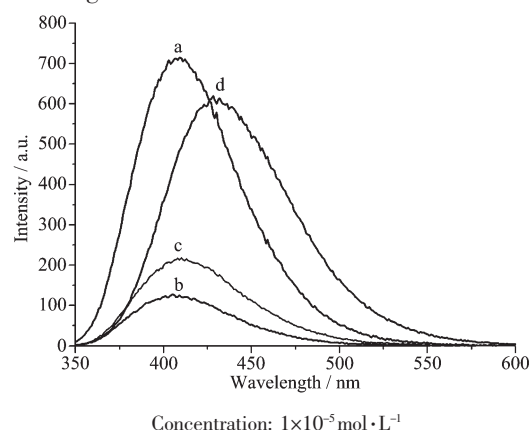


Fig.3 Fluorescence emission spectra of L (a), **1** (b), **2** (c) and **3** (d) in CH₃CN solution at room temperature

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