

含喹啉氧基乙酰胺型配体的锌配合物的合成、 晶体结构及荧光性质

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摘要: 合成并通过单晶衍射表征了一个配合物 $[\text{ZnL}(\text{NO}_3)_2] \cdot \text{CH}_3\text{CN}$ (**1**, $\text{L} = N$ -(1-萘基)-2-(8-喹啉氧基)乙酰胺)。在配合物 **1** 中, 金属锌离子采取扭曲的四方锥的配位构型。来自配体 **L** 的 1 个氧原子, 2 个氮原子及来自 2 个硝酸根的 2 个氧原子和中心锌离子配位。配合物通过分子间的 $\text{N-H} \cdots \text{O}$ 氢键作用构筑成沿 a 轴的链状结构。乙腈溶液中配合物在 414.8 nm 处有强荧光发射。

关键词: 锌配合物; 晶体结构; 荧光

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Zinc Complex with Acetamide Type Ligand Bearing Quinolinylxy Unit: Synthesis, Crystal Structure and Fluorescence Spectra

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Abstract: A complex, $[\text{ZnL}(\text{NO}_3)_2] \cdot \text{CH}_3\text{CN}$ (**1**, $\text{L} = N$ -(naphthalen-1-yl)-2-(quinolin-8-yloxy)acetamide), was synthesized and characterized by X-ray diffraction. In complex **1**, the Zn^{2+} center, possessing a coordination geometry closer to a distorted square-pyramidal, coordinates with one nitrogen atom from the **L** ligand and four oxygen atoms, two of which are from **L** ligand and the others are from two nitrate ligands, respectively. In the crystal, intramolecular $\text{N-H} \cdots \text{O}$ hydrogen bonds link the molecules into chains along the a axis. In CH_3CN solution, the complex **1** exhibits strong emission band at 414.8 nm. CCDC: 848089.

Key words: zinc complex; crystal structure; fluorescence

The amide type ligands with nitrogen and oxygen as electron donor atoms, are effective chelating agents that can form complexes with different metal ions. Recently, bi-, tri-, tetra- and hexapodal amide type ligands have been investigated by Liu and his coworkers^[1-4]. Such ligands, which are flexible in structure, could shield the encapsulated ion from

interaction with the surroundings effectively. They have strong antenna effect to Eu(III) and Tb(III) ^[2-4]. We have also reported some quinolin-8-yloxy substituted acetamide ligands and their fluorescence properties with the rare earth ions^[5-8]. However, the investigations on the complexes of amide ligands with transition metal ions are relatively few. Thus, in this work, a zinc

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complex containing an amide type ligand was synthesized and characterized by X-ray diffraction. In addition, the fluorescence spectra of the ligand and the complex in CH₃CN solution were investigated.

1 Experimental

1.1 Materials and measurements

Solvents and starting materials for synthesis were purchased commercially and used as received. Elemental analyses were carried out on an Elemental Vario EL analyzer. The infrared spectra (IR, $\nu=4\,000\sim 400\text{ cm}^{-1}$) were determined by the KBr disc method on a Nicolet-170SX FTIR spectrophotometer. The UV spectra were recorded on a Shimadzu UV-240 spectrophotometer. Fluorescence spectra were determined on a Hitachi F-4500 FL spectrophotometer. In the measurements of emission and excitation spectra the pass width was 5 nm.

1.2 Preparations of [ZnL(NO₃)₂]·CH₃CN (1)

The ligand *N*-(naphthalen-1-yl)-2-(quinolin-8-yloxy)acetamide (L)^[5] (0.38 g, 1 mmol) was dissolved in acetonitrile (10 mL), then an acetonitrile solution (10 mL) containing zinc nitrate hexahydrate (0.295 g, 1 mmol) was added dropwise at room temperature. After stirring for 2 h, the mixture was filtered and set aside to

crystallize at room temperature for 1 d, giving colorless block crystals, which were collected by filtration, washed with Et₂O and dried in air. Yield ca. 45% based on L. Anal. Calcd. for C₂₃H₁₉N₅O₈Zn (%): C, 49.43; H, 3.43; N, 12.53. Found(%): C, 49.08; H, 3.67; N, 12.20.

1.3 X-ray crystallography

A colorless block crystal with dimensions of 0.20 mm×0.18 mm×0.18 mm was put on 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 at 294 (2) K. Total of 5 962 reflections were collected in the range of $1.88^\circ \leq \theta \leq 25.50^\circ$, of which 4 264 were independent with $R_{\text{int}}=0.027\,4$, and 2 523 with $I>2\sigma(I)$ were considered as observed. Semi-empirical absorption correction was applied to the intensity data using the SADABS program^[9]. The structure was solved by direct methods and refined by fullmatrix least-square on F^2 using the SHELXTL-97 program^[10]. All non-hydrogen atoms were refined anisotropically. All H atoms bounded to C and N atoms were generated geometrically and refined isotropically using the riding mode. A summary of crystal data and details of the structure refinements are listed in Table 1.

CCDC: 848089.

Table 1 Crystal data and structure refinement for the title complex

Empirical formula	C ₂₃ H ₁₉ N ₅ O ₈ Zn	V/nm^3	1.1869(3)
Formula weight	558.8	$D_c/(\text{g}\cdot\text{cm}^{-3})$	1.564
Temperature / K	294(2)	μ/mm^{-1}	1.09
Wavelength / nm	0.071 073	$F(000)$	572
Crystal system	Triclinic	Crystal size / mm	0.16×0.15×0.10
Space group	$P\bar{1}$	θ range for data collection / (°)	1.88 to 25.50
Z	2	Reflections collected	5962
a/nm	0.806 05(13)	Independent reflections (R_{int})	4 264 (0.027 4)
b/nm	1.150 9(2)	Observed reflections ($I>2\sigma(I)$)	2 523
c/nm	1.404 1(2)	Final GooF	1.056
$\alpha/^\circ$	78.571(2)	R_1, wR_2 ($I>2\sigma(I)$)	$R_1=0.069\,7, wR_2=0.148\,8$
$\beta/^\circ$	75.958(3)	R_1, wR_2 (all data)	$R_1=0.123\,8, wR_2=0.173\,8$
$\gamma/^\circ$	71.332(2)		

2 Result and discussion

2.1 Crystal structure of complex 1

As shown in Fig.1, the title complex contains one solvate acetonitrile molecule, with a composition of

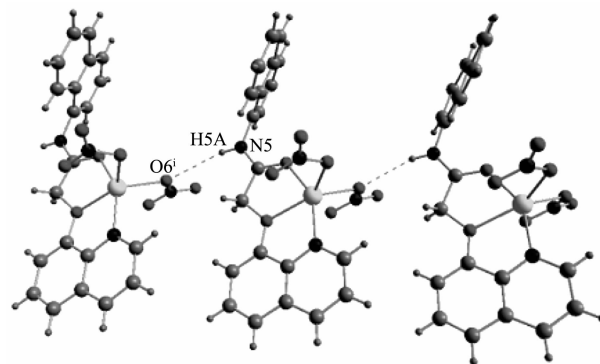
[ZnL(NO₃)₂]·CH₃CN. Selected bond lengths and angles are summarized in Table 2. It can be confirmed that the Zn²⁺ center coordinates with one nitrogen atom from the L ligand and four oxygen atoms, two of which are from L

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$) in the title complex

Zn1-O3	0.204 2(5)	Zn1-O5	0.205 1(4)	Zn1-O7	0.222 4(4)
Zn1-O8	0.203 5(4)	Zn1-N4	0.204 9(5)	O4-N1	0.124 0(7)
O5-N1	0.127 9(7)	O6-N1	0.122 1(7)	O1-N2	0.123 0(8)
O2-N2	0.120 1(8)	O3-N2	0.125 4(8)		
O8-Zn1-O3	98.28(19)	O8-Zn1-N4	146.85(19)	O3-Zn1-N4	104.1(2)
O8-Zn1-O5	101.52(18)	O3-Zn1-O5	87.77(19)	N4-Zn1-O5	103.43(19)
O8-Zn1-O7	72.46(16)	O3-Zn1-O7	135.0(2)	N4-Zn1-O7	74.41(17)
O5-Zn1-O7	137.03(19)				

ligand and the others are from two nitrate ligands, respectively. The distances of $\text{Zn1} \cdots \text{O1}$ and $\text{Zn1} \cdots \text{O4}$ are both 0.254 9 nm, indicating that O1 and O4 atoms do not take part in coordination. The maximal two angles between the coordinate atoms and Zn^{2+} ion are $146.85(19)^{\circ}$ and $137.03(19)^{\circ}$, respectively. According to the Addison rule^[11], the geometric index is 0.16, indicating that the Zn^{2+} ion possesses a coordination geometry closer to a distorted square-pyramidal. However, most bond angles are highly deviated from those of the ideal geometry. Its structure is different from that of aqua [*N*-phenyl-2-(quinolin-8-yloxy)-acetamide]dinitratizinc(II), in which the six-coordinated Zn atom is in a distorted octahedral geometry and an additional water O atom takes part in the coordination^[12]. The basal plane of the square-pyramid is made up of N4, O5, O7 and O8. The bond lengths from Zn^{2+} center to these atoms are in the range of 0.203 5(4)~0.222 4(4) nm. The fifth coordination site is occupied by O3 located axially at 0.204 2 (5) nm. The N-O bond lengths in the two nitrate groups are different. It is obvious that the two nitrate groups lie in dissimilar

coordination environments. In the crystal, intramolecular $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds link the complex molecules into chains along the *a* axis (Fig.2).



Solvent molecules were omitted for clarity; Symmetry code: $i = -1 + x, y, z$

Fig.2 Intramolecular hydrogen bonds of extended chain-like structure along *a* axis

2.2 IR spectra

The IR spectra of L show strong band at $1\,694\text{ cm}^{-1}$, which are attributable to stretch vibrations of the carbonyl group of amide ($\nu(\text{C}=\text{O})$). The peak at $1\,630\text{ cm}^{-1}$ should be assigned to the $\nu(\text{C}=\text{N})$, and the peak at $1\,262\text{ cm}^{-1}$ to $\nu(\text{Ar}-\text{O}-\text{C})$. Upon coordination with Zn^{2+} , the $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{Ar}-\text{O}-\text{C})$ shift by 44, 59 and 5 cm^{-1} , respectively; indicating that carbonyl oxygen atom, ethereal oxygen atom and quinoline nitrogen atom take part in coordination to the metal ion^[13-16]. In addition, two intense absorption bands in the spectra associated with the asymmetric stretching appear at $1\,319\text{ cm}^{-1}$ (ν_4) and $1\,477\text{ cm}^{-1}$ (ν_1), clearly establishing that the NO_3^- groups (C_{2v}) take part in coordination. The difference between the two bands is 158 cm^{-1} , suggesting that the NO_3^- groups in the complexes are monodentate ligands^[17]. It is in accordance with the result of the crystal structure study.

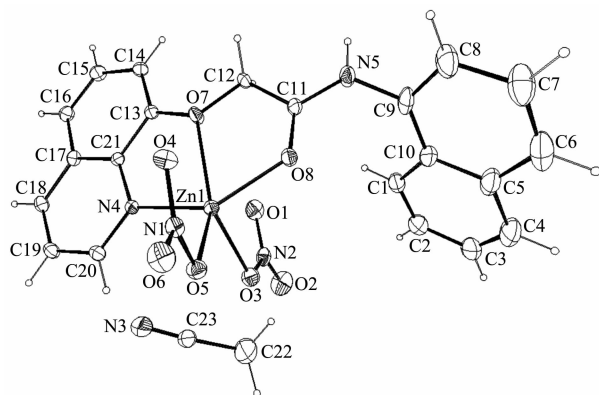


Fig.1 Molecular structure of the title complex shown with 30% probability displacement ellipsoids

2.3 UV spectra

The UV spectra of L and **1** in CH₃CN solution (concentration: 1×10^{-5} mol·L⁻¹) was measured at room temperature (Fig.3). The spectra of L feature three main bands located around 200 ($\epsilon=89\,553$ L·mol⁻¹·cm⁻¹), 221 ($\epsilon=82\,308$ L·mol⁻¹·cm⁻¹) and 292 nm ($\epsilon=14\,322$ L·mol⁻¹·cm⁻¹)^[18]. The bands could be assigned to characteristic π - π^* transitions centered on naphthalene, quinoline ring and the acetamide unit, respectively. They shift to 202 ($\epsilon=115\,032$ L·mol⁻¹·cm⁻¹), 218 ($\epsilon=107\,785$ L·mol⁻¹·cm⁻¹) and 292 nm ($\epsilon=15\,413$ L·mol⁻¹·cm⁻¹) in complex **1**, respectively. The hyperchromicities indicate that the ligand L takes part in the coordination in complex **1**.

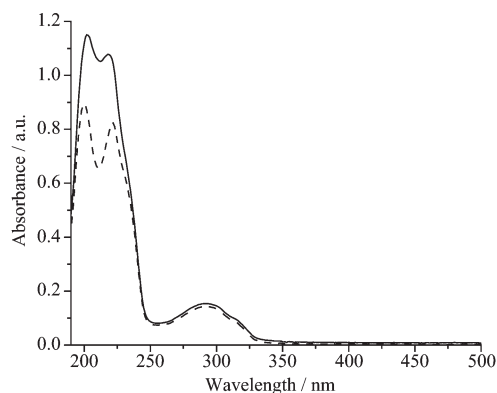


Fig.3 UV spectra of L (dashed line) and complex **1**

2.4 Fluorescence spectra

The fluorescence spectra of L and **1** in CH₃CN solution (concentration: 1×10^{-5} mol·L⁻¹) was measured at room temperature. The excitation wavelengths are both at 314 nm. The emission peak of the complex **1** is at 414.8 nm, but that of the ligand L is at 364.2 nm (Fig.4). It also can be seen that the emission intensity of the complex is much higher than that of the ligand. This

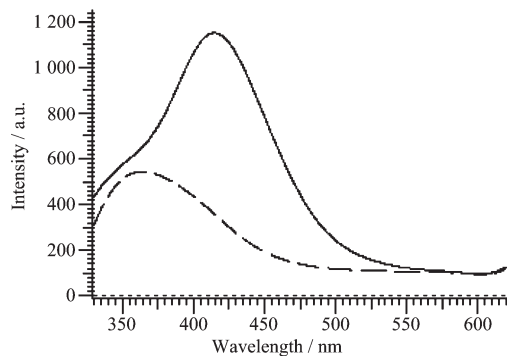


Fig.4 Fluorescence emission spectra of L (dashed line) and complex **1**

is probably due to the energy transfer from the ligand to the Zn(II) ion^[19]. The behavior of Zn²⁺ coordinated to the ligand is in general as that of emissive species leading to a CHEF effect (chelation enhancement of the fluorescence emission).

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