

## 喹啉氧基乙酰胺型配体镉配合物的合成、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  $[\text{CdL}(\text{H}_2\text{O})(\text{NO}_3)]\text{NO}_3 \cdot \text{CH}_3\text{COCH}_3$  (**1**) ( $\text{L} = N$ -甲基  $N$ -苯基-2-(8-喹啉氧基)乙酰胺)。在配合物 **1** 中, 金属镉离子采取扭曲的八面体配位构型。来自配体 **L** 的 1 个氧原子和 2 个氮原子, 2 个硝酸根的 2 个氧原子及配位水分子的 1 个氧原子与中心镉离子配位。配合物通过分子间的  $\text{O}-\text{H} \cdots \text{O}$  氢键作用构筑成沿  $a$  轴的一维链状结构。乙腈溶液中配体 **L** 和配合物 **1** 均在 390 nm 有荧光发射, 但配合物的荧光强度要远低于配体。

**关键词:** 8-羟基喹啉; 乙酰胺; 镉配合物; 晶体结构; 荧光

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### A Cadmium(II) Complex with a Quinolinyloxy Acetamide Ligand: Synthesis, Crystal Structure and Fluorescence Spectra

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**Abstract:**  $[\text{CdL}(\text{H}_2\text{O})(\text{NO}_3)]\text{NO}_3 \cdot \text{CH}_3\text{COCH}_3$  (**1**) ( $\text{L} = N$ -methyl- $N$ -phenyl-2-(quinolin-8-yloxy)acetamide), was synthesized and characterized by X-ray diffraction. In complex **1**, the Cd(II) center is coordinated with two O atoms and one N atom from one ligand **L**, two O atoms from two mono-dentate nitrate anions and one O atom from one water molecule, possessing a distorted octahedral coordination geometry. In the crystal, intramolecular  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds between the coordinated water molecules and free nitrate O atoms link the complexes into chains along the  $a$  axis. In  $\text{CH}_3\text{CN}$  solution, both ligand **L** and complex **1** exhibit emission band at 390 nm. However, the emission intensity of **1** is much lower than that of the ligand **L**. CCDC: 958121.

**Key words:** 8-hydroxyquinoline; acetamide; cadmium complex; crystal structure; fluorescence

## 0 Introduction

Recently, quinolinyloxy acetamide ligands and their fluorescence properties with rare earth ions have attracted much more attention due to their strong antenna effect to Eu(III) or Tb(III) ion<sup>[1-5]</sup>. On the other hand, such ligands could form stable complexes with transition metal ions and thus to act as fluorescent

sensor for Cd(II) or Zn(II) ion<sup>[6-8]</sup>. In addition, Cd(II) ion with  $d^{10}$  configuration can adopt a variety of coordination geometries and is particularly useful for the construction of coordination<sup>[6-7]</sup>. Thus, in this work, a Cd(II) complex containing a quinolin-8-yloxy acetamide ligand **L** ( $\text{L} = N$ -methyl- $N$ -phenyl-2-(quinolin-8-yloxy)acetamide) was synthesized and characterized by X-ray diffraction. In addition, the fluorescence

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spectra of the ligand and complex **1** in CH<sub>3</sub>CN 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 <sup>1</sup>H NMR spectra were recorded with a Bruker AV400 NMR instrument in deuterated acetone with TMS as internal standard. The mass spectrum was obtained on a TRACE DSQ GC/MS. 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. The UV spectra were recorded on a Purkinje General TU-1901 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 the ligand L and [CdL(H<sub>2</sub>O)(NO<sub>3</sub>)]NO<sub>3</sub>·CH<sub>3</sub>COCH<sub>3</sub> (**1**)

The ligand L was synthesized according to the literature procedure<sup>[9]</sup>. M.p. 117~118 °C; <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, ppm):  $\delta$  3.48 (3H, s, CH<sub>3</sub>), 4.78 (2H, s, CH<sub>2</sub>), 7.05~8.88 (11H, m, phenyl and quinoline); MS,  $m/z$ : 293 [M+1]<sup>+</sup>. IR (KBr, cm<sup>-1</sup>):  $\nu$ (C=O) 1 681,  $\nu$ (C=N) 1 618,  $\nu$ (Ar-O-C) 1 258.

The ligand L (0.029 2 g, 0.1 mmol) was dissolved in acetone (3 ml), then an acetone solution (2 ml)

containing cadmium nitrate tetrahydrate (0.031 8 g, 0.1 mmol) was added dropwise at room temperature. After stirring for 2 h, the mixture was filtered and set aside to crystallize for several days, giving colorless block crystals of **1**, which were collected by filtration, washed with Et<sub>2</sub>O and dried in air. Yield ca. 52% based on L. Anal. calc. for C<sub>21</sub>H<sub>22</sub>N<sub>4</sub>O<sub>10</sub>Cd (%): C, 41.84; H, 3.68; N, 9.29. Found(%): C, 41.57; H, 3.42; N, 9.00. IR (KBr, cm<sup>-1</sup>):  $\nu$ (OH) 3 428,  $\nu$ (C=O) 1 634,  $\nu$ (C=N) 1 588,  $\nu$ (Ar-O-C) 1 218,  $\nu_4$ (NO<sub>3</sub>) 1 478,  $\nu_1$ (NO<sub>3</sub>) 1 326,  $\nu$ (OH) 618.

### 1.3.1 X-ray crystallography

The X-ray diffraction measurement for **1** was 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<sup>[10]</sup>. The structures were solved by direct methods and refined by full matrix least-square on  $F^2$  using the SHELXTL-97 program<sup>[11]</sup>. All non-hydrogen atoms were refined anisotropically. H atoms for the 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 **1** are summarized in Table 1.

CCDC: 958121.

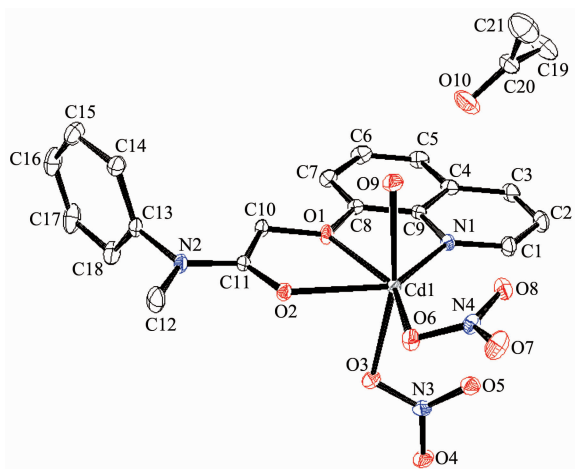
Table 1 Crystal data and structure refinement for **1**

Empirical formula	C <sub>21</sub> H <sub>22</sub> N <sub>4</sub> O <sub>10</sub> Cd	$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.543
Formula weight	602.83	Absorption coefficient / mm <sup>-1</sup>	0.9
$T / \text{K}$	296(2)	Crystal size / mm	0.21×0.16×0.02
$\lambda / \text{nm}$	0.071 073	$F(000)$	1 216
Crystal system	Monoclinic	$\theta$ range for data collection / (°)	$2.07 \leq \theta \leq 28.26$
Space group	$P2_1/c$	Index ranges ( $h, k, l$ )	$-10 \leq h \leq 10, -15 \leq k \leq 26, -20 \leq l \leq 22$
$a / \text{nm}$	0.815 85(5)	Reflections collected / Unique ( $R_{int}$ )	16 626 / 6 294 (0.033 2)
$b / \text{nm}$	1.971 75(12)	Data / restraints / parameters	6 294 / 3 / 334
$c / \text{nm}$	1.670 15(10)	Goodness-of-fit (GOF) on $F^2$	1.034
$\beta / (^\circ)$	104.965(3)	Final $R$ indices ( $I > 2\sigma(I)$ )	$R_1=0.030\,5; wR_2=0.078\,9$
$V / \text{nm}^3$	2.595 6(3)	$R$ indices (all data)	$R_1=0.040\,4; wR_2=0.083\,8$
$Z$	4	Largest peak and hole / ( $\text{e}\cdot\text{nm}^{-3}$ )	598 and -376

## 2 Results and discussion

### 2.1 Crystal structure of complex **1**

As shown in Fig.1, the title complex contains one solvate acetone molecule, with a composition of  $[\text{CdL}(\text{H}_2\text{O})(\text{NO}_3)]\text{NO}_3 \cdot \text{CH}_3\text{COCH}_3$ . Selected bond lengths and angles are summarized in Table 2. It can be confirmed that the Cd(II) center possesses a coordination geometry closer to a distorted octahedral geometry with the donor centers of two O atoms and one N atom from the ligand, two O atoms from two mono-dentate nitrate anions and one O atom from one water molecule. The bond angles of O6-Cd1-O1 and O9-Cd1-O3 are  $151.54(6)^\circ$  and  $167.10(7)^\circ$ , respectively; confirming that in **1**, the four atoms O1 (from the ligand L), O3, O6 (from two nitrate groups) and O9 (from water molecule) are in the basal plane. The axial positions are occupied with N1 atom and O2 atom from the ligand L. In complex **1**, most bond angles are highly deviated from those of the ideal geometry. Although the coordination behavior of the



$\text{m}^{-1}$  should be assigned to the  $\nu(\text{C}=\text{N})$ , and the peak at  $1\,258\text{ cm}^{-1}$  to  $\nu(\text{Ar}-\text{O}-\text{C})$ . Upon coordination with  $\text{Cd}(\text{II})$  ion, the  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}=\text{N})$  and  $\nu(\text{Ar}-\text{O}-\text{C})$  shift by 47, 30 and  $40\text{ cm}^{-1}$ , respectively; indicating that carbonyl oxygen atom, ethereal oxygen atom and quinoline nitrogen atom take part in coordination to the metal ion<sup>[7-8]</sup>. The aqueous  $\nu(\text{OH})$  bands appear at  $3\,428\text{ cm}^{-1}$  and  $\rho(\text{OH})$  bands at  $618\text{ cm}^{-1}$  showing that there is coordinative water molecule in **1**<sup>[8]</sup>. In addition, two intense absorption bands in the spectra associated with the asymmetric stretching appear at  $1\,478\text{ cm}^{-1}$  ( $\nu_1$ ) and  $1\,326\text{ cm}^{-1}$  ( $\nu_4$ ), clearly establishing that the  $\text{NO}_3^-$  groups ( $C_{2v}$ ) take part in coordination. The difference between the two bands is  $1\,52\text{ cm}^{-1}$ , suggesting that the  $\text{NO}_3^-$  groups in **1** are mono-dentate ligands<sup>[7-8,12]</sup>. It is in accordance with the result of the crystal structure study.

### 2.3 UV spectra

The UV spectra of **L** and **1** in  $\text{CH}_3\text{CN}$  solution (concentration:  $1 \times 10^{-5}\text{ mol} \cdot \text{L}^{-1}$ ) was measured at room temperature (Fig.3). The spectra of **L** feature three main bands located around 200 ( $\varepsilon=106\,538\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ), 239 ( $\varepsilon=74\,512\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) and 298 nm ( $\varepsilon=8\,103\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ )<sup>[13]</sup>. The bands could be assigned to characteristic  $\pi-\pi^*$  transitions centered on naphthalene, quinoline ring and the acetamide unit, respectively. They shift to 201 ( $\varepsilon=56\,623\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ), 240 ( $\varepsilon=25\,041\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) and 299 nm ( $\varepsilon=2\,619\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) in complex **1**, respectively. The hypochromicities indicate that the ligand **L** takes part in the coordination in complex **1**.

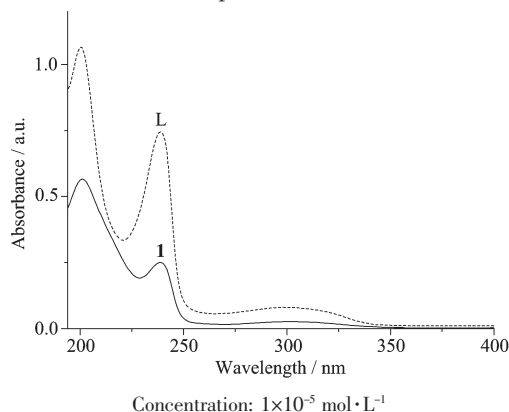


Fig.3 UV spectra of **L** and **1** in  $\text{CH}_3\text{CN}$  solution at room temperature

### 2.4 Fluorescence spectra

The fluorescence spectra of the ligand **L** and **1** in  $\text{CH}_3\text{CN}$  solution (concentration:  $1 \times 10^{-5}\text{ mol} \cdot \text{L}^{-1}$ ) was measured at room temperature. The excitation and emission wavelengths of both compounds are at 240 and 390 nm, respectively (Fig.4). It also can be seen that the emission intensity of **1** is much lower than that of the ligand **L**. This is probably due to the coordination of  $\text{Cd}(\text{II})$  ion influencing the fluorescence emission of the ligand **L**<sup>[14]</sup>.

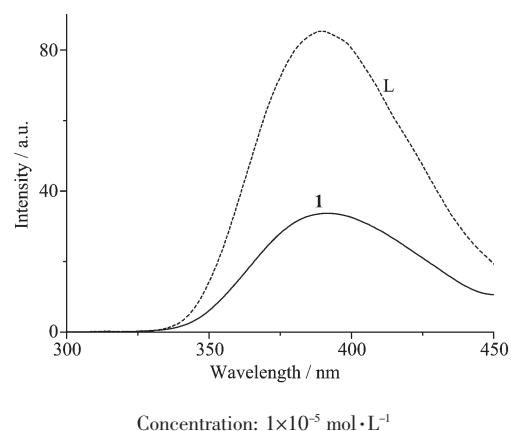


Fig.4 Fluorescence emission spectra of **L** and **1** in  $\text{CH}_3\text{CN}$  solution at room temperature

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