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喹啉-8-甲醛乙酰腙锌/镉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{[Zn(HL)(H_2O)(SO_4)]·H_2O}$_n$ (**1**),[Cd(HL)Cl_2] (**2**)和[Cd(HL)I_2] (**3**)的结构(HL 为喹啉-8-甲醛乙酰腙)。单晶衍射结果表明,配合物 **1** 中,中心 Zn(Ⅱ)离子的配位构型为扭曲的八面体,与来自 1 个中性三齿配体 HL 的 ONN 原子供体,1 个水分子和 2 个 μ_2 桥联的硫酸根配位,从而形成沿 *b* 轴方向的一维链。配合物 **2** 和 **3** 中 Cd(Ⅱ)与 1 个中性三齿配体 HL 和 2 个卤素阴离子(**2** 中为氯离子,**3** 中为碘离子)配位,配位构型为扭曲的四方锥。乙腈溶液中,配合物 **3** 与配体 HL 几乎无荧光发射,而配合物 **1** 和 **2** 分别在 428 和 408 nm 处有强荧光。

关键词: 酰腙; 锌配合物; 镉配合物; 喹啉; 荧光

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Crystal Structures and Fluorescence Property of Zn(Ⅱ)/Cd(Ⅱ) Complexes Based on *N*-((quinolin-8-yl)methylene)acetohydrazide

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Abstract: Three complexes, namely {[Zn(HL)(H_2O)(SO_4)]·H_2O}$_n$ (**1**), [Cd(HL)Cl_2] (**2**) and [Cd(HL)I_2] (**3**) (HL=*N*-((quinolin-8-yl)methylene)acetohydrazide) have been synthesized and characterized by single crystal X-ray diffraction, elemental analysis and IR spectroscopy. X-ray diffraction analysis results show that in complex **1**, the Zn(Ⅱ) ion with a distorted octahedron coordination geometry is six-coordinated, involving one coordinated water molecule, one ONN donor set of an neutral ligand HL, and two O atoms from two independent μ_2-bridged sulfate anions, thus forming one dimension chain-like framework along *b* axis. However, the coordination geometry of the Cd(Ⅱ) ion in each of complexes **2** and **3** is a distorted square planar geometry with a tridentate acylhydrazone ligand and two halide anions (chloride for **2**, while iodide for **3**). In CH_3CN solution, the ligand HL and complex **3** exhibit almost none fluorescence emission, whilst complexes **1** and **2** show remarkable peaks at about 428 and 408 nm, respectively. CCDC: 1562151, **1**; 1562152, **2**; 1562153, **3**.

Keywords: acylhydrazone; Zn(Ⅱ) complex; Cd(Ⅱ) complex; quinoline; fluorescence

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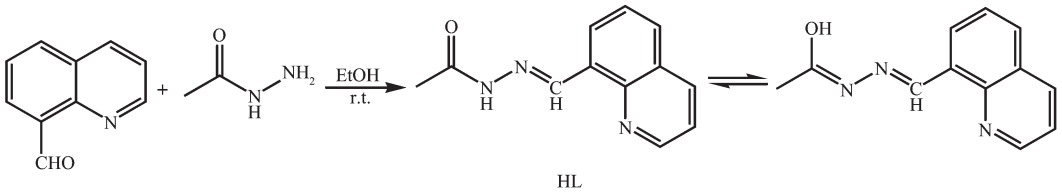
Schiff bases are an important class of ligands in coordination chemistry and have been found extensive application in different fields [1-2]. As one of the most promising systems, the relevant semicarbazones and thiosemicarbazones involve condensed heterocycle, especially quinoline, have been paid much attention due to their potentially biological activities[3-6]. However, acylhydrazones, as their structurally analogous, have been paid much less attention[7-8]. Recently, several quinoline based acylhydrazone chemosensors for the fluorescent detection of metal ions have been reported in the literature, most of which function by coordination reaction with ions[9-11]. Nevertheless, the crystal structures of corresponding complexes are relatively scarce[11].

Our previous work also shows that the acylhydrazone ligand HL (Scheme 1), namely *N*-((quinolin-8-yl)methylene)acetohydrazide is an excellent fluorescent probe for the detection for Zn(Ⅱ) ions[11]. Therefore, in this paper, three Zn(Ⅱ) and Cd(Ⅱ) complexes with HL have been synthesized and structural determined by single-crystal X-ray diffraction. In addition, the fluorescence properties of the complexes in CH_3CN solution were investigated.



HL

Scheme 1 Synthesis route of HL

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 (ν=4 000~400 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-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 1~3

As shown in Scheme 1, the ligand HL was produced by condensation of 8-formylquinoline and acethydrazide in ethanol at room temperature according to the literature method[11]. The complexes **1~3** were generated by reaction of the ligand HL (5 mmol) with equimolar of $ZnSO_4$, $CdCl_2$ and CdI_2 in methanol solution (10 mL) at room temperature for 1 h, respectively. Crystals suitable for X-ray diffraction analysis were obtained by evaporating the corresponding reaction solutions at room temperature.

1: Colorless plates. Anal. Calcd. for $C_{12}H_{15}N_3O_7SZn$ (%): C: 35.09; H: 3.68; N: 10.23. Found(%): C: 34.75; H: 3.85; N: 9.94. FT-IR (cm^{-1}): ν(C=O) 1 655, ν(C=N) 1 592, $\nu(C=N)_{pyrazine}$ 1 560.

2: Colorless blocks. Anal. Calcd. For $C_{12}H_{11}N_3OCl_2Cd$(%):C: 36.35; H: 2.80; N: 10.60. Found (%): C: 36.42; H: 3.05; N: 10.37. FT-IR (cm^{-1}): ν(C=O) 1 654, ν(C=N) 1 590, $\nu(C=N)_{pyrazine}$ 1 558.

3: Colorless blocks. Anal. Calcd. For $C_{12}H_{11}N_3OI_2Cd$(%): C: 24.87; H: 1.91; N: 7.25. Found(%): C: 25.00; H: 2.18; N: 7.02. FT-IR (cm^{-1}): ν(C=O) 1 646, ν(C=N) 1 586, $\nu(C=N)_{pyrazine}$ 1 555.

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 (λ=0.071 073 nm) by using φ-ω scan mode at 296(2) K. Semi-empirical absorption correction was applied to the intensity data using the SADABS program[12]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELX-97 program[13]. 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: 1562151, **1**; 1562152, **2**; 1562153, **3**.

Table 1　Crystal data and structure refinement for complexes 1~3

	1	2	3
Empirical formula	$C_{12}H_{15}N_3O_7SZn$	$C_{12}H_{11}N_3OCl_2Cd$	$C_{12}H_{11}N_3OI_2Cd$
Formula weight	410.70	396.54	579.44
Size / mm	0.15×0.12×0.06	0.20×0.18×0.16	0.18×0.16×0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a / nm	1.033 9(7)	0.792 90(19)	0.746 79(12)
b / nm	0.664 5(4)	1.523 4(3)	1.659 7(2)
c / nm	2.179 5(14)	1.404 0(3)	1.263 00(12)
β / (°)	93.915(11)	123.322(10)	90.132 0(10)
V / nm^3	1.493 8(16)	1.417 1(5)	1.565 4(3)
Z	4	4	4
D_c / (g·cm^{-3})	1.826	1.859	2.459
Unique	2 616	2 495	2 756
R_{int}	0.072 7	0.021 1	0.022 0
GOF	1.032	1.070	1.053
R indices [$I>2\sigma(I)$]	R_1=0.044 3, wR_2=0.079 5	R_1=0.026 0, wR_2=0.063 5	R_1=0.026 9, wR_2=0.059 7
R indices (all data)	R_1=0.091 6, wR_2=0.092 7	R_1=0.031 4, wR_2=0.066 8	R_1=0.032 7, wR_2=0.062 5

2　Results and discussion

2.1　Crystal structures description

The diamond drawings of complexes **1~3** are shown in Fig.1. Selected bond distances and angles are listed in Table 2. As shown in Fig.1a, **1** contains one discrete cationic Zn(Ⅱ) complex and one crystal water molecule in the asymmetric unit. The center Zn(Ⅱ) ion

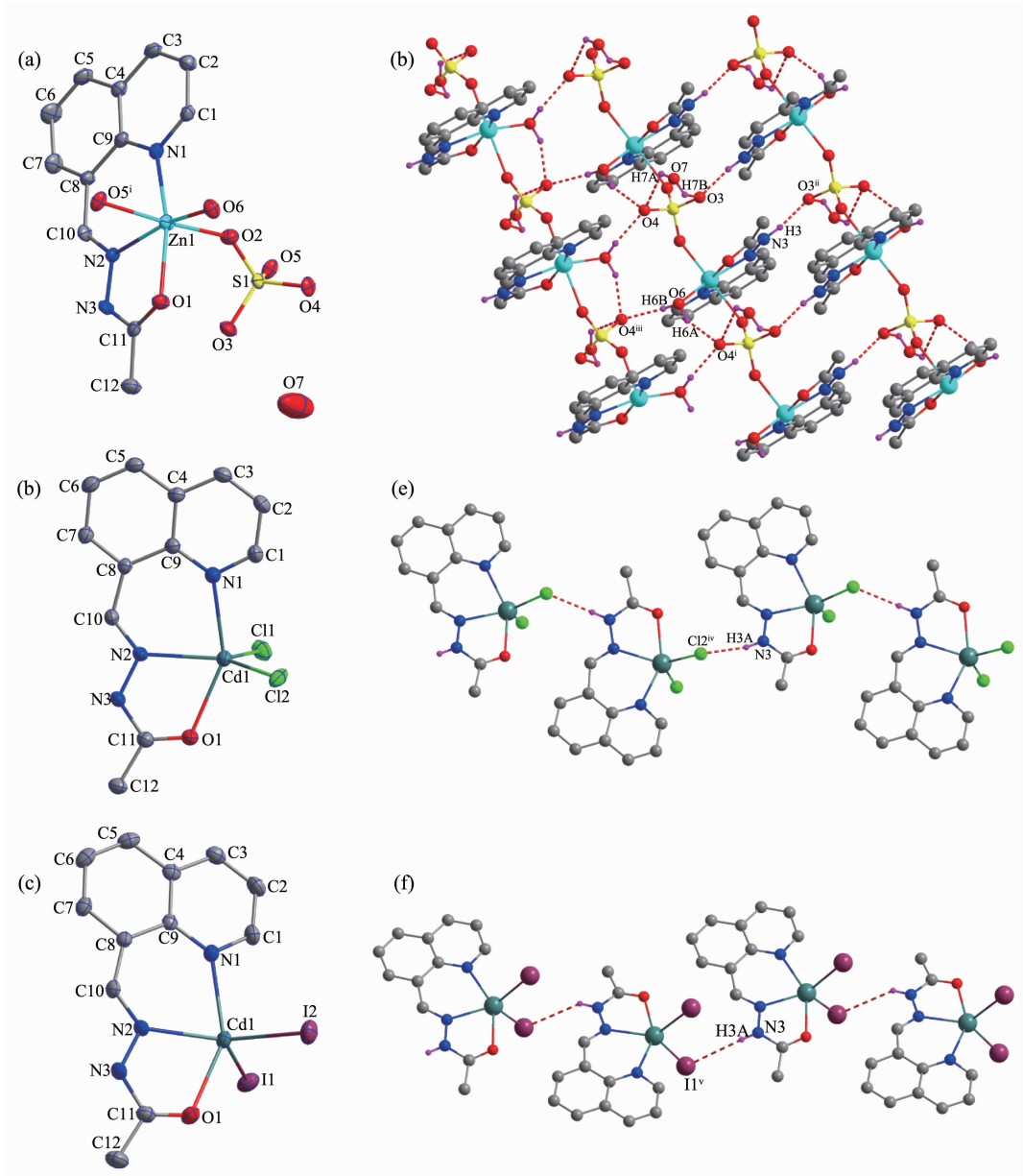
Table 2　Selected bond lengths (nm) and angles (°) in complexes 1~3

1					
Zn1-N1	0.209 9(4)	Zn1-N2	0.205 9(4)	Zn1-O1	0.215 8(3)
Zn1-O2	0.211 4(3)	Zn1-O6	0.200 0(3)	Zn1-O5^i	0.227 9(3)
O6-Zn1-N2	161.91(14)	N1-Zn1-O2	87.73(14)	O6-Zn1-O5^i	86.08(12)
O6-Zn1-N1	107.02(15)	O6-Zn1-O1	87.47(14)	N2-Zn1-O5^i	86.09(13)
N2-Zn1-N1	88.97(15)	N2-Zn1-O1	76.09(15)	N1-Zn1-O5^i	87.98(13)
O6-Zn1-O2	95.30(13)	N1-Zn1-O1	164.90(13)	O2-Zn1-O5^i	175.71(12)
N2-Zn1-O2	93.70(13)	O2-Zn1-O1	95.28(13)	O1-Zn1-O5^i	88.83(12)
2					
Cd1-N1	0.235 6(2)	Cd1-N2	0.231 4(2)	Cd1-O1	0.236 0(2)
Cd1-Cl1	0.241 82(11)	Cd1-Cl2	0.244 57(10)		
Cl1-Cd1-Cl2	116.27(4)	N2-Cd1-N1	79.00(8)	N2-Cd1-Cl1	117.11(7)
N2-Cd1-Cl2	126.40(7)	N2-Cd1-O1	69.66(8)	N1-Cd1-Cl1	97.34(7)
N1-Cd1-Cl2	98.92(7)	N1-Cd1-O1	147.27(8)	O1-Cd1-Cl1	105.00(6)
O1-Cd1-Cl2	92.37(6)				

Continued Table 2

			3		
Cd1-N1	0.237 8(4)	Cd1-N2	0.230 8(3)	Cd1-O1	0.238 4(3)
Cd1-I1	0.274 72(7)	Cd1-I2	0.273 21(5)		
I2-Cd1-I1	109.208(16)	N2-Cd1-N1	78.88(12)	N2-Cd1-I2	127.43(9)
N2-Cd1-I1	122.37(9)	N2-Cd1-O1	69.29(12)	N1-Cd1-I2	100.14(9)
N1-Cd1-I1	102.92(9)	N1-Cd1-O1	148.15(12)	O1-Cd1-I2	98.28(9)
O1-Cd1-I1	95.17(10)				

Symmetry codes: [i] x, $-1+y$, z



(a~c) H atoms are omitted for clarity; Symmetry codes: [i] x, $-1+y$, z; [ii] $1-x$, $1-y$, $-z$; [iii] $1.5-x$, $-0.5+y$, $0.5-z$; [iv] x, $0.5-y$, $0.5+z$; [v] $-0.5+x$, $1.5-y$, $-0.5+z$

Fig.1 Diamond drawing of **1~3** (a~c) with 30% thermal ellipsoids; Extended 2D supramolecular structure in complex **1** (d); Chain-like structures in complex **2** (e, along c axis) and **3** (f) formed by hydrogen bonds (shown in dashed line), respectively

Table 3　Hydrogen bonds information for complexes 1~3

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠DHA / (°)
		1		
O6–H6A···O4^{i}	0.085	0.191	0.270 9(5)	155.1
N3–H3···O3^{ii}	0.086	0.193	0.274 4(5)	158.2
O6–H6B···O4^{iii}	0.085	0.189	0.270 1(5)	159.6
O7–H7A···O4	0.085	0.26	0.317 4(6)	125.9
O7–H7B···O3	0.085	0.25	0.297 4(7)	116
		2		
N3–H3A···Cl2^{iv}	0.086	0.235	0.318 9(3)	164.3
		3		
N3–H3A···I1^{v}	0.086	0.311	0.383 1(4)	142.3

Symmetry codes: ^{i} x, $-1+y$, z; ^{ii} $1-x$, $1-y$, $-z$; ^{iii} $1.5-x$, $-0.5+y$, $0.5-z$; ^{iv} x, $0.5-y$, $0.5+z$; ^{v} $-0.5+x$, $1.5-y$, $-0.5+z$

with a distorted octahedron geometry is coordinated by one neutral hydrazone with ONN donor set, one coordinated water molecule and two O atoms from two independent μ_2-bridged sulfate anions, thus forming one dimension chain-like framework along *b* axis. In addition, in the solid state, the chains were further linked into a 2D supramolecular network by intermolecular N–H···O and O–H···O hydrogen bonds (Fig.1d and Table 3).

Similarly, the hydrazone HL acts as a neutral tridentate ligand in complexes **2** and **3** (Fig.1b and 1c). Coordinated by two additional halide anions (chloride for **2**, while iodide for **3**), the Cd(Ⅱ) ion adopts a distorted square pyramid coordination geometry (τ= 0.348 and 0.345 for complex **2** and **3**, respectively)[7]. In the crystal, intermolecular N–H···Cl or N–H···I hydrogen bonds link the complex molecules of **2** or **3** into one dimension chains (Fig.1e and 1f).

2.2　IR spectra

The FT-IR spectral region for both complexes is more or less similar due to the similar coordination modes of the ligands. The ν(C=O), $\nu(C=N)_{imine}$ and ν $(C=N)_{quinoline}$ bands are at 1 673, 1 615 and 1 584 cm^{-1}, respectively. They shift to lower frequency values in the complexes, indicating that the carbonyl O, imine N and quinoline N atoms take part in the coordination[7-8,14-15]. It is in accordance with the crystal structure study.

2.3　UV spectra

The UV spectra of the ligand HL, complexes **1~3** in CH_3CN solution (c=1×10^{-5} mol·L^{-1}) were measured at room temperature (Fig.2). The spectra of HL features two main band located around 230 nm (ε=35 288 L·mol^{-1}·cm^{-1}) and 320 nm (ε=16 955 L·mol^{-1}·cm^{-1}), which could be assigned to characteristic π-π* transition of quinoline and imine units, respe-ctively[8]. Both bands have no shift while with absorption intensity change in the spectra of complexes **1~3** (ε_1= 34 327, 16 575 L·mol^{-1}·cm^{-1}; ε_2=30 131, 14 854 L·mol^{-1}·cm^{-1}; ε_3=38 244, 14 870 L·mol^{-1}·cm^{-1}). This fact supports the neutral mode of the ligand HL in three complexes[7].

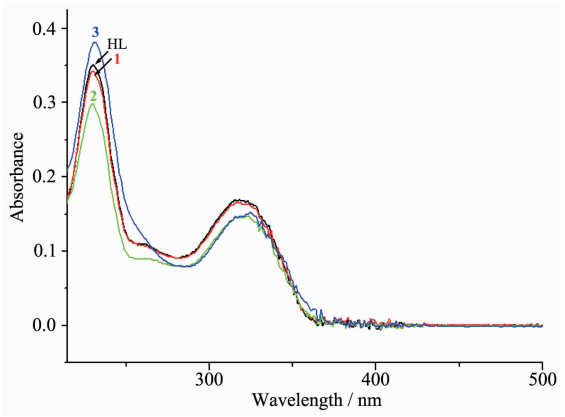


Fig.2　UV spectra of the ligand HL, complexes **1~3** in CH_3CN solution at room temperature

2.4　Fluorescence spectra

The fluorescence spectra of the ligand HL and complexes **1~3** have been studied in CH_3CN solution (c =1×10^{-5} mol·L^{-1}) at room temperature. The free Schiff base ligand HL exhibits almost none

fluorescence emission when excited at 320 nm, primarily due to C=N isomerization. However, complexes **1** and **2** show remarkable peaks at about 428 and 408 nm under the same tested condition, respectively. Obviously, binding with Zn^{2+}/Cd^{2+} inhibits the isomerization of C=N, thereby increasing the fluorescence intensity through the CHEF mechanism[9-11]. In addition, it should be noted that complex **3** gives similar emission as the free ligand because of the heavy atom effect of the coordinated iodide anions.

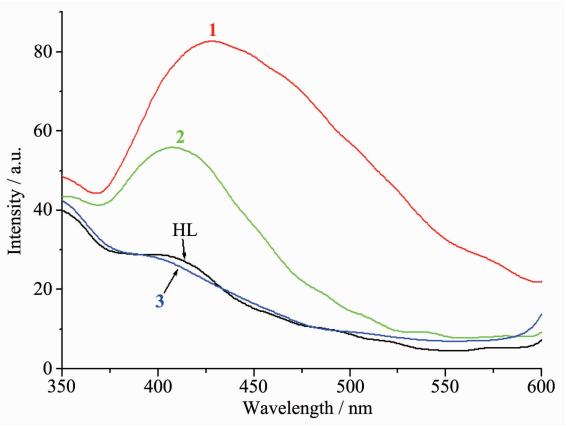


Fig.3 Fluorescence emission spectra of the ligand HL, complexes **1**~**3** in CH_3CN solution at room temperature

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