第 31 卷第 11 期
2015 年 11 月

无 机 化 学 学 报
CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.31 No.11
2265-2271

两个喹啉酰腙镉配合物的合成、结构及荧光性质

李晓静 吴伟娜* 徐周庆* 李守杰 赵 亮
(河南理工大学物理化学学院,焦作 454000)

摘要: 合成并通过单晶衍射表征了配合物[Cd(L)(H_2O)(NO_3)$_2$] (**1**)和[Cd(L)I_2]·CH_3OH (**2**)(L=喹啉-8-甲醛对羟基苯甲酰腙)。单晶衍射结果表明, 在配合物 **1** 中,Cd(Ⅱ)分别与 1 个三齿配位的酰腙配体,1 个水分子,1 个单齿配位和 1 个双齿配位的硝酸根配位,从而拥有单帽三棱柱配位构型。然而,配合物 **2** 中,Cd(Ⅱ)离子采取扭曲的四方锥配位构型,与来自配体 L 的 N_2O 电子供体以及 2 个碘离子配位。此外还详细研究了配合物 **1** 和 **2** 的热稳定性及荧光性质。

关键词: 喹啉; Cd(Ⅱ)配合物; 荧光; 晶体结构; 热稳定性
中图分类号: O614.24+2 **文献标识码**: A **文章编号**: 1001-4861(2015)11-2265-07
DOI:10.11862/CJIC.2015.303

Two Cadmium(Ⅱ) Complexes of an Acylhydrazone Ligand Bearing Quinoline Unit: Syntheses, Structures and Fluorescent Properties

LI Xiao-Jing WU Wei-Na* XU Zhou-Qing* LI Shou-Jie ZHAO Liang
(*Department of Physics and Chemistry, Henan Polytechnic University, Jiaozuo, Henan* 454000, *China*)

Abstract: Two complexes [Cd (L) (H_2O) (NO_3)$_2$] (**1**) and [Cd (L)I_2] ·CH_3OH (**2**) (L =4-hydroxy-*N*-((quinolin-8-yl) methylene)benzohydrazide) have been synthesized and structurally determined by single-crystal X-ray diffraction. The results show that the Cd(Ⅱ) ion in **1** with a mono-capped trigonal prismatic geometry is surrounded by one acylhydrazone ligand with N_2O donor set, one water molecule, one mono-dendate and one bidendate nitrate anions. However, the coordination geometry of the Cd(Ⅱ) ion in **2** is a distorted tetragonal pyramid with oxygen and two nitrogen atoms provided by the ligand L and two iodide anions. The thermal stabilities and luminescent properties of both complexes are also investigated in detail. CCDC: 1034567, **1**; 1405135, **2**.

Key words: quinoline; Cd(Ⅱ) complex; fluorescence; crystal structure; thermostability

0 Introduction

The interest in coordination chemistry of acylhydrazone ligands with transition metal ions has been stimulated by their interesting physicochemical properties[1-4] and potentially biological activities. In the past, most works on the relevant acylhydrazones involve various simple aromatic rings, such as substituted benzene, pyridine, pyrazine, as well as pyrrole[5-7]. However, complexes of the acylhydrazone ligands bearing condensed heterocycle have not been paid much attention. In view of a variety of coordination geometries and photoluminescent properties of Cd(Ⅱ) complexes[8-9], and as part of our ongoing work on metal-acylhydrazones, we report here the structure and fluorescence property of two Cd(Ⅱ) complexes with an

收稿日期:2015-07-10。收修改稿日期:2015-10-06。
国家自然科学基金(No.21404033,21401046,21001040)和河南省教育厅自然科学基金(No.12B150011,14B150029)资助项目。
*通讯联系人。E-mail:wuwn08@hpu.edu.cn,zhqxu@hpu.edu.cn;会员登记号:S06N6704M112。

acylhydrazone ligand derived from quinoline-8-carbaldehyde and 4-hydroxylbenzoyl hydrazide.

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. ^1H NMR spectra of L was acquired with Bruker AV400 NMR instrument in d_6-DMSO 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. The thermal behavior was monitored on a Perkin Elmer TG-7 thermal analyzer.

1.2 Preparations of the ligand, complexes 1 and 2

As shown in scheme 1, the ligand L was prepared by condension of quinoline-8-carbaldehyde (1.57 g, 10 mmol) and 4-hydroxylbenzoyl hydrazide[10] (1.52 g, 10 mmol) in methanol solution (300 mL) under refluxing for 4 h[11]. The slight yellow solid was filtered and washed three times by methanol. Yield: 2.01g (69%). m.p.: 134~137 ℃. Elemental analysis Calcd. for $C_{17}H_{13}N_3O_2$ (%): C, 70.09; H, 4.50; N, 14.42; Found(%): C, 70.22; H, 4.34; N, 14.49. FT-IR (cm^{-1}): ν(N-H) 3 286, ν(O=C-N) 1 654, ν(C=N-N) 1 606, ν(quinoline C=N) 1 574. ^1H NMR (400 MHz, DMSO-d_6) δ 11.95 (1H, s, NH-C=O); 10.16 (1H, s, OH); 9.00~9.01 (1H), 8.45~8.87 (2H), 8.08~8.10(1H), 7.63~7.73 (2H) for quinoline-H; 6.87~6.89 (2H), 8.08~8.10 (2H) for phenyl-H.

The complexes **1** and **2** were generated by reaction of L (5 mmol) with equimolar of $Cd(NO_3)_2\cdot 4H_2O$ and CdI_2 in methanol solution (15 mL), respectively. Crystals of **1** and **2** suitable for X-ray diffraction analysis were obtained by evaporating the corresponding reaction solutions at room temperature.

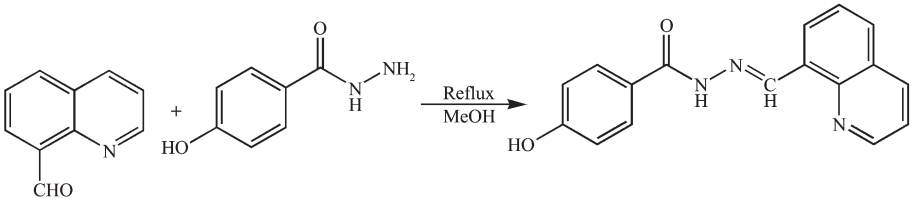
1: Yellow blocks. Anal. Calcd. for $C_{17}H_{15}N_5O_9Cd$ (%): C, 37.41; H, 2.77; N, 12.83. Found(%): C, 37.52; H, 2.73; N, 12.95. FT-IR (cm^{-1}): ν (O-H) 3 397, ν(N-C=O) 1 625, ν(C=N-N) 1 601, ν(quinoline C=N) 1 556. $\nu_1(NO_3)$ 1 480, $\nu_4(NO_3)$ 1 381, 1 301, ρ(O-H) 858.

2: Yellow blocks. Anal. Calcd. for $C_{18}H_{17}N_3O_3I_2Cd$ (%): C, 31.35; H, 2.48; N, 6.09. Found (%): C, 31.41; H, 2.39; N, 6.15. FT-IR (cm^{-1}): ν(O-H) 3 307, ν(N-C=O) 1 618, ν(C=N-N) 1 605, ν(quinoline C=N) 1 583.

1.3 X-ray crystallography

The X-ray diffraction measurement for 1 and 2 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. 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 SHELXTL-97 program[13]. All non-hydrogen atoms were refined anisotropically. The O3 atom in complex **2** is disordered, the occupancy values for O3A and O3B are 75.23% and 24.77%, respectively. H atoms for water molecules in complex **1** 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** and **2** are summarized in Table 1.

CCDC: 1034567, **1**; 1405135, **2**.



Scheme 1 Reaction scheme for the synthesis of L

Table 1　Crystal data and structure refinement for the complexes 1 and 2

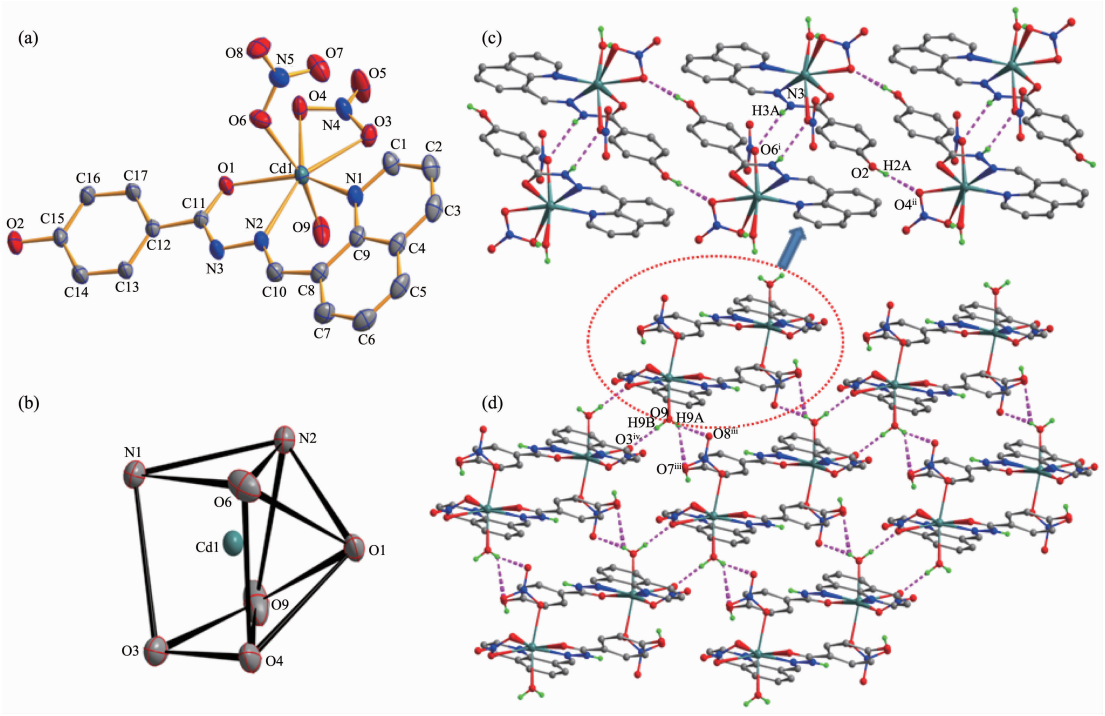
Empirical formula	$C_{17}H_{15}CdN_5O_9$	$C_{18}H_{17}CdI_2N_3O_3$
Formula weight	545.74	689.55
T / K	293(2)	296(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	0.820 1(7)	0.779 5(6)
b / nm	1.067 8(9)	0.981 6(7)
c / nm	1.293 7(12)	1.434 1(10)
α / (°)	77.427(15)	101.845(10)
β / (°)	72.197(15)	90.464(12)
γ / (°)	74.312(15)	102.027(12)
V / nm^3	1.027 1(16)	1.049 0(13)
Z	2	2
D_c / (g·cm^{-3})	1.765	2.183
Absorption coefficient / mm^{-1}	1.125	4.007
Crystal size / mm	0.15×0.12×0.08	0.24×0.22×0.20
F(000)	544	648
θ range for data collection / (°)	1.67~25.00	1.45~25.00
Index ranges (h, k, l)	$-9 \leqslant h \leqslant 7, -12 \leqslant k \leqslant 12, -15 \leqslant l \leqslant 14$	$-9 \leqslant h \leqslant 4, -11 \leqslant k \leqslant 11, -17 \leqslant l \leqslant 17$
Reflections collected	5 214	4 998
Unique (R_{int})	3 588 (0.023 8)	3 631 (0.037 9)
Data/restraints/parameters	3 588 / 3 / 297	3 631 / 1 / 247
Goodness-of-fit (GOF) on F^2	1.031	1.027
Final R indices [$I>2\sigma(I)$]	R_1=0.037 0, wR_2=0.072 6	R_1=0.047 5, wR_2=0.116 6
R indices (all data)	R_1=0.051 6, wR_2=0.079 5	R_1=0.066 0, wR_2=0.125 7
Largest peak and hole / (e·nm^{-3})	459 and −567	1 374 and −1 201

2　Results and discussion

2.1　Crystal structures of 1 and 2

As show in Fig.1a, the seven-coordinated Cd(Ⅱ) ion in complex **1** is coordinated by one acylhydrazone ligand with N_2O donor set, one water molecule, one mono-dendate and one bidendate nitrate anions, thus giving a distorted mono-capped trigonal prismatic geometry (Fig.1b). Selected bond lengths and angles are summarized in Table 2. The Cd-N and Cd-O bond lengths are in the range of 0.228 7(4)~0.247 4(4) nm, comparable to the Cd(Ⅱ) complexes with similar donor sets[14]. It should be noted that in complex **1**, the acylhydrazone ligand is in a ketone form, since the bond lengths of carbonyl C11-O1 (0.124 5(5) nm) and amide C11-N3 (0.136 1(5) nm) are comparable to those of the reported acylhydrazones[15]. In the crystal of **1**, two complex molecules are linked with each other by pairs of intermolecular N–H⋯O hydrogen bonds between amide nitrogen and monodendate nitrate oxygen atoms (Fig.1c and Table 3), forming a centrosymmetry dimer. Similarly, a further chain-like structure along b axis is constructed by pairs of intermolecular O–H⋯O hydrogen bonds between the dimers. In addition, large amount of O–H⋯O hydrogen bonds between the chains (Fig.1d) are helpful to consolidate the three-dimensional network.

The coordination behavior of the acylhydrazone ligand in complex **2** is same as that in complex **1**. In complex **2**, the Cd(Ⅱ) center (Fig.2a) is surrounded by two iodide anions and one tridentate neutral ligand L. The geometric index τ is 0.146 7 according to the Addison rule[16], indicating that the coordination geometry of the Cd(Ⅱ) ion in **2** is a distorted tetragonal



Symmetry code: [i] $-x, -y+1, -z$; [ii] $-x, -y+2, -z$; [iii] $x+1, y, z$; [iv] $-x, -y+1, -z+1$

Fig.1 (a) Molecular structure of the complex **1** shown with 30% probability displacement ellipsoids; (b) Coordination geometry of the center Cd(Ⅱ) ion, coordination atoms shown with 30% probability displacement ellipsoids; (c) Chain-like structure along *b* axis formed by intermolecular hydrogen bonds (dashed line); (d) Extended structure parallelling to (101) plane formed by intermolecular hydrogen bonds between chains

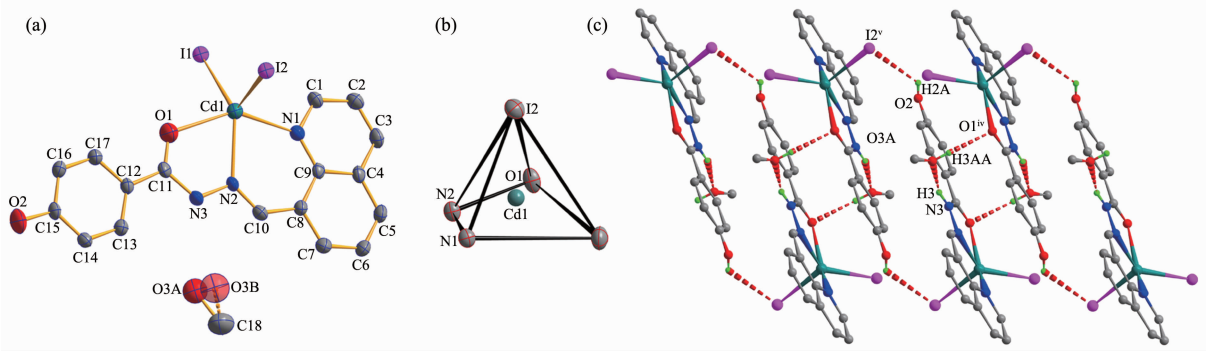
Table 2 Selected bond lengths (nm) and angles (°) in 1 and 2

		1			
Cd1-O9	0.228 7(4)	Cd1-O6	0.233 4(3)	Cd1-N2	0.235 7(4)
Cd1-O1	0.236 7(3)	Cd1-N1	0.236 7(4)	Cd1-O4	0.246 1(3)
Cd1-O3	0.247 4(4)	O1-C11	0.124 5(5)	N3-C11	0.136 1(5)
O6-Cd1-N2	88.77(13)	O9-Cd1-O1	82.01(13)	O6-Cd1-O1	81.14(12)
N2-Cd1-O1	69.02(12)	O9-Cd1-N1	101.43(15)	O6-Cd1-N1	93.47(13)
N2-Cd1-N1	79.23(12)	O1-Cd1-N1	147.83(11)	O9-Cd1-O4	90.26(16)
O6-Cd1-O4	85.17(12)	N2-Cd1-O4	147.11(11)	O1-Cd1-O4	78.11(11)
N1-Cd1-O4	133.34(12)	O9-Cd1-O3	76.52(14)	O6-Cd1-O3	112.63(12)
N2-Cd1-O3	155.09(11)	O1-Cd1-O3	124.85(11)	N1-Cd1-O3	86.60(11)
O4-Cd1-O3	52.22(9)	O9-Cd1-O6	163.11(13)	O9-Cd1-N2	86.27(16)
		2			
Cd1-N2	0.231 9(6)	Cd1-O1	0.236 7(5)	Cd1-N1	0.237 4(6)
Cd1-I1	0.272 43(15)	Cd1-I2	0.274 67(15)	O1-C11	0.122 3(8)
N3-C11	0.136 8(9)				
I1-Cd1-I2	110.63(5)	N1-Cd1-I2	102.61(16)	N2-Cd1-O1	68.49(18)
N2-Cd1-N1	78.9(2)	O1-Cd1-N1	145.6(2)	N2-Cd1-I1	136.80(15)
O1-Cd1-I1	94.31(14)	N1-Cd1-I1	102.63(16)	N2-Cd1-I2	111.04(16)
O1-Cd1-I2	98.93(15)				

Table 3　Hydrogen bonds in complexes 1 and 2

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠DHA / (°)
1				
N3–H3A···O6^{i}	0.086	0.229	0.294 4(5)	132.5
O2–H2A···O4^{ii}	0.082	0.206	0.287 9(5)	178.4
O9–H9A···O7^{iii}	0.084 2(10)	0.249(4)	0.316 6(6)	138(4)
O9–H9A···O8^{iii}	0.084 2(10)	0.204(2)	0.285 1(5)	160(5)
O9–H9B···O3^{iv}	0.084 8(10)	0.196 0(11)	0.280 8(5)	179(6)
2				
N3–H3···O3A	0.086	0.213	0.293 0(10)	154.3
O2–H2A···I2^{v}	0.082	0.288	0.348 1(6)	131.8
O3A–H3AA···O1^{vi}	0.082	0.235	0.305 5(11)	144.2

Symmetry code: ^{i} $-x$, $-y+1$, $-z$; ^{ii} $-x$, $-y+2$, $-z$; ^{iii} $x+1$, y, z; ^{iv} $-x$, $-y+1$, $-z+1$; ^{v} $-x+1$, $-y$, $-z+1$; ^{vi} $x+2$, y, $z+1$



Symmetry code ^{v} $-x+1$, $-y$, $-z+1$; ^{vi} $x+2$, y, $z+1$

Fig.2　(a) Molecular structure of the complex **2** shown with 30% probability displacement ellipsoids; (b) Coordination geometry of the center Cd(Ⅱ) ion, coordination atoms shown with 30% probability displacement ellipsoids; (c) Chain-like structure formed along *a* axis by intermolecular hydrogen bonds (dashed line) (O3B was deleted for clarity)

pyramid (Fig.2b). Moreover, in the crystal of **2**, pairs of the crystal methanol molecules link the complexes into centrosymmetry dimmers by intermolecular O–H···O and N–H···O hydrogen bonds. Furthermore, the chain-like structure along *a* axis is formed via intermolecular O–H···I hydrogen bonds between the dimers.

2.2　IR spectra

The IR spectra of free ligand L show strong band at 1 654 cm^{-1}, which is attributable to stretch vibrations of the carbonyl group (ν(C=O)). The peak at 1 606 and 1 574 cm^{-1} should be assigned to the vibration of imine groups for acylhydrazone and quinoline units, respectively. Upon coordination with Cd(Ⅱ) ion, the ν(C=O), ν(C=N-N) and ν(quinoline C=N) shift by 29, 5, 18 cm^{-1} and 36, 1, 9 cm^{-1} in the complexes **1** and **2**, respectively; indicating that carbonyl oxygen atom, imine nitrogen atom and quinoline nitrogen atom take part in coordination[2]. In addition, the intense absorption bands in the spectra associated with the asymmetric stretching appear at 1 381 or 1 301 cm^{-1} (ν_4) and 1 477 cm^{-1} (ν_1), clearly establishing that two NO_3^- groups in the complex **1** are mono-dentate and bidentate ligands, respectively[18]. The ν(O-H) bands in complexes **1** and **2** appear at about 3 397 and 3 307 cm^{-1}, respectively. Moreover, the medium intensity bands at about 890 cm^{-1} shows that there are some coordinative water molecules in the complex **1**.

2.3　Thermal decomposition process of complexes 1 and 2

For detecting the thermal stabilities of complexes **1** and **2**, thermal gravimetric (TG) analyses were carried out from the room temperature to 800 ℃ with the linear heating rate of 10 ℃·min^{-1} under argon

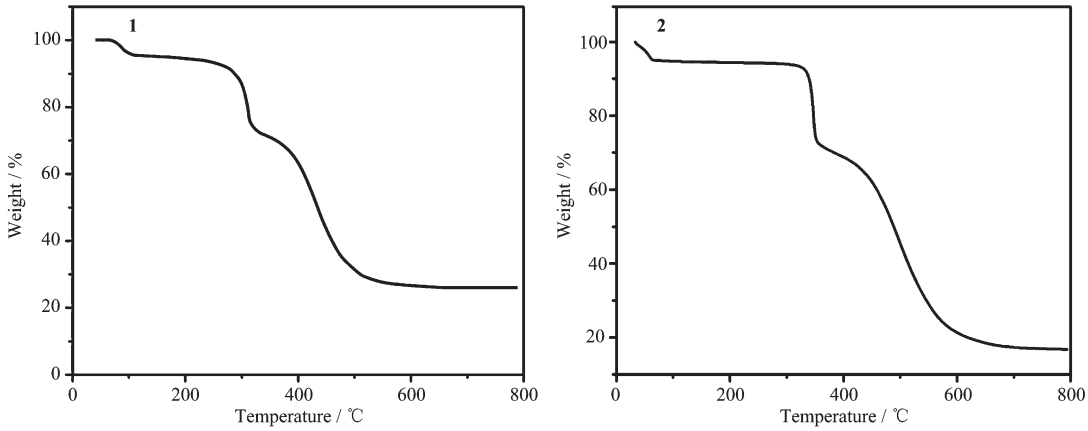


Fig.3 TG curves for complexes **1** and **2**

atmosphere. As shown in Fig.3, the thermal decomposition processes of complexes **1** and **2** are similar as each other, and can be divided into three stages. The first stage occurs with weight loss of 3.75% and 4.64% below 100 ℃ for complexes **1** and **2**, respectively, corresponding to the loss of one coordinated water molecule in **1** (Calcd. 3.29%) and one lattice CH_3OH molecule in **2** (Calcd. 4.38%); the second process of weight loss appears between 285 to 352 ℃, considered as the decomposition of $NNH(CO)C_6H_4(OH)$ part of the ligand L with weight loss of 26.78% and 21.26%, consistent with the calculated value of 27.48% and 21.70% in complexes **1** and **2**, respectively; the final step from 352 to 596 ℃ is assigned as the decomposition of the remaining organic components. The remainder may be CdO because the residue weights (23.43% and 18.33%) are in agreement with the calculated values (23.74% and 18.55%) for complexes **1** and **2**, respectively.

2.4 UV spectra

The UV spectra of the ligand L, **1** and **2** in CH_3OH solution (concentration: 1×10^{-5} mol·L^{-1}) were measured at room temperature (Fig.4). The spectra of L features three main bands located around 231 (ε= 32 390 L·mol^{-1}·cm^{-1}), 283 (ε=14 701 L·mol^{-1}·cm^{-1}) and 324 nm (ε=23 933 L·mol^{-1}·cm^{-1}), respectively. The bands could be assigned to characteristic π-π* transitions centered on benzene ring, quinoline ring and imine unit, respectively[18]. Different bonds can be observed in the spectra of **1** (261 (ε=9 983 L·mol^{-1}·cm^{-1}), 320 (ε=13 049 L·mol^{-1}·cm^{-1}), 385 nm (ε=9 810 L·mol^{-1}·cm^{-1})) and **2** (221 (ε=38 933 L·mol^{-1}·cm^{-1}), 324 (ε=16 274 L·mol^{-1}·cm^{-1}), 382 nm (ε=5 877 L·mol^{-1}·cm^{-1})), respectively, clearly indicating that the acylhydrazone ligand takes part in the coordination in complexes **1** and **2**.

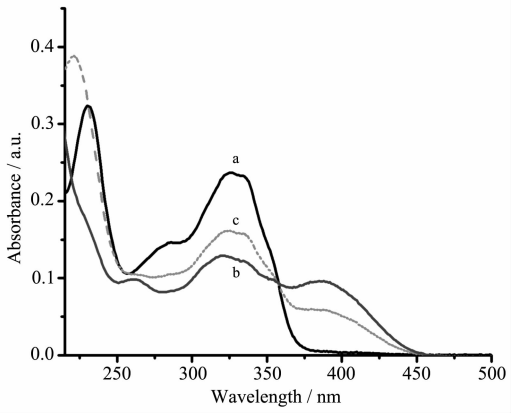


Fig.4 UV spectra of the ligand L (a), **1** (b) and **2** (c) in CH_3OH solution at room temperature

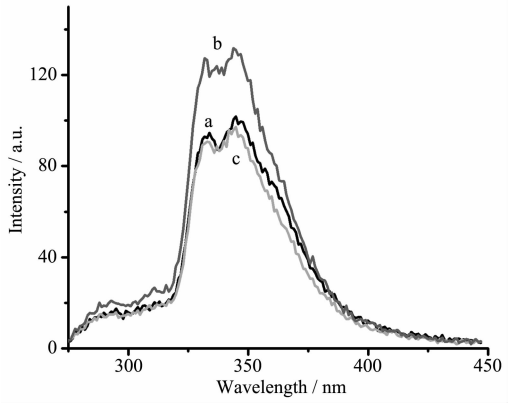


Fig.5 Fluorescence emission spectra of the ligand L (a), **1** (b) and **2** (c) in CH_3OH solution at room temperature

2.5 Fluorescence spectra

The fluorescence spectra of the ligand L, **1** and **2** in CH_3OH solution (concentration: 1×10^{-5} mol·L^{-1}) are quite similar. When exited at 233 nm, the three compounds show two emission bands at 333 and 343 nm, respectively (Fig.5). It is obvious that complexes **1** and **2** are photoluminescent with the emission peaks corresponding to $\pi\rightarrow\pi^*$ transition of metal-perturbed intraligand[19].

References:

[1] Yang Z Y, Yang R D, Li F S, et al. *Polyhedron*, **2000**,**19**: 2599-2604

[2] Yang Z Y, Wang B D, Li Y H. *J. Organomet. Chem.*, **2006**, **691**:4159-4166

[3] Zhai Q G, Li S N, Gao X, et al. *Inorg. Chem. Commun.*, **2010**,**13**:211-214

[4] Wang Y, Yang Z Y. *J. Lumin.*, **2008**,**128**:373-376

[5] HUANG Chao(黄超), WU Juan(吴娟), CHEN Dong-Mei(陈冬梅), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2015**, **31**:109-113

[6] Ye X P, Zhu T F, Wu W N, et al. *Inorg. Chem. Commun.*, **2014**,**47**:60-62

[7] Costes J P, Duhayon C, Vendier L. *Inorg. Chem.*, **2014**,**53**: 2181-2187

[8] Liu S G, Zuo J L, Li Y Z, et al. *J. Mol. Struct.*, **2004**,**705**: 153-157

[9] Chandrasekhar V, Azhakar R, Zacchini S, et al. *Inorg. Chem.*, **2005**,**44**:4608-4615

[10]CHENG Mei-Ling(程美令), CAO Xiang-Qian(曹向前), WANG Chun-Lan(王春兰), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2006**,**22**:1222-1226

[11]Ye X P, Zhu T F, Wu W N, et al. *Inorg. Chem. Commun.*, **2014**,**47**:60-62

[12]Sheldrick G M. *SADABS*, University of Göttingen, Germany, **1996**.

[13]Sheldrick G M. *SHELX*-97, *Program for the Solution and the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[14]YE Xing-Pei(叶行培), WU Wei-Na(吴伟娜), LI Fei-Fei(李飞飞), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2013**, **29**:2678-2682

[15]Wang Y, Wu W N, Wang Q, et al. *J. Coord. Chem.*, **2010**, **63**:147-155

[16]Addison A W, Rao T N. *J. Chem. Soc. Dalton Trans.*, **1984**,**5** (11):1349-1356

[17]YE Xing-Pei(叶行培), WANG Guan-Jie(王冠杰), PAN Peng (潘鹏), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2014**, **30**:2789-2795

[18]Song X Q, Zang Z P, Liu W S, et al. *J. Solid State Chem.*, **2009**,**182**:841-848

[19]ZHUO Xin(卓馨), PAN Zhao-Rui(潘兆瑞), WANG Zuo-Wei (王作为), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2006**,**22**:1847-1851