

2-乙酰吡嗪缩胍基甲酸甲酯的镍和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 X 射线单晶衍射、元素分析及红外光谱表征了配合物 $[\text{Ni}(\text{L})_2]$ (**1**) 和 $[\text{Cd}(\text{HL})(\text{CH}_3\text{OH})(\text{NO}_3)_2]$ (**2**) 的结构 (HL 为 2-乙酰吡嗪缩胍基甲酸甲酯)。单晶衍射结果表明, 配合物 **1** 中, Ni(II) 离子与来自 2 个阴离子配体 L 的 N_2O 电子供体配位, 形成扭曲的八面体配位构型。在配合物 **2** 中, Cd(II) 离子拥有双帽三棱柱配位构型, 与 1 个中性配体 HL, 2 个双齿配位硝酸根和 1 分子甲醇配位。此外还研究了配合物 **1** 和 **2** 的荧光及热性质。

关键词: 胍基甲酸甲酯; 吡嗪; 荧光; 晶体结构; 热稳定性

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Ni(II) and Cd(II) Complexes with a Schiff Base Ligand Derived from 2-Acetyl Pyrazine and Methyl Hydrazinocarboxylate: Crystal Structures and Fluorescence Properties

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Abstract: Two complexes, namely $[\text{Ni}(\text{L})_2]$ (**1**) and $[\text{Cd}(\text{HL})(\text{CH}_3\text{OH})(\text{NO}_3)_2]$ (**2**) (HL is derived from 2-acetyl pyrazine and methyl hydrazinocarboxylate) have been synthesized and characterized by single-crystal X-ray diffraction, elemental analysis and IR spectroscopy. X-ray diffraction analysis results show that the central Ni(II) ion in complex **1** is surrounded by two independent anionic ligands with N_2O donor set, thus possesses a distorted octahedral coordination geometry. However, in complex **2**, the Cd(II) ion with bicapped-triangular prism geometry is coordinated with one neutral ligand HL, two bidentate nitrate anions and one methanol molecule. In addition, the thermal stability and luminescent properties of the complexes are also studied in detail. CCDC: 1424257, **1**; 1424258, **2**.

Keywords: methyl hydrazinocarboxylate; pyrazine; fluorescence; crystal structure; thermostability

Schiff bases as an important class of ligands play a crucial role in coordination chemistry and have been widely applied in different fields mainly due to their wide-spectrum biological applications^[1-7]. In recent years, there are many reports about the acylhydrazones,

thiosemicarbazones derived from acetyl-pyridine/pyrazine, and their transition metal complexes because of high biological and pharmaceutical activities^[3,8-10]. By contrast, as their structurally analogous, carbazates (R-O-CO-NH-NH_2) and their metal complexes have

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been paid much less attention^[6].

Generally, Cd(II) ion is closely related to biochemistry, clinical diagnostics as well as environmental pollution^[11]. Furthermore, a large amount of Cd(II) complexes have been reported for their fluorescence properties^[12-13]. Therefore, in this paper, Ni(II) and Cd(II) complexes with a Schiff base ligand derived from 2-acetyl pyrazine and methyl hydrazinocarboxylate have been synthesized and structural determined by single-crystal X-ray diffraction. In addition, the thermal stability and luminescent properties of the complexes are also 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 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 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 ligand, complexes 1 and 2

As shown in Scheme 1, the ligand HL was produced by condensation of 2-acetyl pyrazine (1.22 g, 0.01 mol) and methyl hydrazinocarboxylate (0.90 g, 0.01 mol) in anhydrous methanol solution (30 mL) with continuous stirring at room temperature for 3 h. The white solid was filtered and washed three times by cold methanol. Yield: 1.13 g (58%). m.p. 183~185 °C. Elemental analysis Calcd. for $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ (%): C: 49.48; H: 5.19; N: 28.85; Found (%): C: 49.26; H: 5.34; N: 29.00. FT-IR (cm^{-1}): $\nu(\text{C}=\text{O})$ 1 748, $\nu(\text{C}=\text{N})$ 1 613, $\nu(\text{C}=\text{N})_{\text{pyrazine}}$ 1 558. ^1H NMR (400 MHz): δ

10.52 (1H, s, NH), 9.09 (1H)/8.55~8.58 (2H) for pyrazine-H, 3.70 (3H, s, CH_3), 2.24(3H, s, CH_3).

The complexes **1** and **2** were generated by reaction of the ligand HL (5 mmol) with equimolar of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in methanol solution (10 mL), respectively. Crystals suitable for X-ray diffraction analysis were obtained by evaporating the corresponding reaction solutions at room temperature.

1: Brown blocks. Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{N}_8\text{O}_4\text{Ni}$ (%): C: 43.18; H: 4.08; N: 25.18. Found(%): C: 43.05; H: 4.00; N: 25.33. FT-IR (cm^{-1}): $\nu(\text{N}=\text{C}-\text{O})$ 1 606, $\nu(\text{C}=\text{N})$ 1 594, $\nu(\text{C}=\text{N})_{\text{pyrazine}}$ 1 535.

2: Colorless blocks. Anal. Calcd. for $\text{C}_9\text{H}_{14}\text{N}_6\text{O}_9\text{Cd}$ (%): C: 23.36; H: 3.05; N: 18.16. Found(%): C: 23.22; H: 3.17; N: 18.27. FT-IR (cm^{-1}): $\nu(\text{O}-\text{H})$ 3 532, $\nu(\text{C}=\text{O})$ 1 720, $\nu(\text{C}=\text{N})$ 1 579, $\nu(\text{C}=\text{N})_{\text{pyrazine}}$ 1 523. $\nu_1(\text{NO}_3)$ 1 494, $\nu_4(\text{NO}_3)$ 1 311.

1.3 X-ray crystallography

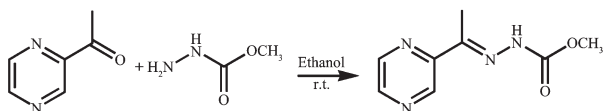
The X-ray diffraction measurement for complexes **1** and **2** were performed on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) by using φ - ω scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program^[14]. The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-97 program^[15]. 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** and **2** are summarized in Table 1.

CCDC: 1424257, **1**; 1424258, **2**.

2 Results and discussion

2.1 Crystal structures description

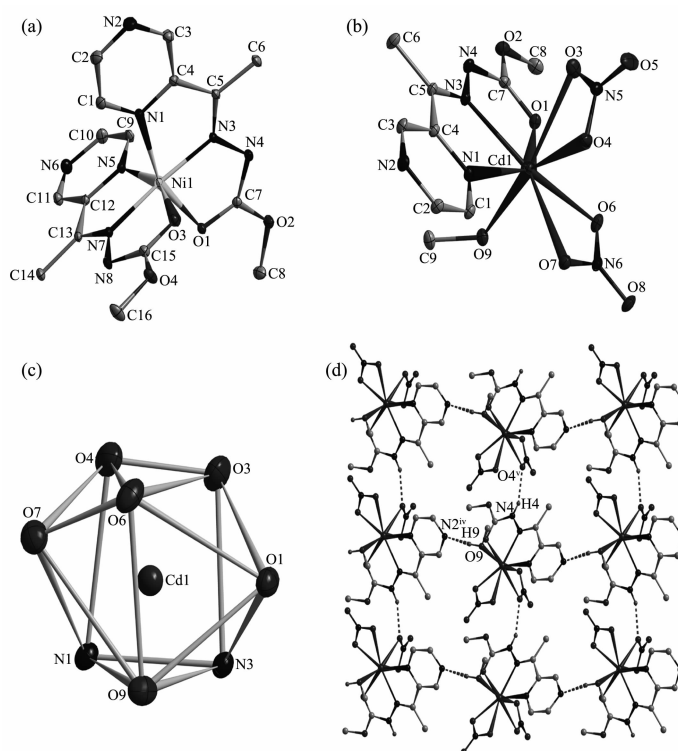
Selected bond distances and angles, hydrogen bonds information for both complexes are listed in Table 2 and 3, respectively. As shown in Fig.1a, the central Ni(II) ion in complex **1** is surrounded by two independent anionic ligands with N_2O donor set, thus possesses a distorted octahedral coordination geometry. The enolization of $\text{C}=\text{O}$ bond of the ligand



Scheme 1 Synthesis route of HL

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

	1	2
Empirical formula	C ₁₆ H ₁₈ N ₈ O ₄ Ni	C ₉ H ₁₄ N ₆ O ₉ Cd
Formula weight	445.09	462.66
<i>T</i> / K	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> <i>n</i>
<i>a</i> / nm	0.906 4(9)	0.883 92(11)
<i>b</i> / nm	1.749 7(16)	0.760 58(9)
<i>c</i> / nm	1.477 6(10)	1.268 82(15)
β / (°)	126.67(4)	103.554(2)
<i>V</i> / nm ³	1.880(3)	0.829 26(17)
<i>Z</i>	4	2
<i>D_c</i> / (g·cm ⁻³)	1.573	1.853
Absorption coefficient / mm ⁻¹	1.075	1.375
<i>F</i> (000)	920	460
Reflections collected, unique (<i>R_{int}</i>)	9 379, 3 304 (0.047 0)	4 051, 1 967 (0.022 8)
Data, restraints, parameters	3 304, 0, 262	1 967, 5, 232
Goodness-of-fit (GOF) on <i>F</i> ²	1.032	1.044
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ =0.039 2, <i>wR</i> ₂ =0.094 9	<i>R</i> ₁ =0.024 2, <i>wR</i> ₂ =0.060 9
<i>R</i> indices (all data)	<i>R</i> ₁ =0.064 3, <i>wR</i> ₂ =0.105 8	<i>R</i> ₁ =0.024 4, <i>wR</i> ₂ =0.061 1
Largest peak and hole / (e·nm ⁻³)	279 and -469	969 and -771



In (a)~(c): H atoms are omitted for clarity; In (d): H atoms of C-H bonds are omitted for clarity, Symmetry codes: ^{iv} *x*-1/2, -*y*+1, *z*+1/2; ^v *x*, *y*-1, *z*

Fig.1 Diamond drawing of **1** (a) and **2** (b) with 30% thermal ellipsoids; (c) Coordination environment of Cd(II) ion in complex **2** (coordination atoms shown with 30% thermal ellipsoids); (d) Extend 2D supramolecular structure along *c* axis in complex **2**

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

1					
Ni1-N7	0.197 1(3)	Ni1-O3	0.206 0(2)	Ni1-N1	0.208 4(3)
Ni1-N3	0.197 6(3)	Ni1-N5	0.207 3(3)	Ni1-O1	0.209 5(2)
N7-Ni1-N3	174.45(10)	O3-Ni1-N5	155.57(10)	N7-Ni1-O1	101.54(11)
N7-Ni1-O3	77.09(11)	N7-Ni1-N1	103.23(12)	N3-Ni1-O1	76.81(11)
N3-Ni1-O3	97.74(10)	N3-Ni1-N1	78.63(12)	O3-Ni1-O1	96.33(11)
N7-Ni1-N5	78.50(12)	O3-Ni1-N1	90.35(12)	N5-Ni1-O1	87.70(11)
N3-Ni1-N5	106.62(12)	N5-Ni1-N1	96.03(12)	N1-Ni1-O1	155.20(10)
2					
Cd1-O6	0.230 7(3)	Cd1-O9	0.236 9(3)	Cd1-O7	0.250 2(4)
Cd1-N3	0.234 2(4)	Cd1-O1	0.240 5(3)	Cd1-O3	0.260 8(6)
Cd1-N1	0.235 4(4)	Cd1-O4	0.243 7(5)		
O7-Cd1-O3	117.56(14)	O6-Cd1-N3	151.74(12)	O9-Cd1-O1	79.52(12)
O9-Cd1-O7	84.82(15)	O6-Cd1-N1	139.14(12)	O6-Cd1-O4	83.04(17)
O1-Cd1-O7	135.09(15)	N3-Cd1-N1	68.34(12)	N3-Cd1-O4	111.68(16)
O4-Cd1-O7	71.04(17)	O6-Cd1-O9	84.44(12)	N1-Cd1-O4	83.98(18)
O6-Cd1-O3	98.27(17)	N3-Cd1-O9	88.74(12)	O9-Cd1-O4	155.74(14)
N3-Cd1-O3	76.62(13)	N1-Cd1-O9	92.11(12)	O1-Cd1-O4	119.39(16)
N1-Cd1-O3	102.00(17)	O6-Cd1-O1	83.45(12)	O6-Cd1-O7	53.13(14)
O9-Cd1-O3	153.98(12)	N3-Cd1-O1	68.34(12)	N3-Cd1-O7	153.32(14)
O1-Cd1-O3	75.13(14)	N1-Cd1-O1	135.98(11)	N1-Cd1-O7	86.02(14)
O4-Cd1-O3	49.18(14)				

Table 3 Hydrogen bonds information in complexes **1** and **2**

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠D-H...A / (°)
1				
C8-H8A...O4 ⁱ	0.096	0.246	0.327 0(5)	141.8
C10-H10A...N6 ⁱⁱ	0.093	0.258	0.326 1(5)	130.9
C11-H11A...O3 ⁱⁱⁱ	0.093	0.232	0.315 9(5)	149.5
2				
O9-H9...N2 ^{iv}	0.0858(10)	0.201(2)	0.283 7(5)	160(5)
N4-H4...O4 ^v	0.086	0.212	0.291 3(6)	153.9

Symmetry operations ⁱ -x+1, y-1/2, -z+1/2; ⁱⁱ -x+2, -y+1, -z; ⁱⁱⁱ x, -y+3/2, z-1/2; ^{iv} x-1/2, -y+1, z+1/2; ^v x, y-1, z

can be confirmed by the bond lengths of C-O being 0.125 3(4) and 0.124 1(4) nm, which are in excellent agreement with previously known semicarbazone complexes in the literature^[6-7]. The distances of Ni-N/O bonds were in the range of 0.197 1 (3)~0.209 5(2) nm, comparable with those in some reported complexes with similar donor set^[3]. As expected, there exist none classic hydrogen bonds in the crystal of **1**.

However, certain C-H...N and C-H...O interactions are helpful to construct three dimensional net work.

By contrast, the molar ratio of the ligand HL and metal is 1:1, and the ligand is neutral tridentate in complex **2** (Fig.1b) with C-O bond length being 0.121 1(5) nm. The Cd(II) ion is also coordinated with two bidentate nitrate anions and one methanol molecule, giving bicapped-triangular prism geometry

(Fig.1c). In the crystal, intermolecular $O9-H9 \cdots N2^{iv}$ and $N4-H4 \cdots O4^v$ (Symmetry codes: $^{iv} x-1/2, -y+1, z+1/2$; $^v x, y-1, z$) hydrogen bonds link the complexes into extended 2D supramolecular structure (Fig.1d).

2.2 IR spectra

The $\nu(C=O)$ of the free ligand is $1\,748\text{ cm}^{-1}$, it shifts to lower frequency value in complex **2**, confirming the coordination of the carbonyl group^[3]. However, such absorption is disappeared in complex **1**, meanwhile, new $(N=C-O)$ stretching vibration absorption is observed at $1\,606\text{ cm}^{-1}$, revealing that the $C=O$ in $O=C-N$ moiety has enolized and the oxygen atom coordinates to the $Ni(II)$ ion^[6-7]. The $\nu(C=N)$ bands of the imine group and pyrazine ring in the ligand HL shift to lower frequency values in the complexes, indicating that the N atoms of both units take part in the coordination^[8]. Meanwhile, the bands at $1\,494$ and $1\,311\text{ cm}^{-1}$ in complex **2** could be assigned to the two split bands ν_1 and ν_4 of the coordinated nitrate group, respectively, showing that the nitrate group is bidentate^[16]. It is in accordance with the crystal structure study.

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 $800\text{ }^\circ\text{C}$ with the linear heating rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ under argon atmosphere. Complex **1** (Fig.2a) is thermally stable up to about $300\text{ }^\circ\text{C}$, indicating there exist no solvent molecules in the complex. A sharp weight loss for complex **1** could be observed from 300 to $330\text{ }^\circ\text{C}$, then gradually smooth until to about $700\text{ }^\circ\text{C}$, corresponding to the decomposition of two organic ligands. However, the first stage occurs with weight loss of 3.62% below $150\text{ }^\circ\text{C}$ for complex **2**, contributing to the loss of one coordinated methanol molecule (Calcd. 6.89%). The second process of weight loss appears between 150 to $780\text{ }^\circ\text{C}$, considered as the decomposition of the ligand L and two nitrate anions. The remainders of the complexes **1** and **2** might be the metal oxides because the residue weights (11.53% and 15.08%) are agreement with the calculated values

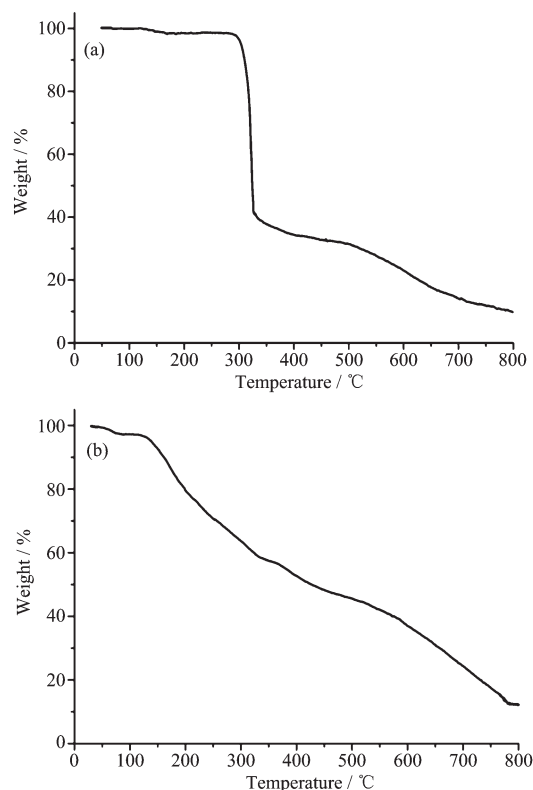


Fig.2 TG curves for complexes **1** (a) and **2** (b)

of 10.12% , and 15.72% , respectively.

2.4 UV spectra

The UV spectra of HL, complexes **1** and **2** in CH_3OH solution (concentration: $1 \times 10^{-5}\text{ mol} \cdot \text{L}^{-1}$) were measured at room temperature (Fig.3). The spectra of HL features only one main band located around 290 nm ($\epsilon = 10\,674\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), which could be assigned to characteristic $\pi-\pi^*$ transition of pyrazine unit^[3]. Similar bands are observed at 289 nm ($\epsilon = 12\,422\text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) in the complex **2**. However, there are

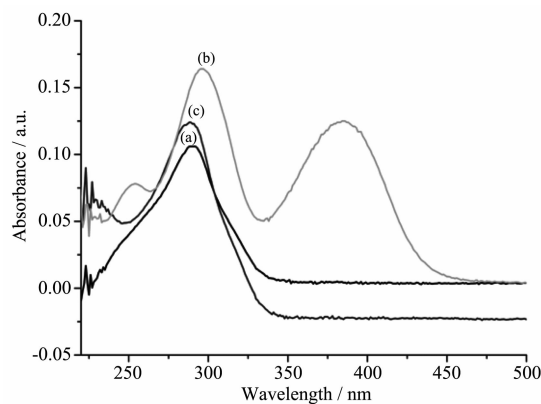


Fig.3 UV spectra of the ligand HL (a), **1** (b) and **2** (c) in CH_3OH solution at room temperature

three bonds in spectra of **1** at 252 ($\varepsilon=7914 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), 296 ($\varepsilon=16\,464 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and 385 nm ($\varepsilon=12\,538 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). The former two could be contributed to the characteristic $\pi\text{-}\pi^*$ transition of pyrazine and imine unit, respectively^[16], while the final one is probably due to the ligand-to-metal charge transfer (LMCT)^[3]. This indicates that an extended conjugation is formed in anionic ligand after complexation in complex **1**.

2.4 Fluorescence spectra

The fluorescence spectra of the ligand HL, complexes **1** and **2** have been studied in CH_3OH solution (concentration: $1\times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$) at room temperature. The results show that the emission spectra of all three compounds exhibit one emission peak at 380 nm when excited at 340 nm, while complex **2** shows another peak at 550 nm. The behavior of Cd(II) ion coordinated to the ligand is regarded as that of emissive species resulted in a CHEF (chelation enhancement of the fluorescence emission) effect^[17].

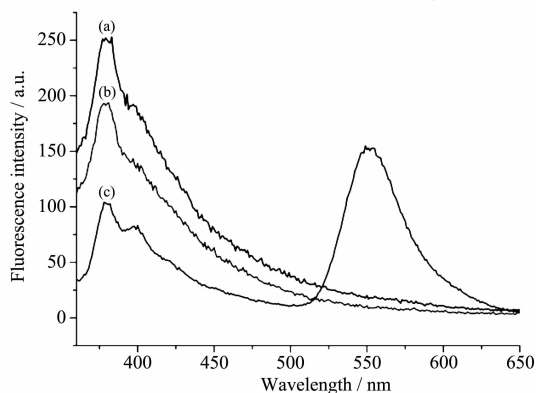


Fig.4 Fluorescence emission spectra of the ligand L (a), **1** (b) and **2** (c) in CH_3OH solution at room temperature

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