

4, 5-二氰基咪唑构筑的锌(II)、钴(II)配合物的合成、晶体结构及荧光性质

胡拖平* 刘建锋 吕旭燕 肖立群 宋江锋

(中北大学理学院, 化学实验室, 太原 030051)

摘要: 以 4, 5-二氰基咪唑(HIMDN)配体, 用常温扩散法合成了 2 个新颖的金属-有机配合物 $[[\text{Zn}_2(\text{IMDN})_4(\text{H}_2\text{O})_3] \cdot (\text{H}_2\text{O})_3]_n$ (**1**) 和 $[\text{Co}(\text{IMDN})_2(\text{H}_2\text{O})_2]_n$ (**2**), 并通过元素分析、红外分析、热重分析和 X-射线单晶衍射对其进行了表征。结果表明配合物 **1** 中 2 个中心 Zn(II) 离子的配位环境不同, 一个是四配位, 另一个是六配位。配合物 **2** 的中心钴(II) 离子为六配位。2 个配合物都为一维链状结构, 并且均通过氢键作用显示出三维结构。此外还研究了配合物 **1** 的荧光性质。

关键词: 4, 5-二氰基咪唑; 一维链; 晶体结构; 荧光

中图分类号: O614.24+1; O614.81+2

文献标识码: A

文章编号: 1001-4861(2013)091928-07

DOI: 10.3969/j.issn.1001-4861.2013.00.270

Syntheses, Crystal Structures and Fluorescent Properties of Two Complexes (Zn(II) and Co(II)) Based on 2H-Imidazole-4, 5-dicarbonitrile

HU Tuo-Ping* LIU Jian-Feng LÜ Xu-Yan XIAO Li-Qun SONG Jiang-Feng

(Department of Chemistry, College of Science, North University of China, Taiyuan 030051, China)

Abstract: Two novel metal-organic complexes $[[\text{Zn}_2(\text{IMDN})_4(\text{H}_2\text{O})_3] \cdot (\text{H}_2\text{O})_3]_n$ (**1**) and $[\text{Co}(\text{IMDN})_2(\text{H}_2\text{O})_2]_n$ (**2**) (HIMDN=2H-imidazole-4,5-dicarbonitrile) based on HIMDN have been synthesized by the method of normal temperature diffusion, and characterized by elemental analysis, FTIR, thermal gravimetric analysis and X-ray diffraction single-crystal structural analysis. The coordination environment of two Zn(II) ions is different in **1**. One Zn(II) ion is four-coordinated and the other is six-coordinated. The central Co(II) ion is six-coordinated in **2**. Both complexes show one dimensional (1D) chain structure and connected by hydrogen bonds to form three-dimensional structure. Moreover, the fluorescent property of complex **1** had been investigated in the solid state. CCDC: 889348, **1**; 889349, **2**.

Key words: 2H-imidazole-4,5-dicarbonitrile; 1D chain; crystal structure; fluorescence

A lot of attention has been received in supramolecular chemistry and crystal engineering of metal-organic frameworks (MOFs) due to their potential power in the design and synthesis of functional materials with interesting structures, applications and desired topologies^[1-5]. Of the many MOFs investigated, the nitrogen-containing ligands constitute an important family and give rise to

fascinating crystal structures^[6-10]. As is known, 2H-imidazole-4,5-dicarbonitrile (HIMDN) is a potential versatile nitrogen-containing ligand in the construction of MOFs due to (i) four coordination sites N atoms with different orientations; (ii) versatile deprotonated forms; (iii) vulnerable CN group which can form a carboxylate or tetrazole group through in situ ligand reaction^[11-12]. So the complexes constructed by

收稿日期: 2013-10-09。收修改稿日期: 2013-05-01。

国家国际科技合作(No.2011DFA51980)和省自然科学基金(No.2011081022)资助项目。

*通讯联系人。E-mail: hutuopingx@yahoo.com.cn

imidazole and its derivatives with transition metal ions have gained considerable attention for a long time, and some of them can be used potentially to optics, magnetic, catalysis materials [13-17]. Nevertheless, because the cyano groups strongly withdraw the charge on the easily formed IMDN anion bridge and diminish the electron count on the π pathway between the metal centres, the complexes including IMDN are scarce [18]. So, we choose nitrogen-containing ligands HIMDN as ligand and transition metal Zn(II) and Co(II) ions to construct MOFs materials by the method of normal temperature diffusion.

1 Experimental

1.1 Materials and methods

All reagents were commercially available and used without further purification. The structures of the complexes were determined on a Bruker Apex II CCD diffractometer and solved by direct methods using the SHELXTL program. Elemental analyses were performed by a Vario EL analyzer. The IR spectra (KBr pellets) was recorded on a FTIR-8400S spectrometer in the range of 4 000 ~400 cm^{-1} . The thermogravimetric analyses were carried out on a ZCT-A analyzer at the heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$ under air atmosphere. Luminescence spectra of solid sample were recorded with a F-2500 FL fluorescence spectrophotometer.

1.2 Synthesis of complex 1

A H_2O solution (2 mL) of $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ (30 mg, 0.015 mmol) was placed at the bottom of a straight glass tube, upon which a solution of HIMDN (15 mg, 0.013 mmol) in water (3 mL) with pH=6~7 adjust by 0.5 $\text{mol} \cdot \text{L}^{-1}$ LiOH was carefully layered. Colorless crystals of **1** suitable for X-ray analysis were obtained at the junction of the layer after a few days (Yield: 65 %). Anal. Calcd.

for $\text{C}_{20}\text{H}_{16}\text{N}_{16}\text{O}_6\text{Zn}_2$ (%): C, 33.898; H, 2.400; N, 31.628. Found (%): C, 33.70; H, 4.52; N, 31.45. IR (KBr pellet, cm^{-1}): 3 515(s), 3 120(s), 2 355(w), 2 240(s), 1 630(m), 1 455(s), 1 300(s), 1 220(w), 1110(s), 650(s).

1.3 Synthesis of complex 2

A H_2O solution (2 mL) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (30 mg, 0.010 mmol) was placed at the bottom of a straight glass tube, upon which a solution of HIMDN (15 mg, 0.013 mmol) in water (3 mL) with pH=6~7 adjust by 0.5 $\text{mol} \cdot \text{L}^{-1}$ NaOH was carefully layered. Red crystals of **2** suitable for X-ray analysis were obtained at the junction of the layer after a few days (Yield: 55%). Calcd for $\text{C}_{10}\text{H}_6\text{CoN}_8\text{O}_2$ (%): C, 36.235; H, 2.416; N, 33.819. Found (%): C, 35.46; H, 2.58; N, 34.22. IR (KBr pellet, cm^{-1}): 3 435(m), 2 970(w), 2 355(w), 2 240(s), 1 615(w), 1450(s), 1315(s), 1112(s), 975(w), 870(m), 655(s).

1.4 Structure determination

Crystallographic data for complex **1** (size: 0.2 mm×0.15 mm×0.1 mm) and **2** (0.15 mm×0.12 mm×0.1 mm) were collected on a Bruker Smart APEXII CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda = 0.071073 \text{ nm}$) at room temperature. Semi-empirical absorption correction was applied (SADABS) and the program SAINT was used to reduce the data [19]. The structures were solved by direct methods with SHELXS-97 program [20] and refined by the full-matrix least-squares techniques on F^2 using SHELXL-97 [21]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined by a riding mode. A summary of the crystallographic data and structure refinement of complex **1** and **2** are listed in Table 1. The selected bond lengths and bond angles are listed in Table 2.

CCDC: 889348, **1**; 889349, **2**.

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

complex	1	2
Empirical formula	$\text{C}_{20}\text{H}_{16}\text{N}_{16}\text{O}_6\text{Zn}_2$	$\text{C}_{10}\text{H}_6\text{CoN}_8\text{O}_2$
Formula weight	707.23	329.16
Temperature / K	296.15	296.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$

Continued Table 1

<i>a</i> / nm	1.445 9(3)	1.311 4(5)
<i>b</i> / nm	1.179 9(2)	0.767 3(3)
<i>c</i> / nm	1.805 1(4)	1.217 0(5)
β / (°)	112.973(4)	94.298(5)
Volume / nm ³	2.835 3(10)	1.221 1(8)
<i>Z</i>	4	4
<i>D_c</i> / (g·cm ⁻³)	1.657	1.790
μ / mm ⁻¹	1.759	1.425
<i>F</i> (000)	1424.0	660.0
Crystal size / mm ³	0.2×0.15×0.1	0.15×0.1×0.1
2 θ range for data collection / (°)	4.24 to 56.28	6.16 to 58.76
Index ranges	-19 ≤ <i>h</i> ≤ 12, -11 ≤ <i>k</i> ≤ 15, -23 ≤ <i>l</i> ≤ 22	-18 ≤ <i>h</i> ≤ 17, -10 ≤ <i>k</i> ≤ 10, -16 ≤ <i>l</i> ≤ 16
Reflections collected	19 740	8 678
Independent reflections	6 930 (<i>R</i> _{int} =0.0829)	1 690 (<i>R</i> _{int} =0.0328)
Data/restraints/parameters	6 930/21/433	1 690/8/103
Goodness-of-fit on <i>F</i> ²	0.961	1.049
Final <i>R</i> indexes (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ =0.054 4, <i>wR</i> ₂ =0.122 4	<i>R</i> ₁ =0.025 2, <i>wR</i> ₂ =0.062 5
Final <i>R</i> indexes (all data)	<i>R</i> ₁ =0.124 9, <i>wR</i> ₂ =0.153 5	<i>R</i> ₁ =0.030 4, <i>wR</i> ₂ =0.065 3
Largest diff. peak and hole / (e·nm ⁻³)	820 and -1 240	330 and -420

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

1					
Zn(1)-N(1)	0.1989(4)	Zn(2)-N(15)	0.2120(4)	Zn(2)-O(3)	0.2096(4)
Zn(1)-N(9)	0.2008(4)	Zn(2)-N(11)#1	0.2169(4)	Zn(2)-O(2)	0.2151(5)
Zn(1)-N(13)	0.2023(4)	Zn(2)-N(3)#2	0.2166(4)	Zn(2)-O(1)	0.2109(4)
Zn(1)-N(5)	0.2007(4)				
N(1)-Zn(1)-N(9)	110.76(17)	O(1)-Zn(2)-N(3) #2	93.23(15)	N(5)-Zn(2)-N(11)#1	91.03(15)
N(1)-Zn(1)-N(13)	114.58(16)	O(1)-Zn(2)-O(2)	81.1(2)	N(5)-Zn(2)-O(3)#2	92.11(15)
N(1)-Zn(1)-N(5)	104.32(17)	O(3)-Zn(2)-N(15)	94.78(18)	N(5)-Zn(2)-O(2)	174.34(19)
N(9)-Zn(1)-N(13)	105.54(16)	O(3)-Zn(2)-N(11)#1	89.34(15)	O(3)-Zn(2)-O(2)	90.9(2)
N(5)-Zn(1)-N(9)	114.06(16)	O(3)-Zn(2)-N(3) #2	87.34(15)	O(2)-Zn(2)-N(11)	88.51(16)
N(5)-Zn(1)-N(13)	107.79(18)	O(3)-Zn(2)-O(1)	171.96(19)	O(2)-Zn(2)-N(3)#2	88.67(16)
O(1)-Zn(2)-N(11)#1	89.66(15)				
2					
Co(1)-N(1)	0.21366(14)	Co(1)-O(1)	0.20743(19)	Co(1)-O(2)	0.20393(19)
Co(1)-N(1)#3	0.21366(14)	Co(1)-N(3)#4	0.21846(15)		
N(1)-Co(1)-N(1)#3	91.2(2)	O(1)-Co(1)-N(1)#3	88.72(3)	O(2)-Co(1)-O(1)	180.0
N(1)1-Co(1)-N(3)#4	88.9(2)	O(1)-Co(1)-N(1)	88.72(3)	O(2)-Co(1)-N(1)#3	91.28(3)
N(1)-Co(1)-N(3)#5	90.7(2)	O(1)-Co(1)-N(3)#5	90.75(4)	O(2)-Co(1)-N(3)#5	89.25(4)
N(1)-Co(1)-N(3)#4	89.3(2)	O(1)-Co(1)-N(3)#4	90.75(4)	O(2)-Co(1)-N(3)#4	89.25(4)
N(1)1-Co(1)-N(3)#5	178.51(6)	O(2)-Co(1)-N(1)	91.28(3)		

Symmetry codes: 1: #1: -*x*, 1/2+*y*, 1/2-*z*; #2: -*x*, -1/2+*y*, 1/2-*z*; 2: #3: 1-*x*, +*y*, 1/2-*z*; #4: 1-*x*, 1-*y*, 1-*z*; #5: +*x*, 1-*y*, -1/2+*z*

2 Results and discussion

2.1 Crystal structures of the complex 1 and 2

2.1.1 $\{[\text{Zn}_2(\text{IMDN})_4(\text{H}_2\text{O})_3] \cdot (\text{H}_2\text{O})_3\}_n$ (**1**)

Complex **1** crystallizes in monoclinic system, $P2_1/c$ space group. The scheme of the asymmetric unit of complex **1** is in Fig.1. The asymmetric unit of **1** consists of two Zn (II) ions, four IMDN⁻ anions and three coordinated and three uncoordinated water molecules. One nitrogen atom in every imidazole ring is deprotonated. The coordination environment of two zinc ions is different. The Zn (1) ion is four-coordinated with four nitrogen atoms (N1,N5,N9,N13) from four IMDN⁻ anions to form a tetrahedron configuration. The minimum bond angle (N1-Zn1-N5) is 104.32 (17) and the biggest bond angle (N1-Zn1-N13) is 114.58 (16)°. The Zn (2) ion is six-coordinated with three oxygen atoms (O1, O2, O3) from three coordinated water molecules and three nitrogen atoms (N15, N11#1, #1: $-x, 1/2+y, 1/2-z$; N3#2, #2: $-x, -1/2+y, 1/2-z$) from three IMDN⁻, respectively. The Zn-N bonds length are in the range 0.198 9~0.202 3 nm. The average length of Zn-O bonds are 0.211 8 nm, all of which are accordant with the normal reported Zn-N and Zn-O bonds lengths^[22-23]. The Zn(1) and Zn(2) ions are connected through IMDN⁻ anions to expand a one dimensional (1D) double chains (Fig.2). The distance of Zn(1)-Zn (2) are 0.605 9 and 0.613 4 nm, respectively.

There are abundant H-bonding interactions in the complex **1**. The intramolecular H-bonding interactions between uncoordinated water molecules and coordinated water molecules (O(2)-H(2B)···O(5), O(3)-H(3B)···O(4), O(5)-H(5A)···O(2), O(6)-H(6A)···O(1)) firmly fix the three uncoordinated water molecules on

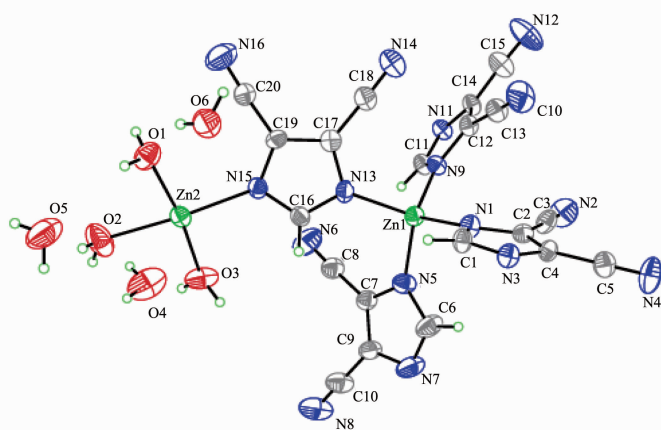
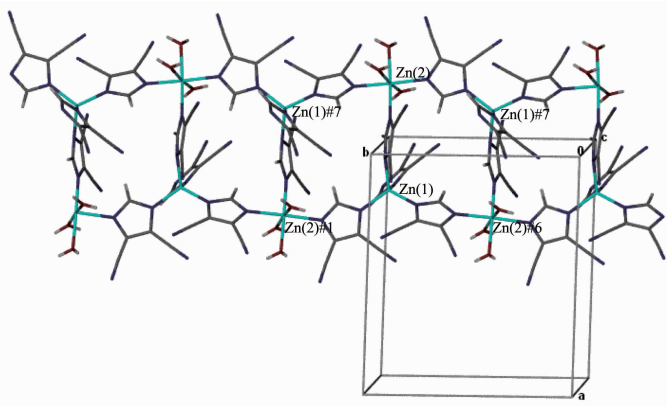
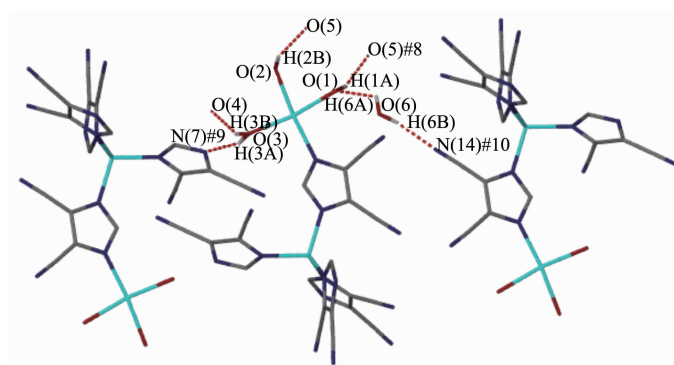


Fig.1 Asymmetric unit of complex **1**



Symmetry codes: #1: $-x, 1/2+y, 1/2-z$; #6: $-x, y-1/2, 1/2-z$; #7: x, y, z

Fig.2 1D double chain of complex **1**



Symmetry codes: #8: $-1-x, 2-y, -z$; #9: $-x, 2-y, 1-z$; #10: $-x, 2-y, -z$; the irrelevant H atoms are omitted for clarity

Fig.3 H-bonding interactions of complex **1**

Table 3 Hydrogen bond lengths and bond angles for complex **1** and **2**

Donor-H...Acceptor	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{D-H}\cdots\text{A} / (^\circ)$
1				
O(1)-H(1A) \cdots O(5)#8	0.085(3)	0.205(4)	0.2838(6)	153(7)
O(2)-H(2B) \cdots O(5)	0.085(4)	0.208(5)	0.2869(7)	155(6)
O(3)-H(3A) \cdots N(7)#9	0.085(3)	0.202(3)	0.2815(6)	156(7)
O(3)-H(3B) \cdots O(4)	0.085(4)	0.203(7)	0.2804(7)	153(7)
O(5)-H(5A) \cdots O(2)	0.085(7)	0.250(7)	0.2869(7)	108(7)
O(6)-H(6A) \cdots O(1)	0.085(6)	0.199(7)	0.2693(7)	138(6)
O(6)-H(6B) \cdots N(14)#10	0.085(7)	0.207(8)	0.2903(8)	169(7)
2				
O(1)-H(1A) \cdots N(4)#11	0.084	0.203	0.28407	162
O(2)-H(2) \cdots N(2)#12	0.085	0.197	0.28110	170

Symmetry codes: **1**: #8: $-1-x, 2-y, -z$; #9: $-x, 2-y, 1-z$; #10: $-x, 2-y, -z$; **2**: #11: $1/2-x, 1/2-y, 1-z$; #12: $1/2-x, 1/2+y, 1/2-z$

1D chain. In addition, the adjacent 1D chains further extend to be 3D structure by H-bonding interactions (O(3)-H(3A) \cdots N(7)#9, #9: $-x, 2-y, 1-z$; O(6)-H(6B) \cdots N(14)#10, #10: $-x, 2-y, -z$) (Fig.3). The data of all H-bonding interactions for **1** are listed in Table 3.

2.1.2 $[\text{Co}(\text{IMDN})_2(\text{H}_2\text{O})_2]_n$ (**2**)

Complex **2** crystallizes in monoclinic system, $C2/c$ space group. The scheme of the asymmetric unit of complex **2** is shown in Fig.4. Unlike **1**, there are no free water molecules in **2**. The asymmetric unit of **2** consists of $1/2$ Co (II) ion, one IMDN $^-$ anion and two $1/2$ coordinated water molecules. One nitrogen atom in every imidazole ring is deprotonated. The central Co(II) ion is six-coordinated by four nitrogen atoms from four IMDN $^-$ anions and two oxygen atoms from two coordinated water molecules to form an octahedron configuration. Its equatorial plane is occupied by four

coordinated nitrogen atoms from two imidazole rings and two cyano groups. While two oxygen atoms occupy the axial position (the O2-Co1-O1 bond angle is 180°). The average lengths of Co-O and Co-N bonds are 0.207 43(19) nm and 0.213 66(14) nm, respectively. All of which are accordant with the normal reported Co-N and Co-O bonds lengths^[24]. The adjacent Co(II) centers

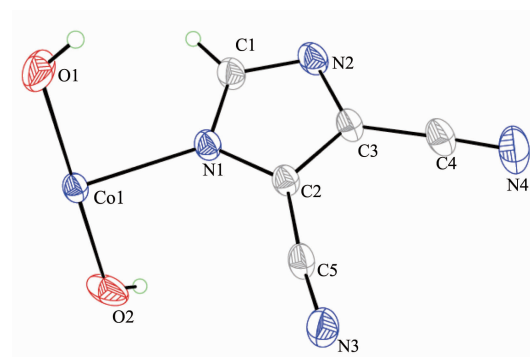
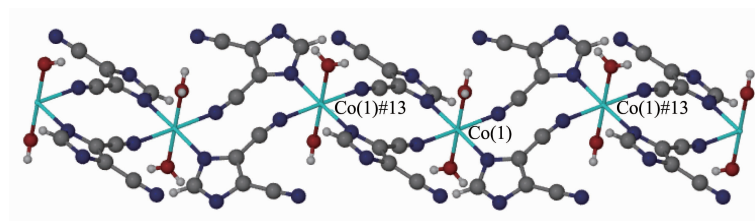


Fig.4 Asymmetric unit of complex **2**

are connected by the IMDN^- anions to afford a 1D chain motif ($\text{Co}\cdots\text{Co}=0.623\ 8\ \text{nm}$) (Fig.5).

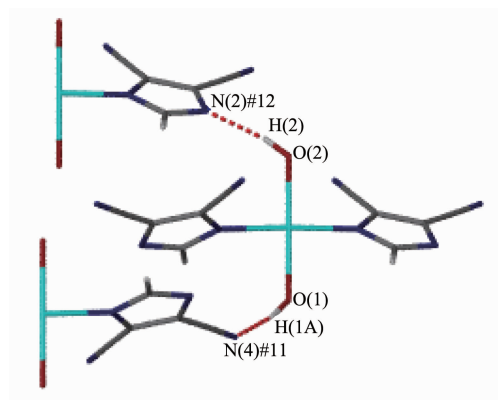
There are also H-bonding interactions in the complex **2** (Fig.6). The H-bonding interactions between coordinated water molecules and IMDN^-

anions ($\text{O}(1)\cdots\text{H}(1\text{A})\cdots\text{N}(4)\#11$, $\#11: 1/2-x, 1/2-y, 1-z$; $\text{O}(2)\cdots\text{H}(2)\cdots\text{N}(2)\#12$, $\#12: 1/2-x, 1/2+y, 1/2-z$) expand complex **2** to a 3D wave-like layer supramolecular architecture. The data of all H-bonding interactions for **2** are listed in table 3.



Symmetry codes: #13: $1-x, 1-y, 1-z$

Fig.5 View of the 1D chain of the complex **2**



Symmetry codes: #11: $1/2-x, 1/2-y, 1-z$; #12: $1/2-x, 1/2+y, 1/2-z$; the irrelevant H atoms are omitted for clarity

Fig.6 H-bonding interactions of complex **2**

2.2 IR spectra of the complex **1** and **2**

In the IR spectrum of complex **1**, the broad peak centered at $3\ 515\ \text{cm}^{-1}$ indicates the O-H characteristic stretching vibrations of uncoordinated water molecular. The sharp characteristic peak at $2\ 240\ \text{cm}^{-1}$ is attributed to the characteristic stretching vibrations of cyano group. The very characteristic bands $\nu(-\text{NH}-)$, $\nu(\text{C}=\text{N})$ of HIMDN ligand moved from $3\ 100$ and $1\ 650\ \text{cm}^{-1}$ to $3\ 120$ and $1\ 630\ \text{cm}^{-1}$ indicate the nitrogen atoms of imidazole ring coordinated with $\text{Zn}(\text{II})$ ion.

In the IR spectrum of complex **2**, the sharp characteristic peak at $2\ 240\ \text{cm}^{-1}$ is also attributed to the characteristic stretching vibrations of cyano group. The very characteristic bands $\nu(-\text{NH}-)$, $\nu(\text{C}=\text{N})$ of HIMDN ligand moved to $3\ 435$ and $1\ 615\ \text{cm}^{-1}$ indicate the nitrogen atoms of imidazole ring

coordinated with $\text{Co}(\text{II})$ ion.

2.3 Thermogravimetric analysis

Thermogravimetric analysis has been measured for complex **1** and **2**. The thermostability of complex **1** is weak, it begins to loss weight from $45\ ^\circ\text{C}$. The weight loss of 14.8% from 45 to $225\ ^\circ\text{C}$ corresponds to the loss of uncoordinated and coordinated water molecules (Calcd. 15.3 %). The weight loss of 64.1% from 225 to $646\ ^\circ\text{C}$ dues to the removal of coordinated IMDN^- anions (Calcd. 66.4%). No weight loss is observed after $646\ ^\circ\text{C}$, and the resulting residue is zinc oxide (ZnO) (Obsd. 21.1%, Calcd. 20.6%).

The complex **2** is stable up to $130\ ^\circ\text{C}$, the weight loss of 8.10% from 130 to $280\ ^\circ\text{C}$ corresponds to the loss of coordinated water molecules (Calcd. 10.8%). The weight loss of 72.8% from 280 to $565\ ^\circ\text{C}$ dues to the removal of coordinated IMDN^- anions (Calcd. 70.7%). No weight loss is observed after $565\ ^\circ\text{C}$, and the resulting residue is cobalt oxide (Obsd. 20.1%, Calcd. 22.6%).

2.4 Fluorescence properties

The emission spectra of complex **1** and free HIMDN in the solid state were investigated at room temperature. Complex **1** exhibits blue photoluminescence with two emission peaks at 450 nm and 472 nm upon excitation at 237 nm (Fig.7). However, no obvious emission bands are observed for the free HIMDN in the range of 400~800 nm under the same experimental conditions. Thus, The

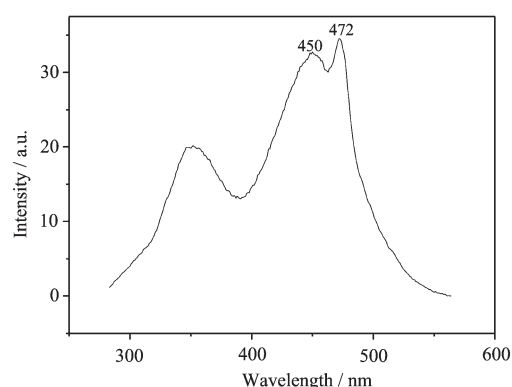


Fig.7 Solid-state emission spectrum of **1** at room temperature

fluorescence emission of **1** could be assigned to the emission of ligand-to metal charge transfer (LMCT)^[25]. For possesses strong fluorescent intensity, it appears to be good candidates for novel hybrid inorganic-organic photoactive materials.

References:

- [1] Moulton B, Zaworotko M J. *Chem. Rev.*, **2001**,**101**:1629-1658
- [2] Kitagawa S, Kitaura R, Noro S I. *Angew., Chem. Int. Ed.*, **2004**,**43**:2334-2375
- [3] Evans O R, Lin W. *Acc. Chem. Res.*, **2002**,**35**:511-522
- [4] Zhang J P, Chen X M. *J Am. Chem. Soc.*, **2008**,**130**:6010-6017
- [5] Michael O K. *Chem. Soc. Rev.*, **2009**,**38**:1215-1217
- [6] Sarah E J, Bowman, Kara L B. *Inorg. Chem.*, **2010**,**49**(17): 7890-7897
- [7] Telfer S G, Kuroda R. *Coord. Chem. Rev.*, **2003**,**242**:33-46
- [8] Maji T K, Matsuda R, Kitagawa S A. *Nature Mater.*, **2007**,**6**: 142-148
- [9] Sano T, Negishi N, Koike K, et al. *J. Mater. Chem.*, **2004**, **14**:380-384
- [10] Hu T P, Bi W H, Hu X Q, et al. *Cryst. Growth Des.*, **2010**, **10**:3324-3326
- [11] Hu T P, Bi W H, Sun D F, et al. *RSC Adv.*, **2011**,**1**:1682-1686
- [12] HU Xiao-Qin (胡晓琴). *Thesis for the Master of North University of China*(中北大学硕士论文). **2011**.
- [13] Akihiro T, Takuya K, Hiroshi F. *Inorg. Chem.*, **2009**,**48**(6): 2614-2625
- [14] Yang H, Chen J M, Sun J J, et al. *Dalton Trans.*, **2009**: 2540-2551
- [15] Akordi M H, Liu Y L, Larsen R W, et al. *J. Am. Chem. Soc.*, **2008**,**130**:12639-12641
- [16] Lu W G, Su C Y, Lu T B, et al. *J. Am. Chem. Soc.*, **2006**, **128**:34-35
- [17] REN Chun-Xia (任春霞). *Thesis for the Doctorate of Zhongshan University*(中山大学硕士论文). **2004**.
- [18] Prasad B L V, Sato H, Enoki T, et al. *Chem. Soc., Dalton Trans.*, **1999**:25-30
- [19] Sheldrick G M. SADABS 2.05, University of Göttingen, Germany.
- [20] Sheldrick G M. *SHELXL97, Program for the Refinement of Crystal Structure*, University of Gottingen, Germany, **1997**.
- [21] Sheldrick G M. *SHELXL97, Program for the Refinement of Crystal Structure*, University of Gottingen, Germany, **1997**.
- [22] SONG Jin-Hao(宋金浩), GU Ya-Kun(顾雅琨), LI Xia(李夏). *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2010**,**26**(8): 1457-1462
- [23] ZHANG Deng-Qing(张灯青), ZHANG Wen-Hua(张文华), CHEN Jin-Xiang(陈金香). *Acta Chimica Sinica (Huaxue Xuebao)*, **2005**,**63**(22):2089-2092
- [24] Zhang B S, Zheng M, Wu C S, et al. *Chinese J. Struct. Chem.*, **2012**,**4**:577-581
- [25] Fu Z Y, Wu X T, Dai J C, et al. *Eur. J. Inorg. Chem.*, **2002**: 2730-2735