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基于 5-羟基-2-吡啶羧酸的五个过渡金属配合物的合成、结构及荧光性质

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摘要: 以 5-羟基-2-吡啶羧酸为配体,通过水热法与过渡金属盐合成了 5 个配合物,其分子式分别为[$M(HL)_2(H_2O)_2$](M=Zn,**1**;Mn,**2**;Co,**3**;Ni,**4**),[$Cu(HL)_2$] (**5**)。由元素分析,红外光谱,X-射线单晶衍射对化合物 **1~5** 的结构进行了表征。化合物 **1~5** 为单核结构的配合物,它们均通过氢键形成了三维超分子结构。测试了配合物 **1** 的光致发光及 **1~5** 的热稳定性。研究发现,配合物 **1** 发光归因于配体内的跃迁。

关键词: 过渡金属; 配合物; 水热合成; 晶体结构
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Five Transition Metal Complexes with 5-Hydroxy-pyridine-2-carboxylic Acid: Syntheses, Crystal Structures and Luminescence Properties

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Abstract: Five transition metal complexes based on the 5-hydroxy-pyridine-2-carboxylic acid (H_2L) were synthesized under hydrothermal conditions, namely, [$M(HL)_2(H_2O)_2$] (M=Zn, **1**; Mn, **2**; Co, **3**; Ni, **4**), [$Cu(HL)_2$] (**5**). Compounds **1~5** were structurally characterized by the elemental analyses, infrared spectra, and single crystal X-ray diffractions. The structural analyses show that **1~5** are discrete mononuclear complexes, which are extended to form the 3D supramolecular frameworks by hydrogen bonds interactions. The solid-state photoluminescence of **1** and thermal properties of **1~5** were further explored, respectively. CCDC: 949732, **1**; 949731, **2**; 1056084, **3**; 1056085, **4**; 1056086, **5**.

Key words: transition metal; coordination compound; hydrothermal synthesis; crystal structure

Recently, the design and synthesis of coordination polymers (CPs) have been acquired tremendous attentions for their intriguing architectures and potential applications in the fields of catalysis[1-2], magnetism[3-5], gas adsorption[6], luminescence[7-10], and so on. The structural construction of CPs is still a great challenge for the chemists since the self-assembly of CPs is probably influenced by the temperature, pH value, solvent of reaction system, and the ratios between metal salts and ligands, etc. The symmetric and asymmetric ligands for the construction of coordination compounds have been attracted the increasing focus, in which possess the versatile donor atoms to assemble with metal centers to generate a great many of CPs[11]. Moreover, the multidentate ligands containing N- and O-donor, such as symmetric 4-hydroxy-pyridine-2,6-dicarboxylic acid, have been extensively used for the synthesis of CPs in the recent

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years[12-15]. The analogous pyridyl multi-carboxylic acids are frequently employed for the synthesis of transition and/or lanthanide metal CPs[16-18]. Furthermore, the controlled design of zero-dimensional aggregates is still a principal field in the crystal engineering[19-20]. In addition, hydrogen bonds and π-π interactions are especially considerable in supramolecular construction of CPs, which are important not only in the viewpoint of coordination chemistry, but also for the development of intricate coordination networks of crystal engineering[21-22].

Based on the above reasons, we chose an asymmetric rigid ligand, 5-hydroxy-pyridine-2-carboxylic acid (H_2L), which owns the multiple coordination sites and probably exhibits plenty of coordination modes with metal centers. Herein, five transition metal complexes have been synthesized, namely, $[M(HL)_2(H_2O)_2]$ (M=Zn, **1**; Mn, **2**; Co, **3**; Ni, **4**), and $[Cu(HL)_2]$ (**5**). These compounds have been characterized by the elemental analyses, IR spectra, TG, and single crystal X-ray crystallography. The crystal structures, thermal properties and photoluminescent properties of **1** ~**5** were investigated in this paper. To the best of our knowledge, the crystal structures of compounds based on H_2L ligand are firstly reported.

1　Experimental

1.1　Materials and physical measurements

The chemical reagents and metal salts were commercially available and used without further purification. The infrared spectra within the frequency range 4 000 ~400 cm^{-1} were recorded on a Nicolet Avatar-360 spectrometer. The elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 analyzer. Thermogravimetric Analysis (TGA) was measured on a Perkin-Elmer TG-7 analyzer heated from room temperature to 900 ℃ under nitrogen atmosphere. Powder X-ray diffraction (PXRD) was performed on a PANalytical Empyrean instrument by using Cu $K\alpha$ radiation at room temperature. The luminescence spectra were measured on a FLS920 spectrophotometer.

1.2　Preparation of complexes

$[Zn(HL)_2(H_2O)_2]$ (**1**). A mixture of $ZnSO_4 \cdot 7H_2O$ (0.1 mmol, 28.8 mg), H_2L (0.1 mmol, 13.9 mg) and 4.0 mL H_2O was sealed in a 23 mL Teflon-lined stainless steel container, and stirred for 30 min in air and heated at 170 ℃ for 72 h, then cooled to 30 ℃ at a rate of 2 ℃·h^{-1}. After filtration, the product was washed with distilled water and then dried, colorless block crystal of **1** was obtained. Yield: 60% (based on Zn). Anal. Calcd. for $C_{12}H_{12}N_2O_8Zn$ (%): C, 38.13, H, 3.18, N, 7.42; Found(%): C, 38.26, H, 3.22, N, 7.43. IR (KBr pellet, cm^{-1}): 3 450(s), 3 074(m), 1 616(s),1 584 (s), 1 560(s), 1 494(m), 1 413(s), 1 384(s), 1 349(m), 1 281 (s), 1 129(m), 826(m), 697(m), 673(w), 562(m).

$[Mn(HL)_2(H_2O)_2]$ (**2**). The complex was obtained following the same procedure described above for **1** except that the $ZnSO_4 \cdot 7H_2O$ was replaced by $MnCl_2 \cdot 4H_2O$ (0.1 mmol, 19.8 mg). Yellow block crystal of **2** was obtained suitable for single crystal X-ray diffraction analysis. Yield: 56% (based on Mn). Anal. Calcd. for $C_{12}H_{12}N_2O_8Mn$ (%): C, 39.22, H, 3.27, N, 7.63; Found (%): C, 40.23, H, 3.32, N, 7.75. IR (KBr pellet, cm^{-1}): 3 441(s), 3 260(m), 1 610(m), 1 594(s), 1 550(s), 1 495(m), 1 380(s), 1 334(m), 1 287(s), 1 129 (m), 945(w), 825(m), 668(m), 554(m).

$[Co(HL)_2(H_2O)_2]$ (**3**). A mixture of $CoCl_2 \cdot 6H_2O$ (0.1 mmol, 23.8 mg), H_2L (0.05 mmol, 6.95 mg) , bpy (0.05 mmol, 78.1 mmg), and 10.0 mL H_2O was sealed in a 23 mL Teflon-lined stainless steel container, and stirred for 30 min in air and heated at 160 ℃ for 72 h, then cooled to 30 ℃ at a rate of 2 ℃·h^{-1} . After filtration, the product was washed with distilled water and then dried, pink block crystal of **3** was obtained. Yield: 52% (based on Co). Anal. Calcd. for $C_{12}H_{12}N_2O_8Co$ (%): C, 38.83, H, 3.25, N, 7.55; Found (%): C, 38.25, H, 3.07, N, 7.33. IR (KBr pellet, cm^{-1}): 3 425 (s), 3 198(m), 1 616(m), 1 595(s), 1 549(s), 1 493(m), 1 382(s), 1 332(m), 1 291(s), 1 128(m), 939(w), 830 (m), 697(m), 562(m).

$[Ni(HL)_2(H_2O)_2]$ (**4**). A mixture of $NiCl_2 \cdot 6H_2O$ (0.1 mmol, 23.7 mg), H_2L (0.1 mmol, 13.9 mg), 8.0 mL H_2O, and 2.0 mL C_2H_5OH was sealed in a 23 mL Teflon-lined stainless steel container, and stirred for 30 min in air and heated at 160 ℃ for 72 h, cooled to 100 ℃ for 48 h, then cooled to 30 ℃ at a rate of 2 ℃

·h $^{-1}$. After filtration, the product was washed with distilled water and then dried, blue block crystal of 4 was obtained. Yield: 54% (based on Ni). Anal. Calcd. for $C_{12}H_{12}N_2O_8Ni$ (%): C, 38.86, H, 3.26, N, 7.55; Found (%): C, 38.34, H, 3.22, N, 7.38. IR (KBr pellet, cm^{-1}): 3 429(s), 3 187(m), 1 621(m), 1 594(s), 1 552(s), 1 489(m), 1 380(s), 1 331(m), 1 289(s), 1 127 (m), 936(w), 833(m), 694(m), 567(m).

[Cu(HL)$_2$] (**5**). The complex was obtained following the same procedure described above for **4** except that the $NiCl_2·6H_2O$ was replaced by $CuCl_2·6H_2O$ (0.1 mmol, 17.0 mg). Blue block crystal of **5** was obtained. Yield: 57% (based on Mn). Anal. Calcd. for $C_{12}H_8N_2O_6Cu$ (%): C, 42.42, H, 2.37, N, 8.25; Found (%): C, 42.23, H, 2.54, N, 8.45. IR (KBr pellet, cm^{-1}): 3 041 (m), 1 610(m), 1 570(s), 1 505(w), 1 457(m), 1 376(s), 1 323(m), 1 287(s), 1 131(m), 945(w), 841(m), 691(m), 573(m).

1.3 X-ray crystallography

Single-crystal X-ray diffraction data for **1**~**5** were collected on a Bruker Apex Ⅱ Smart CCD diffractometer, using the graphite-monochromatic Mo $K\alpha$ radiation (λ=0.071 073 nm) at the room temperature. Semi-empirical absorption corrections were applied using the SADABS program[23]. All of the structures were resolved by direct methods using SHELXS-97[23] and refined by full-matrix least-squares fitting on F^2 of the SHELXTL-97 program[23]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on C and hydroxyl were geometrically generated, the hydrogen atoms of water molecules were located from difference Fourier maps and refined with the common isotropic thermal parameter. The crystal parameters, data collection and refinement for complexes **1**~**5** are summarized in Table 1. The selected bond lengths and angles of **1**~**5** are listed in Table S1. The selected hydrogen bonds distances and angles in crystal packing for **1**~**5** are listed in Table S2.

CCDC: 949732, **1**; 949731, **2**; 1056084, **3**; 1056085, **4**; 1056086, **5**.

Table 1 Crystal data for 1~5

Compound	1	2	3	4	5
Formula	$C_{12}H_{12}N_2O_8Zn$	$C_{12}H_{12}N_2O_8Mn$	$C_{12}H_{12}N_2O_8Co$	$C_{12}H_{12}N_2O_8Ni$	$C_{12}H_8N_2O_6Cu$
Formula weight	377.63	367.18	371.17	370.93	339.75
T / K	296	296	296(2)	296	296
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / nm	0.580 3(6)	0.570 8(6)	0.580 1(12)	0.581 7(5)	0.523 6(3)
b / nm	1.186 2(13)	1.219 4(14)	1.185 6(2)	1.172 2(9)	1.520 0(9)
c / nm	0.969 1(11)	0.974 6(11)	0.967 4(2)	0.964 1(9)	0.727 5(5)
β / (°)	101.701(2)	101.398(2)	101.762(2)	102.184(9)	97.468(12)
V / nm^3	0.653 2(12)	0.665 1(13)	0.651 4(2)	0.642 7(10)	0.574 1(6)
Z	2	2	2	2	2
D_c / (g·cm^{-3})	1.920	1.957	2.079	1.917	1.965
μ / mm^{-1}	1.930	1.042	1.368	2.684	1.936
F(000)	416	376	392	380	342
R_{int}	0.041 9	0.024 5	0.022 0	0.043 5	0.068 2
GOF	1.062	1.099	1.060	1.048	1.144
R_1[a] [$I>2\sigma(I)$]	0.041 9	0.024 5	0.022 0	0.043 5	0.068 2
wR_2[b] [$I>2\sigma(I)$]	0.110 0	0.069 0	0.061 3	0.108 9	0.196 0
R_1 (all data)	0.044 4	0.026 0	0.025 8	0.055 7	0.100 6
wR_2 (all data)	0.112 0	0.070 2	0.064 5	0.120 9	0.215 9

[a] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$; [b] $wR_2=[\sum[w(F_o^2-F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$.

2　Results and discussion

2.1　General characterization

Complexes **1~5** are stable in air and insoluble in water or in common organic solvents. The IR spectra of **1~5** show strong absorption bands about 1 380 and 1 610 cm^{-1} for **1**, 1 382 and 1 595 cm^{-1} for **2**, 1 387 and 1 592 cm^{-1} for **3**, 1 380 and 1 594 cm^{-1} for **4**, 1 376 and 1 570 cm^{-1} for **5**, which are attributed to the asymmetric and symmetric stretching vibrations of carboxylate groups, respectively. The broad bands at around 3 400 cm^{-1} of **1~4** are assigned to the vibration of water molecules[24].

2.2　Description of crystal structures

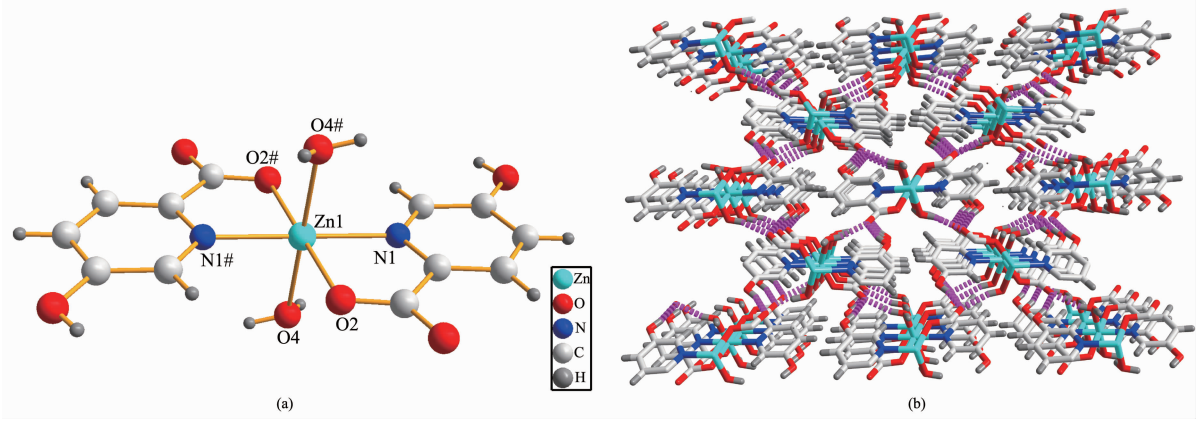
2.2.1　Crystal structures of compounds **1~4**

The single-crystal X-ray diffraction analyses reveal that structures of **1~4** are isostructural mononuclear complexes and crystallize in the monoclinic symmetry with space group $P2_1/c$. Although bpy ligand was added in the preparation of complex **3**, it is uncoordinated with the metal ions and probably acts as the role of template agent. The crystal of **1** is described here in detail as a representative example. The asymmetric unit of **1** contains an independent Zn(Ⅱ) ion (with an occupancy of 0.5), a chelating HL^- anion ligand and a coordinated water molecule. The coordination environment of Zn(Ⅱ) ion is shown in Fig. 1a. Zn(Ⅱ) ion is six-coordinated with two carboxylate oxygen atoms (O2, O2#), and two nitrogen atoms (N1, N1#) belonging to HL^- ligands, two oxygen atoms of coordination water molecules (O4, O4#), which resemble an octahedral coordination sphere. Two carboxylate oxygen atoms and two nitrogen atoms from HL^- ligands occupy the horizontal positions of octahedral coordination sphere. The vertical sites of octahedral coordination sphere are taken up by two coordinated water molecules. The Zn-O (O2, O4) bond lengths are 0.210 2(7) nm and 0.217 7(7) nm, respectively; and the distance of Zn-N (N1) is 0.209 23(7) nm, which are in good agreement with the values in the literature[25-26]. The carboxylate group is slight twisted out of the pyridyl ring with dihedral angles of 1.64°.

The hydrogen bonds are formed between uncoordinated hydroxyl oxygen atom (O3) and uncoordinated carboxylate oxygen atom (O1#), coordinated water molecule (O4) and uncoordinated carboxylate oxygen atom (O1#), and coordinated water molecules (O4) and coordinated carboxylate oxygen (O2#), respectively; the distances of O3…O1#, O4…O1#, and O4…O2# are 0.254 19, 0.271 42 and 0.345 31 nm, respectively[27]; the corresponding angles of DHA are 158.0°, 164.3°, and 161.0°, respectively. These hydrogen bonds connect the unit of $Zn(HL)_2(H_2O)_2$ to form a 3D supramolecular network along *a* axis, as shown in Fig.1b (Symmetry codes: # $-x+2$, $-y$, $-z$).

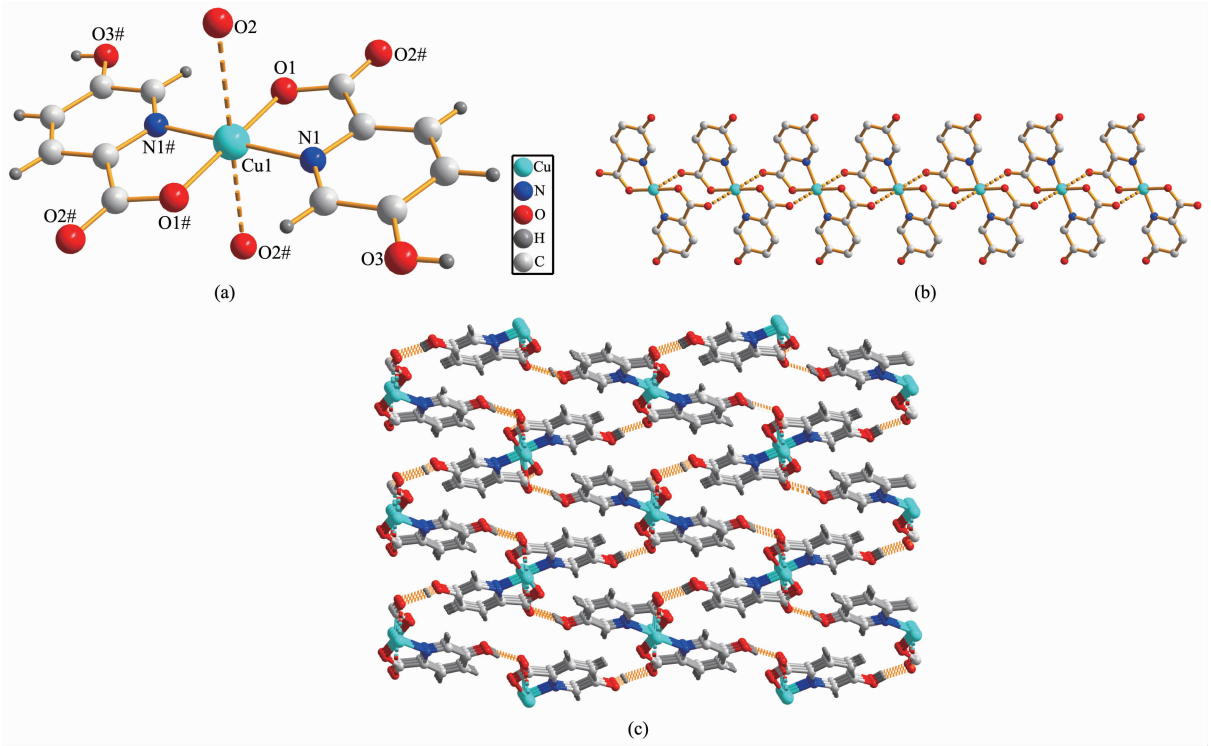
2.2.2　Crystal structure of compound **5**

Compound **5** is a mononuclear complex and crystallizes in the monoclinic symmetry with $P2_1/c$ space group. The asymmetric unit of **5** contains an independent Cu(Ⅱ) ion (with an occupancy of 0.5), a chelating HL^- anion. The coordination environment of



Symmetry code: # $-x+2$, $-y$, $-z$

Fig.1　(a) Coordination environment of Zn(Ⅱ) in **1**; (b) 3D supramolecular structure of **1**



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

Fig.2 (a) Coordination environment of Cu(Ⅱ) in **5**; (b) A view showing a 1D chain along *c* axis; (c) 3D supramolecular structure of **5**

Cu(Ⅱ) ion is shown in Fig.2a. Cu(Ⅱ) ion is four-coordinated with two carboxylate oxygen atoms (O1, O1#), and two nitrogen atoms (N1, N1#) belonging to the HL^- ligands, which resemble an square planar geometry. Two carboxylate oxygen atoms and two nitrogen atoms from HL^- ligands inhabit the horizontal sites of coordination sphere. The bond length of Cu-O (O1) is 0.194 0(2) nm, and the distance of Cu-N is 0.194 6(3) nm. There exists the weak bond of Cu···O2 in **5** with the distance of 0.285 9(2) nm[28]. Cu(Ⅱ) ions are bridged by Cu···O2 bonds to form a 1D infinite linear chain along *c* axis (Fig.2b).

The hydrogen bonds are formed between uncoordinated hydroxyl oxygen atom (O3) and carboxylate oxygen atom (O2). The distance of O3···O2 is 0.261 0 nm[29]; and the corresponding angle of DHA is 164.9°. Finally, the 1D infinite chains are combined through the intermolecular hydrogen bonds to generate a 3D supramolecular architecture (Fig.2c) (Symmetry codes: # $-x+1, -y+1, z-1/2$).

The phase purity of products for complexes **1**~**5** was further confirmed by PXRD, and each of PXRD patterns in the as-synthesized samples is well consistent with the simulated one of crystals **1**~**5** (Supporting information Fig.S1~S5).

2.3 Thermogravimetric analysis

To examine the thermal stabilities of **1**~**5**, TG analyses were carried out in nitrogen atmosphere from ambient temperature to 900 ℃ at the rate of 5 ℃·min^{-1} (Fig.3). The loss of two coordinated water molecules of **1**~**4** are observed with their dehydration temperatures of 140, 180, 200 and 180 ℃, respectively; the weight losses are 9.7% (Calcd. 9.5%) for **1**, 9.7% (Calcd. 9.8%) for **2**, 10.2% (Calcd. 10.3%) for **3**, and 9.9% (Calcd. 9.7%) for **4**, respectively. Further exothermal processes of the complexes appear at temperatures of 270 ℃ for **1**, 264 ℃ for **2**, 290 ℃ for **3**, and 310 ℃ for **4**, respectively, corresponding the decomposition of ligands and the remains are ZnO (Obsd. 25.2%, Calcd. 21.6%), MnO_2 (Obsd. 25.7%, Calcd. 23.7%) and Co_2O_3 (Obsd. 24.2%, Calcd. 20.2%), Ni_2O_3 (Obsd. 24.3%, Calcd. 20.2%), respectively. Complex **5** loses weight at about 182 ℃ and then successively decomposed to 900 ℃. The results

indicate that compounds **1**~**4** exhibit the similar thermal behavior since these compounds are isostruc-tural. Moreover, complex **4** remains stable up to 310 ℃ after the dehydration.

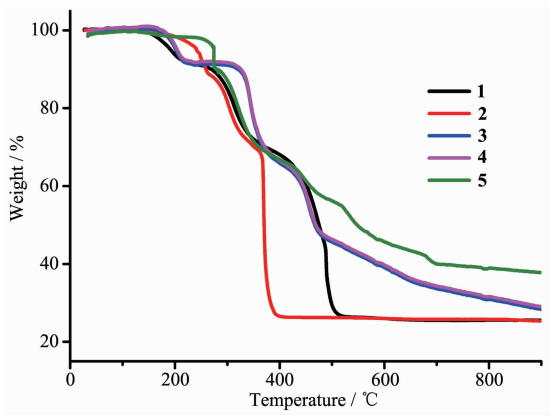


Fig.3　TGA curves of **1**~**5**

2.4　Photoluminescence properties

The complexes with d^{10} metal centers have attracted more interests for their potential applications in the filed of photochemistry[30]. In the present work, the solid-state photoluminescent properties of complex **1** and H_2L ligand were determined at room temperature. As shown in Fig.4, H_2L displays the weak photoluminescence with a maximal emission at 466 nm (λ_{ex}=421 nm), which is assigned to the $\pi^*\rightarrow\pi$ or $\pi^*\rightarrow n$ intraligand transitions. The emission spectra of **1** presents a maximum emission peak at 474 nm (λ_{ex}= 406 nm), which is probably attributed to the $\pi^*\rightarrow\pi$ or $\pi^*\rightarrow n$ intraligand transitions[31]. Comparing with H_2L ligand, complex **1** exhibits the enhanced luminescent intensities. The phenomenon should be attributed to the coordination of H_2L with metal ion centers, which increases the rigidity of complex and reduces the loss of energy by radiationless decay[32].

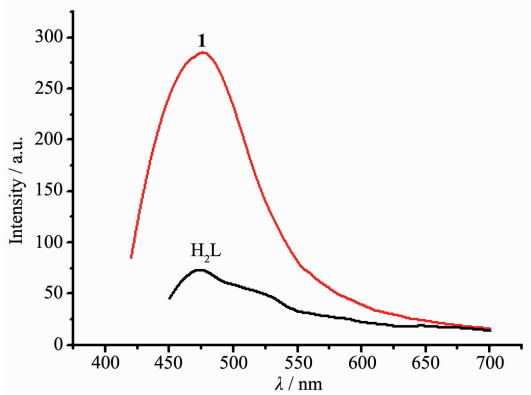


Fig.4　Photoluminescence spectra of **1** and H_2L ligand in the solid state at room temperature

3　Conclusions

Five divalent transition metal coordination compounds based on H_2L ligand have been synthesized by the hydrothermal method. Compounds **1**~**5** demonstrate the mononuclear structures, which are extended to form the 3D supramolecular frameworks by hydrogen bonds. The thermal stabilities of **1**~**5** were discussed. The solid-state luminescence of **1** has been investigated at room temperature, which is probably attributed to the intraligand transitions.

Supporting information is available at http://www.wjhxxb.cn

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