

基于 *N*-((3-吡啶基)磺酰基)天冬氨酸的 Co(II)、Zn(II)、Cd(II) 配位聚合物的合成、磁性和荧光性质

廖蓓玲^{1,2} 李石雄^{1,2} 银秀菊^{1,2} 贾晶晶² 蒋毅民^{*2}

(¹ 河池学院化学与生命工程学院, 宜州 546300)

(² 广西师范大学化学与药学学院, 桂林 541004)

摘要: 以 *N*-((3-吡啶基)磺酰基)天冬氨酸(H₂L)为配体, 采取水热合成的方法, 合成了配位聚合物[M(HL)₂]_n (M=Co, **1**; Zn, **2**; Cd, **3**)。X 射线单晶衍射分析表明, 它们的晶体同构。**1** 的磁性分析表明, **1** 的 Curie 常数为 4.66 cm³·mol⁻¹·K, Curie-Weiss 常数为 -21.23 K; 与配体 H₂L 相比, **2** 和 **3** 的发射光谱发生了明显的蓝移, 可能归因于配体到金属的电荷转移。

关键词: 配位聚合物; *N*-((3-吡啶基)磺酰基)天冬氨酸; 荧光; 磁性

中图分类号: O614.81²; O614.24¹; O614.24²

文献标识码: A

文章编号: 1001-4861(2016)07-1255-06

DOI: 10.11862/CJIC.2016.157

Co(II), Zn(II) and Cd(II) Coordination Polymers Based on *N*-((3-Pyridine)sulfonyl)aspartate: Syntheses, Magnetic and Fluorescence Properties

LIAO Bei-Ling^{1,2} LI Shi-Xiong^{1,2} YIN Xiu-Ju^{1,2} JIA Jing-Jing² JIANG Yi-Min^{*2}

(¹College of Chemistry and Biological Engineering, Hechi University, Yizhou, Guangxi 546300, China)

(²College of Chemistry and Pharmacy, Guangxi Normal University, Guilin, Guangxi 541004, China)

Abstract: The title coordination polymers of [M(HL)₂]_n (M=Co, **1**; Zn, **2**; Cd, **3**) based on H₂L (H₂L=*N*-((3-pyridine)sulfonyl)aspartate) have been synthesized under hydrothermal conditions. X-ray diffraction analysis of three complexes show that they are isomorphous. The values of the Curie and Curie-Weiss constants of **1** are C_m=4.66 cm³·mol⁻¹·K and θ=-21.23 K. The fluorescence spectra indicate that emission of **2** and **3** show obvious blue shift due to the ligand-to-metal charge-transfer (LMCT) effect. CCDC: 1445365, **1**; 1426017, **2**; 1426018, **3**.

Keywords: coordination polymer; *N*-((3-pyridine)sulfonyl)aspartate; fluorescence; magnetic

0 Introduction

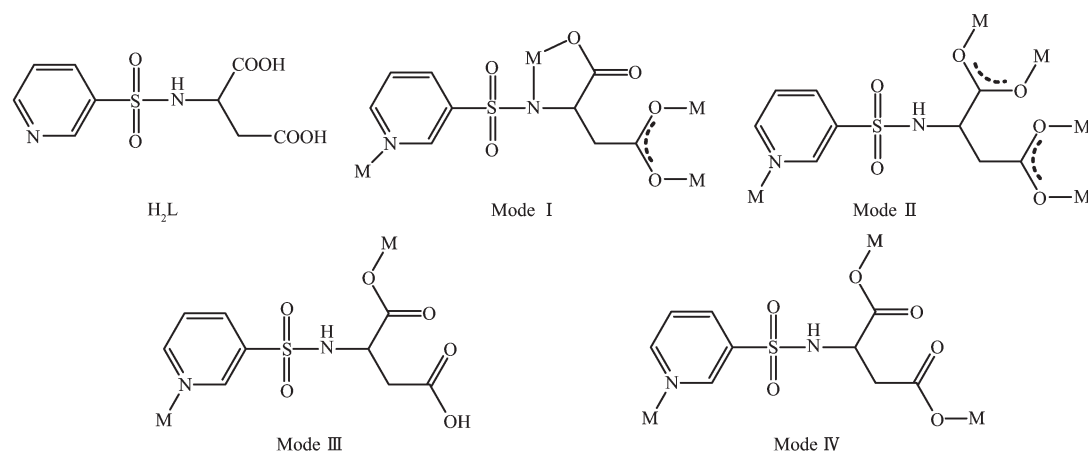
Amino acids are the basic unit of building blocks of proteins giving a specific protein molecular structure and morphology, and they have biological activity. When amino acids and metal ions form amino acid complexes by coordination bond, these complexes not only still have biological activity, but also

maintain the life macromolecular complex structures and function as an active center. Over the years, the *N*-acylated amino acid complexes catch much attention of researchers^[1-5], and a number of innovative results were reported^[6-8]. *N*-sulphonylated amino acid refers to the introduction of sulphonyl in the nitrogen-containing carbonic acid ligands. From the viewpoint of biological effects, not only the *N*-sulphonylated

收稿日期: 2016-01-05。收修改稿日期: 2016-05-15。

广西自然科学基金(No.2014GXNSFAA11803)、广西高校科研项目(No.YB2014331)和广西教育厅基础研究(No.200807MS090)项目资助。

*通信联系人。E-mail: 790223684@qq.com

Scheme 1 Ligand H_2L and its coordination modes

amino acid contains the peptide bond, but also the carboxyl-terminal is very similar to peptide chain. So, *N*-sulphonylated amino acid and its derivatives are a very promising ligand^[9-11]. Studies have shown that when the amino acid changes, the protein molecules will lose the biological activity. At the same time, the fluorescent probes can be applied to the detection of amino acids. Therefore, the study of small molecular fluorescent probe technique and its application for protein detection are very important. In this article we report three new coordination polymers based on *N*-((3-pyridine)sulfonyl)aspartate (H_2L) ligand: $[Co(HL)_2]_n$ (**1**); $[Zn(HL)_2]_n$ (**2**); $[Cd(HL)_2]_n$ (**3**), and their magnetic and fluorescent properties.

1 Experimental

All solvents, chemicals were commercial reagents and used without further purification. H_2L was synthesized according to the reference^[12]. Elemental analyses (carbon, hydrogen and nitrogen) were performed with a Perkin-Elmer 240 elemental analyzer. The crystal structure was determined by an Agilent supernova diffractometer. The magnetic measurements were carried out with a Quantum Design MPMS-XL7 and a PPMS-9 ACMS magnetometer.

1.1 Synthesis of polymers

1.1.1 Synthesis of $[Co(HL)_2]_n$ (**1**)

A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.058 2 g; 0.2 mmol), H_2L (0.054 8 g, 0.2 mmol), 10 mL of water and 10 mL of methanol was stirred for 10 min at room temperature,

and the pH value was adjusted to about 6 with triethylamine solution. Then the solution was sealed in a 25 mL Teflon-lined stainless steel container and heated at 100 °C for 3 days. The mixture was cooled to room temperature at a rate of 10 °C · h⁻¹, and red needle crystals of **1** were obtained with yield of 46% (based on Zn). Anal. Calcd. for $C_{18}H_{18}CoN_4O_{12}S_2$ (%): C, 35.68; H, 2.97; N, 9.25; S, 10.57. Found (%): C, 35.60; H, 2.87; N, 9.26; S, 10.50.

1.1.2 Synthesis of $[Zn(HL)_2]_n$ (**2**)

A mixture of $Zn_2(OH)_2CO_3$ (0.089 9 g, 0.4 mmol), H_2L (0.054 8 g, 0.2 mmol) and 20 mL distilled H_2O was stirred for 10 min at room temperature, and the following procedure was similar to synthesis of **1** except that the reaction temperature was 120 °C. Colorless needle crystals of **2** were obtained with yield of 50% (based on Zn). Anal. Calcd. for $C_{18}H_{18}N_4ZnO_{12}S_2$ (%): C, 35.30; H, 2.94; N, 9.15; S, 10.46. Found (%): C, 35.27; H, 2.96; N, 9.25; S, 10.51.

1.1.3 Synthesis of $[Cd(HL)_2]_n$ (**3**)

The procedures were similar to the synthesis of **2** except that the reaction temperature was 130 °C, and colorless columnar crystals of **3** were obtained with a yield of 70% (based on Cd), Anal. Calcd. for $C_{18}H_{18}CdN_4O_{12}S_2$ (%): C, 32.78; H, 2.73; N, 8.50; S, 9.71. Found (%): C, 32.76; H, 2.63; N, 8.54; S, 9.65.

1.2 Crystallographic data collection and refinement

Diffraction intensities for three polymers were collected on a computer controlled Agilent supernova

diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation with radiation wavelength of 0.071 073 nm by using the X-scan technique. Lorentz polarization and absorption corrections were applied. The structure was solved by direct methods using Olex2 program^[13] and refined with Olex2 program^[14]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms.

The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Crystallographic data for **1**~**3** are listed in Table 1. Selected bond lengths and bond angles for **1**~**3** are listed in Table 2 and hydrogen bonds for **1** and **2** are listed in Table 3.

CCDC: 1445365, **1**; 1426017, **2**; 1426018, **3**.

Table 1 Crystallographic data and structure refinement parameters for **1**~**3**

Complex	1	2	3
Empirical formula	C ₁₈ H ₁₈ N ₄ CoO ₁₂ S ₂	C ₁₈ H ₁₈ N ₄ ZnO ₁₂ S ₂	C ₁₈ H ₁₈ N ₄ CdO ₁₂ S ₂
Formula weight	601.38	603.37	658.91
Temperature / K	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / nm	1.018 01(11)	1.018 01(11)	1.018 01(11)
<i>b</i> / nm	0.717 30(6)	0.717 30(6)	0.717 30(6)
<i>c</i> / nm	1.568 89(16)	1.568 89(16)	1.568 89(16)
β / (°)	97.359(1)	97.359(1)	97.359(1)
Volume / nm ³	1.136 2(19)	1.136 2(19)	1.136 2(19)
<i>Z</i>	2	2	2
<i>D_c</i> / (mg·m ⁻³)	1.758	1.764	1.819
Limiting indices	-12 ≤ <i>h</i> ≤ 13, -9 ≤ <i>k</i> ≤ 8, -18 ≤ <i>l</i> ≤ 20	-12 ≤ <i>h</i> ≤ 13, -9 ≤ <i>k</i> ≤ 8, -18 ≤ <i>l</i> ≤ 20	-12 ≤ <i>h</i> ≤ 13, -9 ≤ <i>k</i> ≤ 8, -18 ≤ <i>l</i> ≤ 20
<i>F</i> (000)	611	614	624
θ range / (°)	2.6~28.3	2.6~28.3	2.6~28.3
<i>S</i>	1.04	0.9	0.88
Total collected reflections, unique	2 814, 1 805 (<i>R</i> _{int} =0.074)	2 814, 1 805 (<i>R</i> _{int} =0.074)	2 814, 1 805 (<i>R</i> _{int} =0.074)
Data, restraints, parameters	2 814, 0, 168	2 814, 0, 168	2 814, 0, 168
Final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ =0.065, <i>wR</i> ₂ =0.192	<i>R</i> ₁ =0.063, <i>wR</i> ₂ =0.18	<i>R</i> ₁ =0.073, <i>wR</i> ₂ =0.215
Largest diff. peak and hole / (e·nm ⁻³)	1 490 and -940	1 080 and -930	1 220 and -1 600

Table 2 Selected bond lengths (nm) and bond angles (°) for **1**~**3**

1					
Co1-O1	0.207 1(3)	Co1-N1 ^B	0.211 1(4)	Co1-O4 ^D	0.228 0(3)
Co1-O1 ^A	0.207 1(3)	Co1-N1 ^C	0.211 1(4)	Co1-O4 ^E	0.228 0(3)
O1 ^A -Co1-O1	180.0	N1 ^C -Co1-N1 ^B	180.0	O4 ^D -Co1-N1 ^C	92.03(14)
N1 ^C -Co1-O1	89.89(14)	O4 ^D -Co1-O1	81.19(13)	O4 ^E -Co1-N1 ^C	87.97(14)
N1 ^B -Co1-O1	90.11(14)	O4 ^E -Co1-O1	98.81(13)	O4 ^E -Co1-N1 ^B	92.03(14)
N1 ^B -Co1-O1 ^A	89.89(14)	O4 ^E -Co1-O1 ^A	81.19(13)	O4 ^D -Co1-N1 ^B	87.97(14)
N1 ^C -Co1-O1 ^A	90.11(14)	O4 ^D -Co1-O1 ^A	98.81(13)		
2					
Zn1-O1	0.207 1(3)	Zn1-O3 ^B	0.228 3(3)	Zn1-N1 ^D	0.211 2(4)
Zn1-O1 ^A	0.207 1(3)	Zn1-O3 ^C	0.228 3(3)	Zn1-N1 ^E	0.211 2(4)

Continued Table 2

O1 ^A -Zn1-O1	180.0	O3 ^B -Zn1-O3 ^C	180.0	N1 ^D -Zn1-O3 ^B	87.75(13)
O3 ^B -Zn1-O1	81.10(12)	N1 ^D -Zn1-O1	90.31(13)	N1 ^E -Zn1-O3 ^B	92.25(13)
O3 ^C -Zn1-O1	98.90(12)	N1 ^E -Zn1-O1	89.69(13)	N1 ^E -Zn1-O3 ^C	87.75(13)
O3 ^C -Zn1-O1 ^A	81.10(12)	N1 ^E -Zn1-O1 ^A	90.31(13)	N1 ^D -Zn1-O3 ^C	92.25(13)
O3 ^B -Zn1-O1 ^A	98.90 (12)	N1 ^D -Zn1-O1 ^A	89.69(13)		
3					
O1-Cd1	0.207 4(4)	O3-Cd1	0.228 6(4)	N1-Cd1	0.211 1(5)
N1 ^A -Cd1-N1 ^C	180.0	O3 ^E -Cd1-N1 ^C	92.41(16)	O1 ^F -Cd1-O3 ^D	99.05(15)
O3 ^D -Cd1-N1 ^C	87.59(16)	O1-Cd1-N1 ^C	90.44(16)	O1-Cd1-O3 ^D	80.95(15)
O3 ^E -Cd1-N1 ^A	87.59(16)	O1-Cd1-N1 ^A	89.56(16)		
O3 ^D -Cd1-N1 ^A	92.41(16)	O1 ^F -Cd1-N1 ^C	89.56(16)		

Symmetry codes: ^A $-x+2, -y+1, -z+1$; ^B $x, y-1, z$; ^C $-x+2, -y+2, -z+1$; ^D $-x+2, y-1/2, -z+1/2$; ^E $x, -y+3/2, z+1/2$; ^F $x, -y+3/2, z-1/2$; ^G $-x+2, y-1/2, -z+3/2$.

Table 3 Hydrogen bond parameters for **1** and **2**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{D-H}\cdots\text{A} / (^\circ)$
1				
N2-H2...O6 ^G	0.86	0.208(1)	0.285 3(6)	150(1)
2				
N2-H2...O6 ^G	0.86	0.213(1)	0.284 5(5)	136(1)

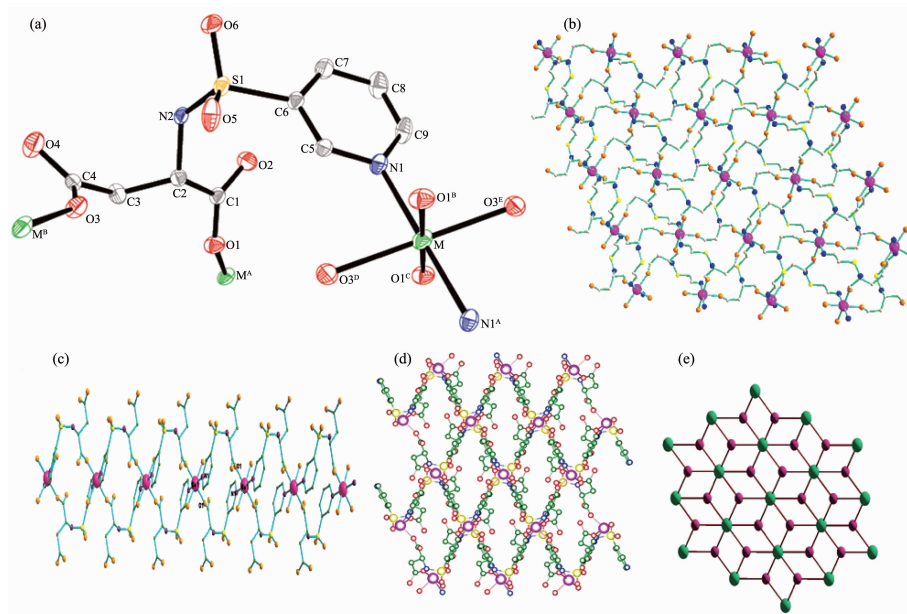
Symmetry codes: ^G $-x+2, y-1/2, -z+3/2$.

2 Results and discussion

2.1 Crystal structures of **1~3**

X-ray single-crystal diffraction analysis reveals

that **1~3** crystallizes in monoclinic system, space group $P2_1/c$. They are allomerism. The coordination environment of $\text{M}(\text{II})$ in **1~3** is shown in Fig.1a ($\text{M}=\text{Co}, \text{Zn}, \text{Cd}$). The asymmetric unit consists of one $\text{M}(\text{II})$ ion, two



Symmetry codes in (a): ^A $-x+2, -y+1, -z+1$; ^B $x, y-1, z$; ^C $-x+2, -y+2, -z+1$; ^D $-x+2, y-1/2, -z+1/2$; ^E $x, -y+3/2, z+1/2$

Fig.1 (a) Coordination environment of $\text{M}(\text{II})$ ($\text{M}=\text{Co}, \text{Zn}, \text{Cd}$) ions in **1~3** with thermal ellipsoids at 50% level; (b) 1D chain along the a -axis of **1~3**; (c) 2D network structure of **1~3**; (d) 2D fishing net structure of **1~3**; (e) Topology ($4^3.4^{12}$) of **1~3**

HL⁻ ligands. The M(II) ion in **1**~**3** is coordinated by two nitrogen atoms (N1, N1^A) and four oxygen atoms (O1^B, O1^C, O3^D, O3^E) of two different HL⁻ ligands. For complex **1**, the Co-O distances fall in the range of 0.207 1(3)~0.228 0(3) nm and the Co-N distance is 0.211 2(4) nm. The bond angles of O1^A-Co1-O1 and O4^E-Co-O1 are 180.0° and 98.81(13)°, respectively. For complex **2**, the Zn-O distances fall in the range of 0.207 1(3)~0.228 3(3) nm and the Zn-N distance is 0.211 2(4) nm. For **3**, the Cd-O distances fall in the range of 0.207 4(4)~0.228 6(4) nm and the Cd-N distance is 0.211 1(5) nm. These bond angles and bond distances all fall in the normal ranges^[15-18].

The atoms of O1^B, O1^C, N1, N1^A are on the same plane and occupy the octahedral equatorial plane, while the atoms of O3^D and O3^E occupy the axial position. In addition, a smooth hand-dimensional double rope structure (Fig.1b) is formed by two atoms (O1, N1) from two ligands connecting two adjacent M(II) ions. Meanwhile, the two-dimensional fishing net structure (Fig.1d) is formed parallel to the *bc* plane by two atoms (O1, O3) from two ligands connecting two adjacency Co(II) ions. The topology of **1**~**3** is (4³.4¹²) (Fig.1e).

2.2 Magnetic analysis of polymer 1

Polymer **1** is a Co(II) (*d*⁷) complex having unpaired electrons, so its magnetic properties are studied. The magnetic susceptibilities, χ_m of **1** were measured in the 2~300 K temperature range, and shown as χ_m and $\chi_m T$ versus *T* plots in Fig.2a and $1/\chi_m$ versus *T* in Fig.2b, respectively. As shown in Fig.2a, the molar magnetic susceptibility χ_m increases gradually as the temperature

lowers, and increases more rapidly below 25 K, then reaches a maximum value of 0.92 cm³·mol⁻¹ at 2 K. Combined with the decrease in the $\chi_m T$ value when cooling, this result indicates the presence of weak antiferromagnetic interactions in complex **1**. The thermal variation of the molar magnetic susceptibility obeys the Curie-Weiss law ($\chi_m = C/(T - \theta)$ or $1/\chi_m = (T - \theta)/C_m$) in the whole process (2~300 K) (Fig.2b). The values of the Curie and Curie-Weiss constants of **1** are $C_m = 4.66$ cm³·mol⁻¹·K and $\theta = -21.23$ K. The negative θ value supports the presence of overall antiferromagnetic interactions in complex **1**. At 300 K, $\chi_m T = 4.32$ cm³·mol⁻¹·K, and the magnetic moment (μ_{eff}) of cobalt(II), which is determined by the equation $\mu_{\text{eff}} = 2.828(\chi_m T)^{1/2}$, reaches the peak value of 5.88 μ_B . This value is slightly higher than that expected for an isolated divalent high-spin Co(II) system with $\mu_{\text{eff}} = 3.87 \mu_B$.

2.3 Fluorescence properties of ligand and complexes 2~3

The solid fluorescence spectra of H₂L and complexes **2**~**3** are shown in Fig.3. The ligand has a maximum emission peak at 447 nm with an excitation wavelength of 419 nm (Fig.3a), which could be attributed to the transition of $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ of the ligand. As shown in Fig.3b and Fig.3c, though H₂L ligand displays a very weak fluorescence in the solid state at room temperature, its complexes **2**~**3** all exhibit different intense fluorescence. For complexes **2** and **3**, blue-shifted emission peak has occurred with a peak broadening, but the degree of blue-shift is not same. For example, the emission peak (438 nm) of

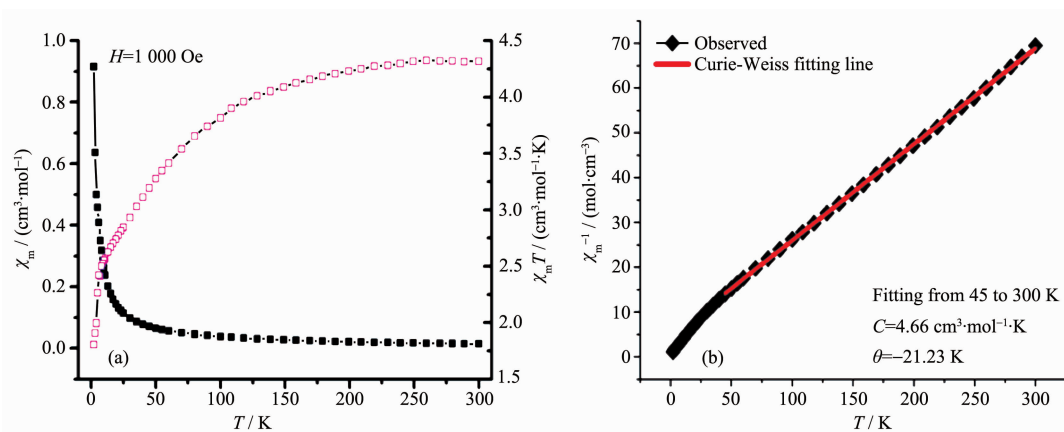
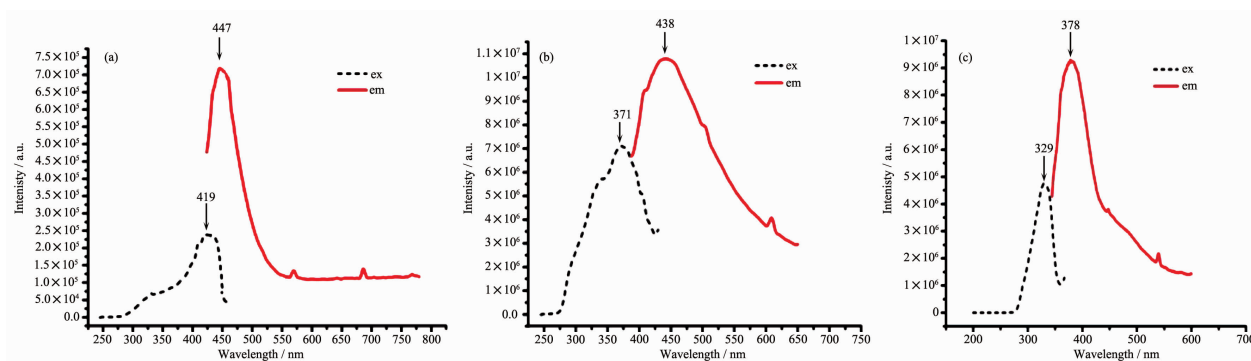


Fig.2 (a) χ_m and $\chi_m T$ vs *T* plots of polymer **1**; (b) $1/\chi_m$ vs *T* plot of polymer **1**

Fig.3 Solid fluorescence spectra of H₂L (a), **2** (b) and **3** (c)

complex **2** occurred with a slight blue shift of 9 nm (Fig.3b, $\lambda_{\text{ex}}=371$ nm), while the emission peak of complex **3** has a blue-shift of 69 nm (Fig.3c, $\lambda_{\text{em}}=378$ nm, $\lambda_{\text{ex}}=329$ nm). So, the fluorescence spectra indicate that emission of **2** and **3** show obvious blue shift due to the ligand-to-metal charge-transfer (LMCT) effect, which may be resulted from coordination environments around the metal ion, since photoluminescence behavior is closely associated with the metal center and the ligands^[19].

3 Conclusions

In summary, three new coordination polymers based on the *N*-((3-pyridine)sulfonyl)aspartate had been synthesized and characterized. Single-crystal X-ray diffraction study reveals that the complexes **1**~**3** are isostructural and have 2D network structure with (4³.4¹²) topology. Magnetic analysis showed that in complex **1** antiferromagnetic coupling is dominant and the values of the Curie and Curie-Weiss constants are $C_m=4.66 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ and $\theta=-21.23 \text{ K}$. The fluorescence spectra indicate that the emissions of **2** and **3** show obvious blue shift due to the ligand-to-metal charge-transfer (LMCT) effect.

References:

- [1] Fleischer B, Shachter A M. *Inorg. Chem.*, **1991**,**30**:3763-3769
- [2] Withersby M A, Blake A J, Champness N R, et al. *J. Am. Chem. Soc.*, **2000**,**122**:4044-4046
- [3] Holliday B J, Mirin C A. *Angew. Chem. Int. Ed.*, **2001**,**113**:2076-2097
- [4] Takashi U, Tetsuya K, Susumu K. *Chem. Mater.*, **2013**,**25**:3772-3776
- [5] Mujahuddin M S, Joel T M, Maravanji S B. *Inorg. Chem.*, **2015**,**54**(13):6063-6065
- [6] Kall P O, Grins J, Fahlman, et al. *Polyhedron*, **2001**,**20**:2747-2753
- [7] Brueckner S, Menabue L, Tolazzi M, et al. *Inorg. Chim. Acta*, **1993**,**214**:185-191
- [8] Ma L F, Wang Y Y, Wang L Y, et al. *Eur. J. Inorg. Chem.*, **2008**,**5**:693-703
- [9] Ma L F, Wang L Y, Chen S H. et al. *Polyhedron*, **2009**,**28**:2494-2502
- [10] Cheng M Q, Ma L F, Wang L Y. *Chin. J. Chem.*, **2007**,**25**:498-502
- [11] Li S X, Liao B L, Yang G G, et al. *Synth. React. Inorg. Met.-Org. Chem.*, **2015**,**45**:926-929
- [12] Panchaud P, Renaud P. *Adv. Synth. Catal.*, **2004**,**346**:925-928
- [13] Dolomanov O V, Bourhis L J, Gildea R J, et al. *J. Appl. Crystallogr.*, **2009**,**42**:339-341
- [14] Bourhis L J, Dolomanov O V, Gildea R J, et al. *Acta Crystallogr. A*, **2015**,**A71**:59-75
- [15] Ghames A, Douadi T, Haffar D. *Polyhedron*, **2006**,**25**:3201-3208
- [16] ZHANG Qi-Long(张奇龙), CHEN Ming-Hua(陈明华), RAN Xia(冉霞), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2015**,**31**:1387-1392
- [17] LI Shi-Xiong(李石雄), LIAO Bei-Ling(廖蓓玲), LUO Pei(罗培), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2015**,**31**:291-296
- [18] GUO Hai-Fu(郭海福), LEI Jia-Mei(雷佳眉), MA De-Yun(马德运). *Chinese J. Inorg. Chem.*(无机化学学报), **2015**,**31**:2385-2392
- [19] Glen G, Briand A D, Smith G S, et al. *Inorg. Chem.*, **2007**,**46**:8625-8637