

## 吡咯甲亚胺镍/铜/锌配合物的合成、荧光性质及 镍、铜配合物的晶体结构

毛盼东<sup>1</sup> 闫玲玲<sup>\*1</sup> 吴伟娜<sup>\*1</sup> 宋艺赫<sup>2</sup> 姚必鑫<sup>2</sup>

(<sup>1</sup> 河南理工大学物理化学学院, 焦作 454000)

(<sup>2</sup> 河南理工大学材料科学与工程学院, 焦作 454000)

**摘要:** 合成并表征了 3 个配合物 NiL (1), Cu<sub>2</sub>L<sub>2</sub> (2) 和 Zn<sub>2</sub>L<sub>2</sub> (3) (H<sub>2</sub>L=1,2-双(3,5-二甲基-4-乙氧羰基-吡咯-2-基)苯)。单晶衍射结果表明在配合物 1 中, 脱质子配体用 4 个氮原子与金属 Ni(II) 配位, 中心金属离子为扭曲的平面正方形配位构型。而双核配合物 2 拥有双螺旋结构, 每个配体桥联 2 个具有平面正方形配位构型的铜中心。推测配合物 3 和 2 的结构类似。此外还研究了配体和配合物的荧光性质。

**关键词:** 席夫碱; 配合物; 吡咯; 荧光

中图分类号: O614.81+3; O614.121; O614.24+1

文献标识码: A

文章编号: 1001-4861(2016)05-0879-05

DOI: 10.11862/CJIC.2016.098

## Ni(II)/Cu(II)/Zn(II) Complexes Based on a Bis(pyrrol-2-yl-methyleneamine) Ligand: Syntheses, Characterization, Fluorescence Properties and Crystal Structures of Ni(II)/Cu(II) Complexes

MAO Pan-Dong<sup>1</sup> YAN Ling-Ling<sup>\*1</sup> WU Wei-Na<sup>\*1</sup> SONG Yi-He<sup>2</sup> YAO Bi-Xin<sup>2</sup>

(<sup>1</sup>Department of Physics and Chemistry, Henan Polytechnic University, Jiaozuo, Henan 454000, China)

(<sup>2</sup>School of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo, Henan 454000, China)

**Abstract:** Three complexes, NiL (1), Cu<sub>2</sub>L<sub>2</sub> (2) and Zn<sub>2</sub>L<sub>2</sub> (3) based on H<sub>2</sub>L (where H<sub>2</sub>L=1,2-bis(3,5-dimethyl-4-ethoxy-carbonyl-pyrrol-2-yl-methyleneamino)benzene) were synthesized and characterized. The X-ray diffraction analyses results show that in complex 1, the deprotonated ligand uses all of its N atoms to bind to the Ni(II) ion, which displays a distorted square planar geometry. However, the binuclear complex 2 possesses a double-stranded helical geometry, in which each Cu(II) ion is also four-coordinated with an extremely distorted square-planar geometry. The proposed structure of complex 3 is similar as that of 2. In addition, the fluorescence properties of all compounds are investigated in detail. CCDC: 1433711, 1; 1433712, 2.

**Keywords:** Schiff base; complex; pyrrole; fluorescence

### 0 Introduction

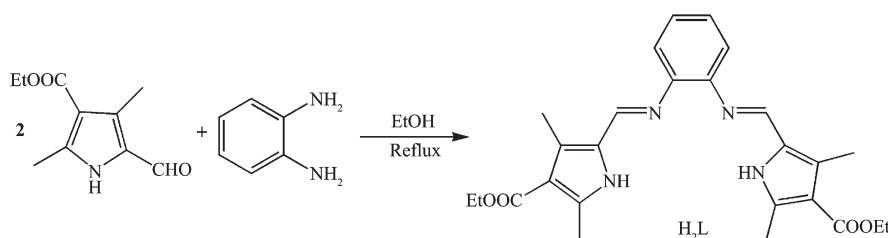
The metal complexes of Schiff base bearing pyrrole units have been extensively investigated for a

long time<sup>[1-2]</sup>. In particular, linear spaced bis(pyrrol-2-yl-methyleneamine) ligands have attracted much recent attention due to the excellent fluorescent properties and good solubilities of their complexes. By varying

收稿日期: 2015-12-06。收修改稿日期: 2016-01-30。

国家自然科学基金(No.21001040, 21404033, 21401046)和河南省教育厅自然科学基金(No.12B150011, 14B150029)资助项目。

\*通信联系人。E-mail: yll@hpu.edu.cn, wuwn08@hpu.edu.cn; 会员登记号: S06N6704M1112。

Scheme 1 Synthesis route of  $H_2L$ 

the spacers, mono-, bi-, tri- and tetra-nuclear metal complexes of such ligands have been generated<sup>[3-7]</sup>.

In fact, our previous work demonstrated that several Zn(II)/Cu(II) complexes with pyrrol-2-yl-methyleneamine ligands show considerable DNA-binding abilities<sup>[8-9]</sup>. Therefore, as a continuation of our research, Ni(II), Cu(II) and Zn(II) complexes with a pyrrol-2-yl-methyleneamine ligand derived from ethyl 5-formyl-2,4-dimethyl-pyrrole-3-carboxylate and benzene-1,2-diamine (Scheme 1) have been synthesized. In addition, the fluorescence properties of the ligand and complexes were discussed in detail.

## 1 Experimental

### 1.1 Materials and measurements

Solvents and starting materials for synthesis were purchased commercially and used as received. The melting point of the ligand was determined on a SGWX-4 microscopic melting point apparatus (uncorrected, made in Shanghai Precision Scientific Instrument Co., Ltd., China). Elemental analyses were carried out on an Elemental Vario EL analyzer. The IR spectra ( $4\,000\sim400\text{ cm}^{-1}$ ) were determined by the KBr pressed disc method on a Bruker V70 FT-IR spectrophotometer.  $^1\text{H}$  NMR spectra of  $H_2L$  was acquired with Bruker AV400 NMR instrument using  $\text{DMSO-d}_6$  solvent. The UV spectra were recorded on a Purkinje General TU-1800 spectrophotometer. Fluorescence spectra were determined on a Varian CARY Eclipse spectrophotometer, and the pass width is 5 nm in the measurements of emission and excitation spectra.

### 1.2 Synthesis of $H_2L$

The ligand  $H_2L$  was prepared by condensation of ethyl 5-formyl-2,4-dimethyl-pyrrole-3-carboxylate (0.38

g, 2 mmol) and benzene-1,2-diamine (0.11 g, 1 mmol) in ethanol (10 mL) solution under refluxing for 4 h. The separated solids were filtered and washed with cold ethanol. Yield: 0.34 g (74%). m.p.  $156\sim157\text{ }^\circ\text{C}$ . Elemental analysis calcd. for  $\text{C}_{26}\text{H}_{30}\text{N}_4\text{O}_4$ (%): C 67.51, H 6.54, N 12.11; Found(%): C 67.43, H 6.68, N 11.98.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 8.29 (2H, s,  $\text{CH}=\text{N}$ ), 7.02~7.12 (4H, m, Ar-H), 4.15~4.20 (4H, q,  $\text{CH}_2\text{CH}_3$ ), 2.40 (6H, s,  $\text{CH}_3$ ), 2.28 (6H, s,  $\text{CH}_3$ ), 1.23~1.27 (6H, t,  $\text{CH}_3\text{CH}_2$ ). FT-IR ( $\text{cm}^{-1}$ ):  $\nu(\text{N-H})$  3 245,  $\nu(\text{O}=\text{C})$  1 697,  $\nu(\text{C}=\text{N})$  1 640.

### 1.3 Syntheses of complexes 1~3

Complexes **1**~**3** were synthesized by reacting  $H_2L$  (0.5 mmol) with  $\text{Ni}(\text{OAc})_2\cdot4\text{H}_2\text{O}$  (1:1 ligand-metal molar ratio),  $\text{Cu}(\text{OAc})_2\cdot2\text{H}_2\text{O}$  and  $\text{Zn}(\text{OAc})_2\cdot2\text{H}_2\text{O}$  (2:1 ligand-metal molar ratio) in methanol/THF (10 mL, 1:1, V/V) solution, respectively. The block crystals of **1** and **2** suitable for X-ray diffraction analysis were obtained by evaporating the reaction solutions at room temperature. Yellow powder of complex **3** is generated under same conditions. All complexes are soluble in DMF, DMSO and THF, slightly soluble in methanol, ethanol, ethyl acetate and acetone, insoluble in water and ether.

**1**: brown block, yield: 78%. Anal. Calcd. for  $\text{C}_{26}\text{H}_{28}\text{N}_4\text{O}_4\text{Ni}$ (%): C 60.14, H 5.44, N 10.79; Found(%): C 60.01, H 5.60, N 10.68. FT-IR ( $\text{cm}^{-1}$ ):  $\nu(\text{O}=\text{C})$  1 662,  $\nu(\text{C}=\text{N})$  1 601.

**2**: dark green block, yield: 66%. Anal. Calcd. for  $\text{C}_{52}\text{H}_{56}\text{N}_8\text{O}_8\text{Cu}_2$ (%): C 59.59, H 5.39, N 10.69; Found(%): C 59.40, H 5.51, N 10.55. FT-IR ( $\text{cm}^{-1}$ ):  $\nu(\text{O}=\text{C})$  1 692,  $\nu(\text{C}=\text{N})$  1 589.

**3**: yellow powder, yield: 84%. Anal. Calcd. for  $\text{C}_{52}\text{H}_{56}\text{N}_8\text{O}_8\text{Zn}_2$ (%): C 59.38, H 5.37, N 10.65; Found(%): C 59.48, H 5.26, N 10.49. FT-IR ( $\text{cm}^{-1}$ ):  $\nu(\text{O}=\text{C})$

1 693,  $\nu(\text{C}=\text{N})$  1 588.

#### 1.4 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 ( $\lambda=0.071\ 073\ \text{nm}$ ) by using  $\varphi$ - $\omega$  scan mode. Semi-empirical absorption correction was applied to the intensity data using the SADABS program<sup>[10]</sup>. The structures were solved by direct methods and refined by full matrix least-square on  $F^2$  using the SHELXTL-97 program<sup>[11]</sup>. All the H atoms were positioned geometrically and refined using a riding model. A summary of crystal data and details of the structure refinements are listed in Table 1.

CCDC: 1433711, **1**; 1433712, **2**.

## 2 Results and discussion

### 2.1 Crystal structures of **1** and **2**

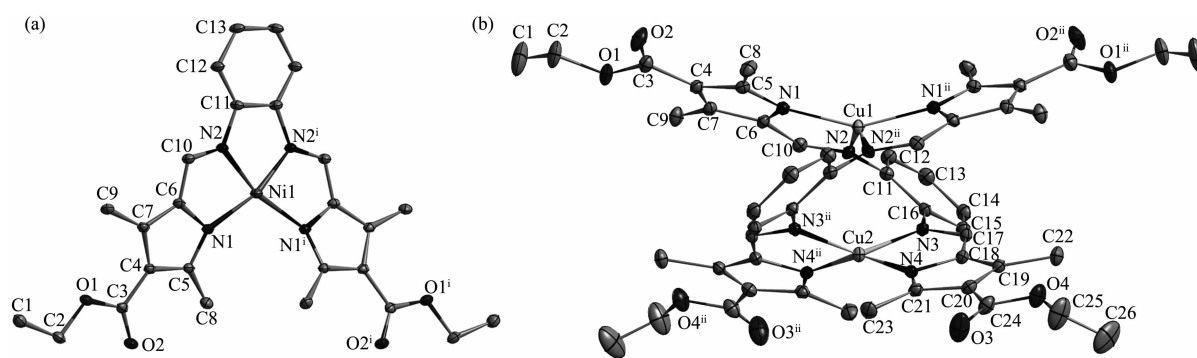
As shown in Fig.1a, the asymmetric unit of complex **1** contains one half of a molecule with Ni(II) ion lying on the two fold rational axis. The

deprotonated ligand uses all of its N atoms to bind to the Ni(II) ion, which displays a distorted square planar geometry. The dihedral angle between two pyrrole ring is  $22.66^\circ$ , which is equal divided by the phenyl bridge ring.

The crystal structure of **2** (Fig.1b) consists of two unsymmetrical Cu(II) ions situated on the two fold rational axis, and each one bound to four nitrogen atoms from two ligands in an extremely distorted square-planar geometry. Also, the molecule of **2** possesses a double-stranded helical geometry. The twist around phenyl bridge divides the ligand into two pyrrol-2-yl-methyleneamine subunits, each of which is bound to a different Cu(II) ion. Different from complex **1**, the phenyl ring of each independent ligand in complex **2** makes the dihedral angle of  $41.20^\circ$  and  $45.28^\circ$  with two pyrrole units, respectively. In addition, the N-Cu-N angles range from  $83.70(11)^\circ$  to  $153.86(17)^\circ$  and the bonds distances of Cu-N span from  $0.195\ 5(3)$  to  $0.201\ 3(3)\ \text{nm}$ . The distance between two copper centers is  $0.320\ 8\ \text{nm}$ . Its molecular structure is similar

Table 1 Selected crystallographic data for **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{26}\text{H}_{28}\text{N}_4\text{O}_4\text{Ni}$	$\text{C}_{52}\text{H}_{56}\text{N}_8\text{O}_8\text{Cu}_2$
Formula weight	519.23	1 048.13
$T / \text{K}$	296(2)	296(2)
Crystal system	Orthorhombic	Monoclinic
Space group	$Pbcn$	$C2/c$
$a / \text{nm}$	0.829 9(7)	2.950(3)
$b / \text{nm}$	1.576 7(14)	0.776 3(7)
$c / \text{nm}$	1.799 8(16)	2.177(2)
$\beta / (^\circ)$	90	95.980(17)
$V / \text{nm}^3$	2.355(4)	1.113 09(6)
$Z$	4	4
$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.464	1.404
Absorption coefficient / $\text{mm}^{-1}$	0.865	0.920
$F(000)$	1 088	2 184
Reflections collected	10 939	11 675
Unique reflections ( $R_{\text{int}}$ )	2 080 (0.076 1)	4 357 (0.041 1)
Data, restraints, parameters	2 080, 0, 161	4 357, 1, 317
Goodness-of-fit (GOF) on $F^2$	1.010	1.027
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1=0.046\ 3$ , $wR_2=0.122\ 0$	$R_1=0.044\ 0$ , $wR_2=0.117\ 0$
$R$ indices (all data)	$R_1=0.087\ 7$ , $wR_2=0.144\ 4$	$R_1=0.070\ 4$ , $wR_2=0.133\ 2$
Largest peak and hole / ( $\text{e}\cdot\text{nm}^{-3}$ )	245 and -455	328 and -396



Symmetry code: <sup>i</sup>  $-x+1, y, -z+1/2$  for **1**; <sup>ii</sup>  $-x, y, -z+1/2$  for **2**

Fig.1 ORTEP drawing of **1** (a) and **2** (b) with 10% thermal ellipsoids

Table 2 Selected bond lengths (nm) and angles ( $^{\circ}$ ) in **1** and **2**

<b>1</b>					
Ni1-N2	0.185 4(3)	Ni1-N1	0.192 9(3)		
N2 <sup>i</sup> -Ni1-N2	82.8(2)	N2i-Ni1-N1	163.69(13)	N2-Ni1-N1	83.43(15)
N1-Ni1-N1 <sup>i</sup>	111.4(2)				
<b>2</b>					
Cu1-N1	0.196 1(3)	Cu1-N2	0.201 3(3)	Cu2-N3	0.201 1(3)
Cu2-N4	0.195 5(3)				
N1 <sup>ii</sup> -Cu1-N2	105.03(13)	N1-Cu1-N2	83.85(13)	N1-Cu1-N2 <sup>ii</sup>	105.03(13)
N2-Cu1-N2 <sup>ii</sup>	143.87(17)	N4 <sup>ii</sup> -Cu2-N4	153.86(17)	N4 <sup>ii</sup> -Cu2-N3	104.70(11)
N4-Cu2-N3	83.70(11)	N3-Cu2-N3 <sup>ii</sup>	142.87(17)		

Symmetry code: <sup>i</sup>  $-x+1, y, -z+1/2$  for **1**; <sup>ii</sup>  $-x, y, -z+1/2$  for **2**

as that of  $\text{Cu}_2\text{L}^{\text{a}}$  ( $\text{H}_2\text{L}^{\text{a}}$ =bis(3-ethyl-4-methyl-5-ethoxy-carbonyl-pyrrol-2-yl-methyleneamino)benzene)<sup>[3]</sup> and  $\text{Cu}_2\text{L}^{\text{b}}$  ( $\text{H}_2\text{L}^{\text{b}}$ =1,2-bis[3,4-dimethyl-5-ethoxy-carbonyl-pyrrol-2-yl-methyleneamino]benzene)<sup>[9]</sup>.

## 2.2 IR spectra

IR spectra of three complexes **1~3** are similar to those of complexes previously reported<sup>[9-10]</sup>. The  $\nu_{\text{NH}}$  vibration of the free ligand is at  $3\,279\text{ cm}^{-1}$ <sup>[9]</sup>, but disappeared in the corresponding complexes, indicating that nitrogen of the pyrrole takes part in coordination and active hydrogens are substituted by metal ions. The  $\nu_{\text{N=C}}$  of the ligand shifts from  $1\,640$  to  $1\,588\sim 1\,601\text{ cm}^{-1}$  in the complexes, indicating azomethine nitrogens coordinate to metal ions<sup>[10]</sup>. The  $\nu_{\text{O=C}}$  of ester in the complexes **2** and **3** ( $1\,693$  and  $1\,692\text{ cm}^{-1}$ , respectively) is similar as that in the ligand ( $1\,697\text{ cm}^{-1}$ ). However, this band shifts to  $1\,662\text{ cm}^{-1}$  in complex **1**, probably due to the strong coordination

between nitrogen of the pyrrole and metal centers<sup>[9-10]</sup>.

## 2.3 UV spectra

The UV spectra of  $\text{H}_2\text{L}$  and complexes **1~3** in THF solution (concentration:  $1\times 10^{-5}\text{ mol}\cdot\text{L}^{-1}$ ) were measured at room temperature (Fig.2). The spectra of HL features two main bands located around  $293$  ( $\epsilon=20\,982\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) and  $368\text{ nm}$  ( $\epsilon=3\,472\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ). The bands could be assigned to characteristic  $\pi\text{-}\pi^*$  transitions centered on pyrrole rings and imine units, respectively<sup>[12]</sup>. The blue shift and hypochromicity of pyrrole  $\pi\text{-}\pi^*$  transitions bands could be observed in complexes **1~3** ( $275\text{ nm}$ ,  $\epsilon=4\,676\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  for **1**;  $271\text{ nm}$ ,  $\epsilon=9\,370\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  for **2**;  $273\text{ nm}$ ,  $\epsilon=6\,581\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  for **3**). Meanwhile, imine  $\pi\text{-}\pi^*$  transitions bands split into two bands in complexes **1~3** (**1**:  $329\text{ nm}$ ,  $\epsilon=9\,473\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ;  $390\text{ nm}$ ,  $\epsilon=7\,837\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ . **2**:  $342\text{ nm}$ ,  $\epsilon=15\,588\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ;  $422\text{ nm}$ ,  $\epsilon=16\,123\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ . **3**:  $350\text{ nm}$ ,  $\epsilon=25\,892$

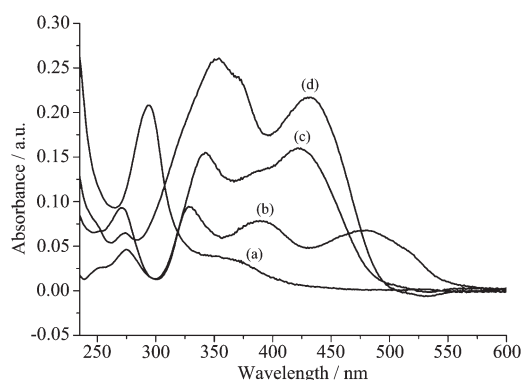


Fig.2 UV spectra of the ligand HL (a), **1** (b), **2** (c) and **3** (d) in THF solution at room temperature

$\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ; 432 nm,  $\varepsilon=21\ 693 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ), accompanying with significantly hyperchromic effect. Furthermore, a new band at 482 nm in complex **1** should be attributed to the Ni(II)  $d-d$  transition<sup>[2]</sup>. Different from that of free ligand and complex **1**, the similar UV spectra of complexes **2** and **3** indicate that both complexes should be isostructural. Therefore, it can be roughly concluded that the possible composition of the Zn(II) complex **3** should be  $\text{Zn}_2\text{L}_2$ .

## 2.4 Fluorescence spectra

The fluorescence spectra of the ligand HL and complexes **1~3** have been studied in THF solution

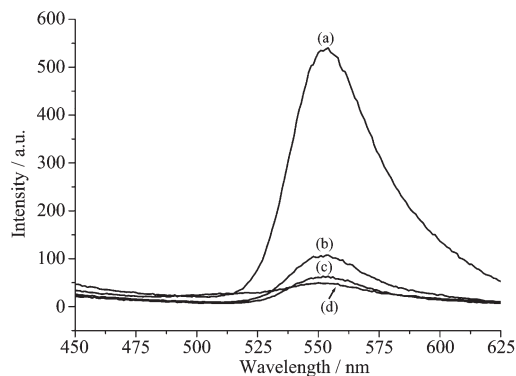


Fig.3 Fluorescence emission spectra of the ligand HL (a), **1** (b), **2** (c) and **3** (d) in THF solution at room temperature

(Concentration:  $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) at room temperature. The results show that the emission spectra of the three complexes exhibit only one main peak at 550 nm when excited at 331 nm, which is similar as that of the ligand (Fig.3). It is obvious that the presence of the metal ions in complexes **1~3** could largely quench the fluorescence emission of the ligand<sup>[13]</sup>.

## References:

- [1] Chakravorty A, Holm R H. *Inorg. Chem.*, **1964**,**3**:1521-1524
- [2] LI Rong-Qing(李荣清), ZHAO Pu-Su(赵朴素), ZHANG Yu (张宇), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2012**, **28**:1025-1030
- [3] Yang LY, Chen Q Q, Li Y, et al. *Eur. J. Inorg. Chem.*, **2004**: 1478-1487
- [4] Wu Z K, Chen Q Q, Xiong S X, et al. *Angew. Chem. Int. Ed.*, **2003**,**42**:3271-3274
- [5] Yang L Y, Chen Q Q, Yang G Q, et al. *Tetrahedron*, **2003**, **59**:10037-10041
- [6] Wu Z K, Yang G Q, Chen Q Q, et al. *Inorg. Chem. Commun.*, **2004**,**7**:249-252
- [7] Wu Z K, Chen Q Q, Yang G Q, et al. *Sens. Actuators B*, **2004**,**99**:511-515
- [8] Wang Y, Yang Z Y, Chen Z N. *Bioorg. Med. Chem. Lett.*, **2008**,**18**:298-303
- [9] Wang Y, Wu W N, Wang Q, et al. *J. Coord. Chem.*, **2010**, **63**:147-155
- [10] Sheldrick G M. *SADABS*, University of Göttingen, Germany, **1996**.
- [11] Sheldrick G M. *SHELX-97, Program for the Solution and the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.
- [12] Song X Q, Zang Z P, Liu W S, et al. *J. Solid. State Chem.*, **2009**,**182**:841-848
- [13] 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