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基于苯并咪唑-5-羧酸和对苯二甲酸配体构筑的二维镉配位聚合物的合成、晶体结构及荧光性质

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摘要: 水热条件下利用苯并咪唑-5-羧酸,1,4-对苯二甲酸和 $Cd(NO_3)_2\cdot 4H_2O$ 为反应物合成出了一个配位聚合物{[Cd(Hbic)$(bdc)_{1/2}$]$\cdot H_2O\}_n$(**1**), 并分别用元素分析,红外谱图,热重分析,X-射线粉末衍射和 X-射线单晶衍射对其结构进行表征。结构分析表明该化合物为二维层状结构,其中每个独立的层都是由两种芳环羧酸配体连接链状的$[Cd(COO)]_n$ 次级构筑单元所构成,有趣的是在二维层中还存在着笼状的空腔结构。邻近的二维层之间通过分子间氢键和 π-π 堆积作用进一步扩展为三维超分子结构。荧光谱图表明常温固态下配合物 **1** 发射绿色荧光,最大发射峰位于 506 nm。

关键词: 水热合成; 晶体结构; 镉配合物; 芳香羧酸配体; 荧光性质
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Synthesis, Structure and Photoluminescent Property of One 2D Cadmium Complex Based on 1*H*-benzimidazole-5-carboxylic Acid and 1,4-Benzenedicarboxylic Acid

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Abstract: A new coordination polymer, {[Cd(Hbic)$(bdc)_{1/2}]\cdot H_2O\}_n$ (**1**), has been synthesized by the self-assembly of 1H-benzimidazole-5-carboxylic acid (H_2bic), 1,4-benzenedicarboxylic acid (H_2bdc) and $Cd(NO_3)_2\cdot 4H_2O$ under hydrothermal conditions, and characterized by elemental analysis, IR, TGA, XRPD and single-crystal X-ray diffraction analysis. Complex **1** shows a 2D layer-like structure formed by mixed aromatic carboxylic acid ligands bridging chain-like $[Cd(COO)]_n$ SBUs, in which there exists cage-like cavity.These 2D layers are extended into a 3D supramolecular framework by intermolecular hydrogen bonds and π-π packing interactions. The photoluminescense of complex **1** in the solid state at room temperature have been studied. CCDC: 909618.

Key words: hydrothermal synthesis; crystal structure; Cd(Ⅱ) complex; aromatic carboxylate ligand; photoluminescent property

0 Introduction

The rapid developments of crystal engineering have produced many interesting metal-organic coordination polymers (CPs) with intriguing variety of architectures and potential applications in catalysis, chirality, conductivity, luminescence, magnetism, and porosity [1-4]. Up to now, the exactly structural predictions for the complexes bearing polydentate N- and O-containing ligands and metal ions with variable coordination geometry are extremely difficult and challenging, because the overall structures of the

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target complexes highly depend on the nature of the metal ions and/or the ligands, the synthetic conditions as well as the preparation methods[5]. Therefore, many new synthetic strategies such as using secondary building units (SBUs), controlling the hydrolysis of metal salts, or selecting organic ligands with appropriate size and specific space conformation and so on, have been extensively applied, in which a mixed-ligand approach by the judicious choice of organic ligands has been proven to be one of most effective and important ways to construct these novel CPs [6-9]. Carboxylate acids constitute an important family of multidentate O-donor ligands and have been extensively employed in the preparation of CPs owing to the carboxylate group can induce core aggregation and bridge metal centers to generate a wide variety of polynuclear complexes ranging from discrete entities to three-dimensional systems [10-12]. Although a large number of CPs built by single carboxylic acid have been reported, the complexes constructed from the mixed carboxylic acid ligands are still not common. As part of an on-going study related to mixed carboxylate ligands system, we are more concerned about the combination of two different aromatic carboxylate acids. Meanwhile, considering that many polynuclear d^{10} metal complexes have exhibited promising luminescent properties, especially those ligands containing hetero-aromatic rings, they can effectively enhance the fluorescence emissions of coordination polymers and are currently of interest in the development of fluorescent materials[13-14]. Herein, we reported the synthesis and structural characterization of a new 2D layer-like Cd(Ⅱ)complex, $\{[Cd(Hbic)(bdc)_{1/2}]\cdot H_2O\}_n$(**1**), built from mixed aromatic carboxylate acid ligands and $Cd(NO_3)_2\cdot 4H_2O$. Complex **1** has been characterized by elemental analysis, IR, TGA, XRPD and single-crystal X-ray diffraction analysis.

1 Experimnetal

1.1 Materials and measurements

The reagents and solvents were commercially available and used as received without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR spectrum (Fig.S1) was recorded in the range 4 000 ~500 cm^{-1} on Mattson Alpha-Centauri spectrometer using KBr pellets. Thermogravimetric analyses (TGA) of the samples were performed using a Perkin-Elmer TG-7 analyzer heated from room temperature to 800 ℃ under nitrogen. XRPD patterns were recorded on a Siemens D5005 diffractometer with Cu $K\alpha$ (λ=0.154 18 nm) radiation in the range of 5°~50°. Solid-state fluorescent spectrum was taken on a Cary Eclipse spectrofluorometer. The solid-state diffuse-reflectance UV-Vis spectrophotometer equipped with an integrating sphere by using $BaSO_4$ as a white standard.

1.2 Synthesis of $\{[Cd(Hbic)(bdc)_{1/2}]\cdot H_2O\}_n$

The title complex was prepared from a mixture of $Cd(NO_3)_2\cdot 4H_2O$ (61.6 mg, 0.2 mmol), H_2bic (32.4 mg, 0.2 mmol), H_2bdc (33.2 mg, 0.2 mmol), NaOH (16 mg, 0.4 mmol) and H_2O (12 mL) in a 30 mL Teflon-lined autoclave under autogenous pressure at 150 ℃ for 72 h. After the mixture was slowly cooled to room temperature, colorless block crystals of **1** suitable for X-ray diffraction were obtained in 55% yield (based on Cd). Anal. Calcd. for $C_{12}H_9N_2O_5Cd$ (%): C 38.57, H 2.42; N 7.49. Found (%): C 38.55, H 2.43, N 7.51. IR (KBr, ν/cm^{-1}): 3 393 (m), 3 124 (w), 3 014 (w), 2 931 (w), 2 814 (w), 1 662 (w), 1572 (s), 1 489 (s), 1393 (s), 1 296 (m), 1 241 (m), 1 131 (w), 1 020 (w), 972 (w), 882 (w), 855 (w), 793 (m), 785 (m), 634 (w), 538(w).

1.3 Crystal structure determination

Single-crystal X-ray diffraction data for **1** was recorded on a Bruker Apex II CCD area-detector diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ =0.071 073 nm) at 293 K. Absorption corrections were applied using multi-scan technique. The structure was solved by Direct Method of SHELXS-97 and refined by full-matrix least-square techniques using the SHELXL-97 program[15-16]. Metal atoms in the complex were located from the E-maps and non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. The hydrogen

atoms attached to carbon atoms were placed in calculated positions and refined using the riding model. The hydrogen atom of dissociative water molecule and the hydrogen atom attached to nitrogen atom were located in the difference Fourier map and refined isotropically. Further details of crystal data and structure refinement for **1** are summarized in Table 1. Selected bond lengths and angles for **1** are listed in Table 2.

CCDC: 909618.

Table 1 Crystal data and structure refinement for 1

Empirical formula	$C_{12}H_9N_2O_5Cd$	Z	4
Formula weight	373.61	D_c / (g·cm^{-3})	2.086
Crystal system	Monoclinic	μ / mm^{-1}	1.858
Space group	$P2_1/c$	F(000)	732
Crystal size / mm	0.20×0.18×0.15	θ range / (°)	2.14~24.99
a / nm	0.954 5(6)	Reflections collected	5 916
b / nm	1.847 4(4)	Unique reflections (R_{int})	2 072(0.020 9)
c / nm	0.677 2(4)	Observed reflections	1 874
β / (°)	94.913(5)	Goodness-of-fit on F^2	1.045
V / nm^3	1.189 7(11)	R, wR ($I>2\sigma(I)$)	0.027 9, 0.072 2

Table 2 Selected Bond Lengths (nm) and Bond Angles (°)

Cd(1)-O(2)^{i}	0.213 5(2)	Cd(1)-O(4)	0.226 23(19)	Cd(1)-O(3)	0.251 2(2)
Cd(1)-N(1)	0.222 5(2)	Cd(1)-O(3)^{ii}	0.243 4(3)	Cd(1)-O(4)^{iii}	0.263 0(3)
O(2)^{i}-Cd(1)-N(1)	107.69(9)	O(4)-Cd(1)-O(3)^{ii}	78.90(8)	O(2)^{i}-Cd(1)-O(4)^{iii}	83.65(7)
O(2)^{i}-Cd(1)-O(4)	121.88(9)	O(2)^{i}-Cd(1)-O(3)	148.78(8)	N(1)-Cd(1)-O(4)^{iii}	81.35(9)
N(1)-Cd(1)-O(4)	129.94(8)	N(1)-Cd(1)-O(3)	86.66(8)	O(4)-Cd(1)-O(4)^{iii}	109.03(7)
O(2)i^{i}-Cd(1)-O(3)^{ii}	91.20(7)	O(4)-Cd(1)-O(3)	54.62(9)	O(3)^{ii}-Cd(1)-O(4)^{iii}	171.99(6)
N(1)-Cd(1)-O(3)^{ii}	94.46(9)	O(3)^{ii}-Cd(1)-O(3)	115.77(7)	O(3)-Cd(1)-O(4)^{iii}	70.98(7)

Symmetry code: ^{i} $-x+1, -y+1, -z+1$; ^{ii} $x, -y+1/2, z-1/2$; ^{iii} $x, -y+1/2, z+1/2$

Table 3 Hydrogen Bond Lengths and Bond Angles

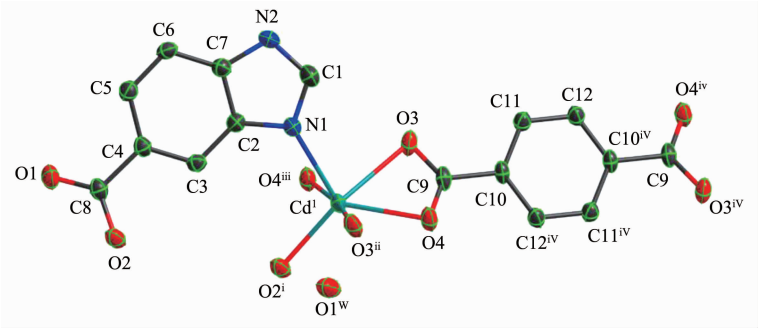
D-H···A	d(D-H) / nm	d(H···A) / nm	d(D···A) / nm	∠DHA / (°)
N(2)-H(4)···O(1W)^{i}	0.076 0	0.198 3	0.272 9	166.85
O(1W)-H(1A)···O(1)^{ii}	0.084 4	0.198 3	0.277 9	156.84
O(1W)-H(1B)···O(1)^{iii}	0.081 9	0.197 2	0.278 6	172.86

Symmetry code: ^{i} $x-1, y, z$; ^{ii} $-x+1, -y+1, -z+2$; ^{iii} $-x+1, y-1/2, -z+3/2$

2 Results and discussion

2.1 Description of the crystal structure

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallized in monoclinic space group $P2_1/c$ and the asymmetric unit of **1** consists of one Cd(Ⅱ) ion, one Hbic- ligand, half of a bdc^{2-} dianion ligand and one dissociative water molecule. As shown in Fig.1, each crystallographically independent Cd(Ⅱ) ion is six-coordinated with one N atom and one O atom from two different Hbic^{-} anion, and four O atoms from three individual bdc^{2-} anions forming a distorted octahedral geometry. In complex **1**, the Cd-N bond length is 0.222 5(2) nm and the Cd-O bond distances in the crystal are in the range of 0.213 5(2)~0.263 0(3) nm. The N(O)-Cd-O angles range from 70.98(7)° to



All hydrogen atoms are omitted for clarity. Symmetry code: [i] $-x+1, -y+1, -z+1$; [ii] $x, -y+1/2, z-1/2$; [iii] $x, -y+1/2, z+1/2$; [iv] $-x+1, -y, -z+1$

Fig.1 View of the coordination environment of Cd(Ⅱ) ion in complex **1** at the 50% probability level

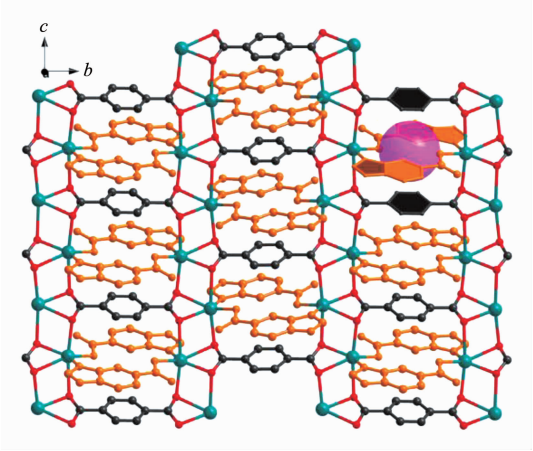
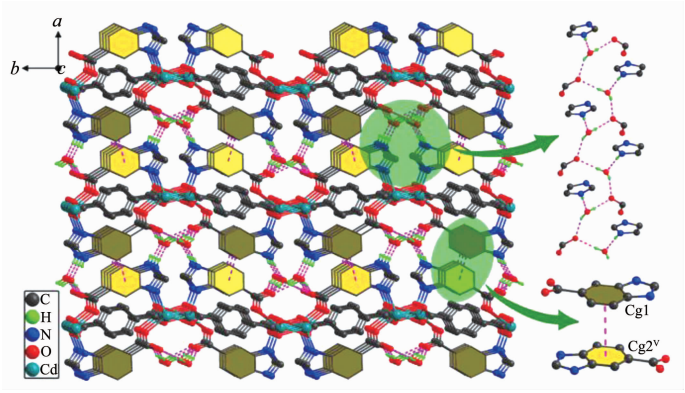


Fig.2 View of the 2D coordination layer and cage-like cavity in complex **1** along the crystallographic *a*-axis

171.99(6)°, all of which are consistent with those reported in other aromatic carboxylate Cd (Ⅱ) complexes[17-18]. In complex **1**, the adjacent Cd(Ⅱ) ions were linked together by the carboxylate groups of bdc^{2-} anions in μ_2-η^2:η^2 mode forming a infinite $[Cd(COO)]_n$ chain along the c axis (Fig.2). Each infinite $[Cd(COO)]_n$ chain can be considered as a secondary building unit (SBU), where the neighbouring Cd(Ⅱ) ions are separated by 0.390 7(2) nm. These SBUs are further connected by the benzene rings of bdc^{2-} anions into a two-dimensional (2D) layer, exhibiting a ladder-like network with the $[Cd(COO)]_n$ chains as sharing sidepieces and benzene rings as rungs. The $Hbic^-$ ligands lies on two sides of ladder-like network and bridge the Cd(Ⅱ) ions located at the grid via bis-monodentate fashion leading to the closed rings with the two adjacent Cd(Ⅱ) centers distances of 0.735 64(20) nm. Interestingly, there exists cage-like cavity in the 2D layer built by two pairs of bdc^{2-} and $Hbic^-$ ligands connecting metal nodes. The minimum diameter of the cavity is 0.429 8 nm. To our knowledge, the 2D complexes with cavity structure of this type are not common. The unsaturated aromatic ligands and dissociative water molecules may be important for providing potential supramolecular recognition sites. The neighbouring 2D covalent structures were further interconnected resulting in a 3D supramolecular framework (Fig.3) via two main types of intermolecular interactions. One is the intermolecular hydrogen bonds between the carboxylate oxygen atoms, imidazole ring nitrogen atoms and lattice water molecules. (N(2)⋯O1W 0.272 9 nm, N(2)-H(4)⋯O(1W) 166.85°, O(1W)⋯O(1) 0.277 9 nm, O(1W)-H(1A)⋯O(1) 156.84°, O(1W)⋯O(1) 0.278 6 nm, O(1W)-H(1B)⋯O(1) 172.86°) (Table 3). The other one is the strong offset π-π stacking interactions between benzene rings of $Hbic^-$ ligands. The distance of center to center, Cg1⋯Cg2^v, is 0.336 8 nm and the dihedral angle is close to 0° (Cg1 and



Symmetry code: v −*x*, −*y*+1, −*z*+1

Fig.3　View of the 3D supramolecular framework in **1** formed by intermolecular hydrogen bonds and the π-π stacking interactions

Cg2^{v} are the aromatic C2/C3/C4/C5/C6/C7 and C2^{v}/C3^{v}/C4^{v}/C5^{v}/C6^{v}/C7^{v} from two Hbic^{-} ligands, respectively).

2.2　X-ray powder diffraction and thermal analysis

In order to check the phase purity of complex **1**, the X-ray powder diffraction (XRPD) pattern of **1** was checked at room temperature. As shown in Fig.4, the peak positions of the simulated and as-synthesized XRPD patterns are in agreement with each other, demonstrating the good phase purity of the complex. The TGA curve of complex **1** reveals two main steps of weight losses (Fig.5). The first observed weight loss of 5.15% in the region of 40 ~160 ℃ may be attributable to the dehydration process (Calcd. 4.81%). Subsequent to this, no obvious weight loss occurred from 160 to 350 ℃. The second step covers a temperature range of 350~580 ℃ with the weight loss of 60.48% (Calcd. 60.82%), which corresponds to the release of organic components. The remaining weight (38.60%) indicated that the final product was CdO (Calcd. 37.47%).

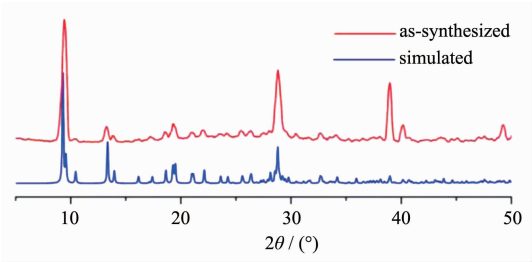


Fig.4　As-synthesized and simulated XRPD patterns for **1**

2.3　Photoluminescent property

The luminescent property of complex **1** was investigated in the solid state at room temperature. Excitation at 375 nm leads to strong green-fluorescent emission bands observed at 506 nm for **1**, as indicated in Fig.6. According to the reported literature, the free H_2bic ligand exhibit fluorescent emission bands at 550 upon excitation at 380 nm[19], while the H_2bdc ligand is observed without emission in the range of 400~700

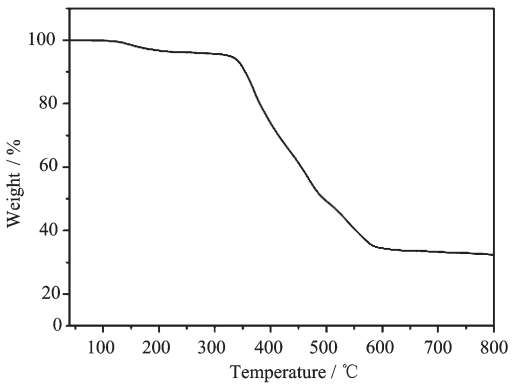


Fig.5　TGA curve of complex **1**

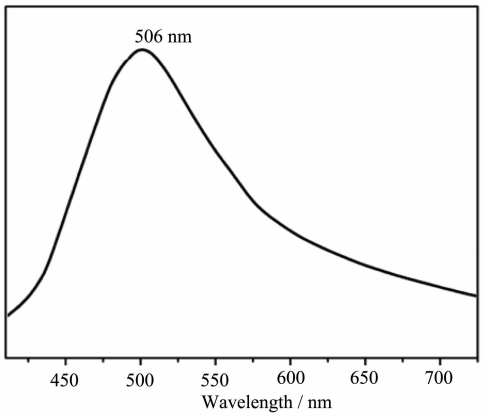


Fig.6　Solid-state emission spectrum for complex **1** at room temperature

cm^{-1} [20]. Therefore, we assign the emissions described above for **1** should originate from the intraligand π-π^* transitions mainly through the H_2bic, namely ligand-to-ligand charge transfer (LLCT). Compared with the H_2bic ligand, the blue shift of 44 nm for **1** should be ascribed to the metal-ligand coordinative interaction.

2.4 UV-Vis spectrum

The solid-state UV-Vis spectra of H_2bdc, H_2bic and complex **1** are displayed in Fig.7. The H_2bdc and H_2bic ligands display strong sbsorption bands in the UV spectral region from 200 to 400 nm, arising from the π-π^* transition of aromatic rings. These bands are not strongly perturbed upon its coordination to Cd (Ⅱ), suggesting that coordination of the metal ions hardly alters the intrinsic electronic properties of ligands. The absorption spectra of complex **1** are similar to the free H_2bic ligand, so the absorption band can be assigned to the intraligand π-π^* transition of the H_2bic ligand. The result is accorded with the analysis of luminescent spectra of complex **1** and free H_2bic ligand.

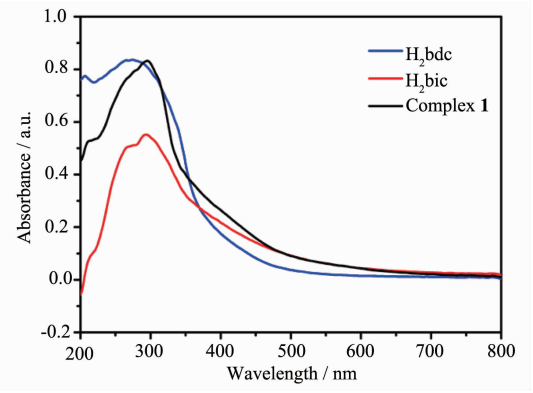


Fig.7 UV-Vis diffuse-reflectance spectra of the H_2bic ligand and the title complex with $BaSO_4$ as the background

3 Conclusion

In summary, by use of H_2bic with H_2bdc, a Cd(Ⅱ) coordination polymer $\{[Cd(Hbic)(bdc)_{1/2}]\cdot H_2O\}_n$ was obtained. Complex **1** features a 2D layer-like structure built by two aromatic carboxylic acid ligands linking chain-like SBUs and the 2D arrangement further extend into 3D supramolecular architecture by hydrogen bonds and π-π packing interactions. In addition, such complex displays modest thermal stability and strong solid-state fluorescent emission.

References:

[1] Ye B H, Tong M L, Chen X M. *Coord. Chem. Rev.*, **2005**,**249**:545-565

[2] Hill R J, Long D L, Champness N R, et al. *Acc. Chem. Res.*, **2005**,**38**:337-350

[3] Batten S R, Murray K S. *Coord. Chem. Rev.*, **2003**,**246**:103-130

[4] Chen B L, Yang Y, Zapata F, et al. *Inorg. Chem.*, **2006**,**45**:8882-8886

[5] Yang E C, Feng Y, Liu Z Y, et al. *CrystEngCom*, **2011**,**13**:230-242

[6] Pan L, Liu H M, Lei X, et al. *Angew. Chem. Int. Ed.*, **2003**,**42**:542-546

[7] Pan L, Adams K M, Hernandez H E, et al. *J. Am. Chem. Soc.*,**2003**,**125**:3062-3067

[8] Bürgstein M R, Gamer M T, Roesky P W. *J. Am. Chem. Soc.*, **2004**,**126**:5213-5218

[9] Saito K, Arai T, Takahashi N, et al. *Dalton Trans.*, **2006**,**37**:4444-4448

[10]Eddaoudi M, Kim J. *Nature*, **2003**,**423**:705-714

[11]Chael H K, Siberio-Pérez D Y, Kim J, et al. *Nature*, **2004**,**427**:523-527

[12]Rosi N L, Kim J, Eddaoudi M, et al. *J. Am. Chem. Soc.*, **2005**,**127**:1504-1518

[13]Grummt U W, Birckner E, Klemm E, et al. *J. Phys. Org. Chem.*,**2000**,**13**:112-116

[14]Hu R F, Zhang J, Kang Y, et al. *Inorg. Chem. Commun.*, **2005**,**8**:828-830

[15]Sheldrick G M. *SHELXS*-97, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**.

[16]Sheldrick G M. *SHELXL*-97, *Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, **1997**.

[17]Guo Z G, Cao R, Li X J, et al. *Eur. J. Inorg. Chem.*, **2007**:742-748

[18]Wei Y Q, Yu Y F, Wu K C. *Cryst. Growth Des.*, **2008**,**8**:2087-2089

[19]Liu Z, Chen Y, Wang J, et al. *J. Solid. State. Chem.*, **2005**,**178**:2306-2312

[20]Fang Q R, Zhu G S, Shi X, et al. *J. Solid. State. Chem.*, **2004**,**177**:1060-1066