

以 4'-羟基-联苯-4-羧酸和 1,3-二(4-吡啶基)丙烷构筑的一维锌配位聚合物的晶体结构与荧光性质

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摘要: 水热条件下采用 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 4'-羟基-联苯-4-羧酸和 1,3-二(4-吡啶基)丙烷作为反应物合成出一个新的一维锌金属配位聚合物 $[\text{Zn}(\text{Hhbc})_2(\text{bpp})] \cdot \text{H}_2\text{O}$ (**1**) (Hhbc=4'-羟基-联苯-4-羧酸, bpp=1,3-二(4-吡啶基)丙烷), 并分别用元素分析、红外光谱、差热分析、X-射线粉末衍射和 X-射线单晶衍射等表征了该结构。晶体结构分析结果表明: 化合物 **1** 为一维链状锌(II)配位聚合物, 通过分子间的 O-H...O 氢键作用, 一维链进一步被连接成二维超分子结构。荧光分析表明常温固态下配合物 **1** 发射蓝色荧光, 荧光寿命为 3.08 ns(480 nm)。

关键词: 锌(II)配位聚合物; 晶体结构; 4'-羟基-联苯-4-羧酸; 1,3-二(4-吡啶基)丙烷; 荧光性质

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Synthesis, Structure and Luminescence of a 1D Zinc(II) Coordination Polymer Constructed from 4'-Hydroxyl-biphenyl-4-carboxylate and 1,3-Bis(4-pyridyl)propane Ligands

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Abstract: A new 1D zinc(II) coordination polymer $[\text{Zn}(\text{Hhbc})_2(\text{bpp})] \cdot \text{H}_2\text{O}$ (**1**) (Hhbc=4'-Hydroxyl-biphenyl-4-carboxylate, bpp=1,3-bis (4-pyridyl)propane) has been synthesized by hydrothermal method and characterized by elemental analysis, IR, TGA, powder X-ray diffraction and single-crystal X-ray diffraction. The carboxylate oxygens of two different Hhbc ligands connect one Zn^{II} ion in bidentate-chelating and monodentate coordinated modes to form mononuclear zinc building blocks, which are further linked into a 1D infinite chain through trans-bpp ligands. These chains are further linked into a 2D supramolecular network through water-hydroxyl tetramers involving the free water molecules and hydroxyl groups of Hhbc ligands. Furthermore, the luminescent property of complex **1** was investigated at room temperature. CCDC: 919045.

Key words: zinc(II) coordination polymer, hydrothermal synthesis, crystal structure, luminescence

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0 Introduction

The rational design and synthesis of new metal-organic coordination polymers have received increasing attention due to their potential applications in the fields such as catalysis, materials science, biochemistry and so on^[1-7]. The rational selection of organic ligands and metals play an important role in constructing functional coordination polymers, and the weaker non-covalent interactions, such as hydrogen bonds, π - π stacking interactions also play key roles in the recognition process forming final 3D architectures^[8-10]. Metal-organic coordination polymers containing carboxylates and flexible *N*-bridging ligands constitute a new family^[11-13]. As a multidentate ligand, the 4'-hydroxyl-biphenyl-4-carboxylic acid (Hhbc) molecule possesses one oxygen of the hydroxyl group and two oxygen atoms of carboxylate group, and might be utilized as a versatile linker for constructing interesting coordination polymers with abundant hydrogen bonds interactions^[14-16]. Moreover, it is well known that the flexible 1,3-bis(4-pyridyl)propane (bpp) ligand is an excellent candidate for constructing novel structures as the auxiliary ligands^[13,17,26-27]. So far, work on the construction of transition metals coordination polymers involving 4',4'-H₂hbc ligand and *N*-containing auxiliary ligands is still scarce^[14-16]. On the basis of the above consideration, we report herein the hydrothermal synthesis, crystal structure and luminescent properties of a new 1D coordination framework based on the H₂hbc and bpp ligands, namely, {[Zn(Hhbc)₂(bpp)]·H₂O}_{*n*} (**1**). The photoluminescent properties of **1** are also reported in this paper.

1 Experimental

1.1 Materials and measurements

All chemicals purchased were of reagent grade and used without further purification. All syntheses were carried out in 23 mL Teflon-lined autoclaves under autogenous pressure. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. Infrared spectra were recorded (4 000~400 cm⁻¹) as KBr disks on Shimadzu IR-440

spectrometer. Powder XRD investigations were carried out on a Bruker AXS D8-Advanced diffractometer at 40 kV and 40 mA with Cu *K* α (λ =0.154 06 nm) radiation. Luminescence spectra for crystal solid samples were recorded at room temperature on an Edinburgh FLS920 phosphorimeter. Thermogravimetry analyses (TGA) were performed on an automatic simultaneous thermal analyzer (DTG-60, Shimadzu) under a flow of N₂ at a heating rate of 10 °C·min⁻¹ between ambient temperature and 800 °C.

1.2 Synthesis of complex 1

Complex **1** was prepared by the addition of stoichiometric amounts of Zn(NO₃)₂·6(H₂O) (0.15 g, 0.5 mmol) and 1,3-bis(4-pyridyl)propane (0.1 g, 0.5 mmol) to a hot aqueous solution (15 mL) of H₂hbc (0.107 g, 0.5 mmol) which the pH was adjusted to 7.0~8.0 with NaOH (0.021 g, 0.25 mmol). The resulting solution was sealed in a 23 mL Teflon reactor and kept under autogenous pressure at 170 °C for 72 h. The mixture was cooled to room temperature at a rate of 5 °C·h⁻¹, and colorless block crystals were obtained in a yield of 49% based on Zn. Element analysis found (%): C, 66.10; H, 4.80; N, 3.95. Calcd. for C₃₉H₃₄N₂O₇Zn(%): C, 66.03; H, 4.83; N, 3.99. IR (KBr pellet) (cm⁻¹): 3 441(s), 3 078(w), 2 960(m), 1 667(vs), 1 573(s), 1 541(s), 1 477(s), 1 405(vs), 1 348(m), 1 315(w), 1 279(s), 1 261(m), 1 228(s), 1 160(m), 1 107(s), 1 071(vs), 1 038(s), 1 017(w), 930(m), 870(s), 834(m), 805(s), 776(s), 751(m), 723(m), 701(s), 647(m).

1.3 Crystal structure determination

A single crystal with dimensions of 0.33 mm×0.28 mm×0.22 mm was mounted on a glass fiber for data collection which was performed on a Bruker SMART APEXII CCD diffractometer operating at 50 kV and 30 mA using a Mo *K* α radiation (λ =0.071 073 nm) at 296(2) K by using a ω scan mode. In the range 1.73°≤ θ ≤27.00°, a total of 21 425 reflections were collected, of which 7 310 were unique (R_{int} =0.065 5) and 3 752 observed ones ($I>2\sigma(I)$) were used in the succeeding structure calculations. Data collection and reduction were performed using the APEX II software^[18]. Multi-scan absorption corrections were applied using the SADABS^[18]. The structure was solved by direct

methods and refined on F^2 by full-matrix least squares technique using the SHELX-97 program package^[19]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Water H atoms were tentatively located in difference Fourier maps and were refined with distance restraints of O-H 0.082 nm and HH 0.138 nm, with an standard deviation of 0.001 nm, and with $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O})$. $R_1=0.056\ 7$ and $wR_2=0.113\ 7$ ($w=1/[\sigma^2(F_o^2)+(0.052\ 0P)^2+1.950\ 0P]$, where $P=(F_o^2+2F_c^2)/3$) for 3 752 observed reflections with $I>2\sigma(I)$. $S=1.031$, $(\Delta/\sigma)_{\text{max}}=0.000$, $(\Delta\rho)_{\text{max}}=483\ \text{e}\cdot\text{nm}^{-3}$ and $(\Delta\rho)_{\text{min}}=-300\ \text{e}\cdot\text{nm}^{-3}$. Crystal parameters and details of the data collection and refinement are given in Table 1.

Selected bond lengths and angles are given in Table 2. H-bonding parameters are given in Table 3.

CCDC: 919045.

2 Results and discussion

2.1 Structure description

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic space group $C2/c$ and has a 1D infinite chain structure. As shown in Fig.1, the Zn(II) center is five-coordinated by three carboxylate oxygen atoms from two different Hhbc ligands and two nitrogen atom from two different bpp ligands, adopting a distorted trigonal biyramidal geometry. The Zn-O, Zn-N bond lengths and O-Zn-O, O-Zn-N bond angles range from 0.195 0(3) to 0.220 1(3)

Table 1 Crystal data and structure refinements of complex **1**

Empirical formula	C ₃₉ H ₃₄ N ₂ O ₇ Zn	$\gamma / (^\circ)$	90.00
Formula weight	708.05	V / nm^3	6.741 8(15)
Temperature / K	296(2)	Z	8
Size / mm	0.33×0.28×0.22	μ / mm^{-1}	0.783
θ range for data collection / $(^\circ)$	1.73 to 27.00	$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.395
Crystal system	Monoclinic	$F(000)$	2 944
Space group	$C2/c$	Reflections collected	21 425
a / nm	2.023 2(2)	Independent reflections (R_{int})	7 310 (0.065 5)
b / nm	1.527 53(18)	Goodness of fit on F^2	1.014
c / nm	2.377 6(4)	R_1, wR_2 ($I>2\sigma(I)$)	0.056 7, 0.113 7
$\alpha / (^\circ)$	90.00	R_1, wR_2 (all data)	0.133 8, 0.138 6
$\beta / (^\circ)$	113.435(2)	$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}} / (\text{e}\cdot\text{nm}^{-3})$	483, -300

Table 2 Selected bond lengths (nm) and bond angles $(^\circ)$

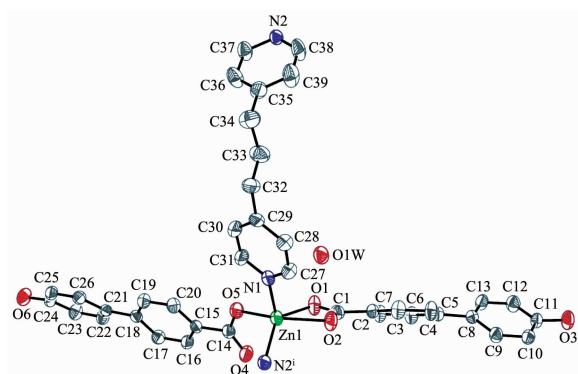
Zn(1)-O(5)	0.195 0(3)	Zn(1)-O(1)	0.216 6(3)	Zn(1)-N(2) ⁱ	0.205 2(3)
Zn(1)-O(2)	0.220 1(3)	Zn(1)-N(1)	0.206 2(3)		
O(5)-Zn(1)-N(2) ⁱ	102.01(12)	O(5)-Zn(1)-O(2)	160.20(11)	O(5)-Zn(1)-N(1)	95.88(12)
N(1)-Zn(1)-O(1)	111.48(12)	N(2) ⁱ -Zn(1)-N(1)	105.54(12)	N(2) ⁱ -Zn(1)-O(2)	93.23(12)
O(5)-Zn(1)-O(1)	101.15(11)	N(1)-Zn(1)-O(2)	92.07(12)	N(2) ⁱ -Zn(1)-O(1)	133.51(12)
O(1)-Zn(1)-O(2)	59.05(11)				

Symmetry cod: ⁱ $-0.5+x, -0.5+y, z$.

Table 3 Hydrogen bonds for complex **1**

D-H \cdots A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
O(1W)-H(1W) \cdots O(1)	0.083 1(19)	0.197(2)	0.279 0(5)	168(6)
O(1W)-H(2W) \cdots O(3) ⁱⁱ	0.081 8(19)	0.210(3)	0.288 1(5)	159(5)
O(6)-H(6A) \cdots O(4) ⁱⁱⁱ	0.081 8(19)	0.200(3)	0.275 7(4)	155(6)
O(3)-H(3A) \cdots O(1W) ^{iv}	0.080(2)	0.193(3)	0.267 8(4)	156(6)

Symmetry codes: ⁱⁱ $0.5-x, 1.5-y, 1-z$; ⁱⁱⁱ $0.5+x, -0.5+y, z$; ^{iv} $-0.5+x, 0.5+y, z$.



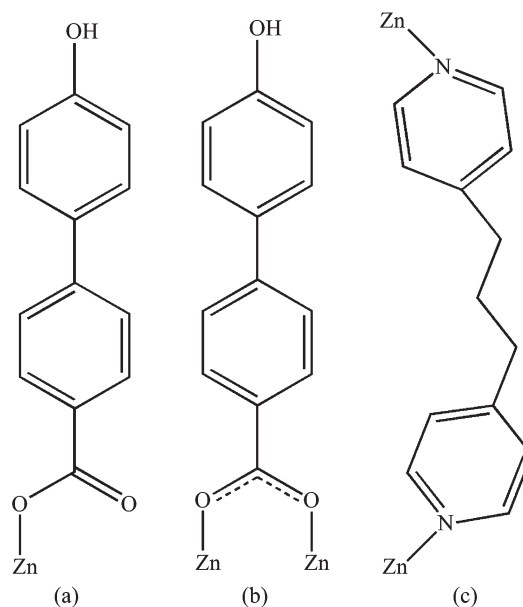
Symmetry codes: $i -0.5+x, -0.5+y, z$

Fig.1 View of the asymmetric unit of **1** with 30% probability ellipsoids

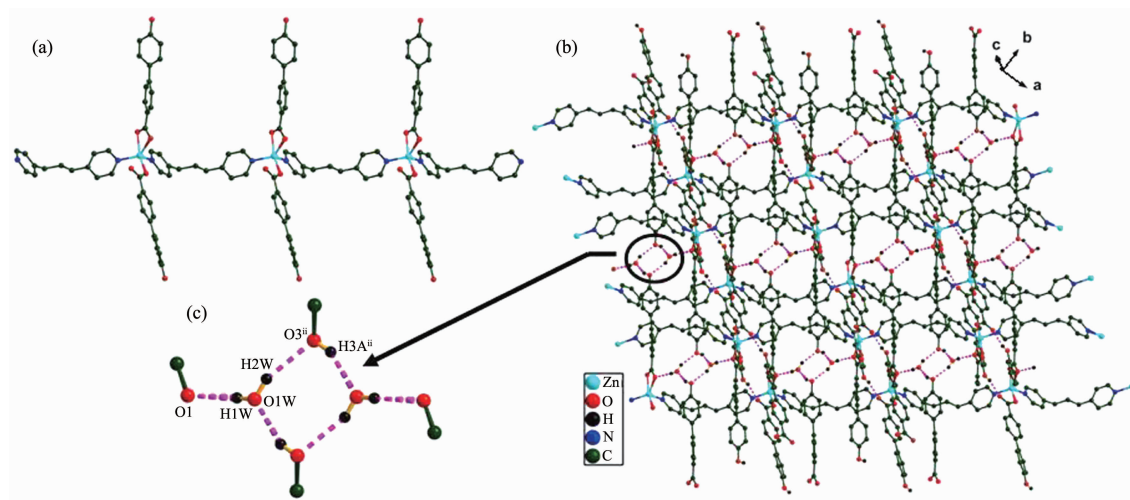
nm and $59.05(11)^\circ$ to $160.20(11)^\circ$, respectively, which is within the reasonable range of observed values for other five-coordinated Zn(II) complexes with oxygen and nitrogen donating ligands^[20-21].

In the complicated polymeric structure of **1**, the Hhbc ligands are terminal and adopt monodentate and bidentate-chelating coordination modes (Scheme 1a, 1b), respectively, and the bpp ligand has TG conformation (the two pyridyl groups of bpp ligand show different trans(T) and gauche(G) orientations)^[17] and adopts two end pyridyl N atoms that link to two Zn(II) atoms (Scheme 1c). In this manner, every two Hhbc ligands coordinated one Zn^{II} center to form a mononuclear zinc building block, which can be regarded as a knot. Each bpp ligand bridges two

neighbouring knots to form a one-dimensional infinite chain (Fig.2a), with the Zn...Zn separation being 1.267 (5) nm. These chains are further linked into a 2D supramolecular network through the O-H...O hydrogen bonding interactions involving the free water molecules and hydroxyl groups of Hhbc ligands (Fig. 2b). These hydrogen bonds all fall in the normal range; details are available in Table 3. It should be point out that the water-hydroxyl tetramers have been observed in the 2D structure (Fig.2c). Interactions



Scheme 1 Coordination mode of Hhbc and bpp ligands in the structure of complex **1**



Symmetry codes: $ii 0.5-x, 1.5-y, 1-z$

Fig.2 View of structure **1** (a) the 1D infinite chain; (b) 2D layer network formed by hydrogen bonds (dash lines); (c) Water-hydroxyl tetramers

between water aggregates and their surroundings can be important for the stability of metal-organic complexes^[22].

2.2 IR and TGA

The IR spectra of compound **1** shows broad bands at 3 441 cm^{-1} , which may be assigned to the $\nu(\text{O-H})$ stretching vibrations of the free water molecules and hydroxyl groups of Hhbc ligands. The moderate absorption bands observed at 3 078, 2 960 cm^{-1} are attributed to the $\nu(\text{C}_{\text{methylene}}-\text{H})$ vibration of bpp ligand. The features at 1 667 and 1 573, 1 405 cm^{-1} are associated with the asymmetric (COO) and symmetric (COO) stretching vibrations. The $\Delta\nu(\nu_{\text{as}}(\text{COO}^-)-\nu_{\text{s}}(\text{COO}^-))$ value are 94 and 262 cm^{-1} , respectively, indicating the coordination of Hhbc with Zn(II) in monodentate and bidentate-chelating modes^[23], respectively, which is well consistent with X-ray diffraction structural analysis.

The thermogravimetric analyses (TGA) of compound **1** were performed in a N_2 atmosphere when the sample was heated to 800 $^{\circ}\text{C}$ at a constant rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$. The TG and DTA curves of **1** are depicted in Fig.3, which shows that compound **1** has three weight loss steps. The first corresponding to the escape of one free water molecule is observed from 40 to 100 $^{\circ}\text{C}$ (Obsd. 2.61%, Calcd. 2.54%). The second corresponding to the escape of one bpp ligand is observed from 200 to 380 $^{\circ}\text{C}$ (Obsd. 28.29%, Calcd. 27.96%). The sharp weight loss above 500 $^{\circ}\text{C}$ corresponds to the decomposition of framework structure. Finally, **1** was completely degraded into ZnO with total loss of 87.93% (Calcd. 88.51%).

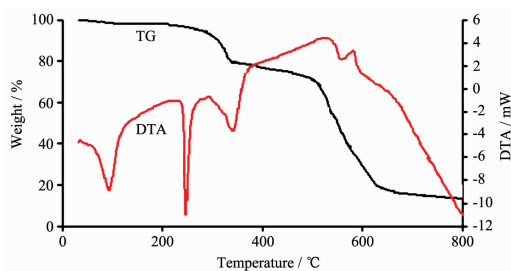


Fig.3 Thermogravimetric curves (DTA and TG) for complex **1**

2.3 Powder X-ray diffraction analysis

Samples of complex **1** were measured by X-ray

powder diffraction at room temperature. As shown in Fig.4, the peak positions of the experimental patterns are in a good agreement with the simulated patterns, which clearly indicates the good purity of the complex.

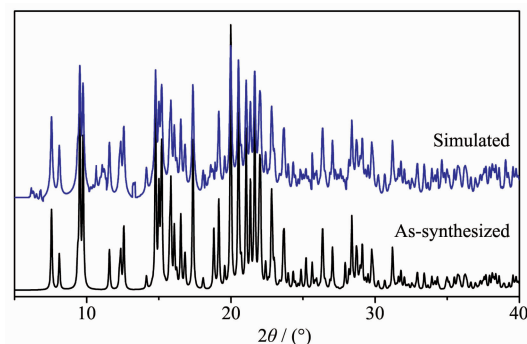


Fig.4 PXRD patterns of complex **1**

2.4 Photoluminescent properties

Photoluminescence experiments for Zn^{II}-containing polymers, as a typical d^{10} transition-metal configuration which exhibits photoluminescent property^[24], were performed at room temperature in the solid state. The Hhbc and bpp ligands with their extended aromaticity, is thus regarded to be excellent candidates for enhanced emissive properties. As illustrated in Fig.5, complex **1** exhibits indigotin photoluminescence with an emission maximum of 480 nm upon excitation at 388 nm. From the emission maximum of **1**, which is clearly red-shifted compared with the free ligand H₂hbc^[14]. Complex **1** represents an obvious qualitative change of luminescence property resulted from the interaction between metal ion and ligand. The emission of **1** probably origins from ligand-to-metal charge transfer (LMCT)^[25] excited state, because both ligands have relatively large π -conjugated system of

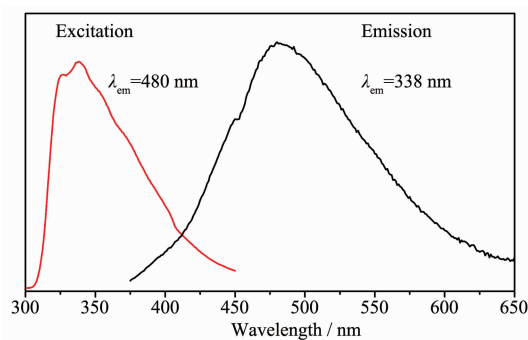


Fig.5 Solid-state excitation and emission spectra of complex **1** at room temperature

benzene-pyridyl rings and uses carboxylate oxygen and nitrogen donors to coordinate to Zn(II) ions, which benefits the charge transfer between Zn(II) ion and organic ligands. The luminescent lifetime of solid complex **1** using an Edinburgh FLS920 phosphorimeter with 450 W xenon lamp as excitation source show lifetime for complex **1** of 3.08 ns at 480 nm (Fig.6).

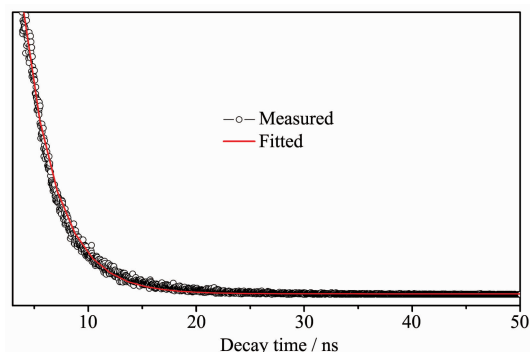


Fig.6 Luminescent lifetime for complex **1** in solid state at room temperature

3 Conclusions

In conclusion, we have successfully constructed a new one-dimensional coordination polymer $\{[\text{Zn}(\text{Hhbc})_2(\text{bpp})] \cdot \text{H}_2\text{O}\}_n$ based on Hhbc and bpp ligands under hydrothermal reaction. Complex **1** emits the intensely indigotin luminescence of Zn^{2+} ion with the fluorescence lifetime of 3.08 ns (480 nm) in the solid state at room temperature, which may have potential applications as luminescent materials in indigotin light-emitting devices.

References:

- [1] Yi L, Din B, Zhao B, et al. *Inorg. Chem.*, **2004**,**43**:33-43
- [2] Glasner M E, Bergman N H, Bartel D P. *Biochem.*, **2002**,**41**: 8103-8112
- [3] Kluge S, Weston J. *Biochem.*, **2005**,**44**:4877-4885
- [4] Withersby M A, Blake A J, Champness N R, et al. *Inorg. Chem.*, **1999**,**38**:2259-2266
- [5] Ma D, Li Y, Li Z. *Chem. Commun.*, **2011**,**47**:7377-7379
- [6] Cui Y, Yue Y, Qian G, et al. *Chem. Rev.*, **2012**,**112**:1126-1162
- [7] Zhang J P, Zhang Y B, Lin J B, et al. *Chem. Rev.*, **2012**, **112**:1001-1033
- [8] Mahata P, Natarajan S. *Inorg. Chem.*, **2007**,**46**:1250-1258
- [9] Ma L F, Wang L Y, Huo X K, et al. *Cryst. Growth Des.*, **2008**,**8**:620-628
- [10] Ma L F, Wang Y Y, Wang L Y, et al. *Eur. J. Inorg. Chem.*, **2008**:693-703
- [11] Qin C, Wang X, Carlucci L, et al. *Chem. Commun.*, **2004**: 1876-1877
- [12] Pan L, Liu H, Lei X, et al. *Angew. Chem. Int. Ed.*, **2003**,**42**: 542-546
- [13] Li B, Li G, Liu D, et al. *CrystEngComm*, **2011**,**13**:1291-1298
- [14] Zhu Z B, Lu X W. *Chin. J. Struct. Chem.*, **2010**,**29**:465-470
- [15] Ma D Y, Guo H F, Lu K, et al. *Z. Anorg. Allg. Chem.*, **2012**, **638**:992-995
- [16] Wu W P, Wang J, Lu L, et al. *Acta Cryst.*, **2011**,**E67**:m568
- [17] Carlucci L, Ciani G, Proserpio D M, et al. *CrystEngComm*, **2002**,**4**:121-129
- [18] Bruker. *APEXII Software, Version 6.3.1*, Bruker AXS Inc, Madison, Wisconsin, USA, **2004**.
- [19] Sheldrick G M. *Acta Cryst.*, **2008**,**A64**:112-122
- [20] Li X, Cao R, Sun D, et al. *Cryst. Growth Des.*, **2004**,**4**:775-780
- [21] Zhang J, Gao S, Che Z M. *Eur. J. Inorg. Chem.*, **2004**:956-959
- [22] Michaelides A, Skoulika S, Bakalbassis E G, et al. *Cryst. Growth Des.*, **2003**,**3**:487-492
- [23] Zheng Y, Xu D M, Liu S X. *Inorg. Chim. Acta*, **1999**,**294**: 163-169
- [24] Tian Z, Lin J, Su Y, et al. *Cryst. Growth Des.*, **2007**,**7**:1863-1867
- [25] de Bettencourt-Dias A, Viswanathan S. *Chem. Commun.*, **2004**:1024-1025
- [26] Li X, Cao R, Sun D, et al. *Cryst. Growth Des.*, **2004**,**4**:775-780
- [27] Liu G X, Huang Y Q, Chu Q, et al. *Cryst. Growth Des.*, **2008**,**8**:3233-3245