第 26 卷第 4 期 无 机 化 学 学 报 Vol.26 No.4
2010 年 4 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 609-614

两个基于间苯二甲酸和咪唑衍生物 Zn(Ⅱ) 配位聚合物的合成、晶体结构和电化学性能

李荣勋*,[1] 邓月义[2] 刘保成[2] 刘法谦[2] 吴其晔[2]
([1]北京科技大学材料科学与工程学院,北京 100083)
([2]青岛科技大学新材料研究重点实验室,青岛 266042)

摘要:合成了 2 个配位聚合物{[Zn(ip)(Eim)$_2$]·H_2O}(**1**)和 Zn(ip)(Mim)$_2$(**2**)(ip 为间苯苯二甲酸阴离子,Eim 为 1-乙基咪唑,Mim 为 1-甲基咪唑),并用 X 射线单晶衍射仪测定了其晶体结构。2 个配合物的结构中都含有沿晶体 *a* 轴方向的 zigzag 聚合链,每个 Zn 原子分别与 2 个来自不同间苯二甲酸离子氧原子和 2 个来自乙基咪唑或甲基咪唑的 N 原子配位,形成了配位四面体。在配合聚合物 **2** 中各链间只存在范德法力相互作用,而在配合物 **1** 中一维链通过 O–H···O 氢键相互作用进一步连接形成了三维网络结构。电化学研究表明在配合物 **1** 和 **2** 中 Zn^{2+}/Zn^{+}对的氧化还原是一个准可逆的过程。

关键词:间苯二甲酸配合物;羧酸锌(Ⅱ)盐;晶体结构;循环伏安法
中图分类号:O614.24+1 **文献标识码**:A **文章编号**:1001-4861(2010)04-0609-06

Two Zn(Ⅱ) Coordination Polymers Based on Isophthalate and Imidazole Derivatives: Synthesis, Crystal Structures, and Electrochemical Properties

LI Rong-Xun[1] DENG Yue-Yi[2] LIU Bao-Cheng[2] LIU Fa-Qian*,[2] WU Qi-Ye[2]
([1]*School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing* 100083)
([2]*Key Laboratory of Advanced Materials, Qingdao University of Science and Technology, Qingdao, Shandong* 266042)

Abstract: Two Zn(Ⅱ) coordination polymers {[Zn(ip)(Eim)$_2$]·H_2O} (**1**) and Zn(ip)(Mim)$_2$ (**2**) (where ip^{2-}=isophthalate dianion; Eim=1-ethyl-1H-imidazole; Mim=1-methyl-1H-imidazole), have been synthesized and characterized by X-ray single crystal diffractometry. Complexes **1** and **2** contain polymeric zigzag chains extended along a axis, and each Zn(Ⅱ) atom is tetrahedrally coordinated to two O atoms from different isophthalate ions and two N atoms from Eim or Mim. There are only van der Waals interactions between the chains in **2**, while 1D Zigzag chains in **1** are connected to form a 3D network by O–H···O contacts. The electrochemical studies reveal that redoxes of Zn^{2+}/Zn^{+} in the complexes **1** and **2** are quasi-reversible processes. CCDC: 762257, **1**; 762258, **2**.

Key words: isophthalate compound; Zn(Ⅱ) carboxylate; crystal structure; cyclic voltammetry

The crystal engineering approach is extensively used to control material structure and dimensionality[1-3]. The crystal engineering of coordination polymers has held great potential for applications in many areas, such as molecular magnetism, heterogeneous catalysis, molecular sieving, storage, and non-linear optics [4-9]. Bridging metals with organic ligands is used to construct lower dimensional coordination polymers, which can be further assembled by hydrogen-bonding, π-π interaction or other intermolecular contacts to form

收稿日期:2009-11-25。收修改稿日期:2009-12-25。
国家自然科学基金(No.20601015,20871072)、山东省博士基金(No.2007BS04023)和山东省自然科学基金(No.2009ZRA02071)资助项目。
*通讯联系人。E-mail:qdplastics@163.com
第一作者:李荣勋,男,38 岁,副教授;研究方向:材料学。

extended networks with higher dimensionality[10-12]. On the other hand, more subtle conditions can also be used to modify structures, such as choice of solvents or counter ions. By judicious choice of bridging ligands and metal coordination geometries, control over the topology and geometry of the infinite networks can be gained.

Lots of Zn(Ⅱ) coordination polymers based on isophthalate as bridging ligands and N-donors as auxiliary ligands have been reported[13-20], but ones containing N-donors of imidazole derivatives are rare[21-23]. Imidazole derivatives can not only coordinate with metal ion, but also donate hydrogen bonds, which may result in the formation of higher dimensional structures.

Here we report on crystal structures and characterization of two coordination polymers, {[Zn(ip)(Eim)$_2$]·H_2O} (**1**) and Zn(ip)(Mim)$_2$ (**2**). The 1D Zigzag chains in **1** and **2** are assembled to form 3D networks by hydrogen bonds and van der Waals interactions, respectively.

1 Experimental

1.1 Materials and instruments

All the chemical reagents for synthesizing the title compounds were purchased commercially and used without further purification. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 1400C analyzer. Voltammetry was performed by using a CHI 832B electrochemical analysis system (China) with a three-electrode system consisting of a glass carbon (GC) electrode (U=3 mm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the auxiliary electrode. All the electrochemical measurements were carried out in a 10 mL electrolyte cell with 0.01 mol·L^{-1} pH 6.86 KH_2PO_4-Na_2HPO_4 buffer solution as electrolyte. TG curve was recorded on a NETZSCH-TG209 GmbH thermoanalyser in flow of N_2, in the temperature range from 20~700 ℃, with a heating rate of 10 ℃·min^{-1}.

1.2 Preparation

Complex **1** was prepared as follows. $ZnSO_4·7H_2O$ (1.15 g, 4 mmol) was added to a solution of Eim (0.75 g, 8 mmol) in 10 mL of distilled water and 40 mL of ethanol. The resulting solution was added to a solution of disodium isophthalate (0.84 g, 4 mmol) in 10 mL of distilled water and 40 mL of ethanol (under continuous stirring at room temperature), and the mixture was refluxed for 7 h. The powder precipitate formed was filtered off, and the colorless filtrate was allowed to stay at ambient temperature for a period of about 3 weeks, gave 0.53 g (24% yields) of colorless block crystals suitable for structural determinations. Anal. Calcd. for $C_{18}H_{17}ZnN_4O_5$: C 49.27, H 4.82, N 12.77; found: C 50.01, H 4.99, N 12.82.

The colorless crystal of complex **2** was obtained by a similar procedure as for **1** except for using Mim (0.66 g, 8 mmol) instead of Eim, yield: 0.45g, 49%. Anal. Calcd. for $C_{16}H_{16}ZnN_4O_4$: C 48.81, H 4.10, N 14.23; found: C 48.72, H 4.02, N 14.49.

1.3 Crystal structure determination

Single crystals of **1** and **2** were mounted on a Bruker SMART 1000 CCD area detector X-ray single crystal diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm) and a φ/ω scanning mode at 293(2) K. Intensities were corrected for Lorentz and polarization effects and empirical absorption.

The structure was solved by direct methods via SHELXS 97 program[24] and refined by full-matrix least squares on F^2 via SHELXL 97 program[25]. All the non-hydrogen atoms were located from the difference Fourier map and refined anisotropically. H atoms were positioned geometrically (C-H=0.093 nm, 0.096 nm) and allowed to ride on their parent atoms with U_{iso}(H)= 1.2 times U_{eq}(C). Crystallographic data for **1** and **2** are listed in Table 1.

CCDC: 762257, **1**; 762258, **2**.

Table 1 Crystallographic data for the complexes 1 and 2

Complex	**1**	**2**
Empirical formula	$C_{18}H_{21}ZnN_4O_5$	$C_{16}H_{16}ZnN_4O_4$
Formula weight	438.76	393.7
Crystal size / mm	0.30×0.20×0.20	0.20×0.10×0.10

Continued Table 1

Temperature / K	293(2)	293(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pbca*
a / nm	1.587 6(3)	0.968 20(19)
b / nm	1.345 0(3)	1.322 4(3)
c / nm	0.974 60(19)	2.6983(5)
V / nm^3	2.081 1(7)	3.454 8(12)
Z	4	8
D_c / (Mg·m^{-3})	1.4	1.514
μ / mm^{-1}	1.215	1.45
F(000)	908	1 616
θ range / (°)	2.45~25.17	1.51~25.15
Reflections collected	1 954	3 091
Unique reflections	1 876	2 956
Goodness-of-fit on F^2	1.012	1.054
R_{int}	0.0225	0.0116
R_1 [$I>2\sigma(I)$]	0.073 7	0.068 0
wR_2 [$I>2\sigma(I)$]	0.167 2	0.183 8
R_1 (all data)	0.122 9	0.1028
wR_2 (all data)	0.191 9	0.207 1

2　Result and discussion

2.1　Crystal structures

The X-ray diffraction analysis indicates that each Zn atom adopts a distorted tetrahedral geometry formed by two N atoms from Eim or Mim molecules and two O atoms of different ip ligands (Fig.1). The complexes **1** and **2** contain infinite 1D polymeric zigzag chains consisting of [Zn(L)$_2$](L=Eim for **1**; Mim for **2**) building units connected by bridging isophthalate ligands in the μ_2-1,3 coordination mode. Fig.2a and Fig.2b show a fragment of the chains in the complexes **1** and **2** respectively. The Zn-O and Zn-N bond lengths are comparable to those of the structurally analogous complex [Zn(ip)(im)$_2$]$_n$·3nH$_2$O (Zn-O=0.198 0(2) and 0.193 3(3)nm, Zn-N=0.200 0(3) and 0.201 1(3)nm)[21].

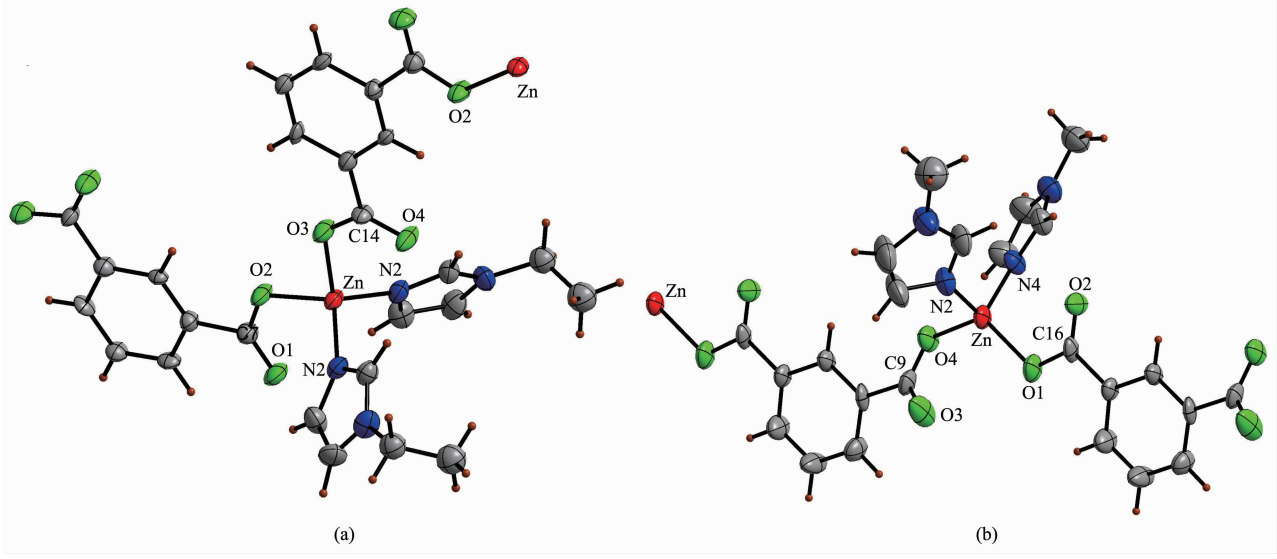

Fig.1　ORTEP representation of the local geometry around the Zn centers in **1**(a) and **2**(b) (30% probability ellipsoids)

The bond angles for Zn atoms in the complexes **1** and **2** lie in the range of 95.5(3)°~114.9(3)° and 96.6(18)°~117.2(19)°, respectively. (Table 2) In the bridging isophthalate anions with amphimonodentate coordination mode, the average C-O distance for the coordinated oxygen atom (0.128 5(10) nm in **1** and 0.128 7(6) nm in **2**) is slightly longer than for uncoordinated ones (0.122 1(10) nm in **1** and 0.120 8(6) nm in **2**). The carboxylate groups and benzene rings in **1** are almost coplanar, but the dihedral angle between two carboxylates in **2** is 35.33(3)°.

In the complexes **1** and **2**, the polymer backbone propagates along the crystallographic *a*-axis. The metal-metal distances across each polymer backbone are 0.959 4(21) nm in **1** and 0.968 2(21) nm in **2**, which are shorter than those found in $[Zn(ip)(im)_2]_n \cdot 3nH_2O$ (1.039 1(14) nm)[21]. The closest metal-metal distances between neighboring strands for **1** are 0.905 5(21) nm, which are longer than those of 0.673 4(17) nm and 0.743 8(14) nm in **2** and $[Zn(ip)(im)_2]_n \cdot 3nH_2O$[21], respectively.

In the complex **1**, the adjacent metal-organic chains are connected into a 3D network via hydrogen bonds between solvent water molecules and the uncoordinated oxygen atoms of the carboxylate groups (Ow–HWA···O(4)=0.291 0(14) nm), which control the

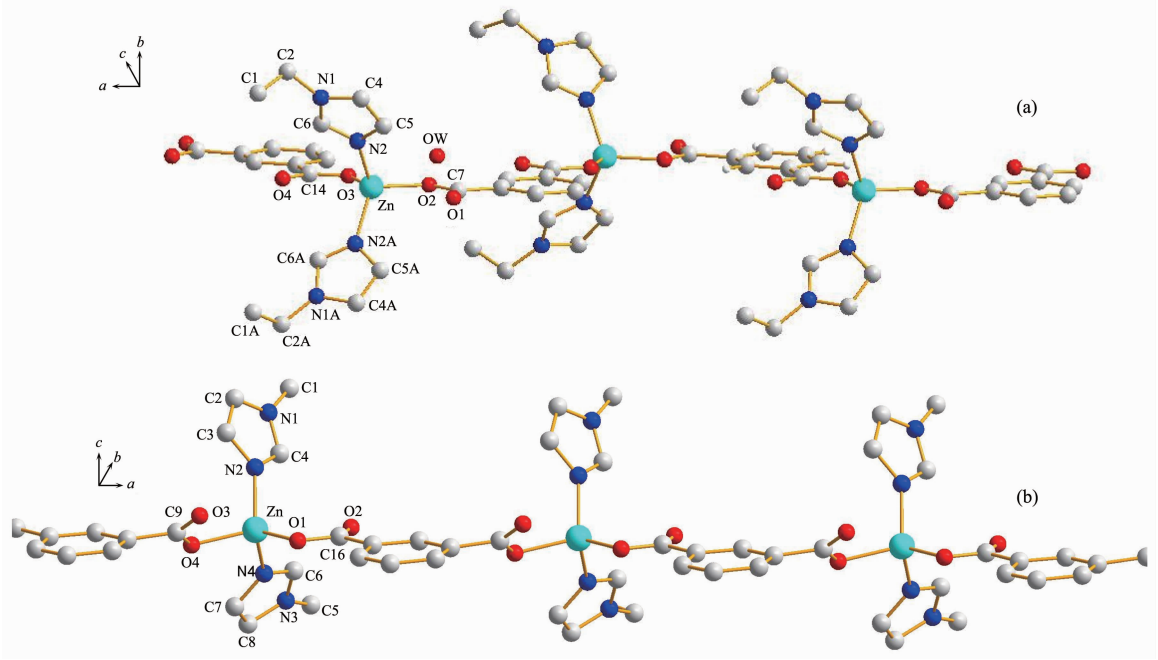

Fig.2 View of the coordination polymeric chains in 1(a) and 2(b)

Table 2 Selected bond lengths (nm) and bond angles (°) for the complexes

Complex **1**					
Zn-O(2)	0.194 4(6)	Zn-O(3)	0.194 3(6)	Zn-N(2)	0.200 1(6)
O(2)-Zn-O(3)	95.5(3)	O(3)-Zn-N(2)	111.77(18)	N(2)#1-Zn-N(2)	114.9(3)
O(2)-Zn-N(2)	111.64(17)				
Complex **2**					
Zn-O(1)	0.193 0(4)	Zn-N(2)	0.199 6(6)	Zn-N(4)	0.203 2(5)
Zn-O(4)	0.197 6(4)				
O(1)-Zn-O(4)	117.2(19)	O(4)-Zn-N(2)	105.8(19)	O(4)-Zn-N(4)	96.6(18)
O(1)-Zn-N(2)	115.5(2)	O(1)-Zn-N(4)	111.5(19)	N(2)-Zn-N(4)	108.3(2)

Symmetry operations: #1: *x*, −*y*+1/2, *z*.

packing of the adjacent chains (Fig.3a and Table 3). In complex **2** there are only van der Waals interactions between the adjacent chains in contrast to **1** (Fig.3b). Some potentially weak (C–H···O) intramolecular interactions exist in the complexes **1** and **2** (Table 3), which further stabilize the structures of zigzag chains.

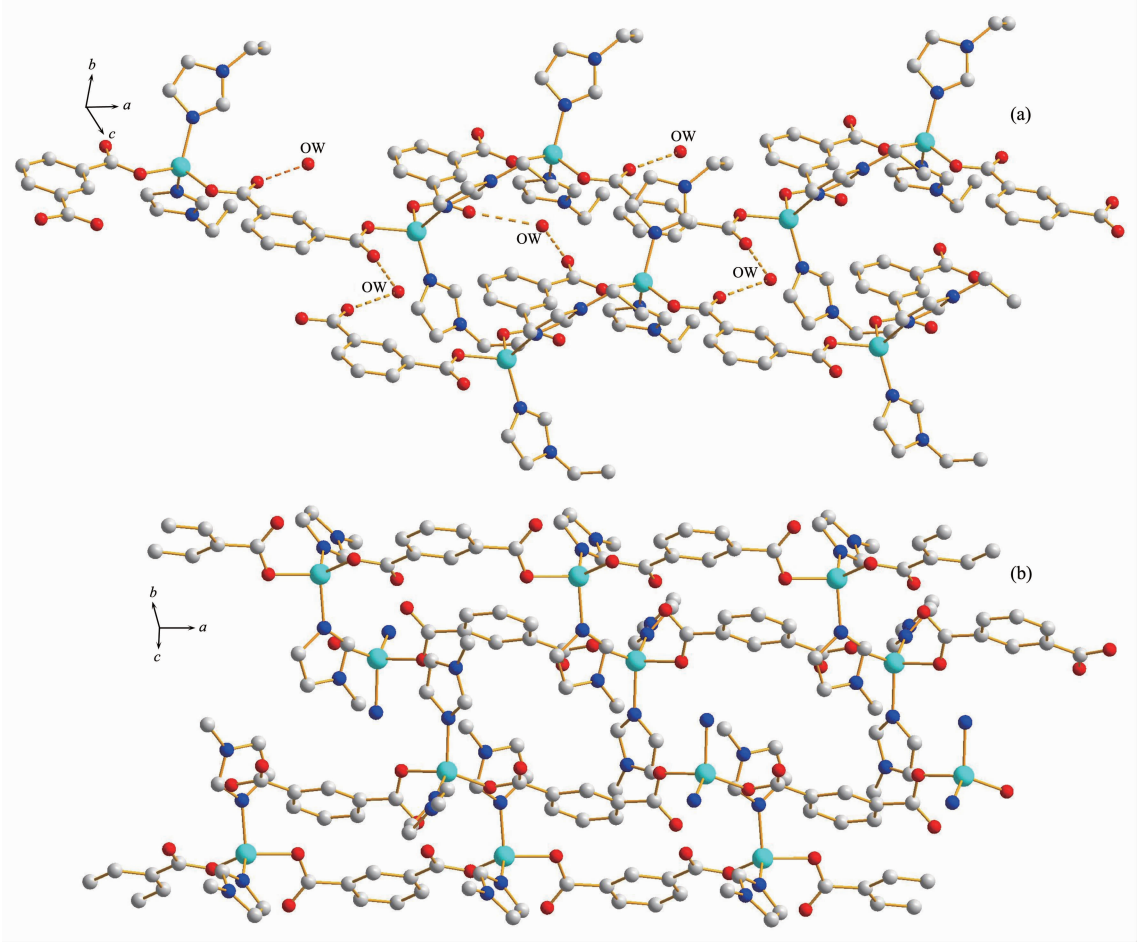

Fig.3　View of supramolecular networks in **1**(a) and **2**(b)

Table 3　Hydrogen bonds of the complexes 1 and 2 (nm and °)

D–H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
Complex **1**				
Ow–HWA···O(4)#1	0.085	0.250	0.291 0(14)	111
C(6)–H(6A)···O(4)	0.093	0.259	0.331 4(8)	135
C(13)–H(13A)···O(2)	0.093	0.240	0.271 8(10)	100
Complex **2**				
C(1)–H(1A)···O(3)#2	0.096	0.255	0.342 1(9)	150
C(4)–H(4B)···O(3)#3	0.093	0.231	0.315 0(2)	150
C(11)–H(11A)···O(2)#4	0.093	0.254	0.345 6(6)	171

Symmetry code: #1: 1–*x*, –1/2+*y*, –*z*; #2: 3/2–*x*, 1/2+*y*, *z*; #3: 3/2–*x*, 1/2+*y*, *z*; #4: 3/2–*x*, –1/2+*y*, *z*.

2.2　Thermal properties

Thermal analyses of the complex 1 reveal that the first weight loss of about 4.95% occurs in the temperature range of 82~250 ℃, which corresponds to the loss of water molecules (calculated 4.14%). On further heating polymeric chains decompose via two unidentified steps in the temperature range of 250~580 ℃ and the weight loss of 79.04% was ascribed to the release of Eim and ip ligands.(calculated 78.21%). The final product was ZnO with the remaining percentage of

16.68% (calculated 17.65%). For the complex **2** the first weight loss of 40.38% around 220~390 ℃ corresponds to the loss of two Mim molecules(calculated 41.71%). In the temperature range of 390 ~520 ℃ weight loss of 38.17% was ascribed to the release of ip ligand (calculated 37.59%), to give the expected oxides (observed 18.95%, calculated 20.61%).

2.3 Electrochemistry

Typical cyclic voltammetry curves for the complexes **1** and **2** in 0.01 mol·L^{-1} pH 6.86 KH_2PO_4-Na_2HPO_4 buffer solutions are shown in Fig.4.

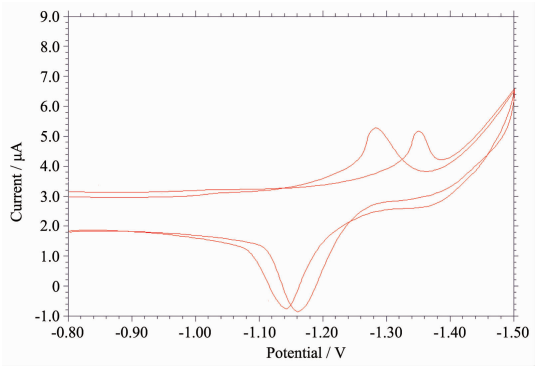

Fig.4 Cyclic voltammetry of 3.00×10^{-4} mol·L^{-1} complexes **1** and **2** in 0.01 mol·L^{-1} pH 6.86 KH_2PO_4-Na_2HPO_4 buffer solution, at a scan rate: 0.03 V·s^{-1}

The complexes **1** and **2** at 0.03 V·s^{-1} have anodic peaks at −1.161 V and −1.141 V, and cathodic peaks at −1.345 V and −1.282 V, respectively, corresponding to the electrochemical process of Zn^{2+}/Zn^{+}[26]. The separations of the cathodic and anodic peaks potential, ΔE= 0.184 V for **1** and 0.141 V for **2**, indicate that the electrochemical behaviors of both complexes **1** and **2** on the glass carbon electrode are quasi-reversible processes.

References:

[1] Subramanian S, Zaworotko M J. *Angew. Chem., Int. Ed. Engl.*, **1995**,**34**:2127-2131

[2] Moulton B, Zaworotko M J. *Chem. Rev.*, **2001**,**101**:1629-1653

[3] Zaworotko M J. *Cryst. Growth Des.*, **2007**,**7**:4-11

[4] Batten S R. *Curr. Opin. Solid State Mater. Sci.*, **2001**,**5**:107-114

[5] Huang X C, Lin Y Y, Zhang J P, et al. *Angew. Chem. Int. Ed.*, **2006**,**45**:1557-1560

[6] Janiak C. *J. Chem. Soc., Dalton Trans.*, **2003**:2781-2787

[7] Rowsell J L C, Yaghi O M. *Microporous Mesoporous Mater.*, **2004**,**73**:3-12

[8] Kitagawa S, Kitaura R, Noro S I. *Angew. Chem., Int. Ed.*, **2004**,**43**:2334-2339

[9] Yamaguchi T, Tashiro S, Tominaga M, et al. *Adv. Inorg. Biochem.*, **2007**,**15**(2):468-472

[10]Lewinski J, Zachara J, Justyniak I, et al. *Coord. Chem. Rev.*, **2005**,**249**:1185-1205

[11]Chen H J, Zhang J, Feng W L, et al. *Inorg. Chem. Commun.*, **2006**,**9**:300-302

[12]Song J F, Chen Y, Li Z G, et al. *J. Mol. Struct.*, **2005**,**743**:243-248

[13]LI Bin(李 彬), SUN Yue-Fei(孙跃飞), GOU Shao-Hua(苟少华), et al. *Chinese J. Inorg. Chem.* (*Wuji Huaxue Xuebao*), **2001**,**17**(6):917-920

[14]Zhou Y F, Zhao Y J, Sun D F, et al. *Polyhedron.*, **2003**,**22**:1231-1235

[15]Wang S P, Gao D Z, Liao D Z, et al. *Transition Met. Chem.*, **2006**,**31**:214-228

[16]Hao Z M, Zhang X M. *Inorg. Chem. Commun.*, **2006**,**9**:57-62

[17]Che G B, Liu C B, Liu B, et al. *CrystEngComm.*, **2008**,**10**:184-190

[18]Qin Y Y, Zhang J, Li Z J, et al. *Chem. Commun.*, **2008**:2532-2534

[19]Wang X L, Xu Y H, Li L C, et al. *Chin. J. Struct. Chem.*, **2008**,**27**(7):797-801

[20]Hu T L, Zou R Q, Li J R, et al. *Discussion of Faraday Soc.*, **2008**:1302-1307

[21]Li X M, Cui Y C, Wang Q W, et al. *Chin. J. Struct. Chem.*, **2006**,**25**(4):481-485

[22]Li W H, Zhao G F, Huang Z G, et al. *Chin. J. Chem.*, **2008**,**26**(9):1607-1610

[23]Li S X, Zhao G F, Liu F Q, et al. *Chin. J. Chem.*, **2008**,**26**(9):1732-1736

[24]Sheldrick G M. *Acta Crystallogr., Sect. A*, **1990**,**46**:467-471

[25]Sheldrick G M. *SHELXL*-97, *Program for X-ray Crystal Structure Refinement*, University of Gttingen, Germany, **1997**.

[26]Xi P X, Xu Z H, Chen F J, et al. *J. Inorg. Biochem.*, **2009**,**103**:210-217