Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Molecular Structure 733 (2005) 63–68
Journal of MOLECULAR STRUCTURE
www.elsevier.com/locate/molstruc

Hydrothermal synthesis and crystal structures of two zinc(II) coordination polymers with benzophenone-4,4′-dicarboxylic acid

Changyan Sun, Linpei Jin*

Department of Chemistry, Beijing Normal University, Xinjiekou Road, Beijing 100875, China

Received 19 June 2004; revised 28 July 2004; accepted 3 August 2004
Available online 18 September 2004

Abstract

Two new coordination polymers, $[Zn(bpndc)(4,4'\text{-bpy})_{1.5}]_n \cdot 0.5n(4,4'\text{-bpy}) \cdot 0.5nH_2O$ (**1**) and $[Zn(bpndc)(phen)(H_2O)]_n$ (**2**) (H_2bpndc = benzophenone-4,4′-dicarboxylic acid; 4,4′-bpy = 4,4′-bipyridine; phen = 1,10-phenanthroline) were synthesized by the hydrothermal reactions and characterized by single crystal X-ray diffraction, elemental analysis, IR spectrum and thermal analysis. In **1**, 4,4′-bpy molecules link Zn(II) ions into one-dimensional ladders, and these ladders are bridged by $bpndc^{2-}$ ligands, resulting in an infinite two-dimensional rhombohedral network. Such rhombohedral grids interweave each other, forming a three-dimensional structure. In **2**, Zn_2O_2 cores are interconnected by $bpndc^{2-}$ ligands to generate a one-dimensional centripede-like double-chain structure, and further assembled by O–H···O hydrogen bonds and π–π stacking interactions to form three-dimensional supramolecular network with one-dimensional channels.

Keywords: Benzophenone-4,4′-dicarboxylic acid; Hydrothermal synthesis; Coordination polymer; Hydrogen bond; Supramolecular architecture

1. Introduction

Design and synthesis of coordination polymers with well-defined pores are of great interest for potential applications in catalysis [1–4], adsorption [5–8], ion-exchange [9,10], sensor technology [11,12], optoelectronics [13], and nanowires [14]. A large number of three-dimensional coordination polymers with porous structures have been prepared and characterized using a variety of benzene-polycarboxylic acid. Of these, benzene-1,4-dicarboxylic acid (H_2BDC) with a 180° separation between the two carboxylic groups and benzene-1,3,5-tricarboxylic acid (H_3BDC) with a 120° separation have been proven to yield interesting structures [4,8,15–18]. It seems that rigid linear ligands are profitable to construct porous coordination polymers. The introduction of neutral ligands, such as 4,4′-bipyridine, 1,10-phenanthroline, often changes the frameworks of the coordination polymers. In general, 4,4′-bipyridine is a useful spacer to link metal ions and is beneficial to the formation of porous network; while 1,10-phenanthroline, for its large volume and steric effect, seldom forms porous network.

Benzophenone-4,4′-dicarboxylic acid (H_2bpndc) is a long spacer with two exo carboxylate groups. Although there is not any report about its coordination chemistry, we expect that it can coordinate to metal ions in various modes to give novel coordination polymers. Herein, we report two new Zn(II) coordination polymers with H_2bpndc, $[Zn(bpndc)(4,4'\text{-bpy})_{1.5}]_n$ $0.5n(4,4'\text{-bpy})$ $0.5nH_2O$ (**1**) and $[Zn(bpndc)(phen)(H_2O)]_n$ (**2**).

2. Experimental

2.1. Materials and apparatus

All reagents were used as received without further purification. The C, H, N microanalyses were carried out with a Vario EL elemental analyzer. The IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer

---

* Corresponding author. Tel.: +86-106-220-5522; fax: +86-106-220-2075.

E-mail address: lpjin@bnu.edu.cn (L. Jin).

0022-2860/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2004.08.001

using the KBr pellet technique. Thermogravimetric analyses were conducted on a ZRY-2P Thermal Analyzer using a heating rate of 20 °C/min from room temperature to 700 °C.

2.2. Synthesis of the two complexes

[Zn(bpndc)(4,4′-bpy)$_{1.5}$]$_n$·0.5n(4,4′-bpy)·0.5nH$_2$O (**1**). A mixture of $Zn(CH_3COO)_2$ 2H_2O (0.022 g, 0.1 mmol), H_2bpndc (0.027 g, 0.1 mmol), 4,4′-bpy (0.016 g, 0.1 mmol), 0.042 ml Et_3N and 5 ml deionized water was sealed in a Teflon-lined stainless vessel (25 ml) and heated at 140 °C for 72 h under autogenous pressure, and then cooled slowly to room temperature. Colourless and column single crystals were obtained by filtration, washed with deionized water and ethanol, and dried in air. Yield: 0.024 g (36.6%) Anal. Calc. for $C_{35}H_{25}N_4O_{5.5}Zn$ (%): C, 64.13; H, 3.82; N, 8.55; Found (%): C, 63.78; H, 4.09; N,8.09. IR data (KBr pellet, cm^{-1}): 3433(s), 1662(m), 1608(s), 1542(m), 1491(w), 1384(s), 1297(w), 1258(m), 1217(w), 1137(w), 1069(w), 1067(w), 929(w), 837(w), 810(m), 731(m), 627(m), 569(w), 503(w).

[Zn(bpndc)(phen)(H$_2$O)]$_n$ (**2**). A mixture of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.022 g, 0.1 mmol), H_2bpndc (0.027 g, 0.1 mmol), phen·H_2O (0.02 g, 0.1 mmol), 0.028 ml Et_3N and 5 ml deionized water was sealed in a Teflon-lined stainless vessel (25 ml) and heated at 140 °C for 72 h under autogenous pressure, and then cooled slowly to room temperature. Colourless and plate-like single crystals were obtained by filtration, washed with deionized water and ethanol, and dried in air. Yield: 0.028 g (52.6%) Anal. Calc. for $C_{27}H_{18}N_2O_6Zn$ (%): C, 60.93; H, 3.38; N, 5.27; Found (%): C, 60.72; H, 3.59; N, 5.16. IR data (KBr pellet, cm^{-1}): 3373(s), 1655(s), 1598(s), 1545(m), 1519(m), 1431(w), 1386(s), 1339(s), 1304(m), 1275(m), 1128(w), 1106(w), 933(w), 847(w), 813(w), 788(w), 729(m), 640(w), 494(w).

2.3. X-ray diffraction determination

Diffraction intensities for the two complexes were collected at 293 K on a Bruker SMART 1000 CCD area detector diffractometer employing graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) in ϕ and ω scan modes. Semi-empirical absorption correction was applied using the SADABS program [19]. The structures were solved by direct methods [20] and refined by full-matrix least squares method on F^2 using SHELXS 97 and SHELXL 97 programs, respectively [20,21]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. The crystallographic data for the two complexes are listed in Table 1, and selected bond lengths (Å) and bond angles (deg) in Table 2.

Table 1
Crystal data and structure refinement parameters for **1** and **2**

	1	**2**
Chemical formula	$C_{35}H_{25}N_4O_{5.5}Zn$	$C_{27}H_{18}N_2O_6Zn$
Formula weight	654.96	531.80
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.306(6)	7.745(3)
b (Å)	11.507(6)	11.620(5)
c (Å)	13.796(7)	13.563(5)
α (deg)	74.806(10)	82.994(6)
β (deg)	73.198(9)	83.969(7)
γ (deg)	64.976(8)	70.966(7)
V (Å^3)	1536.6(14)	1142.5(8)
Z	2	2
F(000)	674	544
D_c (mg m^{-3})	1.416	1.546
T (°C)	293(2)	293(2)
θ range (deg)	1.56 to 25.01	1.52 to 25.01
Absorption coefficient	0.851 mm^{-1}	1.123 mm^{-1}
Goodness-of-fit on F^2	1.074	1.034
Final R indices [$I>2\sigma(I)$]	$R_1=0.0847$, $wR_2=0.1919$	$R_1=0.0492$, $wR_2=0.1072$
largest diff. peak and hole	0.734 and -0.413e Å^{-3}	0.845 and -0.486e Å^{-3}

Table 2
Selected bond lengths (Å) and angles (deg) for **1** and **2**

1

Zn(1)–O(1)	2.101(4)	Zn(1)–N(1)	2.218(4)
Zn(1)–O(2)	2.480(5)	Zn(1)–N(2)#2	2.241(4)
Zn(1)–O(5)#1	1.983(3)	Zn(1)–N(3)	2.133(4)
O(1)–Zn(1)–O(2)	55.23(17)	O(5)#1–Zn(1)–N(3)	124.25(13)
O(1)–Zn(1)–N(1)	94.40(14)	N(1)–Zn(1)–O(2)	87.37(14)
O(1)–Zn(1)–N(2)#2	90.12(14)	N(1)–Zn(1)–N(2)#2	174.58(13)
O(1)–Zn(1)–N(3)	138.14(16)	N(2)#2–Zn(1)–O(2)	92.79(14)
O(5)#1–Zn(1)–O(1)	97.61(16)	N(3)–Zn(1)–O(2)	83.09(14)
O(5)#1–Zn(1)–O(2)	152.44(13)	N(3)–Zn(1)–N(1)	86.65(13)
O(5)#1–Zn(1)–N(1)	90.63(14)	N(3)–Zn(1)–N(2)#2	87.99(13)
O(5)#1–Zn(1)–N(2)#2	91.73(13)		

Symmetry transformations used to generate equivalent atoms: #1 $x+1$, y, $z-1$; #2 x, $y-1$, z.

2

Zn(1)–O(1)	2.051(3)	Zn(1)–O(6)	2.087(3)
Zn(1)–O(5)#1	2.127(3)	Zn(1)–N(1)	2.194(4)
Zn(1)–O(5)#2	2.146(3)	Zn(1)–N(2)	2.132(4)
O(1)–Zn(1)–O(5)#1	99.03(12)	O(5)#2–Zn(1)–N(1)	92.18(12)
O(1)–Zn(1)–O(5)#2	89.47(11)	O(6)–Zn(1)–O(5)#1	89.05(12)
O(1)–Zn(1)–O(6)	88.70(12)	O(6)–Zn(1)–O(5)#2	165.40(12)
O(1)–Zn(1)–N(1)	88.57(13)	O(6)–Zn(1)–N(1)	102.25(13)
O(1)–Zn(1)–N(2)	165.11(13)	O(6)–Zn(1)–N(2)	92.04(13)
O(5)#1–Zn(1)–O(5)#2	76.94(12)	N(2)–Zn(1)–O(5)#2	93.44(12)
O(5)#1–Zn(1)–N(1)	166.57(11)	N(2)–Zn(1)–N(1)	76.74(13)
O(5)#1–Zn(1)–N(2)	95.85(12)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y$, $-z+1$; #2 x, y, $z-1$.

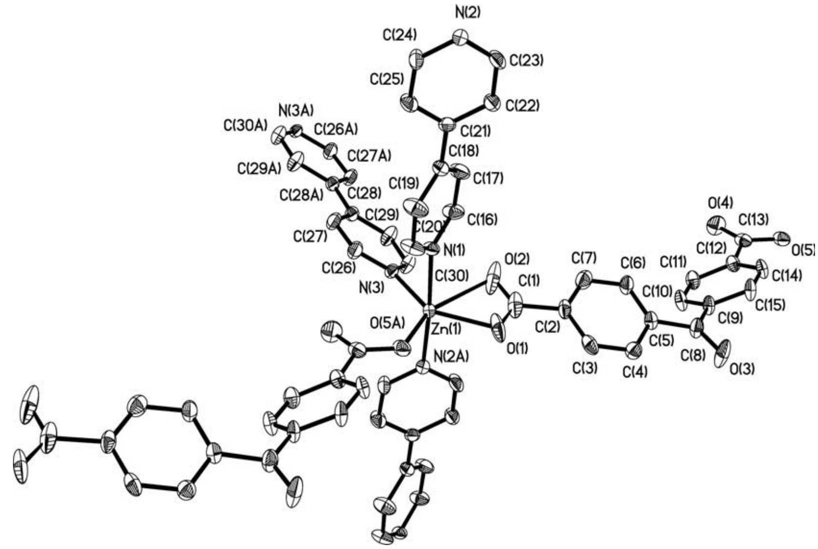


Fig. 1. The coordination environment of Zn(II) ion in complex **1** with thermal ellipsoids at 30% probability.

3. Results and discussion

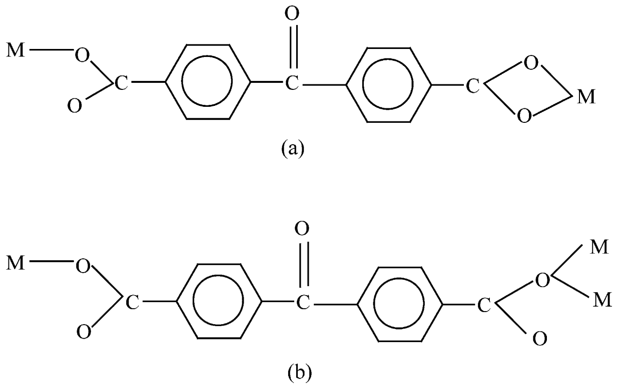
3.1. Structural description of *[Zn(bpndc)(4,4′-bpy)$_{1.5}$]$_n$ 0.5n(4,4′-bpy) 0.5nH$_2$O (**1**)*

The coordination environment of Zn(II) ion in **1** is shown in Fig. 1. Each Zn(II) ion is six-coordinated by three oxygen atoms of two bpndc^{2-} ligands and three nitrogen atoms from three 4,4′-bpy molecules, leading to a distorted octahedron geometry. There is only one kind of crystallographically independent bpndc^{2-} ligand, acting as a tridentate ligand. One carboxylate group adopts a bidentate chelating mode, chelating one Zn(II) ion. While the other carboxylate group adopts a monodentate mode, coordinating to one Zn(II) ion (see Scheme 1a). The bpndc^{2-} ligand is not in linear, but in 'V' shape with C(5)–C(8)–C(9) 118.93°.

In **1**, 4,4′-bpy molecules link metal ions into a one-dimensional ladder, as shown in Fig. 2. The one-dimensional ladders are bridged by bpndc^{2-} ligands, resulting in an infinite two-dimensional rhombohedral network (Fig. 3). The Zn–Zn–Zn angles in each rhombohedron are 85.6° and 94.4°. Owing to the larger length of bpndc^{2-} and 4,4′-bpy ligands, there is a larger void space in **1**. The dimensions of rhombohedral grid are about 11.507×15.099 Å. However, no channel is formed in **1** because of the interweaving of each four independent rhombohedral grids (Fig. 4). Free 4,4′-bipy and water molecules are encased in **1**.

3.2. Structural description of *[Zn(bpndc)(phen)(H$_2$O)]$_n$ (**2**)*

There is only one metal environment in **2**, as shown in Fig. 5. The coordination geometry around the Zn(II) ion, comprising N$_2$O$_4$ from three bpndc^{2-} ligands, one water molecule and one phen molecule, can be described as a distorted octahedron. Two oxygen atoms (O(5A) and O(6)) from a bpndc^{2-} ligand and a coordinated water molecule occupy the axial positions. There is also one kind of crystallographically independent bpndc^{2-} ligand, acting as a tridentate ligand(Scheme 1b). But the coordination mode is different from that in **1**. Scheme 1b shows that one oxygen atom of a carboxylate group adopts a bidentate bridging mode, connecting two Zn(II) ions. While the other carboxylate group adopts a monodentate mode, coordinating to one Zn(II) ion. The bpndc^{2-} ligand is in 'V' shape, too. The angle of C(5)–C(8)–C(9) is 119.75°. So in **2**, the neighboring Zn(II) ions are held together by the carboxylate bridging oxygens with Zn–Zn distance of 3.345 Å. It is very interesting that Zn$_2$O$_2$ cores including Zn(1), Zn(1A), O(5A) and O(5B) in parallelogram geometry are interconnected by bpndc^{2-} bridging ligands to generate



Scheme 1. The coordination modes of bpndc^{2-} ligands in complexes **1** and **2**.

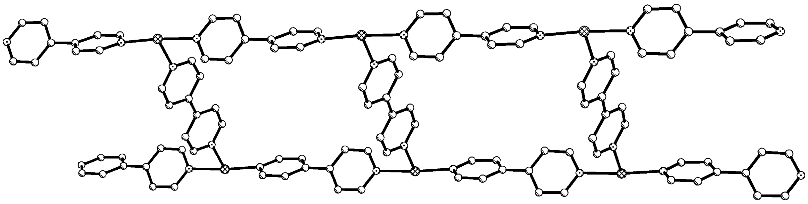


Fig. 2. The one-dimensional ladder linked by 4,4′-bpy in **1**.

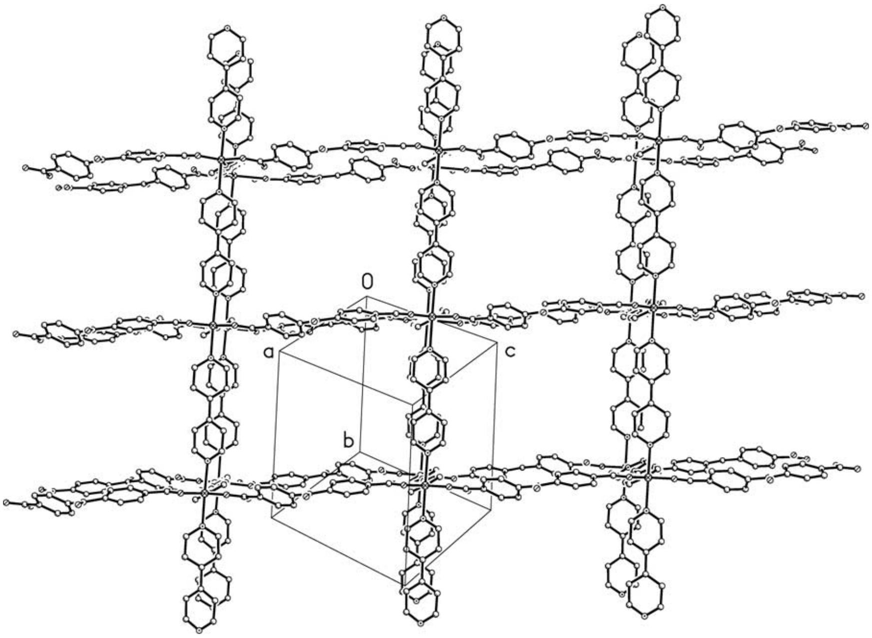


Fig. 3. View of the two-dimensional rhombohedral grid structure of **1**.

a one-dimensional centripede-like double-chain structure (Fig. 6).

These chains are further connected with O–H···O hydrogen bonds between the coordinated water molecules and the uncoordinated carboxylate oxygen atoms: O(6)–H(6A)···O(2) 163.37°, O(6)···O(2) 2.659 Å; O(6)–H(6B)···O(4)*i* 151.43°, O(6)···O(4)*i* 2.659 Å (symmetry code *i*: $x-1$, y, $z-1$). All the phen rings in **2** are parallel to each other. The nearest distance of two phen planes from neighbor chains is 3.37 Å. Therefore, there are π–π stacking interactions between the phen molecules. The hydrogen bonds and π–π stacking interactions result in the formation of three-dimensional supramolecular network with one-dimensional channels of about 3.345×13.563 Å, as shown in Fig. 7.

3.3. Thermogravimetric analyses

Thermogravimetric analyses of the two complexes were carried out to examine their thermal stabilities. For **1**, the first weight loss of 13.5% from 84 to 115 °C corresponds to the loss of the free 4,4′-bpy and water molecules in the complex (calcd 13.3%). Increasing temperature led to the further decomposition of the compound at 255 °C. The final pyrolysis was completed at 520 °C, giving a powder of ZnO. **2** is similar to **1**, with the first weight loss (the one coordinating water molecule) of 3.7% (calcd 3.4%) from 122 to 228 °C. The further decomposition of the complex begun at 331 °C and finished at 693 °C, giving the compound $ZnCO_3$.

4. Conclusions

In this work, we report the syntheses and structures of two new zinc(II) coordination polymers with H_2bpndc,

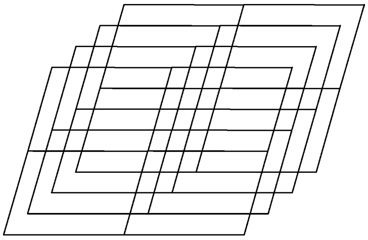


Fig. 4. A schematic view of the interweaving of the four independent rhombohedral grids in **1**.

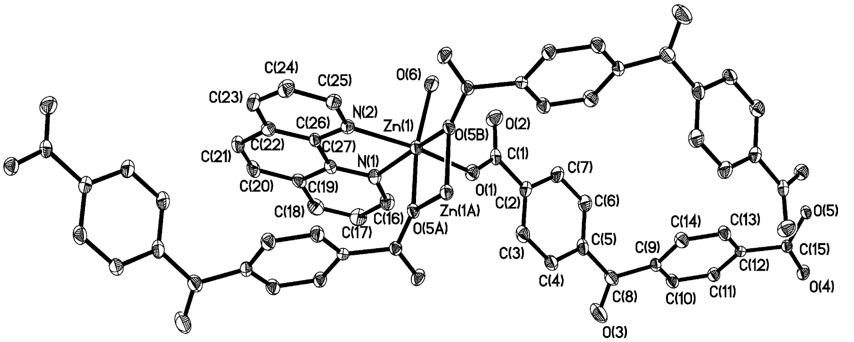


Fig. 5. The coordination environment of Zn(II) ion in **2** with thermal ellipsoids at 30% probability.

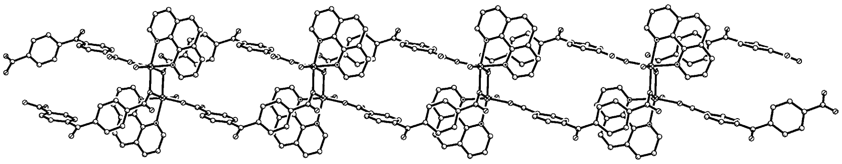


Fig. 6. The one-dimensional centripede-like double-chain structure viewed along *a*-axis in **2**.

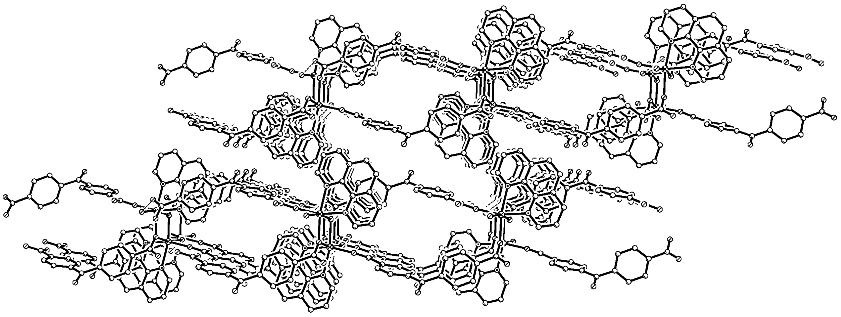


Fig. 7. The three-dimensional network viewed along *a*-axis in **2**.

$[Zn(bpndc)(4,4'\text{-}bpy)_{1.5}]_n \cdot 0.5n(4,4'\text{-}bpy) \cdot 0.5nH_2O$ (**1**) and $[Zn(bpndc)(phen) \cdot (H_2O)]_n$ (**2**). The introduction of 4,4′-bpy in **1** and phen in **2** makes $bpndc^{2-}$ ligands coordinate to metal ions in different mode, and thus results in the formation of different three-dimensional structures.

5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 241595, 241596 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

Acknowledgements

This project is supported by National Nature Science Foundation of China (20331010).

References

[1] K. Endo, T. Kake, T. Sawaki, O. Hayashida, H. Masuda, H. Aoyama, J. Am. Chem. Soc. 119 (1997) 4117.
[2] T. Sawaki, T. Dewa, Y. Aoyama, J. Am. Chem. Soc. 120 (1998) 8539.
[3] J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim, Nature 404 (2000) 982.
[4] B.G. Lor, E.G. Puebla, M. Iglesias, M.A. Monge, C.R. Valero, N. Snejko, Inorg. Chem. 41 (2002) 2429.
[5] B.F. Abrahams, P.A. Jackson, R. Robson, Angew. Chem. Int. Ed. 37 (1998) 2656.
[6] M. Kondo, T. Okubo, A. Asami, S. Noro, S. Kitagawa, T. Ishii, H. Matsuzaka, K. Seki, Angew. Chem. Int. Ed. 38 (1999) 140.
[7] H. Eddaudi, H.L. Li, O.M. Yaghi, J. Am. Chem. Soc. 122 (2000) 1391.

[8] J.W. Ko, K.S. Min, M.P. Suh, Inorg. Chem. 41 (2002) 2151.
[9] O.M. Yaghi, H. Li, J. Am. Chem. Soc. 118 (1996) 295.
[10] K.S. Min, M.P. Suh, J. Am. Chem. Soc. 122 (2000) 6834.
[11] J.A. Real, E. Andrés, M.C. Muñoz, M. Julve, T. Granier, A. Boussekou, F. Varret, Science 268 (1995) 265.
[12] M. Albrecht, M. Lutz, A.L. Spek, G. van Koten, Nature 406 (2000) 970.
[13] O.R. Evans, W. Lin, Chem. Mater. 13 (2001) 2705.
[14] B.H. Hong, S.C. Bae, C.-W. Lee, S. Jeong, K.S. Kim, Science 294 (2001) 348.
[15] T.M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley, O.M. Yaghi, J. Am. Chem. Soc. 121 (1999) 1651.
[16] K. Barthelet, J. Marrot, D. Riou, G. Ferey, Angew. Chem. Int. Ed. 41 (2002) 281.
[17] C. Serre, F. Millange, C. Thouvenot, M. Nogues, G. Marsolier, D. Louer, G. Ferey, J. Am. Chem. Soc. 124 (2002) 13519.
[18] W. Chen, J.Y. Wang, C. Chen, Q. Yue, H.M. Yuan, J.S. Chen, S.N. Wang, Inorg. Chem. 42 (2003) 944.
[19] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area detector Data, University of Göttingen, Germany, 1997.
[20] G.M. Sheldrick, SHELXS 97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.
[21] G.M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.