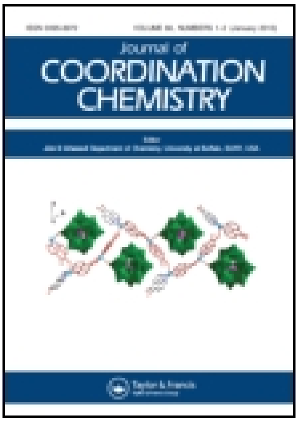
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:49
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Tuning the topological net of two new copper(II) coordination polymers based on a paddle-wheel secondary building unit via altering the auxiliary ligands

Lu Zhao [a] & Feng Guo [a]

[a] Key Laboratory of Coordination Chemistry and Functional Materials in Universities of Shandong, Dezhou University, Shandong, P.R. China

Accepted author version posted online: 25 Jun 2013.Published online: 24 Jul 2013.

To cite this article: Lu Zhao & Feng Guo (2013) Tuning the topological net of two new copper(II) coordination polymers based on a paddle-wheel secondary building unit via altering the auxiliary ligands, Journal of Coordination Chemistry, 66:16, 2940-2947, DOI: 10.1080/00958972.2013.819090

To link to this article: http://dx.doi.org/10.1080/00958972.2013.819090

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Coordination Chemistry, 2013
Vol. 66, No. 16, 2940–2947, http://dx.doi.org/10.1080/00958972.2013.819090

Tuning the topological net of two new copper(II) coordination polymers based on a paddle-wheel secondary building unit via altering the auxiliary ligands

LU ZHAO and FENG GUO*

Key Laboratory of Coordination Chemistry and Functional Materials in Universities of Shandong, Dezhou University, Shandong, P.R. China

(*Received 16 February 2013; in final form 6 June 2013*)

Two new coordination polymers, $[Cu(BDC)(L_1)_{0.5}]_n$ (**1**) and $[Cu(BDC)(L_2)_{0.5}]_n$ (**2**) [H_2BDC=5-methyl-1,3-benzenedicarboxylic acid, L_1=1,4-bis(2-methyl-imidazol-1-yl) butane and L_2=1,4-bis (1-imidazol-yl)-2,5-dimethylbenzene], were synthesized from Cu(II), H_2BDC, and L_1/L_2. The carboxylate groups in **1** and **2** are bis-monodentate. By changing the N-donor ligands, **1** and **2** exhibit different topologies from a rob topological net to a twofold interpenetrating pcu net; however, they possess the same paddle-wheel secondary building unit in which Cu(II) has square-pyramidal geometry. The thermal stabilities of **1** and **2** are investigated.

Keywords: Coordination polymer; Copper(II); Paddle-wheel structure

1. Introduction

Coordination polymers have attracted interest for potential applications in porous materials [1–3], luminescence [4–6], and magnetism [7–9] and for intriguing topologies [10–12]. Objectives within coordination polymers are the construction and analysis of new topologies to understand complicated structures and provide a role in design of functional materials with desirable properties. If the external environment (including metal ion and ligand) is well defined, synthetic methodologies and strategies play key roles in formation of these materials [13–15]. Designing secondary building units (SBU) can be an effective strategy in construction of a topological net [16–18]. A number of factors, such as solvents, the coordination geometry of metal centers, and the addition of auxiliary ligands, significantly affect the final framework [19–22]. To get desired architecture in the final molecule, selection of ligand and metal/metal cluster nodes is important. The paddle-wheel structural unit of Cu(II) ions is a well-known SBU and has been used to construct many coordination polymers such as HKUST-1 [23–25]. In this paper, we chose 5-methylisophthalic acid, imidazole-containing ligands and Cu(II) ion to construct two new coordination polymers, $[Cu(BDC)(L_1)_{0.5}]_n$ (**1**) and $[Cu(BDC)(L_2)_{0.5}]_n$ (**2**), both of which possess a

---

*Corresponding author. Email: guofeng1510@yeah.net paddle-wheel structure. In addition, **1** and **2** display different topological nets, i.e., rob and pcu topology.

2. Experimental

2.1. *Materials and physical measurements*

All reagents and solvents were commercially available and used as received. Elemental analysis was carried out with a Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded from 400 to 4000 cm^{-1} with a Bruker Equinox 55 FT-IR spectrometer as a dry KBr pellet. Thermal analysis was carried out with a Netzsch STA449C thermal analyzer under nitrogen at a heating rate of 10 °C min^{-1}. X-ray powder diffraction (XRPD) measurements were performed on a Bruker D8 diffractometer operated at 40 kV and 40 mA using Cu-Kα radiation ($\lambda = 0.15418$ nm).

2.2. *Syntheses of 1 and 2*

2.2.1. Synthesis of [Cu(BDC)(L_1)$_{0.5}$]$_n$ (1). **1** is hydrothermally synthesized by reaction of $Cu(NO_3)_2 \cdot 3H_2O$ (0.241 g, 1.0 mM), H_2BDC (0.180 g, 1.0 mM), L_1 (0.218 g, 1.0 mM), NaOH (0.08 g, 2 mM), and deionized water (18 mL) in a sealed 25-mL teflon-lined stainless steel vessel at 160 °C for 96 h. After cooling to room temperature, green block crystals were obtained and washed with alcohol several times (Yield 40%). Anal. Calcd (%) for $C_{15}H_{15}CuN_2O_4$: C, 51.35; N, 7.99; H, 4.31. Found: C, 51.33; N, 7.98; H, 4.33. IR/cm^{-1} (KBr): 1616 s, 1453, 1381, 1247, 1121, 1088, 942, 876, 763, 622, and 576 m.

2.2.2. Synthesis of [Cu(BDC)(L_2)$_{0.5}$]$_n$ (2). **2** was prepared in a similar manner to **1**. In this case, L_2 (0.238 g, 1.0 mM) was used instead of L_1. Green crystals of **2** were obtained (Yield 43%). Anal. Calcd (%) for $C_{16}H_{13}Cu\ N_2O_4$: C, 53.26; N, 7.76; H, 3.63. Found: C, 53.28; N, 7.74; H, 3.62. IR/cm^{-1} (KBr): 1609 s, 1441, 1352, 1214, 1157, 1072, 976, 861, 752, and 633 m.

2.3. *X-ray crystallography*

Single-crystal X-ray diffraction analyses of **1** and **2** were carried out with a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using a ω-scan mode. An empirical absorption correction was applied using SADABS [26]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHEXL 97 [27]. All non-hydrogen atoms were refined anisotropically. Hydrogens were located by geometric calculations and their positions, and thermal parameters were fixed during structure refinement. The crystallographic data and experimental details of structural analyses for the coordination polymers are summarized in table 1. Selected bond and angle parameters are listed in table 2.

Table 1. Crystallographic data and structure refinement summary for **1** and **2**.

Empirical formula	$C_{15}H_{15}CuN_2O(4)$	$C_{16}H_{13}CuN_2O_4$
Formula weight	350.83	360.82
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Unit cell dimensions	$a = 11.678(2)$ Å	$a = 9.8110(8)$ Å
	$b = 14.596(3)$ Å	$b = 13.5050(11)$ Å
	$c = 18.893(3)$ Å	$c = 11.1750(9)$ Å
	$\beta = 104.110(2)°$	$\beta = 96.6020(11)°$
Volume (Å^3)	3123.2(9)	1470.8(2)
Z	4	4
Calculated density (mg/m^3)	1.492	1.629
Independent reflections ($I > 2\sigma(I)$)	5069	2836
F (000)	1440	736
Goodness-of-fit on F^2	1.017	1.024
θ range for data collection	2.28–24.98	2.37–27.45
Limiting indices	$-15 \leqslant h \leqslant 15$	$-12 \leqslant h \leqslant 12$
	$-18 \leqslant k \leqslant 18$	$-15 \leqslant k \leqslant 17$
	$-18 \leqslant l \leqslant 24$	$-12 \leqslant l \leqslant 14$
$R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	$R_1 = 0.0385$, $wR_2 = 0.0836$	$R_1 = 0.0256$, $wR_2 = 0.0668$
$R_1{}^a$, $wR_2{}^b$ (all data)	$R_1 = 0.0647$, $wR_2 = 0.0953$	$R_1 = 0.0330$, $wR_2 = 0.0705$
Largest diff. peak and hole (e/Å^3)	0.397 and −0.303	0.407 and −0.263

^aR = S(||F_0|-|F_C||)/S|F_0|; ^bwR = [Sw(|F_0|^2-|F_C|^2)^2/Sw($F_0{}^2$)]$^{1/2}$

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

Compound **1**			
Cu(1)–O(1)^b	1.974(2)	Cu(1)–O(8)^a	1.994(2)
Cu(1)–O(2)^c	1.962(2)	Cu(1)–O(7)	1.970(2)
Cu(1)–N(1)	2.156(2)		
O(1)^b–Cu(1)–N(1)	92.67(9)	O(2)^c–Cu(1)–O(8)^a	90.45(10)
O(1)^b–Cu(1)–O(8)^a	87.20(10)	O(2)^c–Cu(1)–O(7)	86.80(10)
O(2)^c–Cu(1)–Cu(1)^a	84.42(6)	O(8)^a–Cu(1)–N(1)	98.39(9)
O(2)^c–Cu(1)–O(1)^b	165.20(9)	O(7)–Cu(1)–O(1)^b	91.67(11)
O(7)–Cu(1)–O(8)^a	164.89(9)		
Compound **2**			
Cu(1)–O(1)	1.9707(13)	Cu(1)–O(2)^c	1.9848(13)
Cu(1)–O(4)^a	1.9750(14)	Cu(1)–N(1)	2.1564(16)
Cu(1)–O(3)^b	1.9841(14)		
O(1)–Cu(1)–O(4)^a	88.92(6)	O(1)–Cu(1)–N(1)	93.83(6)
O(1)–Cu(1)–O(3)^b	88.62(7)	O(4)^a–Cu(1)–N(1)	105.17(6)
O(4)^a–Cu(1)–O(3)^b	166.56(6)	O(3)^b–Cu(1)–N(1)	88.17(6)
O(1)–Cu(1)–O(2)^c	166.36(6)	O(2)^c–Cu(1)–N(1)	99.71(6)
O(4)^a–Cu(1)–O(2)^c	89.05(6)	O(1)–Cu(1)–O(4)^a	88.92(6)
O(3)^b–Cu(1)–O(2)^c	90.24(7)		

Symmetry code for compounds: (**1**) (a) $-x+1$, $-y+1$, $-z+2$; (b) $-x+3/2$, $y+1/2$, $-z+3/2$; (c) $x-1/2$, $-y+1/2$, $z+1/2$; (**2**) (a) $-x+5/2$, $y+1/2$, $-z+3/2$; (b) $x-1/2$, $-y+3/2$, $z-1/2$; (c) $-x+2$, $-y+2$, $-z+1$.

3. Results and discussion

3.1. *Description of crystal structures*

Single-crystal X-ray diffraction analysis reveals that **1** has a 3-D rob framework crystallizing in the monoclinic space group $P2_1/n$. The asymmetric unit contains one Cu(II), one BDC^{2-}, and a half of L_1. Each Cu(II) is a square-pyramid coordinated by four carboxylate oxygens at basal positions (Cu–O bond lengths range from 1.962(2) to 1.994(2) Å) and one N (Cu(1)–N(1) = 2.156(2) Å) at the apical position (figure 1(a)). Four carboxylates from four symmetry-related BDC^{2-} connect two Cu(II) ions to form a dinuclear paddle-wheel Cu(II) subunit with Cu···Cu separation of 2.745(8) Å. Neighboring $[Cu_2(BDC)_4]$ dimers are connected by BDC^{2-}. If the dinuclear Cu(II) can be four-connected nodes and carboxylates can be viewed as linkers, the Cu(II)-carboxylate structure can be simplified as a cds topological net with short Schläfli symbol of $(6^5 \times 8)$ by TOPOS software [28]. L_1 as linkers connect four-connected nodes to form six-connected nodes, which lead the cds net to the rob net with short Schläfli symbol $(4^8 \times 6^6 \times 8)$ (figure 1(b)). Indeed, the six-connected rob net can be obtained by the net deriving from a cds net and a series of parallel 4^4-net sharing common edges (figure 1(c)).

Compared to **1**, replacement of L_1 with L_2 results in generation of **2** which lead the structure from 3-D rob net to 3-D pcu topology. Single-crystal X-ray diffraction reveals that each Cu(II) is coordinated by four oxygen donors (Cu–O distances from 1.971(2) to 1.985(2) Å) and one N (Cu(1)–N(1) = 2.156(2) Å) (figure 2(a)). Two Cu(II) ions, related by a twofold axis, are bridged by two pairs of carboxylates into a paddle-wheel unit with a Cu(II)…Cu(II) distance of 2.694(4) Å. The $[Cu(CO_2)_4Cu]$ dimers are bonded to four BDC^{2-} ligands. The binuclear Cu(II) ions can be viewed as four-connecting nodes to generate a layer formed by a series of squares (figure 2(b)). Each $[Cu(CO_2)_4Cu]$ unit is bridged to two structural units in the sheet above and below by pairs of L_2. From the topological view, the $[Cu(CO_2)_4Cu]$ unit can be treated as a six-connected node, the BDC^{2-} and L_2 are taken as linkers and the 3-D structure can be classified as a pcu net (α-Po topology) (figure 2(c)). The pcu topology can be described as comprising three intersecting (4,4) nets that share connections. This arrangement leads to layers of (4,4) nets cross-linked by co-linear connections. Due to the absence of guest molecules to fill the large void space in the 3-D framework during assembly, the potential voids in **2** are filled by mutual interpenetration of two identical 3-D nets, which directly lead to the formation of a twofold interpenetrating pcu network (figure 2(d)).

Complexes **1** and **2** are constructed by using dicarboxylate and N-donor ligands and show different topological nets. Complexes **1** and **2** have the same SBUs; the different topological nets may derive from different rigid/flexible ligands. When using the rigid ligand, **2** has a potential void which leads to a twofold interpenetrating net. Using the flexible ligand, the potential void cannot be created, leading to a rob net.

3.2. *Thermogravimetric analyses (TGA) and X-ray powder diffraction (XRPD)*

In order to check the purity and homogeneity of the bulk products of **1** and **2**, the as-synthesized samples were investigated by XRPD at room temperature. As shown in figure S1, in Supplementary material, the peak positions of the experimental patterns are in agreement with the simulated ones, which indicate good purity and homogeneity of the complexes.

TGA analyses of **1** and **2** were carried out under N_2 from 25° to 600° with a heating rate of 10 °C min^{-1}. For **1**, the weight loss of 77.38% (Calcd 77.33%) from 255 to 580 °C indicates loss of carboxylate and L_1. For **2**, TGA exhibits one-weight losses of 77.87% (Calcd 77.96%) from 215 to 550 °C, also attributed to loss of carboxylate and L_2 (figure S2, Supplementary material).

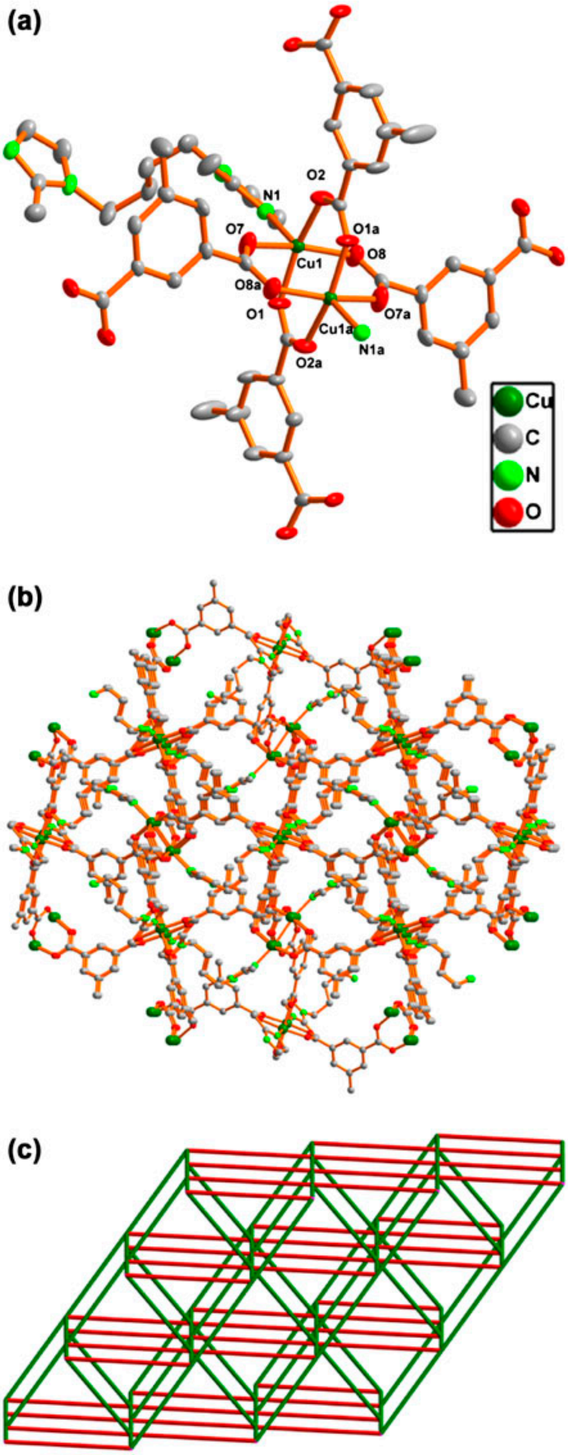


Figure 1. (a) The coordination environment of Cu(II) for **1**; (b) The 3-D topological net for **2** (green: cds net formed by carboxylate; red: L$_1$ as linkers). (see http://dx.doi.org/10.1080/00958972.2013.819090 for color version.)

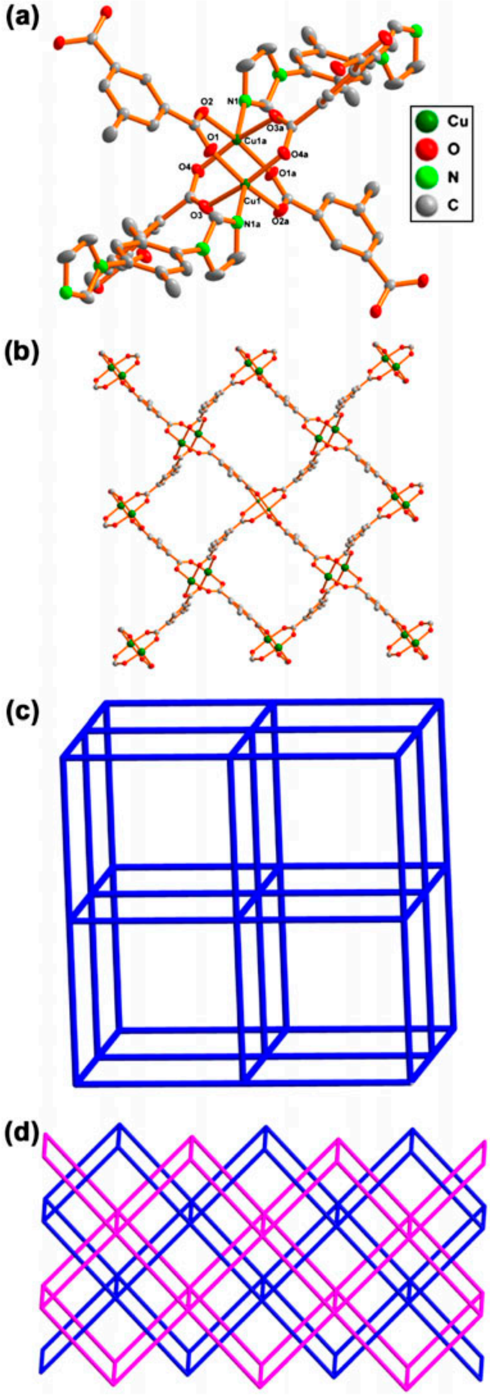


Figure 2. (a) The coordination environment of Cu(II) for **1**; (b) the 2-D layer structure formed by carboxylates; (c) the twofold interpenetrating pcu topology for **2**.

4. Conclusions

In this paper, two new Cu(II) metal-organic frameworks based on dinuclear secondary building blocks have been obtained. Complex **1** is a 3-D rob topology net, while **2** exhibits a twofold interpenetrating 3-D pcu topology. Structure transition from rob to pcu topology between the complexes was realized with the aid of imidazole-containing ligands, which indicate it is an effective method to tune the topological net via changing auxiliary ligands.

Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference numbers: 901067 and 901068. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk (or Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

We thank the support of this work by the Natural Science Foundation of Shandong Province (ZR2011BL024) and the financial support from Dezhou University (318019).

References

[1] D.J. Tranchemontagne, K.S. Park, H. Furukawa, J. Eckert, C.B. Knobler, O.M. Yaghi. *J. Phys. Chem. C*, **116**, 13143 (2012).
[2] H. Yang, F. Wang, Y. Kang, T.H. Li, J. Zhang. *Dalton Trans.*, 2873 (2012).
[3] J.B. Lin, W. Xue, J.P. Zhang, X.M. Chen. *Chem. Commun.*, **47**, 926 (2011).
[4] J. Qin, C. Qin, C.X. Wang, H. Li, L. Cui, T.T. Li, X.L. Wang. *CrystEngComm*, **12**, 4071 (2010).
[5] L.Y. Wang, R.Q. Fan, P. Wang, Y.L. Yang. *Inorg. Chem. Commun.*, **23**, 54 (2012).
[6] G.G. Hou, J.P. Ma, L. Wang, P. Wang, Y.B. Dong, R.Q. Huang. *CrystEngComm*, **12**, 4287 (2010).
[7] J. Li, J. Tao, R.B. Huang, L.S. Zheng. *Inorg. Chem.*, **51**, 5988 (2012).
[8] X.T. Zhang, D. Sun, B. Li, L.M. Fan, B. Li, P.H. Wei. *Cryst. Growth Des.*, **12**, 3845 (2012).
[9] J.E.W. Cull, F. Habib, I. Korobkov, M. Murugesu, J. Scott. *Inorg. Chim. Acta*, **370**, 98 (2011).
[10] S. Zheng, T. Wu, F. Zuo, C.T. Chou, P. Feng, X. Bu. *J. Am. Chem. Soc.*, **134**, 1934 (2012).
[11] H.X. Zhang, F. Wang, H. Yang, Y.X. Tan, J. Zhang, X. Bu. *J. Am. Chem. Soc.*, **133**, 11884 (2011).
[12] Y. Zhang, X. He, J. Zhang, P. Feng. *Cryst. Growth Des.*, **11**, 29 (2011).
[13] Z.X. Li, X. Chu, G.H. Cui, Y. Liu, L. Li, G.L. Xue. *CrystEngComm*, **13**, 1984 (2011).
[14] Z. Wang, S.M. Cohen. *Chem. Soc. Rev.*, **38**, 1315 (2009).
[15] B.F. Hoskins, R. Robson. *J. Am. Chem. Soc.*, **112**, 1546 (1990).
[16] N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi. *Acc. Chem. Res.*, **28**, 176 (2005).
[17] S. Kitagawa, R. Kitaura, S.I. Noro. *Angew. Chem. Int. Ed.*, **43**, 2334 (2004).
[18] J.M. Roberts, O.K. Farha, A.A. Sarjeant, J.T. Hupp, K.A. Scheidt. *Cryst. Growth Des.*, **11**, 4747 (2011).
[19] G.P. Yang, Y.Y. Wang, W.H. Zhang, A.Y. Fu, R.T. Liu, E.K. Lermontova, Q.Z. Shi. *CrystEngComm*, **12**, 1509 (2010).
[20] F.Y. Yi, N. Zhao, W. Wu, J.G. Mao. *Inorg. Chem.*, **48**, 628 (2009).
[21] P.X. Yin, J. Zhang, Y.Y. Qin, J.K. Cheng, Z.J. Li, Y.G. Yao. *CrystEngComm*, **13**, 3536 (2011).
[22] C.A. Williams, A.J. Blake, C. Wilson, P. Hubberstey, M. Schröder. *Cryst. Growth Des.*, **6**, 911 (2008).
[23] S.S.Y. Chui, S.M.F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams. *Science*, **283**, 1148 (1999).
[24] S. Youngme, A. Cheansirisomboon, C. Danvirutai, C. Pakawatchai, N. Chaichit. *Inorg. Chem. Commun.*, **11**, 57 (2008).
[25] I. Eryazici, O.K. Farha, B.G. Hauser, A.Ö. Yazaydın, A.A. Sarjeant, S.T. Nguyen, J.T. Hupp. *Cryst. Growth Des.*, **12**, 1075 (2012).

[26] *SAINT Software Reference Manual*, Version 6.2, Bruker AXS, Inc., Madison, WI, (2001).
[27] G.M. Sheldrick, *SHELXTL NT Version 5.1., Program for Solution and Refinement of Crystal Structures*, University of Göttingen, Göttingen (1997).
[28] V.A. Blatov, M. O'Keeffe, D.M. Proserpio. *CrystEngComm*, **12**, 44 (2010). see also, http://www.topos.ssu.Samara.ru.