

Discovery, Synthesis, and Characterization of an Isomeric Coordination Polymer with Pillared Kagome Net Topology

Hyunghil Chun* and Jumi Moon

Department of Applied Chemistry, College of Science and Technology, Hanyang University, 1271 Sa-1 dong, Ansan 426-791, Republic of Korea

Received January 10, 2007

A topological isomer based on Zn_2 paddlewheel, dicarboxylate, and diamine ligands is synthesized by solvothermal methods after careful modulation of the reaction conditions. The new framework is characterized by a pillared Kagome net topology and possesses a sustainable pore structure with high surface area ($\sim 2400 \text{ m}^2/\text{g}$) and large hexagonal channels ($\sim 15 \text{ \AA}$).

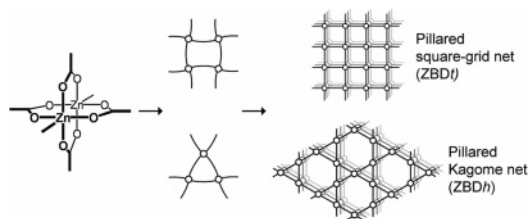
As interest in the study of coordination polymers grows, advances have been made in various aspects of the crystalline open frameworks. Topological analyses¹ have improved our understanding of the three-dimensional nets, and an unprecedented level of surface area has been established.² Also, potentials have been raised toward such applications as storage,³ separation,⁴ catalysis,⁵ and host–guest chemistry.⁶ The last area would benefit greatly if the porous crystalline hosts possess not only high surface areas but also large apertures, which delimit the size of the guest molecules that can be included. Although such properties may be materialized by using extended organic ligands,⁷ the same may be achieved from a different perspective. That is, a given

combination of metal ion and organic ligands can give rise to a large number of topological isomers depending on the three-dimensional connectivity. Therefore, efforts to discover new open frameworks using well-known and easily available ligands are also important.

A recent paper has shown the flexibilities of the 1,4-benzenedicarboxylate (bdc) ligand in a pillared square-grid net of $[Zn_2(\text{bdc})_2(\text{dabco})]_8$ ZBDt hereafter, meaning the tetragonal phase of Zn–bdc–dabco (dabco is 1,4-diazabicyclo-[2.2.2]octane). The unusually bent bdc linkers connecting the paddlewheel nodes in ZBDt have inspired us to explore the possibility of obtaining a new framework in which the dinuclear units are connected in a shape other than a square. The rational expectations would then be triangular or hexagonal connection because, along with the square, triangle and hexagon are the basic building motifs for regular plane nets.⁹ Therefore, we have systematically approached variation

* To whom correspondence should be addressed. E-mail: hchun@hanyang.ac.kr.

- (1) (a) Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *CrystEngComm* **2004**, *6*, 377–395. (b) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keefe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176–182. (c) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res.* **2005**, *38*, 273–282. (d) Hill, R. J.; Long, D.-L.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Acc. Chem. Res.* **2005**, *38*, 337–350.
- (2) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surlbé, S.; Margiolaki, I. *Science* **2005**, *309*, 2040–2042.
- (3) (a) Chen, B.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4745–4749. (b) Chun, H.; Dybtsev, D. N.; Kim, H.; Kim, K. *Chem.—Eur. J.* **2005**, *11*, 3521–3529. (c) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* **2005**, *436*, 238–241. (d) Millward, A. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 17998–17999. (e) Dietzel, P. D. C.; Panella, B.; Hirscher, M.; Blom, R.; Fjellvåg, H. *Chem. Commun.* **2006**, 959–961. (f) Sun, D.; Ma, S.; Ke, Y.; Collins, D. J.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 3896–3897. (g) Lin, X.; Jia, J.; Zhao, X.; Thomas, K. M.; Blake, A. J.; Walker, G. S.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7358–7364. (h) Llewellyn, P. L.; Bourrelly, S.; Serre, C.; Filinchuk, Y.; Férey, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7751–7754. (i) Dincă, M.; Yu, A. F.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 8904–8913.
- (4) (a) Maji, T. K.; Uemura, K.; Chang, H.-C.; Matsuda, R.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3269–3272. (b) Dybtsev, D. N.; Chun, H.; Yoon, S. H.; Kim, D.; Kim, K. *J. Am. Chem. Soc.* **2004**, *126*, 32–33. (c) Bradshaw, D.; Prior, T. J.; Cussen, E. J.; Claridge, J. B.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 6106–6114. (d) Dincă, M.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 9376–9377. (e) Pan, L.; Olson, D. H.; Ciemmolonski, L. R.; Heddy, R.; Li, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 616–619. (f) Wang, X.; Liu, L.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6499–6503. (g) Chen, B.; Liang, C.; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 1390–1393. (h) Pan, L.; Parker, B.; Huang, X.; Olson, D. H.; Lee, J. J.; Li, J. *J. Am. Chem. Soc.* **2006**, *128*, 4180–4181.
- (5) (a) Ohmori, O.; Fujita, M. *Chem. Commun.* **2004**, 1586–1587. (b) Wu, C.-D.; Hu, A.; Zhang, L.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 8940–8941. (c) Perles, J.; Iglesias, M.; Martín-Luengo, M.; Monge, M. A.; Ruiz-Valero, C.; Snejko, N. *Chem. Mater.* **2005**, *17*, 5837–5842. (d) Dybtsev, D. N.; Nuzhdin, A. L.; Chun, H.; Bryliakov, K. P.; Talsi, E. P.; Fedin, V. P.; Kim, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 916–920.
- (6) (a) Moon, H. R.; Kim, J. H.; Suh, M. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 1261–1265. (b) Hermes, S.; Schröter, M.-K.; Schmid, R.; Khodeir, L.; Muhler, M.; Tissler, A.; Fischer, R. W.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6237–6241. (c) Uemura, T.; Kitaura, R.; Ohta, T.; Nagaoka, M.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 4112–4116. (d) Horcajada, P.; Serre, C.; Vallet-Regí, M.; Sebban, M.; Taulelle, F.; Férey, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 5974–5978. (e) Kim, H.; Chun, H.; Kim, C.-H.; Lee, H.-S.; Kim, K. *Chem. Commun.* **2006**, 2759–2761.
- (7) For example, see: Wang, X.-S.; Ma, S.; Sun, D.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 16474–16475.
- (8) Dybtsev, D. N.; Chun, H.; Kim, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5033–5036.

Scheme 1. $[\text{Zn}_2(\text{O}_2\text{C})_4]$ Paddlewheel and Its Role as Nodes in Two Isomeric Nets

of the synthetic conditions and successfully obtained a new phase having the same chemical composition as ZBDt but with a completely different connectivity, which resulted in a higher porosity and much larger open channels. The new phase is referred to ZBDh hereafter, where *h* implies the hexagonal symmetry (Scheme 1).

For synthesis of ZBDh, the relative amounts of reagents, reaction temperatures, and solvents in the solvothermal conditions for ZBDt have been modulated in a systematically controlled manner. Although most of these attempts have not returned encouraging results, we have noticed that a small amount of hexagonal single crystals forms along with the block-shaped crystals of ZBDt when acetonitrile is used as the cosolvent.¹⁰ The synthetic procedure has been optimized further by adopting a ternary solvent system *N,N'*-dimethylformamide (DMF)/ CH_3CN /ethylene glycol (EG) to yield only the hexagonal crystals of ZBDh.¹¹ The composition of ZBDh is $[\text{Zn}_2(\text{bdc})_2(\text{dabco})]$ and is identical with that of ZBDt.

In the structure determined by X-ray diffraction on preevacuated single crystals of ZBDh,¹² Zn_2 paddlewheel nodes are interconnected by slightly bent bdc linkers, as in the case of ZBDt. Unlike ZBDt, however, the same nodes and linkers form two-dimensional sheets composed of triangles and hexagons (Scheme 1). One such layer is known as the Kagome net,¹³ frequently seen in ornamental designs. The Kagome pattern has also been observed in microarrays of colloidal crystals,¹⁴ in a periodic assembly of DNA nucleotides,¹⁵ and, more frequently, in the structure of various inorganic solids with interesting magnetic properties.¹⁶ Coordination polymers related to the Kagome lattice are also

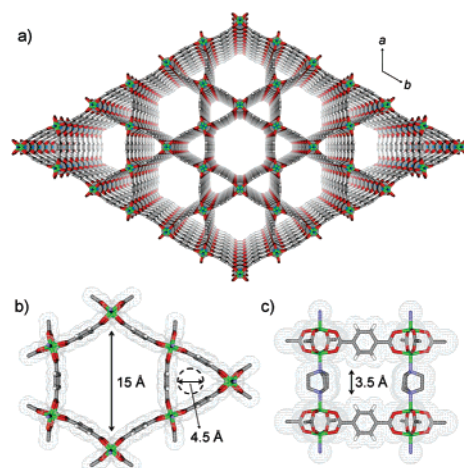


Figure 1. Perspective view of the ZBDh framework showing the two types of open channels (a) and enlarged views of the free apertures (b) and side windows (c) after considering the van der Waals surface of the framework depicted as a wire mesh. Legend: Zn, green; C, gray; H, white; O, red; N, blue.

known;¹⁷ however, three-dimensionally connected Kagome nets showing a reversible sorption behavior have been reported only twice.¹⁸

The solvent sites of the paddlewheel units are exposed above and below the Kagome layer and are occupied by nitrogen atoms of the dabco ligand. Therefore, adjacent Kagome layers are pillared directly on top without a lateral dislocation and form straight open channels running along the *c* axis (Figure 1a).

As shown in Figure 1b, the small, triangular open channel allows an imaginary sphere of 4.5 Å diameter to pass through without touching the van der Waals surface of the framework, implying that only small guest molecules with linear geometry may fit inside. The large, hexagonal channel has widths of 17.1 Å when measured between the centers of two opposite phenyl rings and 21.5 Å when measured between the two nitrogen atoms at the corner. When the van der Waals surface of the framework is considered, the width of the hexagonal window is 13.5–15 Å. Straight open channels with such a large aperture is not common in porous coordination polymers. For comparison, MOF-5 is a well-known metal–organic framework having channel-type pores

(9) Wells, A. F. *Three-dimensional nets and polyhedra*; Wiley-Interscience: New York, 1977; p 5.

(10) The hexagonal phase in the mixture was estimated to be 5–30% based on PXRD analysis.

(11) Synthesis of ZBDh: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.080 g, 0.27 mmol) and $\text{H}_2\text{-bdc}$ (0.044 g, 0.26 mmol) were dissolved in 2.50 mL of a DMF/ CH_3CN mixture (4:1, v/v). After dabco (0.015 g, 0.13 mmol) was added, the mixture was stirred at room temperature for 1 h and filtered after centrifuge, and then 0.70 mL of EG was added. The final solution was charged into a glass vial, which was tightly sealed and heated to 110–120 °C for 2 days. The colorless crystals with hexagonal columnar morphology were collected, washed with DMF and CH_3CN , and soaked in CH_3CN before drying under a dynamic vacuum overnight at room temperature (0.061 g, 82%). Anal. Calcd for $[\text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{C}_6\text{H}_{12}\text{N}_2)] \cdot 0.5\text{H}_2\text{O}$: C, 45.54; H, 3.65; N, 4.83. Found: C, 45.37; H, 3.31; N, 4.43. ZBDh is insoluble and stable in common organic solvents but slowly decomposes in water.

(12) Crystal data for ZBDh: formula $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_8\text{Zn}_2$, $M = 571.14$, hexagonal, space group $P3m1$ (No. 164), $a = 21.620(1)$ Å, $c = 9.628(1)$ Å, $V = 3897.3(5)$ Å³, $Z = 3$, $T = 173$ K, $\rho_{\text{calcd}} = 0.73$ g/cm³, $F(000) = 870$, $\mu(\text{Mo K}\alpha) = 0.95$ mm⁻¹, 2736 reflections observed [$I > 2\sigma(I)$]; $R1 = 0.0520$, $wR2 = 0.1790$.

(13) Syozi, I. *Prog. Theor. Phys.* **1951**, *6*, 306–308.

(14) (a) Schaak, R. E.; Cable, R. E.; Leonard, B. M.; Norris, B. C. *Langmuir* **2004**, *20*, 7293–7297. (b) Shevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O'Brien, S.; Murray, C. B. *Nature* **2006**, *439*, 55–59.

(15) Paukstelis, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 6794–6795.

(16) (a) Greedan, J. E. *J. Mater. Chem.* **2001**, *11*, 37–53. (b) Grohol, D.; Nocera, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 2640–2646. (c) Behera, J. N.; Rao, C. N. R. *Inorg. Chem.* **2006**, *45*, 9475–9479 and references cited therein.

(17) (a) Eddaoudi, M.; Kim, J.; Vodak, D.; Sudik, A.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4900–4904. (b) Moulton, B.; Lu, J.; Hajndl, R.; Hariharan, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2821–2824. (c) Shin, D. M.; Lee, I. S.; Chung, Y. K.; Lah, M. S. *Inorg. Chem.* **2003**, *42*, 5459–5461. (d) Perry, J. J.; McManus, G. J.; Zaworotko, M. J. *Chem. Commun.* **2004**, 2534–2535. (e) Liu, Y.; Kravtsov, V. Ch.; Beauchamp, D. A.; Eubank, J. F.; Eddaoudi, M. *J. Am. Chem. Soc.* **2005**, *127*, 7266–7267. (f) Wang, X.-Y.; Wang, L.; Wang, Z.-L.; Gao, S. *J. Am. Chem. Soc.* **2006**, *128*, 674–675.

(18) (a) Rusanov, E. B.; Ponomarova, V. V.; Komarchuk, V. V.; Stoeckli-Evans, H.; Fernandez-Ibañez, E.; Stoeckli, F.; Sieler, J.; Domashevitch, K. V. *Angew. Chem., Int. Ed.* **2003**, *42*, 2499–2501. (b) Barthelet, K.; Marrot, J.; Férey, G.; Riou, D. *Chem. Commun.* **2004**, 520–521.

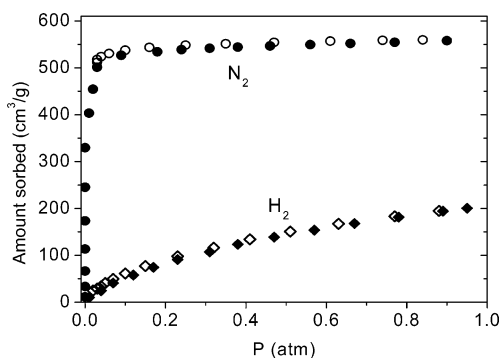


Figure 2. Gas sorption isotherms of ZBDh for nitrogen and hydrogen measured at 78 K. The filled and open symbols represent sorption and desorption data, respectively.

and a surface area of about 3000 m²/g,¹⁹ and its free aperture measures approximately 8 Å. The triangular and hexagonal open channels are interconnected through small windows of 3.5–5 Å (Figure 1c).

The solvent-accessible free volume of ZBDh is estimated to be 65% of the total crystal volume²⁰ and is slightly larger than that of its topological isomer ZBDt (62%). The extraframework space should have been filled by synthetic solvents. Not surprisingly, however, the solvent molecules are severely disordered, and no useful information about the relative amounts or orientation in the pores could be obtained from the single-crystal X-ray analysis on as-synthesized crystals. Nevertheless, we think that CH₃CN with a linear geometry acts as a template for the triangular channels through $\pi\cdots\pi$ contacts, and extensive intermolecular hydrogen bonding between DMF and EG or among EG molecules creates solvent aggregates that help form the hexagonal channels.²¹

ZBDh maintains its structural integrity after complete removal of the solvents occupying the voids. Thermal gravimetric analysis (TGA) shows that the as-synthesized material releases solvents even at room temperature and loses 30% of its weight upon heating to about 250 °C (Figure S1 in the Supporting Information). The decomposition of the framework is observed near 300 °C. Because an open-framework structure may collapse without decomposition upon evacuation, we measured powder X-ray diffraction (PXRD) of ZBDh at various temperatures to check the thermal stability. The PXRD pattern, which also proves the phase purity of the ZBDh product, is maintained at 250 °C (Figure S2 in the Supporting Information). The PXRD peaks gradually disappear upon heating at 300 °C for 2 h. Therefore, it is safe to say that the open-framework ZBDh is stable to 250 °C after a complete evacuation.

The porosity and specific surface area of ZBDh have been estimated by measuring nitrogen gas sorption at 78 K. The isotherm shown in Figure 2 is fully reversible and reproducible.

The abrupt rise and saturation of the sorbed amounts at a low relative pressure are type I behavior characteristics for microporous materials. The Brunauer–Emmett–Teller (BET) and Langmuir surface areas obtained from the adsorption isotherm are 1603 and 2420 m²/g, respectively. The total pore volume of ZBDh is estimated to be 0.86 cm³/g. The topological isomer ZBDt has BET and Langmuir surface areas of 1450 and 2090 m²/g, respectively, and a pore volume of 0.75 cm³/g. The larger values of the surface area and pore volume for ZBDh corroborate with the expectation based on single-crystal structure analysis (see above) and on simple geometric considerations.²²

The hydrogen gas sorption of ZBDh has also been measured at 78 K. The hydrogen uptake at 0.94 atm and 78 K is 200.5 cm³/g (STP). This is equivalent to 1.8 wt % of hydrogen uptake and slightly smaller than that of ZBDt (223 cm³/g). The fact that ZBDh possesses a larger surface area and yet adsorbs a smaller amount of hydrogen than ZBDt under the same conditions is not surprising. As one of us has already proposed, a large open channel is not an optimal pore structure for hydrogen sorption.^{3b} Instead, it may be worth trying to load metallic guests that help hydrogen sorption into the hexagonal channels of ZBDh. If carefully planned, such an inclusion will still leave the triangular channels available for hydrogen storage.

In summary, we have systematically approached the synthesis of a new open-framework ZBDh using a known combination of metal and ligands. The ZBDh framework has a pillared Kagome net and a sustainable pore structure with large hexagonal channels (~15 Å). The novel features of ZBDh may be useful for the inclusion and diffusion of large guest molecules. Although the roles played by cosolvents during the synthesis of ZBDh are yet to be clarified, the synthetic protocol and solvent cocktail used in this work deserve further attention because they may lead to the discovery of new open frameworks from well-known combinations of transition-metal ions and common organic ligands.

Acknowledgment. This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD; Grants KRF-2006-331-C00157 and KRF-2005-070-C00068) and by the research fund of Hanyang University (Grant HY-2005-0016). H.C. is grateful to Prof. K. Kim (POSTECH, Korea) for allowing access to TGA and PXRD and to Dr. D. N. Dybtsev (Nikolaev Institute of Inorganic Chemistry, Russia) for the inspiration of this work.

Supporting Information Available: Experimental details, PXRD and TGA plots, analysis of gas sorption data, and crystallographic information files (CIF) of ZBDh. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC070036T

(19) Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276–279.

(20) Spek, A. L. *PLATON, a multipurpose crystallographic tool*; Utrecht University: Utrecht, The Netherlands, 2001.

(21) The formation of the hexagonal phase is not due to the increased pressure inside the reaction tube resulting from the acetonitrile vapor because the reactions using cosolvents with vapor pressure similar to that of acetonitrile do not produce the hexagonal phase.

(22) Given the same set of pillar and linker ligands, a pillared Kagome net (ZBDh) is expected to have a surface area higher than a pillared square grid net (ZBDt) by 15%. For details, see the Supporting Information.