Establishing Microporosity in Open Metal−Organic Frameworks: Gas Sorption Isotherms for Zn(BDC) (BDC = 1,4-Benzenedicarboxylate)

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Construction of microporous metal−organic frameworks by copolymerization of organic molecules with metal ions has received widespread attention in recent years, with significant strides made toward the development of their synthetic and structural design chemistry.[1] Cognizant of the fact that access to the pores and understanding the inclusion chemistry of these materials are essential to their ultimate utility, we prepared rigid frameworks that maintain their structural integrity and porosity during anion-exchange and guest sorption from solution and in the absence of guests.[2−4] Although gas sorption isotherm measurements are often used to confirm and study microporosity in crystalline zeolites and related molecular sieves,[5] such studies have not been established in the chemistry of open metal−organic frameworks[6] thus leaving unanswered vital questions regarding the existence of permanent porosity in this class of materials. Herein, we present the synthesis, structural characterization, and gas sorption isotherm measurements for the Zn(BDC) microporous framework of crystalline Zn(BDC)·(DMF)(H_2O) (BDC = 1,4-benzenedicarboxylate and DMF = N,N′-dimethylformamide).

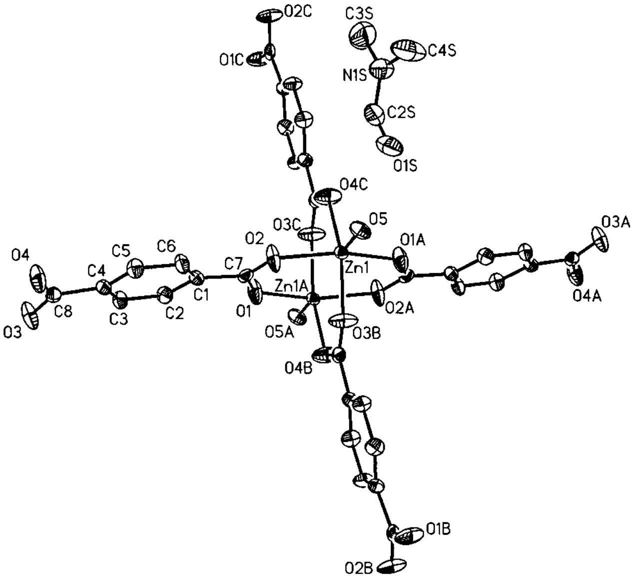
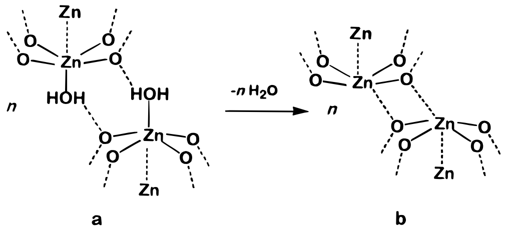


Figure 1. The building block unit including the asymmetric unit present in crystalline Zn(BDC)·(DMF)(H_2O) with non-hydrogen atoms represented by thermal ellipsoids drawn at the 50% probability level. Atoms labeled with an additional letter "A, B or C" are symmetrically equivalent to those atoms without such designation. Atoms of the DMF guest molecule are labeled with an additional letter "S".



Slow vapor diffusion at room temperature of triethylamine (0.05 mL) and toluene (5 mL) into a DMF solution (2 mL) containing a mixture of $Zn(NO_3)_2$·$6H_2O$ (0.073 g, 0.246 mmol) and the acid form of BDC (0.040 g, 0.241 mmol) diluted with toluene (8 mL) yields colorless prism-shaped crystals that were formulated as Zn(BDC)·(DMF)(H_2O).[7] X-ray single-crystal analysis[8] on a sample obtained from the reaction product revealed an extended open-framework structure composed of the building unit shown in Figure 1. A total of four carboxylate units of different, but symmetrically equivalent, BDC building blocks are bonded to two zinc atoms in a di-monodentate fashion. Each zinc is also linked to a terminal water ligand to form an overall arrangement that is reminiscent of the carboxylate bridged M−M bonded molecular complexes. Although the Zn−Zn distance (Zn1−Zn1A = 2.940 (3) Å) is indicative of some M−M interaction, it does not represent an actual bond.[9] The structure extends into the (011) crystallographic plane by having identical Zn−Zn units linked to remaining carboxylate functionalities of BDC to yield 2-D microporous layers. These layers are held together along the *a* axis by hydrogen-bonding interactions between water ligands of one layer and carboxylate oxygens of an adjacent layer as illustrated in **a**. Stacking of the layers in the crystal leads to a 3-D network having extended 1-D pores of nearly 5 Å in diameter where DMF guests reside, as shown in Figure 2. Each DMF guest molecule forms a hydrogen-bonding

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(1) (a) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C.; Niu, T.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 923. (b) Losier, P.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2779. (c) Gardner, G. B.; Venkataraman, D.; Moore, J. S.; Lee, S. *Nature* **1995**, *374*, 792−795. (d) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *378*, 703−706. (e) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287−7288. (f) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2755. (g) Robson, R.; Abrahams, B. F.; Batteen, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. *Supramolecular Architecture*: *Synthetic Control in Thin Films and Solids*; Bein, T., Ed.; American Chemical Society: Washington, DC, 1992; Chapter 19. (h) Iwamoto, T. in *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.: Oxford: New York, 1991; Vol. 5, p 177. (i) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* **1993**, *259*, 1558−1564. (j) Fagan, P. J.; Ward, M. D. *Sci. Am.* **1992**, *267*, 48−54.

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(6) Reports on gas sorption isotherms for metal−organic systems have appeared in the literature for molecular solids such as Werner complexes (a) and a lithium cobalt cyanide compound (b). A recent report of gas sorption into a metal−organic extended network suggests microporosity; however, high pressure (30 atm) conditions were employed, thus prohibiting determination of surface area and pore volume (c). (a) Allison, S. A.; Barrer, R. M. *J. Chem. Soc. A* **1969**, 1717−1723. (b) Ramprasad, D.; Pez, G. P.; Toby, B. H.; Markley, T. J.; Pearlstein, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 10694−10701. (c) Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1725.

(7) Anal. Calcd for Zn(BDC)·(DMF)(H_2O) = $C_{11}H_{13}NO_6Zn$: C, 41.21; H, 4.09; N, 4.37; Zn, 20.39. Found: C, 41.04; H, 4.18; N, 4.52; Zn, 20.33.

(8) Colorless prismatic crystals of Zn(BDC)·(DMF)(H_2O) were analyzed at 20 ± 1°C: monoclinic, space group $P2_1/n$ with $a = 6.718$ (3) Å, $b = 15.488$ (7) Å, $c = 12.430$ (8) Å, $\beta = 102.83$ (4)°, $V = 1261.0$ (11) Å^3, $Z = 4$, $d_{\mathrm{calcd}} = 1.689$ g·cm^{-3} and μ_a (Mo Kα) = 1.970 mm^{-1}. Data were collected on a Siemens R3m/V autodiffractometer using graphite-monochromated Mo Kα radiation and full 1.60° wide ω scans to a maximum of $2\theta = 25.04°$, giving 2508 unique reflections. The structure was solved by direct methods (SHELXTL PC V. 5.03), and the resulting structural parameters were refined by least-squares techniques to a standard discrepancy index $R = 0.0458$ and $R_w = 0.0923$ for 2219 reflections with $F > 2\sigma(F)$ and goodness of fit on $F^2 = 1.079$. Anisotropic thermal parameters were refined for all non-hydrogen atoms, and fixed thermal parameters were used for included hydrogens.

(9) Considering that the mean value for Hg−Hg^{2+} bonds in coordination compounds is 2.51 Å, then similar Zn−Zn interactions should be less. Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984; p 1157.

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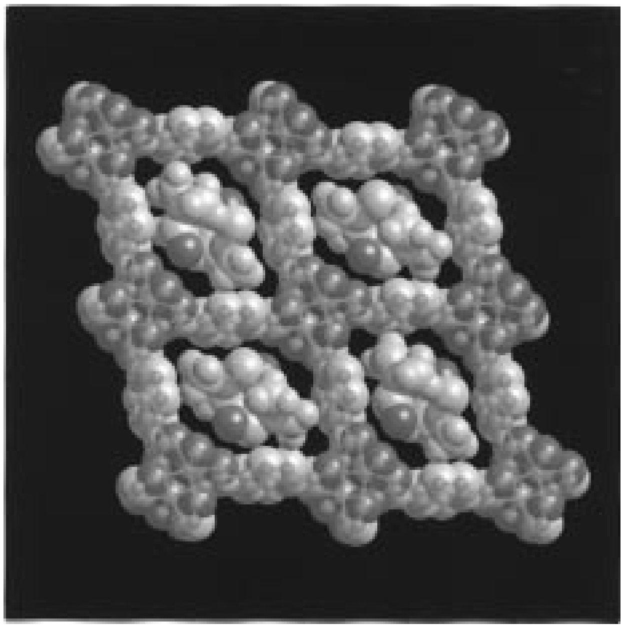

Figure 2. The crystal structure of Zn(BDC)·(DMF)(H_2O) shown approximately down the crystallographic direction (100), where extended 1-D channels are found occupied by DMF molecules. A fragment of the structure is drawn in pink color using stick-and-ball to show the topology, with the remaining part of the framework including the DMF guests represented with space-filling spheres (Zn blue, C and H gray, O green, and N red). Hydrogen atoms on water and BDC have been omitted for clarity.

interaction with the water ligands (O1S−O5 = 2.603 (3) Å); otherwise, it is held in the cavity by van der Waals interactions with the Zn(BDC) framework.

To study the inclusion chemistry of this material, thermogravimetric analysis (TGA) was performed on a polycrystalline sample (39.45 mg) of this material, which showed the following two strikingly clean and well-separated weight loss steps: An initial weight loss of 5.5% at 65 °C, corresponding to the removal of one water molecule per formula unit (5.6% calculated), followed by another weight loss of 22.5% at 160 °C for evacuation of the DMF guests from the pores, with one DMF removed per formula unit (22.8% calculated). Most significant is the fact that no weight loss was observed between the temperature range 190−315 °C, signaling the formation of a stable phase formulated as Zn(BDC).[10a] Furthermore, this phase shows crystalline order as evidenced by the diffraction lines observed in its X-ray powder diffraction pattern, albeit broadened and dissimilar relative to that of the original unevacuated solid.[10b] Close examination of the bonding motif adopted between the layers (shown in **a**) revealed that each zinc atom is ideally positioned from a nearby BDC oxygen of an adjacent layer, in that the C−O···Zn angle is 117.6 (7)°, which, in the absence of water, would be suited for the formation of stronger O···Zn interaction as shown in **b**. This structural transformation scenario (**a**−**b**) may account for the high stability observed in the TGA experiment, which ultimately has allowed the evacuation of the DMF guests leading to a microporous network.[10c]

Anticipating the microporosity of the resulting evacuated Zn(BDC) framework, we proceeded to measure its gas sorption isotherm: The sample (ca. 0.01-mm sized particles) was prepared by heating to 140 °C for 16 h under vacuum (5×10^{-5} Torr) the as-synthesized solid (119.00 mg) in an electromicrogravimetric balance (CAHN 1000) setup, after which the sample showed a weight loss of 28.23% in agreement with the total weight loss measured in the TGA experiments (28.00%). The N_2(g) and CO_2(g) sorption isotherms were obtained by introducing high purity grade gases into the sample chamber with increasing pressure intervals at 78 K (N_2) and 195 K (CO_2) and then by monitoring the resulting weight changes. Rapid sorption of these gas into the pores was observed, with equilibrium pressures achieved within 10 min (N_2) and 20 min (CO_2). A plot of (mg weight sorbed)/[g of Zn(BDC)] vs P/P_0 (P_0 = saturation pressure, 780 Torr for CO_2 and 745 Torr for N_2) revealed a type I isotherm for both gases as shown in Figure 3[11] and was thus indicative of an open Zn(BDC) framework with permanent microporosity. Similar to most zeolites, these isotherms are reversible and show no hysteresis behavior upon desorption of gases from the pores (Figure 3). Langmuir apparent surface areas of 270 m^2/g and 310 m^2/g were calculated, and micropore volumes of 0.11 cm^3/cm^3 (0.094 cm^3/g) and 0.10 cm^3/cm^3 (0.086 cm^3/g) were calculated for N_2 and CO_2, respectively, using the Dubinin-Raduskhvich equation.[12] Typically for zeolites, which generally have higher molar mass than Zn(BDC), pore volumes ranging from 0.18 cm^3/cm^3 for analcime to 0.47 cm^3/cm^3 for zeolite A are obtained.[5]

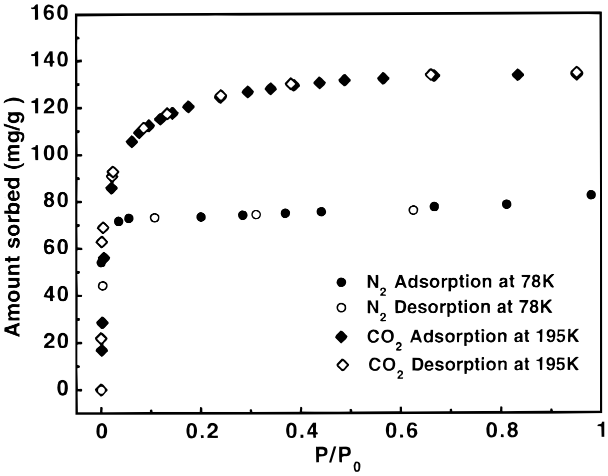

Figure 3. The gas sorption isotherms for the microporous Zn(BDC) evacuated framework.

We believe that this report clearly demonstrates the feasibility of producing microporous metal−organic frameworks with pores accessible in a zeolite-like fashion. This is expected to pave the way to understanding the chemical and physical properties of the pores and their ultimate use for molecular transformations and confinement.

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Supporting Information Available: Crystallographic data for Zn(BDC)·(DMF)(H_2O), including crystal structure analysis report, positional parameters, thermal parameters, and interatomic distances and angles (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(10) (a) Anal. Calcd for Zn(BDC) = $C_8H_4O_4Zn$: C, 41.87; H, 1.76; N, 0.00. Found: C, 40.47; H, 1.82; N, 0.16. (b) XRPD data for the most prominent lines with *d*-spacings in Å and the relative intensities placed in parentheses. Observed: 9.036 (27), 7.493 (18), 6.846 (100), 4.614 (15), 4.070 (16). Attempts to index this pattern did not yield a unique solution. (c) Upon reintroduction of a water/DMF (1:1) mixture, only several XRPD lines belonging to the original solid were observed.

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