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 frameworks6 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)(H2O) (BDC = 1,4-benzenedicarboxylate and DMF = N,N′-dimethylformamide).

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(NO3)2·6H2O (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 characterized by X-ray single-crystal analysis7 on a sample obtained from the reaction product revealed containing a mixture of Zn(NO3)2·6H2O (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 characterized by X-ray single-crystal analysis7 on a sample obtained from the reaction product revealed containing a mixture of Zn(NO3)2·6H2O (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 characterized by X-ray single-crystal analysis7 on a sample obtained from the reaction product revealed containing a mixture of Zn(NO3)2·6H2O (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.

Figure 1. The building block unit including the asymmetric unit present in crystalline Zn(BDC)(DMF)(H2O) 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”.

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 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.


(8) Colorless prismatic crystals of Zn(BDC)(DMF)(H2O) were analyzed at 298 ± 2°C; monoclinic, space group P21/c with a = 6.718 (3), b = 15.488 (7), c = 12.430 (8), β = 102.83 (4)°, V = 1261.0 (11) Å3, Z = 4, dcalc = 1.689 g cm−3 and µ = 1.970 mm−1. Data were collected on a Siemens R3/m Cu autodiffractometer using graphite-monochromated Mo Kα radiation and full 1.60° wide ω scans to a maximum of 2θ = 25.04°, giving 2588 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 Rs = 0.0923 for 2219 reflections with F > 2σ(F) and goodness of fit on F2 = 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 Hg2+–Hg2+ 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.
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). Furthermore, this phase shows crystallographic 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 evacuated solid. 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 allowed the evacuation of the DMF guests leading to a microporous network.

Anticipating the microporosity of the resulting evacuated Zn(BDC) framework, we proceeded to measure its gas sorption isotherms. Figure 3. The gas sorption isotherms for the microporous Zn(BDC) evacuated framework.

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 N2(g) and CO2(g) sorption isotherms were obtained by introducing high purity grade gases into the sample chamber with increasing pressure intervals at 78 K (N2) and 195 K (CO2) 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 (N2) and 20 min (CO2). A plot of (mg weight sorbed)/[g of Zn(BDC)] vs P/P0 (P0 = saturation pressure, 780 Torr for CO2 and 745 Torr for N2) revealed a type I isotherm for both gases as shown in Figure 3 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 m2/g and 310 m2/g were calculated, and micropore volumes of 0.11 cm3/g (0.094 cm3/g) and 0.10 cm3/cm3 (0.086 cm3/g) were calculated for N2 and CO2, respectively, using the Dubinin-Radushkovich equation. Typically for zeolites, which generally have higher molar mass than Zn(BDC), pore volumes ranging from 0.18 cm3/cm3 for analcime to 0.47 cm3/cm3 for zeolite A are obtained.5

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)(H2O), 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. J9A8160X

Figure 2. The crystal structure of Zn(BDC)(DMF)(H2O) 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.

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(10) (a) Anal. Calcd for Zn(BDC) = C10H4O4Zn: C, 41.87; H, 1.76; N, 0.00. Found: C, 40.47; H, 1.32; 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.
