Coordinatively Unsaturated Metal Centers in the Extended Porous Framework of Zn₃(BDC)₃·6CH₃OH (BDC = 1,4-Benzenedicarboxylate)

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The chemistry of soluble inorganic and organometallic complexes is replete with examples of metal centers having one or more labile ligands, whereby the dissociation of such ligands yields unsaturated metal centers, which have been implicated as the active sites of catalysts to many organic[1] and inorganic[2] homogeneous transformations. However, the presence of such accessible metal centers in extended 3-D infinite crystalline solids has been elusive at best, with no established synthetic routes leading to their formation.[3] In this report, we present an example of how coordinatively unsaturated metal centers can be achieved in the chemistry of metal-organic porous frameworks. There has been intense activities devoted to the development of this chemistry[4] due to the expected impact on many technologies including separations of gases and liquids,[5,6] sensors[7] and low-temperature catalysis.[8] Here, we describe the synthetic, structural and inclusion principles of this chemistry as they have been demonstrated for the copolymerization of 1,4-benzenedicarboxylate (BDC), with zinc(II), to give a 3-D porous framework, Zn₃(BDC)₃·6CH₃OH, where coordinatively unsaturated zinc centers allow for highly selective binding of incoming guests—a process that occurs reversibly and without destruction of the Zn−BDC framework.

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(2) For organic transformations using organometallic complexes, see: Parshall, G. W. *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; John Wiley & Sons, New York, 1980.

(3) The catalytic activity of coordinatively unsaturated metal centers has been proposed as the catalytic site in many heterogeneous systems such as the partial oxidation of *n*-butane: Centi, G.; Triffiro, F.; Ebner, J. R.; Franchetti, V. M. *Chem. Rev.* **1988,** *88,* 55−80.

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An *N,N'*-dimethylformamide solution (8.0 mL) of Zn(NO₃)₂·6H₂O (0.56 g, 1.89 mmol) and 1,4-benzenedicarboxylic acid (H₂-BDC) (0.32 g, 1.93 mmol) was diluted with absolute methanol (72.0 mL). To deprotonate the acid and initiate the copolymerization process, an *n*-propanol solution of triethylamine was allowed to diffuse into an aliquot (10 mL) of the mixture at room temperature. Block-shaped crystals of Zn₃(BDC)₃·6CH₃OH appeared after 12 days, which were collected, washed with methanol and acetone, and air-dried to give 0.195 g (35% yield based on zinc nitrate).[9]

X-ray structure performed[10] on a single crystal isolated from the reaction mixture revealed a 3-D porous network composed of the building unit shown in Figure 1a. Three zinc(II) centers, with an inversion center on Zn1, are clustered by virtue of the bidentate functionalities of three symmetry-inequivalent BDC units (the BDC unit is not shown for C31 and C31A). In the asymmetric unit, each two of the zinc centers are bridged by two BDC units through the two oxygen atoms of each carboxylate, and by a third BDC unit through only one carboxylate oxygen (O31 of C31) with the other carboxylate oxygen (O32) unbound. Zn1 is octahedrally bound to carboxylate oxygens, and Zn2 and Zn2A only coordinated to three such oxygens with the remaining positions bound by two methanol molecules (O41, O51 and O41A, O51A, respectively), where O41 and O41A are tightly bonded (Zn2−O41 = 2.071 (6) Å), while O51 and O51A are weakly bonded (Zn2−O51 = 2.135 (7) Å) to zinc.[11] Two additional methanol molecules (O1S and O1SA) per building unit are not bonded to any of the zinc centers; however, they each form one weak hydrogen bond to a coordinated methanol molecule (O1S···O51 = 2.695 (5) Å). In the crystal, these building units are polymerized through the BDC units of C11, C21, and C31 and their symmetry equivalent units into the *ab*, *ac*, and *bc* crystallographic planes, respectively, as shown in Figure 1b. This arrangement yields a 3-D porous material having nearly 7 Å wide-pores that are supported by a tightly held network.

The multidentate functionality of BDC and its ability to generate such tightly held and bulky building units have significant implications on the stability of this material, while the possibility of removing the weakly bound (O51 and O51A) and the guest (O1S and O1SA) methanol molecules presents an opportunity for achieving a porous material with coordinatively unsaturated zinc centers decorating the pores. Preliminary thermal gravimetric studies on this material showed two separate weight losses at 55 and 170 °C that can be attributed to the loss of approximately four and two methanol molecules from the pores, respectively. The first is due to the loss of the guest and weakly bound methanol (OS1, OS1A and O51, O51A, respectively), while the second is due to the loss of the strongly bound methanol (O41 and O41A). The remaining compound was heated to 335 °C without any additional weight loss, indicating a robust Zn−BDC framework.

To examine the inclusion chemistry of this material, the as-synthesized microcrystalline solid was heated to 140 °C under

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(9) Anal. Calcd for Zn₃C₃₀H₃₆O₁₈: C, 40.91; H, 4.12; N, 0.00; Zn, 22.27. Found: C, 40.62; H, 4.08; N, 0.02; Zn, 21.94. FT.-IR (KBr): ν_OH (CH₃OH) = 3177 (s), and ν_COO = 1598 (s), and 1552 (s).

(10) Colorless single crystals of Zn₃(BDC)₃·6CH₃OH were analyzed at 20 ± 1 °C: Triclinic, space group P1̄ with *a* = 9.726 (4) Å, *b* = 9.911 (5) Å, *c* = 10.450 (5) Å, α = 99.72 (4)°, β = 111.11 (4)°, γ = 108.42 (4)°, V = 844.9 (7) Å³, Z = 2, *d*_calcd = 1.731 g·cm⁻³ and μ_a(Mo Kα) = 2.193 mm⁻¹. Data were collected on a Siemens R3m/V autodiffractometer using graphite-monochromated Mo Kα radiation and full 2.00°wide ω scans to a maximum of 2θ = 50.1°, giving 2988 unique reflections. The structure was solved by (SHELXTL PC V.5.03) direct methods and the resulting structural parameters were refined by least-squares techniques to a standard discrepancy index R = 0.0642 and R_w = 0.1395 for 1921 reflections with F > 2 σ(F) and goodness-of-fit on F² = 1.024. Anisotropic thermal parameters were refined for all non-H atoms, and fixed thermal parameters were used for included H.

(11) Prince, R. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1987; Vol. 5, p 925.
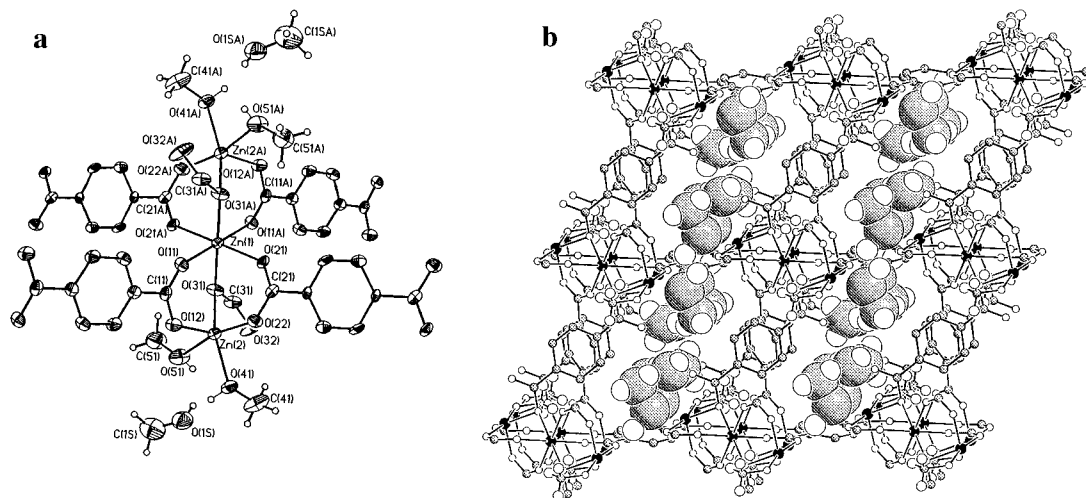
Figure 1. (a) The building block unit including the asymmetric unit present in crystalline $Zn_3(BDC)_3 \cdot 6CH_3OH$ with non-hydrogen atoms represented by thermal ellipsoids drawn to encompass 50% of their electron density. Atoms labeled with an additional letter "A" are symmetry equivalent to those atoms without such designation. Only one carboxylate of C31 and C31A is shown, with the remaining parts of the respective BDC units are omitted for clarity. (b) The crystal structure of $Zn_3(BDC)_3 \cdot 6CH_3OH$ shown approximately down the crystallographic direction [100], where an extended 3-D channel system is found occupied by methanol guests (O1S). The framework atoms including O41 methanol are represented as ball-and-stick: Zn, dark; C, shaded; O, small open; and H, large open. The labile methanol molecules (O1S and O51) are shown as large spheres for clarity, with C and O, shaded, and H, open. In (a) and (b) all hydrogen atoms on BDC have been omitted for clarity.
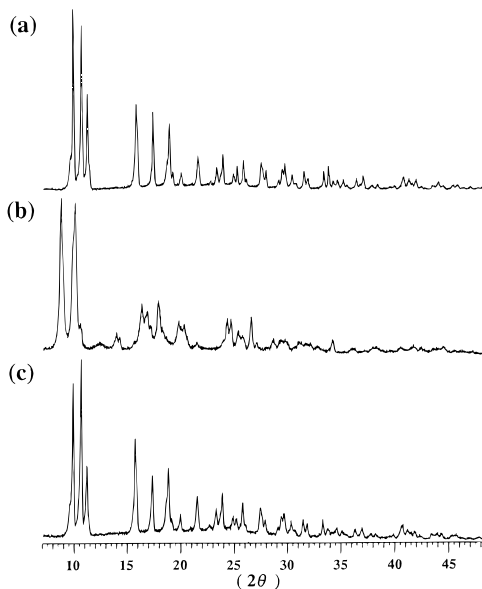
Figure 2. The XRPD patterns of the (a) as-synthesized material, $Zn_3(BDC)_3 \cdot 6CH_3OH$, (b) evacuated solid, $Zn_3(BDC)_3 \cdot 2CH_3OH$, and (c) regenerated solid resulting from the reintroduction of methanol into the channels of the evacuated solid.

0.08 mmHg vacuum for 1 h in order to remove the guest and weakly bound methanol molecules and give a solid that was formulated as $Zn_3(BDC)_3 \cdot 2CH_3OH$[12] (hereafter referred to as the evacuated solid). Comparison of the ^{13}C CPMAS solid-state NMR spectrum of this material to that of the original solid showed a significant reduction, as expected, in the relative intensity of the methanol resonance (δ 48 ppm). Comparison of the X-ray powder diffraction pattern (XRPD) of the starting material (Figure 2a) and that of the evacuated solid (Figure 2b) show that the diffraction lines in the latter remain sharp but with slightly different positions and line widths. Although this may indicate a slight deformation of the pore structure due to the empty space created by methanol evacuation, it points to the stability and high periodicity of the $Zn_3(BDC)_3 \cdot 2CH_3OH$ framework in the presence

of coordinatively unsaturated zinc centers. It is worth noting that upon reintroducing methanol into the pores over a period of only 10 min, the XRPD of the resulting solid (Figure 2c) is instantaneously regenerated with the peak position and their intensity being fully coincident to those observed for the original solid, serving as evidence to the reversibility of the inclusion process.

The thermal and structural stability of the evacuated solid including the inevitable possibility of the presence of accessible metal centers into the porous framework of the evacuated material led us to explore the selectivity of the pores toward the separation of molecules from solution mixtures. Preliminary experiments show a clear preference for the inclusion of alcohols in the expected order: $CH_3OH > C_2H_5OH > n\text{-}C_3H_7OH$, with no evidence for the inclusion of any detectable amounts of acetonitrile or benzene.[13a] In another experiment involving the exposure of the evacuated solid to gaseous amines, a clear preference to NH_3, CH_3NH_2, and $(CH_3)_2NH$, with no evidence for the inclusion of $(CH_3)_3N$ was observed.[13b] We believe that the high-selectivity to alcohols, ammonia, and primary/secondary amines, despite the presence of a potential guest with similar size and shape (CH_3-CN, $(CH_3)_3N$), is a direct consequence of the availability of coordinatively unsaturated zinc centers poised within the pores of the framework. Although we believe that these electronic affects predominate the inclusion process, this does not exclude the involvement of steric factors.

Elaboration on the utility of 1,4-benzenedicarboxylate for the construction of 3-D porous frameworks, and for tailoring pores with coordinatively unstaturated metal centers, is already in progress.

Supporting Information Available: Crystallographic data for $Zn_3(BDC)_3 \cdot 6CH_3OH$—crystal structure analysis report, positional parameters, thermal parameters, and interatomic distances and angles (9 pages). See any current masthead page for ordering and Web access instructions.

(12) Anal. Calcd for $Zn_3C_{26}H_{20}O_{14}$: C, 41.49; H, 2.68; N, 0.00; Zn, 26.06. Found: C, 41.55; H, 2.54; N, 0.09; Zn, 26.10.

(13) (a) The experimental protocol used here was developed earlier (Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc.* **1997**, *119*, 2861−2868) and followed by GC using 50 mg of host in 3.00 mL of toluene solution containing potential guests. The observed amount of guests (mmol) before and **after** the addition of host were CH_3OH (1.88, **1.55**), C_2H_5OH (1.89, **1.76**), C_3H_7OH (1.92, **1.86**), CH_3CN (0.050, **0.050**), and C_6H_6 (0.050, **0.050**). (b) Elemental microanalyses of the nitrogen content in the resulting amine containing solids were as follows (%): NH_3, 10.83; CH_3NH_2, 12.13. $(CH_3)_2$-NH, 8.91. $(CH_3)_3N$, 0.37.