

Design and synthesis of metal-carboxylate frameworks with permanent microporosity

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Metal-carboxylate clusters are ideally suited as secondary building units (SBU) for the assembly of extended open frameworks. Examples extracted from the chemistry of the multidentate building block 1,4-benzenedicarboxylate (BDC) show that Zn(BDC) clusters lead to the formation of rigid, stable and truly microporous metal-carboxylate networks. Gas sorption isotherms measured for this class of materials show type (I) gas uptake that is analogous to those observed for zeolites and molecular sieves.

Keywords: metal-organic, microporous, frameworks, sorption, isotherm

1. Introduction

The discovery of zeolite-like sorption by crystals of Werner complexes, β -m(4-methylpyridyl)₄(NCS)₂ (M = Ni²⁺ or Co²⁺) [1], and Prussian blue compounds, Fe₄[Fe(CN)₆]₃·xH₂O [2], has served as an important precedent to the extensive subsequent interest in developing the chemistry of metal-organic microporous materials [3]. The synthetic approach to these materials involves addition copolymerization of organic building blocks with metal ions at room temperature or in superheated solvents, whereupon controlling the nucleation of the products yields crystalline samples that are amenable to single crystal X-ray diffraction studies. Equipped with an existing library of organic building blocks and an extensive knowledge of their metal-coordination chemistry, many have recognized the potential for designing open frameworks with structural attributes yet unknown in zeolites and molecular sieves [4]. However, the pursuit of metal-organic frameworks with permanent microporosity has been complicated by two factors: (a) the presence of interpenetrated nets, and (b) collapse of the framework structure upon exchange or removal of guests. To overcome these challenges, we have used hydrogen-bonded guest aggregates to prevent interpenetration and multi-bidentate organic building blocks to enhance the rigidity and stability of the resulting open network [5]. We sought to measure gas sorption isotherms for these materials as an initial step toward exploring the prospects of designing solids with tailored pore-size, -shape and -function. In this report, we summarize recent results from our laboratory, which show that by using multidentate building blocks it is possible to prepare stable metal-organic frameworks having zeolite-like *permanent porosity*.

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2. Metal-carboxylate clusters as SBU in microporous solids

Designing strategies for preserving molecular structure and reactivity into assembled solid state networks is one of the most pressing issues facing materials chemistry today. Here, we show how metal-carboxylate clusters can be linked into extended open networks that are characterized by high framework stability even in the absence of guests. In earlier publications we have shown how such clusters also provide opportunities for translating molecular reactivity into the solid state by allowing the formation of ordered arrays of Lewis acid sites within the channels [5(b), 6].

Discrete dinuclear [7], trinuclear [8], and tetranuclear [9] metal-carboxylate clusters are produced when *mono*-carboxylate ligands such as crotonate and benzoate are employed as shown in figures 1(a)–(c). It is instructive to view these clusters as having three components relevant to their polymerization into microporous metal-carboxylate networks: (a) the “Zn–O–C” core structure (SBU) provides the bulk necessary to ultimately prevent interpenetration and support the formation of a rigid network, (b) the monocarboxylate ligands (crotonate and benzylacetate) present opportunities for employing dicarboxylate or multicarboxylate ligands in order to polymerize these clusters into predictable extended networks, and (c) the terminal Lewis base (quinoline) in figures 1(a) and (b) may be exploited for studying the reactivity of the metal center, which is easily done by employing weaker Lewis bases or solvents (methanol or ethanol) to allow their removal from the assembled solid, thereby yielding a microporous network with channels decorated with accessible Lewis acid sites – an aspect of this research that has been presented elsewhere [6]. To link these cluster cores into extended solids, we employed the bifunctional 1,4-benzenedicarboxylate (BDC)

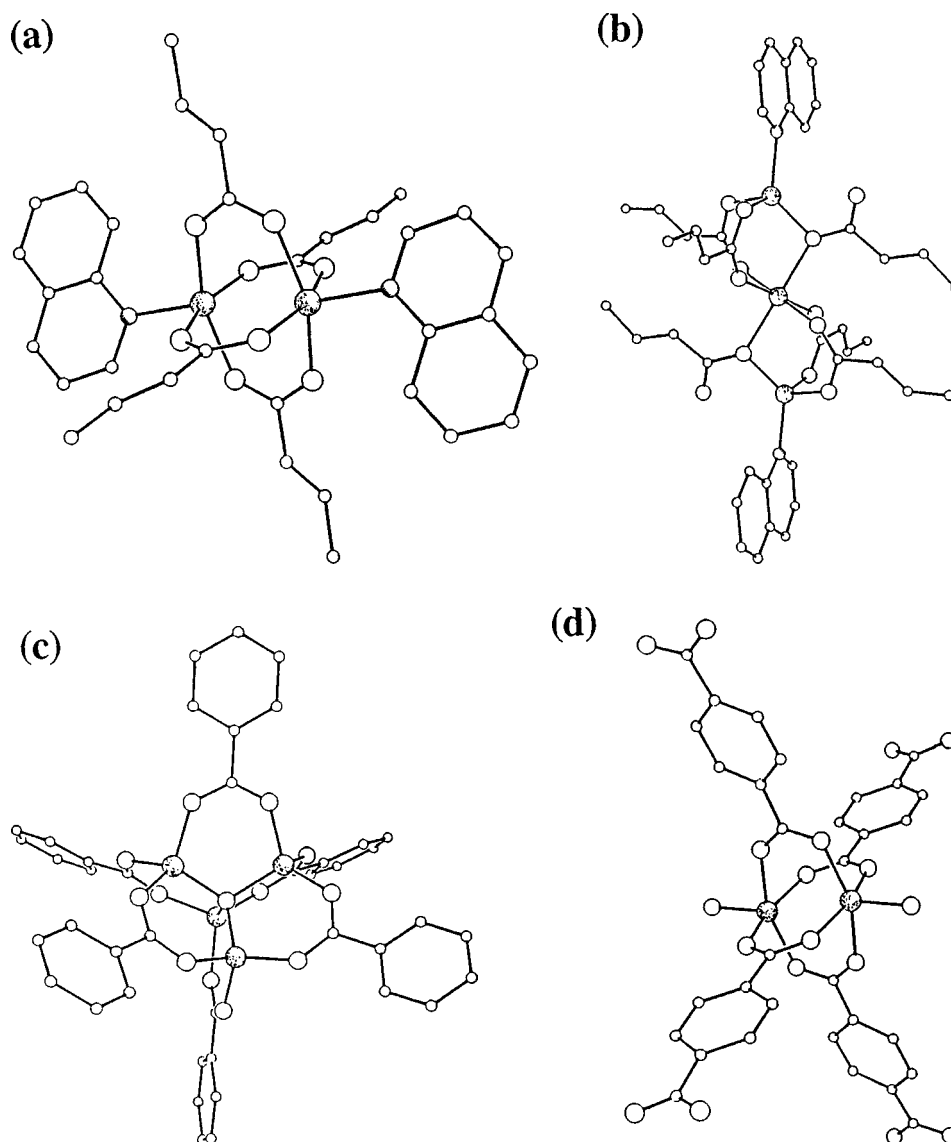


Figure 1. Representations of zinc carboxylate clusters prepared with crotonate (a) and (b), and benzoate (c) to form discrete dinuclear, trinuclear and tetranuclear clusters, respectively. The use of 1,4-benzenedicarboxylate (BDC) yields extended porous networks having cluster unit building blocks (d)–(f) analogous to those observed for the monocarboxylates (a)–(c). Atoms shown as spheres with zinc (shaded), nitrogen (partially shaded), oxygen (large open), carbon (small open) are given arbitrary sizes and hydrogen atoms were omitted for clarity.

building block in reactions involving its copolymerization with Zn(II).

3. Synthesis and structure

Slow diffusion of triethylamine into a solution mixture containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and H_2BDC using a weakly coordinating solvent(s) yields crystalline $\text{Zn}(\text{BDC}) \cdot (\text{DMF})(\text{H}_2\text{O})$, **1** [10], $\text{Zn}_3(\text{BDC})_3 \cdot 6(\text{CH}_3\text{OH})$, **2** [6], $\text{Zn}_4\text{O}(\text{BDC})_3 \cdot x(\text{DMF})$, **3**, (DMF = N,N'-dimethylformamide), which are composed of microporous Zn(BDC) frameworks. Compounds **1** and **2** have been fully characterized and reported in preliminary communications. The essential features of their structures and properties will be presented here in the context of the theme outlined above.

Although compound **3** has just been examined by single crystal X-ray diffraction with only its framework structure resolved thus far, its inclusion in this discussion lends further support to the objectives of the present report. Crystallographic data and positional parameters for the three compounds are listed in tables 1 and 2, respectively.

The extended structures of **1–3** contain the “Zn–O–C” SBU’s found in the molecular clusters as shown in figures 1(d)–(f), respectively. However, in these cases, the BDC building block allows the polymerization of these clusters into three-dimensional networks (figures 2(a)–(c)).

In the structure of **1**, a total of four carboxylate units of different, but symmetry 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 car-

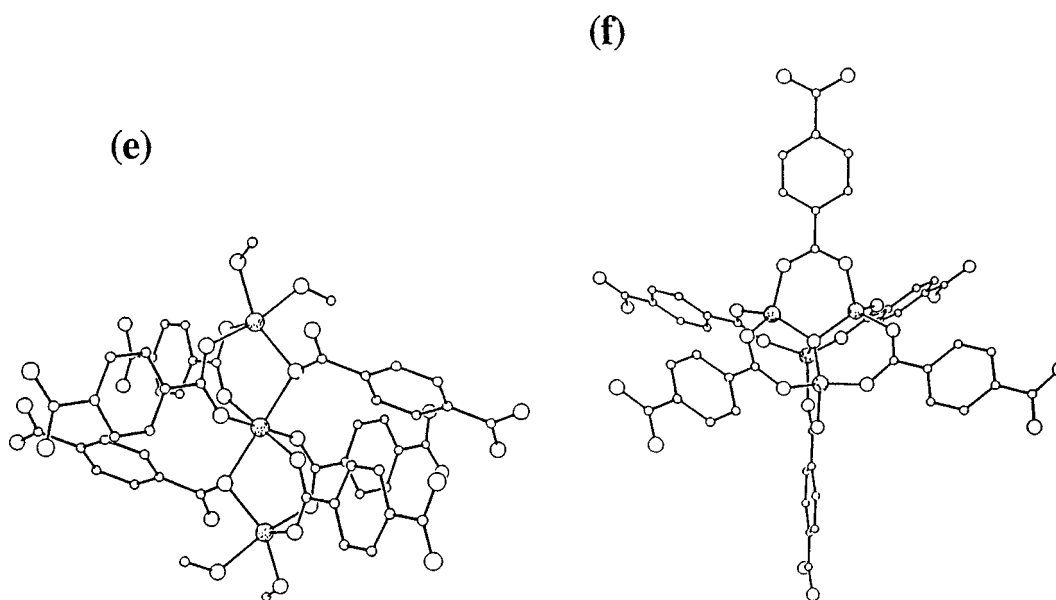


Figure 1. (Continued.)

Table 1
 Crystallographic data for crystalline Zn(BDC)·(DMF)(H₂O), **1**, Zn₃(BDC)₃·6(CH₃OH), **2**, Zn₄O(BDC)₃·*x*(DMF), **3**.

| | 1 | 2 | 3 |
|------------------------------------|--|---|--|
| Chemical formula | C ₁₁ H ₁₃ NO ₆ Zn | C ₁₅ H ₁₈ O ₉ Zn _{1.50} | C _{5.33} H _{2.67} O _{2.89} Zn _{0.89} |
| Formula weight | 320.59 | 440.35 | 171.07 |
| Crystal system | Monoclinic | Triclinic | Cubic |
| Space group | P2 ₁ /n | P ₁ ⁻ | Fm ₃ ⁻ m |
| <i>Z</i> | 4 | 2 | 36 |
| Temperature (K) | 293 (2) | 293 (2) | 213 (2) |
| <i>a</i> (Å) | 6.718 (3) | 9.726 (4) | 25.669 (3) |
| <i>b</i> (Å) | 15.488 (7) | 9.911 (5) | 25.6690 (3) |
| <i>c</i> (Å) | 12.430 (8) | 10.450 (5) | 25.6690 (3) |
| α (°) | 90 | 99.72 (4) | 90 |
| β (°) | 102.83 (4) | 111.11 (4) | 90 |
| γ (°) | 90 | 108.42 (4) | 90 |
| <i>V</i> (Å ³) | 1261.0 (11) | 844.9 (7) | 16913.2 (3) |
| μ (mm ⁻¹) | 1.970 | 2.193 | 1.142 |
| <i>R</i> (<i>R</i> _w) | 0.0458(0.0923) | 0.0642(0.1395) | 0.1106(0.3230) |

boxylate bridged M–M bonded molecular complexes (figure 1(d)). 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. Stacking of the layers in the crystal leads to a 3-D network having extended 1-D pores of nearly 5 Å diameter where DMF guests reside, as shown in figure 2(a). Each DMF guest molecule forms a hydrogen-bonding interaction with the water ligands, otherwise, it is held in the cavity by van der Waals interactions with the Zn(BDC) framework.

The structure of **2** contains three zinc(II) centers, with an inversion center on the central Zn atom. They are clustered by virtue of the bidentate functionalities of three symmetry-

inequivalent BDC units (figure 1(e)). Three zinc(II) centers, with an inversion center on the central Zn, are clustered by virtue of the bidentate functionalities of three symmetry-inequivalent BDC units. In the asymmetric unit, each two 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 with the other carboxylate oxygen unbound. The center zinc is octahedrally bound to carboxylate oxygens, and the remaining zinc centers are only coordinated to three such oxygens with the remaining positions bound by two methanol molecules per zinc. Two additional methanol molecules 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. In the crystal, these trinuclear building units are polymerized through the BDC into the *ab*, *ac* and *bc* crystallographic planes, respectively, as

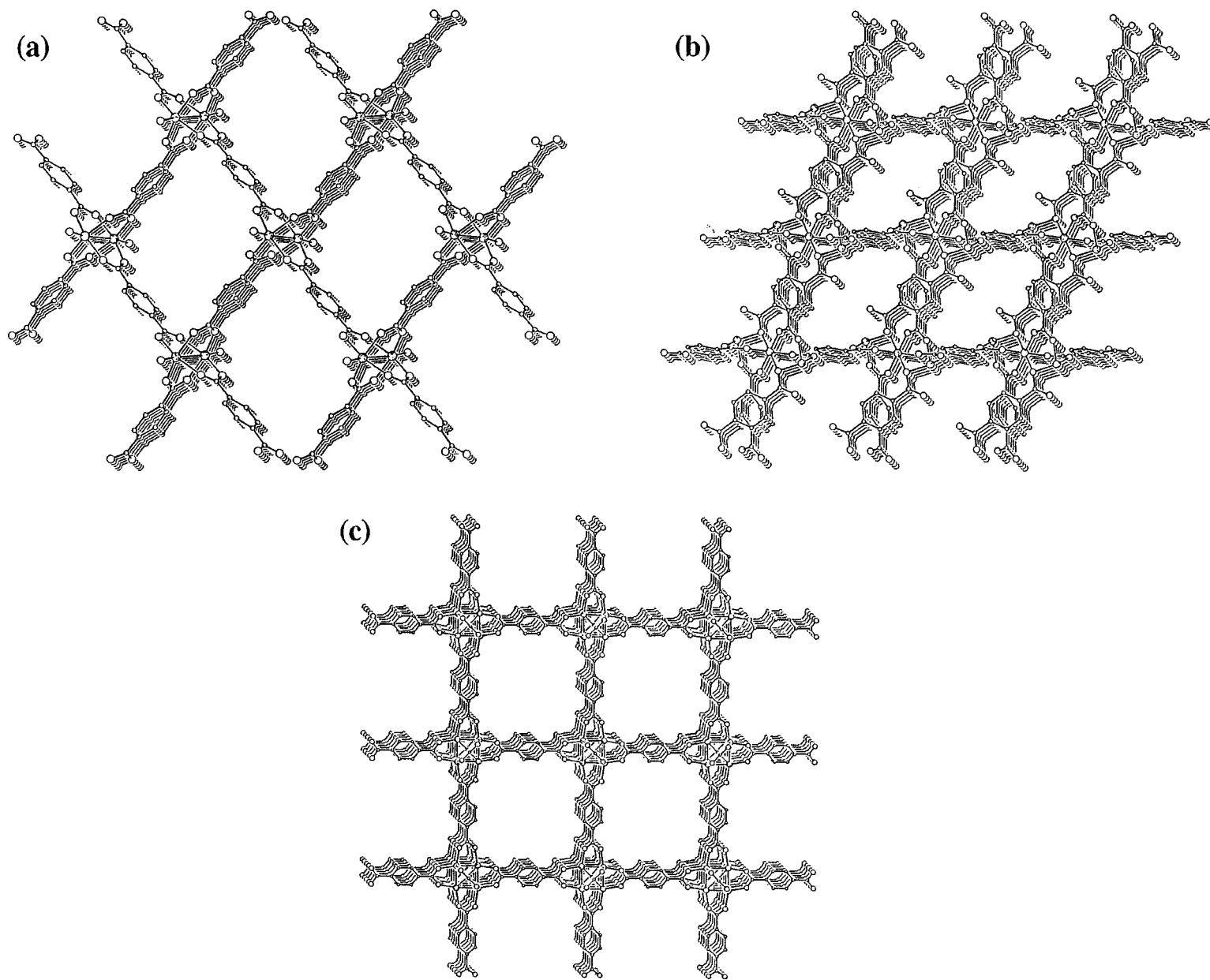


Figure 2. The crystal structures of (a) $\text{Zn}(\text{BDC}) \cdot (\text{DMF})(\text{H}_2\text{O})$, (b) $\text{Zn}_3(\text{BDC})_3 \cdot 6(\text{CH}_3\text{OH})$, (c) $\text{Zn}_4\text{O}(\text{BDC})_3 \cdot x(\text{DMF})$.

Table 2
 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Zn(BDC)·(DMF)(H₂O), **1**,
 Zn₃(BDC)₃·6(CH₃OH), **2**, Zn₄O(BDC)₃·x(DMF), **3**.

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (eq) |
|----------|----------|----------|-----------|---------------|
| 1 | | | | |
| Zn(1) | 2003(1) | 5050(1) | 5771(1) | 17(1) |
| O(1) | −600(6) | 3952(3) | 3669(3) | 41(1) |
| O(2) | 2442(6) | 4030(3) | 4791(3) | 41(1) |
| O(3) | 2841(6) | 796(3) | 587(3) | 43(1) |
| O(4) | 5876(6) | 805(3) | 715(3) | 44(1) |
| O(5) | 4830(5) | 5213(2) | 6569(3) | 29(1) |
| C(1) | 1948(8) | 2990(3) | 3372(4) | 22(1) |
| C(2) | 599(8) | 2584(3) | 2513(4) | 25(1) |
| C(3) | 1280(8) | 1960(3) | 1895(4) | 25(1) |
| C(4) | 3324(8) | 1713(3) | 2125(4) | 22(1) |
| C(5) | 4671(8) | 2112(3) | 3003(4) | 26(1) |
| C(6) | 3991(8) | 2743(3) | 3617(4) | 28(1) |
| C(7) | 1213(8) | 3706(3) | 3998(4) | 22(1) |
| C(8) | 4067(8) | 1054(3) | 1419(4) | 22(1) |
| O(1S) | 6439(7) | 4869(3) | 8628(3) | 53(1) |
| N(1S) | 6382(9) | 3967(4) | 10052(4) | 49(1) |
| C(2S) | 5644(11) | 4286(4) | 9060(5) | 47(2) |
| C(3S) | 5375(13) | 3279(5) | 10506(7) | 74(2) |
| C(4S) | 8278(12) | 4285(6) | 10706(6) | 73(3) |
| 2 | | | | |
| Zn(1) | 5000 | 5000 | 5000 | 17(1) |
| Zn(2) | 5728(1) | 3974(1) | 2107(1) | 20(1) |
| O(11) | 6683(7) | 6733(6) | 4741(7) | 24(1) |
| O(12) | 7417(8) | 6036(6) | 3027(7) | 31(2) |
| C(11) | 7537(11) | 6985(10) | 4088(9) | 23(2) |
| C(12) | 8810(11) | 8548(9) | 4549(9) | 22(2) |
| C(13) | 8996(11) | 9685(9) | 5658(10) | 24(2) |
| C(14) | 9829(11) | 8875(9) | 3907(10) | 27(2) |
| O(21) | 3082(7) | 4758(7) | 3146(6) | 23(1) |
| O(22) | 3821(8) | 4590(7) | 1351(7) | 30(2) |
| C(21) | 2872(11) | 4725(9) | 1894(9) | 20(2) |
| C(22) | 1379(10) | 4857(9) | 905(9) | 18(2) |
| C(23) | 918(11) | 4550(10) | −574(9) | 25(2) |
| C(24) | 421(11) | 5291(10) | 1459(9) | 25(2) |
| O(31) | 5444(8) | 3310(6) | 3785(7) | 25(2) |
| O(32) | 4030(11) | 1335(8) | 1842(7) | 51(2) |
| C(31) | 4725(13) | 1885(10) | 3187(10) | 29(2) |
| C(32) | 4838(12) | 900(10) | 4125(10) | 25(2) |
| C(33) | 5865(11) | 1535(10) | 5586(9) | 25(2) |
| C(34) | 3989(12) | −632(10) | 3547(9) | 26(2) |
| O(41) | 5387(8) | 3376(7) | −17(7) | 34(2) |
| C(41) | 4272(18) | 1977(13) | −1054(12) | 62(4) |
| O(51) | 7529(10) | 3106(9) | 2402(8) | 47(2) |
| C(51) | 8551(17) | 2994(18) | 3669(13) | 64(4) |
| O(1S) | 7869(12) | 1330(11) | 386(10) | 62(2) |
| C(1S) | 9366(21) | 1243(16) | 896(18) | 83(5) |
| 3 | | | | |
| Zn(1) | 2935(1) | 2065(1) | 2065(1) | 51(1) |
| O(1) | 2500 | 2500 | 2500 | 42(5) |
| O(2) | 2818(3) | 2182(3) | 1339(4) | 96(3) |
| C(1) | 2500 | 2500 | 1105(7) | 87(6) |
| C(2) | 2831(4) | 2169(4) | 263(6) | 123(8) |
| C(3) | 2500 | 2500 | 538(6) | 98(8) |

shown in figure 2(b). This arrangement yields a 3-D porous material having nearly 7 Å wide-pores that are supported by a tightly held network.

Preliminary single crystal X-ray studies on compound **3** show that the zinc atoms and BDC carboxylate groups occupy, respectively, the corners and edges of an oxide centered tetrahedron as shown in figure 1(f). The tetrahedra are linked by BDC into a CaB_6 -type network as shown in figure 2(c). The framework thus formed has a 3-D porous system having nearly 7–8 Å diameter pores that are filled with DMF guest molecules as observed by ^{13}C NMR for a solution obtained from the immersion of the as-synthesized solid into CD_3CN , thus indicating solvent exchange with DMF. We have evidence from X-ray powder diffraction, which indicates that the guest molecules can be removed without destruction of the framework. Further structure and sorption experiments are currently being pursued to fully characterize this material.

4. Gas sorption isotherms

The multidentate functionality of BDC and its ability to generate such tightly held and bulky building units have significant implications on the stability of these materials. Thermogravimetric analysis (TGA) on polycrystalline samples of **1** and **2** show sharp weight losses due to the removal of guests. The evacuated $\text{Zn}(\text{BDC})$ frameworks are generally stable up to 350 °C in inert atmosphere. Anticipating the microporosity of the resulting evacuated $\text{Zn}(\text{BDC})$ framework, we measured their gas sorption isotherms. Typically, a sample (ca. 0.01 mm size particles) is prepared by heating the as-synthesized form to a temperature sufficient to remove the guests (140 °C) under vacuum (5×10^{-5} Torr) in an electromicrogravimetric balance (CAHN 1000) setup. The $\text{N}_2(\text{g})$, $\text{Ar}(\text{g})$ and $\text{CO}_2(\text{g})$ sorption isotherms were obtained by introducing high purity grade gases into the sample chamber with increasing pressure intervals at 78 K (N_2 , Ar) and 195 K (CO_2), then monitoring the resulting weight changes. Rapid sorption of these gases into the pores was observed for **1** and **2**, with equilibrium pressures achieved within 10 min (N_2), 13 min (Ar) and 20 min (CO_2). A plot of (mg weight sorbed)/[g of $\text{Zn}(\text{BDC})$ for **1** and $\text{Zn}_3(\text{BDC})_3$ for **2**] vs. P/P_0 revealed type I isotherm figures 3(a) and (b), and is thus indicative of an open $\text{Zn}(\text{BDC})$ framework with permanent microporosity. Similar to most zeolites, these isotherms are reversible and show no hysteresis behavior upon desorption of gases from the pores. Micropore volumes of $0.11 \text{ cm}^3/\text{cm}^3$ for **1** ($300 \text{ m}^2/\text{g}$) and $0.06 \text{ cm}^3/\text{cm}^3$ for **2** ($140 \text{ m}^2/\text{g}$) are calculated for N_2 and CO_2 using the Dubinin–Radushkevich equation. Figure 3(c) shows liquid vapor sorption isotherms for the evacuated solid of compound **2**, which also shows type I behavior as measured at room temperature. It is worth noting that for the four solvents, the same pore volume was observed (figure 3(c)), which is indicative of the homogeneity of the pores. Similar studies on compound **3** are currently in progress.

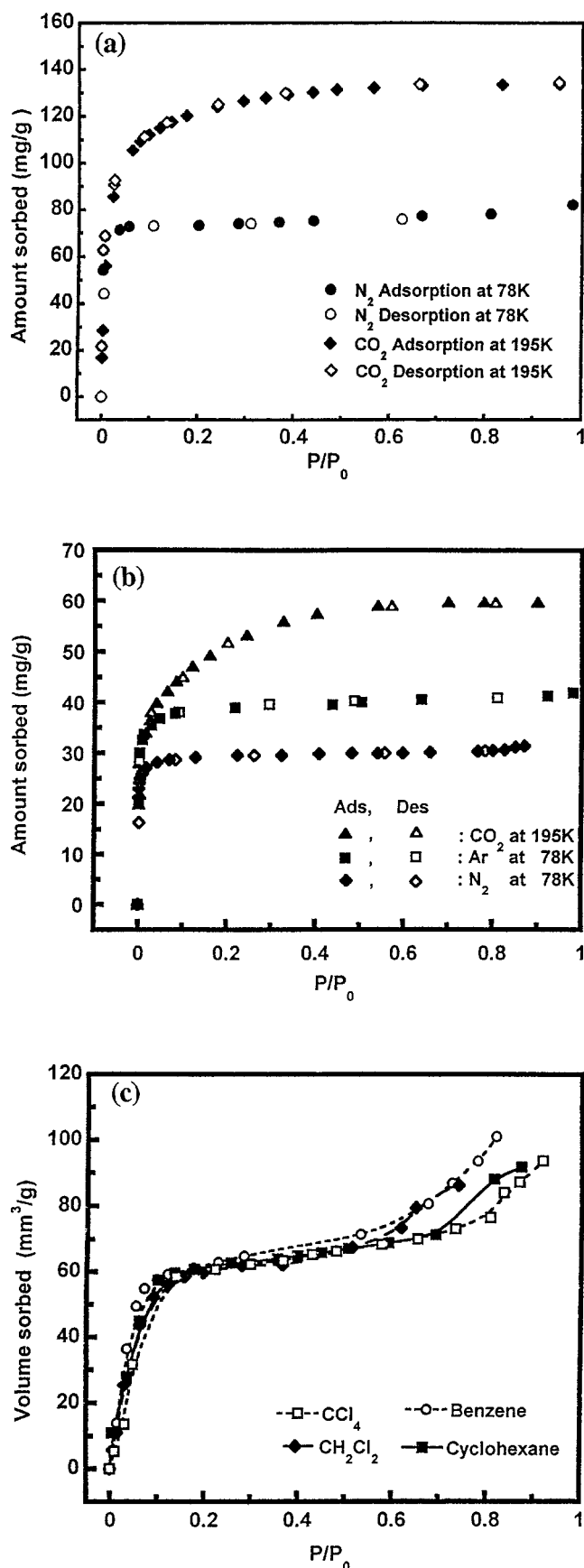


Figure 3. Sorption isotherms for the evacuated frameworks of (a) $\text{Zn}(\text{BDC}) \cdot (\text{DMF})(\text{H}_2\text{O})$, (b) and (c) $\text{Zn}_3(\text{BDC})_3 \cdot 6(\text{CH}_3\text{OH})$.

5. Concluding remarks

It is clear from the foregoing discussion that multidentate organic building blocks such as BDC play an important role in producing molecular metal-carboxylate SBU's that are ideally suited for the formation of open *non-interpenetrated* networks, and achieving frameworks with zeolitic sorption behavior and permanent microporosity. Although this presentation was restricted to BDC, other multidentate carboxylates such as 1,3,5-benzenetricarboxylates (BTC) have been pursued to give microporous Zn(BTC) frameworks with larger pores [5(b)]. In principle, other metal ions can be used in this synthetic scheme to yield similar porous networks having more active metal centers, thus opening many opportunities for their exploration in low temperature catalysis.

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