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Synthesis and Characterization of a 1-D Porous Barium Carboxylate Coordination Polymer, [Ba(HBTB)] (H_3BTB = Benzene-1,3,5-trisbenzoic Acid)

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Supporting Information

ABSTRACT: The synthesis and characterization of [Ba(HBTB)] is reported. This is the first porous framework synthesized with barium using carboxylate ligands. The framework has robust microporous character (Langmuir surface area of 879 $m^2\ g^{-1}$) and possesses unsaturated metal sites when fully desolvated.

Porous coordination polymers (PCPs) or metal–organic frameworks are a new class of microporous solids combining the modularity of inorganic structural building units (nodes) with organic ligands (linkers) that can be easily tailored by organic synthesis.[1] This combination of the designability and structural porosity of PCPs has led to their explosive growth for possible applications such as in gas storage/separation, as catalysts, and in drug delivery.[2]

The development of new PCPs has thus far been focused on first-row transition metals, although there has been interest in main-group elements for reasons such as the oxophilicity and low atomic weight of its earlier members. For example, [Al(OH)(BDC)] (H_2BDC = 1,4-benzenedicarboxylic acid),[3] a framework based on the highly oxophilic Al^{3+} ion, possesses exceptional air, water, and thermal stability. The low atomic weight of lithium and beryllium has been utilized in porous frameworks for gas storage, as embodied in frameworks such as tetralithium tetrakis(4-pyridinolate).[4] Because the ions of alkaline-earth metals possess 2+ charge, a common oxidation state for transition metals, it is not surprising that considerable effort has been expended to form frameworks with these elements. The first porous framework of magnesium, $[Mg_3(NDC)_3]$ (H_2NDC = 2,6-napthalenedicarboxylic acid), possesses ultramicropores and demonstrates selective adsorption of O_2 over N_2, possibly via a size-sieving effect.[5] For calcium and strontium, there has been some activity in this area, but compared to transition metals, porosity is the rare exception rather than the norm.[6] For beryllium, only two porous frameworks of beryllium have been synthesized, $[Be_4O(BDC)_3]$[7] and $[Be_{12}(OH)_{12}(BTB)_4]$ (H_3BTB = benzene-1,3,5-tribenzoic acid).[8]

We are interested in forming porous frameworks with barium, the last stable member of this group, because of its inherent synthetic challenge. Barium coordination polymers have been previously reported using several ligands based on carboxylic acid, such as benzene-1,4-dicarboxylic acid,[9] naphthalene-2,6-dicarboxylic acid,[10] imidazole-4,5-dicarboxylic acid,[11] methylenediisophthalic acid,[12] and thiobenzoic acid.[13] However, to the best of our knowledge, the frameworks reported so far either are nonporous or are porous only in the presence of guest molecules.[14] No gas adsorption isotherm of a barium carboxylate PCP has been published to demonstrate its permanent microporosity in the evacuated state. This may be attributed to the relatively large ionic radii of Ba^{2+}, which leads to high coordination numbers and weak metal–ligand bonds. Inspired by the discovery of the MIL-103 family of lanthanide PCPs utilizing the rigid BTB ligand,[15] the synthesis of barium PCPs with permanent porosity was attempted because of the size similarity between La (i.e., Shannon–Prewitt effective ionic radii for nine-coordinated La^{3+} = 1.22 Å) and Ba ions (Ba^{2+} = 1.47 Å).[16] Here we demonstrate that [Ba(HBTB)], a porous barium framework with good air and thermal stability, can be synthesized with good yield and phase purity. It is noted that $[Mg_{12}(BTB)_8]$ has previously been reported with a 2-fold interpenetrated ReO_3 structure and 54% porosity.[17] However, the structure is somewhat unstable to solvent removal, and only a modest Langmuir surface area of 216 $m^2\ g^{-1}$ was obtained, despite the low atomic weight of magnesium.

[Ba(HBTB)(DMF)]·DMF [**1**(DMF)⊃DMF; DMF = *N*,*N*-dimethylformamide] was synthesized by the solvothermal reaction of $Ba(NO_3)_2$ and H_3BTB in DMF (see the Supporting Information). Its crystal structure was elucidated by single-crystal X-ray diffraction (XRD) and is shown in Figure 1a. The asymmetric unit of **1**(DMF)⊃DMF possesses one Ba^{2+} ion, one HBTB ligand, and one coordinating DMF molecule in the structure. The topology of the framework obtained by Systre[18] with a Ba^{2+} ion as the node and HBTB as the linker is the (3,5)-connected hms[19] net, similar to MIL-103.[15]

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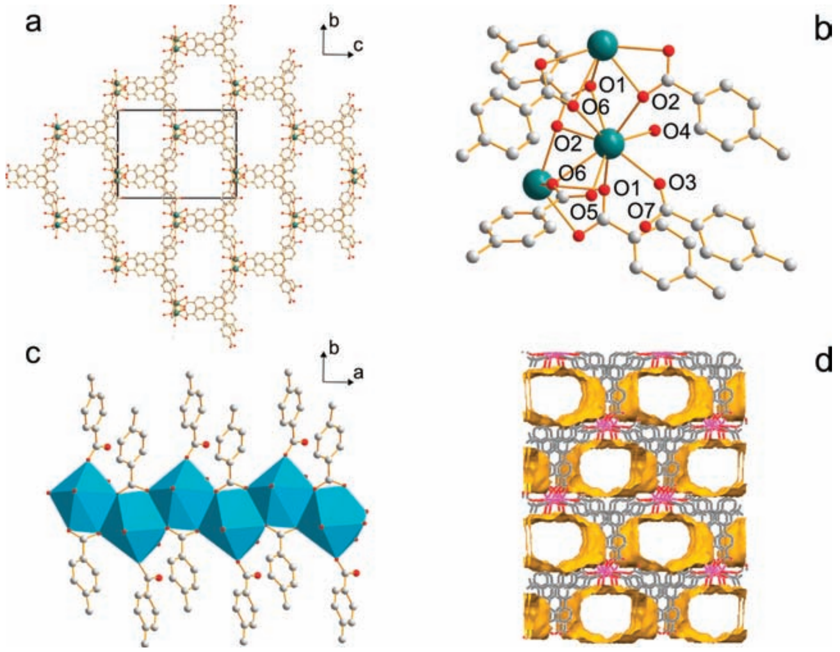

Figure 1. (a) Crystal structure of **1**(DMF)⊃DMF with the unit cell highlighted. Orthorhombic space group $Pna2_1$ (No. 33, $Z = 4$) with a = 7.3162(11) Å, b = 19.404(3) Å, and c = 26.155(4) Å. (b) Local coordination environment around the Ba ion with aromatic H atoms omitted. DMF directly coordinated to the Ba ion is represented by O4. Dark-green spheres represent Ba, red spheres represent O, and gray spheres represent C. There exists possible hydrogen bonding between O5 and the carboxylic H atom at O7. Selected bond distances (Å) and angles (deg): Ba1−O4 2.752(9), Ba1−O2 2.783(5), Ba1−O5 2.825(5), Ba1−O6 2.946(5); O4−Ba1−O1 72.9(3), O4−Ba1−O2 96.9(3), O2−Ba1−O1 150.2(2), O5−Ba1−O1 147.0(0). (c) Zigzag chains of edge-sharing BaO_9 octahedra along the a axis. (d) Contact surface with a probe radius of 1.2 Å emphasizing the undulating 1D channels (gold) present.

Ba^{2+} ions are coordinated to nine O atoms (Figure 1b), with eight of them from the carboxylate groups of the HBTB ligand and one O atom of DMF (O4), to afford a distorted single-capped square-antiprism geometry, similar to [Ba(2,6-PDCO)] (H_2PDCO = pyridine-2,6-dicarboxylic acid *N*-monoxide).[19] The coordination modes of the three carboxylate groups in the HBTB ligand can be described as μ_3-η^1:η^2:η^1 for (O1,O2), μ_2-η^2:η^1 for (O5,O6), and the relatively rare μ^1:η^1 for (O3,O7). The Ba−O bond lengths ranging from 2.752 to 2.943 Å are typical for nine-coordinated Ba ions. Although it is difficult to determine the location of the H atom, it is reasonable that one carboxylate group is protonated because of charge balance and the coordination-free oxygen (O7) in Figure 1b could be protonated with the formation of hydrogen bonding among O7, H, and O5. The distance of O7−O5 is 2.624 Å, and this also supports the formation of hydrogen bonding to stabilize the framework. In the assembled structure of **1** (Figure 1c), zigzag Ba−O chains run parallel to the *a* axis and the BTB ligands lie on the *bc* plane. The adjacent distance of BTB ligands is 3.8 Å with weak π−π interaction. The stacked HBTB ligands align in an ABAB fashion, and each HBTB plane is offset. Because of the mutual stacking of HBTB ligands and the C_3 symmetry of the ligand, the 1D channels along the *a* axis are distorted honeycombs. There were no other guest-accessible spaces in directions perpendicular to the *c* axis. The pore dimension of the honeycomb channel is estimated as 8 × 13 Å^2, and because of the offset of each HBTB ligand, the shape of channel is undulating (Figure 1d) and coordinating DMF molecules to the Ba^{2+} ions are directed toward the pore interior. The guest-accessible void volume, as calculated by *PLATON* software, is 46%, and this value is comparable to that of MIL-103 (49%).[15]

Powder X-ray diffraction (PXRD) of **1**(DMF)⊃DMF and a comparison with simulations show that the sample produced is phase pure (Figure 2). Its XRD pattern is unchanged upon prolonged storage (at least 6 months) in a sealed vial stored at ambient conditions. Upon degassing at 200 °C (temperature used for activation prior to gas adsorption experiments), the XRD pattern is slightly shifted to a larger 2θ angle, indicating a slight contraction of the unit cell, but is largely unchanged, demonstrating that **1** maintains its crystallinity upon evacuation However, the crystallinity of **1** decreased upon prolonged exposure to moist air.

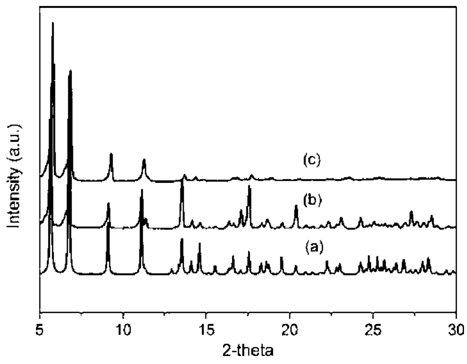

Figure 2. PXRD of (a) **1** as simulated from single-crystal XRD data, (b) as-synthesized **1**(DMF)⊃DMF, and (c) **1** upon degassing at 200 °C overnight.

Thermogravimetric analysis (TGA) was measured for **1**(DMF)⊃DMF under flowing N_2 (Figure S2 in the Supporting Information). Coordination-free guest molecules that are accommodated during the handling of the sample are released below 100 °C, and the coordinated DMF molecules are removed from 140 to 180 °C to form guest-free phase **1**. The expected loss of weight for the release of three DMF molecules and one water molecule per formula unit of **1**(DMF)⊃DMF is 29.2%, which is in agreement with the observed value of 28.1%. The onset of decomposition is around 350 °C; thus, **1** possesses good thermal stability.

1(DMF)⊃DMF was degassed by heating under vacuum at 200 °C overnight to afford **1**. From TGA, under these conditions, all DMF (bound to Ba or in the pores) molecules are removed. The porosity of **1** was unambiguously ascertained from a type I isotherm using N_2 at 77 K (Figure 3a). The N_2 Langmuir surface area is 879 m^2g^{-1} with a pore (Gurvitch) volume of 0.32 mL g^{-1}. CO_2 adsorption at 195 K (Figure 3b) also confirmed robust porosity via a reversible isotherm, which is slightly stepped, indicating possible interaction of CO_2 with the unsaturated Ba^{2+} centers. When the temperature of adsorption was increased to 298 K (Figure 3d), no pronounced curvature was observed at low partial pressures, suggesting no strong interactions between the unsaturated Ba^{2+} metal sites and CO_2. The isosteric heat of adsorption was calculated to be ~28 kJ mol^{-1} by the virial equation (Figure S3 in the Supporting Information). This relatively low value is probably because an unsaturated eight-coordinated Ba^{2+} metal site with low charge density does not interact with CO_2 strongly at room temperature. However, the effect of the unsaturated metal site could be observed for MeOH adsorption of **1** at 298 K (Figure 3c). A two-step profile was obtained with the first plateau at 55 mL g^{-1} of MeOH, which corresponds to 1.4 MeOH molecules per unsaturated Ba center. This is further substantiated by the initial sharp uptake of the adsorption isotherm, suggestive of significant heats of adsorption.

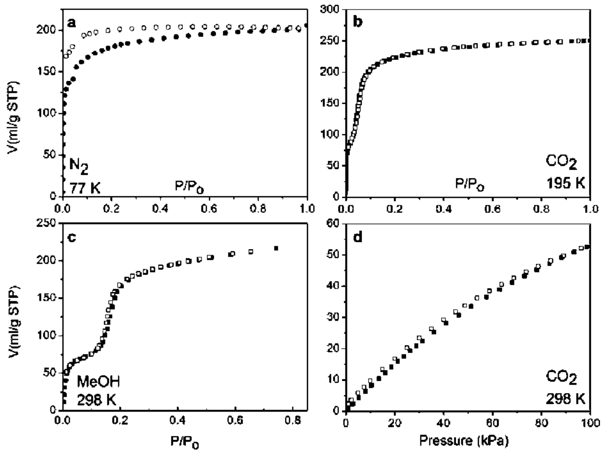

Figure 3. Adsorption/desorption isotherms of **1** with (a) N_2 at 77 K, (b) CO_2 at 195 K, (c) MeOH at 298 K, and (d) CO_2 at 298 K.

In summary, we have synthesized a permanent microporous framework with barium, the last stable member of the alkaline-earth metals by the appropriate choice of bulky carboxylate ligands. **1** remains unequivocally porous after evacuation, as demonstrated by gas adsorption measurements. It contains unsaturated Ba sites when fully degassed and demonstrates preferable affinity for polar molecules such as MeOH at room temperature.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic file (CIF), experimental details, crystallographic data, IR, TGA, and CO_2 gas adsorption isotherms of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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