Synthesis and Hydrogen Storage Properties of Be₁₂(OH)₁₂(1,3,5-benzenetribenzoate)₄

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Owing to their convenient modular synthesis and high surface areas, metal−organic frameworks have come under intense recent scrutiny for potential applications in gas storage.[1] The dense storage of hydrogen for use in fuel cell vehicles presents a particularly difficult challenge as a consequence of its high fugacity, which has prompted development of insulated pressure tanks for cryogenic storage.[2] For an adsorbent within such a system, $Zn_4O(1,4\text{-benzenedicarboxylate})_3$ (MOF-5) offers the best known hydrogen storage properties, exhibiting a total uptake of 10 wt % and 66 g/L at 77 K and 100 bar.[3] One possible means of improving the gravimetric capacity for this type of material would be to replace the typically di- or trivalent transition metal centers with light main group ions such as Be^{2+}, B^{3+}, Mg^{2+}, or Al^{3+}.[4] For example, substitution of the lightest divalent metal, Be^{2+}, for the Zn^{2+} ions in MOF-5 would be expected to result in a roughly 40% increase in both surface area and gravimetric hydrogen storage capacity.[5,6] Although early experiments involving addition of dicarboxylate bridging ligands to beryllium-containing solutions were recognized as leading to three-dimensional polymeric solids (i.e., metal−organic frameworks),[7] the isolation of such materials as pure, crystalline phases has proven elusive. Herein, we report the synthesis and hydrogen storage properties of the first structurally characterized metal−organic framework based upon beryllium: $Be_{12}(OH)_{12}(1,3,5\text{-benzenetribenzoate})_4$ (**1**).

The solvated form of compound **1** was obtained as colorless block-shaped crystals by heating a solution of beryllium nitrate and 1,3,5-benzenetribenzoic acid (H_3BTB) in a mixture of DMSO, DMF, and water at 130 °C for an extended period of 10 days. X-ray analysis of an evacuated single crystal revealed a highly porous network structure consisting of $[Be_{12}(OH)_{12}]^{12+}$ rings connected through the tritopic BTB^{3-} ligands (see Figure 1). The saddle-shaped ring units are composed of tetrahedrally coordinated Be^{2+} ions linked around the inside edge via bridging hydroxide anions and around the periphery via bridging benzoate groups. These rings are observed every 27 Å along the [001] direction in the structure and reside on a $\bar{4}$ symmetry site. Each benzoate group is disposed ∼90° to its neighboring benzoate groups, alternating in an up and down fashion around the ring. To the best of our knowledge, this 12-metal ring structure is without precedent in beryllium chemistry, or indeed in any other metal-carboxylate chemistry.

The overall network structure of **1** consists of an unprecedented 3,12 net, in which 12-connected $[Be_{12}(OH)_{12}]^{12+}$ ring nodes are linked through 3-connected BTB^{3-} ligand nodes. The resulting framework contains large pear-shaped cavities that are ∼27 Å along their long axis and 21 Å in diameter at the widest portion of their base. These pores can be accessed through three different types of openings:
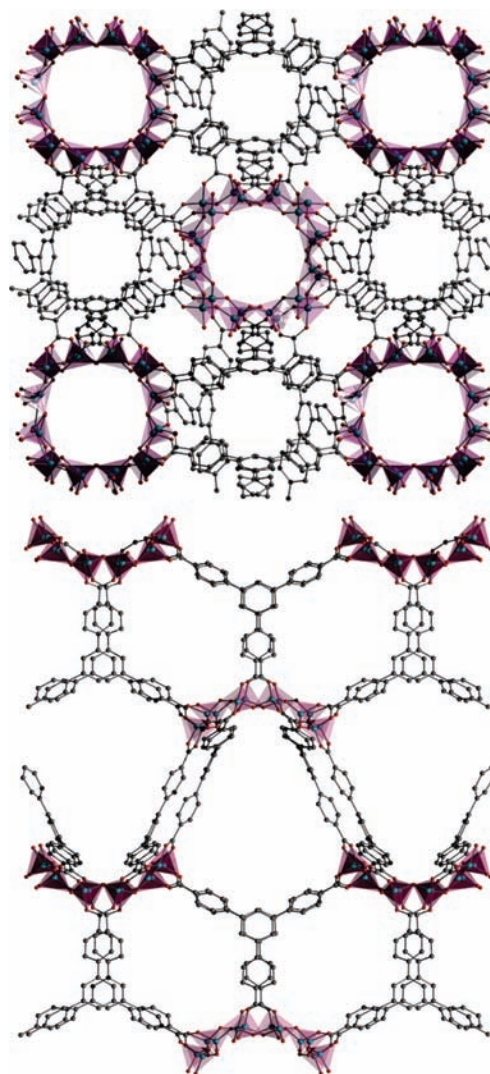

Figure 1. A portion of the crystal structure of $Be_{12}(OH)_{12}(BTB)_4$ (**1**), as viewed down the [001] (upper) and [010] (lower) directions. Turquoise, gray, and red spheres represent Be, C, and O atoms, respectively, while purple tetrahedra highlight the BeO_4 units; H atoms are omitted for clarity. Crystal data: $P\bar{4}c2$, $a = 24.3013(9)$ Å, $c = 54.570(3)$ Å. Selected interatomic distances (Å) and angles (deg): $Be-O_{OH}$ 1.485(3)−1.662(2), $Be-O_{BTB}$ 1.561(2)−1.721(2), $Be-O_{OH}-Be$ 114.7(1)−123.9(1), $O_{OH}-Be-O_{BTB}$ 105.0(1)−117.1(1), $O_{BTB}-Be-O_{BTB}$ 101.6(1)−107.7(2), $Be-O-C$ 122.4(1)−129.8(1).

$[Be_{12}(OH)_{12}]^{12+}$ rings with a diameter of ca. 6 Å (based on van der Waals radii), 7 Å wide hexagonal rings formed by two BTB^{3-} ligands and two $[Be_2(OH)]^{3+}$ segments, and larger 14 × 9 Å² arrowhead-shaped rings involving three BTB^{3-} ligands, two Be^{2+} ions, and a

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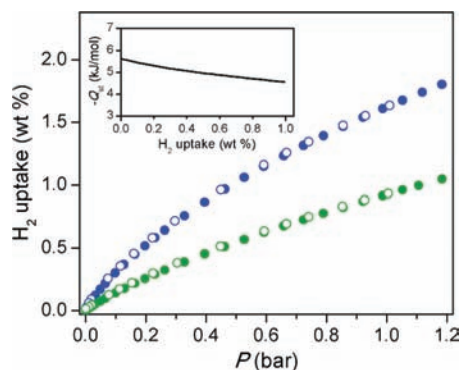∥ General Motors Company.

Figure 2. Low-pressure region of the H₂ adsorption isotherms of **1** recorded at 77 K (blue) and 87 K (green), with filled and open symbols representing adsorption and desorption data, respectively. Inset: Isosteric heat of H₂ adsorption for **1** calculated using the adsorption data.

$[Be_2(OH)]^{3+}$ segment. The solvent-accessible volume calculated from the crystal structure using the PLATON routine[8] is 77%, highlighting the extremely porous nature of the framework.

Low-pressure N₂ adsorption measurements performed on **1** at 77 K afforded a type I isotherm characteristic of a microporous solid. Fits to the data gave a BET surface area of 4030 m²/g and a Langmuir surface area of 4400 m²/g. These values lie slightly above the accessible surface area of 3600 m²/g calculated from the crystal structure,[9] indicating complete evacuation of the pores. Although the BET surface area of **1** exceeds the 3800 m²/g observed for MOF-5, it is still somewhat below that obtained for $Zn_4O(BTB)_2$ (MOF-177; 4750 m²/g)[1e] and at least two other frameworks with larger pore openings.[1i,10] Nevertheless, it represents the highest value yet reported for a main group metal−organic framework or covalent organic framework.

The low-pressure H₂ adsorption isotherms for **1** at 77 and 87 K are shown in Figure 2. The total H₂ uptake of 1.6 wt % at 77 K and 1 bar is completely reversible, and the gradual rise of the isotherm indicates a small adsorption enthalpy. Indeed, a fit to the data yields an initial isosteric heat of adsorption of −5.5 kJ/mol, which gradually increases with loading. Hence, the $[Be_{12}(OH)_{12}]^{12+}$ rings do not serve as strong binding sites for H₂, resulting in a flat adsorption profile. Note that this behavior is actually favorable for a cryogenic storage material, since operation of the fuel cell at pressures above 1.5 bar means that H₂ retained at lower pressures would not ordinarily be utilized.

Consistent with its high surface area, compound **1** shows excellent performance as a hydrogen storage material at higher pressures (see Figure 3). At 77 K, the excess H₂ uptake reaches a maximum of 6.0 wt % at 20 bar, while the total uptake climbs to 9.2 wt % and 43 g/L at 100 bar. Although these capacities are among the highest recorded to date for a metal−organic framework,[1j] the volumetric storage density is still considerably below the 66 g/L achieved in MOF-5.[3] This is due to the larger pores of **1**, wherein a significant amount of H₂ gas can reside far from the influence of the framework walls. Interestingly, while the H₂ storage capacity is dramatically reduced at 298 K, reaching 2.3 wt % and 11 g/L at 95 bar, the combined values are arguably better than those of any other metal−organic framework. To our knowledge, only $Mn_3[(Mn_4Cl)_3(BTT)_8(MeOH)_{10}]_2$ (BTT³⁻ = 1,3,5-benzenetristetrazolate), which possesses open metal coordination sites, has a higher volumetric capacity of 12 g/L at 90 bar and 298 K, although its gravimetric uptake is just 1.5 wt %.[11] Here, the relatively good performance of **1** is likely a consequence of its structure, which contains many rings near the 7 Å diameter calculated as ideal for achieving a high storage density at 298 K.[12]

The foregoing results demonstrate reaction conditions under which the first pure, crystalline beryllium-based metal−organic framework could be isolated. It is likely that similar conditions may now supply
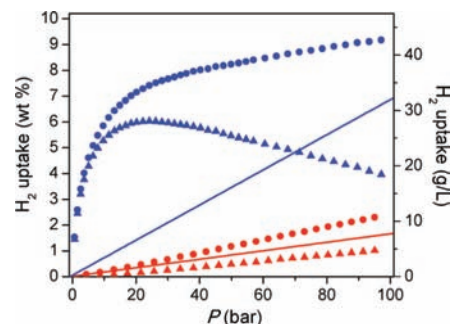

Figure 3. Higher-pressure H₂ uptake in **1** measured at 77 K (blue) and 298 K (red). Triangles and circles represent excess and total H₂ uptake, respectively, while the solid lines show the density of pure H₂.

a range of new beryllium-based frameworks exhibiting exceptionally high surface areas. In particular, the use of 1,4-benzenedicarboxylate as a linker can be expected to afford frameworks with pore sizes near the 10 Å diameter sought for high-density hydrogen storage at cryogenic temperatures.[12] In addition, efforts are underway to functionalize the surfaces within **1** via substitution of the bridging hydroxide ligand protons.

Supporting Information Available: Full experimental details (PDF); an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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