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Synthesis and Hydrogen Storage Properties of  
 $\text{Be}_{12}(\text{OH})_{12}(1,3,5\text{-benzenetribenzoate})_4$ Kenji Sumida,<sup>†</sup> Matthew R. Hill,<sup>\*,‡,§</sup> Satoshi Horike,<sup>†</sup> Anne Dailly,<sup>||</sup> and Jeffrey R. Long<sup>\*,†</sup>

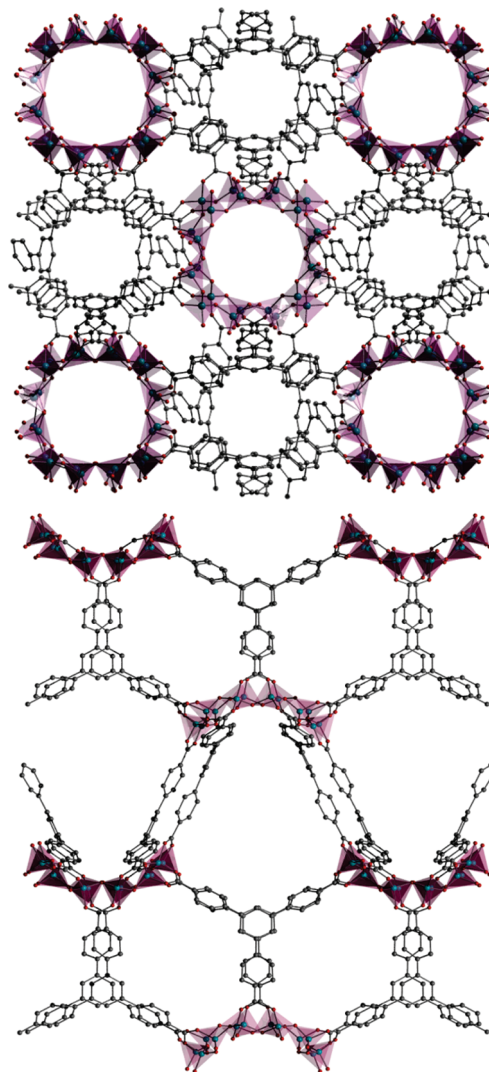
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Owing to their convenient modular synthesis and high surface areas, metal–organic frameworks have come under intense recent scrutiny for potential applications in gas storage.<sup>1</sup> The dense storage of hydrogen for use in fuel cell vehicles presents a particularly difficult challenge as a consequence of its high fugacity, which has prompted development of insulated pressure tanks for cryogenic storage.<sup>2</sup> For an adsorbent within such a system,  $\text{Zn}_4\text{O}(1,4\text{-benzenedicarboxylate})_3$  (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.<sup>3</sup> 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  $\text{Be}^{2+}$ ,  $\text{B}^{3+}$ ,  $\text{Mg}^{2+}$ , or  $\text{Al}^{3+}$ .<sup>4</sup> For example, substitution of the lightest divalent metal,  $\text{Be}^{2+}$ , for the  $\text{Zn}^{2+}$  ions in MOF-5 would be expected to result in a roughly 40% increase in both surface area and gravimetric hydrogen storage capacity.<sup>5,6</sup> 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),<sup>7</sup> 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:  $\text{Be}_{12}(\text{OH})_{12}(1,3,5\text{-benzenetribenzoate})_4$  (**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 ( $\text{H}_3\text{BTB}$ ) 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  $[\text{Be}_{12}(\text{OH})_{12}]^{12+}$  rings connected through the tritopic  $\text{BTB}^{3-}$  ligands (see Figure 1). The saddle-shaped ring units are composed of tetrahedrally coordinated  $\text{Be}^{2+}$  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  $\sim 90^\circ$  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.

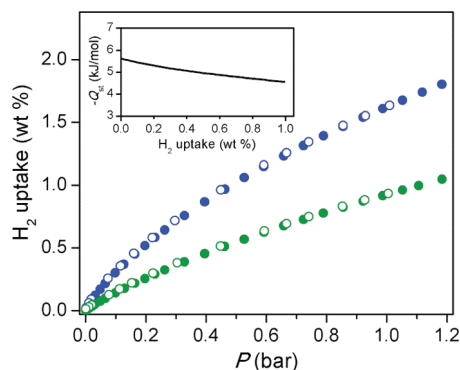
The overall network structure of **1** consists of an unprecedented 3,12 net, in which 12-connected  $[\text{Be}_{12}(\text{OH})_{12}]^{12+}$  ring nodes are linked through 3-connected  $\text{BTB}^{3-}$  ligand nodes. The resulting framework contains large pear-shaped cavities that are  $\sim 27$  Å 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  $\text{Be}_{12}(\text{OH})_{12}(\text{BTB})_4$  (**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  $\text{BeO}_4$  units; H atoms are omitted for clarity. Crystal data:  $P4c2$ ,  $a = 24.3013(9)$  Å,  $c = 54.570(3)$  Å. Selected interatomic distances (Å) and angles (deg):  $\text{Be}-\text{O}_{\text{OH}}$  1.485(3)–1.662(2),  $\text{Be}-\text{O}_{\text{BTB}}$  1.561(2)–1.721(2),  $\text{Be}-\text{O}_{\text{OH}}-\text{Be}$  114.7(1)–123.9(1),  $\text{O}_{\text{OH}}-\text{Be}-\text{O}_{\text{BTB}}$  105.0(1)–117.1(1),  $\text{O}_{\text{BTB}}-\text{Be}-\text{O}_{\text{BTB}}$  101.6(1)–107.7(2),  $\text{Be}-\text{O}-\text{C}$  122.4(1)–129.8(1).

$[\text{Be}_{12}(\text{OH})_{12}]^{12+}$  rings with a diameter of ca. 6 Å (based on van der Waals radii), 7 Å wide hexagonal rings formed by two  $\text{BTB}^{3-}$  ligands and two  $[\text{Be}_2(\text{OH})]^{3+}$  segments, and larger  $14 \times 9$  Å<sup>2</sup> arrowhead-shaped rings involving three  $\text{BTB}^{3-}$  ligands, two  $\text{Be}^{2+}$  ions, and a

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**Figure 2.** Low-pressure region of the  $\text{H}_2$  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  $\text{H}_2$  adsorption for **1** calculated using the adsorption data.

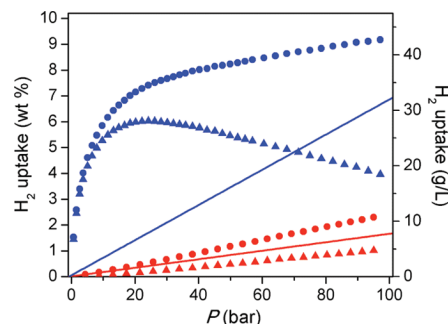
$[\text{Be}_2(\text{OH})]^{3+}$  segment. The solvent-accessible volume calculated from the crystal structure using the PLATON routine<sup>8</sup> is 77%, highlighting the extremely porous nature of the framework.

Low-pressure  $\text{N}_2$  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  $\text{m}^2/\text{g}$  and a Langmuir surface area of 4400  $\text{m}^2/\text{g}$ . These values lie slightly above the accessible surface area of 3600  $\text{m}^2/\text{g}$  calculated from the crystal structure,<sup>9</sup> indicating complete evacuation of the pores. Although the BET surface area of **1** exceeds the 3800  $\text{m}^2/\text{g}$  observed for MOF-5, it is still somewhat below that obtained for  $\text{Zn}_4\text{O}(\text{BTB})_2$  (MOF-177; 4750  $\text{m}^2/\text{g}$ )<sup>1e</sup> and at least two other frameworks with larger pore openings.<sup>1i,10</sup> Nevertheless, it represents the highest value yet reported for a main group metal–organic framework or covalent organic framework.

The low-pressure  $\text{H}_2$  adsorption isotherms for **1** at 77 and 87 K are shown in Figure 2. The total  $\text{H}_2$  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  $[\text{Be}_{12}(\text{OH})_{12}]^{2+}$  rings do not serve as strong binding sites for  $\text{H}_2$ , 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  $\text{H}_2$  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  $\text{H}_2$  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,<sup>1j</sup> the volumetric storage density is still considerably below the 66 g/L achieved in MOF-5.<sup>3</sup> This is due to the larger pores of **1**, wherein a significant amount of  $\text{H}_2$  gas can reside far from the influence of the framework walls. Interestingly, while the  $\text{H}_2$  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  $\text{Mn}_3[(\text{Mn}_4\text{Cl})_3(\text{BTT})_8(\text{MeOH})_{10}]_2$  ( $\text{BTT}^{3-} = 1,3,5$ -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 %.<sup>11</sup> 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.<sup>12</sup>

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  $\text{H}_2$  uptake in **1** measured at 77 K (blue) and 298 K (red). Triangles and circles represent excess and total  $\text{H}_2$  uptake, respectively, while the solid lines show the density of pure  $\text{H}_2$ .

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.<sup>12</sup> In addition, efforts are underway to functionalize the surfaces within **1** via substitution of the bridging hydroxide ligand protons.

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**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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