

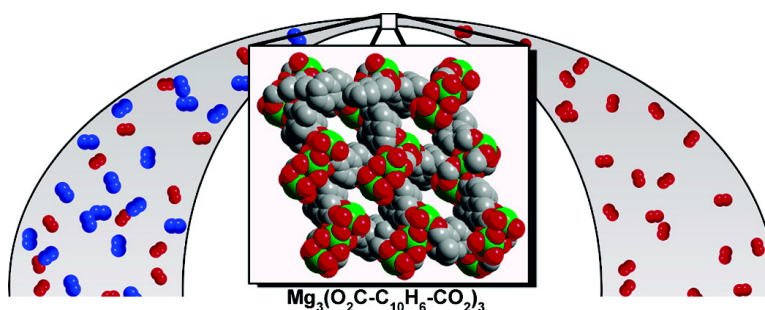
Communication

**Strong H Binding and Selective Gas Adsorption within  
 the Microporous Coordination Solid Mg(OC-CH-CO)**

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## Strong H<sub>2</sub> Binding and Selective Gas Adsorption within the Microporous Coordination Solid Mg<sub>3</sub>(O<sub>2</sub>C-C<sub>10</sub>H<sub>6</sub>-CO<sub>2</sub>)<sub>3</sub>

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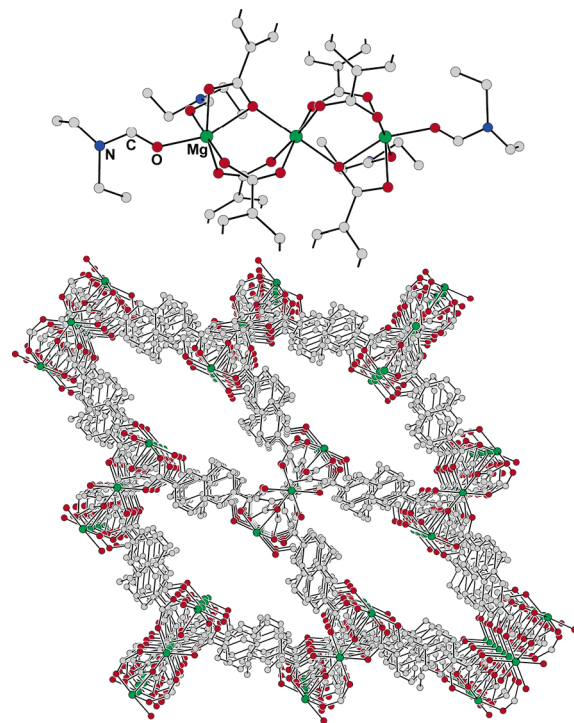
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A possible transition from hydrocarbons to hydrogen as the fuel of choice in mobile applications relies in part on the development of a viable hydrogen storage system.<sup>1</sup> As a consequence, chemical hydrides,<sup>2</sup> metal hydrides,<sup>3</sup> and nanostructured carbon<sup>4</sup> continue to be investigated as potential H<sub>2</sub> storage materials. Recently, it was realized that microporous metal–organic frameworks are also promising candidates for storing hydrogen.<sup>5</sup> In particular, cubic frameworks consisting of tetrahedral [Zn<sub>4</sub>O]<sup>6+</sup> units linked by linear aryldicarboxylates were demonstrated to adsorb reversibly up to 1.6 wt % H<sub>2</sub> at 77 K and 1 atm.<sup>5c</sup> This work was followed by reports of significant hydrogen uptake in other microporous frameworks, wherein Mn<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, or Zn<sup>2+</sup> ions are connected through rigid organic bridging units.<sup>6</sup> Obviously, the hydrogen storage capacities of these materials might improve significantly if the transition metal ions could be replaced with a lighter, main group ion of similar radius, such as Mg<sup>2+</sup>. Herein, we report the synthesis of the first magnesium-based metal–organic framework, which is indeed structurally analogous to a zinc-containing framework. Upon desolvation, the new compound displays an exceptionally high H<sub>2</sub> adsorption enthalpy and, unexpectedly, selective uptake of H<sub>2</sub> or O<sub>2</sub> over N<sub>2</sub> or CO.

Incorporation of Mg<sup>2+</sup> ions into an aryldicarboxylate-bridged framework was accomplished under conditions approximating those employed previously in generating Zn<sup>2+</sup> ion-containing frameworks.<sup>7</sup> Heating an *N,N*-diethylformamide (DEF) solution of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 2,6-naphthalenedicarboxylic acid (H<sub>2</sub>NDC) at 105 °C for 24 h afforded Mg<sub>3</sub>(NDC)<sub>3</sub>(DEF)<sub>4</sub> (**1**) as colorless block-shaped crystals.<sup>8</sup> A similar reaction utilizing Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in a mixture of methanol and DMF produced Zn<sub>3</sub>(NDC)<sub>3</sub>(CH<sub>3</sub>OH)<sub>2</sub>·2DMF·H<sub>2</sub>O (**2**).

X-ray analysis<sup>9</sup> of a single crystal of **1** revealed a structure in which linear Mg<sub>3</sub> units are linked via naphthalenedicarboxylate bridges to form a neutral, three-dimensional framework (see Figure 1). The Mg<sub>3</sub> units consist of a central Mg<sup>2+</sup> ion coordinated octahedrally by six carboxylate oxygen atoms, and two outer Mg<sup>2+</sup> ions, each coordinated by four carboxylate oxygen atoms and two DEF molecules in a distorted octahedral geometry. Note that trinuclear moieties of this type have been observed previously as discrete molecular complexes of formula Mg<sub>3</sub>(O<sub>2</sub>CR)<sub>6</sub>L<sub>4</sub>.<sup>10</sup> In **1**, the Mg<sub>3</sub> units stack along the (101) direction, such that, together with the connecting dicarboxylate ligands of the framework, they define one-dimensional channels in which the DEF molecules reside. An analogous framework is present within the crystal structure of **2**,<sup>9</sup> although here the channels are filled with a mixture of methanol, DMF, and water molecules instead of DEF. Indeed, this structure type appears to be quite general in view of its precedent within the frameworks of Ni<sub>3</sub>(NDC)<sub>3</sub>(Py)<sub>4</sub><sup>11</sup> and Zn<sub>3</sub>(BDC)<sub>3</sub>(CH<sub>3</sub>OH)<sub>4</sub>·2CH<sub>3</sub>OH (BDC = 1,4-benzenedicarboxylate).<sup>12</sup> Thus, Mg<sup>2+</sup> ions are in fact capable of replacing Ni<sup>2+</sup> and Zn<sup>2+</sup> ions within a metal–organic framework.

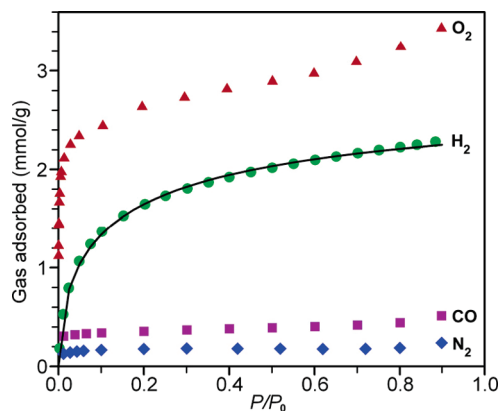
Compound **1** is readily desolvated to generate Mg<sub>3</sub>(NDC)<sub>3</sub>. A thermogravimetric analysis of **1** indicated release of the four bound



**Figure 1.** Portions of the crystal structure of **1**, showing the linear Mg<sub>3</sub> unit (upper) and, upon removing the DEF molecules, the arrangement of channels along the (101) direction (lower). Hydrogen atoms are omitted for clarity.

DEF molecules upon heating in the range 150–200 °C. Accordingly, a preweighed sample of the compound was evacuated by heating at 190 °C under dynamic vacuum, until the outgas rate was less than 1 mTorr/min. The resulting mass loss of 36.3% was very near the 36.1% loss expected upon liberation of four DEF molecules. Subsequent powder X-ray diffraction analysis revealed Mg<sub>3</sub>(NDC)<sub>3</sub> to have a crystal structure different from that of **1**. Significantly, exposure of the solid to DEF converted it back to crystalline **1** (see Figure S2 in the Supporting Information), suggesting that the connectivity of the magnesium–dicarboxylate framework of **1** remains intact upon desolvation. As such, we can expect Mg<sub>3</sub>(NDC)<sub>3</sub> to be a microporous solid featuring coordinatively unsaturated Mg<sup>2+</sup> centers.

The hydrogen storage characteristics of Mg<sub>3</sub>(NDC)<sub>3</sub> were measured using a volumetric gas sorption apparatus. As shown in Figure 2, the H<sub>2</sub> adsorption isotherm at 77 K reveals an uptake of just 2.3 mmol/g (1.7 mol/mol, 0.46 wt %) at 880 Torr. A fit of the Langmuir–Freundlich equation<sup>13</sup> to the data gave a predicted saturation of 3.0 mmol/g (2.2 mol/mol, 0.60 wt %). This represents a rather low storage capacity compared to a number of other metal–organic framework solids,<sup>5,6</sup> and suggests that the pore dimensions in Mg<sub>3</sub>(NDC)<sub>3</sub> are somewhat constricted compared to the framework of **1**. The steepness of the rise in the isotherm, however, indicates a relatively strong H<sub>2</sub> binding interaction. Indeed, by fitting



**Figure 2.** Gas sorption isotherms for the uptake of  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{O}_2$  in  $\text{Mg}_3(\text{NDC})_3$  at 77 K. The solid line represents a Langmuir–Freundlich fit to the  $\text{H}_2$  isotherm.

a second  $\text{H}_2$  adsorption isotherm measured at 87 K and applying a variant of the Clausius–Clapeyron equation, the isosteric heat of adsorption was calculated to lie in the range 7.0–9.5 kJ/mol (see Figure S4). These values are considerably higher than previously reported  $\text{H}_2$  adsorption enthalpies of 4.7–5.2 kJ/mol in  $\text{Zn}_4\text{O}(\text{BDC})_3$  and 5.3–7.4 kJ/mol in the dehydrated Prussian blue analogues  $\text{M}_3\text{–}[\text{Co}(\text{CN})_6]_2$  ( $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ).<sup>14</sup> Consequently,  $\text{Mg}_3(\text{NDC})_3$  can be expected to attain saturation at higher temperatures and lower pressures.<sup>15</sup> The higher binding affinity likely stems in part from the increased van der Waals contact area associated with a very small pore size (as discussed below). Insight into whether interactions with the  $\text{Mg}^{2+}$  centers also contribute will potentially be provided by planned low-temperature, high-pressure infrared spectroscopy experiments.

Unexpectedly, attempts to measure an  $\text{N}_2$  adsorption isotherm for  $\text{Mg}_3(\text{NDC})_3$  at 77 K revealed almost no  $\text{N}_2$  uptake (see Figure 2). In contrast, it was found that significant quantities of  $\text{O}_2$  are adsorbed, and fitting the BET equation to the resulting isotherm gave an estimated surface area of 190  $\text{m}^2/\text{g}$ . Notably, the monolayer coverages predicted by fitting the Langmuir equation to the  $\text{O}_2$  and  $\text{H}_2$  isotherms were nearly identical (2.25 and 2.30 mmol/g, respectively), suggesting that the same number of binding sites are accessible in each case. To our knowledge, preferential adsorption of  $\text{H}_2$  over  $\text{N}_2$  by a coordination solid has been observed previously only in  $\text{Mn}(\text{HCO}_2)_2$ ,<sup>6a</sup> while selective adsorption of  $\text{O}_2$  over  $\text{N}_2$  has never been demonstrated in such a material. This behavior is analogous to the molecular sieving effect observed in zeolite 4A, which shows  $\text{O}_2$  adsorption but no  $\text{N}_2$  uptake at 123 K.<sup>16</sup> In view of the kinetic diameters of 3.46 Å for  $\text{O}_2$  and 3.64 Å for  $\text{N}_2$ ,<sup>17</sup> it was concluded that zeolite 4A has pore openings of ca. 3.6 Å. Similarly, assuming that the framework structure does not change upon gas adsorption, it can be inferred that the pore openings in  $\text{Mg}_3(\text{NDC})_3$  are between 3.46 and 3.64 Å in diameter. As a simple test of this hypothesis, a  $\text{CO}$  adsorption isotherm was measured (see Figure 2). Only a very small amount of  $\text{CO}$  was adsorbed, consistent with prohibited access to the pores due to its larger kinetic diameter of 3.76 Å.<sup>17,18</sup>

The selective adsorption behavior demonstrated by the isotherms depicted in Figure 2 indicates that  $\text{Mg}_3(\text{NDC})_3$  may be of utility in performing certain gas separations. Most remarkably, it could potentially be used for the separation of  $\text{N}_2$  and  $\text{O}_2$  from air, a process currently performed on a scale of billions of tons per year in the United States alone. Similarly,  $\text{Mg}_3(\text{NDC})_3$  could perhaps play a role in the separation of  $\text{H}_2$  from  $\text{CO}$  for fuel cell applications, and in  $\text{H}_2$  enrichment of the  $\text{N}_2/\text{H}_2$  exhaust mixture resulting from ammonia synthesis.<sup>19</sup> Further experiments employing a gas flow

apparatus are necessary, however, for directly testing the efficacy of such separations.

The foregoing results demonstrate the utility of  $\text{Mg}^{2+}$  ions in producing lightweight metal–organic frameworks with sustainable porosity and potential applications in the storage and separation of gases with low liquefaction points. Future work will focus on the incorporation of  $\text{Mg}^{2+}$  ions into more open framework structures, and on the extension of this approach to other light main group cations, such as  $\text{Li}^+$ ,  $\text{B}^{3+}$ , and  $\text{Al}^{3+}$ .

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**Supporting Information Available:** Detailed experimental procedures for the syntheses of **1** and **2**, the method used to calculate the  $\text{H}_2$  adsorption enthalpy, powder X-ray diffraction patterns, and thermogravimetric analysis plots (PDF); X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353–358 and references therein.
- Schüth, F.; Bogdanovic, B.; Felderhoff, M. *Chem. Commun.* **2004**, 2249–2258.
- (a) Sandrock, G.; Gross, K.; Thomas, G.; Jensen, C.; Meeker, D.; Takara, S. *J. Alloys Compd.* **2002**, *330*, 696–701. (b) Bogdanovic, B.; Felderhoff, M.; Kaskel, S.; Pommerin, A.; Schlichte, K.; Schüth, F. *Adv. Mater.* **2003**, *15*, 1012–1015.
- (a) Ding, R. G.; Finnerty, J. J.; Zhu, Z. H.; Yan, Z. F.; Lu, G. Q. *Encycl. Nanosci. Nanotechnol.* **2004**, *4*, 13–33. (b) Züttel, A.; Orimo, S. *MRS Bull.* **2002**, *27*, 705–711.
- (a) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O’Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127–1129. (b) Ferey, G.; Latroche, M.; Serre, C.; Millange, F.; Loiseau, T.; Percheron-Guegan, A. *Chem. Commun.* **2003**, 2976–2977. (c) Rowsell, J. L.; Millward, A. R.; Park, K. S.; Yaghi, O. M. *J. Am. Chem. Soc.* **2004**, *126*, 5666–5667.
- (a) Dybtsev, D. N.; Chun, H.; Yoon, S. H.; Kim, D.; Kim, K. *J. Am. Chem. Soc.* **2004**, *126*, 32–33. (b) Pan, L.; Sander, M. B.; Huang, X.; Li, J.; Smith, M.; Bittner, E.; Bockrath, B.; Johnson, J. K. *J. Am. Chem. Soc.* **2004**, *126*, 1308–1309. (c) Lee, E. Y.; Suh, M. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 2798–2801. (d) Zhao, X.; Xiao, B.; Fletcher, A. J.; Thomas, K. M.; Bradshaw, D.; Rosseinsky, M. J. *Science* **2004**, *306*, 1012–1015. (e) Dybtsev, D. N.; Chun, H.; Kim, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5033–5036. (f) Kesanli, B.; Cui, Y.; Smith, M. R.; Bittner, E. W.; Bockrath, B. C.; Lin, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 72–75. (g) Kubota, Y.; Takata, M.; Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kato, K.; Sakata, M.; Kobayashi, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 920–923.
- Yaghi, O. M.; Eddaoudi, M.; Li, H.; Kim, J.; Rosi, N. U.S. Patent Appl. 2003/0004364.
- Characterization of **1**. IR:  $\nu_{\text{C=O}}$  1648 (s), 1615 (s), 1538 (s), 1428 (m), 1399 (vs), 1359 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{56}\text{H}_{66}\text{Mg}_3\text{N}_4\text{O}_{18}$  ( $\text{1-2H}_2\text{O}$ ): C, 58.18; H, 5.75; N, 4.85. Found: C, 58.51; H, 5.55; N, 4.88.
- Crystal and structure refinement parameters for **1**:  $\text{C}_{56}\text{H}_{66}\text{Mg}_3\text{N}_4\text{O}_{16}$ ,  $T = 129$  K,  $C2/c$ ,  $Z = 4$ ,  $a = 15.045(4)$  Å,  $b = 18.036(5)$  Å,  $c = 20.979(5)$  Å,  $\beta = 101.493(4)^\circ$ ,  $V = 5578(2)$  Å<sup>3</sup>,  $R_1 = 0.0821$ ,  $wR_2 = 0.1859$ . For **2**:  $\text{C}_{44}\text{H}_{38}\text{N}_2\text{O}_{17}\text{Zn}_3$ ,  $T = 133$  K,  $P1$ ,  $Z = 1$ ,  $a = 10.327(3)$  Å,  $b = 11.067(6)$  Å,  $c = 11.692(10)$  Å,  $\alpha = 112.33(5)^\circ$ ,  $\beta = 97.31(6)^\circ$ ,  $\gamma = 106.79(4)^\circ$ ,  $V = 1140.2(12)$  Å<sup>3</sup>,  $R_1 = 0.0364$ ,  $wR_2 = 0.0936$ .
- (a) Yang, K. C.; Chang, C. C.; Yeh, C. S.; Lee, G. H.; Yang, Y. *Organometallics* **2002**, *21*, 1296–1299. (b) Coker, E. N.; Boyle, T. J.; Rodriguez, M. A.; Alam, T. M. *Polyhedron* **2004**, *23*, 1739–1747.
- Kongshaug, K. O.; Fjellvåg, H. *Solid State Sci.* **2003**, *5*, 303–310.
- Li, H.; Davis, C. E.; Groy, T. L.; Kelley, D. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 2186–2187.
- Yang, R. T. *Gas Separation by Adsorption Processes*; Butterworth: Boston, 1997.
- Kaye, S. S.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 6506–6507.
- Ideally, for saturation at 298 K and 1 atm, one would like to achieve an adsorption enthalpy of  $\Delta H_{\text{ads}} = 38.9$  kJ/mol. This value was calculated assuming no activation barrier for  $\text{H}_2$  adsorption, such that at equilibrium  $\Delta H_{\text{ads}} = T\Delta S^\circ$ , where  $S^\circ$  is the standard  $\text{H}_2$  formation entropy of 130.68 J/mol·K (Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere Publ. Co.: New York, 1989).
- Breck, D. W.; Eversole, W. G.; Milton, R. M.; Reed, T. B.; Thomas, T. L. *J. Am. Chem. Soc.* **1956**, *78*, 5963–5971.
- Breck, D. W. *Zeolite Molecular Sieves*; Wiley & Sons: New York, 1974.
- Note that the higher  $\text{CO}$  uptake relative to  $\text{N}_2$  may be attributed to a stronger electrostatic interaction of the  $\text{CO}$  dipole with the external surface of the particles.
- Yang, R. T. *Adsorbents: Fundamentals and Applications*; Wiley & Sons: Hoboken, NJ, 2003.

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