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. As a consequence, chemical hydrides, metal hydrides, and nanostructured carbon continue to be investigated as potential H2 storage materials. Recently, it was realized that microporous metal–organic frameworks are also promising candidates for storing hydrogen. In particular, cubic frameworks consisting of tetrahedral [Zn4O]6+ units linked by linear aromatic dicarboxylate bridges were demonstrated to adsorb reversibly up to 1.6 wt % H2 at 77 K and 1 atm. This work was followed by reports of significant hydrogen uptake in other microporous frameworks, wherein Mn2+, Ni2+, Cu2+, or Zn2+ ions are connected through rigid organic bridging units. 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 Mg2+. 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 H2 adsorption enthalpy and, unexpectedly, selective uptake of H2 or O2 over N2 or CO.

Incorporation of Mg2+ ions into an aromatic dicarboxylate-bridged framework was accomplished under conditions approximating those employed previously in generating Zn2+ ion-containing frameworks. Heating an N,N-diethylformamide (DEF) solution of Mg(NO3)2·6H2O and 2,6-naphthalenedicarboxylic acid (H2NDC) at 105 °C for 24 h afforded Mg3(NDC)3(DEF)4 (1) as colorless block-shaped crystals. A similar reaction utilizing Zn(NO3)2·6H2O in a mixture of methanol and DMF produced Zn3(NDC)3(CH3OH)2·2DMF·H2O (2).

X-ray analysis of a single crystal of 1 revealed a structure in which linear Mg3 units are linked via naphthalenedicarboxylate bridges to form a neutral, three-dimensional framework (see Figure 1). The Mg3 units consist of a central Mg2+ ion coordinated octahedrally by six carboxylate oxygen atoms, and two outer Mg2+ 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 Mg3(O2CR)2L4. In 1, the Mg3 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, 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 Ni3(NDC)3(Py)3 and Zn3(BDC)3(CH3OH)2·2CH3OH (BDC = 1,4-benzenedicarboxylate). Thus, Mg2+ ions are in fact capable of replacing Ni2+ and Zn2+ ions within a metal–organic framework.

Compound 1 is readily desolvated to generate Mg3(NDC)3. A thermogravimetric analysis of 1 indicated release of the four bound methanol molecules. Subsequent powder X-ray diffraction analysis revealed Mg3(NDC)3 to have a crystal structure different from that of 1, which 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 Mg3(NDC)3, 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 Mg3(NDC)3 to be a microporous solid featuring coordinatively unsaturated Mg2+ centers.

The hydrogen storage characteristics of Mg3(NDC)3 were measured using a volumetric gas sorption apparatus. As shown in Figure 2, the H2 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 to the data gave a predicted saturation of 3.0 mmol/g (2.2 mol/mol, 0.63 wt %). This represents a rather low storage capacity compared to a number of other metal–organic framework solids, and suggests that the pore dimensions in Mg3(NDC)3 are somewhat constricted compared to the framework of 1. The steepness of the rise in the isotherm, however, indicates a relatively strong H2 binding interaction. Indeed, by fitting
a second H₂ 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 H₂ adsorption enthalpies of 4.7–5.2 kJ/mol in Zn₉O(BDC)₆ and 5.3–7.4 kJ/mol in the dehydrated Prussian blue analogues Mg₃[Co(CN)₆]₂ (M = Mn, Fe, Co, Ni, Cu, Zn). Consequently, Mg₃(NDC)₃ can be expected to attain saturation at higher temperatures and lower pressures. The higher binding affinity likely stems in part from the increased van der Waals contact area associated with Mg²⁺ centers also contribute which will potentially be provided by planned low-temperature, high-pressure infrared spectroscopy experiments.

Unexpectedly, attempts to measure an N₂ adsorption isotherm for Mg₆(NDC)₃ at 77 K revealed almost no N₂ uptake (see Figure 2). In contrast, it was found that significant quantities of O₂ were adsorbed, and fitting the BET equation to the resulting isotherm gave an estimated surface area of 190 m²/g. Notably, the monolayer coverages predicted by fitting the Langmuir equation to the O₂ and H₂ 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 H₂ over N₂ by a coordination solid has been observed previously only in Mn(HCO₃)₂,7b while selective adsorption of O₂ over N₂ has never been demonstrated in such a material. This behavior is analogous to the molecular sieving effect observed in zeolite 4A, which shows O₂ adsorption but no N₂ uptake at 123 K.6 In view of the kinetic diameters of 3.46 Å for O₂ and 3.64 Å for N₂,17 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 Mg₆(NDC)₃ are between 3.46 and 3.64 Å in diameter. As a simple test of this hypothesis, a CO adsorption isotherm was measured (see Figure 2). Only a very small amount of CO was adsorbed, consistent with prohibited access to the pores due to its larger kinetic diameter of 3.76 Å.17,18

The selective adsorption behavior demonstrated by the isotherms depicted in Figure 2 indicates that Mg₆(NDC)₃ may be of utility in performing certain gas separations. Most remarkably, it could potentially be used for the separation of N₂ and O₂ from air, a process currently performed on a scale of billions of tons per year in the United States alone. Similarly, Mg₆(NDC)₃ could perhaps play a role in the separation of H₂ from CO for fuel cell applications, and in H₂ enrichment of the N₂/H₂ exhaust mixture resulting from ammonia synthesis.19 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 Mg²⁺ 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 Mg²⁺ ions into more open framework structures, and on the extension of this approach to other light major group cations, such as Li⁺, B³⁺, and Al³⁺.

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Supporting Information Available: Detailed experimental procedures for the syntheses of 1 and 2, the method used to calculate the H₂ 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
(19) Note that the higher CO uptake relative to N₂ may be attributed to a stronger electrostatic interaction of the CO dipole with the external surface of the particles.