Inorganic Chemistry
Communication

Inorg. Chem. **2009**, *48*, 8069–8071 **8069**
DOI: 10.1021/ic901056d

Magnesium-Based 3D Metal–Organic Framework Exhibiting Hydrogen-Sorption Hysteresis

Zhiyong Guo,[†,‡] Guanghua Li,[§] Liang Zhou,[†,‡] Shenqqun Su,[†,‡] Yongqian Lei,[†,‡] Song Dang,[†,‡] and Hongjie Zhang*,[†]

[†]*State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China,* [‡]*Graduate School of the Chinese Academy of Sciences, Beijing, People's Republic of China, and* [§]*State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China*

Received June 2, 2009

A new magnesium metal–organic framework (MOF) based on an asymmetrical ligand, biphenyl-3,4′,5-tricarboxylate (H_3BPT), has been synthesized and structurally characterized. MOF $Mg_3(BPT)_2(H_2O)_4$ (**1**) consists of 1D hexagonal nanotube-like channels and exhibits pronounced hydrogen-sorption hysteresis at medium pressure.

A major technical obstacle to the widespread use of hydrogen as a nonpolluting fuel for automobiles is the lack of a safe and efficient system for on-board storage.[1] Recently, a new class of ordered, three-dimensional (3D) extended solids composed of metal ions and organic linkers, known as metal–organic frameworks (MOFs),[2] has emerged as a promising storage alternative to high-pressure and liquefied hydrogen tanks, metal hydrides, and carbon-based adsorbents.[3] However, for hydrogen physisorption, dihydrogen (H_2) adsorption energy (typically 4–7 kJ/mol) of this type of network is usually very discouraging.

Several strategies have been used to enhance H_2 binding within MOFs, thus increasing hydrogen uptake. First, frameworks with very narrow pores that fit the size of the hydrogen molecule can be constructed.[4] Second, particular attention has been paid to the creation of open metal sites, which has proven to be an effective way of strengthening the MOF–H_2 interaction.[5] In addition, the use of alkaline-earth metals such as lithium and magnesium in porous materials is appealing because they are predicted to have strong binding affinities for the hydrogen molecule.[6] In fact, the construction of porous coordination frameworks with lightweight metal centers has been proven to be very advantageous for gravimetric hydrogen uptake.[7]

Recently, the Matzger group reported a MOF (named UMCM-150) based on an unsymmetrically substituted linker named biphenyl-3,4′,5-tricarboxylate (H_3BPT).[8] H_3BPT is an excellent linker for the area of MOFs because of its multiple coordination sites and unsymmetrical structure. Here we choose magnesium and H_3BPT as our candidates for constructing a novel MOF.

The magnesium complex $Mg_3(BPT)_2(H_2O)_4$ (**1**) was synthesized by the solvothermal reaction of H_3BPT with $Mg(NO_3)_2 \cdot 6H_2O$ in 5:1 *N*,*N*-dimethylformamide (DMF)/H_2O at 120 °C for 48 h. The product was isolated as colorless block crystals of $\mathbf{1} \cdot 2DMF \cdot 3H_2O$ at 72% yield, with the overall formula determined by crystallography,[9] elemental analysis, and thermogravimetric analysis (TGA).

---

*To whom correspondence should be addressed. E-mail: hongjie@ciac.jl.cn. Tel: +86-431-85262127. Fax: +86-431-85698041.

[1] Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353.

[2] (a) Kitagawa, S.; Kitaura, R.; Noro, S.-i. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (b) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276. (c) Ferey, G. *Chem. Soc. Rev.* **2008**, *37*, 191. (d) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319.

[3] (a) Zhao, X.; Xiao, B.; Fletcher, A. J.; Thomas, K. M.; Bradshaw, D.; Rosseinsky, M. J. *Science* **2004**, *306*, 1012. (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. (c) Lin, X.; Jia, J.; Zhao, X.; Thomas, K. M.; Blake, A. J.; Walker, G. S.; Champness, N. R.; Hubberstey, P.; Schroder, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7358. (d) Rowsell, J. L.; Millward, A. R.; Park, K. S.; Yaghi, O. M. *J. Am. Chem. Soc.* **2004**, *126*, 5666. (e) Chen, B. L.; Ma, S. Q.; Zapata, F.; Lobkovsky, E. B.; Yang, J. *Inorg. Chem.* **2006**, *45*, 5718. (f) Dinca, M.; Yu, A. F.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 8904. (g) Sun, D.; Ma, S.; Ke, Y.; Collins, D. J.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 3896. (h) Ma, S.; Sun, D.; Simmons, J. M.; Collier, C. D.; Yuan, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2008**, *130*, 1012. (i) Chun, H.; Dybtsev, D. N.; Kim, H.; Kim, K. *Chem.—Eur. J.* **2005**, *11*, 3521. (j) Farha, O. K.; Spokoyny, A. M.; Mulfort, K. L.; Hawthorne, M. F.; Mirkin, C. A.; Hupp, J. T. *J. Am. Chem. Soc.* **2007**, *129*, 12680.

[4] Dinca, M.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 9376.

[5] (a) Chen, B.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4745. (b) Kaye, S. S.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 6506.

[6] Han, S. S.; Deng, W.-Q.; Goddard, W. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 6289.

[7] (a) Rood, J. A.; Noll, B. C.; Henderson, K. W. *Inorg. Chem.* **2006**, *45*, 5521. (b) Loiseau, T.; Lecroq, L.; Volkringer, C.; Marrot, J.; Ferey, G.; Haouas, M.; Taulelle, F.; Bourrelly, S.; Llewellyn, P. L.; Latroche, M. *J. Am. Chem. Soc.* **2006**, *128*, 10223.

[8] Wong-Foy, A. G.; Lebel, O.; Matzger, A. J. *J. Am. Chem. Soc.* **2007**, *129*, 15740.

[9] X-ray crystal data for **1**: $C_{30}H_{22}Mg_3O_{16}$, $M_r = 711.41$, rhombohedral, $R\bar{3}$, $a = 31.642(5)$ Å, $b = 31.642(5)$ Å, $c = 14.873(3)$ Å, $V = 12896(4)$ Å^3, $Z = 9$, $T = 200$ K, $\rho_{calcd} = 0.824$ g/cm^3, R1 [$I > 2\sigma(I)$] = 0.0553, wR2 = 0.1561, GOF = 0.957. CCDC reference number for **1**: 734381.

© 2009 American Chemical Society

Published on Web 07/31/2009

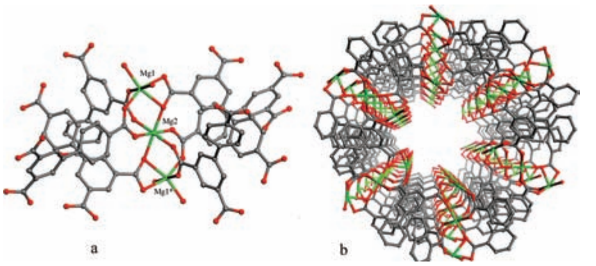

Figure 1. (a) Trinuclear magnesium carboxylate clusters and a representation of the inorganic six-coordinate SBUs in **1**. (b) Network of **1** with a 1D hexagonal nanotube-like channel.

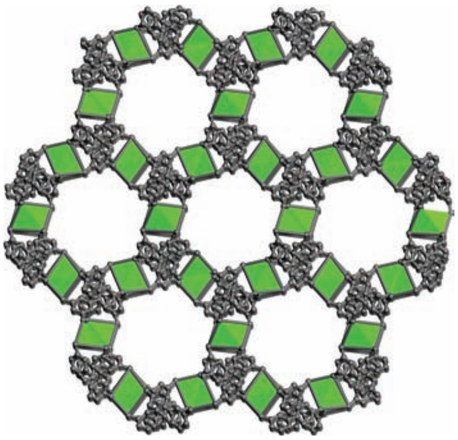

Figure 2. Structure illustrated for **1**, shown from the [001] direction.

A single-crystal X-ray crystallographic study revealed that **1** crystallizes in rhombohedral space group $R\overline{3}$. It adopts a $[Mg_3(\mu_3\text{-}O)_2(\mu_2\text{-}O)_4]$ cluster as its secondary building unit (SBU). It should be noted that the trinuclear SBU is the most important magnesium cluster because the same structural motif was found in all magnesium MOFs with a rigid 3D framework and permanent porosity reported so far.[10] The trinuclear magnesium clusters in **1** are connected by rigid organic linkers (BPT). The BPT ligands in compound **1** adopt two coordination modes that connect six Mg atoms: a bidentate bridging mode and an asymmetric chelating bridging mode. Compound **1** contains two crystallographically independent Mg atoms, as shown in Figure 1a. The central Mg^{2+} cation in each unit lies on an inversion center and is coordinated by six carboxylate O atoms from separate BPT ligands [Mg−O distances range from 2.074(2) to 2.152(3) Å], whereas the terminal Mg^{2+} cations are coordinated by four carboxylate O atoms from three BPT ligands [Mg−O distances range from 1.956(2) to 2.209(1) Å] and two O atoms from aqua ligands.

Every distorted SBU connects with six BPT ligands (Figure 1a), and every BPT connects six SBUs to form a 3D framework (Figure 2). Probably because of the bulkiness of the SBU, no $\pi-\pi$ stacking is allowed in the framework and the structure is noninterpenetrated.[11] It is interesting to note that these Mg_3 SBUs are interconnected through the organic linkers to generate one-dimensional (1D) hexagonal nanotube-like channels of 11.2 Å × 15.0 Å (excluding axial aqua ligands) in the [001] direction (Figure 1b).

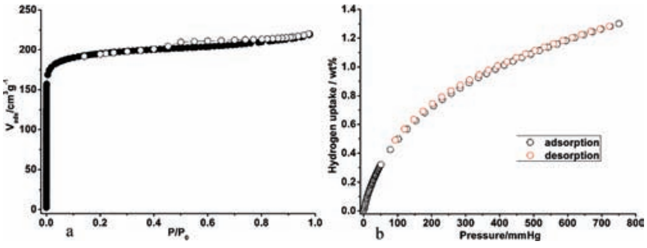

Figure 3. Gas-sorption isotherms (77 K) of **1**: (a) N_2; (b) H_2.

TGA data of **1** show a weight loss of 29.3% in the temperature range of 50—400 °C, corresponding to four coordinated H_2O molecules, three H_2O guest solvent molecules, and two DMF molecules residing in the open channels of **1** (expected 29.85%). It should be noted that **1** is stable up to 350 °C, as evidenced by a comparison of the powder X-ray diffraction (PXRD) patterns collected at temperatures ranging from 100 to 400 °C (see Figures S2 and S3 in the Supporting Information).

PLATON[12] calculations showed that the solvent-accessible volume constitutes ~54% of the total volume of the crystal **1** after being activated. Compound **1** exhibits permanent porosity, which has been confirmed by gas sorption. Prior to gas-sorption experiments, DMF and H_2O guest molecules are removed by solvent exchange.[13] Measured nitrogen adsorption of **1** at 77 K, shown in Figure 3a, displays typical type I sorption behavior. Compound **1** adsorbs 225 cm^3/g of nitrogen at 77 K and 1 atm, corresponding to apparent Brunauer−Emmett−Teller and Langmuir surface areas of 714 and 837 m^2/g, respectively. The average pore size is about 0.98 nm, which is within the limit of the theory pore sizes. The nitrogen adsorption shows very good reversibility.

The hydrogen-sorption isotherm recorded at 77 K under normal pressure shows type I behavior with no hysteresis and no noticeable change in the properties upon repeated cycling. **1** showed an excess gravimetric hydrogen uptake of nearly 1.3 wt % at 1 atm (Figure 3b). Compared with other MOFs with high surface area and high porosity, the H_2 adsorption of this framework is still inspiring. To determine the hydrogen affinity of **1**, a H_2 adsorption isotherm at 87 K was also collected to calculate the heat of adsorption (Figure 4a), and the data were fit using the Langmuir−Freundlich equation.[14] Isosteric adsorption enthalpies as a function of the quantity of hydrogen adsorbed were calculated using a variant of the Clausius−Clapeyron equation.[5b] At low coverage, **1** exhibits a moderately high H_2 adsorption enthalpy of 7.5 kJ/mol (Figure 4b), which is higher than that of MOF-5 (5.2 kJ/mol) and HKUST-1 (6.6 kJ/mol) but is lower than that of MOF-74 (8.3 kJ/mol), IRMOF-11 (9.1 kJ/mol), or PCN-9 (10.1 kJ/mol).[15] The H_2 sorption isotherms at both temperatures show no hysteresis under normal pressure.

The medium-pressure hydrogen storage capability of **1** was evaluated at 308 K. At that temperature, the sorption isotherm of **1** has a type I profile that is saturated at 5 bar

---

[10] Senkovska, I.; Kaskel, S. *Eur. J. Inorg. Chem.* **2006**, 4564.

[11] (a) Xu, X.; Nieuwenhuyzen, M.; James, S. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 764. (b) Reineke, T. M.; Eddaoudi, M.; Moler, D.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 4843.

[12] Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

[13] Rowsell, J. L. C.; Eckert, J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 14904.

[14] Yang, R. T. *Gas Adsorption by Adsorption Processes*; Butterworth: Boston, 1997.

[15] (a) Rowsell, J. L. C.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 1304. (b) Ma, S. Q.; Zhou, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 11734.

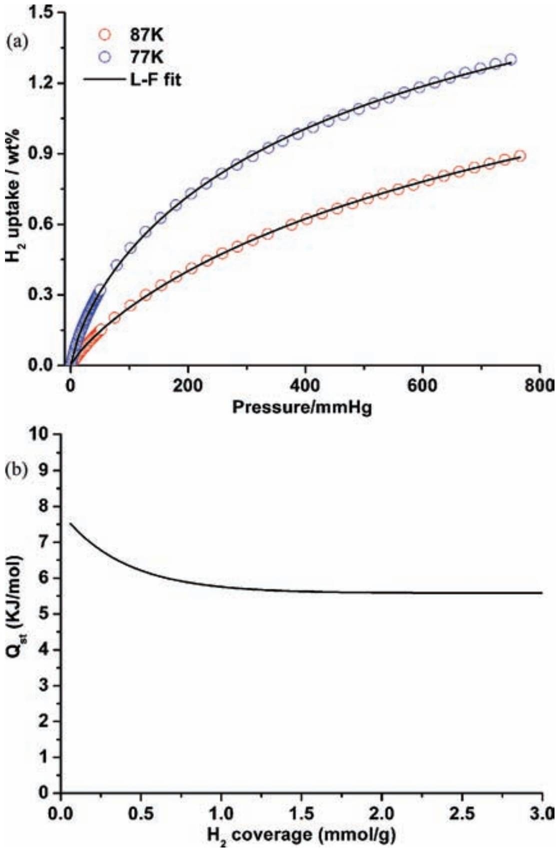

Figure 4. (a) H_2 adsorption isotherms of **1** at 77 K (blue circles) and 87 K (red circles). The solid lines correspond to Langmuir−Freundlich fits to the experimental data. (b) H_2 adsorption enthalpy for **1** calculated from the H_2 adsorption isotherms at 77 and 87 K.

with a hydrogen uptake of about 0.23 wt %. As shown in Figure 5, the sorption isotherms display noticeable hysteresis. We hypothesize that this unusual behavior arises from the size effect of a 1D hexagonal nanotube-like channel. Besides, the kinetic effect may be a contributing factor to the hysteresis because the adsorption/desorption kinetics were very slow.[16] To deeply understand this phenomenon, further studies are needed. The hysteretic hydrogen sorption thus may offer the possibility of developing new porous MOFs, which can upload hydrogen at high pressures and store it at low pressures.

Photoluminescent properties of alkaline-earth metal complexes are not well studied as compared with those of transition-metal complexes, although there are reports on the photoluminescent properties of alkaline-earth metal-containing materials. The photoluminescence properties of **1** and the free ligand were examined in the solid state at room temperature. The free ligand displays photoluminescent emission at 360 nm under 320 nm radiations. Photoluminescence studies of **1** showed that the excitation of the solid samples of **1** at 328 nm produces the same luminescence peak at 372 nm (Figure S4 in the Supporting Information). These intense violet-blue luminescence signals may result from a ligand-based $\pi-\pi^*$ transition.[17] These observations suggest that this compound could find application as a potential fluorescent porous material.[18]

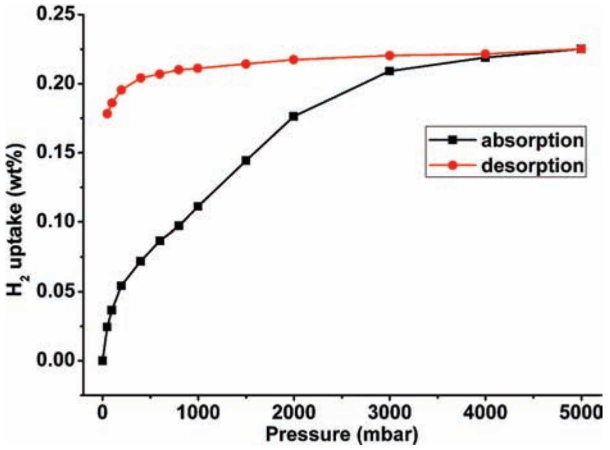

Figure 5. Medium-pressure H_2 adsorption isotherm for **1** at 308 K.

In conclusion, we have successfully synthesized a 3D microporous magnesium MOF (**1**) constructed from $[Mg_3(\mu_3\text{-}O)_2(\mu_2\text{-}O)_4]$ SBUs with 1D hexagonal nanotube-like channels. **1** exhibits very good fluorescence properties and noticeable hydrogen-sorption hysteresis at medium pressure. Future work will continue to focus on constructing magnesium-based microporous frameworks for higher hydrogen adsorption.

Acknowledgment. The authors are grateful for financial aid from the National Natural Science Foundation of China (Grants 20631040 and 20771099) and the MOST of China (Grants 2006CB601103 and 2006DFA42610). The authors thank Professor Jun Chen for help with the hydrogen-sorption measurements.

Supporting Information Available: Experimental procedures, TGA results, PXRD patterns, and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

---

(16) Navarro, J. A. R.; Barea, E.; Salas, J. M.; Masciocchi, N.; Galli, S.; Sironi, A.; Ania, C. O.; Parra, J. B. *Inorg. Chem.* **2006**, *45*, 2397.

(17) Wu, C.; Ngo, H. L.; Lin, W. *Chem. Commun.* **2004**, 1588.

(18) (a) Guo, X. D.; Zhu, G. S.; Fang, Q. R.; Xue, M.; Tian, G.; Sun, J. Y.; Li, X. T.; Qiu, S. L. *Inorg. Chem.* **2005**, *44*, 3850. (b) Chen, W.; Wang, J. Y.; Chen, C.; Yue, Q.; Yuan, H. M.; Chen, J. S.; Wang, S. N. *Inorg. Chem.* **2003**, *42*, 944. (c) Zou, R.-Q.; Bu, X.-H.; Zhang, R.-H. *Inorg. Chem.* **2004**, *43*, 5382. (d) Braverman, M. A.; LaDuca, R. L. *Cryst. Growth Des.* **2007**, *7*, 2343.