JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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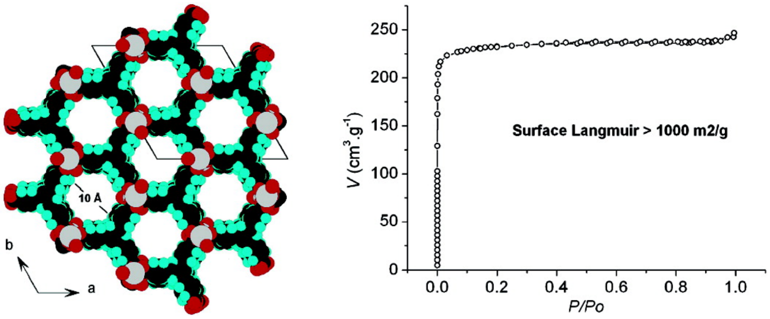
J. Am. Chem. Soc., **2005**, 127 (37), 12788-12789• DOI: 10.1021/ja053992n • Publication Date (Web): 26 August 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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COMMUNICATIONS

MIL-103, A 3-D Lanthanide-Based Metal Organic Framework with Large One-Dimensional Tunnels and A High Surface Area

Thomas Devic,*,† Christian Serre,† Nathalie Audebrand,‡ Jérôme Marrot,† and Gérard Férey*,†

Institut Lavoisier, UMR CNRS 8637, Université de Versailles Saint-Quentin-en-Yvelines, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France, and Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Université Rennes I, Avenue du général Leclerc, 35042 Rennes Cedex, France

Received June 16, 2005; E-mail: ferey@chimie.uvsq.fr; devic@chimie.uvsq.fr

Among the porous polycarboxylate-based metal organic frameworks (MOFs),[1] those based on rare-earth cations have deserved a special attention due to their ability to form multifunctional hybrid materials, combining their intrinsic porous character with physical properties coming from the rare-earth, in the field of magnetism, catalysis, or luminescence.[2] Many lanthanide-based MOFs present relatively open frameworks with included solvent molecules,[3] but collapse or become amorphous under guest removal,[4] even if they present reversible solvent exchange.[3e,5] However, a few solids remain crystallized[5a,h,6] upon solvent departure and present a permanent porosity,[5b,c,6b,e,7] but to our knowledge, only one lanthanide carboxylate ($Tb(BTC)(H_2O)_{1.5}\cdot(DMF)$, MOF-76) has been proven to show a significant porosity relative to nitrogen.[8]

We present here the synthesis, crystal structure, and nitrogen sorption properties of $Tb(BTB)(H_2O)\cdot 2(C_6H_{12}O)$ (BTB = 1,3,5-benzenetrisbenzoate), a three-dimensional lanthanide carboxylate MOF, later denoted MIL-103, presenting a permanent porosity and a high surface area after guest removal.

The BTB ligand, already used by Yaghi and co-workers with transition-metal cations to produce highly porous MOFs,[9] was synthesized starting from 1,3,5-tritolylbenzene[10] following the published procedure.[11] MIL-103 was hydrothermally synthesized from stoichiometric amounts of $TbCl_3\cdot 6H_2O$, H_3BTB, and NaOH in a 1:1 biphasic mixture of water and cyclohexanol[12] (see Supporting Information).[13]

MIL-103 is trigonal ($a = 28.5344(8)$ Å, $c = 12.2148(5)$ Å, space group $R32$),[13] and the structure is a rare case of the (3,5)-coordinated minimal net hms.[14] Tb^{III} ions are 9-fold coordinated by eight carboxylate oxygen atoms and one water molecule, in accordance with bond valence calculations ($\upsilon_{Tb} = 2.91-3.18$, $\upsilon_{Ow} = 0.33-0.36$, depending on the bond valence parameters used[15]). Edge-sharing $[TbO_9]$ polyhedra define chains running in the c direction. They are connected by the extended tritopic BTB^{3-} ligand to afford 1-D hexagonal pores containing the free cyclohexanol molecules (Figure 1). When solvent is removed, free cylinders of ca. 10 Å diameter (taking into account the van der Waals radii of the atoms) are defined (see Figure 1).

Thermogravimetric analysis was performed under oxygen atmosphere (see insert in Figure 2). A 23% weight loss is observed between room temperature and 150 °C, which is consistent with the free solvent departure (theoretical 24−25%). A slightly decreasing plateau follows (2% weight loss, which could be associated with the coordinated water departure) until 400 °C, where MIL-103 collapses. The remaining product is Tb_2O_3, with a residual mass (77% weight loss) consistent with theoretical value (77%).

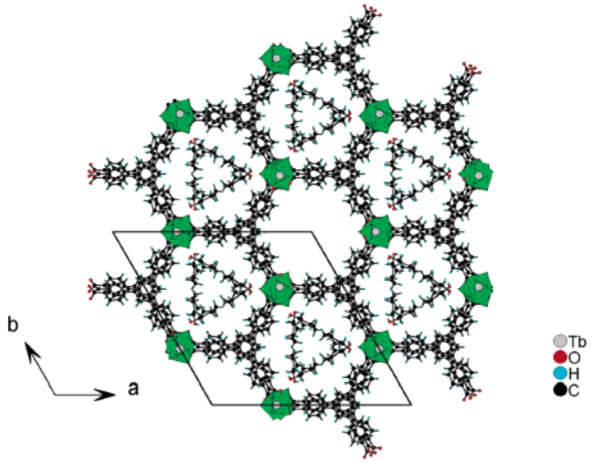

Figure 1. View of MIL-103 along the *c* axis, showing the hexagonal pores filled with free solvent molecules (one pore is pictured empty for clarity).

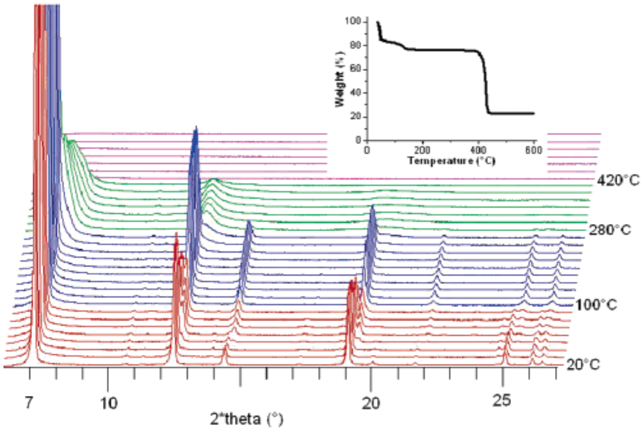

Figure 2. X-ray thermodiffractogram of MIL-103 under air from 20 to 500 °C. The following color code corresponding to the structural changes (see text) was used: red (20−90 °C), blue (100−260 °C), green (280−400 °C), purple (420−500 °C). Insert: TG analysis under oxygen (1 °C/min).

X-ray thermodiffraction analysis was carried under air. Noticeable diffraction intensity variations are observed between 50 and 100 °C, accompanied by a slight position shift of the Bragg peaks. No change occurs until 280 °C, where the long-range order begins to disappear to form an amorphous phase above 420 °C (Figure 2) before apparition of Tb_2O_3 upon further heating.

The first change certainly corresponds to a small structural rearrangement consecutive to the solvent departure (cell indexing at 220 °C: $a = 28.178(1)$ Å, $c = 12.196(1)$ Å). The loss of crystallinity above 280 °C could be associated with the bound water departure, which is consistent with the TG analysis. MIL-103 heated at 300 °C does not recover its crystallinity after rehydration, proving that the transformation is irreversible on the day time scale.

The nitrogen sorption properties of MIL-103 were investigated. The as-synthesized product was degassed at 150 °C for 15 h under

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† Université de Versailles.
‡ Université Rennes I.

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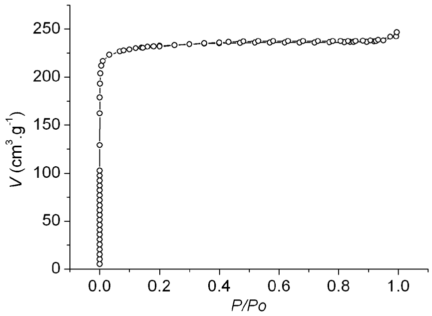

Figure 3. Nitrogen gas adsorption isotherm at 77 K for MIL-103 degassed overnight at 150 °C. P/P_0 is the ratio of gas pressure (P) to saturation pressure ($P_0 = 750$ mmHg). V is the adsorbed volume.

vacuum, and the sorption measurement was performed at 77 K using nitrogen as the sorbed gas. As shown in Figure 3, MIL-103 exhibits a typical type I isotherm, with a Langmuir surface area greater than 1000 $m^2 \cdot g^{-1}$ (ranging from 1030 to 1330 $m^2 \cdot g^{-1}$, depending on the batch used; surfaces between 730 and 930 $m^2 \cdot g^{-1}$ were found using the BET model). The same experiment performed after activation at 300 °C gives a surface of 60 $m^2 \cdot g^{-1}$, confirming that the loss of crystallinity above 280 °C corresponds to the collapse of the structure.

This is so far the largest surface area reported for lanthanide-based porous solids, far beyond the best one previously reported for rare-earth-based MOF ($S_{\text{Langmuir}} = 334$ $m^2 \cdot g^{-1}$ for MOF-76).[8]

MIL-103 could also be synthesized with other light rare-earth elements (RE = Y, La–Ho). Moreover, in the $H_3BTB/RE^{III}X_3$ (X = Cl, NO_3) system, only this single crystalline phase was observed up to now, as checked by powder diffraction, whatever the temperature (100–200 °C), reaction time (10 h to 9 days), NaOH/H_3BTB/LnX_3 ratio, and concentrations were used.

To conclude, we present here the first lanthanide-based MOF keeping its crystalline order upon guest removal and showing both large pores (free diameter >10 Å) and a high surface area (>1000 $m^2 \cdot g^{-1}$) relative to nitrogen. Studies of the lability of the bound water by solid-state NMR, which is of importance for catalytic applications, as well as luminescence measurements and insertion properties are in progress and will be reported in due course.

Acknowledgment. Dr. M. Haouas and Dr. F. Taulelle are gratefully acknowledged for solid-state NMR measurements. We also thank a referee for helpful comments about the net topologies.

Supporting Information Available: Full synthetic method, IR spectra and CIF file for MIL-103(Tb), powder diffraction data for MIL-103(RE) (RE = Y, La–Ho). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For recent reviews, see: (a) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375. (b) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1466–1496. (c) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res.* **2005**, *38*, 273–282. (d) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217–225. (e) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176–182. (f) Suslick, K. S.; Bhyrappa, P.; Chou, J.-H.; Kosal, M. E.; Nakagaki, S.; Smithenry, D. W.; Wilson, S. R. *Acc. Chem. Res.* **2005**, *38*, 283–291.

(2) Guillou, O.; Daiguebonne, C. *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Bünzli, J.-C. G., Pecharsky, V. K., Eds.; Elsevier: New York, 2005; Vol. 34, pp 359–404.

(3) For early work, see: (a) Zhi-Bang, D.; Zhong-Sheng, J.; Ge-Geng, W.; Jia-Zan, N. *J. Huaxue* (*J. Struct. Chem.*) **1990**, *9*, 64–69. (b) Robl, C.; Hentschel, S. *Z. Naturforsch.* **1992**, *47*, 1561–1564. (c) Baggio, R.; Garland, M. T.; Perec, M.; Vega, D. *Inorg. Chem.* **1996**, *35*, 2396–2399. (d) Serpaggi, F.; Férey, G. *J. Mater. Chem.* **1998**, *8*, 2737–2741. (e) Kiritsis, V.; Michaelides, A.; Skoulika, S.; Golhen, S.; Ouahab, L. *Inorg. Chem.* **1998**, *37*, 3407–3410.

(4) (a) Chui, S. S.-Y.; Siu, A.; Feng, X.; Zhang, Z. Y.; Mak, T. C. W.; Williams, I. D. *Inorg. Chem. Commun.* **2001**, *4*, 467–470. (b) Serre, C.; Pelle, F.; Gardant, N.; Férey, G. *Chem. Mater.* **2004**, *16*, 1177–1182. (c) de Lill, D. T.; Gunning, N. S.; Cahill, C. L. *Inorg. Chem.* **2005**, *44*, 258–266. (d) Zhang, Z.-H.; Shen, Z.-L.; Okamura, T.; Zhu, H.-F.; Sun, W.-Y.; Ueyama, N. *Cryst. Growth Des.* **2005**, *5*, 1191–1197.

(5) (a) Serpaggi, F.; Luxbacher, T.; Cheetham, A. K.; Férey, G. *J. Solid State Chem.* **1999**, *145*, 580–586. (b) Reineke, T. M.; Eddaoudi, M.; Fehr, M.; Kelley, D.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 1651–1657. (c) Reineke, T. M.; Eddaoudi, M.; Moler, D.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 4843–4844. (d) Pan, L.; Huang, X.; Li, J.; Wu, Y.; Zheng, N. *Angew. Chem., Int. Ed.* **2000**, *39*, 527–530. (e) Daiguebonne, C.; Guillou, O.; Grault, Y.; Boubekeur, K. *J. Alloys Compds.* **2001**, *323–324*, 199–203. (f) Dimos, A.; Tsaousis, D.; Michaelides, A.; Skoulika, S.; Golhen, S.; Ouahab, L.; Didierjean, C.; Aubry, A. *Chem. Mater.* **2002**, *14*, 2616–2622. (g) Almeida Paz, F. A.; Klinowski, J. *Chem. Commun.* **2003**, 1484–1485. (h) Chen, X.-Y.; Zhao, B.; Shi, W.; Xia, J.; Cheng, P.; Liao, D.-Z.; Yan, S.-P.; Jiang, Z.-H. *Chem. Mater.* **2005**, *17*, 2866–2874.

(6) (a) Serre, C.; Férey, G. *J. Mater. Chem.* **2002**, *12*, 3053–3057. (b) Pan, L.; Adams, K. M.; Hernandez, H. E.; Wang, X.; Zheng, C.; Hattori, Y.; Kaneko, K. *J. Am. Chem. Soc.* **2003**, *125*, 3062–3067. (c) Zheng, X.; Sun, C.; Lu, S.; Liao, F.; Gao, S.; Jin, L. *Eur. J. Inorg. Chem.* **2004**, 3262–3268. (d) Michaelides, A.; Skoulika, S. *Cryst. Growth Des.* **2005**, *5*, 529–533. (e) Maji, T. K.; Mostafa, G.; Chang, H.-C.; Kitagawa, S. *Chem. Commun.* **2005**, 2436–2438.

(7) (a) Reineke, T. M.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 2590–2594. (b) Millange, F.; Serre, C.; Marrot, J.; Gardant, N.; Pellé, F.; Férey, G. *J. Mater. Chem.* **2004**, *14*, 642–645.

(8) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 1504–1518.

(9) See, for example: Chae, H. K.; Siberio-Pérez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523–527.

(10) Elmorsy, S. S.; Pelter, A.; Smith, K. *Tetrahedron Lett.* **1991**, *32*, 4175–4176.

(11) Kim, J.; Chen, B.; Reineke, T. M.; Li, H.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 8239–8247.

(12) Forster, P. M.; Thomas, P. M.; Cheetham, A. K. *Chem. Mater.* **2002**, *14*, 17–20.

(13) A first mixture (sample 1) was placed in a Teflon-lined steel autoclave under autogenous pressure for 5 days at 100 °C. A pale-yellow powder was recovered. An other sample (2) was prepared using the same synthetic conditions but at a higher temperature (200 °C during 4 days, followed by a slow cooling at 4 °C/min). This led to thin-yellow needlelike crystals as a byproduct among an unidentified amorphous pale powder. The X-ray powder diffraction indicated that sample 1 and crystals of sample 2 correspond to the same phase. The powder patterns are in agreement with the theoretical one calculated from the crystal structure. Structure determination was performed using crystals from sample 2, while all other analyses used powder from sample 1. Crystal data for $Tb[C_{27}H_{15}O_6][H_2O] \cdot 2(C_6H_{12}O)$: trigonal, space group $R32$ (No. 155), $a = 28.5344(8)$ Å, $c = 12.2148(5)$ Å, $V = 8613.0(5)$ A^3, $Z = 9$, $D_{\text{calcd}} = 1.406$ $g \cdot cm^{-3}$, $T = 293$ K, $R1 = 0.0628$, $wR2 = 0.1288$ for all data; $R1 = 0.0427$, $wR2 = 0.1034$ for 2560 observed data ($I > 2\sigma(I)$) with 7 restraints and 196 parameters. Elemental analysis found (%) for as synthesized MIL-103: C 47.13, H 4.66, Tb 18.09, Na 0.04. Calcd for $C_{27}H_{17}O_7Tb \cdot 2C_6H_{12}O$: C 57.64, H 5.08, Tb 19.55, Na 0.0. Calcd for $C_{27}H_{17}O_7Tb \cdot C_6H_{12}O \cdot 5H_2O$: C 49.38, H 4.90, Tb 19.80. The later formulation is in agreement with preliminary ^1H NMR solid-state experiments for the powdered La analogue. Cyclohexanol molecules may be partially exchanged with water molecules during the synthesis or the washing process. IR data (KBr pellet), υ (cm^{-1}); as synthesized MIL-103: 3417 (br), 2987 (w), 2854 (w), 1650 (w), 1611 (s), 1581 (s), 1518 (s), 1413 (s); activated MIL-103: 3425 (br), 1650 (w), 1608 (s), 1581 (s), 1515 (s), 1412 (s).

(14) Bonneau, C.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acta Crystallogr.* **2004**, *A60*, 517–520.

(15) (a) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192–197. (b) Trzesowska, A.; Kruszynski, R.; Bartczak, T. J. *Acta Crystallogr.* **2004**, *B60*, 174–178.

JA053992N