DOI: 10.1002/ange.201104688

Crystal Engineering

Network Diversity through Decoration of Trigonal-Prismatic Nodes: Two-Step Crystal Engineering of Cationic Metal–Organic Materials**

*Alexander Schoedel, Lukasz Wojtas, Stephen P. Kelley, Robin D. Rogers, Mohamed Eddaoudi, and Michael J. Zaworotko**

During the past decade porous metal–organic material (MOM) networks constructed from metal-based nodes (metal ions or metal clusters) and bridging organic ligand (linkers) have attracted ever increasing scientific interest.[1] Their modular nature imparts structural and compositional diversity, tunable functionality, and multiple properties within a single material. In particular, that MOMs can exhibit extra-large surface area means that they represent a uniquely promising class of materials to solve technological challenges related to gas storage and separation, environmental remediation, catalysis, sensing, and drug delivery. Crystal engineering[2] played a major role in the early development of MOMs as exemplified by the high symmetry nets that can be generated by linking polygonal or polyhedral nodes such as tetrahedra (**dia**),[3] octahedra (**pcu**),[3c] squares (**nbo**),[3c,4] and trigonal prisms (**acs**).[5] The aforementioned nets might be described as platforms because they are fine-tunable in terms of both scale and properties as there are many nodes and linkers that can sustain these structures. Pyridyl linkers such as 4,4′-bipyridine were initially exploited in such a capacity[6] but the majority of extra-large surface area MOMs are based upon carboxylate linkers such as benzene-1,3-dicarboxylic acid (1,3-BDC),[7] benzene-1,4-dicarboxylic acid (1,4-BDC),[8] and benzene-1,3,5-tricarboxylic acid (BTC).[9] Such linkers complement synthetically accessible and highly symmetrical metal carboxylate nodes such as $[Cu_2(CO_2)_4]$, $[Zn_4(\mu_4\text{-}O)(CO_2)_6]$ and $[\{M_3(\mu_3\text{-}O)(CO_2)\}_6]$ (M = Cr, Fe). The exploitation of $[Cu_2(CO_2)_4]$, the "square paddlewheel", has proven to be particularly fruitful since ligand design[10] or the use of mixed ligands[11] facilitates a plethora of highly porous polyhedral nets. $[\{M_3(\mu_3\text{-}O)(CO_2)\}_6]$, the "trigonal prism", has also afforded highly porous materials, as exemplified by MIL-100[12] and MIL-101.[13] However, even though this node is remarkably robust,[14] its structures tend to form only microcrystalline materials and require harsh synthetic conditions. We describe herein a crystal engineering strategy that exploits preformed molecular building blocks (MBBs) based upon water-stable trigonal prisms that are decorated with pyridyl moieties. A two-step modular approach that opens up a broad new class of bimetallic MOMs is thereby facilitated.

Two-step processes to form heterobimetallic frameworks are known[15] and are based on the synthesis of a metal complex that is subsequently connected to a different metal ion. To the best of our knowledge, high-connectivity metal complexes that afford high symmetry nets with extra-large channels have not yet been studied in this context. Our two-step process involves isolation of a trigonal prism decorated by pyridyl moieties and then coordinating this highly soluble *t*rigonal-*p*rismatic *P*rimary *M*olecular *B*uilding *B*lock (tp-PMBB-1) to different metals through its six exodentate pyridyl moieties (Scheme 1). We coin the term PMMB to draw analogies to the primary building unit (PBU) in zeolite chemistry. In this context the different connections of PMBBs to various *S*econdary *M*olecular *B*uilding *B*locks (SMBBs) lead to the structural diversity. This approach enables us to exploit both metal–carboxylate and metal–pyridyl bonds and ensures that the nets thereby generated will be positively charged. The first three examples of such nets, tp-PMBB-1-**snx**-1, -**snw**-1, and -**stp**-1 (nomenclature describes both the primary building block and the topology of the resulting net) are described herein.

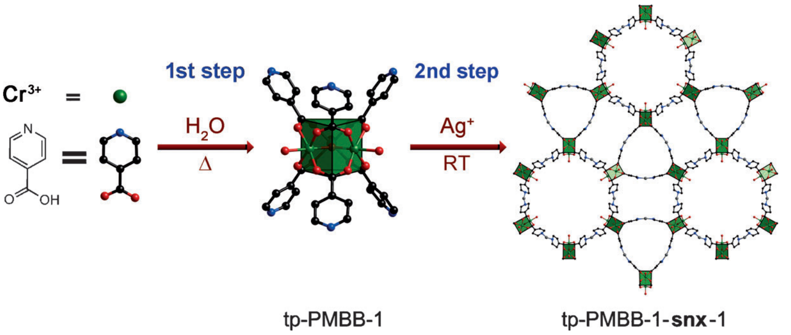
The building block tp-PMBB-1 $[Cr_3(\mu_3\text{-}O)(\text{isonic})_6]^+$ (isonic = pyridine-4-carboxylate)[16] represents a discrete and robust "hexapyridyl" 6-connected node that is well-suited for the subsequent synthesis of a plethora of networks with nanoscale features. Its coordination chemistry with two metals is detailed herein: a linear but bendable linker (Ag^+) and a rigid square-planar metal node (Cd^{2+}). Our results demonstrate the ability of Ag^+ to exist in nonlinear geometry and facilitate two new network topologies for trigonal-prismatic nodes, **snx** (**s**ix-connected **n**et type **x**) (6,6) and **snw** (**s**ix-connected **n**et type **w**) (6,6), rather than the default **acs** net.[5] A cationic net with **acs** topology formed by another tp-PMBB can also be formed and will be reported elsewhere. For the rigid CdN_4 node we anticipated **stp** (**s**quare **t**rigonal **p**rism) (6,4) topology[17] consisting of a trigonal-prismatic and a rectangular-vertex figure, and the first nanoporous variant of this net was indeed isolated.

---

[*] A. Schoedel, Dr. L. Wojtas, Prof. Dr. M. J. Zaworotko
Department of Chemistry, University of South Florida
4202 East Fowler Ave., SCA400, Tampa, FL 33620 (USA)
E-mail: xtal@usf.edu
Homepage: http://chemistry.usf.edu/faculty/zaworotko/
S. P. Kelley, Prof. Dr. R. D. Rogers
Department of Chemistry
Box 870336, The University of Alabama Tuscaloosa
3006D Shelby Hall, 250 Hackberry Lane
Tuscaloosa, AL 35487 (USA)
Prof. Dr. M. Eddaoudi
Chemical Science, King Abdullah University
of Science and Technology
Thuwal 23955-6900 (Kingdom of Saudi Arabia)

[**] This work is supported by Award No. FIC/2010/06, made by the King Abdullah University of Science and Technology (KAUST). We thank Dr. T. T. Ong and Dr. J. A. Perman for the help in sample characterization and S. Elsaidi for fruitful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201104688.



Scheme 1. The two-step process that affords tp-PMBB-1-**snx**-1. The building block tp-PMBB-1 is prepared hydrothermally then dissolved and layered with Ag^+ in an aqueous environment at room temperature to yield crystals of tp-PMBB-1-**snx**-1 (anions, solvent molecules, and hydrogen atoms are omitted for clarity).

The $[Cr_3(\mu_3\text{-}O)(CO_2)_6]$ trigonal-prismatic complexes are well and long known[18] and they are readily accessible by either reflux of stoichiometric amounts of reactants in organic solvents or simply by evaporation of aqueous solutions. The buiding block tp-PMBB-1 is likewise accessible from hydrothermal synthesis (for structural and synthetic details, see the Supporting Information) and based on our experience with [Ag(4,4′-bipyridine)] nets,[19] we linked it with Ag^+ ions. The nets tp-PMBB-1-**snx**-1 and -**snw**-1 were prepared by layering $AgNO_3$ or $AgBF_4$ onto a solution of the nitrate salt of tp-PMBB-1. Light green hexagonal crystals of tp-PMBB-1-**snx**-1 and light green octahedral crystals of tp-PMBB-1-**snw**-1, respectively, were harvested. Planar nets formed from Cd^{II} and 4,4′-bipyridine have been known for some time[20] and dark green needle-shaped hexagonal crystals of tp-PMBB-1-**stp**-1 were obtained by layering a solution of $Cd(NO_3)_2$ onto a solution of the nitrate salt of tp-PMBB-1. The crystal structures of tp-PMBB-1-**snx**-1, -**snw**-1, and -**stp**-1 were determined by single-crystal X-ray diffraction data (see the Supporting Information) and their topologies were determined by using TOPOS[21] and the RCSR database.[22] The RCSR provides unique three-letter codes for each net topology and these codes are used throughout this contribution.

$\{Ag_3[Cr_3O(\text{isonic})_6(H_2O)_3](NO_3)_4\}\cdot x\,H_2O$, tp-PMBB-1-**snx**-1, crystallizes in the hexagonal space group $P6_3/mmc$ and its tp-PMBB-1 moieties possess $\bar{6}m2$ symmetry. The tp-PMBB-1 nodes are linked by two crystallographically distinct Ag^+ ions through the nitrogen atom of the pyridine moiety. The slightly bent geometry of the linkers facilitates the 3-, 4-, and 6-connected SMBBs (Figure 1) needed for the **snx** topology. The 6-connected SMBBs enable mesoporous hexagonal channels with a diameter of approximately 2.4 nm running along [001]. The trigonal and square rings enable channels with a diameter of approximately 1.6 nm and 1.7 nm, and cavities (see the Supporting Information), respectively. The empty space in this structure was calculated to be 85.7 % using PLATON.[23]

$\{Ag_3[Cr_3O(\text{isonic})_6(H_2O)_3](NO_3)_4\}\cdot y\,H_2O$, tp-PMBB-1-**snw**-1, is a second crystalline phase obtained during the reaction that afforded tp-PMBB-1-**snx**-1 and it is a supramolecular isomer[1a] of tp-PMBB-1-**snx**-1 (Figure 2). The N-Ag-N bond angles in tp-PMBB-1-**snw**-1 are different and facilitate corner-sharing 4-connected as well as 6-connected SMBBs as required for the **snw** topology (Figure 2). The hexagonal channels in tp-PMBB-1-**snw**-1 are 2.14 nm in diameter (yellow cylindrical rods in Figure 2b) and they are connected by two trigonal-prismatic vertices compressed in the *c* direction that run along [100] and [010]. There are no channels along [001]. The net tp-PMBB-1-**snw**-1 exhibits the largest empty space of the structures reported herein, with a value of 87.4 %.

$\{[Cd(H_2O)_2]_3[Cr_3O(\text{isonic})_6(H_2O)_3]_2(NO_3)_8\}\cdot x\,\text{solv}$ (solv = DMF, MeCN), tp-PMBB-1-**stp**-1, was obtained by linking tp-PMBB-1 to Cd^{II} and forming a CdN_4 node (Figure 3a). The net tp-PMBB-1-**stp**-1 crystallizes in the hexagonal space group $P6/mmm$ and consists of square-planar linked trigonal prisms

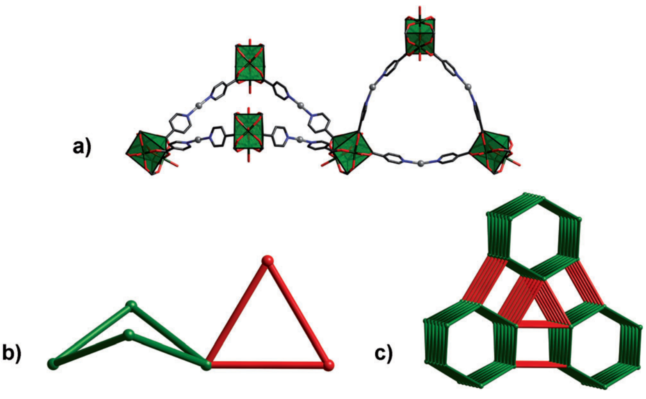


Figure 1. a) In addition to the expected 6-connected secondary molecular building blocks (SMBBs), the framework of tp-PMBB-1-**snx**-1 contains 3- and 4-connected SMBBs. b) Schematic representation of the SMBBs, each corner is a tp-PMBB-1. c) Schematic representation of the **snx** net.

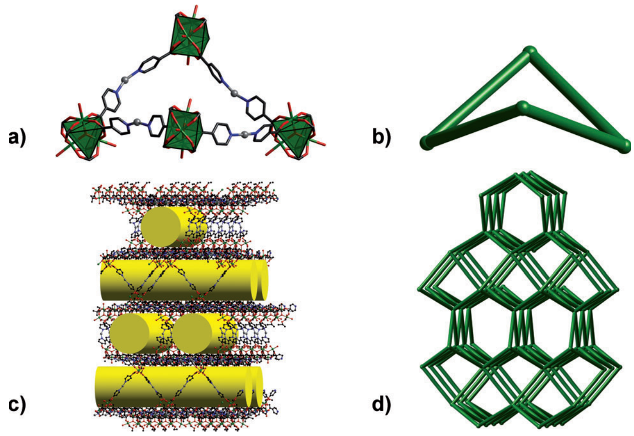


Figure 2. a) Structural and schematic representations of the 4-connected SMBBs in tp-PMBB-1-**snw**-1. b) Left: Single-crystal X-ray structure of tp-PMBB-1-**snw**-1 viewed along [010]. The hexagonal channels also run along [100] (hydrogen atoms, anions, and water molecules are omitted for clarity; hexagonal channels are highlighted with yellow cylindrical rods). Right: Schematic representation of the new **snw** topology.

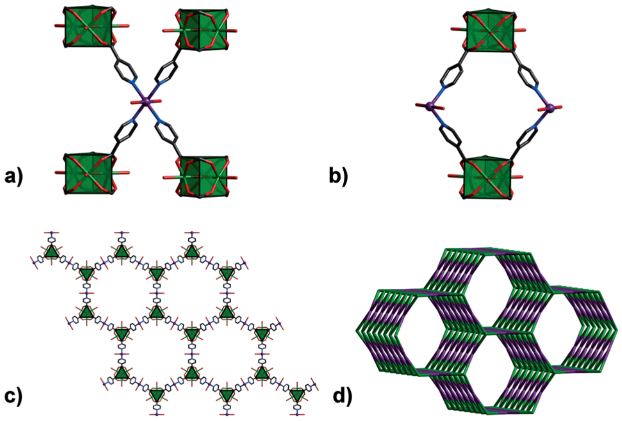


Figure 3. a) Connection of four tp-PMBB-1 nodes by a Cd^{2+} node; b) 4-connected ring SMBB in tp-PMBB-1-**stp**-1; c) structure of tp-PMBB-1-**stp**-1 showing hexagonal channels along [001]; d) schematic representation of the **stp** net comprising of 6- and 4-connected nodes (6,4).

(Figure 3b) that sustain the previously known **stp** (6,4) topology[17] (Figure 3c). The 4-connected ring SMBBs (Figure 3b) enable 1.9 nm channels along [001]. The void volume of tp-PMBB-1-**stp**-1 was calculated to be 69.1 %.

Since all three frameworks possess cationic charge and nanoscale channels we anticipated that they would be suitable for anion exchange. We selected tp-PMBB-1-**stp**-1 to study anion exchange using $NaBF_4$ in DMF at room temperature. The replacement of NO_3^- by BF_4^- was confirmed by FT-IR spectroscopy (see the Supporting information) and the measurement of unit cell parameters before and after anion exchange indicates that this is a single-crystal to single-crystal transformation.

The two-step approach we describe herein has been addressed previously[15] but it remains atypical for synthesis of MOMs. In the present situation the two-step approach is advantageous since it is a modular method and facilitates the growth of large single crystals under ambient aqueous conditions. The flexibility of both the tp-PMBB-1 building block, as exemplified by the series of MIL-88,[24] and the N-Ag-N linkages, facilitate the **snx** and **snw** structures reported herein rather than the default **acs** net. In conclusion, we have demonstrated that tp-PMBB-1, a trigonal-prismatic node decorated with pyridyl groups, can be linked in a two-step process through linear or square metals and thereby afford three nanoporous cationic MOMs. The generality of this approach is likely to be high and we anticipate a large variety of new network structures based upon tp-PMBB-1 and related nodes.

Experimental Section

The nitrate salt of tp-PMBB-1 was synthesized by a modified literature procedure.[25] The nets tp-PMBB-1-**snx**-1 and -**snw**-1 were synthesized by layering either $AgNO_3$ or $AgBF_4$ dissolved in 1:1 PEG(400)/H_2O onto a solution of the nitrate salt of tp-PMBB-1 in 4:1 PEG(400)/H_2O. Pure tp-PMBB-1-**snw**-1 could not be isolated. The net tp-PMBB-1-**stp**-1 was synthesized by layering a $Cd(NO_3)_2$ solution (DMF/MeCN = 1/2) onto a solution of the nitrate salt of tp-PMBB-1 in DMF/MeCN = 2/1 with a separation layer of DMF/MeCN = 1/1 in between (for a detailed procedure, see the Supporting Information).

Received: July 6, 2011

Keywords: chromium · crystal engineering · mesoporous materials · metal–organic frameworks · synthesis design

---

[1] a) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629–1658; b) S. Kitagawa, R. Kitaura, S.-i. Noro, *Angew. Chem.* **2004**, *116*, 2388–2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2375; c) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558–1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494; d) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; e) C. Janiak, *J. Chem. Soc. Dalton Trans.* **2003**, 2781–2804; f) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117–138; g) S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276–288.

[2] G. R. Desiraju, *Angew. Chem.* **2007**, *119*, 8492–8508; *Angew. Chem. Int. Ed.* **2007**, *46*, 8342–8356.

[3] a) O. R. Evans, W. B. Lin, *Acc. Chem. Res.* **2002**, *35*, 511–522; b) M. J. Zaworotko, *Chem. Soc. Rev.* **1994**, *23*, 283–288; c) O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acta Crystallogr. Sect. A* **2003**, *59*, 22–27; d) C. Bonneau, O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acta Crystallogr. Sect. A* **2004**, *60*, 517–520.

[4] a) O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acta Crystallogr. Sect. A* **2003**, *59*, 515–525; b) N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 1504–1518.

[5] A. C. Sudik, A. P. Côté, O. M. Yaghi, *Inorg. Chem.* **2005**, *44*, 2998–3000.

[6] a) L. R. MacGillivray, S. Subramanian, M. J. Zaworotko, *J. Chem. Soc. Chem. Commun.* **1994**, 1325; b) L. Carlucci, G. Ciani, D. M. Proserpio, A. Sironi, *J. Chem. Soc. Chem. Commun.* **1994**, 2755; c) S.-i. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka, M. Yamashita, *J. Am. Chem. Soc.* **2002**, *124*, 2568–2583.

[7] a) M. Eddaoudi, J. Kim, J. B. Wachter, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 4368–4369; b) B. Moulton, J. Lu, A. Mondal, M. J. Zaworotko, *Chem. Commun.* **2001**, 863–864; c) B. Moulton, J. Lu, R. Hajndl, S. Hariharan, M. J. Zaworotko, *Angew. Chem.* **2002**, *114*, 2945–2948; *Angew. Chem. Int. Ed.* **2002**, *41*, 2821–2824.

[8] a) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276–279; b) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469–472.

[9] S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148–1150.

[10] a) F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko, M. Eddaoudi, *J. Am. Chem. Soc.* **2008**, *130*, 1833–1835; b) X.-S. Wang, S. Ma, P. M. Forster, D. Yuan, J. Eckert, J. J. López, B. J. Murphy, J. B. Parise, H.-C. Zhou, *Angew. Chem.* **2008**, *120*, 7373–7376; *Angew. Chem. Int. Ed.* **2008**, *47*, 7263–7266; c) S. Ma, D. Sun, M. Ambrogio, J. A. Fillinger, S. Parkin, H.-C. Zhou, *J. Am. Chem. Soc.* **2007**, *129*, 1858–1859.

[11] J. K. Schnobrich, O. Lebel, K. A. Cychosz, A. Dailly, A. G. Wong-Foy, A. J. Matzger, *J. Am. Chem. Soc.* **2010**, *132*, 13941–13948.

[12] G. Férey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surblé, J. Dutour, I. Margiolaki, *Angew. Chem.* **2004**, *116*, 6456–6461; *Angew. Chem. Int. Ed.* **2004**, *43*, 6296–6301.

[13] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040 – 2042.

[14] a) K. A. Cychosz, A. J. Matzger, *Langmuir* **2010**, *26*, 17198 – 17202; b) S. Bernt, V. Guillerm, C. Serre, N. Stock, *Chem. Commun.* **2011**, *47*, 2838 – 2840.

[15] a) J. M. Ellsworth, H.-C. zur Loye, *Dalton Trans.* **2008**, 5823; b) V. D. Vreshch, A. B. Lysenko, A. N. Chernega, J. A. K. Howard, H. Krautscheid, J. Sieler, K. V. Domasevitch, *Dalton Trans.* **2004**, 2899 – 2903.

[16] D. F. Mullica, D. E. Pennington, J. E. Bradshaw, E. L. Sappenfield, *Inorg. Chim. Acta* **1992**, *191*, 3 – 6.

[17] O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acta Crystallogr. Sect. A* **2006**, *62*, 350 – 355.

[18] a) B. N. Figgis, G. B. Robertson, *Nature* **1965**, *205*, 694 – 695; b) A. Figuerola, V. Tangoulis, J. Ribas, H. Hartl, I. Brüdgam, M. Maestro, C. Diaz, *Inorg. Chem.* **2007**, *46*, 11017 – 11024; c) A. Vlachos, V. Psycharis, C. P. Raptopoulou, N. Lalioti, Y. Sanakis, G. Diamantopoulos, M. Fardis, M. Karayanni, G. Papavassiliou, A. Terzis, *Inorg. Chim. Acta* **2004**, *357*, 3162 – 3172; d) V. Psycharis, C. P. Raptopoulou, A. K. Boudalis, Y. Sanakis, M. Fardis, G. Diamantopoulos, G. Papavassiliou, *Eur. J. Inorg. Chem.* **2006**, 3710 – 3723.

[19] F. Robinson, M. J. Zaworotko, *J. Chem. Soc. Chem. Commun.* **1995**, 2413 – 2414.

[20] M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151 – 1152.

[21] V. A. Blatov, A. P. Shevchenko, V. N. Serezhkin, *J. Struct. Chem.* **1994**, *34*, 820 – 822 – 822.

[22] M. O'Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi, *Acc. Chem. Res.* **2008**, *41*, 1782 – 1789.

[23] A. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7 – 13.

[24] S. Surblé, C. Serre, C. Mellot-Draznieks, F. Millange, G. Férey, *Chem. Commun.* **2006**, 284.

[25] E. Gonzalez-Vergara, J. Hegenauer, P. Saltman, *Inorg. Chim. Acta* **1982**, *66*, 115 – 118.