Structural and zeolitic features of a 3D heterometallic porous architecture constructed from a $\{M(oxalate)_4\}^{4-}$ building unit

Inhar Imaz, Georges Bravic and Jean-Pascal Sutter*

Received (in Cambridge, UK) 16th September 2004, Accepted 24th November 2004
First published as an Advance Article on the web 10th January 2005
DOI: 10.1039/b414190c

The utilization of the tetrahedral pre-formed coordination compound $\{U(C_2O_4)_4\}^{4-}$ permitted the efficient synthesis of a 3D heteronuclear supramolecular nano-porous architecture undergoing a reversible sorption process without collapsing.

The design of supramolecular materials prepared from molecular building blocks has become a challenging field of research according to the new perspectives they open in material science. A very promising approach to such functional systems involves coordination polymers.[1,2] This approach has also been envisaged for the preparation of nano-porous materials.[3–7] Several prototypical examples of such supramolecular nano-porous architectures have been reported and were shown to exhibit promising results in catalysis,[8] gas sorption and storage,[9] or separation.[10] The vast majority of these open frameworks are prepared by the direct assembly of a metal ion with a bridging ligand, the resulting network relying on the formation during the association process of the so-called secondary building units. These nodes, resulting from the connection of the coordinating functional groups of the ligands to the metal ions, determine the net topology and dimensionality of the coordination polymer.[11] The use of a pre-formed coordination compound as a molecular building block has seldom been envisaged for the construction of porous frameworks[12–17] whereas this approach was shown to be very efficient for the preparation of other molecule-based materials. Typically, such a building block consists of a metal center surrounded by ligands which are able to connect to a second metal ion by an available functional group. We are currently considering tetrafunctional synthons, $\{M(C_2O_4)_4\}^{4-}$, with tetrahedrally arranged oxalate linkers. Herein we report that robust heterometallic 3D-coordination polymers exhibiting porous architectures can be prepared by association of the tetrahedral building unit, $\{U(C_2O_4)_4\}^{4-}$, with M^{2+} metal ions. A framework constructed with Mg^{2+} is described. This structure exhibits channels which are easily emptied from solvates without affecting the chemical scaffolds, and become accessible to other molecules.

The reaction of $K_4U(C_2O_4)_4$ with Mg^{2+} in H_2O led to well shaped green single crystals of $[K_2Mg_2\{U_2(C_2O_4)_7\}\cdot 2H_2O];9H_2O$ **1** suitable for X-ray diffraction analysis.† As a result of the reaction, the tetrahedral $\{U(C_2O_4)_4\}^{4-}$ units assemble *via* {U–oxalate–U} linkages in a ladder type arrangement running along the *b* axis (Fig. 1) where each metal center displays five oxalate ligands in its coordination sphere. These ladders are interconnected through the coordination of the external oxalate ligands to the K and Mg ions setting up a 3D framework. This scaffold frames apertures forming channels where both the coordinated H_2O and solvate molecules are located. A view of the resulting architecture revealing the porous nature of the structure is depicted in Fig. 1. The channels are running through the structure in the three directions of space with apertures of 12 Å × 8 Å (along *b*), 6 Å × 6 Å (along *a*), and 5.5 Å × 5.5 Å (along *c*). The potential free volume accessible for a

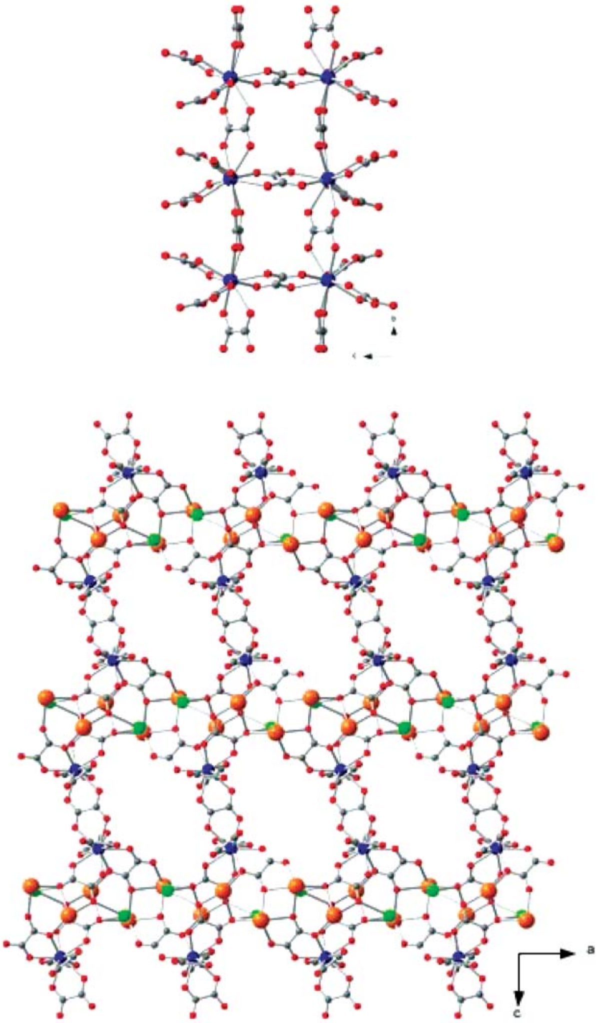

Fig. 1 View of the structure of the supramolecular porous architecture (U^{4+} blue, K^+ orange, Mg^{2+} green, the H_2O molecules are not depicted). *Top*: Detail of the $U(C_2O_4)$ ladder organization. *Bottom*: View of the framework revealing the channels running through the structure along the *b* axis. Selected bond lengths and distances (Å): U–O(oxalate), 2.370(5)–2.551(4); Mg–O(oxalate), 2.800(9)–2.834(9); Mg–O(H_2O), 2.741(9); K–O(oxalate), 2.715(6)–2.810(7); U–U, 6.449(1)–6.392(1).

---

*jpsutter@icmcb-bordeaux.cnrs.fr

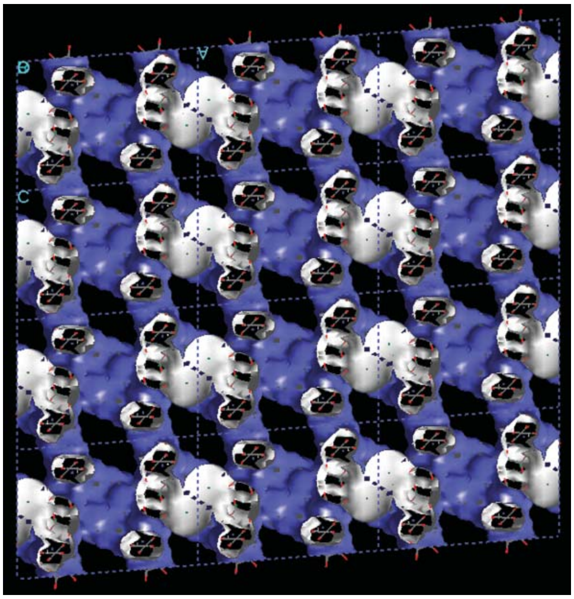

Fig. 2 View of the framework along the *b* axis taking into account the van der Waals volume of the atoms (generated by Cerius 2). The blue surface corresponds to the walls of the porous volume.

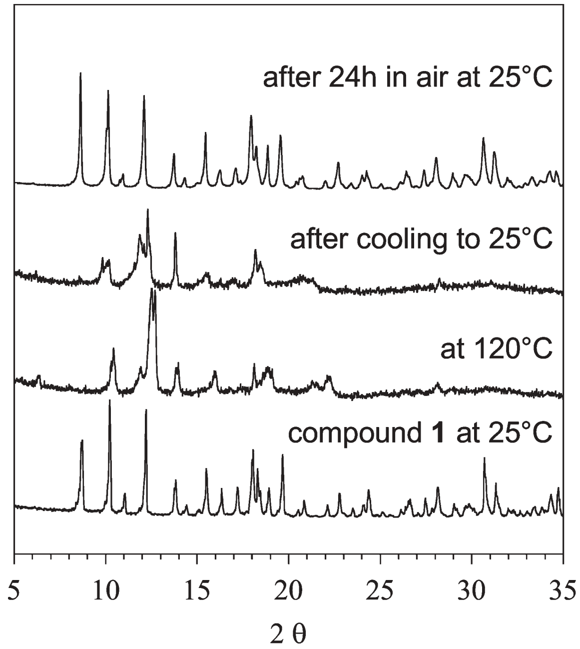

Fig. 3 X-ray powder diffractograms recorded for compound **1**. *From bottom to top*: as synthesized, at 120 °C, at 25 °C after H_2O release, after H_2O re-adsorption at 25 °C.

small molecule (H_2O) determined by PLATON[18] calculations is 1187 Å^3 per unit cell volume (3823 Å^3) which represents 32% of void per unit volume for **1**. The channels running along the *b* axis are highlighted in Fig. 2 where the framework has been plotted by taking into account the van der Waals volume of the atoms. Their effective opening can be described as a diamond-shaped section with sides of *ca.* 5 Å and diagonals of 9 × 4 Å^2.

The H_2O molecules contained in the framework are released in mild conditions. Thermo-gravimetric analyses revealed that all solvent is removed at 100 °C and that the compound remains stable up to 230 °C. Further evidence for the persistence and stability of these porous architectures upon solvent release was obtained from the X-ray powder diffractograms (XRPD) recorded at different temperatures. In Fig. 3 are depicted the XRPD for compound **1** (*from bottom to top*) at 25 °C, at 120 °C, just after cooling back to 25 °C, and for the same temperature after 24 h in air. The diffractogram recorded at 120 °C shows that the sample remains crystalline but with crystallographic modifications resulting from the H_2O release. Finally, when the evacuated sample was maintained in air for 24 h the initial X-ray pattern was recovered, indicating the re-adsorption of H_2O. The recovering of the initial diffractogram confirms that the integrity of the framework is not affected by the solvent release. The use of the rigid oxalate ligands was indeed anticipated to prevent the framework from collapsing. A related behavior has been reported recently for a similar metal–oxalate lattice.[19] The nano-porous architecture **1** thus belongs to the compounds of type 1 of the 3rd generation of solvated solids, *i.e.* the sample retains its crystalline nature during the desorption/adsorption process.[6,20]

Preliminary sorption experiments show that the freed space becomes accessible for small molecules. We mentioned above the capability of the supramolecular porous architecture to re-absorb H_2O but it was also found to absorb molecules like MeOH or EtOH. The sorption capacity per gram of **1** was roughly estimated by TGA to be in the order of 1.2 and 0.93 mmol of alcohols, respectively MeOH and EtOH.

The utilization of the tetrahedral pre-formed coordination compound $\{M(C_2O_4)_4\}^{4-}$ permitted the efficient construction of a rare example of heteronuclear supramolecular nano-porous architecture. This result further demonstrates that the use of a coordination compound as a primary building unit is certainly a valuable and versatile approach for the construction of robust open frameworks. Moreover, this approach appears perfectly suited for the design of open frameworks with various compositions of metal ions.

Inhar Imaz, Georges Bravic and Jean-Pascal Sutter*
Institut de Chimie de la Matière Condensée de Bordeaux – CNRS, Université Bordeaux 1, 87 Avenue du Dr. Schweitzer, Pessac, F-33608, France. E-mail: jpsutter@icmcb-bordeaux.cnrs.fr; Fax: (+33) 540002649

Notes and references

† Preparation of $[K_2Mg_2\{U_2(C_2O_4)_7\}\cdot 2H_2O];9H_2O$: $K_4U(C_2O_4)_4$[21] was synthesized *in situ* from $U(C_2O_4)_2\cdot 6H_2O$ (0.2 g, 0.4 mmol) and $K_2(C_2O_4)\cdot H_2O$ (0.15 g, 0.8 mmol) in H_2O (12 mL) at 80 °C. To the hot green solution, a solution of $Mg(ClO_4)_2\cdot 6H_2O$ (0.15 g, 0.4 mmol) in H_2O (2 mL) was added. The reaction mixture was allowed to cool, and ethanol was added by vapor diffusion. After 7 days green crystals were obtained that were manually separated from precipitated white magnesium oxalate and light-green uranium oxalate. Anal. (%) Calcd. for $C_{14}H_{22}O_{39}K_2Mg_2U_2$: C, 11.87; H, 1.56; Mg, 3.43; U, 33.59. Found: C, 11.81; H, 1.36; Mg, 3.11; U, 34.01. IR (KBr, cm^{-1}): 3397 (s), 1667 (s), 1633 (s), 1443 (m), 1372 (m), 1323 (m), 830 (m), 490 (m). Crystal data: $C_{14}H_{22}O_{39}K_2Mg_2U_2$, M_r = 1417.20 g mol^{-1}, crystal dimension 0.34 × 0.30 × 0.20 mm^3, monoclinic, space group *C*2/*m*, a = 20.437(3) Å, b = 12.841(4) Å, c = 14.614(5) Å, β = 94.52(6)°, V = 3823.4(1) Å^3, Z = 4, $\rho_{\text{calcd.}}$ = 2.462 g cm^{-3}, $F(000)$ = 2656, $\mu(\text{Mo}_{K\alpha})$ = 8.838 mm^{-1}, T = 298 K, $2\theta_{\max}$ = 72.6°. A total of 22286 reflections were collected in the range of $4.1° \leqslant \theta \leqslant 36.3°$ of which 9529 were unique reflections and 6805 with ($I > 4\sigma(I)$) were collected for the analysis. The H atoms have been included in theoretical positions but not refined. The final indices were $R1$ = 0.052,

*Rw*2 = 0.142 with *S* = 1.082. CCDC 246085. See http://www.rsc.org/suppdata/cc/b4/b414190c/ for crystallographic data in .cif or other electronic format. These data can be obtained online free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk.

1 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
2 C. Janiak, *Dalton Trans.*, 2003, 2781.
3 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546.
4 O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705 (and cited references).
5 C. N. R. Rao, S. Natarajan and R. Vaidhyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466 (and cited references).
6 S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334 (and cited references).
7 A. K. Cheetham, G. Férey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268 (and cited references).
8 K. Endo, T. Koike, T. Sawaki, O. Hayashida, H. Masuda and Y. Aoyama, *J. Am. Chem. Soc.*, 1997, **119**, 4117.
9 N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127.
10 D. Bradshaw, T. J. Prior, E. J. Cussen, J. B. Claridge and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2004, **126**, 6106.
11 R. Robson, *J. Chem. Soc., Dalton Trans.*, 2000, 3735.
12 P. Gravereau, E. Garnier and A. Hardy, *Acta Crystallogr., Sect. B*, 1979, **35**, 2843.
13 L. G. Beauvais, M. P. Shores and J. R. Long, *J. Am. Chem. Soc.*, 2000, **122**, 2763.
14 R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S. Noro and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 2684.
15 M. Shmilovits, Y. Diskin-Posner, M. Vinodu and I. Goldberg, *Cryst. Growth Design*, 2003, **3**, 855.
16 D. W. Smithenry, S. R. Wilson and K. S. Suslick, *Inorg. Chem.*, 2003, **42**, 7719.
17 F. Tuna, S. Golhen, L. Ouahab and J.-P. Sutter, *C. R. Chim.*, 2003, **6**, 377.
18 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht, The Netherlands, 2001.
19 P. A. W. Dean, D. Craig, I. Dance, V. Russel and M. Scudder, *Inorg. Chem.*, 2004, **43**, 443.
20 S. Kitagawa and M. Kondo, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1739.
21 M. C. Favas, D. L. Kepert, J. M. Patrick and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 571.