ChemComm
www.rsc.org/chemcomm

Synthesis and structure determination from powder data of the first organically templated tin(IV) phosphate : MIL-76 or $Sn_3^{IV}O_2(H_2O)(HPO_4)_4.\{H_2N–C_2H_4–NH_2\}_{2.5.}\{H_2O\}_2$†

Christian Serre and Gérard Férey
Institut Lavoisier, UMR CNRS 8637, Université de Versailles Saint-Quentin-en-Yvelines, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France

Received (in Cambridge, UK) 1st May 2003, Accepted 17th June 2003
First published as an Advance Article on the web 1st July 2003

The first organically templated tin(IV) phosphate has been isolated and its structure solved from powder X-ray diffraction data; it exhibits a one-dimensional inorganic network built up from chains of trimers of tin(IV) octahedra on which phosphate tetrahedral groups are grafted interacting with water molecules and organic moieties.

Metallophosphates have attracted a lot of interest in the past decade and a large number of three-dimensional solids containing metals such as Zn, Ni, Co, Al, Ga, Fe, Zr, V… have been characterized to date.[1] Among them, tetravalent phosphates such as the titanium phosphates αTiP,[2] γTiP[3] or KTP,[4] are very attractive materials for their applications in ion conductivity, ion exchange and non-linear optics. An increasing number of open framework solids have been isolated recently using zirconium or titanium(IV) cations.[5–16] Concerning tin(IV) phosphates, results are still very scarce and only the lamellar alpha-SnP and its partially ammonium exchanged form have been characterised to date.[17] A large number of open framework tin(II) phosphate have however been reported in the last few years by the groups of Cheetham and Rao.[18–25] However, the tin(II) and tin(IV) chemistries in water are very different with a threefold coordination in the case of tin(II) and an octahedral environment for tin(IV) centres. ‡

We reported recently some hexagonal and cubic mesoporous tin(IV) phosphates using a fluoride route and alkylammonium surfactants.[26] Herein we describe the synthesis and structure from powder data of the first organically templated tin(IV) phosphate obtained under hydrothermal conditions.

MIL-76 was isolated as a pure (MIL for Material of Institut Lavoisier), polycrystalline powder from a reaction mixture of composition 1.0 $SnCl_4 \cdot xH_2O$:1.0 H_3PO_4 :1.0 HF :3.0 en : 280 H_2O (en = ethylenediamine) that was held at 180°C in a Teflon-lined autoclave for 5 days. The pH remains basic (> 10) throughout the synthesis. The light white solid product was recovered by filtration, washed with deionized water, and dried at room temperature. A laboratory powder X-ray diffraction pattern showed that a novel crystalline phase had been produced. It was not possible to obtain crystals of suitable size whatever the synthesis conditions. Without any HF in the starting solution, only poorly crystallised resulting materials are isolated. Elemental analysis indicated P/Sn, C/Sn, N/Sn and H/C ratios of 1.35(5), 1.71(4), 1.70(4) and 5.9(1) which is in good agreement with the formula based on the structure determination (calc: 1.33, 1.67, 1.67 and 5). Only residual traces of fluorine have been detected (< 200 ppm). Thermal analysis (TGA2050 TA apparatus, O_2 flow, heating rate 5 K min^{-1}) has shown three weight losses between 298 and 873 K. The two first (~ 3.1 and 2.3%, respectively) at 373 K and 423 K are attributed to the departure of the free and bound water molecules, respectively. The third weight loss (~ 18.4%) at 573 K is related to the departure of the organic template. These losses are in agreement with the theoretical values (calc. : 3.6, 1.8 and 15.3%). The residual solid has been identified as a mixture of poorly crystallised tin(IV) oxide and a dense tin(IV) phosphate. The pattern of **MIL-76** was indexed with the Dicvolgv program[12] and a monoclinic solution with adequate figures of merit was found.‡

The pattern matching was performed with Fullprof2k using the Winplotr software package.[14] Structure determination was realised using the EXPO package.[15] The structure of **MIL-76** was then refined using also Fullprof2k. Seventeen experimental point values were introduced during the refinement to adjust the background. The peak profile was determined using a Pseudo-Voigt function and two asymmetry parameters. Soft distances constraints, two thermal parameters, one for tin atoms and one for lighter atoms (P, O, N, C) and a preferred orientation vector were used. Satisfactory reliability factors were obtained for this complex structure (38 independent atoms) despite the use of laboratory data: R_{Bragg} = 6.7% and Rp = 8.2%. Bond valence calculation gives for tin values above 4 (4.2–4.6) confirming the tetravalent state of the tin centres. The structure determination was consistent with analytical results leading to a $Sn_3^{IV}O_2(H_2O)(HPO_4)_4 \cdot \{H_2N–C_2H_4–NH_2\}_{2.5} \cdot \{H_2O\}_2$ formula for **MIL-76**. The final Rietveld plot is shown in Fig. 1. Details of the structure determination are reported in the ESI.†

MIL-76 exhibits a one-dimensional structure. It is built up from tin(IV) octahedra and phosphate tetrahedral groups (Fig. 2). The tin octahedra share μ_3 oxo groups to produce trimers of octahedra and finally chains of tin octahedra along the *c* axis (Fig. 3). The remaining oxygen atoms of the tin octahedra are shared with the phosphorus atoms. Organic moieties and free water molecules are located between the chains and interact with terminal P–OH and Sn–H_2O groups (Fig. 2). Interatomic distances are in agreement with those usually observed for tetravalent phosphates (M = Ti, Zr, Sn): Sn–O distances are between 1.90 and 2.14 Å. Unlike in the case of distorted titanium oxo chains observed previously, Sn–(μ_3O) distances

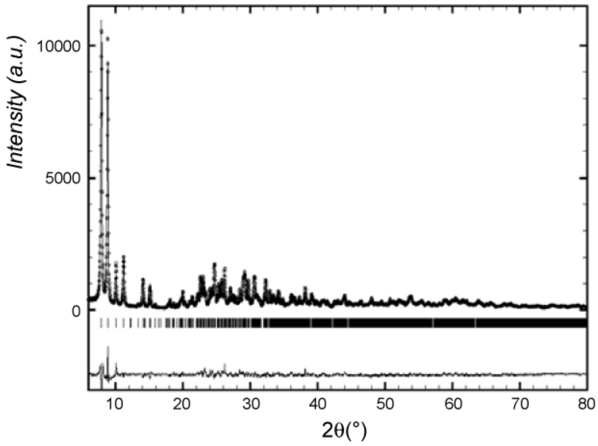

Fig. 1 Final Rietveld refinement plot for $Sn_3^{IV}O_2(H_2O)(HPO_4)_4 \cdot \{H_2N–C_2H_4–NH_2\}_{2.5} \cdot \{H_2O\}_2$ (**MIL-76**) in the space group $P2_1/c$. Observed, calculated and difference profiles are plotted on the same scale. Bragg peaks are indicated by tick marks.

---

† Electronic supplementary information (ESI) available: tables of X-ray crystallographic data and TGA of MIL-76 under air atmosphere. See http://www.rsc.org/suppdata/cc/b3/b304900k/

DOI: 10.1039/b304900k

are similar to other Sn–O distances, within 1.92 and 2.14 Å. P–O, N–C and C–C distances are typical, (1.4–1.58 Å and 1.49–1.54 Å, respectively).

The ligands around the three octahedrally coordinated tin atoms are different. Sn(1) has three oxygens bridging tin and phosphorus atoms, two μ_3O atoms, relating tin centres, and one terminal water molecule (O(19)). Sn(2) and Sn(3) atoms exhibit similar environments with respectively four and two μ_2O and μ_3O atoms. Three phosphorus atoms ((P(1), P(3), P(4)) exhibit three bridging oxygens and one terminal group while the last phosphorus atom (P(2)) exhibits two μ_2O and two terminal P–O groups. Due to powder data, the accurate nature of the terminal P–O groups (O(6), O(8), O(10), O(11) and O(12)) cannot be determined using only interatomic distances. However, considering the basicity of the synthesis medium and the relative pK_a of H_3PO_4 and ethylenediamine species (2.1/7.2/12.7 for H_3PO_4 and 7.3 and 9.8 for en), amino groups would be better described as non protonated and P–O groups as P–OH entities. An exception concerns the two terminal P–O groups of P(2) where neutrality of **MIL-76** imposes the presence of one PO_4 and one HPO_4 group. This latter case has been observed previously on a gallofluorophosphate.[27]

The structure of **MIL-76** is original for several reasons. First, its inorganic chains exhibit a topology never encountered before, whereas chains are usually built up either from *trans*-linked corner sharing octahedra related to the mineral Tancoïte type[28] (M = Ti) or from corner sharing MO_6 octahedra and PO_4 tetrahedra. These chains can also be described as a reminiscence of the mineral Leucophosphite type.[29] However, the tetramers present in the structure of Leucophosphite are isolated from each other which is not the case for **MIL-76** where two consecutive trimers of octahedra can be decomposed into one Leucophosphite tetramer and one dimer of edge-sharing octahedra. Secondly, under similar synthesis conditions, isostructural aluminium, iron, vanadium and titanium phosphates with the ULM-11 type were previously obtained;[30,31] the organic molecule was found to be directly bounded to the metal centres. This is not the case for **MIL-76** where organic moieties are neutral. This would allow the synthesis of other organically tin(IV) phosphate under basic conditions where template extraction could be performed without any charge compensation.

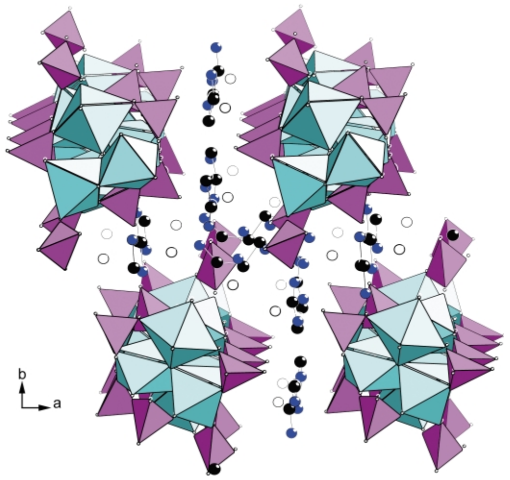

Fig. 2 Polyhedral representation of the structure of **MIL-76** along the *c* axis. Tin, phosphorus, oxygen, carbon and nitrogen atoms are represented in cyan, purple, white, black and dark grey, respectively.

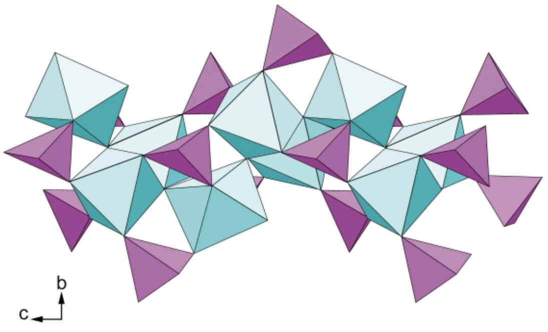

Fig. 3 Polyhedral representation of an inorganic chain of **MIL-76**. Tin, and phosphorus atoms are represented in cyan and purple, respectively.

Finally, we report a tin(IV) phosphate incorporating organic template with an original inorganic complex chain of octahedra. This opens the way to the synthesis of new open-framework materials based on tin(IV) centres with potential applications.

Notes and references

‡ Powder X-ray diffraction data were collected from **MIL-76** at room temperature on a Siemens D5000 diffractometer using CuKα radiation (λ = 1.5418 Å). Crystal data for **MIL-76** : monoclinic space group $P2_1/c$ with a = 11.152(1) Å, b = 22.193(1)Å, c = 9.532(2) Å, β = 95.57(1)°. CCDC 209927.

1 A. K. Cheetham, G. Férey and T. Loiseau, *Angew. Chem. Int. Ed.*, 1999, **38**, 3269.
2 A. Clearfield and J. A. Stynes, *J. Inorg. Nucl. Chem.*, 1964, **26**, 117.
3 S. Alluli, C. Ferragina, C. La Ginestra, M. A. Massucci and N. Tomassini, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1043.
4 R. Masse and J. C. Grenier, *Bull. Soc. Fr. Mineral. Crystallogr.*, 1971, **94**, 437.
5 E. Kemnitz, M. Wloka, S. Trojanov and A. Stiewe, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2677.
6 H.-Y. Sung, J. Yu and I. D. Williams, *J. Solid State Chem.*, 1998, **140**, 46.
7 M. Wloka, S. Trojanov and E. Kemnitz, *J. Solid State Chem.*, 1998, **135**, 293.
8 D. M. Poojary, A. I. Bortun, L. N. Bortun and A. Clearfield, *J. Solid State Chem.*, 1997, **132**, 213.
9 C. Serre and G. Férey, *C. R. Acad. Sci.*, 1999, **2**, 147.
10 C. Serre and G. Férey, *J. Mater. Chem.*, 1999, **9**, 579.
11 C. Serre, N. Guillou and G. Férey, *J. Mater. Chem.*, 1999, **9**, 1185.
12 C. Serre, F. Taulelle and G. Férey, *Solid State Sci.*, 2001, **3**, 623.
13 C. Serre, F. Taulelle and G. Férey, *Chem. Mater.*, 2002, **14**, 998.
14 Y. Zhao, G. Zhu, X. Jiao, W. Liu and W. Pang, *J. Mater. Chem.*, 2000, **10**, 463.
15 Z. Y. S. Liu, L. Zhang, Y. Fu, J. Chen, B. Li, J. Hua and W. Pang, *Chem. Mater.*, 2001, **13**(6), 2017.
16 Y. Guo, Z. Shi, J. Yu, J. Wang, Y. Liu, N. Bai and W. Pang, *Chem. Mater.*, 2001, **13**, 203.
17 L. Roces, S. A. Khainakov, J. R. Garcia, P. Pertierra, M. A. Salvado and S. Garcia-Granda, *Inorg. Chem. Comm.*, 2002, **5**, 685.
18 Y.-L. Liu, G.-S. Zhu, J.-S. Chen, L.-Y. Na, W.-Q. Pang and R.-R. Xu, *Inorg. Chem.*, 2000, **39**, 1820.
19 S. Natarajan, S. Ayyappan, A. K. Cheetham and C. N. R. Rao, *Chem. Mater*, 1998, **10**, 1627.
20 S. Natarajan, M. Eswaramoorthy, A. K. Cheetham and C. N. R. Rao, *Chem. Commun.*, 1998, 1561.
21 S. Natarajan and A. K. Cheetham, *J. Solid State Chem.*, 1998, **140**, 435.
22 S. Natarajan and A. K. Cheetham, *Chem. Commun.*, 1997, 1089.
23 S. Natarajan, M. P. Attfield and A. K. Cheetham, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 978.
24 S. Ayyappan, X. Bu, A. K. Cheetham, S. Natarajan and C. N. R. Rao, *Chem. Commun.*, 1998, 2181.
25 S. Ayyappan, A. K. Cheetham, S. Natarajan and C. N. R. Rao, *J. Solid State Chem.*, 1998, **139**, 207.
26 C. Serre, A. Auroux, A. Gervasini, M. Hervieu and G. Ferey, *Angew. Chem. Int. Ed.*, 2002, **41**, 1594.
27 C. Livage, F. Millange, R. I. Walton, T. Loiseau, N. Simon, D. O'Hare and G. Férey, *Chem. Commun.*, 2001, 994.
28 F. C. Hawthorne, *Acta Crystallogr.*, 1994, **B50**, 481.
29 P. B. Moore, *Am. Mineral.*, 1972, **57**, 397.
30 D. Riou and G. Férey, *J. Solid State Chem.*, 1994, **111**, 422.
31 M. Riou-Cavellec, C. Serre and G. Férey, *C. R. Acad. Sci.*, 1999, **2**, 85.