

Synthesis of open-framework zinc phosphates from organophosphorus amides

S. Neeraj and A. K. Cheetham*

Materials Research Laboratory, University of California, Santa Barbara, CA 93106, USA.

E-mail: cheetham@mrl.ucsb.edu

Received (in Columbia, MO, USA) 22nd February 2002, Accepted 5th June 2002

First published as an Advance Article on the web 12th July 2002

The use of hexamethylphosphoramide as a single source of amine and phosphorus has made it possible to synthesize new three-dimensional zinc phosphate frameworks under solvothermal conditions.

Open framework metal phosphates have been of interest because of their chemical and physical properties and their applications in catalysis, enantioselective separations and ion exchange.^{1–4} The synthesis of these compounds employs a wide range of temperatures (from -20 to 650 °C) and synthetic techniques. The most commonly employed method is the hydrothermal reaction of metal ions with a phosphorus source in the presence of an organic amine. The other technique, the molten salt method,⁵ is limited to the synthesis of frameworks based solely on inorganic species owing to the reaction conditions employed. The hydrothermal method has greater versatility, and typical modifications involve variations in the choice of solvent and the use of organometallic, metal–organic and inorganic metal complex precursors.^{6–8} Such variations are especially important because the formation of open-framework structures is kinetically controlled and can be highly sensitive to the reaction conditions. Our recent investigations have shown that organophosphate esters ($\text{O}=\text{P}(\text{OR})_3$) can be employed in place of H_3PO_4 to synthesize a range of open-framework metal phosphates.⁹ By varying the alkyl chain (R) of the phosphate ester, the reaction media can be switched from aqueous to non-aqueous. In addition, the slow hydrolysis of the ester helps to control the release of phosphate ions into solution. The present study investigates the role of organophosphorus amides as a common source for delivery of both the phosphate and amine to synthesize framework phosphates. The organophosphorus amides, ($\text{O}=\text{P}(\text{NR}_2)_3$), have three P–N linkages which hydrolyze under solvothermal conditions to release phosphoric acid and amine in the synthesis media, similar to that observed in the amine phosphate route.¹⁰ We have chosen the reaction of zinc ions with hexamethylphosphoramide (HMP, $\text{O}=\text{P}(\text{N}(\text{CH}_3)_2)_3$) as a prototype case, and report the first successful synthesis of open-framework zinc phosphates by this route.

Two new three-dimensional zinc phosphates $[\text{C}_2\text{NH}_8][\text{Zn}_3(\text{PO}_4)(\text{HPO}_4)_2]\cdot\text{H}_2\text{O}$ **I** and $[(\text{C}_2\text{NH}_8)(\text{H}_3\text{O})][\text{Zn}_4(\text{PO}_4)_3(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ **II** were obtained by reaction of zinc ions with HMP in a butan-2-ol–water mixture,[†] and have been characterized by single crystal X-ray diffraction,[‡] powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA).

The three-dimensional structure of **I** is formed by linking zinc phosphate layers perpendicular to the *a*-axis with zinc phosphate ladders that are parallel to the *b*-axis (Fig 1(a)). The connectivity of the ZnO_4 and PO_4 moieties within the zinc phosphate layers produces two types of chains (along the *b*-axis); type A chains consist of four-membered rings (2Zn, 2P) only, whereas type B chains consist of three-membered rings (2Zn, P) (Fig 1(b)). The zinc and phosphate tetrahedra form the ladder with edge-shared 4-rings similar to type A (Fig 1(b)), which link these the layers to form a three-dimensional architecture containing channels of 16-membered rings along the *b*-axis. The protonated *N,N*-dimethylamine and water molecules are present in the middle of 16-membered channels

and interact with the framework oxygens *via* hydrogen-bonding (Fig 1(a)). The framework of **I** is also characterized by the presence of infinite Zn–O–Zn chains, which involve three-coordinated oxygen atoms (Fig 1(b)). The structure of **I** bears a close resemblance to that of a zinc phosphate reported using tributylphosphate.⁹

The three-dimensional structure of **II** is comprised of zinc phosphate layers perpendicular to the *b*-axis (Fig. 2(a)) linked together by ZnO_4 tetrahedra to form the three-dimensional architecture. The connectivity of the ZnO_4 and PO_4 moieties within the zinc phosphate layer produces three types of chains, labeled as A, B, C (along the *c*-axis) in Fig 2(b). The type A chain consists of four-membered rings (2Zn, 2P), while the type B chain comprises three-membered rings (2Zn, P). The C type chain contains alternating three- and four-membered rings. The chains are connected to each other forming the layer as shown in Fig 2(b). A two-dimensional zinc phosphate with similar layer topology already exists in literature.¹³ The phosphate tetrahedra of the layer connect to another ZnO_4 tetrahedra which further link to the phosphate tetrahedra of the adjacent layer to form the three-dimensional architecture containing two differ-

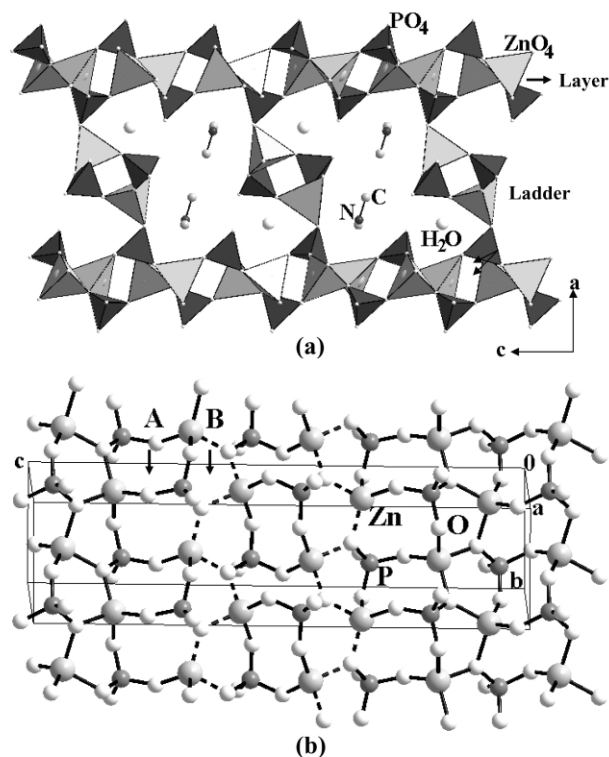


Fig. 1 (a) Polyhedral view of **I**, showing the 16-membered channels along the *b*-axis. Also marked are the ladders and the layers forming the channels with 16-membered rings; large tetrahedra are ZnO_4 and small ones are PO_4 . The amine and water molecules are shown in ball-and-stick view. (b) A section of **I**, showing the layer mentioned in (a) formed from A and B type chains. Note the presence of infinite Zn–O–Zn chains shown in dotted lines.

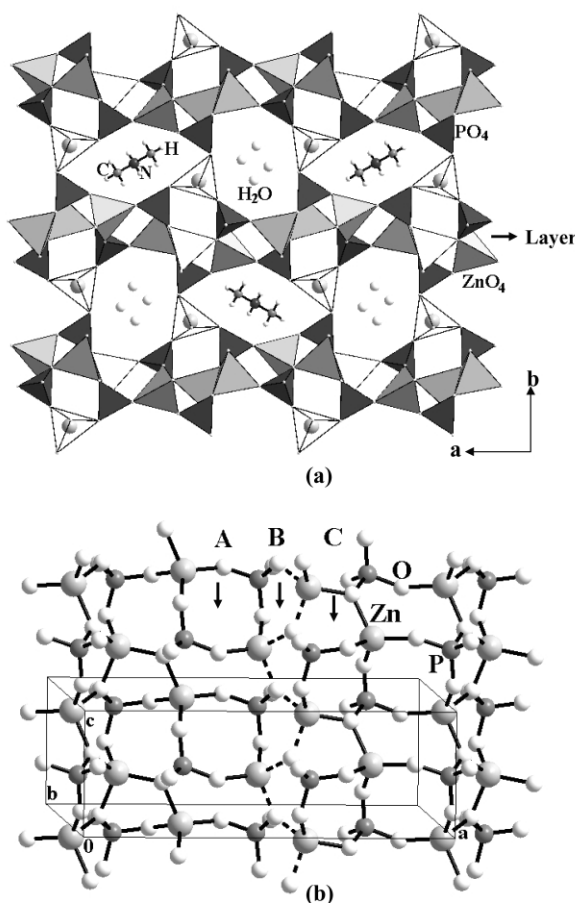


Fig. 2 Polyhedral view of **II**, showing two different types of eight-membered channels containing amine and water molecules. Also marked are the layers and the zinc polyhedra (with open faces), which link these layers to form **II**. (b) A section of **II**, showing the layer mentioned in (a). Note the presence of three types of chains A, B and C and the infinite Zn–O–Zn chains shown in dotted lines.

ent types of eight-membered channels along the *c*-axis (Fig 2(a)). The first channel contains diprotonated *N,N*-dimethylamine molecules whereas the other contains water molecules. The guest species interact with the framework oxygen atoms *via* hydrogen bonding. The zinc tetrahedra linking the layers bear terminal oxygen, which has been assigned as a water molecule. The framework of **II** is also characterized by the presence of infinite Zn–O–Zn chains (Fig 2(b)). The trigonal and tetrahedral coordination of oxygen atoms have been observed in large numbers of divalent metal phosphate systems.^{8,14,15}

The present results show that organophosphorus amides can be successfully employed to synthesize open-framework phosphates. In principle, any primary or secondary amine can be delivered as a phosphorus amide in the reaction, and tertiary amines can be introduced as quaternary phosphoammonium salts. Apart from being a single source for the phosphate and amine, as with the amine phosphates,¹⁰ the organophosphorus amides also offer controlled release of phosphate and amine (structure-directing agent or template) in the reaction media. The rates of hydrolysis of these organophosphorus amides are affected by the R group of the amine molecule. We have also carried out reactions of Co(II) and Mn(II) ions with phosphorus amides, and the structural characterization of these phases is still in progress. The scope of this method can be extended to organosulfuramides or organosulfates in order to synthesize metal–sulfate frameworks. Amides and esters of organic acids also can be reacted with metal ions to yield metal–organic frameworks with or without amines.

We thank Unilever plc for generous support of this work. The work also made use of central MRL facilities, which are

supported by the MRSEC program of the National Science Foundation under award No. DMR00-80034.

Notes and references

† *Synthesis*: in a typical synthesis of **I**, 0.136 g (1 mmol) of ZnCl₂ was reacted with 0.358 g (2 mmol) of hexamethylphosphoramide in a (60:40) butan-2-ol–water mixture. The homogenized gel mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 180 °C for 2 days. The resulting product exclusively consisted of thick needle like crystals. **II** was synthesized by employing an identical procedure in which 0.272 g (2 mmol) of ZnCl₂ was reacted with 0.537 g (3 mmol) of hexamethylphosphoramide in a (60:40) butan-2-ol–water mixture. The crystals were filtered off and washed thoroughly with deionized water. Both **I** and **II** contain Zn(H₃O)PO₄ as a minor impurity phase. TGA revealed that both **I** and **II** lose the water molecules in the range 100–200 °C, with a gradual weight loss in the temperature range 200–450 °C due to loss of amine and other water molecules (calc. 14.8%, obs. 15.0% for **I**; calc. 9.74%, obs. 13.3% for **II**). The final decomposition products in both cases are dense zinc phosphates.

‡ *Crystal data*: [C₂NH₈][Zn₃(PO₄)(HPO₄)₂]-H₂O **I**: monoclinic, space group = *P*2₁/*c* (no. 14) *a* = 12.6528(11), *b* = 5.1909(4), *c* = 21.1457(18) Å, β = 95.088(2)°, *V* = 1383.4(2) Å³, *Z* = 4, *R*_{int} = 0.0599, *D*_c = 2.617 g cm⁻³, μ(Mo-Kα) = 5.575 mm⁻¹, *R*₁(*I* > 2σ(*I*)) = 0.034, *wR*₂ (all data) = 0.0904.

[C₂NH₈](H₃O)[Zn₄(PO₄)₃(H₂O)]₂·H₂O **II**: orthorhombic, space group *P*mm2 (no. 34) *a* = 15.284(3), *b* = 17.726(3), *c* = 5.1882(10) Å, *V* = 1405.6(5) Å³, *Z* = 4, *R*_{int} = 0.1247, *D*_c = 2.842 g cm⁻³, μ(Mo-Kα) = 7.157 mm⁻¹, *R*₁(*I* > 2σ(*I*)) = 0.072, *wR*₂(all data) = 0.1813.

Single crystal X-ray data were collected using a Siemens SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-Kα radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with ψ-scans (width 0.30° and exposure time of 20 s per frame). The structures were solved by direct methods using SHELX-97¹¹ and difference Fourier syntheses. Full-matrix least-squares refinement against |*F*²| was carried out using the SHELXTL-PLUS¹² package of programs. CCDC reference numbers 179397 and 179398 for **I**, and **II**, respectively. See <http://www.rsc.org/suppdata/cc/b2/b205557k/> for crystallographic files in .cif or other electronic format.

- 1 A. K. Cheetham, T. Loiseau and G. Férey, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268.
- 2 *Handbook of Heterogeneous Catalysis*, ed. G. Ertl, H. Knözinger and J. Weitkamp, VCH, Berlin, 1997.
- 3 A. Baiker, *Curr. Opin. Solid State Mater. Sci.*, 1998, **3**, 86.
- 4 J. M. Thomas, *Angew. Chem., Int. Ed.*, 1994, **33**, 913; J. M. Thomas, *Chem. Eur. J.*, 1997, **3**, 1557; M. E. Davis, *Chem. Eur. J.*, 1997, **3**, 1745.
- 5 Q. Huang, M. Ulutagay, P. A. Michener and S.-J. Hwu, *J. Am. Chem. Soc.*, 1999, **121**, 10323; Q. Huang, S.-J. Hwu and X. Mo, *Angew. Chem., Int. Ed.*, 2001, **40**, 1690.
- 6 K. Morgan, G. Gainsford and N. Milestone, *J. Chem. Soc., Chem. Commun.*, 1995, 425; D. A. Bruce, A. P. Wilkinson, M. G. White and A. J. Bertrand, *J. Chem. Soc., Chem. Commun.*, 1995, 2059; D. A. Bruce, A. P. Wilkinson, M. G. White and A. J. Bertrand, *J. Solid State Chem.*, 1996, **125**, 228.
- 7 J. Yu, Y. Wang, Z. Shi and R. Xu, *Chem. Mater.*, 2001, **13**, 2972.
- 8 S. Natarajan, S. Neeraj, A. Choudhury and C. N. R. Rao, *Inorg. Chem.*, 2000, **39**, 1426; A. Choudhury, S. Neeraj, S. Natarajan and C. N. R. Rao, *Angew. Chem., Int. Ed.*, 2000, **39**, 3091.
- 9 S. Neeraj, P. M. Forster, C. N. R. Rao and A. K. Cheetham, *Chem. Commun.*, 2001, 2716.
- 10 C. N. R. Rao, S. Natarajan and S. Neeraj, *J. Am. Chem. Soc.*, 2000, **122**, 2810.
- 11 G.M. Sheldrick, SHELXL-97, A Program for Crystal Structure Determination, University of Göttingen, Göttingen, 1997.
- 12 G.M. Sheldrick, SHELXTL-PLUS, Program for Crystal Structure Solution and Refinement, University of Göttingen, Göttingen, 1993.
- 13 S. Neeraj, S. Natarajan and C. N. R. Rao, *Chem. Mater.*, 1999, **11**, 1390.
- 14 J. R. D. DeBord, R. C. Haushalter and J. Zubieta, *J. Solid State Chem.*, 1996, **125**, 270.
- 15 J. Escobal, J. L. Pizarro, J. L. Mesa, L. Lezama, R. Olazcuaga, M. I. Arriortua and T. Rojo, *Chem. Mater.*, 2000, **12**, 376; K. O. Kongshaug, H. Fjellvåg and K. P. Lillerud, *J. Solid State Chem.*, 2001, **156**, 32.