JOURNAL OF Materials CHEMISTRY

$H_3N(CH_2)_6NH_3{\cdot}Zn_4(PO_4)_2(HPO_4)_2{\cdot}3H_2O$: a novel three-dimensional zinc phosphate framework containing 5- and 20-rings

Jennifer A. Rodgers and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Aberdeen, UK AB24 3UE.
E-mail: w.harrison@abdn.ac.uk

Received 22nd June 2000, Accepted 2nd October 2000
First published as an Advance Article on the web 8th November 2000

The solution-mediated synthesis, single crystal structure, and some properties of $H_3N(CH_2)_6NH_3{\cdot}Zn_4(PO_4)_2(HPO_4)_2{\cdot}3H_2O$, a novel organically-templated zinc phosphate containing 3-, 4-, 5-, 6- and 20-rings, are described. Vertex-linked ZnO_4, PO_4, and HPO_4 building units self-assemble into a complex three-dimensional network incorporating extra-framework 1,6-diammoniohexane and water molecules. The organic species interacts with the framework by way of N–H···O hydrogen bonds. Previously unseen "trimers" of ZnO_4 tetrahedra are a feature of the framework.

Introduction

Organically-templated zincophosphates (ZnPOs) containing inorganic frameworks built up from vertex-linked ZnO_4 and PO_4 tetrahedra show considerable structural diversity.[1] The recently reported[2] $[H_2DACH]Zn_3(PO_4)_2(HPO_4){\cdot}2H_2O$ (DACH = 1,2-diaminocyclohexane) contains the largest pore (a 24-ring, *i.e.* 24 tetrahedral centres) yet seen in a microporous, tetrahedral framework phase. Interesting features, such as 3-rings and infinite chains of –Zn–O–Zn–O– bonds are shown by the inorganic component of various examples of ZnPO phases.[1,3] The conformation and H-bonding properties of the organic cation have a strong structure-directing effect, and linear diamines are particularly successful in templating ZnPOs.[1] For each of the series $[H_3N(CH_2)_nNH_3]^{2+}$ ($n = 2$, 3, 4, 6), templated ZnPOs have been prepared, although, even for a particular protonated diamine, it is very difficult to control or even to predict the structural features of the resulting ZnPO phases.[4] One reason for this is that reaction mechanisms are essentially unknown in most hydrothermal reactions and the "black-box" nature of the sealed hydrothermal reactor makes conventional sampling of any intermediate phases tedious or impossible.[5] Thus, following the example of aluminosilicate zeolites, exploratory synthesis continues to play a vital role in preparing new ZnPO phases which may demonstrate further points of correlation between preparation conditions and the resulting crystal structures.

Here, we report solution-mediated syntheses, the single-crystal structure, and some properties of $H_3N(CH_2)_6NH_3{\cdot}Zn_4(PO_4)_2(HPO_4)_2{\cdot}3H_2O$, a new 1,6-diammoniohexane zinc phosphate hydrate, which contains a three-dimensional Zn–P–O bonding network. Typically, the structure is quite distinct from those of any previously observed ZnPOs: novel features include isolated trimers of ZnO_4 groups, and 5- and 20-rings.

Experimental

Synthesis and initial characterisation

First, 4.4761 g $Zn(NO_3)_2$ (BDH Analar, 98%) was added to 30 ml of 1 M H_3PO_4 (made up from 85% BDH Analar H_3PO_4 solution) in a glass beaker. Once the $Zn(NO_3)_2$ had dissolved, 37.277 g of ethylene glycol was added, followed by 1.7872 g of 1,6-diaminohexane (Acros Organics, 99.5%), and the mixture was stirred for 10 min. A yellow–white precipitate appeared and heat was evolved. The mixture was then placed in an oven at 90 °C for 4 days. The solids (yield = 0.605 g) were recovered by suction filtration and rinsing with acetone, providing light brown needle-like crystals (maximum linear dimension *ca.* 1 cm) of $H_3N(CH_2)_6NH_3{\cdot}Zn_4(PO_4)_2(HPO_4)_2{\cdot}3H_2O$ and small amounts of powder. The product appears to be completely stable when stored in a sealed vessel in dry air. Hydrothermal treatment (*ca.* 66% filled 23 ml teflon-lined bomb) of the same reaction mixture at 150 or 180 °C for 4 days also led to similar crystals of the title compound.

The powder pattern of $H_3N(CH_2)_6NH_3{\cdot}Zn_4(PO_4)_2(HPO_4)_2{\cdot}3H_2O$ (Stoe STADI diffractometer, Cu-Kα_1 radiation, $\lambda = 1.54054$ Å) was in good agreement with simulated peak positions and intensities based on the single crystal structure, confirming the phase purity of the crystalline component. Thermogravimetric analysis (TGA) data for the title compound were collected on a STA 1500 instrument (ramp at 10 °C min^{-1} in air and N_2). The post-TGA residue yielded a null diffraction pattern. Cross-polarized (CP) ^{13}C MAS NMR spectra were collected on a Varian Unityplus spectrometer with a Doty Scientific MAS probe and referenced to a standard of $(CH_3)_4Si$.

Single crystal structure study

A needle of $H_3N(CH_2)_6NH_3{\cdot}Zn_4(PO_4)_2(HPO_4)_2{\cdot}3H_2O$ ($\sim 0.05 \times 0.05 \times 0.50$ mm) was selected and mounted on a Bruker SMART 1000 CCD area detector diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å, $T = 25 \pm 2$ °C). After routine data collection and reduction,[6] the structural model was developed in space group $P\bar{1}$ (no. 2). H atoms associated with the organic cation were positioned geometrically [d(X–H) = 1.00 Å] and refined by riding on their appropriate N or C atoms. The H atoms associated with the extra-framework water molecules and the Zn–P–O framework component of the structure were not located. The site occupation factors of the three extra-framework water molecule oxygen atoms (O17, O18, and O19) were refined, and converged to unity within experimental error. Thus, for the final refinement cycles, these values were fixed at 1.00. Crystal data are summarised in Table 1.

CCDC reference number 1145/252. See http://www.rsc.org/suppdata/jm/b0/b004994h/ for crystallographic files in .cif format.

DOI: 10.1039/b004994h

Table 1 Crystallographic parameters for $H_3N(CH_2)_6NH_3{\cdot}Zn_4(PO_4)_2(HPO_4)_2{\cdot}3H_2O$

Empirical formula	$Zn_4P_4O_{19}N_2C_6H_{26}$
Formula weight	815.69
Crystal system	Triclinic
a/Å	5.2016(4)
b/Å	13.6024(11)
c/Å	17.2394(13)
α/°	97.869(2)
β/°	93.302(2)
γ/°	91.828(2)
V/Å^3	1205.3
Z	2
Space group	$P\bar{1}$ (no. 2)
T/K	298(2)
μ/cm^{-1}	42.8
Total data	6986
Observed data^a	2385
$R(F)^b$	0.044
$wR(F)^c$	0.054

$^a I > 2\sigma(I)$ after the merging of systematically equivalent and multiply-measured reflections. $^b R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^c R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Results

Crystal structure

Selected geometrical data for $H_3N(CH_2)_6NH_3{\cdot}Zn_4(PO_4)_2(HPO_4)_2{\cdot}3H_2O$ are presented in Table 2. This phase is a new framework zincophosphate with three-dimensional character containing 20-ring pores. An ORTEP-3[7] view of the asymmetric unit is shown in Fig. 1, and a polyhedral representation[8] of the complete crystal structure is given in Fig. 2.

The 16 distinct framework oxygen atoms in $H_3N(CH_2)_6NH_3{\cdot}Zn_4(PO_4)_2(HPO_4)_2{\cdot}3H_2O$ divide into 12 Zn–O–P bridges [$\theta_{av} = 131.3°$], two terminal P–OH links, and the two three-coordinate (to two Zn and one P) O3 and O4 species. The Zn–O–P bond angles around these two atoms are much smaller than those of the simple Zn–O–P bridges (Table 2). The overbonded situations of O3 and O4 are probably responsible for their rather long bonds to Zn and P, although their bond valences[9] of 2.03 and 2.07, respectively (expected 2.00), are satisfied by this geometry. The three extra-framework O atoms must be parts of water molecules. The thermal parameters for O18 and, especially, O19 are large and anisotropic, with the highest degree of thermal motion occurring roughly along [100], the 20-ring channel direction. Such behaviour is not unexpected for "zeolitic" water molecules which weakly interact with the framework part of the structure and is quite distinct from "bound" water molecules which form parts of $ZnO_3(H_2O)$ tetrahedra as seen in some ZnPOs.[10]

There are 35 distinct non-hydrogen atoms in $H_3N(CH_2)_6NH_3{\cdot}Zn_4(PO_4)_2(HPO_4)_2{\cdot}3H_2O$, all of which occupy general positions in the unit cell. The four distinct zinc atoms adopt tetrahedral coordination with typical[1,2] geometrical parameters (Table 2). Some Zn–O–(Zn,P) links are present, *via* the three-coordinate oxygen species O3 and O4. The connectivity for Zn1, Zn2 and Zn3 results in novel, isolated (from each other and from Zn4), trimers of three ZnO_4 groups connected by Zn–O–Zn bonds (Fig. 3). As expected, the four distinct P atoms form the centres of tetrahedral (hydrogen) phosphate groups. Bond length/bond strength considerations[9] strongly suggest that the long, terminal, P3–O15 and P4–O16 bonds are parts of P–OH groups, which is consistent with the charge balancing requirement.

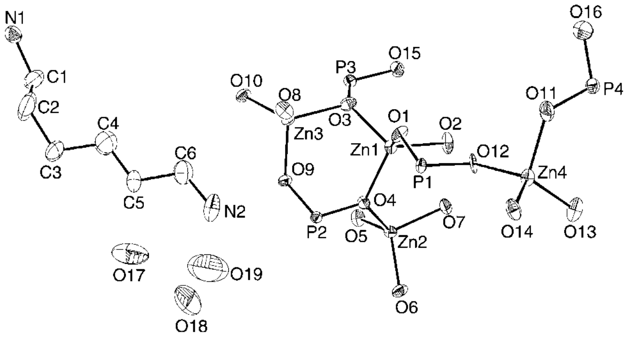

Fig. 1 Asymmetric unit of $H_3N(CH_2)_6NH_3{\cdot}Zn_4(PO_4)_2(HPO_4)_2{\cdot}3H_2O$ (50% thermal ellipsoids) showing the atom labelling scheme. H atoms omitted for clarity.

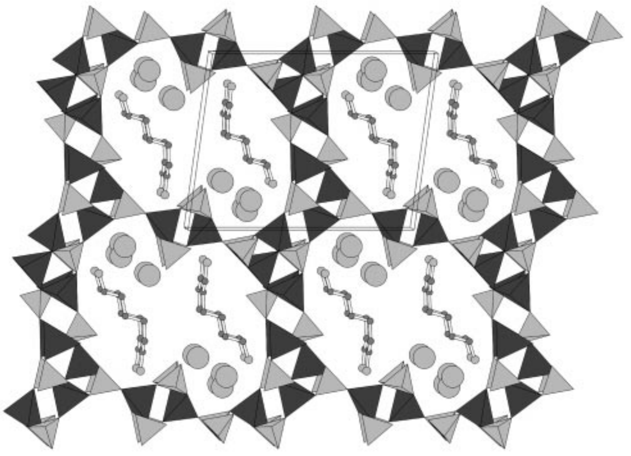

Fig. 2 Polyhedral view down [100] of the $H_3N(CH_2)_6NH_3{\cdot}Zn_4(PO_4)_2(HPO_4)_2{\cdot}3H_2O$ crystal structure showing the network of ZnO_4 (dark) and PO_4 (light) tetrahedra surrounding the 20-ring channels occupied by the water molecules (isolated spheres) and 1,6-diammoniohexane cations.

The polyhedral connectivity in this complex phase may be envisaged in terms of various types of sub-units propagating along [100]. Various types of rings are apparent in these subunits, including 3- and 4-rings associated with the Zn1, Zn2, P1 and P2-centered polyhedra, rather similar to the situation in $(CN_3H_6)_2{\cdot}Zn_4H_5(PO_4)_5$.[11] The Zn3 and P3 tetrahedra form 4-ring ladders, akin to the connectivity of similar building blocks in phases such as $H_3N(CH_2)_3NH_3{\cdot}Zn(HPO_4)_2$.[4] These first two sub-units are fused together *via* polyhedral 3- and 5-rings into corrugated sheets which propagate normal to [001]. The novel 5-ring grouping is illustrated in Fig. 4. Lastly, the Zn4 and P4 units also form 4-ring ladders and these groupings link the

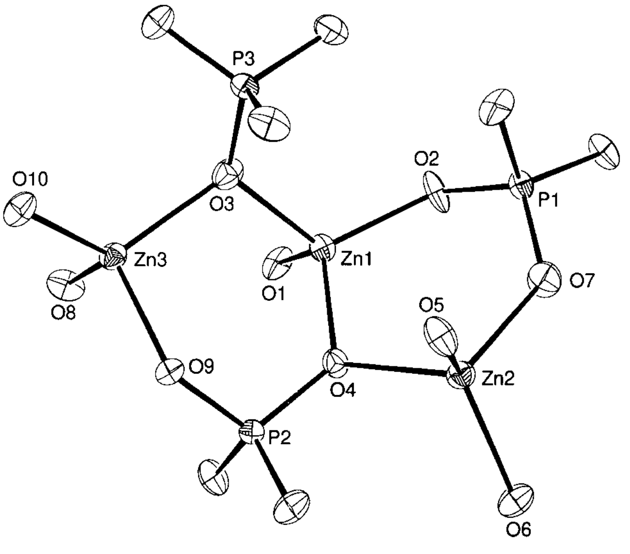

Fig. 3 Detail of the $H_3N(CH_2)_6NH_3{\cdot}Zn_4(PO_4)_2(HPO_4)_2{\cdot}3H_2O$ structure showing a trimer of ZnO_4 tetrahedra and its associated PO_4 groups. Note the three-coordinate O3 and O4 species.

Table 2 Selected bond distances (Å)[a] and angles (°) for $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$

Zn1–O1	1.914(7)	Zn1–O2	1.905(7)	Zn1–O3	1.990(7)
Zn1–O4	1.966(7)	Zn2–O4	2.026(7)	Zn2–O5	1.926(7)
Zn2–O6	1.920(7)	Zn2–O7	1.943(7)	Zn3–O3	2.017(7)
Zn3–O8	1.911(7)	Zn3–O9	1.942(7)	Zn3–O10	1.914(7)
Zn4–O11	1.979(8)	Zn4–O12	1.926(7)	Zn4–O13	1.930(8)
Zn4–O14	1.942(7)	P1–O1	1.553(7)	P1–O2	1.548(7)
P1–O7	1.517(8)	P1–O12	1.525(7)	P2–O4	1.564(7)
P2–O5	1.507(7)	P2–O6	1.519(8)	P2–O9	1.542(7)
P3–O3	1.570(7)	P3–O8	1.512(8)	P3–O10	1.494(7)
P3–O15	1.565(7)	P4–O11	1.523(8)	P4–O13	1.511(8)
P4–O14	1.520(7)	P4–O16	1.589(9)		

Zn1–O1–P1	127.8(4)	Zn1–O2–P1	125.7(4)	Zn1–O3–Zn3	109.2(3)
Zn1–O3–P3	127.2(4)	Zn3–O3–P3	115.6(4)	Zn1–O4–Zn2	114.9(3)
Zn1–O4–P2	125.7(4)	Zn2–O4–P2	116.1(4)	Zn2–O5–P2	142.2(5)
Zn2–O6–P2	126.9(4)	Zn2–O7–P1	130.5(5)	Zn3–O8–P3	141.5(5)
Zn3–O9–P2	127.2(4)	Zn3–O10–P3	132.3(5)	Zn4–O11–P4	128.6(5)
Zn4–O12–P1	135.3(4)	Zn4–O13–P4	136.7(5)	Zn4–O14–P4	120.4(4)

N1–H1···O12	1.00	2.01	2.84(2)	N1–H2···O2	1.00	1.82	2.82(2)
N1–H3···O11	1.00	1.98	2.88(2)	N2–H4···O5	1.00	2.13	3.02(2)
N2–H5···O9	1.00	1.94	2.83(2)	N2–H6···O18	1.00	1.94	2.92(2)

[a] For the hydrogen bonds, the three distances refer to the N–H, H···O, and N···O separations, respectively.

sheets into a three-dimensional network *via* 6-rings. The resulting tetrahedral network encloses 20-ring pores propagating along [100] with maximum atom-to-atom dimensions of *ca.* 8.03 × 16.06 Å.

The C–N and C–C geometrical parameters of the doubly protonated 1,6-diammoniohexane cation are in good accord with those seen in related structures.[3] Its general conformation could be described as irregular, or "floppy". Pairs of 1,6-diammoniohexane cations and six water molecules occupy each 20-ring window. The organic moieties bond to the zincophosphate framework by way of N–H···O hydrogen bonds (Table 2). Based on the geometrical placement of the hydrogen atoms, all six N–H protons are involved in H-bonding, with d(H···O) ranging between 1.82 and 2.13 Å. Five of the acceptor O atoms are parts of Zn–O–P bonds and one oxygen atom belongs to a water molecule. Based on $O_w \cdots O_f$ (w = water, f = framework) contact distances < 3 Å for O17, O18, and O19, the water molecules may also weakly interact with the framework by way of O–H···O bonds.

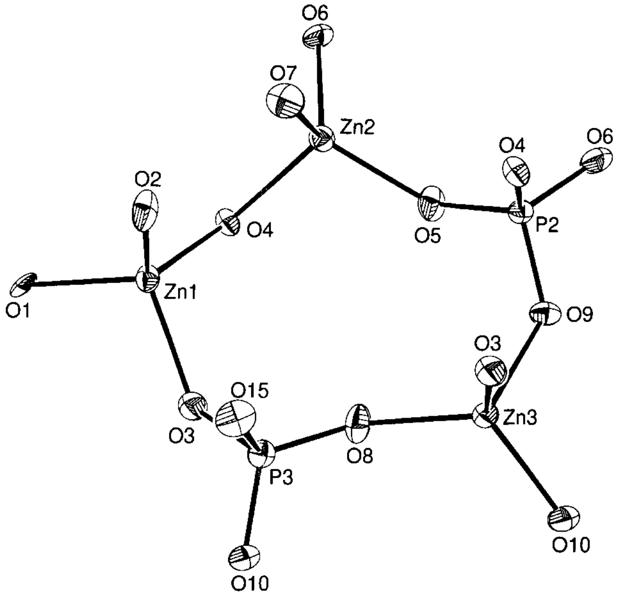

Fig. 4 Detail of the $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$ structure showing a tetrahedral 5-ring. The maximum deviation of the constituent Zn and P nodal atoms from their best least-squares plane is less than 0.08 Å.

Physical data

When heated in air, $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$ reacts vigorously and expands to many times its initial volume. Therefore, TGA/DTA runs were made with the minimum possible amount of sample. The average weight loss for two runs was 25.2%. This is in good agreement with a scheme involving the loss of all the C, N and H, and five O to result in a residue of nominal formula "$Zn_4P_4O_{14}$" (calculated weight loss = 25.3%), and offers some supporting evidence for the existence of three fully-occupied extra-framework water molecule sites, as noted above. Powder diffraction indicated that the TGA residue was amorphous/glassy. The weight loss was essentially continuous from ambient to *ca.* 700 °C, with a strong exothermic event apparent at *ca.* 512 °C, possibly corresponding to combustion of some of the organic material. There were no identifiable steps corresponding to separate loss of the water and organic molecules. A TGA run carried out under N_2 was very similar, with a broad, unresolved weight loss occurring over a wide temperature range.

The ^{13}C CP-MAS NMR spectrum for $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$ showed six signals at δ values of 41.05, 39.01, 29.87, 28.76, 26.33, and 25.26 (Fig. 5). The spectrum was deconvoluted to yield relative peak intensities of unity, within experimental error. The crystallographic evidence indicates that the six carbon atoms are in distinct environments which correspond to the six peaks produced. The ^{13}C signal for $-CH_2NH_2$ is expected to occur at about 43 ppm and the peak

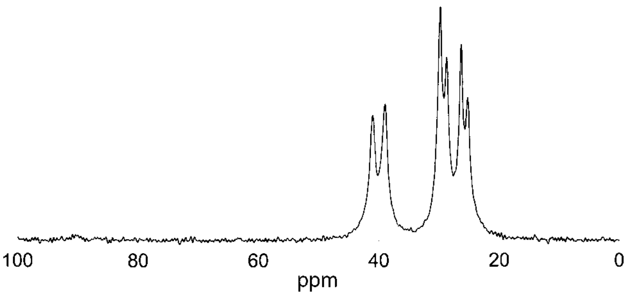

Fig. 5 ^{13}C MAS NMR spectrum of $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$ [chemical shifts relative to $(CH_3)_4Si$].

for $–CH_2NH_3^+$ is expected at 40 ppm.[12] Therefore, we assume that the two peaks at $\delta = 41.05$ and 39.01 ppm result from carbon atoms adjacent to protonated NH_3^+ groups. This provides further evidence that the cation is doubly protonated.

Discussion

$H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$, a new 1,6-diammoniohexane zinc phosphate hydrate, has been prepared as single crystals by a typical solution-mediated reaction and structurally characterised by X-ray diffraction methods. In this case, a predominantly non-aqueous environment was used to synthesise the product in reasonable yield and high purity. The reaction seems to be fairly insensitive to temperature. The product has a completely different structure to $H_3N(CH_2)_6NH_3 \cdot Zn_3(HPO_4)_4 \cdot H_2O$,[3] the only other ZnPO phase templated by the same cation characterised so far. The latter material is layered and contains 8-membered rings. It is notable that both these phases contain extra-framework water molecules, which is unusual for organically-templated ZnPOs. We assume that $O_w–H \cdots O_f$ hydrogen bonds are present in $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$, as well as the typical[2] $N–H \cdots O_f$ interactions. Thus we might tentatively describe this situation as one of "co-templating" by both the organic species and water molecules. Presumably the title compound would not be stable in the absence of water, however, we have not succeeded in preparing it under purely aqueous conditions.

As is common for organically-templated ZnPOs,[1] the framework of $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$ does not survive template/water removal, at least by simple thermal methods. The broad temperature range for removal of the extra-framework species superficially resembles the thermal behaviour of hydrated aluminosilicate zeolites, but here, the change is irreversible and the porous structure collapses, whereas zeolites readily readsorb water. This is a frustrating general problem[13] in templated, porous solids.

Structurally, $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$ consists of the expected polyhedral units of ZnO_4 and $(H)PO_4$ tetrahedra, sharing vertices. Recently, efforts have been made[14] to identify a "primary building unit," or PBU (somewhat akin to the concept of groups of tetrahedra, or secondary building units,[15] used in rationalising zeolite structures) in framework phosphates. The proposed ZnPO PBU 4-ring unit, containing strictly alternating Zn and P nodes[14] is indeed observed in $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$, but rationalisation of the overall structure is still elusive. One reason for this is the presence of trigonally coordinated (to 2 Zn and 1 P) oxygen atoms. This feature, which has never been seen in aluminosilicates or aluminophosphates, invariably leads to odd-numbered rings, rather than just even-numbered rings, which would follow from a perfectly alternating array of Zn and P nodes. A number of ZnPOs containing 3-rings (nodes: Zn, Zn, P) have been seen previously,[16] whereas the 5-ring (Zn, Zn, P, Zn, P) in $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$ is novel.

As expected for a tetrahedral framework containing 20-rings, the structure of $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$ is very open. The templating effect of the 1,6-diammoniohexane species is broadly as expected in terms of $N–H \cdots O$ interactions from the terminal, protonated amine groups, and the space-filling role of the hydrocarbon chain. $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$ contains the largest ring system seen in a ZnPO templated by a diamine. It is tempting to assign this feature to the space-filing needs of the longer carbon chain in the 1,6-diamine, but this would be simplistic, as the majority of ZnPOs templated by diamines are layered. However, it seems worthwhile to attempt to prepare three-dimensional ZnPOs with yet longer chain diamines and such efforts are currently in progress.

The framework density (FD; number of nodal Zn and P atoms per 1000 Å^3)[17] of $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$ is 13.3, which is only slightly greater than that of aluminosilicate faujasite (typical FD = 12.7).[15] The amount of void space[18] in $H_3N(CH_2)_6NH_3 \cdot Zn_4(PO_4)_2(HPO_4)_2 \cdot 3H_2O$, defined as the fraction of the unit cell volume *not* occupied by the framework (Zn, P, and O) atoms, assuming typical van der Waals' radii for these species, is 551.3 Å^3 (45.7% of the unit cell volume). However, when the extra-framework species are included, there is no "solvent accessible" volume, indicating that the channels are essentially filled by the extra-framework species. The recently reported gallophosphate $H_3N(CH_2)_4NH_3 \cdot Ga_4(PO_4)_3(HPO_4)_2(OH)_3 \cdot 5.4H_2O$[19] also contains 20-ring windows built up from GaO_6 octahedra and $(H)PO_4$ tetrahedra.

Acknowledgements

We thank Jim Marr for experimental assistance and David Apperley (EPSRC National NMR Service, University of Durham) for running the MAS NMR spectra.

References

1 W. Liu, Y. Liu, Z. Shi and W. Pang, *J. Mater. Chem.*, 2000, **10**, 1451 and references therein.
2 G.-Y. Yang and S. C. Sevov, *J. Am. Chem. Soc.*, 1999, **121**, 8389.
3 D. Chidambaram, S. Neeraj, S. Natarajan and C. N. R. Rao, *J. Solid State Chem.*, 1999, **147**, 154.
4 W. T. A. Harrison, Z. Bircsak, L. Hannooman and Z. Zhang, *J. Solid State Chem.*, 1998, **136**, 93.
5 P. Amorós, M. Dolores Marcos, A. Beltrán-Porter and D. Beltrán-Porter, *Curr. Opin. Solid State Mater. Sci.*, 1999, **4**, 123.
6 Data collection software: SMART, SAINT and SADABS, software for area-detector diffractometers, Bruker Analytical X-Ray Systems, Madison, WI, USA, 1999; Structure solution: SHELXS-86, G. M. Sheldrick, University of Göttingen, Germany, 1986; Refinement: CRYSTALS, J. R. Carruthers, D. J. Watkin and P. W. Betteridge, University of Oxford, UK, 1999.
7 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.
8 ATOMS, Shape Software, Kingsport, Tennessee, USA, 1999.
9 I. D. Brown, *J. Appl. Crystallogr.*, 1996, **29**, 479.
10 W. T. A. Harrison, T. M. Nenoff, M. M. Eddy, T. E. Martin and G. D. Stucky, *J. Mater. Chem.*, 1992, **2**, 1127.
11 W. T. A. Harrison, M. L. F. Phillips, W. Clegg and S. J. Teat, *J. Solid State Chem.*, 1999, **148**, 433.
12 D. Apperley, University of Durham, UK, private communication, 2000.
13 A. K. Cheetham, G. Férey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3269.
14 S. Neeraj, S. Natarajan and C. N. R. Rao, *J. Solid State Chem.*, 2000, **150**, 417.
15 W. M. Meier and D. H. Olson, *Atlas of Zeolite Structure Types*, 3rd revised edn., Butterworth-Heinmann, New York, 1992.
16 S. B. Harmon and S. C. Sevov, *Chem. Mater.*, 1998, **10**, 3020.
17 G. O. Brunner and W. M. Meier, *Nature (London)*, 1989, **337**, 146.
18 A. L. Spek, PLATON for Windows, Utrecht University, Utrecht, The Netherlands, 2000.
19 A. M. Chippindale, K. J. Peacock and A. R. Cowley, *J. Solid State Chem.*, 1999, **145**, 379.