Journal of Solid State Chemistry 183 (2010) 1625–1631

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Ionothermal synthesis and crystal structures of metal phosphate chains

David S. Wragg [a,*,1], Benjamin Le Ouay [a], Andrew M. Beale [b], Matthew G. O'Brien [b], Alexandra M.Z. Slawin [a], John E. Warren [c], Timothy J. Prior [c], Russell E. Morris [a]

[a] EaSt CHEM School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, UK
[b] Inorganic Chemistry and Catalysis, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands
[c] STFC Daresbury Laboratory, Warrington, Cheshire, WA4 4AD, UK

ARTICLE INFO

Article history:
Received 19 January 2010
Received in revised form
23 April 2010
Accepted 2 May 2010
Available online 11 May 2010

Keywords:
Ionothermal synthesis
X-ray diffraction
Crystal structure
Chain

ABSTRACT

We have prepared isostructural aluminium and gallium phosphate chains by ionothermal reactions in 1-ethyl-3-methylimidazolium bromide and 1-ethylpyridinium bromide under a variety of conditions. The chains can be prepared as pure phases or along with three dimensional framework phases. The chains are favoured at shorter heating times and the crystallinity can be improved by addition of transition metal acetates and amines which are not included in the final structure. The chain can be prepared with or without the presence of hydrofluoric acid.

1. Introduction

Ionothermal synthesis is a recently developed method for synthesising framework-type materials using ionic liquids as solvent and template. A range of three dimensional and layered metal phosphate and metal–organic framework structures have been prepared by this route [1]. We have extended the set of structure types prepared in this way by isolating a well known one dimensional chain structure from ionothermal metal phosphate syntheses under a range of conditions.

The first zeotype aluminium phosphates were synthesised by Wilson and co workers in 1982 [2] and over the subsequent years numerous metal phosphate systems have yielded zeolite like frameworks of great interest [3–11], for example the extremely large pore cloverite [12] and VSB-1 [13] structures and the catalytically important SAPO-34[14]. One dimensional metal phosphates based on the same tetrahedral MO_4 and PO_4 building blocks as the zeotypes are also well known in the literature [15–31] (there are 22 different 1-D aluminium phosphates in the AlPO database) [32]. The first of these to be prepared, a chain of AlO_4 and $PO_4(H_2)$ tetrahedra arranged in corner sharing rings [14], is found in a range of synthetic systems and is one of the basic units for the "chain to layer" synthetic mechanism for aluminophosphates proposed by Ozin and co workers [33]. The structure is composed of rings of four alternating tetrahedral aluminium and phosphorus centres linked by oxygen atoms. The aluminium tetrahedra (opposite corners of the 4 tetrahedral atom ring) are shared by two rings to create a straight chain while the phosphorus centred tetrahedra have two uncondensed pendant oxygen atoms which link adjacent chains in a hydrogen bonded network which also includes the organic template used in the synthesis. Short O–O contacts can also exist between pendant oxygens within the individual chains. The basic chain is shown without an organic template in Fig. 1.

This corner sharing chain has already been reported in ionothermal systems in which the solvent is a deep eutectic mixture [26,28] but not in syntheses using single component ionic liquids; indeed, the only chain so far synthesised in a single component ionic liquid is probably not formed by an ionothermal route but by a solid state or hydrothermal reaction under a layer of hydrophobic ionic liquid [27].

In this paper we describe the ionothermal synthesis of the MP_2O_8 chain under a surprising variety of conditions with $M{=}Al$ and Ga and report well determined crystal structures for the aluminium version with 1-ethyl-3-methyl imidazolium bromide (at 150 and 100 K) and 1-ethylpyridinium bromide (150 K). The effects of mixing tetraethylammonium hydroxide and tripropylamine, well known templates for porous materials, with the ionic liquid are discussed. Also the addition of zinc, which can substitute for M^{3+} in MPO_4 metal phosphate frameworks producing a charged framework, and fluoride, a common mineralising agent in framework synthesis, are studied. All of these modifications to the synthesis lead to the same chain structure (sometimes together with other phases) which also appears to be favoured at shorter heating times.

---

[*] Corresponding author.
E-mail address: david.wragg@smn.uio.no (D.S. Wragg).
[1] Current address: Centre for Materials Science and Nanotechnology, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway.

0022-4596/$ - see front matter © 2010 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2010.05.002

2. Experimental

1-ethyl-3-methylimidazolium bromide (EMIM Br) and 1-ethylpyridinium bromide (EPB) ionic liquids (ILs) were prepared by reaction of an amine (1-methylimidazole or pyridine) with a slight molar excess of bromoethane under dry conditions [34]. Other chemicals were obtained from Aldrich and used without further purification. In a typical synthesis phosphoric acid (0.17 g, 3 mmol) and aluminium isopropoxide (0.1 g, 0.5 mmol) were placed in an autoclave or sealed glass tube and the chosen IL (5 g, 26 mmol for EMIM Br and 3 g, 16 mmol for EPB) was added. In some reactions additional reagents were added after the IL:

- Hydrofluoric acid (40% solution, 0.015 ml, 0.3 mmol)
- Tripropylamine (0.1 ml)
- Tetraethylammonium hydroxide (0.03 g, 35% weight solution)
- Zinc acetate

In the syntheses with zinc the amounts of aluminium isopropoxide and zinc acetate were varied in order to give several molar ratios of Zn:Al. The ratios used and the resulting products are given in the results section below.

The mixtures thus prepared were heated in an oven at 150 °C for 3 days (compounds 1 and 3) or 24 h (compounds 2 and 4), cooled at room temperature and filtered to recover the solid product. The white, crystalline powder products were washed with water and acetone and dried in air.

The gallium phosphate chain (compound 5) was prepared from a mixture of gallium sulphate hydrate (0.05 g, 0.1 mmol), phosphoric acid (0.17 g, 3 mmol) and EMIM Br (2.4 g, 13 mmol) sealed in a glass tube and heated at 150 °C for 24 h. The product was recovered as above. The specific synthesis mixtures and conditions used to prepare the 5 reported chain compounds are given in Table 1.

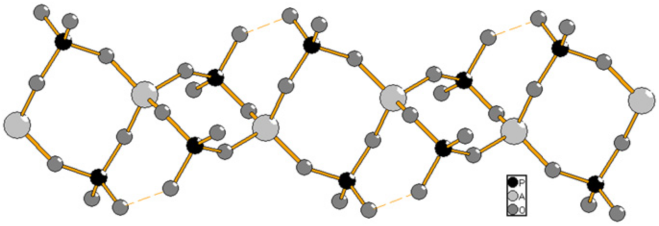

Fig. 1. The MP_2O_8 linear corner sharing chain, shown without any of the possible organic structure directing agents which can produce it, to illustrate the basic structure. Internal hydrogen bonds between dangling phosphate groups are shown as dashed lines. Hydrogen atoms are omitted for clarity.

Initial characterisation of the products was by powder X-ray diffraction on a Stoe STADIP diffractometer equipped with an automatic sample changer using copper $K\alpha$ radiation in transmission mode or a Bruker D8 diffractometer using Co $K\alpha$ radiation in reflective mode.

Single crystal X-ray diffraction (SCXRD) data for compounds 1, 2 and 5 were collected on diffractometers comprising Rigaku Cu/Mo MM007 high brilliance generators with Saturn 92 CCDs and XStream low temperature accessories. Data were processed using the Crystal Clear program suite [35]. SCXRD data for compounds 3 and 4 were collected at stations 16.2 smx and 9.8, respectively, of the Synchrotron Radiation Source, Daresbury, UK [36]. The diffractometers were modified Bruker instruments with APEX II CCD area detectors. Full spheres of data were collected, integrated and scaled using the Bruker software [37]. All structures were solved by direct methods using SHELXS-97 and refined by full matrix least squares on F^2 in the program SHELXL-97 as implemented in Farrugia's WinGX program suite [38,39].

EDX microanalysis of the samples prepared using zinc acetate was carried out on a JEOL 5600 SEM using an Oxford instruments' INCA EDX system.

3. Results and discussion

The corner sharing $[AlP_2O_8]$ chain has been prepared from four different ionothermal reaction mixtures:

1. Aluminium phosphate with EPB.
2. Aluminium phosphate with EMIM Br and Zn acetate.
3. Aluminium phosphate with EMIM Br and tripropylamine.
4. Aluminium phosphate with EMIM Br and tetraethylammonium hydroxide. Synthesis with hydrofluoric acid.

The chain has also been prepared as a gallium phosphate $[GaP_2O_8]$ using EMIM Br as solvent and template (compound **5**).

The crystal structures of the chains show slight differences in unit cell parameters depending on the synthesis route and data collection temperature, Table 2.

Table 1
Synthesis conditions for the five compounds described in the structural investigations.

Compound	$Al(Oipr)_3$/g	$Ga_2(SO_4)_3$/g	H_3PO_4/g	IL	additives	Heating time (h)	Product
1	0.1		0.17	EPB, 3 g		72	Chain
2	0.05		0.17	EMIM Br, 5 g	$Zn(Oac)_2$, 0.175 g	24	Chain+SIZ-1 [40]
3	0.1		0.17	EMIM Br, 5 g	tripropylamine, 0.1 ml	72	Chain
4	0.1		0.17	EMIM Br, 5 g	TEAOH, 0.03 g; HF, 0.015 ml	24	SIZ-4 [40]+chain
5		0.05	0.17	EMIM Br, 2.4 g		24	Chain+hexagonal GaPO phase [39]

Table 2
Summary of unit cell data for compounds 1–5.

Structure and formula	T/K	Space group	R ($F_{obs} > 4\sigma F_{obs}$)	a, b, c/Å	α, β, γ/°
1 $AlP_2O_8H_2$, $C_7H_{10}N$	173	$P2_1/c$ (14)	0.0529	7.8237(14), 14.2901(17), 12.7884(14)	90, 118.18(1), 90
2 $AlP_2O_8H_2$, $C_6H_{11}N_2$	173	$P2$ (3)[a]	N.A.	8.0611(13), 13.0760(20), 13.5150(20)	90, 114.245(12), 90
3 $AlP_2O_8H_2$, $C_6H_{11}N_2$	150	$P2_1/c$ (14)	0.0668	8.078(4), 13.111(6), 13.534(5)	90, 114.19(2), 90
4 $AlP_2O_8H_2$, $C_6H_{11}N_2$	100	$P-1$ (2)	0.0883	8.0786(32), 12.5799(50), 12.9740(52)	88.510(6), 86.240(6), 79.848(6)
5 $GaP_2O_8H_2$, $C_6H_{11}N_2$	93	$P-1$ (2)	N.A.	7.9240(31), 12.5626(50), 12.9397(50)	88.640(22), 87.037(24), 79.685(21)

Note that the structures of compounds 2 and 5 could not be refined by the least squares method against the SCXRD data.

[a] The true space group of structure 2 is in fact likely to be $P2_1/c$ rather than the lower symmetry group determined from the poor quality SCXRD data.

Structures **4** and **5**, collected below 100 K, have triclinic symmetry while at higher temperatures (above 150 K) the symmetry is monoclinic. The SCXRD data were obtained from rather small crystals and for compounds **2** and **5** were not good enough to give an acceptable least squares refinement (or indeed to fully determine the space group symmetry for compound **2**—we believe that the true symmetry is in fact $P2_1/c$ as for the other structures collected above 150 K). The chain structure could be seen from the direct methods structure solution in both cases, however, and the unit cells are well determined and consistent with the results obtained for compounds **1**, **3** and **4**. These unit cell parameters do not match any other structures containing aluminium or gallium phosphate in the Cambridge structural database [40,41]. We therefore include these data to illustrate the range of synthetic conditions which can yield the chain structure and as further evidence (compound **5**) of the existence of the triclinic low temperature structure. The slightly high residual (R=0.088) value for the refinement of structure **4** is explained by the small and weakly scattering nature of the crystals obtained for this material. The SCXRD data for this structure were collected using synchrotron radiation and it is highly unlikely that structural data for this material could have been obtained at all by other means. The estimated standard deviations in the bond lengths and angles and atomic positions also suggest that the structure is reliable and of comparable quality to those of compounds **1** and **3**. The asymmetric units of compounds **1**, **3** and **4** are shown in Fig. 2.

Despite the fact that the unit cells vary significantly for the different AlP_2O_8 structural types (**1**; **2** and **3**; **4)** the bond lengths and angles in the chain are very similar in all cases. Within the rings the Al–O distances range from 1.731 to 1.749 Å and the P–O distances from 1.542 to 1.551 Å. The pendant oxygen atoms of the phosphorus tetrahedra comprise pairs with a shorter distance of 1.49–1.50 Å (indicating a P=O double bond) and a longer distance of 1.534–1.564 Å (indicating a P–O single bond). The existence of double bond character in these bonds is also suggested by the O–P–O angles for the pendant oxygens of 112°–113°. These values are consistent with those reported elsewhere for the chain.

The monoclinic EPB templated chain (compound **1**) has a very different packing arrangement to the monoclinic EMIM structure (**2**, **3**), which is clearly apparent from comparison of the unit cell dimensions. When viewed along the *a*-axis (Fig. 3) the chains in **1** appear to be connected in a zig-zag pattern with distances of 2.512(6) Å between pendant oxygen atoms on adjacent chains (each chain is linked to two others in this manner) and 2.529(7) Å within the chains. The closest contacts from the pendant oxygen atoms to the ethylpyridinium ion are 3.517(9) and 4.077(11) Å. Clearly the strongest links between the chains come from direct hydrogen bond type interactions, however, the comparison to the EMIM templated structures shows that the weaker interactions

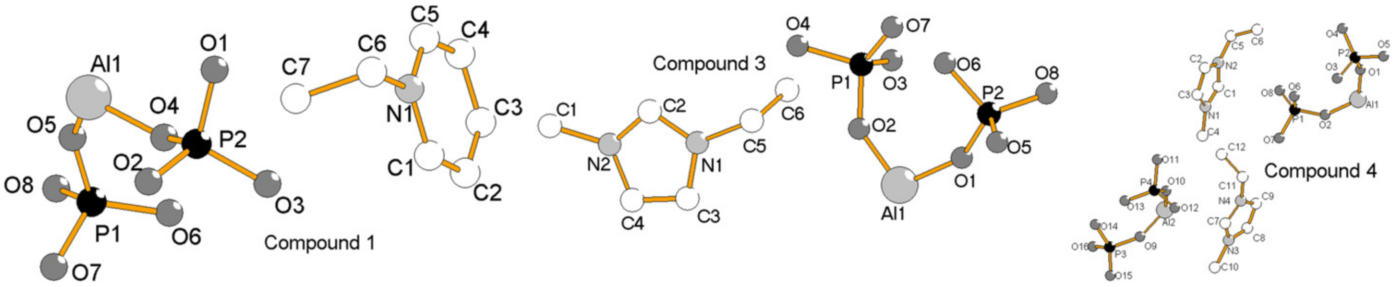

Fig. 2. Asymmetric units for compounds 1, 3 and 4. Hydrogen atoms are omitted for clarity.

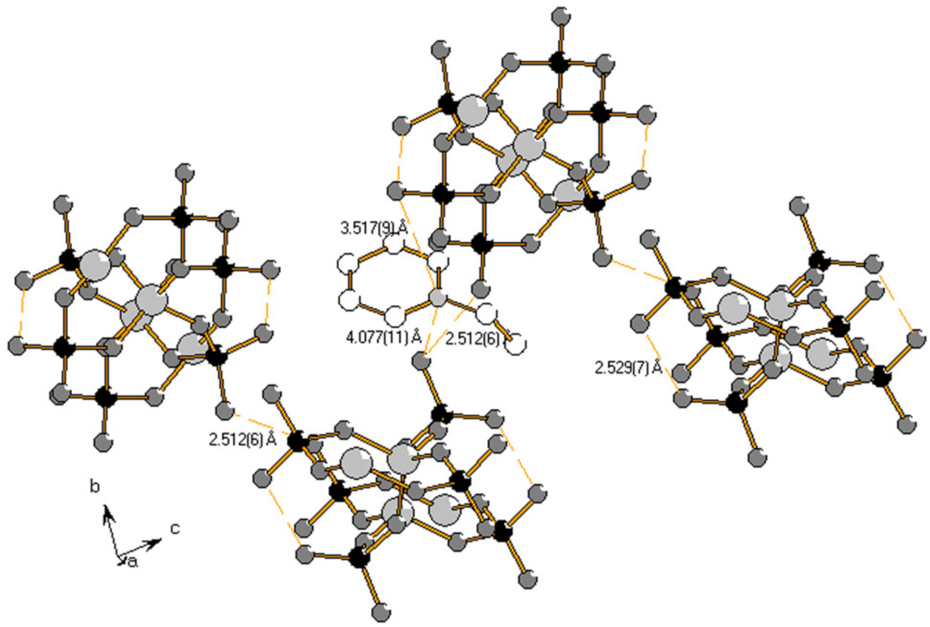

Fig. 3. The hydrogen bonding between AlP_2O_8 chains in **1** viewed along the *a*-axis showing the zig-zag arrangement of neighbouring chains. Short contacts are shown as dotted lines hydrogen atoms are omitted for clarity.

with the organic molecule are very important in the final packing. The arrangement of the chains in **3** and **4** viewed along the *a*-axis (Fig. 4) is more cross-shaped with each chain linked to four others by close pendant oxygen contacts of 2.493(6) Å in **3** and 2.482(9)/2.523(11) Å in **4**. The shortest internal O–O contacts are close to 2.50 Å in both structures. The asymmetry introduced at lower temperature causes the shift from monoclinic to triclinic symmetry. The template is connected to the pendant oxygen atoms by contacts of 3.697(6) and 3.866(7) Å in structure **3** and 3.571(12) and 3.927(11) Å in structure **4**. The slight shift of the organic molecule to one side of the space between the chains is also a factor in the symmetry change, which may also be related to a slight change in the N–C–C angle in the ethyl group from 108.3(5)° in **3** to 112(1)° in **4**. The packing differences between **3** and **4** are also apparent in the chain separations: the monoclinic version has a minimum separation of 8.65 Å between adjacent aluminium atoms in neighbouring chains compared to horizontal separation of 8.64 Å and vertical separation of 8.48 Å in the triclinic structure.

The involvement of the organic template in the hydrogen bonding of other examples of this chain structure seems to be much greater than in these ionothermally synthesised examples, with O–N distances of 2.72–2.85 Å being common in the literature [15–28]. The difference in hydrogen bonding between the compound synthesised with EBP and those prepared with EMIM Br is therefore all the more surprising. It may be that this weak interaction is due to the ionic nature of the solvent.

The crystal data collection details coordinates and isotropic thermal parameters for compounds 1, 3 and 4 are shown in Tables 3 and 4. Full crystallographic data in CIF format are available as supplementary information.

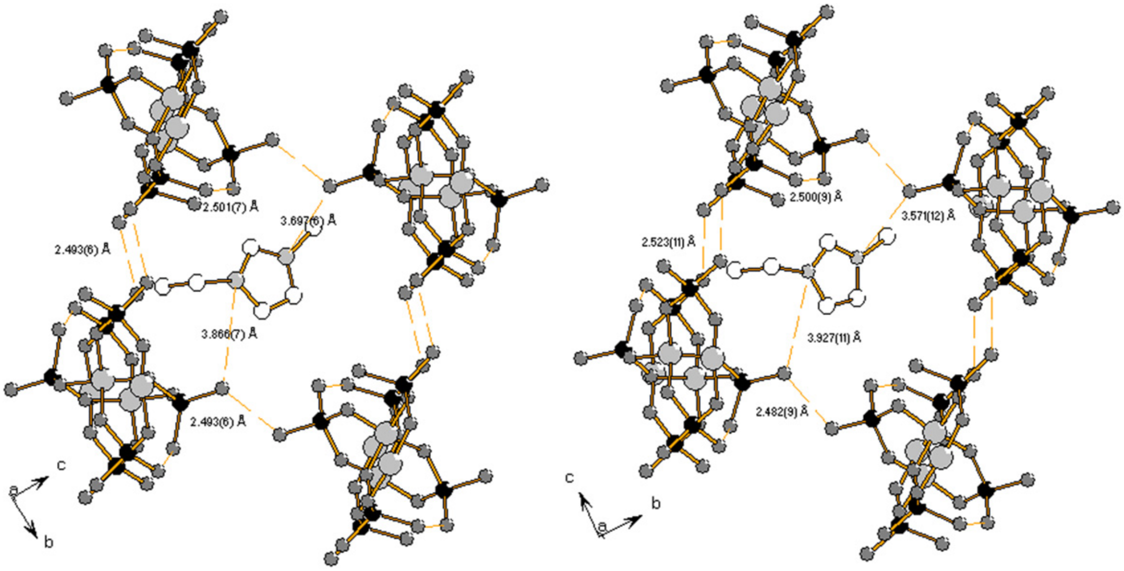

Fig. 4. Views of **3** (left) and **4** (right) along the *a*-axis showing the cross shaped hydrogen bonded arrangement of the chains. Short contacts are shown as dotted lines and hydrogen atoms are omitted for clarity.

Table 3
Data collection and crystal structure refinement details for compounds 1, 3 and 4.

	Compound 1	Compound 3	Compound 4
Formula	$AlP_2O_8H_2$, $C_7H_{10}N$	$AlP_2O_8H_2$, $C_6H_{11}N_2$	2($AlP_2O_8H_2$, $C_6H_{11}N_2$)
Formula weight	325.08	330.1	659.20
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P21/c$ (no. 14)	$P-1$ (no. 2)
a, *b*, *c* (Å)	7.8237(14), 14.2901(17), 12.7884(14)	8.078(4), 13.111(6), 13.534(5)	8.079(3), 12.580(5), 12.974(5)
α, β, γ (°)	90, 118.18(1), 90	90, 114.19(2), 90	88.510, (6)86.240(6), 79.848(6)
V (Å^3)	1260.3(3)	1307.5(10)	1295.0(9)
Z	4	4	2
D (calc) (g/cm^3)	1.713	1.677	1.691
Mu (/mm)	4.196	0.788	0.440
F (000)	664	680	678
Crystal size (mm)	0.10 × 0.02 × 0.01	0.01 × 0.005 × 0.005	0.07 × 0.05 × 0.02
Temperature (K)	173	150	100
Radiation (Å)	Cu*K*α, 1.54051	SRS station 16.2, 0.84620	SRS station 9.8, 0.69390
Theta min–max (°)	5.0, 68.3	3.0, 27.3	1.5, 23.2
Dataset	−7:7; −13:13; −10:10	−10: 10; −16: 15; −16: 17	−9:9; −14:14; −14:14
Tot., uniq. data, R(int)	2345, 2345, 0.077	9433, 2807, 0.165	8801, 3968, 0.070
Observed data [$I > 2.0$ sigma(I)]	864	1362	2584
N_{ref}, N_{par}	1000,172	2807, 182	3968,356
R, wR^2, S	0.0529, 0.1338, 1.14	0.0668, 0.1536, 0.94	0.0867, 0.2444, 1.13
Max. and avg. shift/error	0.00, 0.00	0.14, 0.00	0.02, 0.00
Min. and max. resd. dens. (e/Å^3)	−0.40, 0.32	−0.60, 0.46	−0.58, 0.81

Table 4
Atomic coordinates for the crystal structures of compounds 1, 3 and 4.

Atom	x	y	z	$U_{(eq)}$ (Å^2)
Compound 1, $AlP_2O_8H_2$, $C_7H_{10}N$				
P1	0.0860 (3)	0.41654 (14)	0.67567 (17)	0.0256 (8)
P2	−0.4534 (3)	0.38314 (13)	0.36770 (17)	0.0240 (9)
Al1	−0.2355 (3)	0.51836 (15)	0.53839 (18)	0.0250 (9)
O1	−0.6272 (6)	0.4278 (4)	0.3772 (4)	0.0363 (19)
O2	−0.3939 (6)	0.4080 (3)	0.2541 (4)	0.0302 (17)
O3	−0.4739 (7)	0.2766 (3)	0.3819 (4)	0.0393 (19)
O4	−0.3248 (6)	0.4138 (3)	0.4781 (4)	0.0339 (19)
O5	−0.0478 (6)	0.4939 (3)	0.6357 (4)	0.0264 (17)
O6	0.0071 (7)	0.3267 (3)	0.7022 (4)	0.0356 (19)
O7	0.1950 (6)	0.4067 (3)	0.5742 (4)	0.0285 (17)
O8	0.2071 (6)	0.4550 (3)	0.7866 (4)	0.0313 (17)
N1	−0.9859 (8)	0.2229 (5)	0.2733 (6)	0.033 (3)
C1	−0.8918 (12)	0.1474 (7)	0.2596 (8)	0.046 (4)
C2	−0.8382 (12)	0.0895 (6)	0.3506 (11)	0.057 (4)
C3	−0.8764 (13)	0.1094 (7)	0.4611 (9)	0.051 (4)
C4	−0.9704 (13)	0.1872 (8)	0.4755 (8)	0.053 (4)
C5	−1.0236 (11)	0.2432 (7)	0.3808 (10)	0.047 (4)
C6	−1.0462 (11)	0.2828 (6)	0.1696 (8)	0.053 (4)
C7	−0.9017 (11)	0.3397 (6)	0.1319 (7)	0.049 (3)
Compound 3, $AlP_2O_8H_2$, $C_6H_{11}N_2$				
P1	0.9101 (2)	0.15453 (10)	0.41317 (12)	0.0197 (5)
P2	0.6495 (2)	0.11375 (10)	0.62276 (12)	0.0181 (5)
Al1	0.7399 (2)	−0.03716 (12)	0.47124 (14)	0.0179 (5)
O1	0.7189 (5)	0.0219 (2)	0.5793 (3)	0.0190 (11)
O2	0.8233 (5)	0.0481 (3)	0.4046 (3)	0.0204 (12)
O3	1.1156 (5)	0.1417 (3)	0.4816 (3)	0.0229 (14)
O4	0.8872 (6)	0.1815 (3)	0.2969 (3)	0.0333 (16)
O5	0.4669 (5)	0.0843 (2)	0.6242 (3)	0.0199 (12)
O6	0.6044 (6)	0.2032 (3)	0.5399 (3)	0.0259 (14)
O7	0.8317 (5)	0.2337 (2)	0.4615 (3)	0.0265 (16)
O8	0.7829 (5)	0.1418 (3)	0.7340 (3)	0.0231 (12)
N1	0.2260 (7)	0.0733 (3)	0.0729 (4)	0.0313 (19)
N2	0.2421 (7)	0.0563 (3)	−0.0812 (4)	0.0280 (17)
C1	0.2415 (10)	0.0823 (5)	−0.1877 (5)	0.053 (3)
C2	0.2307 (8)	0.1235 (4)	−0.0116 (5)	0.031 (2)
C3	0.2403 (9)	−0.0292 (4)	0.0574 (5)	0.035 (2)
C4	0.2478 (8)	−0.0398 (4)	−0.0393 (5)	0.033 (2)
C5	0.2083 (9)	0.1213 (5)	0.1687 (5)	0.043 (3)
C6	0.3912 (10)	0.1598 (5)	0.2442 (6)	0.057 (3)
Compound 4, 2($AlP_2O_8H_2$, $C_6H_{11}N_2$)				
P1	0.5094 (3)	0.4228 (2)	0.8389 (2)	0.0187 (8)
P3	0.0444 (3)	0.6236 (2)	0.8903 (2)	0.0175 (8)
Al6	0.2676 (4)	0.4667 (2)	1.0364 (2)	0.0175 (9)
O1	0.1458 (8)	0.5796 (5)	0.9831 (5)	0.018 (2)
O3	0.0835 (9)	0.5392 (6)	0.8017 (5)	0.024 (2)
O4	0.4216 (8)	0.4048 (5)	0.9460 (5)	0.019 (2)
O6	0.6395 (9)	0.4960 (6)	0.8553 (5)	0.023 (3)
O7	0.3892 (8)	0.4697 (6)	0.7597 (5)	0.022 (2)
O9	−0.1452 (8)	0.6284 (5)	0.9197 (6)	0.023 (2)
O11	0.0827 (8)	0.7330 (5)	0.8587 (5)	0.020 (2)
O17	0.6155 (9)	0.3114 (6)	0.8069 (6)	0.027 (2)
P2	1.4801 (3)	−0.1199 (2)	0.3813 (2)	0.0196 (9)
P4	1.0206 (3)	0.0961 (2)	0.3482 (2)	0.0196 (8)
Al5	1.2282 (4)	0.0254 (3)	0.5396 (2)	0.0195 (10)
O2	1.3582 (8)	−0.0785 (6)	0.4732 (5)	0.022 (2)
O5	1.0842 (8)	0.0965 (6)	0.4579 (5)	0.022 (2)
O8	1.6622 (8)	−0.1168 (6)	0.4100 (5)	0.021 (2)
O10	1.4508 (9)	−0.0363 (6)	0.2907 (6)	0.028 (2)
O12	0.9401 (9)	0.2136 (6)	0.3260 (5)	0.024 (2)
O13	1.1538 (8)	0.0530 (6)	0.2664 (5)	0.028 (3)
O14	0.8780 (9)	0.0278 (6)	0.3549 (5)	0.025 (2)
O15	1.4635 (9)	−0.2310 (6)	0.3552 (6)	0.027 (2)
N16	0.7273 (12)	0.5943 (8)	0.5798 (7)	0.028 (3)
N20	0.8346 (11)	0.4258 (7)	0.5566 (7)	0.026 (3)
C19	0.8107 (14)	0.5055 (9)	0.6242 (9)	0.027 (4)
C24	0.9128 (15)	0.3146 (9)	0.5764 (10)	0.036 (4)
C26	0.6965 (15)	0.5715 (10)	0.4802 (9)	0.035 (4)
C27	0.6745 (13)	0.6981 (10)	0.6322 (10)	0.033 (4)
C28	0.7612 (14)	0.4678 (10)	0.4649 (9)	0.030 (4)
C32	0.4863 (15)	0.7245 (10)	0.6532 (10)	0.039 (4)
N18	1.3184 (11)	−0.0764 (7)	0.9477 (7)	0.025 (3)
N21	1.1459 (11)	0.0732 (7)	0.9236 (7)	0.026 (3)
C22	1.4279 (14)	−0.1816 (9)	0.9296 (9)	0.032 (4)

Table 4 (*continued*)

Atom	x	y	z	$U_{(eq)}$ (Å^2)
C23	1.1768 (13)	0.0668 (9)	1.0264 (9)	0.026 (4)
C25	1.2341 (14)	−0.0144 (9)	0.8774 (9)	0.027 (4)
C29	1.0388 (15)	0.1632 (10)	0.8720 (9)	0.035 (4)
C30	1.2876 (14)	−0.0256 (10)	1.0423 (9)	0.029 (4)
C31	1.1402 (16)	0.2503 (9)	0.8341 (9)	0.032 (4)

Table 5
Masses of aluminium isopropoxide and zinc acetate and molar Al to Zn ratios used in the ionothermal synthesis of chain phases with EPB.

Experiment name	Zinc acetate mass/g	Aluminium isopropoxide mass/g	Zn:Al ratio	Products
dswil216a	0.1	0.1	0.930524	Chain
dswil216b	0	0.2	0	Chain (very poor crystallinity)
dswil216c	0.05	0.16	0.290789	Chain
dswil216d	0.02	0.19	0.09795	Chain
dswil216e	0.21	0	–	No solid
dswil216f[a]	0.175	0.05	3.256834	Chain+SIZ-1 [38]

[a] dswil216f is the reaction from which the crystal of compound 2 was taken.

Careful examination of the powder pattern of compound **5** shows that the chain is the major phase with a significant impurity of a hexagonal porous gallium phosphate previously reported by Yang et al. [42]. We have also prepared the latter compound as a pure phase in ionothermal gallium phosphate preparations with EPB as solvent and template with longer heating times.

Compound **2** appears to consist of a mixture of the chain and the three dimensional interrupted framework SIZ-1 [43]. A Le Bail [44] fit using the two unit cells gives a good agreement. The aluminium to zinc ratios and products obtained in the series of reactions with aluminium isopropoxide and zinc acetate are given in Table 5.

XRD analysis of the products shows that crystallinity (as measured by XRD line width and intensity) increases drastically with zinc content. At zero zinc the product is a poorly crystallised version of the chain with a large amount of amorphous background scattering in the powder XRD pattern. Peak intensities gradually increase and line widths narrow up to 76.5% zinc. The zinc appears to be strongly solvated by the ionic liquid. Reactions using zinc acetate only (no aluminium isopropoxide) gave no solid product and EDX microanalysis shows that the solids prepared in the presence of zinc acetate do not contain zinc. Chippindale and coworkers have observed that in solvothermal systems transition metals appear to improve the crystallinity of the product without becoming a part of it [29,45]. It appears that the same holds true in ionothermal framework synthesis using transition metal acetates. This may be in part due to the ability of halide ionic liquids to form very stable complexes with metals, especially metal halides [46,47]. We explored several IL/metal acetate mixtures and found them to give mixed chain and 3D products (as discussed above) with the 3D phases favoured by longer heating times as observed by Rao et al. [21] in the hydrothermal synthesis of zinc phosphates.

The presence of crystalline chain material (compound 4) in a mixture whose main product is SIZ-4 shows that the synthesis conditions for these phases are related, although the chain was not observed during *in situ* energy dispersive XRD studies [48]. This is the only case in our ionothermal synthesis work so far in which this corner sharing chain structure has been prepared in the presence of fluoride although it should be noted that the chain structure prepared by Parnham and Morris [27] is made with hydrofluoric acid in the mixture. It is likely that the fluoride in the mixture is used up in the synthesis of the dominant SIZ-4 phase (fluoride is incorporated into this chabazitic zeotype balancing the charge of the ionic liquid template) and the chain forms as a minor side product with good crystallinity. The synthesis of compounds **3** and **4** suggests that amines added to the aluminophosphate synthesis mixture help to stabilise the chain without being incorporated as a template into the final product; an effect similar to that observed for metal acetates. They key factor here may well be modification of the acidity of the mixture, however, this is difficult to quantify in an ionothermal reaction mixture [49].

4. Conclusions

These chain structures prepared by ionothermal synthesis extend the set of metal phosphate structure types which have been prepared by this relatively novel route to include 1 dimensional as well as 2 dimensional layered and 3 dimensional microporous structures. The structure of the chain material contains a well known linear M_2PO_4 corner sharing chain whose internal bonding is not affected by the synthesis conditions. The hydrogen bonding network which links the neighbouring chains, however, seems to be strongly affected by changes in the organic material used as structure directing agent despite the fact that the contacts between the chain and the organic molecules are longer than the chain to chain contacts. Synthesis with EMIM Br can lead to monoclinic and triclinic structures with the triclinic structures being observed at low temperature. The isolation of a chain material from a reaction mixture containing HF in which the major product was SIZ-4 is also extremely interesting, showing that the chain can exist in the same reaction mixtures as the microporous phase. The crystallinity of the chain in EMIM Br is increased by the addition of transition metal acetates but this is not the case for systems where EPB is the solvent, in which the product is SIZ-3 or 4 or a mixture of the two depending on the amount of acetate added. TEAOH and TPA also stabilise the chain in EMIM Br without being included in the final structure. We also observed that many of the reactions led to mixtures of chain and 3 dimensional products with the 3D products being favoured at longer heating times.

The supplementary material has been sent to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, as supplementary material and can be obtained by contacting the CCDC (quoting the article details).

DSW and REM thank the UK Science and Technology Facilities Council for providing beamtime at the SRS and the Engineering and Physical Sciences Research Council for funding. AMB thanks NOW-CW for a VENI research fellowship. We acknowledge use of the UK chemical database service.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2010.05.002.

References

[1] E.R. Parnham, R.E. Morris, Acc. Chem. Res. 40 (2007) 1005.
[2] S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannan, E.M. Flanigen, J. Am. Chem. Soc. 104 (1982) 1146.
[3] Y. Ma, W. Tong, H. Zhou, S.L. Suib, Microporous Mesoporous Mater. 37 (2000) 243.
[4] T. Loiseau, G. Férey, J. Fluorine Chem. 128 (2007) 413.
[5] G. Férey, Chem. Mater. 13 (2001) 3084.
[6] A.K. Cheetham, G. Férey, T. Loiseau, Angew. Chem. Int. Ed. 38 (1999) 3268.
[7] S. Natarajan, S. Mandal, Angew. Chem. Int. Ed. 47 (2008) 4798.
[8] J. Yu, R. Xu, Acc. Chem. Res. 36 (2003) 481.
[9] G. Férey, Comptes Rendus de l'Académie des Sciences – Series IIC – Chemistry 1 (1998) 1–13.
[10] R.E. Morris, S.J. Weigel, Chem. Soc. Rev. 26 (1997) 309.
[11] R. Murugavel, A. Choudhury, M.G. Walawalkar, R. Pothiraja, C.N.R. Rao, Chem. Rev. 108 (2008) 3549.
[12] M. Estermann, L.B. McCusker, C. Baerlocher, A. Merrouche, H. Kessler, Nature 352 (1991) 320.
[13] N. Guillou, Q. Gao, M. Nogues, R.E. Morris, M. Hervieu, G. Férey, A.K. Cheetham, Comptes Rendus de l'Académie des Sciences – Series IIC – Chemistry 2 (1999) 387.
[14] B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gajek, T.R. Cannan, E.M. Flanigen, J. Am. Chem. Soc. 106 (1984) 6092.
[15] R.H. Jones, J.M. Thomas, R. Xu, Q. Huo, Y. Xu, A.K. Cheetham, D.J. Bieber, Chem. Soc., Chem. Commun. (1990) 1170.
[16] Q. Gao, J. Chen, S. Li, R. Xu, J.M. Thomas, M. Light, M.B. Hursthouse, J. Solid State Chem. 127 (1996) 145.
[17] J. Jasper, A. Wilkinson, Chem. Mater. 10 (1998) 1664.
[18] K. Sugiyama, K. Hiraga, J. Yu, S. Zheng, S. Qiu, R. Xu, O. Terasaki, Acta Crystallogr. C55 (1999) 1615.
[19] S. Phan Thanh, J. Marrot, J. Renaudin, V. Maisonneuve, Acta Crystallogr. C56 (2000) 1073.
[20] A.A. Ayi, A. Choudhury, S.J. Natarajan, Solid State Chem. 156 (2001) 185.
[21] C. Rao, S. Natarajan, A. Choudhury, S. Neeraj, A. Ayi, Acc. Chem. Res. 34 (2001) 80.
[22] N. Rajic, N.Z. Logar, A. Golobic, V. Kaucic, J. Phys. Chem. Solids 64 (2003) 1097.
[23] T. Loiseau, L. Beitone, F. Millange, F. Taulelle, D. O'Hare, G. Ferey, J. Phys. Chem. B 108 (2004) 20020.
[24] T. Loiseau, L. Beitone, C. Huguenard, F. Taulelle, M. Henry, G. Ferey, J. Phys. Chem. B 108 (2004) 20011.
[25] P. Chen, J. Li, J. Yu, Y. Wang, Q. Pan, R. Xu, J. Solid State Chem. 178 (2005) 1929.
[26] E.R. Parnham, E.A. Drylie, P.S. Wheatley, A.M.Z. Slawin, R.E. Morris, Angew. Chem., Int. Ed. 45 (2006) 4962.
[27] E.R. Parnham, R.E. Morris, J. Mater. Chem. 16 (2006) 3682.
[28] E.A. Drylie, D.S. Wragg, E.R. Parnham, P.S. Wheatley, A.M.Z. Slawin, J.E. Warren, R.E. Morris, Angew. Chem., Int. Ed. 46 (2007) 7839.
[29] A.M. Chippindale, A.D. Bond, A.D. Law, A.R. Cowley, J. Solid State Chem. 136 (1998) 227.
[30] T. Loiseau, F. Serpaggi, G. Ferey, Chem. Commun. (1997) 1093.
[31] J.L. Kissick, A.R. Cowley, A.M. Chippindale, J. Solid State Chem. 167 (2002) 17.
[32] http://mezeopor.jlu.edu.cn/alpo/.
[33] S. Oliver, A. Kuperman, G.A. Ozin, Angew. Chem., Int. Ed. 37 (1998) 46.
[34] C.M. Gordon, in: Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003, pp. 9.
[35] Cystal Clear, Rigaku/MSC Inc., (2006).
[36] R.J. Cernik, W. Clegg, C.R.A. Catlow, G. Bushnell-Wye, J.V. Flaherty, G.N. Greaves, M. Hamichi, I. Burrows, D.J. Taylor, S.J. Teat, J. Synchrotron Radiat. 4 (1997) 279.
[37] APEX suite, Bruker AXS, 2007.
[38] G.M. Sheldrick, University of Gottingen, 1997.
[39] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[40] D.A. Fletcher, R.F. McMeeking, D. Parkin, J. Chem. Inf. Comput. Sci. 36 (1996) 746.
[41] F.H. Allen, Acta Crystallogr. B58 (2002) 380.
[42] G. Yang, S. Feng, R. Xu, J. Chem. Soc., Chem. Commun. (1987) 1254–1255.
[43] E.R. Cooper, C.D. Andrews, P.S. Wheatley, P.B. Webb, P. Wormald, R.E. Morris, Nature 430 (2004) 1012.
[44] A. Le Bail, Powder Diffr. 20 (2005) 316.
[45] A.M. Chippindale, R.I. Walton, C.J. Turner, J. Chem. Soc. Chem. Commun. (1995) 1261.
[46] T. Welton, Chem. Rev. 99 (1999) 2071.
[47] A. Chaumont, G. Wipff, J. Phys. Chem. B 108 (2004) 3311.
[48] D.S. Wragg, P.J. Byrne, G. Giriat, B. Le Ouay, R. Gyepes, A. Harrison, A.G. Whittaker, R.E. Morris, J. Phys. Chem. C 113 (2009) 20553.
[49] C. Thomazeau, H. Olivier-Bourbigou, L. Magna, S. Luts, B. Gilbert, J. Am. Chem. Soc. 125 (2003) 5264.