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Ambient-temperature syntheses of layered iron(III) phosphates in silica gels

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Two layered iron(III) phosphates, $[C_5NH_6][Fe(HPO_4)_2(H_2O)_2]$ and $[C_3N_2H_5][Fe(HPO_4)_2(H_2O)_2]$, have been prepared in silica-gel media at ambient temperature and pressure. Their structures have been determined by single-crystal X-ray diffraction. The compounds contain similar inorganic layers constructed from FeO_6 octahedra and PO_4 tetrahedra, but differ in their layer stacking patterns. The compounds are the first layered iron phosphates to be reported in which the Fe : P ratio is 1 : 2.

Introduction

There is considerable interest in the synthesis and characterisation of organically templated phosphates because of their potential applications in fields such as catalysis and ion exchange. The conventional synthetic route to these materials is through solvothermal treatment of a gel precursor. Such syntheses generally require prolonged heating at typically 100–200 °C, with the consequence that thermally unstable templates cannot be used. We have previously reported the use of silica gels as crystallisation media for the preparation of layered alumino- and gallo-phosphates at ambient temperature and pressure.[1] The products, which have general formula $[HT][M(HPO_4)_2(H_2O)_2]$ (T = pyridine or imidazole, M = Al or Ga), adopt a common layered structure. A conventional solvothermal synthesis at 160 °C of $[C_3N_2H_5][Al(HPO_4)_2(H_2O)_2]$ has been reported subsequently,[2] as has that of a structurally related material, $[CN_3H_6][Al(HPO_4)_2(H_2O)_2]$.[3] There have, however, been no reports of syntheses of phosphates of other metals with this structure.

We here report the extension of the ambient-temperature gel synthetic method to iron(III) phosphates. The material $[C_5NH_6][Fe(HPO_4)_2(H_2O)_2]$ **I** is isostructural with its pyridine-templated aluminium and gallium analogues. $[C_3N_2H_5][Fe(HPO_4)_2(H_2O)_2]$ **II** has similar iron–phosphate layers to those of **I**, but the stacking pattern of these differs from that found in the previously reported imidazole-templated alumino- and gallo-phosphates. Whilst a number of organically templated 3-D iron phosphates have been synthesized under hydrothermal conditions,[4–6] there are still relatively few layered examples in the literature.[4–9] One example, $[NH_3(CH_2)_2NH_3]_{0.5}[Fe(OH)(PO_4)]$,[10,11] is isostructural with a previously reported gallium phosphate.[12] The compounds described in this work, synthesized under ambient conditions, are the first templated iron phosphates to be prepared with a Fe : P ratio of 1 : 2.

Experimental

The silica gels described in this work were prepared by dissolving 0.5 g $Fe(NO_3)_3\cdot 9H_2O$ in 5 cm^3 deionised water. 1.5 cm^3 85% aqueous H_3PO_4 were added and the solution was stirred until homogeneous. 1 cm^3 tetraethyl orthosilicate was added and the mixture shaken until the ester had dissolved (*ca.* 30 minutes). The organic template was then added (0.6 cm^3 pyridine for **I**, 0.6 g imidazole for **II**) and the mixture again stirred until homogeneous. The resulting, almost colourless solutions (molar compositions $Fe(NO_3)_3 : 20\ H_3PO_4 : 2.1\ Si(OEt)_4 : 6.7\ C_5H_5N : 280\ H_2O$ for **I**, $Fe(NO_3)_3 : 20\ H_3PO_4 : 2.1\ Si(OEt)_4 : 6.7\ C_5H_5N : 280\ H_2O$ for **II**) were filtered into soda-glass test tubes, stoppered tightly and allowed to stand undisturbed at ambient temperature until firm gels formed (*ca.* 3 days). After 2 weeks, the gels began to acquire a yellow colour, accompanied by the formation of small colourless crystals. Both reactions produced square plate-like crystals, although many of those resulting for **II** were aggregated in stacks. After a further week the gels were removed from the tube and stirred vigorously with a large excess of deionised water. The resulting suspensions of finely divided silica gel were decanted from the solid products, which were washed further and dried in air at 60 °C for 24 hours.

Combustion analysis of the crystalline products **I** and **II** showed good agreement with the formulae obtained from the corresponding single-crystal X-ray diffraction studies described below (Compound **I**: observed contents 16.20% C, 3.38% H, 3.76% N; calculated for $[C_5NH_6][FeH_6P_2O_{10}]$ 16.50% C, 3.32% H, 3.85% N. Compound **II**: observed contents 10.12% C, 3.30% H, 7.82% N; calculated for $[C_3N_2H_5][FeH_6P_2O_{10}]$ 10.21% C, 3.14% H, 7.94% N). Energy-dispersive X-ray analyses of the products were carried out using a JEOL 2000FX analytical electron microscope, with α-$FePO_4$ used as a calibration standard. All crystallites studied contained Fe and P in approximate ratio 1 : 2. None of the crystallites contained any detectable amount of Si.

Single-crystal X-ray diffraction data were measured for each compound at ambient temperature using an Enraf-Nonius MACH3 diffractometer (graphite-monochromated Cu-Kα radiation (λ = 1.5418 Å)). Experimental information is given in Table 1. Both structures were solved using direct methods (SIR 92)[13] and all non-hydrogen atoms located. Subsequent full-matrix least-squares refinements and Fourier syntheses were carried out using the CRYSTALS program suite.[14]

For compound **I** the framework hydroxyl hydrogen atoms were located in Fourier difference maps and their coordinates subsequently refined. The hydrogen atoms of the pyridinium cation were positioned geometrically after each cycle of refinement. Selected bond lengths and angles are listed in Table 2. The local co-ordination geometry of the asymmetric unit is shown in Fig. 1(a).

During structure refinement of compound **II** it was observed

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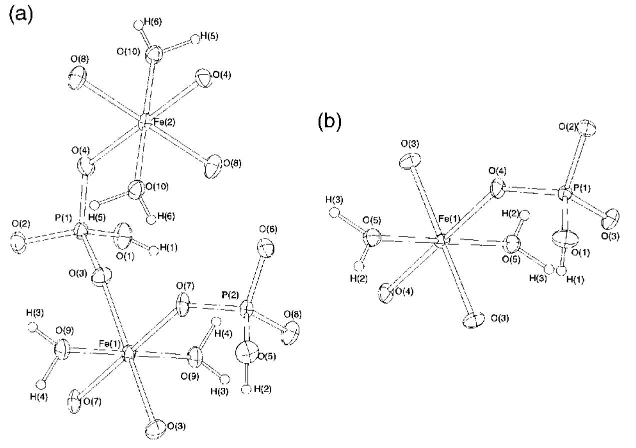

Fig. 1 Views of the local co-ordination geometry of the atoms of the inorganic layers of (a) compound **I** and (b) **II**. Both structures are viewed along an arbitrary crystallographic vector. Thermal ellipsoids are shown at 50% probability. Drawing package: ATOMS for Windows.[15]

that the geometry of the imidazolium cation was distorted and the thermal parameters of the C and N atoms appeared excessively large. The ion was thus modelled as disordered over two sites related by the crystallographic mirror plane. Geometric restraints were applied to the bond lengths and angles of the C_3N_2 ring, derived from the geometry of the imidazolium cation of the corresponding gallophosphate $[C_3N_2H_5][Ga(HPO_4)_2(H_2O)_2]$. Framework hydroxyl hydrogen atoms were again located in Fourier difference maps and subsequently their coordinates were refined. The imidazolium hydrogen atoms were positioned geometrically after each cycle of refinement. Selected bond lengths and angles are listed in Table 3. The local co-ordination geometry of the asymmetric unit is shown in Fig. 1(b).

CCDC reference number 186/2126.

See http://www.rsc.org/suppdata/dt/b0/b003618h/ for crystallographic files in .cif format.

Discussion

The materials described in this work adopt structures in which corrugated Fe–phosphate layers are separated by either pyridinium or imidazolium cations. Compound **I** is isostructural with the previously reported alumino- and gallo-phosphate analogues incorporating pyridine. The inorganic layers are constructed from alternating FeO_6 octahedra and PO_4 tetrahedra (Fig. 2). Each of the two crystallographically distinct Fe atoms is located on a centre of inversion, and there are no significant differences between the local co-ordination geometries of the two sites. In addition to four phosphate groups, each metal atom is co-ordinated to two water molecules which occupy *trans* positions of the octahedra. Bond-valence calculations[16] show that the Fe–O bond lengths are consistent with the presence of trivalent iron (calculated valencies 3.13 and 3.07 for Fe(1) and Fe(2) respectively).

The structure also contains two crystallographically distinct phosphorus atoms, neither of which occupies a site with any crystallographic symmetry. Both of the phosphorus atoms are co-ordinated to four O atoms, two of which are also co-ordinated to an iron atom. One of the remaining P–O bonds of each site, P(1)–O(1) and P(2)–O(5), is considerably longer than the other, consistent with the presence of P–OH groups. This assignment is supported by the location of the hydrogen atoms in Fourier difference maps and by bond-valence calculations. The relatively short lengths of the remaining P–O bond of each phosphate group, P(1)–O(2) and P(2)–O(6), suggest some multiple-bond character.

There are a number of hydrogen bonds within each layer, but no direct hydrogen bonds between the layers (Fig. 3). The two crystallographically distinct P–OH groups each form a hydrogen bond to a P=O group (O(1) · · · O(6) 2.663(4), O(5) · · · O(2) 2.582(5) Å), as does one of the hydroxyl groups of each water molecule (O(9) · · · O(6) 2.672(4), O(10) · · · O(2) 2.637(4) Å). The second hydroxyl of each water molecule is hydrogen bonded to a P–O–Fe bridge (O(9) · · · O(4) 2.724(4), O(10) · · · O(7) 2.758(4) Å). The pyridinium cations occupy sites between the layers. The nitrogen atom of the template molecule is hydrogen bonded to a P=O group of one of the adjacent layers (N(1) · · · O(6) 2.671(5) Å).

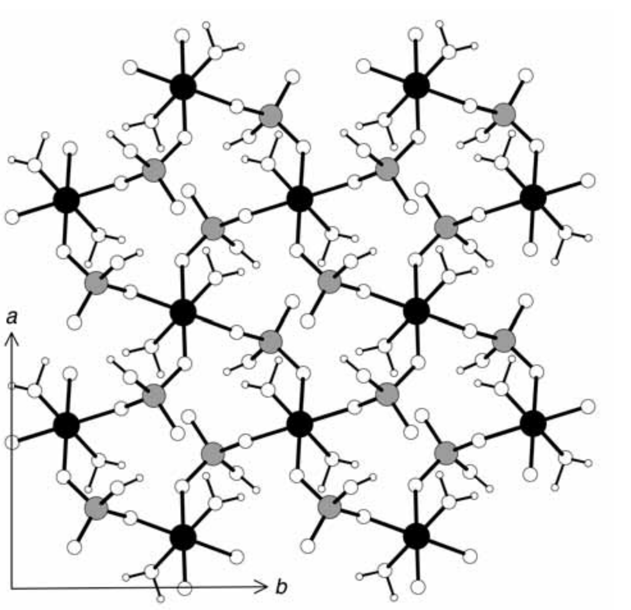

Fig. 2 Projection of the inorganic layer of compound **I** on the (0 0 1) plane. Key: black circles, Fe; grey circles, P; large white circles, O; small white circles, H.

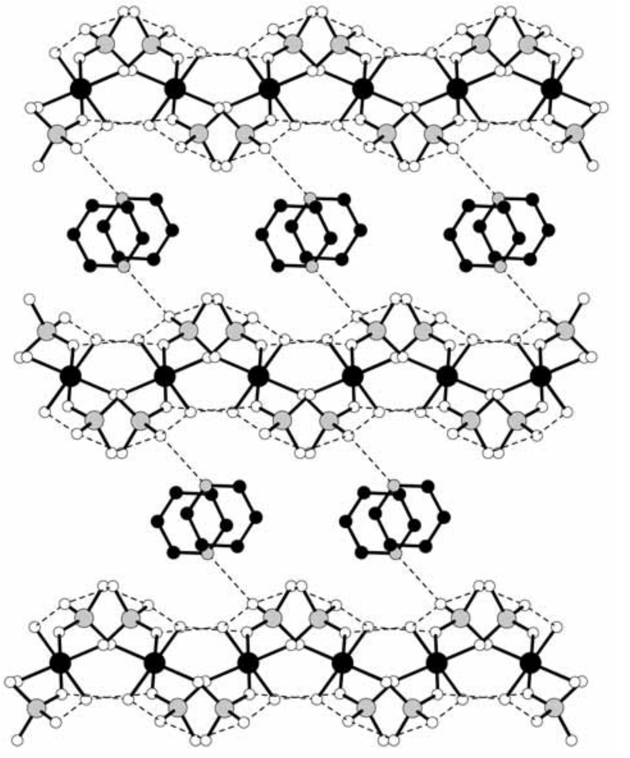

Fig. 3 View of compound **I** along the crystallographic *a* axis, with the *b* axis running horizontally. H atoms have been omitted. Hydrogen bonds are shown as dashed lines. Key: large black circles, Fe; large grey circles, P; white circles, O; small black circles, C; small grey circles, N.

Compound **II** has layers with a similar geometry to those of **I**, although as a consequence of the change in crystallographic

Table 1 Summary of crystallographic data for compounds **I** and **II**

	I	**II**
Molecular formula	$[C_5NH_6][Fe(HPO_4)_2(H_2O)_2]$	$[C_3N_2H_5][Fe(HPO_4)_2(H_2O)_2]$
Formula weight	363.95	352.92
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pnam*
T/K	293	293
a/Å	7.1166(4)	7.127(1)
b/Å	7.3711(7)	7.323(1)
c/Å	12.181(1)	21.292(4)
α/°	105.538(7)	
β/°	105.474(6)	
γ/°	90.237(6)	
U/Å^3	591.31	1111.2
Z	2	4
μ/mm^{-1}	13.43	14.29
Data	2553, of which 2244 unique	1848, of which 1160 unique
Merging R (%)	5.0	10.7
R (%)	5.95	5.75
R_w (%)	7.15	6.82

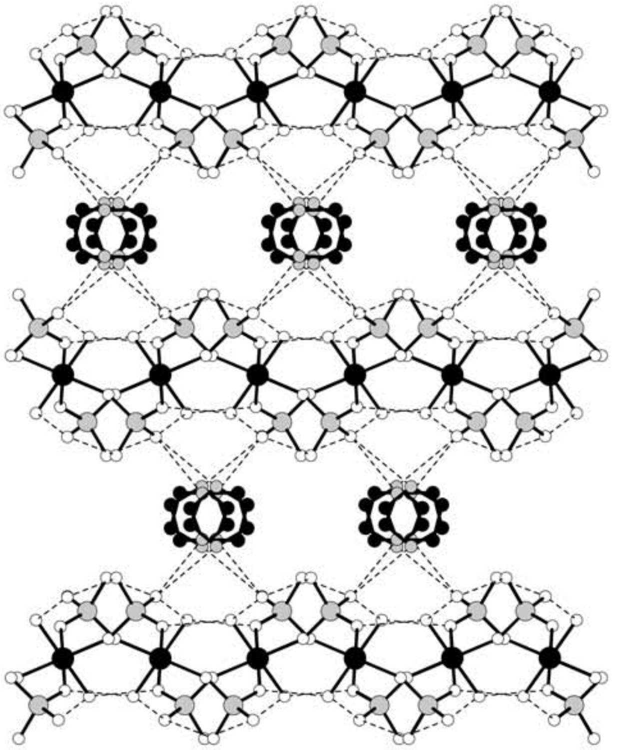

Fig. 4 View of compound **II** along the crystallographic *a* axis, with the *b* axis running horizontally. H atoms have been omitted. Hydrogen bonds are shown as dashed lines. Key as for Fig. 3.

symmetry there is only a single iron site (which occupies a centre of inversion) and a single phosphate group (which occupies a site with no crystallographic symmetry). The Fe atom is again co-ordinated to four phosphate O atoms and two water molecules. Bond-valence calculations show the iron to be trivalent (calculated valence 3.12). Two of the O atoms of the phosphate group are co-ordinated to Fe atoms, and again one of the remaining P–O bonds, P(1)–O(1), is elongated, indicative of a P–OH group, while the second, P(1)–O(2), is shortened, indicative of some multiple-bond character. The *intra*layer hydrogen bonds are analogous to those in compound **I**, with the single P–OH group being bonded to the P=O oxygen of a neighbouring phosphate (O(1) ··· O(2) 2.625(5) Å). One hydroxyl group of the single water molecule is bonded to the P=O group (O(5) ··· O(2) 2.648(5) Å) and the remaining hydroxyl is bonded to a P–O–Fe bridge (O(5) ··· O(4) 2.730(5) Å).

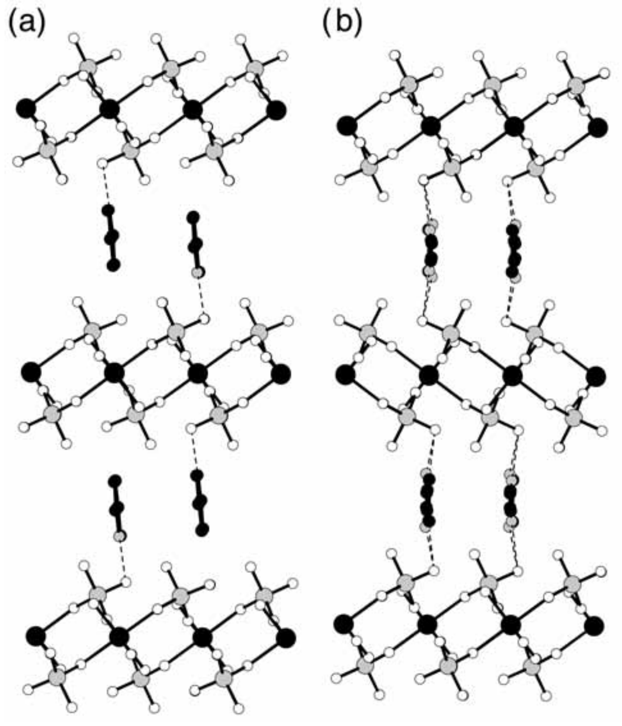

Fig. 5 Views of (a) compound **I** and (b) **II**, viewed along the crystallographic *b* axes, with the *a* axes running horizontally. Note the different orientations of the central inorganic layers in the two diagrams.

The imidazolium cation occupies a site between the layers which lies on a crystallographic mirror plane. Whilst this symmetry is not inconsistent with that of an ordered template, the best fit to the diffraction data was obtained by modelling the ion as disordered over two sites related by crystallographic symmetry (Fig. 4). Each of the two nitrogen atoms is hydrogen bonded to a P=O group in one of the neighbouring layers (N(1) ··· O(2) 2.78(1), N(2) ··· O(2) 2.98(1) Å).

Unlike compound **I**, **II** is *not* isostructural with its alumino- and gallo-phosphate analogues. The latter materials are monoclinic, space group *C*2/*c*, and have a different stacking pattern of the layers. In these materials (and also in **I** and its analogues) the layers are stacked directly above one another in an *AAAA* pattern (Fig. 5a), whereas in **II** alternate layers are reflected, resulting in an *ABAB* arrangement (Fig. 5b). A similar alternation of layers has been observed in the aluminophosphate $[CN_3H_6][Al(HPO_4)_2(H_2O)_2]$.[3] Powder X-ray diffraction of a sample of compound **II** shows the single-crystal structure to be representative of the majority of the crystalline products, but

Table 2 Selected bond lengths (Å) and angles (°) for compound **I**

Fe(1)–O(3)	1.937(3)	Fe(2)–O(8)	1.947(3)
Fe(1)–O(7)	2.022(3)	Fe(2)–O(4)	2.019(3)
Fe(1)–O(9)	2.051(3)	Fe(2)–O(10)	2.064(3)
P(1)–O(1)	1.578(3)	P(2)–O(5)	1.572(3)
P(1)–O(2)	1.509(3)	P(2)–O(6)	1.522(3)
P(1)–O(3)	1.517(3)	P(2)–O(8)	1.524(3)
P(1)–O(4)	1.530(3)	P(2)–O(7)	1.512(3)
O(3)–Fe(1)–O(7)	87.0(1)	O(8)–Fe(2)–O(4)	87.7(1)
O(3)–Fe(1)–O(9)	89.8(1)	O(8)–Fe(2)–O(10)	88.6(1)
O(7)–Fe(1)–O(9)	89.6(1)	O(4)–Fe(2)–O(10)	89.9(1)
O(1)–P(1)–O(2)	106.6(2)	O(5)–P(2)–O(6)	103.9(2)
O(1)–P(1)–O(3)	108.1(2)	O(5)–P(2)–O(8)	108.9(2)
O(2)–P(1)–O(3)	113.3(2)	O(6)–P(2)–O(8)	112.6(2)
O(1)–P(1)–O(4)	108.7(2)	O(5)–P(2)–O(7)	110.0(2)
O(2)–P(1)–O(4)	110.8(2)	O(6)–P(2)–O(7)	109.4(1)
O(3)–P(1)–O(4)	110.8(2)	O(8)–P(2)–O(7)	111.7(2)
Fe(1)–O(3)–P(1)	158.9(2)	Fe(2)–O(8)–P(2)	159.2(2)
Fe(2)–O(4)–P(1)	134.8(2)	Fe(1)–O(7)–P(2)	137.6(2)

Table 3 Selected bond lengths (Å) and angles (°) for compound **II**

Fe(1)–O(3)	1.941(3)	P(1)–O(1)	1.578(3)
Fe(1)–O(4)	2.016(3)	P(1)–O(2)	1.509(3)
Fe(1)–O(5)	2.054(3)	P(1)–O(3)	1.517(3)
		P(1)–O(4)	1.530(3)
O(3)–Fe(1)–O(4)	87.6(1)	O(1)–P(1)–O(2)	104.5(2)
O(3)–Fe(1)–O(5)	89.0(1)	O(1)–P(1)–O(3)	108.7(2)
O(4)–Fe(1)–O(5)	89.2(1)	O(2)–P(1)–O(3)	112.7(2)
		O(1)–P(1)–O(4)	109.5(2)
Fe(1)–O(3)–P(1)	158.7(2)	O(2)–P(1)–O(4)	110.2(2)
Fe(1)–O(4)–P(1)	136.6(2)	O(3)–P(1)–O(4)	111.0(2)

does not preclude the presence of a small amount of an *AAAA*-stacked polymorph. Attempts to produce a pure sample of an *AAAA*-stacked form of $[C_3N_2H_5][Fe(HPO_4)_2(H_2O)_2]$ by 'seeding' the initial reaction mixture with a trace of finely ground $[C_3N_2H_5][Ga(HPO_4)_2(H_2O)_2]$ led to precipitation of a poorly crystalline solid within a few minutes. Similarly, attempts to prepare an *ABAB*-stacked form of $[C_3N_2H_5][Ga(HPO_4)_2(H_2O)_2]$ failed to produce a crystalline product.

In conclusion, this work shows that the technique of crystal growth in silica gel media may be extended to organically templated iron phosphates. Further work is in progress to extend this synthetic method to phosphates of other transition metals, especially those which have not been obtained using conventional solvothermal syntheses.

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