

The solid solution (Fe_{0.81}Al_{0.19})-(H₂PO₄)₃ with a strong hydrogen bond

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Single crystals of the solid solution iron aluminium tris-(dihydrogenphosphate), (Fe_{0.81}Al_{0.19})(H₂PO₄)₃, have been prepared under hydrothermal conditions. The compound is a new monoclinic variety (γ -form) of iron aluminium phosphate (Fe,Al)(H₂PO₄)₃. The structure is based on a two-dimensional framework of distorted corner-sharing MO₆ ($M = \text{Fe, Al}$) polyhedra sharing corners with PO₄ tetrahedra. Strong hydrogen bonds between the OH groups of the H₂PO₄ tetrahedra and the O atoms help to consolidate the crystal structure.

Comment

Microporous materials find their origin in the discovery by Crönsted during the thirteenth century of the zeolitic property of the mineral stilbite. The zeolite family is made up of the aluminosilicate minerals with formula $\{M_{x/n}^{n+}[(\text{AlO}_2)_x(\text{SiO}_2)_y]^{x-} \cdot w\text{H}_2\text{O}\}$, where x indicates the number of M^{n+} cations necessary to compensate the negative charge of the whole framework. All these phases exhibit three-dimensional structures built up exclusively from corner-sharing TO₄ ($T = \text{Al, Si}$) tetrahedra, defining tunnels in which the M^{n+} cations and water molecules are located. Wilson *et al.* (1982) discovered a new family of compounds, the microporous aluminophosphates. Since 1992, the research groups of Cavellec (Cavellec *et al.*, 1995; Cavellec, Riou & Férey, 1997; Cavellec, Férey & Grenèche, 1997; Riou-Cavellec *et al.*, 1998) have been interested in the synthesis of these microporous materials. This work was followed by studies of microporous oxides by several groups (Debord *et al.*, 1997; Lii & Huang, 1997*a,b,c*; Huang *et al.*, 1998; Zima *et al.*, 1998; Zima & Lii, 1998). Microporous materials derived from octahedral and tetrahedral frameworks currently boast an extensive chemistry and a number of them display useful properties as catalysts, sorbents and ionic exchangers (Davis & Lobo, 1992; Breck, 1974; Venuto, 1994).

Two polymorphs of Al(H₂PO₄)₃ have been reported to date. The α -form is hexagonal with cell parameters $a = 7.849$ (1) Å and $c = 24.87$ (3) Å (Yoire, 1961), and the hexagonal β -form has parameters $a = 13.69$ (1) Å and $c = 9.135$ (1) Å (Yoire, 1961), also found by Brodalla *et al.* (1981). The α -form is isostructural with Fe(H₂PO₄)₃ (Baies *et al.*, 2006) and consists of a three-dimensional framework of corner-sharing FeO₆ and PO₂(OH)₂ tetrahedra. The synthesis of a new monoclinic variety of iron aluminium phosphate, (Fe_{0.81}Al_{0.19})(H₂PO₄)₃ (γ -form), is reported in this work.

(Fe_{0.81}Al_{0.19})(H₂PO₄)₃ is composed of a highly puckered sheet structure containing interconnected M₂P₂ units ($M = \text{Fe, Al}$) connected laterally by Fe–O–P mixed bridges to form two-dimensional layers perpendicular to the b axis (Fig. 1). The oligomeric M₂P₂ units are built up from alternating corner sharing of octahedral MO₆ and tetrahedral PO₄ units. The MO₆ octahedra share six O atoms with adjacent P atoms, whereas the PO₄ tetrahedra share only two O atoms. The projection of the sheet is shown in Fig. 2, viewed down the [010] axis. The M –O distances in (Fe_{0.81}Al_{0.19})(H₂PO₄)₃ have values intermediate between 1.944 (4) and 2.063 (4) Å (Table 1), consistent with the occupation of Fe and Al valencies in these sites. The interatomic angles reveal distortions of the octahedra, varying from O6–Fe1–O2($x, y, z - 1$) = 86.66 (17)° to O1–Fe1–O6 = 178.84 (18)°. The dihydrogen phosphate ions, [H₂PO₄][−], can be described as slightly distorted tetrahedra, with a mean value for the P–OH bond distances of 1.578 Å and with P=O bond distances ranging from 1.504 (4) to 1.525 (4) Å. The O–P–O angles are in the range 101.6 (3)–118.1 (2)°.

The crystal structure of (Fe_{0.81}Al_{0.19})(H₂PO₄)₃ is characterized by an extended hydrogen-bonding network. The layers are held together through strong hydrogen bonds between the terminal O atoms attached to the two-connected phosphate groups in adjacent layers. Analysis of the hydrogen bonds in (Fe_{0.81}Al_{0.19})(H₂PO₄)₃ shows two different types of

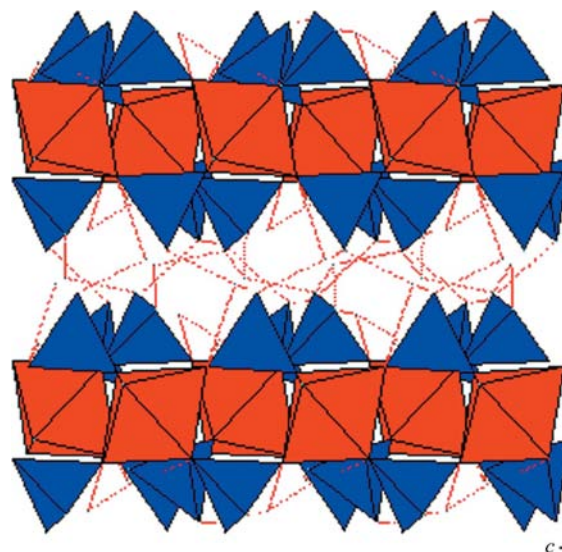
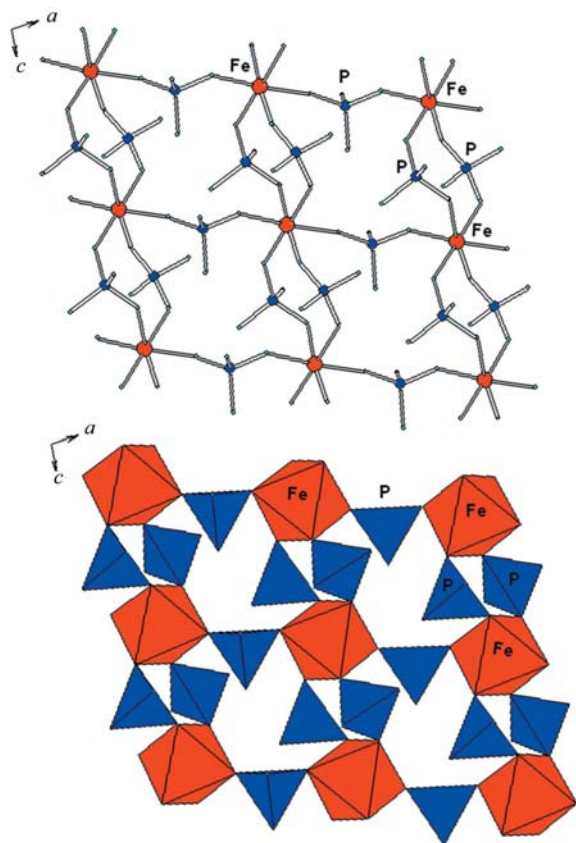


Figure 1
The structure of (Fe_{0.81}Al_{0.19})(H₂PO₄)₃. Dashed lines show the intra- and inter-layer hydrogen bonds.

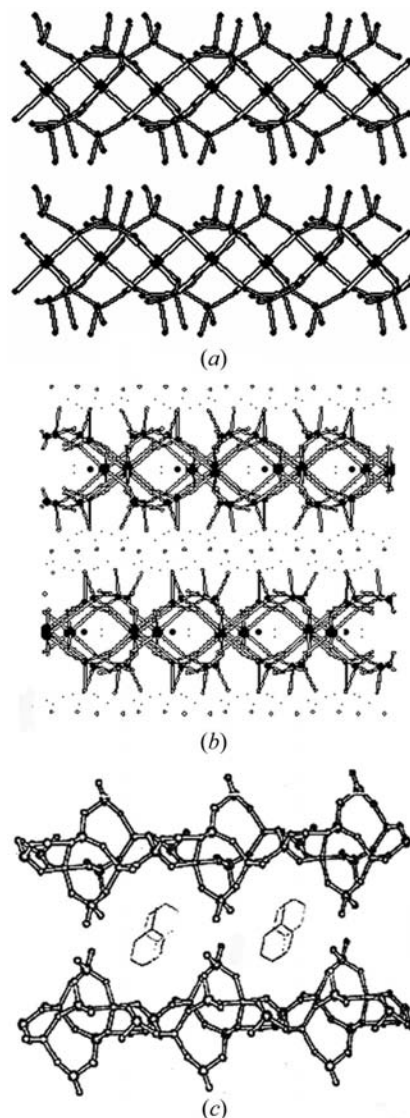

Figure 2

The sheet structure of $(\text{Fe}_{0.81}\text{Al}_{0.19})(\text{H}_2\text{PO}_4)_3$, viewed along the b axis, showing the oligomeric $M_2\text{P}_2$ units ($M = \text{Fe}, \text{Al}$) connected laterally by Fe–O–P mixed bridges. The labels show the sites of the elements in the structure.

P–O–H \cdots O–P bridges. Within the layer, adjacent $[\text{H}_2\text{PO}_4]^-$ ions are connected into chains by short hydrogen bonds (Table 2) with an O \cdots O distance of 2.614 (5) Å formed by one of the hydroxy groups, O3–H3 \cdots O6($x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$). Adjacent layers are linked by longer hydrogen bonds, viz. O4–H4 \cdots O4($x, -y + 1, z + \frac{1}{2}$) [2.775 (6) Å], O12–H12 \cdots O12($x, -y + 2, z - \frac{1}{2}$) [3.055 (8) Å] and O11–H11 \cdots O12($x, -y + 2, z + \frac{1}{2}$) [3.220 (7) Å], which allow the layers to connect as observed in Fig. 1.

A comparison between $(\text{Fe}_{0.81}\text{Al}_{0.19})(\text{H}_2\text{PO}_4)_3$ and the series of compounds $(\text{NH}_4, \text{H}_3\text{O}, \text{K})(\text{Fe}, \text{Al})_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_6 \cdot 4\text{H}_2\text{O}$ and $(\text{C}_6\text{H}_8\text{N})[\text{Al}_2\text{P}_3\text{O}_{10}(\text{OH})_2]$ is shown in Fig. 3. Detailed descriptions of their topology are also reported here. The aim of this comparison is to provide a review of possible approaches that can be used to establish the topology of microporous structures. For obvious reasons, we do not consider related octahedral–tetrahedral frameworks here. Most attention will be focused on network topology and the possibility of intercalating alkaline cations or organic molecules in the solid-state inorganic framework, which is important for both mineralogy and material sciences.

$(\text{Fe}_{0.81}\text{Al}_{0.19})(\text{H}_2\text{PO}_4)_3$ is considered a normal solid-state inorganic framework. A comparison between this compound and the series of compounds $(\text{NH}_4, \text{H}_3\text{O}, \text{K})(\text{Fe}, \text{Al})_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_6 \cdot 4\text{H}_2\text{O}$ is shown in Figs. 3(a) and (b). The common


Figure 3

(a) The stacking sheets of $(\text{Fe}_{0.81}\text{Al}_{0.19})(\text{H}_2\text{PO}_4)_3$. (b) The structure of the series of compounds $(\text{NH}_4, \text{H}_3\text{O}, \text{K})(\text{Fe}, \text{Al})_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_6 \cdot 4\text{H}_2\text{O}$, with the water molecules lying in the interlayer space. (c) The two-dimensional layered compound $(\text{C}_6\text{H}_8\text{N})[\text{Al}_2\text{P}_3\text{O}_{10}(\text{OH})_2]$, with the 4-methylpyridine lying in the interlayer space.

characteristic of these compounds is their bidimensionality. In $(\text{NH}_4, \text{H}_3\text{O}, \text{K})(\text{Fe}, \text{Al})_3(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_6 \cdot 4\text{H}_2\text{O}$, the NH_4^+ , H_3O^+ and K^+ cations are located inside 12-sided polyhedra, which are generated by the corner-sharing MO_6 ($M = \text{Fe}, \text{Al}$) and $[\text{H}_2\text{PO}_4]^-$ units, while water molecules are located in the interlayer space (Mgaidi *et al.*, 1999; Bosman *et al.*, 1986; Anisimova *et al.*, 1997). Figs. 3(a) and (c) show the comparison between $(\text{Fe}_{0.81}\text{Al}_{0.19})(\text{H}_2\text{PO}_4)_3$ and the two-dimensional layered compound $(\text{C}_6\text{H}_8\text{N})[\text{Al}_2\text{P}_3\text{O}_{10}(\text{OH})_2]$. This structure contains macroanionic $[\text{Al}_2\text{P}_3\text{O}_{10}(\text{OH})_2]^-$ sheets that are charge-balanced by protonated 4-methylpyridine. The inorganic layers are constructed from alternating Al-centred units (AlO_4 and AlO_5) and P-centred units [PO_4 , $\text{PO}_3(\text{OH})$ and $\text{PO}_2(=\text{O})(\text{OH})$] with triply and doubly bridging phosphate groups (Yu *et al.*, 2000). This comparison provides an example of the concept of scale chemistry (Férey, 2000). The cavities

created by the framework, which are very small in typical solid-state inorganic frameworks and only able to accept alkaline cations or organic molecules, become larger and larger.

Experimental

The title compound was prepared from a reaction mixture of H_3PO_4 (4 mmol), FeO (5 mmol) and Al_2O_3 (5 mmol) in water (approximately 6 ml). The starting mixture was sealed inside a 23 ml Teflon-lined stainless steel Parr autoclave under autogenous pressure, filled to approximately 25% volume capacity, and the reactants were stirred briefly before heating. The reaction mixture was heated at 343 K for 3 d to obtain $(\text{Fe}_{0.81}\text{Al}_{0.19})(\text{H}_2\text{PO}_4)_3$, followed by slow cooling to room temperature. The product was filtered off, washed with de-ionized water and dried in air. A needle-shaped single crystal of $(\text{Fe}_{0.81}\text{Al}_{0.19})(\text{H}_2\text{PO}_4)_3$ was selected under a polarizing microscope.

Table 1

Selected geometric parameters (\AA , $^\circ$).

Fe1—O5 ⁱ	1.945 (4)	P1—O4	1.593 (4)
Fe1—O10	1.958 (4)	P2—O5	1.512 (4)
Fe1—O1	1.979 (4)	P2—O6	1.521 (4)
Fe1—O9 ⁱⁱ	1.980 (4)	P2—O7	1.567 (4)
Fe1—O2 ⁱⁱⁱ	2.017 (4)	P2—O8	1.587 (4)
Fe1—O6	2.063 (4)	P3—O9	1.504 (4)
P1—O1	1.513 (4)	P3—O10	1.507 (4)
P1—O2	1.525 (4)	P3—O11	1.570 (4)
P1—O3	1.563 (4)	P3—O12	1.590 (4)
O5 ⁱ —Fe1—O10	91.98 (17)	O5—P2—O6	116.7 (2)
O5 ⁱ —Fe1—O1	92.76 (18)	O5—P2—O7	112.0 (3)
O10—Fe1—O1	92.04 (17)	O6—P2—O7	108.1 (2)
O5 ⁱ —Fe1—O9 ⁱⁱ	90.27 (19)	O5—P2—O8	108.9 (2)
O10—Fe1—O9 ⁱⁱ	174.9 (2)	O6—P2—O8	106.4 (2)
O1—Fe1—O9 ⁱⁱ	92.37 (17)	O7—P2—O8	103.7 (2)
O5 ⁱ —Fe1—O2 ⁱⁱⁱ	174.10 (19)	O9—P3—O10	114.1 (2)
O10—Fe1—O2 ⁱⁱⁱ	90.69 (17)	O9—P3—O11	111.7 (2)
O1—Fe1—O2 ⁱⁱⁱ	92.40 (16)	O10—P3—O11	109.3 (2)
O9 ⁱⁱ —Fe1—O2 ⁱⁱⁱ	86.67 (18)	O9—P3—O12	110.2 (3)
O5 ⁱ —Fe1—O6	88.21 (17)	O10—P3—O12	109.1 (3)
O10—Fe1—O6	87.29 (17)	O11—P3—O12	101.6 (3)
O1—Fe1—O6	178.84 (18)	P1—O1—Fe1	139.6 (2)
O9 ⁱⁱ —Fe1—O6	88.25 (17)	P1—O2—Al1 ⁱ	136.6 (2)
O2 ⁱⁱⁱ —Fe1—O6	86.66 (17)	P1—O2—Fe1 ⁱ	136.6 (2)
O1—P1—O2	118.1 (2)	P2—O5—Al1 ⁱⁱⁱ	156.0 (3)
O1—P1—O3	111.5 (2)	P2—O5—Fe1 ⁱⁱⁱ	156.0 (3)
O2—P1—O3	107.4 (2)	P2—O6—Fe1	135.7 (2)
O1—P1—O4	105.7 (2)	P3—O9—Al1 ^{iv}	169.0 (3)
O2—P1—O4	107.0 (2)	P3—O9—Fe1 ^{iv}	169.0 (3)
O3—P1—O4	106.4 (2)	P3—O10—Fe1	146.5 (3)

Symmetry codes: (i) $x, y, z + 1$; (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $x, y, z - 1$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

D—H...A	D—H	H...A	D...A	D—H...A
O3—H3...O6 ^v	0.86 (7)	1.94 (7)	2.614 (5)	134 (7)
O3—H3...O7 ^v	0.86 (7)	2.42 (8)	3.207 (6)	152 (7)
O4—H4...O4 ^{vi}	0.84 (7)	1.95 (7)	2.775 (6)	167 (8)
O7—H7...O3 ^{vii}	0.91 (7)	1.91 (7)	2.765 (6)	156 (7)
O8—H8...O8 ^{viii}	0.89 (7)	1.92 (7)	2.764 (6)	159 (7)
O11—H11...O12 ^{ix}	0.92 (7)	2.47 (6)	3.220 (7)	139 (6)
O12—H12...O12 ^{viii}	0.94 (6)	2.23 (7)	3.055 (8)	146 (7)

Symmetry codes: (v) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (vi) $x, -y + 1, z + \frac{1}{2}$; (vii) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (viii) $x, -y + 2, z - \frac{1}{2}$; (ix) $x, -y + 2, z + \frac{1}{2}$.

Crystal data

$(\text{Fe}_{0.81}\text{Al}_{0.19})(\text{H}_2\text{PO}_4)_3$
 $M_r = 341.32$
 Monoclinic, Cc
 $a = 11.700$ (1) \AA
 $b = 15.590$ (1) \AA
 $c = 5.030$ (1) \AA
 $\beta = 98.00$ (1) $^\circ$

$V = 908.6$ (2) \AA^3
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.98$ mm^{-1}
 $T = 293$ K
 $0.15 \times 0.15 \times 0.1$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.703$, $T_{\max} = 0.754$

1104 measured reflections
 1104 independent reflections
 1043 reflections with $I > 2\sigma(I)$
 2 standard reflections every 120 min
 intensity decay: 0.4%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.074$
 $S = 1.04$
 1104 reflections
 166 parameters
 10 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.55$ e \AA^{-3}
 $\Delta\rho_{\min} = -0.64$ e \AA^{-3}
 Absolute structure: Flack (1983), with 1104 Friedel pairs
 Flack parameter: 0.00 (3)

During refinement, the occupancy of the Fe site exhibited a significant deviation from full occupancy, indicating a substitution with Al; the final occupancies were constrained to sum to 1.0 and refined to 0.807 (7) and 0.193 (7), respectively, for Fe1 and Al1. The positions of all H atoms were located from a difference electron-density map and were then refined with an O—H bond-length restraint of 0.95 (5) \AA and with $U_{\text{iso}}(\text{H})$ fixed at a value of 0.05 \AA^2 .

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Maciček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3041). Services for accessing these data are described at the back of the journal.

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