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The iron phosphate $K_3Fe_5(PO_4)_6$

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The crystal structure of tripotassium pentairon hexaphosphate has been determined by single-crystal X-ray diffraction. The structure contains one Fe atom on a center of symmetry, one K, two Fe and two P atoms on twofold axes, and one Fe, two P and one K atom in general positions. The $K_3Fe_5(PO_4)_6$ structure consists of a complex three-dimensional framework of corner-sharing between iron polyhedra, and corner- and edge-sharing between PO_4 tetrahedra and iron polyhedra (FeO_5 and FeO_6). This linkage between iron and phosphorus forms intersecting channels containing the K atoms.

Comment

Iron phosphates generate considerable interest not only because of their magnetic properties, due to the great number of possible different cation arrangements, but also because of their potential practical applications, including corrosion inhibition (Meisel *et al.*, 1983), passivation of metal surfaces (Attali *et al.*, 1980) and heterogeneous catalysis (Moffat, 1978). These materials offer a considerable number of complex and versatile network structures due to the ability of iron to be in both the +2 and +3 oxidation states, and to adopt various coordination environments. In the monophosphates, iron(III) coordinates, in most cases, to six O atoms and rarely to five O atoms (Belkhiria *et al.*, 1998; Pintard-Scrépel *et al.*, 1978; Andrew-Allen & Robinson, 1988). It is four-coordinated in a few cases, such as in $FePO_4$ (Ng & Calvo, 1975). Moreover, it can exhibit two different coordination modes in the same structure, such as in $K_3Fe_2(PO_4)_3$ (Pintard-Scrépel *et al.*, 1983) and $Cs_7Fe_7(PO_4)_8O_2$ (Andrew-Allen & Robinson, 1988), in which iron(III) adopts five- and six-coordination. The potassium iron phosphate $K_3Fe_5(PO_4)_6$, reported in this paper, falls into the latter category of compounds.

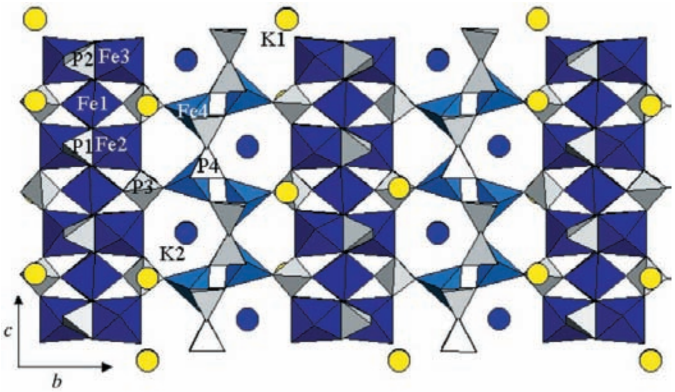

Figure 1
A projection of the structural network of $K_3Fe_5(PO_4)_6$ along the [100] direction.

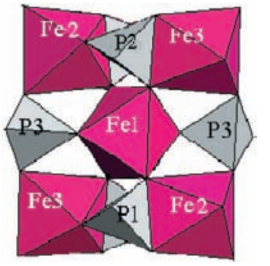

Figure 2
The association mode of iron and phosphorus polyhedra in layers.

Fig. 1 illustrates the complete crystal structure of $K_3Fe_5(PO_4)_6$ projected along the [100] direction. There are four crystallographically distinct Fe atoms in this structure. Fe1 is located on a center of symmetry, Fe2 and Fe3 lie on twofold axes and Fe4 is located in a general position. The Fe atoms are both five- and six-coordinated. Atoms P1, P2 and K2 lie on twofold axes, while atoms P3, P4 and K1 are in general positions. The $K_3Fe_5(PO_4)_6$ structure consists of a three-dimensional complex framework constructed of either iron polyhedra connected to each other by corner-linkage or phosphate tetrahedra connected *via* corner- and edge-sharing. The structure can be easily described as the association of two building blocks. The first gathers Fe1, Fe2 and Fe3 octahedra, P1, P2 and P3 tetrahedra, and K atoms. It consists of iron–phosphate layers, in the *ac* plane, with the interlayer space filled by K^+ cations, as illustrated in the perspective view parallel to the [100] direction shown in Fig. 1. There are two iron–phosphate layers within the repeat distance *b*; each layer lies on a medium plane perpendicular to the *b* axis at $y = \frac{1}{4}$ and $y = \frac{3}{4}$. The layers are formed by corner-sharing FeO_6 octahedra, which are further connected by phosphate tetrahedra through corner- and edge-sharing. The mode of association connecting the iron octahedra and the phosphorus tetrahedra in layers is indicated in Fig. 2. Each $Fe1O_6$ octahedron shares a first corner with, simultaneously, one $Fe2O_6$ octahedron and one $P1O_4$ tetrahedron, a second corner with, simultaneously, one $Fe3O_6$ octahedron and one $P2O_4$ tetrahedron, and finally a third corner with a $P3O_4$ tetrahedron. The $P1O_4$ and $P2O_4$ tetrahedra share one edge, respectively, with $Fe2O_6$ and $Fe3O_6$ octahedra, and share corners of the common edge with two different $Fe1O_6$ octahedra. The remaining corners are coordinated to two $Fe3O_6$ octahedra in the case of $P1O_4$, and two $Fe2O_6$ octahedra in the case of $P2O_4$. $P3O_4$ coordinates to Fe atoms (Fe1, Fe2 and Fe3) through three O atoms. The distortion observed in the $Fe2O_6$ and $Fe3O_6$ octahedra and in the $P1O_4$ and $P2O_4$ tetrahedra is a result of the edge-sharing between these polyhedra, since the existence of the common

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edge induces a strong repulsion between the positive charges carried by the Fe and P atoms, and consequently atoms Fe2, Fe3, P1 and P2 are forced to shift to off-centred positions within their respective polyhedra and the lengths of the common edges are shorter than the other O···O distances in order to efficiently screen this repulsion effect. It is of interest to note that atoms O31, O32 and O34 all bond to P and only one Fe atom, whereas atoms O11, O12, O21 and O22 bond to P and two Fe atoms. Thus, the Fe—O bonds are weaker when the O atom bonds to two Fe atoms, as one would expect. The sharing of edges also affects the geometry, but this may only be possible because the Fe—O bonds are already longer. Fig. 3 shows the atomic displacement ellipsoids connected in layers.

The structural arrangement adopted by the first building block is similar to that observed in the $K_3Fe_3(PO_4)_4{\cdot}H_2O$ structure (Lii, 1995), which is made up of layers involving corner-linkage between FeO_6 octahedra, and corner- and edge-sharing between FeO_6 octahedra and PO_4 tetrahedra. The layers are linked by seven- or six-oxygen-coordinated K^+ cations and hydrogen bonding.

The second building block, formed by Fe4 and $P4O_4$ tetrahedra, is found in the interlayer space between the first building blocks, which has the result of destroying the layered arrangement. Atom Fe4 is pentacoordinated and shares its corners with one $P3O_4$ and four different $P4O_4$ tetrahedra. $Fe4O_5$ polyhedra are connected to each other and to the other iron octahedra by phosphate tetrahedra *via* corner-sharing. The average Fe4—O distance is 1.941 Å, a value close to that observed in $K_3Fe_2(PO_4)_3$ for pentacoordinated iron (1.935 Å; Pintard-Screpel *et al.*, 1983). Each $P4O_4$ tetrahedron shares its four corners with four different $Fe4O_5$ polyhedra.

The three-dimensional structural arrangement formed by the P, Fe and O atoms contains interstitial spaces forming intersecting channels in which K atoms are located. K1 has an environment formed by eight O atoms, with K—O distances ranging from 2.587 (2) to 3.213 (2) Å, while K2 is six-coordinated, with K—O distances between 2.8830 (18) and 3.0257 (15) Å (Table 1). The coordination number of each K^+ cation was determined on the basis of the maximum cation–anion distance; L_{max} = 3.35 Å for K—O according to Donnay & Allman (1970).

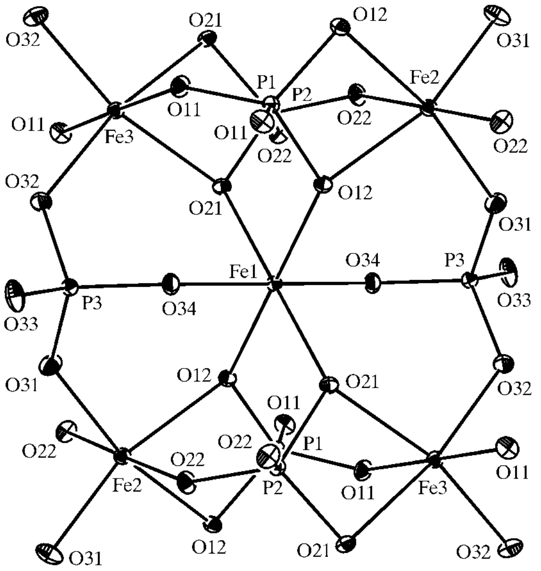

Figure 3
The connectivity of atoms in layers, shown with 50% probability displacement ellipsoids.

Experimental

Crystals of $K_3Fe_5(PO_4)_6$ were prepared by the flux method from K_2CO_3, $(NH_4)_2HPO_4$, MoO_3 and $Fe(NO_3)_3{\cdot}9H_2O$. The starting materials (equimolar ratio) were placed in a platinum crucible (in air) and heated at 1073 K for 1 h. The mixture was cooled to 773 K at a rate of 10 K h^{-1}. Finally, parallelepiped-shaped brown crystals of $K_3Fe_5(PO_4)_6$ were obtained after washing the mixture with boiling water.

Table 1
Selected geometric parameters (Å, °).

Fe1—O34^{i}	1.9544 (12)	P3—O32	1.5220 (13)
Fe1—O12^{i}	2.0351 (14)	P3—O34	1.5302 (12)
Fe1—O21	2.0376 (14)	P3—O31	1.5387 (13)
Fe2—O31	1.9289 (12)	P4—O42	1.5220 (14)
Fe2—O22^{ii}	2.0312 (16)	P4—O43	1.5310 (14)
Fe2—O12^{iii}	2.0987 (12)	P4—O44	1.5366 (13)
Fe3—O32	1.8977 (12)	P4—O41	1.5380 (13)
Fe3—O11^{iv}	2.0293 (16)	K1—O32^{viii}	2.5870 (19)
Fe3—O21^{v}	2.0859 (12)	K1—O33	2.6045 (18)
Fe4—O44^{vi}	1.8736 (13)	K1—O31^{viii}	2.757 (2)
Fe4—O41	1.8867 (12)	K1—O34	2.7579 (17)
Fe4—O33	1.9273 (12)	K1—O42^{vii}	2.7867 (15)
Fe4—O42^{vii}	1.9992 (17)	K1—O11^{ix}	2.8746 (13)
Fe4—O43^{v}	2.0173 (17)	K1—O22^{x}	2.9934 (13)
P1—O11	1.5105 (13)	K1—O43^{vii}	3.2132 (16)
P1—O12	1.5756 (11)	K2—O44^{xi}	2.8830 (18)
P2—O22^{v}	1.5158 (13)	K2—O41^{xi}	2.9890 (16)
P2—O21	1.5772 (11)	K2—O31^{xii}	3.0257 (15)
P3—O33	1.5193 (12)		
O34^{i}—Fe1—O12^{i}	90.92 (5)	O44^{vi}—Fe4—O42^{vii}	95.42 (7)
O34—Fe1—O12^{i}	89.08 (5)	O41—Fe4—O42^{vii}	92.22 (6)
O34^{i}—Fe1—O21	85.42 (5)	O33—Fe4—O42^{vii}	82.67 (5)
O34—Fe1—O21	94.58 (5)	O44^{vi}—Fe4—O43^{v}	91.83 (7)
O12^{i}—Fe1—O21	84.99 (6)	O41—Fe4—O43^{v}	90.22 (7)
O12—Fe1—O21	95.01 (6)	O33—Fe4—O43^{v}	89.08 (5)
O31—Fe2—O31^{iii}	94.31 (7)	O42^{vii}—Fe4—O43^{v}	170.10 (6)
O31—Fe2—O22^{ii}	87.33 (6)	O11—P1—O11^{iii}	111.48 (10)
O31^{iii}—Fe2—O22^{ii}	94.41 (6)	O11—P1—O12	112.32 (7)
O22^{ii}—Fe2—O22^{i}	177.45 (6)	O11^{iii}—P1—O12	110.93 (7)
O31—Fe2—O12^{iii}	166.43 (5)	O12—P1—O12^{iii}	98.24 (9)
O31^{iii}—Fe2—O12^{iii}	98.49 (5)	O22^{v}—P2—O22	111.89 (10)
O22^{ii}—Fe2—O12^{iii}	87.20 (5)	O22^{v}—P2—O21	110.59 (6)
O22^{i}—Fe2—O12^{iii}	90.70 (5)	O22—P2—O21	112.54 (7)
O12^{iii}—Fe2—O12	69.17 (6)	O21—P2—O21^{v}	97.97 (9)
O32—Fe3—O32^{v}	98.84 (8)	O33—P3—O32	110.52 (7)
O32—Fe3—O11^{iv}	85.58 (6)	O33—P3—O34	109.29 (7)
O32^{v}—Fe3—O11^{iv}	95.63 (6)	O32—P3—O34	109.54 (7)
O11^{iv}—Fe3—O11^{i}	178.15 (7)	O33—P3—O31	108.39 (7)
O32—Fe3—O21^{v}	163.62 (5)	O32—P3—O31	108.80 (8)
O32^{v}—Fe3—O21^{v}	96.26 (5)	O34—P3—O31	110.28 (7)
O11^{iv}—Fe3—O21^{v}	86.68 (5)	O42—P4—O43	108.11 (8)
O11^{i}—Fe3—O21^{v}	91.81 (5)	O42—P4—O44	111.53 (8)
O21^{v}—Fe3—O21	69.57 (6)	O43—P4—O44	109.92 (8)
O44^{vi}—Fe4—O41	118.61 (6)	O42—P4—O41	111.36 (8)
O44^{vi}—Fe4—O33	103.56 (6)	O43—P4—O41	111.95 (8)
O41—Fe4—O33	137.82 (6)	O44—P4—O41	103.96 (7)

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

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Crystal data

$K_3Fe_5(PO_4)_6$
$M_r = 966.37$
Monoclinic, $C2/c$
$a = 6.460$ (4) Å
$b = 30.997$ (7) Å
$c = 10.665$ (2) Å
$\beta = 90.22$ (4)°
$V = 2135.6$ (15) Å^3
$Z = 4$
$D_x = 3.006$ Mg m^{-3}
$D_m = 3.05$ (5) Mg m^{-3}
D_m measured by pycnometry
Ag $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7$–12°
$\mu = 2.30$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, brown
0.30 × 0.20 × 0.16 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (Katayama, 1986)
$T_{\min} = 0.630$, $T_{\max} = 0.710$
7763 measured reflections
3823 independent reflections
3354 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 25.0$°
$h = -9 \rightarrow 9$
$k = -46 \rightarrow 9$
$l = -16 \rightarrow 16$
2 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.051$
$S = 1.08$
3823 reflections
177 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0214P)^2 + 4.5065P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.76$ e Å^{-3}
$\Delta\rho_{\min} = -0.79$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00198 (13)

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1386). Services for accessing these data are described at the back of the journal.

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