Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

$K_2Fe[H(HPO_4)_2]F_2$

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(P–O) = 0.002 Å
R factor = 0.023
wR factor = 0.064
Data-to-parameter ratio = 13.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 21 June 2005
Accepted 28 June 2005

The crystal structure of dipotassium iron(III) {hydrogen bis[hydrogenphosphate(V)]} difluoride, $K_2Fe[H(HPO_4)_2]F_2$, obtained by hydrothermal synthesis, was determined from single-crystal X-ray diffraction data. The structure is characterized by K^+ cations and hydrogen-bonded $\{[Fe[H(HPO_4)_2]F_2]^{2-}\}_n$ chains, which consist of centrosymmetric $Fe[F_2O_4]$ octahedra linked to their four neighbouring phosphate tetrahedra *via* common O corners, developing a three-dimensional structure.

Comment

Compounds with open framework structures, including iron phosphates such as cacoxenite (Moore & Shen, 1983), have attracted great interest due to their potential applications (Cheetham *et al.*, 1999). In the anhydrous potassium iron fluorophosphate system, only two compounds have previously been reported, namely $KFe(PO_4)F$ (Matvienko *et al.*, 1979) and $K_2Fe_2(P_2O_7)F_2$ (Yakubovich *et al.*, 1984). To our knowledge, the title compound, (I), reported here is the first potassium iron fluoro-hydrogenphosphate.

A disordered H-atom position in the structure was clearly shown in the difference Fourier peaks after full-matrix least-squares refinement including non-H anisotropic displacement parameters. If an H atom had occupied the special position 2c $(0, \frac{1}{2}, 0)$ for a symmetric arrangement, the O—H bond distance would have been about 1.20 Å. Finally, atom H2 was located and fixed at the position of the difference Fourier peak in a disordered fashion, as described for $Li_2Fe[(PO_4)(HPO_4)]$ (Mi *et al.*, 2004). This gives a reliable value of U_{iso}(H2) = 0.023 (16) Å^2 with 50% occupancy.

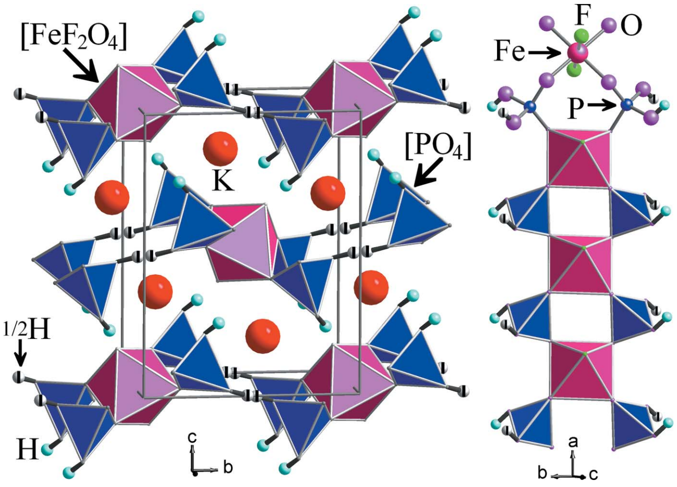

Figure 1
Two views of the crystal structure of $K_2Fe[H(HPO_4)_2]F_2$.

doi:10.1107/S1600536805020635

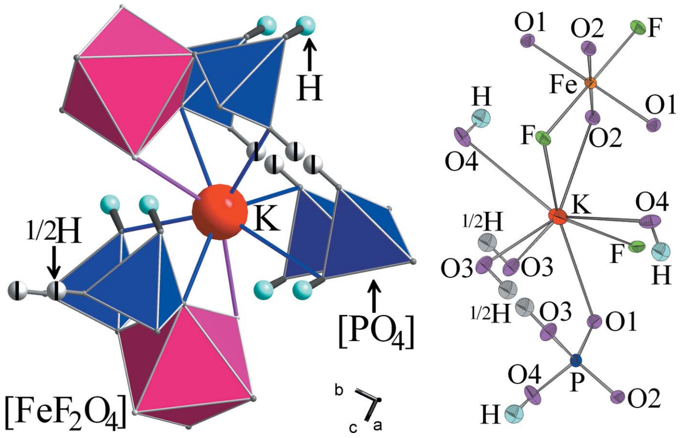

Figure 2
Two views of the environment of the K^+ cation. The second view shows displacement ellipsoids of all atoms drawn at the 50% probability level.

Four O and two F atoms bond to the central Fe atom, which lies on an inversion centre forming an octahedral coordination, with four long equatorial Fe—O bonds and two slightly shorter Fe—F bonds in *trans* positions (Table 1). According to the bond-valence sum calculation for Fe (BVS = 3.16; Brese & O'Keeffe, 1991), it was confirmed that the Fe ions have an oxidation state of 3+ in the title compound.

Each phosphate tetrahedron is connected to two $Fe[F_2O_4]$ octahedra, sharing its two O vertices that are not bonded to H, and each $Fe[F_2O_4]$ octahedron is linked to phosphate units through all four of its O vertices, to form a chain along the *a* axis (Fig. 1). The structure is completed by K^+ cations and hydrogen bonds, which link the $\{[Fe[H(HPO_4)_2]F_2]^{2-}\}_n$ chains into a three-dimensional structure. The large K^+ cation is seven-coordinate with respect to five nearby O and two F atoms. One additional outer O atom has a K—O bond distance of 3.236 Å (Fig. 2).

Experimental

The title compound was synthesized hydrothermally from a typical mixture of Fe_2O_3 (0.399 g), KH_2PO_4 (1.360 g), K(OH) (0.561 g) and 60% HF (1.5 ml) in the molar ratio of Fe:P:K = 1:2:4. The mixture was dissolved in distilled water (4 ml) and heated at 403 K for 4 d under autogenous pressure in a 20 ml Teflon-lined autoclave filled to 40% capacity. All starting materials were analytical grade and used without further purification. Pale-pink transparent crystals of (I) were obtained in *ca* 67% yield (based on Fe) and could be easily separated from a dark roseate powder (unreacted Fe_2O_3). The X-ray powder diffraction pattern of manually selected crystals agreed well with that calculated from the single-crystal data. The chemical composition was confirmed by a chemical semi-quantitative energy-dispersive X-ray diffraction analysis (Oxford Instruments). The FT–IR spectrum was recorded for the sample (2 mg dispersed in 200 mg KBr) in the ranges 4000–400 cm^{-1} using a Nicolet AVATAR 360 ESP spectrometer; IR (ν, cm^{-1}): 3018 (*m*), 1419 (*m*), 1177 (*s*), 1106 (*s*), 1027 (*s*), 942 (*m*), 865 (*m*), 797 (*m*), 589 (*m*), 517 (*m*), 450 (*m*).

Crystal data

$K_2Fe[H(HPO_4)_2]F_2$
$M_r = 365.01$
Monoclinic, $P2_1/c$
$a = 4.7586 (10)$ Å
$b = 8.2530 (17)$ Å
$c = 10.758 (2)$ Å
$\beta = 92.845 (2)^\circ$
$V = 421.97 (15)$ Å^3
$Z = 2$
$D_x = 2.873$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4590 reflections
$\theta = 3$–28.3°
$\mu = 3.21$ mm^{-1}
$T = 295 (2)$ K
Prism, pale pink
0.33 × 0.26 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.417$, $T_{max} = 0.783$
4590 measured reflections
1012 independent reflections
1011 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 28.3^\circ$
$h = -6 \rightarrow 6$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.064$
$S = 1.27$
1012 reflections
73 parameters
Only H-atom displacement parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0241P)^2 + 0.5078P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.035 (3)

Table 1
Selected geometric parameters (Å, °).

$Fe1—F1^{i}$	1.9208 (12)	$K1—O2^{iii}$	2.6900 (16)
$Fe1—F1^{ii}$	1.9208 (12)	$K1—F1^{vi}$	2.6957 (15)
$Fe1—O2^{iii}$	1.9867 (15)	$K1—F1^{i}$	2.6984 (14)
$Fe1—O2^{iv}$	1.9867 (15)	$K1—O3^{vi}$	2.7711 (17)
$Fe1—O1^{iii}$	1.9942 (15)	$K1—O3^{vii}$	2.7785 (18)
$Fe1—O1^{iv}$	1.9942 (15)	$K1—O1^{vii}$	2.7963 (16)
$P1—O1^{v}$	1.4970 (15)	$K1—O4^{iii}$	2.8156 (18)
P1—O2	1.4974 (15)	$K1—O4^{vi}$	3.2362 (19)
P1—O3	1.5265 (16)	O3—H2	0.8722
$P1—O4^{v}$	1.5748 (16)	O4—H1	0.8521
$F1^{i}—Fe1—F1^{ii}$	180	$O1^{v}—P1—O3$	110.90 (9)
$F1^{i}—Fe1—O2^{iii}$	88.03 (6)	O2—P1—O3	109.27 (9)
$F1^{ii}—Fe1—O2^{iii}$	91.97 (6)	$O1^{v}—P1—O4^{v}$	104.82 (9)
$O2^{iii}—Fe1—O2^{iv}$	180	$O2—P1—O4^{v}$	108.30 (9)
$F1^{i}—Fe1—O1^{iii}$	91.23 (6)	$O3—P1—O4^{v}$	107.37 (10)
$F1^{ii}—Fe1—O1^{iii}$	88.77 (6)	$P1^{viii}—O1—Fe1^{ix}$	136.70 (10)
$O2^{iii}—Fe1—O1^{iii}$	90.52 (6)	$P1—O2—Fe1^{ix}$	134.28 (10)
$O2^{iv}—Fe1—O1^{iii}$	89.48 (6)	P1—O3—H2	122.27 (14)
$O1^{iii}—Fe1—O1^{iv}$	180	$P1^{viii}—O4—H1$	113.31 (14)
$O1^{v}—P1—O2$	115.76 (9)		

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

Table 2
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$O4—H1\cdots F1^{x}$	0.85	1.75	2.589 (2)	168
$O3—H2\cdots O3^{xi}$	0.87	1.53	2.400 (2)	172

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

H-atom coordinates are located and fixed at the positions of the difference Fourier peaks and only their displacement parameters were refined.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

This project was supported by funds from the National Natural Science Foundation of China (grant No. 40472027), the Natural Science Foundation of Fujian Province (grant No. E0410003) and the project sponsored by the SRF for ROCS, SEM, in China.

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