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$\text{K}_2\text{Fe}[\text{H}(\text{HPO}_4)_2]\text{F}_2$

Jin-Xiao Mi,^{a*} Cheng-Xin Wang,^a
Zan-Bin Wei,^b Fu-Jin Chen,^a
Chun-Yan Xu^a and Shao-Yu Mao^b

^aDepartment of Materials Science and Engineering, Xiamen University, Xiamen 361005, Fujian Province, People's Republic of China, and ^bDepartment of Chemistry, Xiamen University, Xiamen 361005, Fujian Province, People's Republic of China

Correspondence e-mail:
jxmi@jingxian.xmu.edu.cn

Key indicators

Single-crystal X-ray study

$T = 295 \text{ K}$

Mean $\sigma(\text{P}-\text{O}) = 0.002 \text{ \AA}$

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>.

The crystal structure of dipotassium iron(III) {hydrogen bis[hydrogenphosphate(V)]} difluoride, $\text{K}_2\text{Fe}[\text{H}(\text{HPO}_4)_2]\text{F}_2$, obtained by hydrothermal synthesis, was determined from single-crystal X-ray diffraction data. The structure is characterized by K^+ cations and hydrogen-bonded $\{[\text{Fe}[\text{H}(\text{HPO}_4)_2]\text{F}_2]^{2-}\}_n$ chains, which consist of centrosymmetric $\text{Fe}[\text{F}_2\text{O}_4]$ octahedra linked to their four neighbouring phosphate tetrahedra *via* common O corners, developing a three-dimensional structure.

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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 $\text{KFe}(\text{PO}_4)\text{F}$ (Matvienko *et al.*, 1979) and $\text{K}_2\text{Fe}_2(\text{P}_2\text{O}_7)\text{F}_2$ (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 $\text{Li}_2\text{Fe}[(\text{PO}_4)(\text{HPO}_4)]$ (Mi *et al.*, 2004). This gives a reliable value of $U_{\text{iso}}(\text{H}2) = 0.023(16) \text{ \AA}^2$ with 50% occupancy.

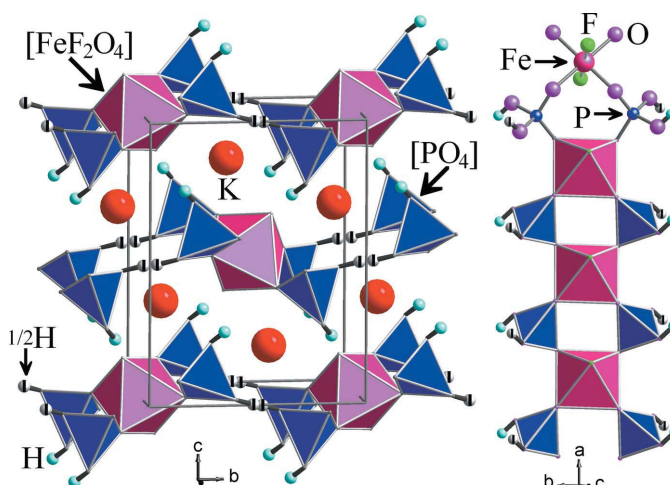


Figure 1
Two views of the crystal structure of $\text{K}_2\text{Fe}[\text{H}(\text{HPO}_4)_2]\text{F}_2$.

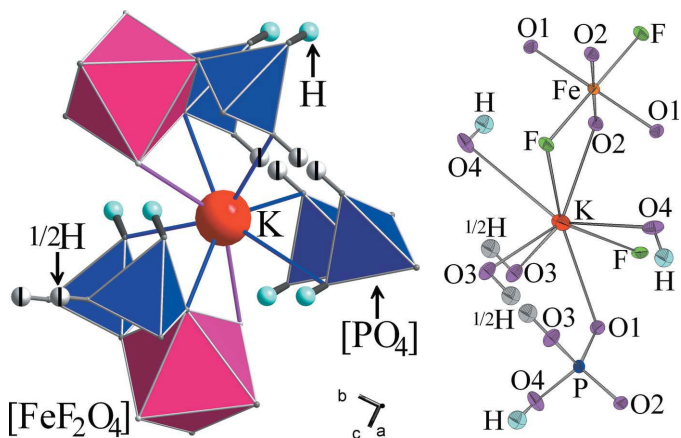


Figure 2
Two views of the environment of the K^+ cation. The second view shows displacement ellipsoids of all atoms drawn at the 50% probability level.

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'Keefe, 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)°
 $V = 421.97$ (15) Å³
 $Z = 2$

$D_x = 2.873$ 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 ^{viii}	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) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (viii) $x - 1, y, z$; (ix) $x, y + 1, z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O4—H1...F1 ^x	0.85	1.75	2.589 (2)	168
O3—H2...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*.

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