$RbFe(HPO_4)_2$: an Iron(III) Phosphate with an Intersecting Tunnel Structure†

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A new iron(III) phosphate, $RbFe(HPO_4)_2$, has been synthesised hydrothermally at 230 °C and characterized by single-crystal X-ray diffraction. The crystal is trigonal with a very long *c* axis: space group $R\bar{3}c$, $a = 8.160(1)$, $c = 52.75(1)$ Å, $Z = 18$ and $R = 0.0207$. The compound adopts an intersecting tunnel structure, with the rubidium cations in the tunnels. The framework consists of corner-sharing FeO_6 octahedra and HPO_4 groups. A triclinic polymorph was also obtained.

We have recently synthesised and structurally characterized several new compounds in the iron phosphate system. The use of mainly hydrothermal methods gave $AFe(P_2O_7)$ (A = Cs or Rb),[1] $Sr_2Fe(PO_4)_2(H_2PO_4)$,[2] $SrFe_3(PO_4)_3(HPO_4)$,[3] $CaFe_2(PO_4)_2(HPO_4)$,[4] $AFe_3(P_2O_7)_2$ (A = Sr or Ba)[5] and $AFe_5(PO_4)_5(OH){\cdot}H_2O$ (A = Ca or Sr).[6] They include iron-(III), -(II) and mixed-valence compounds. Their structures cover discrete FeO_6 octahedra, FeO_5 trigonal bipyramids, dimers of corner-, edge- and face-sharing FeO_6 octahedra, and infinite chains of FeO_6 octahedra sharing either *trans* or skew edges. These phosphates are of interest for their complex crystal structures and present a challenge to complete structural characterization. Attempts to add new members to the system have yielded the iron(III) rubidium hydrogenphosphate $RbFe(HPO_4)_2$. It crystallizes in the trigonal space group $R\bar{3}c$ with a very long *c* axis (52.7 Å). A triclinic polymorph was also obtained. This paper reports the synthesis and single-crystal structure of the trigonal phase.

Experimental

Synthesis.—Crystals of $RbFe(HPO_4)_2$ were obtained by heating a mixture of RbOH (1.271 g, 50%), $FePO_4{\cdot}2H_2O$ (0.386 g), NMe_2H (0.699 g, 40%), $MePO(OH)_2$ (0.198 g), H_3PO_4 (1.5 cm^3, 85%) and water (10 cm^3) in a Teflon-lined autoclave (23 cm^3) at 230 °C for 4 d followed by slow cooling to room temperature. The product was filtered off, washed with water, rinsed with ethanol, and dried in a desiccator at ambient temperature. It contained colourless parallelepiped crystals of $RbFe(HPO_4)_2$, polycrystalline material, and rod-like crystals. The polycrystalline material was the major product. Powder X-ray diffraction analysis of a sample of manually selected parallelepiped crystals agreed well with that calculated from single-crystal data. Energy-dispersive X-ray fluorescence analysis on a parallelepiped crystal showed that the Rb:Fe:P mole ratio was 1.04:1:1.96, in accord with the structural analysis. Interestingly, the polycrystalline material had the same X-ray powder pattern as that of the vanadium(III) compound $RbV(HPO_4)_2$, which is triclinic and has a similar structure to that of $RbFe(HPO_4)_2$.‡ The polycrystalline material was further characterized by thermogravimetric analysis (TGA) under air using a DuPont thermal analyser. The sample began to decompose at about 350 °C and exhibited a weight loss of 5.44% at 550 °C. The weight loss corresponds to the loss of one water molecule and can be compared with the calculated value of 5.40% assuming that the material also has the stoichiometry $RbFe(HPO_4)_2$. The decomposition product from TGA should have the nominal composition $RbFe(P_2O_7)$. Subsequently, it was found that the decomposition product had the same X-ray powder pattern as that of $RbFe(P_2O_7)$ previously synthesised hydrothermally at 500 °C by us.[1] It can be concluded that the polycrystalline material is a triclinic polymorph of $RbFe(HPO_4)_2$. The rod-shaped crystals could not be indexed because of twinning. An optimum reaction condition to prepare a single-phase product was not found.

Single-crystal X-Ray Diffraction.—A colourless parallelepiped crystal of dimensions 0.09 × 0.09 × 0.19 mm was used for indexing on an Enraf-Nonius CAD4 diffractometer with κ-axis geometry using monochromated Mo-Kα radiation. Unit-cell parameters were determined by a least-squares fit of 25 peak maxima having $13 < 2\theta < 33°$. Axial oscillation photographs were taken to check the cell parameters. Since the *c* axis is 52.7 Å, the crystal was transferred to a Rigaku AFC5R four-circle diffractometer equipped with Cu-Kα radiation for intensity data collection because long-wavelength radiation gives a better separation between the reflections. Based on the statistics of the intensity distribution, systematic absences and successful solution of the structure, the space group was determined to be $R\bar{3}c$. The Patterson method was used to locate the Rb and Fe atoms with the remaining non-hydrogen atoms being found from successive Fourier difference maps. However, the least-squares refinement converged at a rather high *R* factor, 0.10, due to strong absorption of Cu-Kα radiation by the heavy elements in the crystal and inadequate correction for absorption. Subsequently, we collected intensity data on the CAD4 diffractometer with Mo-Kα radiation because of the systematic absences of the space group $R\bar{3}c$. The intensity data were corrected for Lorentz polarization and absorption effects. Correction for absorption was based on ψ scans of a few suitable reflections with χ values close to 90° using the NRC VAX program package.[8] During the structure refinement, bond-valence calculations[9] were carried out to help locate any hydrogen atoms. Bond-valence sums (Σ*s*) showed that both Fe atoms were trivalent, O(3) was considerably undersaturated ($\Sigma s = 1.36$), O(4) was a little undersaturated ($\Sigma s = 1.79$), and all other atoms had values close to those of their formal oxidation states. To balance the charge, one H atom must be included in the formula. The values suggested that O(3) is

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

‡ $RbV(HPO_4)_2$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.186(1)$, $b = 8.826(2)$, $c = 9.446(7)$ Å, $\alpha = 65.36(3)$, $\beta = 70.43(3)$, $\gamma = 69.76(2)°$, $U = 498.0(4)$ Å^3, $Z = 3$ and $R = 0.0267$.[7]

bonded to a hydrogen atom and O(4) is involved in hydrogen bonding. The presence of hydrogen bonding can also be inferred from the short O(3) $\cdots$ O(4) distance of 2.59 Å which involves a different co-ordination polyhedron. The H atom was located from a Fourier difference map. The final cycle of least-squares refinement including the atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms, and fixed atomic coordinates and isotropic thermal parameters for the H atoms, converged at $R = 0.0207$, $R' = 0.0228$ and goodness of fit = 0.984. The structure solution and refinement were performed on a MicroVax computer using the SHELXTL-PLUS program package.[10] Corrections for anomalous dispersion and secondary extinction were applied. Neutral atom scattering factors for all atoms were used.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

The crystallographic data are listed in Table 1, atomic coordinates in Table 2, and bond distances, angles, and bond-valence sums in Table 3. Both Fe atoms are six-co-ordinated. The co-ordination number of each Rb atom was determined on the basis of the maximum gap in the Rb–O distances ranked in increasing order. The maximum cation–anion distance, L_{max}, according to Donnay and Allmann[11] was also considered. Therefore, Rb(1) and Rb(2) are co-ordinated by twelve and nine oxygen atoms, respectively. The valence sum for Rb(1) is significantly higher than 1, indicative of tight binding. The values for all other atoms are in good accord with their formal oxidation states. Atoms Rb(2) and Fe(1) sit on three-fold axes, Rb(1) has a local symmetry of 32, Fe(2) is at $\bar{3}$, and all other atoms are at general positions. As shown by the Fe–O distances, O–Fe–O bond angles, and O $\cdots$ O distances of 2.720–2.940 Å for Fe(1)O$_6$ and 2.760–2.888 Å for Fe(2)O$_6$, both FeO$_6$ octahedra are quite regular and Fe(1)O$_6$ is slightly more distorted than Fe(2)O$_6$. The P atom is within a somewhat distorted tetrahedron. The P–O(3) distance is the longest since O(3) is the hydroxyl oxygen.

The compound RbFe(HPO$_4$)$_2$ reveals a new structural type. As shown in Fig. 1 it is constructed from corner-sharing FeO$_6$ octahedra and HPO$_4$ groups. Each Fe(1)O$_6$ octahedron shares corners with six different HPO$_4$ groups, which in turn are co-ordinated to three Fe(1)O$_6$ and four Fe(2)O$_6$ octahedra. Each Fe(2)O$_6$ octahedron also shares corners with six HPO$_6$ groups, which are co-ordinated to eight Fe(1)O$_6$ octahedra. Since the framework Fe(HPO$_4$)$_2$ contains octahedral Fe, the co-ordination number of phosphate anion should be three (= 6/2). The actual structure is in agreement with this since the hydroxyl oxygen is unshared. The fundamental building block of the framework is a trimer consisting of one Fe(2), two Fe(1) atoms and the associated HPO$_4$ groups, Fe(1)$_2$Fe(2)(HPO$_4$)$_{12}$. Each HPO$_4$ group is co-ordinated to one Fe(1)O$_6$ and one Fe(2)O$_6$ within a trimer and one Fe(1)O$_6$ of an adjacent trimer such that a three-dimensional framework with the stoichiometry $^3_\infty$[Fe(1)$_2$Fe(2)(HPO$_4$)$_6$] is formed, where the superscript number indicates the dimensionality of the structure. The H atom is bonded to O(4) belonging to an adjacent trimer through a hydrogen bond (1.74 Å) O(3)–H $\cdots$ O(4) bond. These trimers are arranged so as to form spirals, with six trimers per spiral of unit-cell length along the c axis (Fig. 2). Each trimer is shared by

Table 1 Crystal data and intensity-collection parameters for RbFe(HPO$_4$)$_2$

M	333.27
Crystal symmetry	Trigonal
Space group	$R\bar{3}c$
a/Å	8.160(1)
c/Å	52.75(1)
U/Å^3	3041.8(7)
Z	18
D_c/g cm^{-3}	3.275
F(000)	2862
μ(Mo-Kα)/cm^{-1}	98.7
T/°C	23
Scan rate/° min^{-1}	5.49
Scan mode	θ–2θ
Scan width/°	0.85 + 0.35 tan θ
2θ Range/°	2–55
No. of reflections collected	2190
No. of unique reflections	783
Unique observed reflections	533 [$I > 3\sigma(I)$]
Refined parameters	57
R^a	0.0207
R'^b	0.0228
$(\Delta\rho)_{max,min}$/e Å^{-3}	0.40, −0.42

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. Weighting scheme $w^{-1} = \sigma^2(F) + gF^2$, where $g = 0.000\,347$.

Table 2 Atomic coordinates for RbFe(HPO$_4$)$_2$

Atom	X/a	Y/b	Z/c
Rb(1)	0	0	$\frac{3}{4}$
Rb(2)	0	0	0.666 59(1)
Fe(1)	$\frac{1}{3}$	$\frac{2}{3}$	0.752 69(1)
Fe(2)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$
P	−0.409 3(1)	−0.380 7(1)	0.712 73(1)
O(1)	−0.502 6(3)	−0.398 1(3)	0.687 52(4)
O(2)	−0.437 1(3)	−0.257 7(3)	0.731 90(4)
O(3)	−0.187 7(3)	−0.278 3(3)	0.707 45(4)
O(4)	−0.534 8(3)	−0.112 5(3)	0.776 99(4)

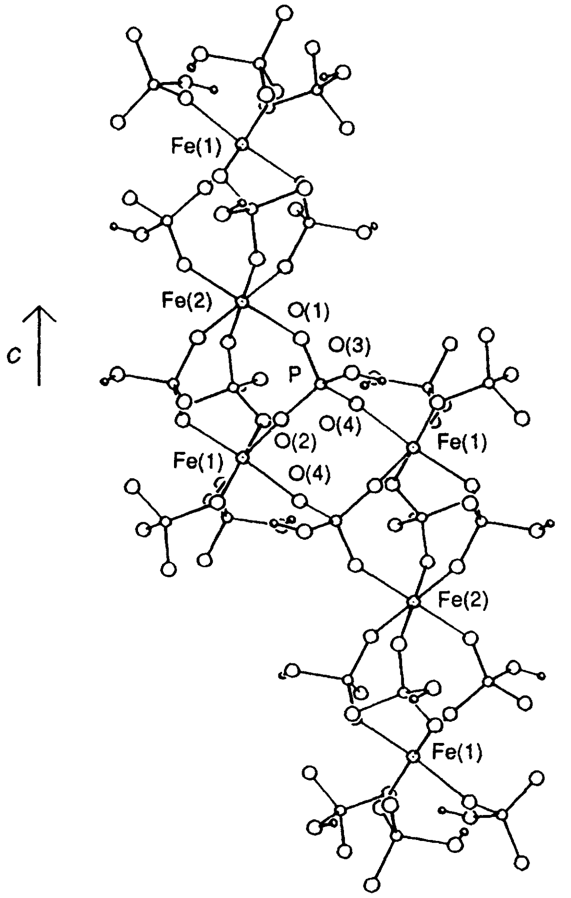

Fig. 1 Section of a spiral chain showing the co-ordination of HPO$_4$ groups around Fe atoms

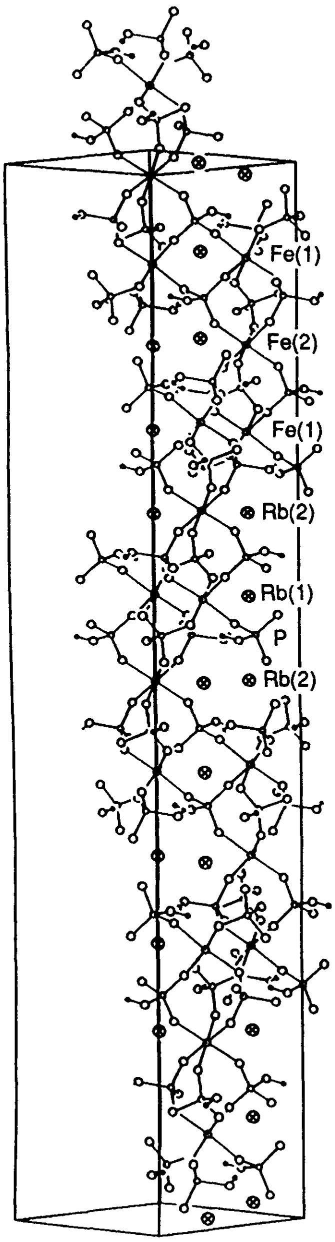

Fig. 2 A spiral chain viewed along the [110] direction

six spirals. As shown in Figs. 3 and 4, the framework contains tunnels along the [100] and [110] directions and the rubidium cations are located at the intersections of these tunnels. In the *ab* plane, sheets formed of Fe(1) and Rb(1) metal atoms alternate with those of Fe(2) and Rb(2). These metal-atom sheets are interleaved with HPO_4 groups. All metal atoms sit on three-fold axes. Columns of metal atoms along the *c* axis form a close-packed array with the interstitial space filled with HPO_4 groups (Fig. 5). In each column the metal atoms are arranged in the sequence . . . Fe(1)Fe(2)Fe(1)Rb(2)Rb(1)Rb(2)Fe(1) . . . .

As indicated earlier, there is a triclinic polymorph of this compound, crystals of which suitable for structure determination have not yet been obtained. Based on powder X-ray diffraction, it is isostructural with the vanadium(III) analogue $RbV(HPO_4)_2$. The latter is well characterized by single-crystal X-ray diffraction, having a similar structure to that of $RbFe(HPO_4)_2$ with rubidium cations in intersecting tunnels. Since the ionic radii for V^{3+} and high-spin Fe^{3+} are very similar, phosphates of iron(III) and vanadium(III) are often isostructural. For example, $Ca_2V(PO_4)(HPO_4)\cdot H_2O$,[12] $Sr_2V(PO_4)_2(H_2PO_4)$,[2] $BaV_2(HPO_4)_4\cdot H_2O$,[13] $CaV_2(PO_4)_2(HPO_4)$[4] and $AV(P_2O_7)$ (A = alkali metal)[14] are isostructural

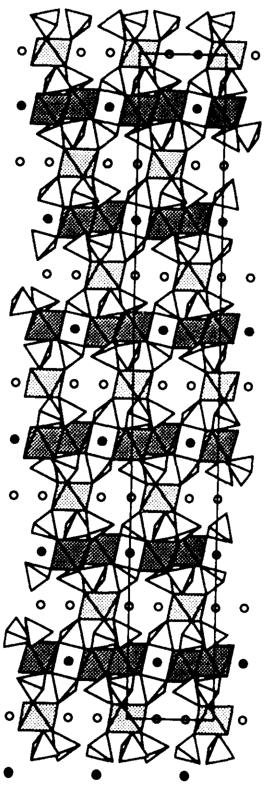

Fig. 3 View of the $RbFe(HPO_4)_2$ structure along the [100] direction. The corners of the octahedra and tetrahedra are O atoms and the Fe and P atoms are at the centre of each octahedron and tetrahedron, respectively. Octahedra with darker and lighter shading are $Fe(1)O_6$ and $Fe(2)O_6$, respectively. Atoms Rb(1) and Rb(2) are represented by solid and open circles, respectively; H atoms are omitted for clarity

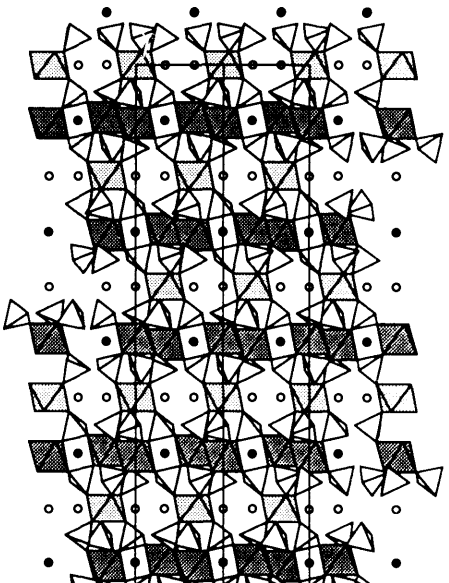

Fig. 4 View of the $RbFe(HPO_4)_2$ structure along the [110] direction

Table 3 Selected bond lengths (Å), angles (°) and bond-valence sums (Σs) for $RbFe(HPO_4)_2$

Rb(1)–O(2)	3.249(2) (6 ×)	Rb(1)–O(3)	3.010(2) (6 ×)
Σs[Rb(1)–O] = 1.21			
Rb(2)–O(1)	3.307(3) (3 ×)	Rb(2)–O(3)	2.944(2) (3 ×)
Rb(2)–O(4)	3.358(2) (3 ×)		
Σs[Rb(2)–O] = 1.01			
Fe(1)–O(2)	1.984(2) (3 ×)	Fe(1)–O(4)	2.027(2) (3 ×)
Σs[Fe(1)–O] = 3.09			
Fe(2)–O(1)	1.997(2) (6 ×)		
Σs[Fe(2)–O] = 3.15			
P–O(1)	1.504(2)	P–O(2)	1.520(3)
P–O(3)	1.592(2)	P–O(4)	1.534(2)
Σs(P–O) = 4.98			
O(3)–H	0.863	O(4) ··· H	1.740
O(2)–Fe(1)–O(2)	92.4(1) (3 ×)	O(2)–Fe(1)–O(4)	94.2(1) (3 ×)
O(2)–Fe(1)–O(4)	89.0(1) (3 ×)	O(4)–Fe(1)–O(4)	84.3(1) (3 ×)
O(1)–Fe(2)–O(1)	92.6(1) (6 ×)	O(1)–Fe(1)–O(1)	87.4(1) (6 ×)
O(1)–P–O(2)	114.5(2)	O(1)–P–O(3)	106.5(1)
O(1)–P–O(4)	110.0(1)	O(2)–P–O(3)	106.0(1)
O(2)–P–O(4)	113.1(1)	O(3)–P–O(4)	106.1(1)
P–O(3)–H	108.3(2)	O(3)–H ··· O(4)	168.5(1)

with their iron analogues. Therefore, one would expect the existence of a trigonal polymorph of $RbV(HPO_4)_2$. Further research on these interesting polymorphs is in progress.

Acknowledgements

Support for this study by the Institute of Chemistry, Academia Sinica and the National Science Council is acknowledged. We thank Dr. Hanna Yuan at the Institute of Molecular Biology and Ms. Chou at the Institute of Chemistry, Academia Sinica for X-ray intensity-data collection.

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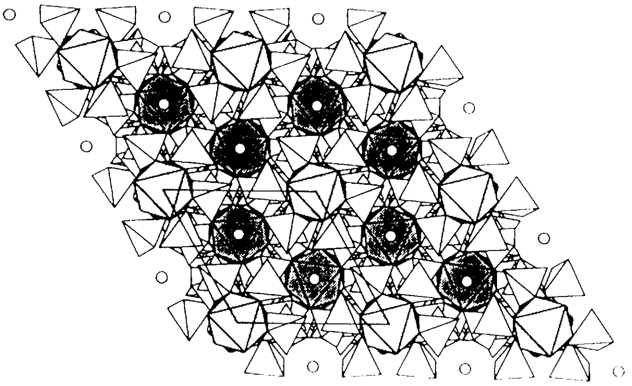

Fig. 5 View of the $RbFe(HPO_4)_2$ structure along the [001] direction

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Received 17*th December* 1993; *Paper* 3/07435H