

Fe₂P₂O₇(H₂O)₂Henry G. Giesber III,^a Michael B. Korzenski,^b William T. Pennington^a and Joseph W. Kolis^{a*}^aDepartment of Chemistry, Clemson University, Clemson, SC 29634-1905, USA, and ^bLaboratoire Crismat-ISMRA, 6 Boulevard du Marechal Juin, 14050 Caen CEDEX, France

Correspondence e-mail: kjoseph@clemson.edu

Received 21 June 1999

Accepted 8 November 1999

The compound diiron diphosphate dihydrate, Fe₂P₂O₇(H₂O)₂, was synthesized hydrothermally and crystallizes in the monoclinic space group *P*₂₁/*n*. The compound has a somewhat open framework made up of edge-sharing iron(II) octahedra that form chains connected by five bridging diphosphates. The remaining octahedral site of each iron is occupied by coordinated water. The H atoms of the water molecules all point into a common channel.

Comment

We have been interested in making low-density iron phosphates for the last few years (Korzenski *et al.*, 1998, 2000). These compounds exhibit interesting magnetic and structural properties, and can possibly form large microporous frameworks under appropriate conditions. We report herein a new iron(II) diphosphate synthesized hydrothermally. The title compound crystallizes in the monoclinic space group *P*₂₁/*n*. There are two crystallographically unique iron sites. Both have octahedral coordination with one water and five diphosphate O atoms. Two O atoms are bridging, forming edge-sharing iron octahedra. The Fe—O distances for Fe1 and Fe2 range from 2.022 (2) to 2.197 (2) Å [average 2.14 (5) Å], in good agreement with those reported for a series of iron(II) phosphate hydrates (Moore & Araki, 1975; Warner *et al.*, 1992) and iron diphosphates (Le Meins & Courbion, 1999). There are also two unique phosphorus sites. Both are tetrahedrally bound to four O atoms and share a common vertex at O4 to form the diphosphate group. The average P—O distance for the terminal O atoms is 1.518 Å (standard deviation 0.007 Å), those to the bridging O atom are longer [1.608 (1) and 1.614 (1) Å] and the average O—P—O angle is 109° (standard deviation 4°), comparable to other iron phosphates (Warner *et al.*, 1992; Stefanidis & Nord, 1984).

All of the atoms in the unit cell sit on general positions. The asymmetric unit (Fig. 1) shows the connectivity of the atoms and how they bond to symmetry-related units. The compound comprises edge-sharing iron octahedra that are linked by bridging diphosphates. This connectivity forms a cavity that houses the H atoms of the two water molecules (Fig. 2). Like

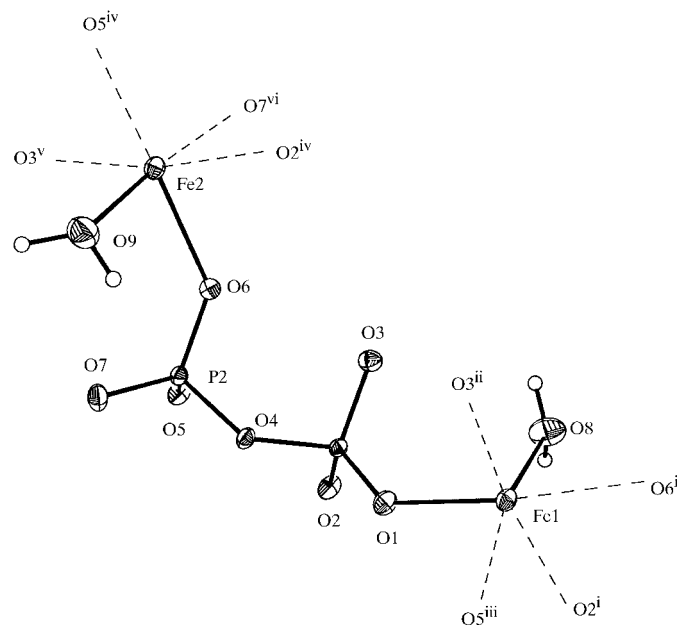


Figure 1
Asymmetric view of the Fe₂P₂O₇(H₂O)₂ unit showing 70% probability displacement ellipsoids.

most hydrated iron(II) phosphates, the water molecules are coordinated to the iron (Mori & Ito, 1950; Eversheim & Kleber, 1953; Moore & Araki, 1976). One of the H atoms on each water is hydrogen bonded to an oxygen of another iron. The remaining H atoms have no obvious interactions. The synthesis of this compound requires titanium oxide (TiO) to be present although it does not become incorporated into the compound, as confirmed by EDAX. Attempts to synthesize

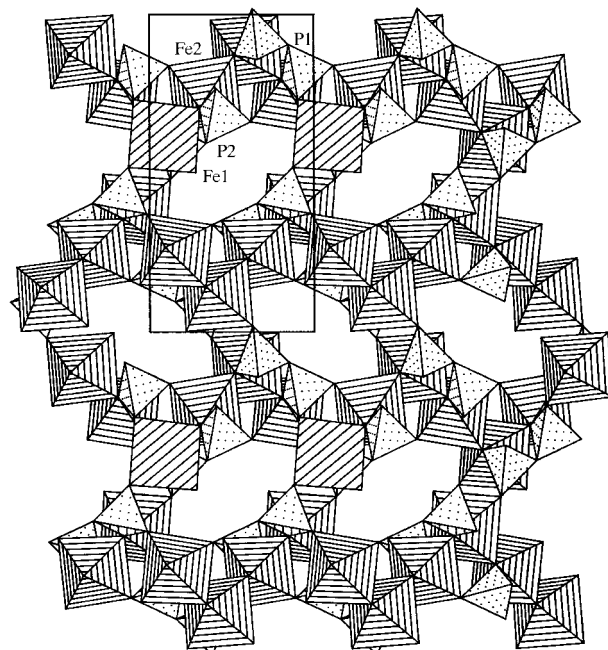


Figure 2
Packing of Fe₂P₂O₇(H₂O)₂ diagram viewed down the *a* axis with positive *z* towards the right and positive *y* downwards.

this compound in the absence of titanium oxide have not been successful.

Experimental

Colorless single crystals of $\text{Fe}_2\text{P}_2\text{O}_7(\text{H}_2\text{O})_2$ were obtained from a reaction mixture of iron metal (42 mg, 752 mmol), TiO (48 mg, 752 mmol) and 25% aqueous H_3PO_4 (0.7 ml) which was placed in a quartz tube. The tube was then put in an autoclave with a counter-pressure of 18.62 MPa of argon gas. The reaction was heated for 3 d at 648 K and cooled in air to room temperature. Upon visual inspection of the quartz tube, the only crystalline material present were colorless truncated diamond-shaped crystals of the title compound and black polyhedral-shaped crystals precipitated from a clear solution. The yield for the colorless crystals was approximately 5–7%. The black polyhedral crystals are currently being characterized.

Crystal data

$\text{Fe}_2\text{P}_2\text{O}_7(\text{H}_2\text{O})_2$	$D_x = 3.188 \text{ Mg m}^{-3}$
$M_r = 321.7$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 50 reflections
$a = 6.400$ (2) Å	$\theta = 25.09$ – 27.53°
$b = 14.181$ (3) Å	$\mu = 4.832 \text{ mm}^{-1}$
$c = 7.416$ (1) Å	$T = 297 \text{ K}$
$\beta = 95.43$ (2)°	Truncated diamond, colorless
$V = 670.1$ (2) Å ³	$0.480 \times 0.240 \times 0.168 \text{ mm}$
$Z = 4$	

Data collection

Nicolet R3m/V diffractometer	$R_{\text{int}} = 0.016$
$\omega/2-\theta$ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 8$
$T_{\text{min}} = 0.185$, $T_{\text{max}} = 0.416$	$k = 0 \rightarrow 18$
1754 measured reflections	$l = -9 \rightarrow 9$
1547 independent reflections	3 standard reflections
1454 reflections with $F > 4\sigma(F)$	every 97 reflections
	intensity decay: 1.0%

Table 1

Selected geometric parameters (Å, °).

Fe1—O1	2.022 (2)	Fe2—O5 ^{iv}	2.181 (2)
Fe1—O8	2.142 (2)	Fe2—O7 ^{vi}	2.081 (2)
Fe1—O2 ⁱ	2.130 (2)	P1—O1	1.505 (2)
Fe1—O3 ⁱⁱⁱ	2.181 (2)	P1—O2	1.517 (1)
Fe1—O5 ⁱⁱⁱ	2.166 (2)	P1—O3	1.524 (1)
Fe1—O6 ⁱⁱ	2.197 (1)	P1—O4	1.614 (1)
Fe2—O6	2.167 (2)	P2—O4	1.608 (1)
Fe2—O9	2.151 (2)	P2—O5	1.532 (2)
Fe2—O2 ^{iv}	2.144 (2)	P2—O6	1.521 (1)
Fe2—O3 ^v	2.118 (2)	P2—O7	1.511 (1)
P1—O4—P2	125.9 (1)		

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

Refinement

Refinement on F	$(\Delta/\sigma)_{\text{max}} = 0.042$
$R = 0.019$	$\Delta\rho_{\text{max}} = 0.548 \text{ e \AA}^{-3}$
$wR = 0.030$	$\Delta\rho_{\text{min}} = -0.582 \text{ e \AA}^{-3}$
$S = 1.180$	Extinction correction: (Larson, 1970)
1454 reflections	Extinction coefficient: 4.861 (3) $\times 10^{-7}$
135 parameters	
H atoms were refined isotropically	
$w = 1/[\sigma^2(F) + 0.0005F^2]$	

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O8—H1 \cdots O7	0.85 (4)	1.95 (4)	2.770 (4)	162 (4)
O9—H4 \cdots O5	0.95 (4)	2.00 (4)	2.898 (4)	157 (4)

The refined hydroxy O—H distances are in the range 0.85 (4)–0.95 (4) Å.

Data collection: *P3 Software* (Siemens, 1989); cell refinement: *P3 Software*; data reduction: *SHELXTL-Plus* (Sheldrick, 1990); program(s) used to solve structure: *SHELXTL-Plus*; program(s) used to refine structure: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

This work was supported by the National Science Foundation grant (CHE-9714408).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1253). Services for accessing these data are described at the back of the journal.

References

- Eversheim, P. & Kleber, W. (1953). *Acta Cryst.* **6**, 215–216.
- Korzenski, M. B., Kolis, J. W. & Long, G. J. (2000). *J. Solid State Chem.* In the press.
- Korzenski, M. B., Schimek, G. L., Kolis, J. W. & Long, G. J. (1998). *J. Solid State Chem.* **139**, 152–160.
- Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
- Le Meins, J.-M. & Courbion, G. (1999). *Acta Cryst.* **C55**, 481–483.
- Moore, P. B. & Araki, T. (1975). *Am. Mineral.* **60**, 454–459.
- Moore, P. B. & Araki, T. (1976). *Inorg. Chem.* **15**, 316–321.
- Mori, H. & Ito, T. (1950). *Acta Cryst.* **3**, 1–6.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1990). *SHELXTL-Plus*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1989) *P3 Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Stefanidis, T. & Nord, A. G. (1984). *Acta Cryst.* **C40**, 1995–1999.
- Warner, J. K., Cheetham, A. K., Cox, D. E. & Von Dreele, R. D. (1992). *J. Am. Chem. Soc.* **114**, 6074–6080.