inorganic papers

Sodium diiron(III) diphosphate hydroxide dihydrate

Shan Gao[a] and Seik Weng Ng[b]*

[a]College of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China, and [b]Department of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia

Correspondence e-mail: seikweng@um.edu.my

The title compound, poly[sodium [aqua-μ_3-hydroxo-di-μ_4-phosphatodiferrate(III)] hydrate], $NaFe_2(OH)(PO_4)_2(H_2O)_2$, is isostructural with the mineral leucophosphite, $Fe_2H_5KO_{11}P_2$.

Comment

The crystal structure of leucophosphite, $Fe_2H_5KO_{11}P_2$, was first reported by Moore (1972); a powder diffraction study by Dick & Zeiske (1997) established the hydrogen-bonding interactions. The formula unit has a coordinated water molecule as well as an uncoordinated water molecule; these interact through hydrogen bonds that further consolidate the three-dimensional structure. The sodium analog crystallizes with matching cell dimensions, and is isostructural with leucophosphite. The two independent Fe atoms show octahedral coordination (Fig. 1 and Table 1), and the phosphate groups interact with the hydroxy groups and water molecules through hydrogen bonds (Table 2). However, the environment around the Na atom is not a regular polyhedron; all Na···O distances exceed 2.8 Å.
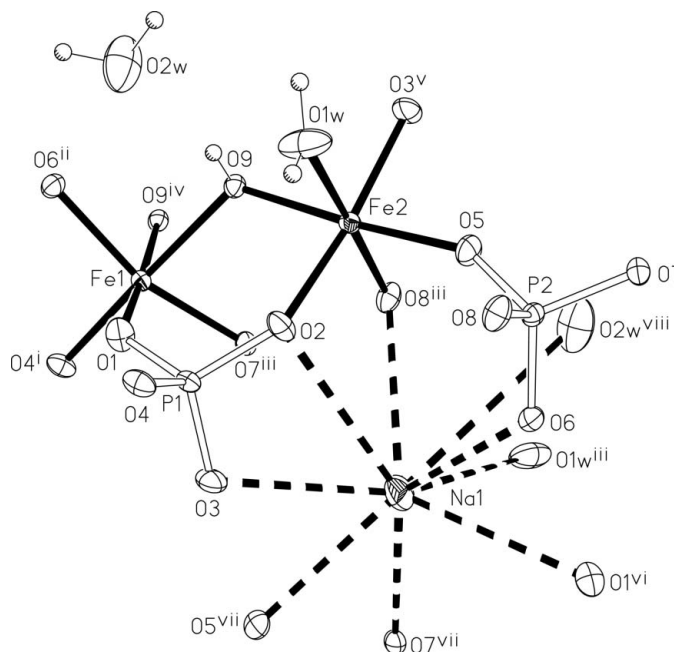
Figure 1
ORTEPII plot (Johnson, 1976) illustrating a portion of the three-dimensional network structure of sodium diiron(II) diphosphate hydroxide dihydrate. Displacement ellipsoids are drawn at the 70% probability level and H atoms are drawn as spheres of arbitrary radius. The Na···O interactions are shown as dashed lines. Symmetry codes are as in Table 1.

The four shortest distances give a bond-valence sum of only 0.21, which is much too small for a regular sodium environment (it should be 1.0). Positional disorder was ruled out as the atomic displacement parameters are normal. Furthermore, attempts to refine the sodium as ammonium, oxonium and potassium gave high R indices. The possibility of the uncoordinated water molecule being an oxonium ion is also excluded as the hydrogen-bonding geometry is satisfactory. If longer distances are considered, the sodium ion then interacts with nine O atoms. However, even with the distances calculated to 3.5 Å, the bond valence sum (0.33) is still too low. Most probably, the sodium cation forced into place in the rigid network motif.

Experimental

Ferric chloride hexahydrate (1.35 g, 5 mmol) and phosphoric acid (0.5 g, 5 mmol) were dissolved in water (30 ml) and to this was added 4,4'-bipyridine (0.8 g, 5 mmol). 0.2 M Sodium hydroxide was added in drops until the solution registered a pH of 7. The mixture was heated in a 50-ml Teflon-lined stainless steel bomb at 450 K for 5 d. The bomb was allowed to cool to room temperature to give light-yellow (almost colorless) prismatic crystals.

Crystal data

NaFe2(OH)(PO4)2(H2O)2	$D_x = 2.767$ Mg m^{-3}
$M_r = 377.67$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 8478
$a = 9.766$ (2) Å	reflections
$b = 9.692$ (2) Å	$\theta = 3.0–27.5°$
$c = 9.811$ (2) Å	$\mu = 3.65$ mm^{-1}
$\beta = 102.53$ (2)°	$T = 295$ (2) K
$V = 906.4$ (3) Å^3	Prism, light yellow
$Z = 4$	$0.31 \times 0.24 \times 0.18$ mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer	2070 independent reflections
ω scans	1955 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{int} = 0.015$
$T_{min} = 0.363$, $T_{max} = 0.518$	$\theta_{max} = 27.5°$
8694 measured reflections	$h = -12 \rightarrow 12$
	$k = -12 \rightarrow 12$
	$l = -10 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 1.9035P]$
$R[F^2 > 2\sigma(F^2)] = 0.022$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.072$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.09$	$\Delta\rho_{max} = 0.85$ e Å^{-3}
2070 reflections	$\Delta\rho_{min} = -0.34$ e Å^{-3}
165 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å).

Fe1—O1	1.935 (2)	P1—O4	1.550 (2)
Fe1—O4^i	1.961 (2)	P2—O5	1.516 (2)
Fe1—O6^{ii}	1.972 (2)	P2—O6	1.541 (2)
Fe1—O7^{iii}	1.960 (2)	P2—O7	1.547 (2)
Fe1—O9	2.155 (2)	P2—O8	1.542 (2)
Fe1—O9^{iv}	2.165 (2)	Na1—O1^{vi}	3.050 (2)
Fe2—O2	1.940 (2)	Na1—O2	3.280 (2)
Fe2—O3^v	1.950 (2)	Na1—O3	2.872 (2)
Fe2—O5	1.946 (2)	Na1—O5^{vii}	2.945 (2)
Fe2—O8^{iii}	1.967 (2)	Na1—O6	2.825 (2)
Fe2—O9	2.154 (2)	Na1—O7^{vii}	2.947 (2)
Fe2—O1w	2.094 (2)	Na1—O8^{iii}	3.045 (2)
P1—O1	1.532 (2)	Na1—O1w^{iii}	3.376 (3)
P1—O2	1.524 (2)	Na1—O2w^{viii}	3.269 (3)
P1—O3	1.525 (2)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O9—H9$\cdots$O2w	0.84	2.16	2.988 (3)	165 (6)
O1w—H1$\cdots$O4^{ix}	0.85	1.91	2.746 (3)	167 (4)
O1w—H2$\cdots$O2w^{ix}	0.85	1.97	2.798 (3)	165 (4)
O2w—H3$\cdots$O4^{ix}	0.85	2.09	2.900 (3)	162 (5)
O2w—H4$\cdots$O8^{ix}	0.84	2.01	2.847 (3)	176 (5)

Symmetry code: (ix) $-x + 1, -y + 1, -z + 1$.

The H atoms were located in a difference Fourier map. The O—H distances were constrained to 0.85 (1) Å; the displacement parameters were freely refined.

Data collection: RAPID-AUTO (Rigaku, 1998); cell refinement: RAPID-AUTO; data reduction: CrystalStructure (Rigaku/MSC, 2002); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

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