Crystal structure of synthetic $(NH_4)H_8Fe_3^{3+}(PO_4)_6 \cdot 6H_2O$

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Abstract

Product K, $(NH_4)H_8Fe_3^{3+}(PO_4)_6 \cdot 6H_2O$, is based on corner-linking octahedra and tetrahedra and is structurally related to coquimbite, paracoquimbite, and the synthetic $Fe_2(SO_4)_3$ dimorphs. It is trigonal, $a_1 = 9.151(2)$, $c = 16.862(4)$A, $Z = 2$, space group $P31c$; usually merohedrally twinned leading to $6/m\ 2/m\ 2/m$ intensity distributions.

$R = 0.042$ for 1200 non-equivalent reflections. The general formula can be written $(NH_4)Fe_3^{3+}[PO_3(OH)_{2/3}O_{1/3})]_3[PO_2(OH)_2]_3(H_2O)_3 \cdot 3H_2O$. Average bond distances are Fe(1)–(O,H_2O) 2.010A, Fe(2)–O 1.983A, Fe(3)–O 2.005A, P(1)–(O,OH) 1.538A, P(2)–(O,OH) 1.545A, NH_4^+–(OH,H_2O) 3.06A; the ammonium cation is in distorted octahedral coordination. Two of the three independent Fe–O octahedra (M) on three-fold rotors and all of the phosphate tetrahedra (T) link at ϕ (linking oxygen) to form a framework structure of stoichiometry $MT_3\phi_6$.

Introduction

We have been much interested in anisodesmic oxysalts of ferric iron and aluminum and extended our study to phases which arise under more acid conditions. Particularly in the phosphates, considerable uncertainty exists in the explicit expression of the structure formula, since the presence of protons suggests the possibility of "acid phosphate" anions. One problem concerns the distribution of these protons and the consequent effect on structure geometry. The compound whose structure we report is called Product K and was studied, along with four other related compounds, by Smith and Brown (1959). One of these compounds is taranakite, $H_6K_3Al_5(PO_4)_8 \cdot 18H_2O$, whose complex structure is unknown but may be related to Product K, which has not as yet been found as a natural phase. We hoped that knowledge of Product K's structure would assist in eventual deciphering of taranakite, which so far has not been found in suitable crystals. Our results provide structural relationships between acid phosphates and other anisodesmic oxysalts, particularly sulfates. In addition, the structure suggests a family of corner-sharing framework structures based on octahedral and tetrahedral corner-sharing linkages, which may represent a new class of zeolitic structures.

Experimental section

Single crystals of Product K were kindly provided by Mr. James R. Lehr of the Tennessee Valley Authority. Smith and Brown (1959) reported $2[H_8(NH_4)Fe_3^{3+}(PO_4)_6 \cdot 6H_2O]$, space group $P6_3/mmc$, $P6_3mc$, or $P\bar{6}2c$, specific gravity (pycnometric) 2.36, computed density 2.36 g cm^{-3}, $a = 9.14$, $c = 16.88$A. In addition they reported synthesis of potassium and aluminum analogues, and found that the structure can tolerate a range of alkali contents and possibly can form without these cations, an observation which added interest to its structure.

The crystal selected for our structure analysis measured 0.10mm ($\|a_1$) × 0.12mm ($\|a_2$) × 0.20mm ($\|c$). Data were collected by ω-scan on a Picker automated diffractometer (graphite monochromator, MoKα radiation, $\lambda = 0.70926$A) to $2\theta = 60.0°$ with scan speed 2° min^{-1} and base scan width of 2°. Background counting times were 20 sec on each side of the peak. Refined cell data from the orientation matrix are $a = 9.151(2)$, $c = 16.862(4)$A, in good agreement with the earlier study. A total of 2545 reflections was collected in the reciprocal space sector ($\bar{h}kl$), including $h = 12$ to 0, $k = 0$ to 12 and $l = 0$ to 23. No absorption correction was applied because of favorable crystal shape and low linear absorption coefficient of $u =$

Table 1. Atomic coordinate parameters for Product K, $(NH_4)H_8Fe_3^{3+}(PO_4)_6 \cdot 6H_2O$[†]

Atom	x	y	z
Fe(1)	0	0	0
Fe(2)	2/3	1/3	0.1983(1)
Fe(3)	2/3	1/3	-0.0806(1)
N	1/3	2/3	0.1635(11)
P(1)	0.8885(2)	0.2730(2)	0.0603(2)
O(1)	0.7912(10)	0.2459(8)	-0.0156(4)
O(2)	0.9598(8)	0.1535(8)	0.0652(5)
OH(3)	1.0433(8)	0.4595(8)	0.0598(5)
O(4)	0.7902(11)	0.2493(8)	0.1373(4)
P(2)	0.5583(3)	0.5267(3)	0.3310(2)
O(5)	0.5296(9)	0.4040(9)	0.2650(4)
OH(6)	0.7122(11)	0.7053(10)	0.3107(6)
O(7)	0.3999(9)	0.5354(10)	0.3482(4)
OH(8)	0.6110(10)	0.4684(10)	0.4089(5)
OW(1)	0.1644(8)	0.1878(8)	-0.0755(5)
OW(2)	0.1845(13)	0.2786(18)	0.2050(6)

[†]Estimated standard errors refer to last digit.

$23.26cm^{-1}$. Symmetry-equivalent reflections were inspected, found satisfactory and averaged for space group $P31c$, yielding 1200 independent reflections. We obtained $|F_o|$ through applying Lorentz and polarization corrections.

We note that $6/m\ 2/m\ 2/m$ point symmetry was found on the crystals studied earlier, but the possibility of $\bar{3}1\ 2/m$ was indicated by the intensity distributions of our crystal-data set. Crystals of this compound were then believed to be frequently merohedrally twinned with [11.0] as twin axis and/or (11.0) as twin plane. The data were refined on the basis of volume concentration of the individuals

starting with 50 percent concentration of one individual (see Araki, 1977, for further details of the program). This twinning was confirmed by applying the same correction for twinning on a data set from a crystal which showed $6/m\ 2/m\ 2/m$ intensity distributions.

An N(z) test on general (hkl) for Z < 0.6 indicated intensity distributions of a twinned non-centric crystal (see Stanley, 1972); therefore our attention focussed on the space groups $P\bar{6}2c$, $P6_3mc$ and $P31c$.

Solution and refinement of the structure

Three-dimensional Patterson maps, $P(uvw)$, were the basis of the structure solution. Both $P\bar{6}2c$ and $P6_3mc$ were ruled out on the basis of vector density distributions on the higher-symmetry Patterson maps. The solution of the structure was obtained for space group $P31c$ on the Patterson map with point symmetry $\bar{3}1\ 2/m$. The Fe–Fe and Fe–P vectors were resolved without difficulty when the locations of three independent Fe atoms in special positions along the 3-fold rotor and two independent P atoms in general positions were deciphered. The structure study of coquimbite (Fang and Robinson, 1970) assisted in unravelling some of the finer details, particularly the polyhedral orientations.

Fourier β- and γ-syntheses (Ramachandran and Srinivasan, 1970) resolved the positions of oxygen atoms and the $(NH_4)^+$ cation center, and afforded more precise locations for the Fe and P atoms. The final cycle of least-squares refinement included 39 atomic coordinate parameters among the 16 non-equivalent atoms, 1 crystal-ratio parameter (owing to twinning), 1 scale factor, and 80 anisotropic thermal

Table 2. Product K: anisotropic thermal vibration parameters ($\times 10^4$)[†]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	31.6(24)	31.6	8.6(5)	15.8	0	0
Fe(2)	32.7(30)	32.7	3.1(6)	16.4	0	0
Fe(3)	32.2(31)	32.2	6.0(6)	16.1	0	0
N	210.3(419)	210.3	40.9(92)	105.1	0	0
P(1)	31.9(28)	40.8(29)	6.6(6)	17.5(23)	0.6(19)	-0.3(19)
O(1)	46.8(112)	63.0(140)	12.6(24)	34.3(113)	14.2(40)	10.1(49)
O(2)	30.4(87)	92.9(105)	9.3(21)	25.7(78)	7.2(48)	18.2(52)
OH(3)	120.5(117)	88.3(114)	20.4(25)	84.4(99)	0.6(68)	1.6(66)
O(4)	29.9(112)	89.1(158)	11.9(23)	27.8(113)	-2.3(41)	-10.7(51)
P(2)	63.0(36)	56.5(37)	12.0(7)	37.4(34)	1.1(13)	-7.3(15)
O(5)	51.0(127)	62.4(132)	14.4(30)	18.8(116)	11.8(46)	-1.1(48)
OH(6)	42.8(148)	53.8(172)	39.7(32)	4.6(81)	7.3(61)	-20.9(64)
O(7)	53.8(131)	54.3(131)	17.7(30)	28.9(116)	9.9(47)	-7.0(46)
OH(8)	188.0(192)	161.4(174)	15.3(23)	142.3(167)	2.6(56)	3.9(57)
OW(1)	64.1(115)	70.8(121)	18.1(25)	27.0(97)	20.0(50)	-2.3(47)
OW(2)	226.9(244)	604.9(508)	36.5(45)	298.2(297)	-44.3(87)	-97.4(122)

[†]Coefficients in the expression $\exp-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell]$. Estimated standard errors refer to the last digit except for those coefficients related by symmetry.

Table 3. Product K: parameters for the ellipsoids of vibration[†]

Atom	i	u_i	θ_{ia}	θ_{ib}	θ_{ic}	$\left(\begin{smallmatrix}B_{equiv.}\\ Å^2\end{smallmatrix}\right)$	Atom	i	u_i	θ_{ia}	θ_{ib}	θ_{ic}	$\left(\begin{smallmatrix}B_{equiv.}\\ Å^2\end{smallmatrix}\right)$
Fe(1)	1	0.100(5)	····not determined····			0.86(4)	O(4)	1	0.092(19)	163(90)	77(90)	89(37)	1.47(15)
	2	0.100	····not determined····					2	0.117(15)	84(31)	114(15)	155(23)	
	3	0.111(4)	90	90	0			3	0.184(15)	74(10)	152(25)	65(13)	
Fe(2)	1	0.067(6)	90	90	0	0.67(5)	P(2)	1	0.097(6)	124(8)	40(11)	52(9)	1.37(4)
	2	0.102(6)	····not determined····					2	0.142(4)	146(19)	86(15)	113(22)	
	3	0.102	····not determined····					3	0.150(4)	88(19)	130(10)	46(20)	
Fe(3)	1	0.093(5)	90	90	0	0.76(5)	O(5)	1	0.100(18)	136(14)	84(17)	51(19)	1.60(15)
	2	0.101(6)	····not determined····					2	0.139(15)	91(17)	141(25)	115(19)	
	3	0.101	····not determined····					3	0.177(13)	46(26)	128(25)	49(27)	
N	1	0.243(27)	90	90	0	5.07(66)	OH(6)	1	0.103(15)	61(55)	59(14)	83(10)	2.53(14)
	2	0.259(34)	····not determined····					2	0.136(12)	36(43)	138(43)	116(16)	
	3	0.259	····not determined····					3	0.259(10)	71(4)	115(5)	27(5)	
P(1)	1	0.096(6)	120(45)	80(16)	31(35)	0.87(3)	O(7)	1	0.091(19)	139(37)	47(33)	56(23)	1.55(15)
	2	0.102(6)	142(34)	85(17)	120(48)			2	0.133(17)	65(90)	55(90)	90(9)	
	3	0.116(4)	70(36)	169(90)	84(26)			3	0.182(13)	60(11)	117(12)	34(17)	
O(1)	1	0.081(19)	139(27)	81(20)	53(10)	1.32(14)	OH(8)	1	0.140(13)	45(90)	146(90)	63(90)	2.89(17)
	2	0.125(17)	124(28)	24(62)	113(29)			2	0.150(12)	67(53)	113(59)	153(49)	
	3	0.167(13)	70(12)	68(15)	46(13)			3	0.261(13)	54(23)	66(14)	87(3)	
O(2)	1	0.075(24)	117(26)	103(12)	44(19)	1.44(11)	OW(1)	1	0.089(19)	138(12)	73(12)	48(12)	1.89(13)
	2	0.105(16)	148(46)	65(22)	122(37)			2	0.149(13)	93(11)	146(19)	100(10)	
	3	0.196(11)	106(6)	29(15)	64(8)			3	0.205(12)	48(13)	119(13)	44(13)	
OH(3)	1	0.107(12)	42(90)	161(90)	87(28)	2.16(11)	OW(2)	1	0.160(17)	107(31)	63(17)	27(19)	7.34(41)
	2	0.171(10)	86(18)	91(16)	176(19)			2	0.186(16)	163(90)	68(11)	106(36)	
	3	0.203(10)	48(90)	72(34)	87(16)			3	0.468(18)	89(2)	144(4)	68(2)	

[†] $i = i$th principal axis, u_i = rms amplitude, θ_{ia}, θ_{ib}, θ_{ic} = angles (deg.) between the ith principal axis and the cell axes a_1, a_2 and c. The equivalent isotropic thermal parameter, B, is also listed. Estimated standard errors in parentheses refer to the last digit.

vibration parameters leading to the following data: variable parameter ratio of 11:1, R = 0.042 and R_w = 0.039, where

$$R = \frac{\Sigma \left| |F_o| - |F_c| \right|}{\Sigma |F_o|}$$

and

$$R_w = \left[\frac{\Sigma_w(|F_o| - |F_c|)^2}{\Sigma_w F_o^2} \right]^{1/2}$$

for all 1200 non-equivalent reflections. We attempted to resolve hydrogen atom positions, but they could not be decisively located on difference synthesis, probably because of the presence of relatively strong scatterers.

The crystal-ratio parameter converged to 0.554(3), which suggests that crystal and twin occurred in nearly equal proportions (differing in volume by about 10 percent) but in different enough quantity that $\bar{3}1\ 2/m$ point symmetry could be recognized in our data set. No other atoms (including the hydrogen atoms) could be located, so we proposed the empirical formula $H_{24}Fe_3P_6\,O_{30}N$.

We employed scattering curves for N^0, Fe^{3+}, P^{5+} and O^{1-} (Cromer and Mann, 1968) and applied anomalous dispersion corrections for Fe and P (Cromer and Liberman, 1970).

Table 1 lists the refined atomic coordinate parameters, Table 2 the anisotropic thermal vibration parameters, Table 3 the ellipsoids of vibration, Table 4 the bond distances and angles, and Table 5 the electrostatic valence balances. Table 6 lists the observed and calculated structure factors.[1]

Description of the structure

A Parker projection of the polyhedral arrangement is shown in Figure 1, oriented so that the structure can be compared with coquimbite and paracoquimbite (Robinson and Fang, 1971). The general formula for the compound can be written $(NH_4)^+$ $Fe_3^{3+}[PO_3(OH_{2/3}O_{1/3})]_3[PO_2(OH)_2]_3(H_2O)_3 \cdot 3H_2O$, which agrees empirically with $(NH_4)^+H_8Fe_3^{3+}$ $(PO_4)_6 \cdot 6H_2O$ suggested by Smith and Brown (1959). We shall discuss later the likelihood on electrostatic grounds that OH(3) $=(OH)_{2/3}O_{1/3}$ may be statistically distributed. The space group $P31c$ means that the crystal is polar. Merohedral twinning, which seems typical for most crystals of the compound, leads to space group $P6_3mc$.

The underlying feature is a cluster built of two octahedra which share corners with nine tetrahedra in a local configuration, much like that found in monoclinic $Fe_2(SO_4)_3$ (Moore and Araki, 1974) and rhombohedral $Fe_2(SO_4)_3$ (Christidis and Rentzeperis, 1976). In coquimbite and paracoquimbite the next
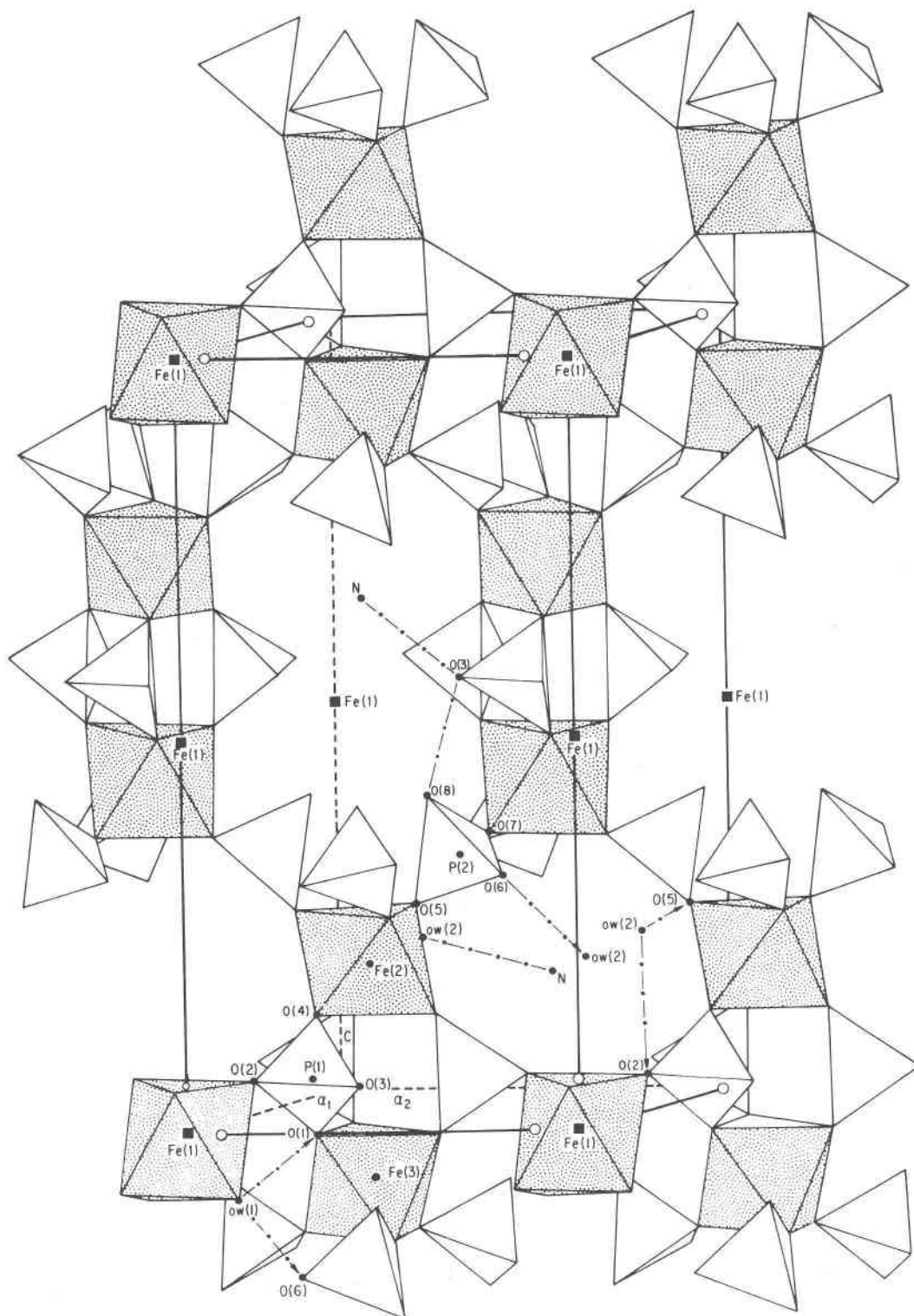
Fig. 1. A polyhedral representation (Parker projection) showing the framework character of Product K. Note that Fe(2)–, Fe(3)–, P(1)– and P(2)–oxygen polyhedra link at corners to form a $MT_3\phi_6$ framework. Atoms are labelled to correspond to Table 1. Potential hydrogen bonds are drawn in dot-dash lines, the arrows pointing to the acceptor. The NH_4^+–OH(3) and –OW(2) bonds are also drawn in. Phosphate oxygens are labelled as oxides and O(3), O(6) and O(8) are OH^- in the ammonium-free salt.

Table 4. Product K: bond distances and angles[†]

Fe(1)			P(1)			$(NH_4)^+$		
3 Fe(1)-O(2)	1.958(7)		P(1)-O(1)	1.507(7)		3 N-OH(3)	2.94(1)	
3 Fe(1)-OW(1)	2.063(7)		P(1)-O(2)	1.530(6)		3 N-OW(2)	3.18(1)	
average	2.010		P(1)-O(4)	1.532(8)		average	3.06	
		O-Fe-O' (°)	P(1)-OH(3)	1.582(6)		3 OW(2)-OH(3)	3.54(1)	70.6(2)
			average	1.538		3 OW(2)-OW(2)[(1)]	3.89(2)	115.3(3)
3 O(2)-O(2)[(1)]	2.806(10)	91.5(3)			O-P-O (°)	3 OW(2)-OH(3)[(1)]	3.91(2)	79.3(2)
3 OW(1)-OW(1)[(1)]	2.810(11)	85.9(3)	O(2)-O(4)	2.452(10)	106.4(4)	3 OH(3)-OH(3)[(1)]	4.10(1)	88.3(5)
3 O(2)-OW(1)	2.810(9)	88.6(3)	O(1)-O(2)	2.501(9)	110.9(4)	average	3.86	88.4
3 O(2)-OW(1)[(1)]	2.941(10)	94.0(3)	O(1)-OH(3)	2.501(10)	108.1(5)			
average	2.842	90.0	O(2)-OH(3)	2.509(8)	107.4(3)	3 OW(2)-OH(3)[(2)]		155.6(6)
			OH(3)-O(4)	2.513(11)	107.6(5)			
Fe(2)			O(1)-O(4)	2.579(7)	116.1(3)			
			average	2.509	109.4	Hydrogen Bonds		
3 Fe(2)-O(4)	1.948(7)							
3 Fe(2)-O(5)	2.018(7)		P(2)			OH(6) → OW(2)[(1)]	2.53(2)	
average	1.983					OH(3) ↔ OH(8)[(3)]	2.67(1)	
			P(2)-O(5)	1.507(7)				
3 O(4)-O(5)	2.658(10)	84.2(3)	P(2)-O(7)	1.518(7)		OW(1) → O(1)[(2)]	2.757(9)	
3 O(4)-O(5)[(2)]	2.786(10)	89.3(3)	P(2)-OH(6)	1.572(6)		OW(1) → OH(6)[(5)]	2.85(1)	
3 O(4)-O(4)[(1)]	2.866(12)	94.7(3)	P(2)-OH(8)	1.581(8)		[OW(1) → OH(6)[(4)]	3.18(1)]	
3 O(5)-O(5)[(1)]	2.900(12)	91.9(3)	average	1.545				
average	2.803	90.0				OW(2) → O(5)	2.95(1)	
			O(5)-O(7)	2.499(7)	111.4(4)	OW(2) → O(2)	2.96(1)	
Fe(3)			OH(6)-OH(8)	2.509(13)	105.4(6)			
			O(7)-OH(8)	2.518(10)	108.6(4)			
3 Fe(3)-O(7)[(3)]	1.997(7)		O(5)-OH(8)	2.520(10)	109.3(4)	Bond Angles		
3 Fe(3)-O(1)	2.013(6)		O(5)-OH(6)	2.526(10)	110.2(5)	O(1)[(1)]-OW(1)-OH(6)[(3)]		70.2(3)
average	2.005		OH(6)-O(7)	2.557(10)	111.7(6)	O(1)[(2)]-OW(1)-OH(6)[(5)]		149.1(4)
			average	2.522	109.4			
3 O(1)-O(7)[(3)]	2.754(10)	86.8(3)						
3 O(7)[(3)]-O(7)[(4)]	2.764(13)	87.6(3)				O(2)[(2)]-OW(2)-O(5)		97.4(3)
3 O(1)-O(7)[(4)]	2.896(10)	92.5(3)				OH(6)[(2)]-OW(2)-O(2)		102.5(4)
3 O(1)-O(1)[(1)]	2.924(12)	93.2(3)				OH(6)[(2)]-OW(2)-O(5)		111.7(5)
average	2.834	90.0				OH(6)[(2)]-OW(2)-O(2)[(2)]		141.8(6)

[†]Estimated standard errors in parentheses refer to the last digit. The equivalent positions (referred to Table 1) are designated as superscripts and are (1) = -y, x-y, z; (2) = y-x, -x, z; (3) = y, x, ½+z; (4) -x, y-x, ½+z; (5) = x-y, -y, ½+z.

corner-sharing condensation of three octahedra and six tetrahedra occurs, resulting in $[Fe_3^{3+}(SO_4)_6$ $(H_2O)_6] \cdot Fe^{3+}(H_2O)_6 \cdot 6H_2O$ (Robinson and Fang, 1971). In this structure the terminal bases of the octahedra in brackets are completed by water molecules. The infinite chain of corner-sharing octahedra and tetrahedra is found in ferrinatrite, Na_3 $(H_2O)_3[Fe(SO_4)_3]$ (Scordari, 1977); the chain is written $FeS_3\phi_6$, where ϕ are identified as linking oxygens between the (FeO_6) octahedra and (SO_4) tetrahedra. An infinite number of framework structures can be conceived with the stoichiometry $MT_3\phi_6$ where M are octahedra and T are tetrahedra. This family includes the limiting chain in ferrinatrite and an infinite number of arrangements based on trigonal symmetry of

which the title compound is a member, including clusters of two octahedra and a girdle of tetrahedra in between, three octahedra and a girdle of two tetrahedra, *etc.* The only requirement is that the terminal octahedra along one 3-fold axis be bridged by tetrahedra to similar clusters along the other 3-fold axis at positions $(1/3 \; 2/3 \; z)$ and $(2/3 \; 1/3 \; z')$. With this motif in mind we have derived a possible structure for taranakite, but that model must be tested with a three-dimensional crystal-structure analysis.

Hydrogen bonding and electrostatic valence balances

Two independent water molecules and three independent hydroxyl groups associated with the phosphate anions provide seven independent hydrogen

Table 5. Product K: electrostatic valence balance of cations and anions[†]

	Coordinating Cations									Bond Length Deviations					
	P(1)	P(2)	Fe(1)	Fe(2)	Fe(3)	NH$_4^+$	H$_d$	H$_a$	ΔP$_O$	P(1)	P(2)	Fe(1)	Fe(2)	Fe(3)	NH$_4^+$
Anions															
O(1)	1	-	-	-	1	-	-	1	-0.08	-0.031	------	------	------	+0.008	-----
O(2)	1	-	1	-	-	-	-	1	-0.08	-0.008	------	-0.052	------	------	-----
OH(3)	1	-	-	-	-	1	1	1	+0.42	+0.044	------	------	------	------	-0.12
O(4)	1	-	-	1	-	-	-	-	-0.25	-0.006	------	------	-0.070	------	-----
O(5)	-	1	-	1	-	-	-	1	-0.08	------	-0.038	------	+0.035	------	-----
OH(6)	-	1	-	-	-	-	1	1	+0.25	------	+0.027	------	------	------	-----
O(7)	-	1	-	-	1	-	-	-	-0.25	------	-0.027	------	------	-0.008	-----
OH(8)	-	1	-	-	-	-	1	1	+0.25	------	+0.036	------	------	------	-----
OW(1)	-	-	1	-	-	-	2	-	+0.17	------	------	+0.053	------	------	-----
OW(2)	-	-	-	-	-	1	2	1	+0.00	------	------	------	------	------	+0.12

[†]A bond length deviation refers to the polyhedral average subtracted from the individual bond distance. H$_d$ = hydrogen bond donor, H$_a$ = hydrogen bond acceptor, ΔP$_O$ = deviation of electrostatic bond strength sum from neutrality (p$_O$ = 2.00 e.s.u.).

bonds. Since the hydrogen atoms were not located, hydrogen bonds cannot be definitely assigned. The most likely bonds are shown as broken lines in Figure 1 with the head of the arrow pointing toward the acceptor. Hydrogen-bond distances range between 2.53 and 2.96A (Table 4), and distances up to 3.3A were examined. OW(2) donates bonds to O(2) and O(5) and receives one bond from OH(6). OW(1) donates to O(1) and OH(6). OH(3) and OH(8) reciprocally donate and receive one bond each. The hydrogen-bond acceptors thus include O(1), O(2), OH(3), O(5), OH(6), OH(8) and OW(2) (Table 5). The list of bond distances and angles in Table 4 shows that OW(2) is surrounded by O(2), O(5) and OH(6) with three angles (97° to 112°) close to the tetrahedral average. One bond in Table 4 is tentatively included, however, since its existence cannot be excluded in the absence of directly-determined hydrogen-atom positions.

Bond-length and bond-strength relations are presented in Table 5. The hydroxyl groups associated with phosphate tetrahedra are easily identified as OH(3), OH(6) and OH(8), as their P–OH distances are greater than +0.03A for the polyhedral averages. OH(3) is the most cation-oversaturated according to this model, and its P(1)–OH(3) distance is 1.58A. But the (NH$_4$)–OH(3) distance is 0.12A shorter than the polyhedral average, which suggests that OH(3) is usually OH$_{2/3}$O$_{1/3}$. This would explain the apparently extensive range of (NH$_4$)$^+$ and alkali contents of synthetic material which may range to a vacant site (Smith and Brown, 1959), that is $\square$Fe$_3^{3+}$ [PO$_3$OH]$_3$[PO$_2$(OH)$_2$]$_3$(H$_2$O)$_3$·3H$_2$O. In addition, OH(3) may lose the proton, thus locally destroying the reciprocal OH(3) $\leftrightarrow$ OH(8)[(3)] hydrogen bond.

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