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Hydrothermal Synthesis and Crystal Structures of $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$ and $Ba_2V_3H(PO_4)_2(P_2O_7)_2$*

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Two new Fe^{III} and V^{III} phosphates, $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$ and $Ba_2V_3H(PO_4)_2(P_2O_7)_2$, have been prepared and their structures have been determined from single-crystal X-ray diffraction data. They crystallize in the triclinic space group $P\bar{1}$ with $a = 4.858(2)$, $b = 7.908(2)$, $c = 11.300(3)$ Å, $\alpha = 89.10(2)$, $\beta = 89.28(2)$, $\gamma = 87.25(2)°$, $V = 433.5(3)$ Å^3, $Z = 1$ and $R = 0.0195$ for $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$, and $a = 4.8433(8)$, $b = 7.902(1)$, $c = 11.308(2)$ Å, $\alpha = 88.77(1)$, $\beta = 89.22(1)$, $\gamma = 87.11(1)°$, $V = 432.09(12)$ Å^3, $Z = 1$ and $R = 0.020$ for $Ba_2V_3H(PO_4)_2(P_2O_7)_2$. The two compounds are isostructural. The framework is built up from corner-sharing $M^{III}O_6$ octahedra, PO_4 tetrahedra and P_2O_7 units. The structure contains tunnels along the [100] direction in which the Ba^{2+} ions are located.

Introduction

A large number of new compounds in the system A–M^{III}–P–O (A = monovalent or divalent cation; M = Fe or V) have been synthesized and structurally characterized, indicating the great ability of PO_4 tetrahedra to form various frameworks with $M^{III}O_6$ octahedra. Among these compounds only a few contain both orthophosphate and diphosphate groups. In 1985, de la Rochere *et al.* (*1*) reported crystal structures of $Na_7(MP_2O_7)_4PO_4$ (M = Al, Fe, or Cr) whose structures can be described as a three-dimensional framework of PO_4 tetrahedra, P_2O_7 units and $M^{III}O_6$ octahedra linked by vertexes. A few years later, the vanadium phosphate $Ca_2V(PO_4)(P_2O_7)$ was reported (*2*). The structure contains intersecting tunnels, and the calcium atoms are located at the intersection of these tunnels. The framework consists of corner-sharing VO_6 octahedra, PO_4 tetrahedra, and P_2O_7 groups. Attempts to add new members to the A–M^{III}–P–O series of compounds by the hydrothermal methods have yielded two new orthodiphosphates of Fe^{III} and V^{III}. These two compounds are isostructural. In this paper we present the syntheses and single-crystal X-ray structures of $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$ and $Ba_2V_3H(PO_4)_2(P_2O_7)_2$.

Experimental

Synthesis

Light-pink plate-shaped crystals of $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$ were prepared by hydrothermal reaction of 0.1500 g of $Ba(OH)_2 \cdot 8$

* Supplementary materials available: tables of anisotropic thermal parameters, bond angles, and observed and calculated structure factors.

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H_2O and 0.1776 g of $FePO_4 \cdot 2\ H_2O$ (molar ratio Ba : Fe = 1 : 2) in 1 ml of 3.75 *M* $H_3PO_{4(aq)}$ in a sealed silica tube. The degree of fill in the glass tube was 43%, including the volume of undissolved solid. The glass ampule was inserted into a cold-seal pressure vessel and the free volume remaining in the bore hole was calibrated with water from a buret. The water was subsequently removed from the bore hole. To balance the pressure inside the glass ampule, water was used. The amount of water that was added to the bore hole was 5% more than the degree of fill in the ampule in order to prevent an explosion. The closed end of the pressure vessel was inserted into a tube furnace, while the joint remained on the outside. The reaction mixture was heated at 450°C for 2 days followed by slow cooling. Visual microscopic inspection showed that the product contained only white powder. Subsequently, the same reaction tube was heated at 550°C for 1 day followed by slow cooling at 2.5°C/h to 450°C. Light-pink crystals of $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$ were obtained. The color suggested that the compound is a ferric phosphate.

Based on powder X-ray diffraction, single phase polycrystalline $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$ was preapred hydrothermally by heating the starting materials in molar ratio Ba : Fe = 2 : 3 at 450°C for 108 hr. The composition deduced from the structural determination of $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$ was checked by energy dispersive X-ray fluorescence analysis which gave a Ba : Fe : P molar ratio equal to 2.09 : 3.02 : 6.15.

The crystal growth of $Ba_2V_3H(PO_4)_2(P_2O_7)_2$ was achieved under the following conditions. A mixture of 0.600 g of $BaHPO_4$, 0.2891 g of V_2O_3, and 2.0 ml of 7.5 *M* $H_3PO_{4(aq)}$ (molar ratio Ba : *V* = 2 : 3) was heated in a sealed silica tube at 450°C for 2 days followed by slow cooling to room temperature. The reaction yielded light green rod-shaped crystals of $Ba_2V_3H(PO_4)_2(P_2O_7)_2$.

Single-Crystal X-ray Diffraction Study

A light-pink crystal of $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$ having dimensions of 0.25 × 0.10 × 0.04 mm and a green crystal of $Ba_2V_3H(PO_4)_2(P_2O_7)_2$ having dimensions of 0.15 × 0.10 × 0.10 mm were selected for indexing and intensity data collection at room temperature on a Nicolet R3m/V four-circle diffractometer and an Enraf-Nonius CAD-4 diffractometer with κ-axis geometry using monochromated Mo$K\alpha$ radiation. Axial oscillation photographs along the three axes were taken to check the symmetry properties and unit cell parameters. Based on the statistical analysis of the intensity data, and successful solution and refinement of the structures, the space groups for both compounds were determined to be $P\bar{1}$. Direct methods (SHELXTL Plus (*3*) for the iron phosphate and NRCVAX (*4*) for the vanadium phosphate) were used to locate metal atoms with the remaining nonhydrogen atoms being found from successive difference maps. Before the H atom was included in the least squares refinement, bond-strength calculations were carried out to help locate the hydrogen atom. One of the oxygen atoms was found to be considerably undersaturated. The values for all the other oxygen atoms were very close to 2.0. It was found that a maximum residual electron density on the difference map was located at the special position ($\frac{1}{2}$, $\frac{1}{2}$, 0). In order to balance the charge, the peak was assigned as a H atom. The presence of a OH group was supported by infrared spectroscopy (vide infra). Subsequent refinement including the atomic coordinates and anisotropic thermal parameters for all nonhydrogen atoms converged at $R = 0.0195$ and $R_w = 0.0223$ for $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$ and $R = 0.020$ and $R_w = 0.026$ for $Ba_2V_3H(PO_4)_2(P_2O_7)_2$. In the final difference Fourier map the deepest hole was -0.57 e/Å^3 (-0.99 e/Å^3) and the highest peak 0.60 e/Å^3 (0.71 e/Å^3) for the iron and vanadium compounds, respectively.

In order to support the presence of H in

TABLE I

CRYSTAL DATA, INTENSITY MEASUREMENTS, AND REFINEMENT PARAMETERS FOR $Ba_2V_3H(PO_4)_2(P_2O_7)_2$ AND $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$

	$Ba_2V_3H(PO_4)_2(P_2O_7)_2$	$Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$
	1. Crystal data	
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Cell constants	a = 4.8433(8) Å	a = 4.858(2) Å
	b = 7.902(1) Å	b = 7.908(2) Å
	c = 11.308(2) Å	c = 11.300(3) Å
	α = 88.77(1)°	α = 89.10(2)°
	β = 89.22(1)°	β = 89.28(2)°
	γ = 87.11(1)°	γ = 87.25(2)°
	V = 432.09(12) Å^3	V = 433.5(3) Å^3
Z	1	1
Density	3.714 g/cm^3	3.758 g/cm^3
Abs. coeff. (Mo$K\alpha$)	6.67 mm^{-1}	7.60 mm^{-1}
Transm coeff.	0.861–0.993	0.647–0.984
	2. Intensity measurements	
λ(Mo$K\alpha$)	0.70930 Å	0.71073 Å
Scan mode	$\theta/2\theta$	$\theta/2\theta$
Maximum 2θ	54.8°	50.0°
Reflection collected	2216	1852
	3. Structure solution and refinement	
Unique reflection	1981 (1887 > $3\sigma(I)$)	1543 (1434 > $3\sigma(I)$)
No. of parameters refined	152	152
Agreement factors[a]	R = 0.020	R = 0.0195
	R^w = 0.026	R_w = 0.0223
GOF	0.92	0.96
$(\Delta\rho)_{max}$; $(\Delta\rho)_{min}$	0.71; −0.99 eÅ^{-3}	0.60; −0.57 eÅ^{-3}

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

the title compounds, infrared spectra were recorded on a Perkin-Elmer 883 spectrometer using dry KBr pellets containing a small amount of the samples. Both samples showed a medium, broad absorption band at ~3400 cm^{-1} which could be attributed to the PO–H stretching. A deuteration study was also performed. $Ba_2V_3D(PO_4)_2(P_2O_7)_2$ was prepared hydrothermally by heating a mixture of $BaHPO_4$, V_2O_3, and 7.5 M D_3PO_4 in D_2O. The X-ray powder pattern of the product compared well with that calculated from the single-crystal data. On deuterium-substitution there is a large decrease in intensity of the IR band near ~3400 cm^{-1}. However, no absorption band at ~2400 cm^{-1} (= 3400 = $1/\sqrt{2}$) could be clearly defined against the background of the spectrum.

Results and Discussion

The crystallographic data for both compounds are listed in Table I. The atomic coordinates, thermal parameters, selected bond distances, and bond valence sums (*5*) are listed in Tables II and III. Atoms Fe(1), V(1), and H lie on inversion centers and all other atoms are at general positions. Bond valence sums are in good accordance with their formal oxidation states. The coordination number of Ba^{2+} was determined on the basis of the maximum gap in the Ba–O distances ranked in increasing order (*6*). In

TABLE II

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR $Ba_2V_3H(PO_4)_2(P_2O_7)_2$ AND $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$

Atom	x	y	z	B_{iso} (Å^2) [a]
$Ba_2V_3H(PO_4)_2(P_2O_7)_2$				
Ba	0.27170(5)	-0.00554(3)	0.82236(2)	0.741(10)
V(1)	0	0	0.5	0.53(3)
V(2)	0.28267(13)	-0.49487(8)	0.79690(6)	0.453(22)
P(1)	0.81889(20)	0.29426(12)	0.94863(9)	0.47(3)
P(2)	-0.23360(20)	0.69706(13)	0.65728(9)	0.53(3)
P(3)	0.47264(20)	0.24363(12)	0.57447(9)	0.51(3)
O(1)	1.0818(6)	0.3190(4)	0.8750(3)	0.76(10)
O(2)	0.5922(6)	0.4331(4)	0.9115(3)	0.82(10)
O(3)	0.7304(6)	0.1148(4)	0.9297(3)	0.95(10)
O(4)	0.8624(6)	0.3197(4)	1.08107(25)	0.76(10)
O(5)	-0.1349(6)	0.8783(4)	0.6524(3)	0.79(10)
O(6)	-0.0131(6)	0.5647(4)	0.6909(3)	0.91(10)
O(7)	0.3234(6)	0.3552(4)	0.4720(3)	0.80(10)
O(8)	0.5088(6)	-0.3059(4)	0.7373(3)	0.80(9)
O(9)	0.3036(6)	0.0853(4)	0.5924(3)	0.76(9)
O(10)	0.7662(6)	0.2028(4)	0.5352(3)	0.87(10)
O(11)	0.4583(6)	0.3420(4)	0.6867(3)	0.93(10)
H[b]	0.5	0.5	0	3.9

both structures the Ba^{2+} cations are coordinated by eight oxygen atoms and the ninth Ba–O distances are at ~3.30 Å. In the following paragraphs only $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$ will be discussed because the two compounds are isostructural.

A perspective view of the structure along the [100] direction shows that the three-dimensional framework consists of isolated FeO_6 octahedra which share their corners with single PO_4 tetrahedra and P_2O_7 units (Fig. 1). There are three different kinds of tunnels: large double tunnels, which are occupied by Ba^{2+} cations, formed by the edges of six FeO_6 octahedra and six PO_4 tetrahedra; empty medium hexagonal tunnels formed by the edges of two octahedra and four tetrahedra; small tetragonal tunnels, occupied by H atoms, formed by the edges of two octahedra and two tetrahedra. One can observe two kinds of FeO_6 octahedra. The neighborhood of $Fe(1)O_6$ octahedra consists of four P_2O_7 units. Two of the P_2O_7 groups are bonded to Fe(1) through bidenate bonding and the other two are monodentate. Each $Fe(2)O_6$ octahedron is linked to three single PO_4 tetrahedra and three different P_2O_7 units. The Fe–O distances and O–Fe–O bond angles show that both octahedra are somewhat distorted. The distortion of an octahedron can be estimated by using the equation $\Delta = (\frac{1}{6})\Sigma((R_i - \bar{R})/\bar{R}))^2$ where R_i = an individual bond length and $\bar{R}$ = average bond length (7). The calcula-

TABLE II–*Continued*

Atom	x	y	z	B_{iso} (Å^2) [a]
$Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$				
Ba	0.26813(5)	-0.00442(2)	0.82401(2)	0.968(10)
Fe(1)	0	0	0.5	0.582(22)
Fe(2)	0.27684(10)	-0.49356(6)	0.79481(5)	0.560(16)
P(1)	0.81638(19)	0.29594(11)	0.94828(8)	0.600(27)
P(2)	-0.23708(19)	0.69837(11)	0.65676(8)	0.568(27)
P(3)	0.47493(19)	0.24287(11)	0.57576(8)	0.547(26)
O(1)	1.08069(54)	0.31959(31)	0.87621(23)	0.980(77)
O(2)	0.59237(54)	0.43370(32)	0.91079(23)	0.919(76)
O(3)	0.72876(54)	0.11554(32)	0.92993(24)	1.088(80)
O(4)	0.85746(56)	0.32246(31)	1.08196(23)	0.951(77)
O(5)	-0.13149(53)	0.87894(30)	0.65064(22)	0.846(75)
O(6)	-0.02033(55)	0.56560(32)	0.69008(24)	1.122(78)
O(7)	0.32675(54)	0.35377(30)	0.47302(23)	0.813(74)
O(8)	0.50769(54)	-0.30134(31)	0.73642(23)	0.875(75)
O(9)	0.30806(53)	0.08481(31)	0.59232(23)	0.781(73)
O(10)	0.76986(55)	0.20280(31)	0.53951(24)	1.013(77)
O(11)	0.45490(54)	0.34465(33)	0.68757(23)	1.060(78)
H [b]	0.5	0.5	0	0.5

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.
[b] The thermal parameters for the H atom are fixed.

tion results show that the distortion in $Fe(2)O_6$ ($\Delta = 10^4 = 8.3$) is considerably more pronounced than that in $Fe(1)O_6$ ($\Delta \times 10^4 = 3.4$). Each PO_4 tetrahedron shares three of its corners with three different $Fe(2)O_6$ octahedra. The fourth corner, O(2), is bonded to a hydrogen atom. Each P_2O_7 unit is bonded by two of its corners to the same $Fe(1)O_6$ octahedron and by four others to one $Fe(1)O_6$ and three different $Fe(2)O_6$ octahedra. The two PO_4 tetrahedra of a P_2O_7 unit are in a nearly eclipsed configuration. The P–O distances in two independent PO_4 tetrahedra can be divided into two groups: one long distance at 1.601 Å corresponding to the P–O bonds involving the bridging oxygen, and three shorter distances at 1.498–1.541 Å and 1.506–1.530 Å. The P–O–P bond angle is 130.2°. The single tetrahedron $P(1)O_4$ is quite regular. The H atom, which is located on a special position, is bonded on two O(2) of two different PO_4 tetrahedra at 1.215 Å. This gives two symmetrical O–H bonds. The O(2) . . . O(2) distance is only 2.429 Å, which can be compared with that in $KH_5(PO_4)_2$ (2.42 Å) and the tetragonal KH_2PO_4 (2.49 Å) (*8*). Infrared spectroscopy studies suggest the presence of H in the title compounds. An IR spectrum of $K_2(VO)_3(HPO_4)_4$ was also measured for comparison. It shows a strong broad band centered at ~3080 cm^{-1} as comapred with the band at ~3400 cm^{-1} for $Ba_2V_3H(PO_4)_2(P_2O_7)_2$. It is unclear to us why the PO–H stretching frequency for $K_2(VO)_3(HPO_4)_4$ is lower than that for $Ba_2V_3H(PO_4)_2(P_2O_7)_2$ since the O-H bond length in the former compound is ~0.3 Å shorter.

TABLE III

BOND LENGTHS (Å), AND BOND VALENCE SUMS (Σs) FOR $Ba_2V_3H(PO_4)_2(P_2O_7)_2$ AND $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$

$Ba_2V_3H(PO_4)_2(P_2O_7)_2$			
Ba-O(1)a	2.755(3)	Ba-O(4)b	2.793(3)
Ba-O(3)b	2.916(3)	Ba-O(5)c	2.962(3)
Ba-O(3)	2.766(3)	Ba-O(8)	2.770(3)
Ba-O(3)a	2.994(3)	Ba-O(9)	2.688(3)
Σs (Ba-O) = 1.91			
V(1)-O(5)c	2.069(3)	V(1)-O(9)	1.970(3)
V(1)-O(5)d	2.069(3)	V(1)-O(9)f	1.970(3)
V(1)-O(10)a	1.959(3)	V(1)-O(10)e	1.959(3)
Σs (V(1)-O) = 3.03			
V(2)-O(1)g	1.989(3)	V(2)-O(6)c	1.915(3)
V(2)-O(2)c	2.046(3)	V(2)-O(8)	1.996(3)
V(2)-O(4)b	2.067(3)	V(2)-O(11)c	1.967(3)
Σs (V(2)-O) = 3.05			
P(1)-O(1)	1.530(3)	P(1)-O(3)	1.522(3)
P(1)-O(2)	1.567(3)	P(1)-O(4)	1.534(3)
Σs (P(1)-O) = 4.95			
P(2)-O(5)	1.532(3)	P(2)-O(7)d	1.599(3)
P(2)-O(6)	1.503(3)	P(2)-O(8)h	1.532(3)
Σs (P(2)-O) = 4.93			
P(3)-O(7)	1.599(3)	P(3)-O(10)	1.506(3)
P(3)-O(9)	1.537(3)	P(3)-O(11)	1.501(3)
Σs (P(3)-O) = 5.01			
H-O(2)i	1.211		
$Ba_2Fe_3H(PO_4)_2(P_2O_7)$			
Ba-O(1)a	2.748(3)	Ba-O(4)b	2.806(3)
Ba-O(3)	2.765(3)	Ba-O(5)c	2.963(3)
Ba-O(3)a	2.986(3)	Ba-O(8)	2.762(3)
Ba-O(3)b	2.903(3)	Ba-O(9)	2.708(3)
Σs (Ba-O) = 1.96			
Fe(1)-O(5)c	2.050(3)	Fe(1)-O(9)	1.984(3)
Fe(1)-O(5)d	2.050(3)	Fe(1)-O(9)f	1.984(3)
Fe(1)-O(10)a	1.964(3)	Fe(1)-O(10)e	1.964 (3)
Σs (Fe(1)-O) = 3.15			
Fe(2)-O(1)g	2.002(3)	Fe(2)-O(6)c	1.914(3)
Fe(2)-O(2)c	2.083(3)	Fe(2)-O(8)	2.029(3)
Fe(2)-O(4)b	2.037(3)	Fe(2)-O(11)c	1.942(3)
Σs (Fe(2)-O) = 3.16			
P(1)-O(1)	1.529(3)	P(1)-O(3)	1.526(3)
P(1)-O(2)	1.560(3)	P(1)-O(4)	1.545(3)
Σs (P(1)-O) = 4.93			
P(2)-O(5)	1.541(3)	P(2)-O(7)d	1.601(3)
P(2)-O(6)	1.498(3)	P(2)-O(8)h	1.523(3)
Σs (P(2)-O) = 4.94			
P(3)-O(7)	1.601(3)	P(3)-O(10)	1.506(3)
P(3)-O(9)	1.530(3)	P(3)-O(11)	1.508(3)
Σs (P(3)-O) = 4.99			
H-O(2)i	1.215		

Note. Symmetry codes: (a) $-1 + x, y, z$; (b) $1 - x, -y, 2 - z$; (c) $x, -1 + y, z$; (d) $-x, 1 - y, 1 - z$; (e) $1 - x, -y, 1 - z$; (f) $-x, -y, 1 - z$; (g) $-1 + x, -1 + y, z$; (h) $-1 + x, 1 + y, z$; (i) $x, y, -1 + z$.

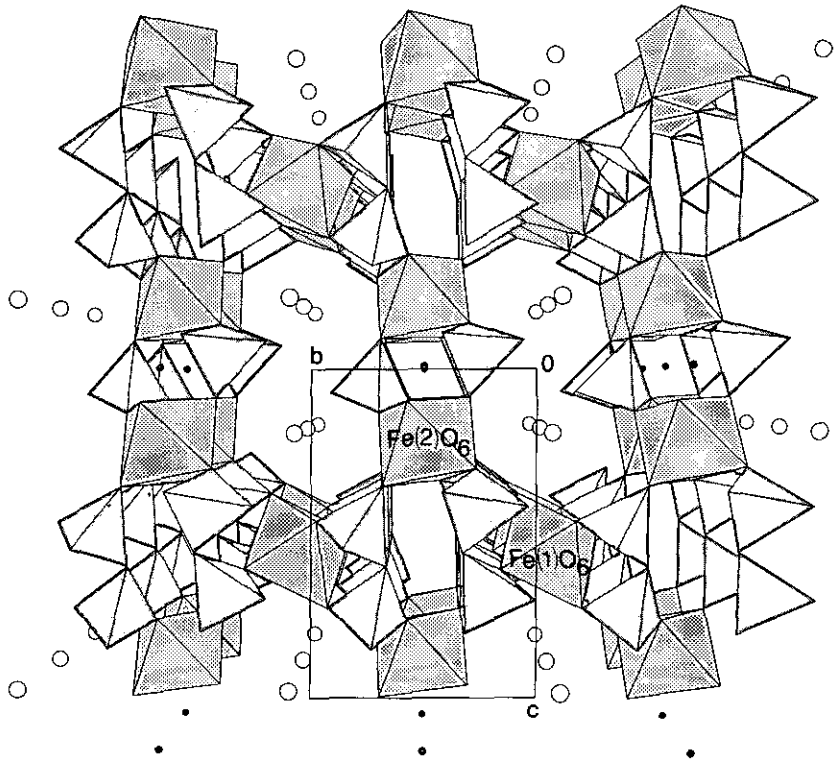

Fig. 1. Perspective view of the structure along the [100] direction in $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$.

The coordination of the barium atom by eight oxygen atoms is shown in Fig. 2. The Ba–O coordination polyhedron is rather distorted and does not clearly show any geometrical relationship with the common structures such as cube, square antiprism, and dodecahedron.

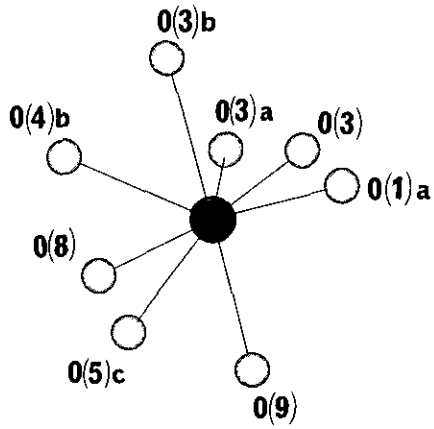

FIG. 2. Projection along [100] showing the environment of the Ba^{2+} ions in $Ba_2Fe_3H(PO_4)_2(P_2O_7)_2$.

Besides the title compounds, a few pairs of isostructural V^{III} and Fe^{III} phosphates have also been synthesized. For examples, $Sr_2V(PO_4)(P_2O_7)$ (*9*), $Sr_2V(PO_4)_2(H_2PO_4)$ (*10*), and AVP_2O_7 (A = alkali metals) are isostructural with their Fe^{III} analogues (*11*). The very similar ionic radii for V^{III} and high-spin Fe^{III} should account for this close structural correspondence.

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