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Crystal Structures of a Cesium Iron(III) Phosphate, $Cs_3Fe_4(PO_4)_5$, and a Cesium Iron(III) Oxyphosphate, $Cs_7Fe_7(PO_4)_8O_2$

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The reaction of $FePO_4$ with molten CsCl produces $Cs_3Fe_4(PO_4)_5$, $Cs_7Fe_7(PO_4)_8O_2$, or Fe_2O_3, depending on the length of the reaction. The crystal structure of $Cs_3Fe_4(PO_4)_5$ consists of an interlocking network of corner-sharing phosphate tetrahedra and iron trigonal bipyramids with cesium atoms situated in tunnels. The $Cs_7Fe_7(PO_4)_8O_2$ structure can be described as a three-dimensional array containing linked phosphate tetrahedra and iron octahedra, trigonal bipyramids, and square pyramids. In addition to the phosphate oxygen atoms, three of the iron polyhedra share a common oxide ion. The cesium atoms are located in tunnels. $Cs_3Fe_4(PO_4)_5$ crystallizes in the orthorhombic space group *Pccn* with $a = 9.838(1)$, $b = 13.913(2)$, $c = 14.076(4)$ Å, and $Z = 4$. $Cs_7Fe_7(PO_4)_8O_2$ is monoclinic, space group $P2_1/c$, with $a = 8.339(4)$, $b = 22.540(4)$, $c = 10.067(2)$ Å, $\beta = 108.63(2)°$, and $Z = 2$.

Introduction

The sizes of the cesium ions and of other large alkali metal and alkaline earth cations preclude close packing in oxyanion salts containing these ions. The cesium ion, for example, has a radius of 1.70 to 1.88 Å, depending on its coordination number (*1*), and this ion crystallizes in more open structures than smaller ions. The interionic O–O distances in Cs_2SO_4 (*2*), for example, are about 10% longer than those in the isostructural K_2SO_4 (*3*). Compounds with cesium ions cocrystallized with network-forming species often exhibit tunnel structures or stuffed networks. Tunnels are found in a wide variety of compounds including $CsMo_3P_{5.8}Si_2O_{25}$ (*4*), $BaCs_4(PO_3)_5$ (*5*), $CsP_8W_8O_{40}$ (*6*), and $CsLiSO_3 \cdot 2H_2O$ (*7*). Substitution of cesium ion for one of the lithium ions in Li_2WO_4 changes the structure from that of a close-packed oxygen array with tetrahedral lithium and tungsten atoms (Li_2WO_4, Ref. (*8*)) to a stuffed structure with 12-coordinate cesium ions in an H-crystobalite-type $LiWO_4^-$ network ($CsLiWO_4$, Ref. (*9*)).

Network structures are sometimes strained in order to accommodate cesium ions. The mineral kalsilite, $KAlSiO_4$ (*10*), and nepheline, $Na_3K(AlSiO_4)_4$ (*11*), are stuffed tridymite derivatives with tetrahedral $(Al,Si)O_4$ frameworks containing interstices filled with potassium and/or sodium ions. The $(Al,Si)O_4$ framework must distort to accommodate the larger cesium ion in $CsAlSiO_4$ (*12*). In the alkali metal nickel phosphate series, M^INiPO_4, the octahedral or tetragonally distorted nickel coordination polyhedra present with the smaller lithium, sodium, and potassium ions are distorted to very irregular tetrahedra in the stuffed net-

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work present in the cesium (and rubidium) compounds (*13*).

The size of the cesium ion also has a pronounced effect on the substitution of M^I and Ti^{4+} for Ba^{2+} and Al^{3+} in barium hollandites (*14*). Potassium and rubidium substitution is possible for the complete series ranging from the end member $Ba_{1.24}(Al_{2.40}Ti_{5.52})O_{16}$ to $K_{1.5}(Al_{1.5}Ti_{6.5})O_{16}$ or $Rb_{1.5}(Al_{1.5}Ti_{6.5})O_{16}$. With cesium, however, substitution is limited to about 0.25 cesium ion per unit cell, a limit imposed by the larger cesium ion's blocking of adjacent sites in the tunnels occupied by Ba^{2+} or M^I.

The cesium iron phosphate $Cs_3Fe_4(PO_4)_5$ and the oxyphosphate $Cs_7Fe_7(PO_4)_8O_2$ reported in his work are tunnel-type structures with networks of iron and phosphate polyhedra forming tunnels which are occupied by cesium ions. $Cs_3Fe_4(PO_4)_5$ forms from the reaction of $FePO_4$ with molten cesium chloride, $Cs_7Fe_7(PO_4)_8O_2$, from the reaction of $FePO_4$ with Cs_2CO_3 and molten CsCl.

Experimental

Synthesis (*15*). $Cs_3Fe_4(PO_4)_5$ was prepared by the reaction of 1 g $FePO_4$ and 4 g CsCl in a covered crucible at 720°C for 1 hr. The mixture was cooled over 5 hr by switching off the furnace and yellow rectangular crystals were obtained after removing excess CsCl with water. An electron microprobe analysis showed a cesium to iron ratio of three to four.

$Cs_7Fe_7(PO_4)_8O_2$ was prepared by the reaction of 0.33 g Cs_2CO_3, 5.1 g CsCl, and 0.60 g $FePO_4$ in a covered crucible at 700°C for 24 hr. The mixture was cooled at 50° hr^{-1} to 500°C and then the furnace was turned off. The products were yellow rectangular needles of $Cs_3Fe_4(PO_4)_5$ and reddish rod-like crystals of $Cs_7Fe_7(PO_4)_8O_2$, which were shown to have a one to one ratio of cesium to iron atoms by electron microprobe analysis.

Longer reaction times or higher temperatures (900°C) produced shiny black crystals that were identified as Fe_2O_3 by their powder patterns. This compound results from formation of the oxide ion and loss of $POCl_3$ as a consequence of the reaction of the chloride ion with the phosphate ion.

Structure determination. Data were collected with an Enraf-Nonius CAD4 X-ray diffractometer using Zr-filtered Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). Twenty-four diffraction maxima were carefully centered and used to determine the cell dimensions reported in Table I. The crystal sizes and other data are also reported in this table.

Reflections were collected using the ω-scan mode with no allowance for systematic absences. Subsequent examination of the data for absences indicated the unique space groups reported in Table I. Examination of several dozen reflections in a hemisphere of reciprocal space confirmed that the diffraction symmetry was appropriate for the space groups selected. The successful refinement of the structure indicates this is an appropriate choice.

Both structures were solved by a combination of standard Patterson and Fourier techniques and refined by full matrix least-squares techniques using the Enraf-Nonius SDP package (*16*). Data collection and correction parameters and refinement parameters are reported in Table I. All atoms of $Cs_3Fe_4(PO_4)_5$ and the nonoxygen atoms of $Cs_7Fe_7(PO_4)_8O_2$ were refined anisotropically. Atom coordinates and (equivalent) isotropic thermal parameters are reported in Tables II and III. Anisotropic thermal parameters and observed and calculated structure factors are available in Ref. (*17*) or upon request to an author (W.R.R.).

Results

The structure of $Cs_3Fe_4(PO_4)_5$. The structure, shown in Fig. 1, consists of an interlocking network of corner-sharing

TABLE I

CRYSTALLOGRAPHIC DATA FOR $Cs_3Fe_4(PO_4)_5$ AND $Cs_7Fe_7(PO_4)_8O_2$

	$Cs_3Fe_4(PO_4)_5$	$Cs_7Fe_7(PO_4)_8O_2$
Mol wt	1096.96	2113.03
Crystal dimens. (mm)	0.20 × 0.20 × 0.10	0.15 × 0.15 × 0.25
Cryst. syst.	Orthorhombic	Monoclinic
Space group	*Pccn* (No. 56)	$P2_1/c$ (No. 14)
Cell dimens. *a* (Å)	9.838(1)	8.339(4)
b (Å)	13.913(2)	22.540(4)
c (Å)	14.076(4)	10.067(2)
β (°)		108.63(2)
Cell volume (Å^3)	1924	1793
Z	4	2
d_{cal}, (g cm^{-3})	3.79	3.91
θ range, (deg)	8–25	8–25
Max scan time	60 sec	100 sec
Scan angle	1 + 0.14 tan θ	1.1 + 0.14 tan θ
Temperature (°C)	21	21
Monitor reflens.	3, every 2 hr	3, every 2 hr
h, *k*, *l* limits	0–11, 0–16, 0–16	−9–9, 0–26, 0–11
Total data	1951	3210
Unique data, $F_0^2 > 3\sigma F_0^2$	1347	1922
No. variables	186	231
Empirical abs. corr. Max. corr. (%)	65.0	51.5
Min. corr. (%)	99.5	99.8
Ave. corr. (%)	85.6	75.3
Residuals, *R*	0.056	0.073
R_{wt}	0.085	0.092
wt	$1/\sigma(F_0^2)^a$	$1/\sigma(F_0^2)^a$
Goodness of fit	2.26	2.19

[a] $1/\sigma(F_0)^2 = 4F_0^2/\sigma(F_0^2)$; $\sigma(F_0)^2 = [\sigma(F_0^2) + (0.05)F_0^2]^{1/2}$.

phosphate tetrahedra and iron trigonal bipyramids with cesium atoms located in sites within tunnels in the structure. Selected bond distances and angles are reported in Tables IV and V.

Two crystallographically distinct iron atoms, both located on general positions, are contained in this structure. The trigonal bipyramid around Fe(1) has an average Fe–O distance of 1.959 Å and only slightly distorted bond angles. The Fe–O distances in the Fe(2) trigonal bipyramid average 1.943 Å. The bond angles are more distorted than corresponding angles in the Fe(1) grouping.

Also present in this structure are three unique phosphorus atoms. P(1) and P(2) are located on general positions. P(3) lies on a twofold axis. Each phosphorus atom is within a distorted tetrahedron.

The cesium atoms in this structure are located in tunnels. Cs(1) is located on a general position in a pocket in the side of a tunnel and Cs(2) is located on a twofold axis in the tunnel. Figure 2 shows the highly anisotropic coordination of Cs(1).

The structure of $Cs_7Fe_7(PO_4)_8O_2$. The structure contains four phosphate tetrahedra and four iron polyhedra, three of which are linked by an oxide ion bridge, with four cesium atoms situated in tunnels (Fig. 3).

There are four crystallographically distinct iron atoms in this structure. The four

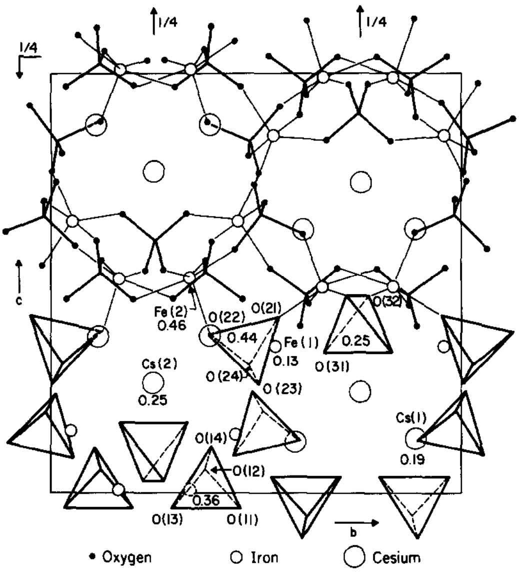

FIG. 1. The unit cell of $Cs_3Fe_4(PO_4)_5$. The bottom half of the cell shows the location of Cs and Fe atoms and the phosphate tetrahedra. The top half shows the network of P–O and Fe–O bonds. The x coordinates of selected Cs and Fe atoms are indicated. Numbers within the tetrahedra indicate the x coordinates of the P atoms.

TABLE II

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DERIVATIONS FOR $Cs_3Fe_4(PO_4)_5$

Atom	x	y	z	B(eq)
Cs(1)	0.1883(1)	0.88792(8)	0.12680(7)	1.49(2)
Cs(2)	$\frac{1}{4}$	$\frac{1}{4}$	0.2630(1)	2.11(3)
Fe(1)	0.1257(2)	0.5439(1)	0.3497(2)	0.36(4)
Fe(2)	0.4625(2)	0.3376(2)	0.5088(2)	0.46(4)
P(1)	0.3597(4)	0.3781(3)	0.0235(3)	1.42(7)
P(2)	0.4422(4)	0.4843(3)	0.3416(3)	1.44(7)
P(3)	$\frac{1}{4}$	$\frac{3}{4}$	0.4006(4)	1.41(9)
O(11)	0.369(1)	0.4670(8)	−0.0379(8)	7.1(3)
O(12)	0.216(1)	0.3697(8)	0.0590(8)	6.7(2)
O(13)	0.397(1)	0.2917(8)	−0.0354(8)	6.9(2)
O(14)	0.453(1)	0.3934(8)	0.1067(7)	6.4(2)
O(21)	0.456(1)	0.5586(8)	0.4206(8)	6.4(2)
O(22)	0.482(1)	0.3851(7)	0.3823(8)	6.5(2)
O(23)	0.5384(9)	0.5090(8)	0.2606(7)	6.2(2)
O(24)	0.300(1)	0.4785(8)	0.3051(8)	6.5(2)
O(31)	0.213(1)	0.6668(8)	0.3354(8)	6.6(2)
O(32)	0.132(1)	0.7715(7)	0.4679(8)	6.6(2)

Note. The equivalent isotropic thermal parameter is defined as: $(\frac{4}{3}) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) + ab(\cos\gamma) * B(1,2) + ac(\cos\beta) * B(1,3) + bc(\cos\alpha) * B(2,3)]$.

TABLE III

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $Cs_7Fe_7(PO_4)_8O_2$

Atom	x	y	z	B(eq)
Cs(1)	0.8679(2)	0.14503(8)	0.7288(2)	1.74(3)
Cs(2)	0.3775(2)	0.43644(8)	0.3886(2)	1.81(3)
Cs(3)	0	$\frac{1}{2}$	0	1.59(5)
Cs(4)	0.5774(2)	0.25740(9)	0.4071(3)	3.45(5)
Fe(1)	$\frac{1}{2}$	$\frac{1}{2}$	0	0.73(9)
Fe(2)	0.1004(4)	0.5772(2)	0.3793(3)	0.87(7)
Fe(3)	0.9845(4)	0.6681(2)	0.0866(3)	0.76(6)
Fe(4)	0.2793(4)	0.1238(2)	0.2786(4)	1.00(7)
P(1)	0.3393(7)	0.3647(3)	0.0657(6)	0.9(1)
P(2)	0.3409(7)	0.5938(3)	0.1873(6)	0.9(1)
P(3)	0.0070(7)	0.2096(3)	0.1162(6)	0.9(1)
P(4)	0.8022(7)	0.4957(3)	0.3214(6)	0.9(1)
O	0.947(2)	0.6078(7)	0.212(1)	0.7(3)*
O(11)	0.381(2)	0.4203(8)	−0.017(2)	1.4(3)*
O(12)	0.170(2)	0.3753(7)	0.092(2)	1.0(3)*
O(13)	0.292(2)	0.3199(8)	−0.057(2)	1.2(3)*
O(14)	0.483(2)	0.3490(8)	0.191(2)	1.1(3)*
O(21)	0.372(2)	0.5364(8)	0.121(2)	1.0(3)*
O(22)	0.496(2)	0.6352(7)	0.228(1)	0.8(3)*
O(23)	0.193(2)	0.6280(8)	0.086(2)	1.1(3)*
O(24)	0.298(2)	0.5751(8)	0.323(2)	1.3(3)*
O(31)	0.196(2)	0.1928(8)	0.152(2)	1.3(3)*
O(32)	−0.101(2)	0.1586(8)	0.035(2)	1.2(3)*
O(33)	−0.029(2)	0.2647(8)	0.025(2)	1.0(3)*
O(34)	−0.039(2)	0.2245(8)	0.249(2)	1.2(3)*
O(41)	0.692(2)	0.4765(8)	0.174(2)	1.3(3)*
O(42)	0.991(2)	0.4974(8)	0.328(2)	1.0(3)*
O(43)	0.777(2)	0.4506(7)	0.426(2)	0.9(3)*
O(44)	0.754(2)	0.5589(8)	0.357(2)	1.6(3)*

Note. Atoms with asterisks were refined isotropically. The equivalent isotropic thermal parameter is defined as: $(\frac{4}{3}) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) + ab(\cos\gamma) * B(1,2) + ac(\cos\beta) * B(1,3) + bc(\cos\alpha) * B(2,3)]$.

iron polyhedra, including the oxide ion bridge, are shown in Fig. 4. Fe(1) is located on a center of symmetry and Fe(2), Fe(3), and Fe(4) are located in general positions. The iron atoms are both five and six coordinated. The polyhedron about Fe(1) is a regular octahedron, about Fe(2) is intermediate between a trigonal bipyramid and a square pyramid, and about Fe(3) and Fe(4) is a square pyramidal with a longer sixth ligand making a distorted octahedron.

TABLE IV

BOND DISTANCES (Å) FOR $Cs_3Fe_4(PO_4)_5$ WITH E.S.D.'S IN PARENTHESES

Atom A	Atom B	Distance
Fe(1)	O(11)$^{\mathrm{vii}}$	1.909(8)
Fe(1)	O(14)$^{\mathrm{vi}}$(ax)^{a}	2.009(8)
Fe(1)	O(23)$^{\mathrm{vi}}$	1.919(7)
Fe(1)	O(24)(ax)	2.037(7)
Fe(1)	O(31)	1.921(7)
Fe(2)	O(12)$^{\mathrm{vii}}$	1.944(7)
Fe(2)	O(13)$^{\mathrm{x}}$(ax)	2.007(8)
Fe(2)	O(21)$^{\mathrm{i}}$(ax)	1.925(7)
Fe(2)	O(22)	1.907(8)
Fe(2)	O(32)$^{\mathrm{v}}$	1.935(7)
P(1)	O(11)	1.511(8)
P(1)	O(12)	1.503(8)
P(1)	O(13)	1.505(8)
P(1)	O(14)	1.500(7)
P(2)	O(21)	1.523(7)
P(2)	O(22)	1.544(8)
P(2)	O(23)	1.521(7)
P(2)	O(24)	1.495(7)
P(3)	O(31)	1.520(7)
P(3)	O(32)	1.524(7)
Cs(1)	O(11)$^{\mathrm{iv}}$	3.554(8)
Cs(1)	O(12)$^{\mathrm{iii}}$	3.625(7)
Cs(1)	O(13)$^{\mathrm{iv}}$	3.414(8)
Cs(1)	O(4)$^{\mathrm{iii}}$	3.414(8)
Cs(1)	O(22)$^{\mathrm{ix}}$	3.248(7)
Cs(1)	O(23)$^{\mathrm{iii}}$	3.251(7)
Cs(1)	O(23)$^{\mathrm{ix}}$	3.546(7)
Cs(1)	O(24)$^{\mathrm{iii}}$	3.120(8)
Cs(1)	O(31)$^{\mathrm{iii}}$	3.186(7)
Cs(1)	O(32)$^{\mathrm{iii}}$	3.123(8)
Cs(1)	O(32)$^{\mathrm{viii}}$	3.276(7)
Cs(1)	O(32)$^{\mathrm{xi}}$	3.195(7)
Cs(2)	O(12)	3.335(8)
Cs(2)	O(13)$^{\mathrm{vii}}$	3.236(8)
Cs(2)	O(14)	3.576(7)
Cs(2)	O(22)	3.397(7)
Cs(2)	O(24)	3.267(7)

Note. Symmetry transformations: $^{\mathrm{i}}(1 - x, 1 - y, 1 - x)$, $^{\mathrm{ii}}(\frac{1}{2} - x, \frac{1}{2} - y, z)$, $^{\mathrm{iii}}(\frac{1}{2} - x, \frac{3}{2} - y, z)$, $^{\mathrm{iv}}(x - \frac{1}{2}, y + \frac{1}{2}, -z)$, $^{\mathrm{v}}(\frac{1}{2} + x, y - \frac{1}{2}, z + \frac{3}{2})$, $^{\mathrm{vi}}(x - \frac{1}{2}, 1 - y, \frac{1}{2} - z)$, $^{\mathrm{vii}}(\frac{1}{2} - x, y, \frac{1}{2} + z)$, $^{\mathrm{viii}}(\frac{1}{2} - x, y, z - \frac{1}{2})$, $^{\mathrm{ix}}(1 - x, + y, \frac{1}{2} - z)$, $^{\mathrm{x}}(x, \frac{1}{2} - y, \frac{1}{2} - z)$, $^{\mathrm{xi}}(x, \frac{3}{2} - y, z - \frac{1}{2})$.

[a] Axial oxygen atom in a FeO_5 trigonal bipyramid.

TABLE V

BOND ANGLES (°) FOR $Cs_3Fe_4(PO_4)_5$

Atom A	Atom B	Atom C	Angle ABC
O(11)$^{\mathrm{vii}}$	Fe(1)	O(14)$^{\mathrm{vi}}$	90.7(3)
O(11)$^{\mathrm{vii}}$	Fe(1)	O(23)$^{\mathrm{vi}}$	117.9(3)
O(11)$^{\mathrm{vii}}$	Fe(1)	O(24)	89.0(3)
O(11)$^{\mathrm{vii}}$	Fe(1)	O(31)	124.9(3)
O(14)$^{\mathrm{vi}}$	Fe(1)	O(23)$^{\mathrm{vi}}$	91.7(3)
O(14)$^{\mathrm{vi}}$	Fe(1)	O(24)	179.2(3)
O(14)$^{\mathrm{vi}}$	Fe(1)	O(31)	91.0(3)
O(23)$^{\mathrm{vi}}$	Fe(1)	O(24)	87.5(3)
O(23)$^{\mathrm{vi}}$	Fe(1)	O(31)	117.1(3)
O(24)	Fe(1)	O(31)	89.4(3)
O(12)$^{\mathrm{vii}}$	Fe(2)	O(13)$^{\mathrm{x}}$	91.6(3)
O(12)$^{\mathrm{vii}}$	Fe(2)	O(21)$^{\mathrm{i}}$	90.9(3)
O(12)$^{\mathrm{vii}}$	Fe(2)	O(22)	110.5(3)
O(12)$^{\mathrm{vii}}$	Fe(2)	O(32)$^{\mathrm{v}}$	145.8(3)
O(13)$^{\mathrm{x}}$	Fe(2)	O(21)$^{\mathrm{i}}$	164.5(3)
O(13)$^{\mathrm{x}}$	Fe(2)	O(22)	93.0(3)
O(13)$^{\mathrm{x}}$	Fe(2)	O(32)$^{\mathrm{v}}$	84.5(3)
O(21)$^{\mathrm{i}}$	Fe(2)	O(22)	100.4(3)
O(21)$^{\mathrm{i}}$	Fe(2)	O(32)	84.8(3)
O(22)	Fe(2)	O(32)$^{\mathrm{v}}$	103.7(3)
O(11)	P(1)	O(12)	108.1(4)
O(11)	P(1)	O(13)	108.8(4)
O(11)	P(1)	O(14)	107.1(4)
O(12)	P(1)	O(13)	110.5(4)
O(12)	P(1)	O(14)	109.0(4)
O(13)	P(1)	O(14)	113.2(4)
O(21)	P(2)	O(22)	108.1(4)
O(21)	P(2)	O(23)	109.8(4)
O(21)	P(2)	O(24)	111.9(4)
O(22)	P(2)	O(23)	108.8(4)
O(22)	P(2)	O(24)	108.4(4)
O(23)	P(2)	O(24)	109.7(4)
O(31)	P(3)	O(31)$^{\mathrm{iii}}$	105.8(6)
O(31)	P(3)	O(32)	109.9(4)
O(31)	P(3)	O(32)$^{\mathrm{iii}}$	114.1(4)
O(32)	P(3)	O(32)$^{\mathrm{iii}}$	104.2(6)

Note. Symmetry transformations: $^{\mathrm{i}}(1 - x, 1 - y, 1 - z)$, $^{\mathrm{ii}}(\frac{1}{2} - x, \frac{1}{2} - y, z)$, $^{\mathrm{iii}}(\frac{1}{2} - x, \frac{3}{2} - y, z)$, $^{\mathrm{iv}}(x - \frac{1}{2}, \frac{1}{2} + y, -z)$, $^{\mathrm{v}}(\frac{1}{2} + x, y - \frac{1}{2}, 1 - z)$, $^{\mathrm{vi}}(x - \frac{1}{2}, 1 - y, \frac{1}{2} - z)$, $^{\mathrm{vii}}(\frac{1}{2} - x, y, \frac{1}{2} + z)$, $^{\mathrm{viii}}(\frac{1}{2} - x, y, z - \frac{1}{2})$, $^{\mathrm{ix}}(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, $^{\mathrm{x}}(x, \frac{1}{2} - y, \frac{1}{2} + y)$, $^{\mathrm{xi}}(x, \frac{3}{2} - y, z - \frac{1}{2})$.

Fe(1) is coordinated to three unique oxygen atoms, which are related in pairs by the center of symmetry. The average Fe(1)–O distance is 2.031 Å. The five-coordinate Fe(2) has a geometry that is intermediate

TABLE VI

BOND DISTANCES (Å) FOR $Cs_7Fe_7(PO_4)_8O_2$ WITH e.s.d.'S IN PARENTHESES

Atom A	Atom B	Distance
Fe(1)	O(11)	2.032(12)
Fe(1)	O(21)	2.028(10)
Fe(1)	O(41)	2.033(12)
Fe(2)	O$^{\mathrm{iii}}$	1.894(11)
Fe(2)	O(24)	1.907(11)
Fe(2)	O(32)$^{\mathrm{ix}}$	2.025(12)
Fe(2)	O(42)$^{\mathrm{iii}}$	2.009(12)
Fe(2)	O(43)$^{\mathrm{vi}}$	1.997(11)
Fe(3)	O	1.946(11)
Fe(3)	O(12)$^{\mathrm{v}}$	2.090(12)
Fe(3)	O(13)$^{\mathrm{v}}$	2.241(11)
Fe(3)	O(23)$^{\mathrm{i}}$	1.959(11)
Fe(3)	O(33)$^{\mathrm{v}}$	1.988(12)
Fe(3)	O(34)$^{\mathrm{x}}$	2.019(12)
Fe(4)	O$^{\mathrm{xi}}$	1.951(10)
Fe(4)	O(11)$^{\mathrm{vii}}$	2.198(12)
Fe(4)	O(13)$^{\mathrm{vii}}$	2.058(12)
Fe(4)	O(22)$^{\mathrm{xi}}$	1.917(10)
Fe(4)	O(31)	1.991(12)
Fe(4)	O(44)$^{\mathrm{xi}}$	1.961(13)
Cs(1)	O(12)$^{\mathrm{viii}}$	3.263(10)
Cs(1)	O(14)$^{\mathrm{vii}}$	3.113(11)
Cs(1)	O(23)$^{\mathrm{xi}}$	3.074(11)
Cs(1)	O(32)$^{\mathrm{ii}}$	3.029(11)
Cs(1)	O(33)$^{\mathrm{viii}}$	3.197(11)
Cs(1)	O(34)$^{\mathrm{viii}}$	3.030(12)
Cs(1)	O(41)$^{\mathrm{vii}}$	3.070(12)
Cs(1)	O(42)$^{\mathrm{vii}}$	3.419(12)
Cs(1)	O(43)$^{\mathrm{vii}}$	3.186(11)
Cs(2)	O(12)	3.242(11)
Cs(2)	O(14)	3.121(11)
Cs(2)	O(21)	3.502(11)
Cs(2)	O(24)	3.219(12)
Cs(2)	O(24)$^{\mathrm{vi}}$	3.289(12)
Cs(2)	O(42)$^{\mathrm{iii}}$	3.376(10)
Cs(2)	O(43)	3.244(10)
Cs(2)	O(43)$^{\mathrm{vi}}$	3.623(11)
Cs(2)	O(44)$^{\mathrm{vi}}$	3.089(11)
Cs(3)	O$^{\mathrm{iii}}$	3.355(11)
Cs(3)	O$^{\mathrm{v}}$	3.355(11)
Cs(3)	O(11)	3.704(11)
Cs(3)	O(12)	3.151(11)
Cs(3)	O(21)	3.063(11)
Cs(3)	O(23)	3.281(12)
Cs(3)	O(24)	3.799(12)
Cs(3)	O(41)$^{\mathrm{iii}}$	3.571(11)
Cs(3)	O(42)$^{\mathrm{iii}}$	3.324(10)
Cs(4)	O(13)$^{\mathrm{vii}}$	3.065(11)
Cs(4)	O(14)	2.922(12)
Cs(4)	O(22)$^{\mathrm{xi}}$	3.047(11)
Cs(4)	O(23)$^{\mathrm{xi}}$	3.480(11)
Cs(4)	O(31)	3.691(12)
Cs(4)	O(32)$^{\mathrm{viii}}$	3.197(11)
Cs(4)	O(33)$^{\mathrm{viii}}$	3.154(11)
Cs(4)	O(34)$^{\mathrm{viii}}$	3.900(12)
P(1)	O(11)	1.585(12)
P(1)	O(12)	1.535(11)
P(1)	O(13)	1.562(12)
P(1)	O(14)	1.481(12)
P(2)	O(21)	1.518(12)
P(2)	O(22)	1.537(11)
P(2)	O(23)	1.532(12)
P(2)	O(24)	1.574(12)
P(3)	O(31)	1.545(12)
P(3)	O(32)	1.527(12)
P(3)	O(33)	1.517(12)
P(3)	O(34)	1.545(12)
P(4)	O(41)	1.536(12)
P(4)	O(42)	1.554(11)
P(4)	O(43)	1.531(12)
P(4)	O(44)	1.554(13)

Note. Symmetry transformations: $^{\mathrm{i}}(x + 1, y, z)$, $^{\mathrm{ii}}(x + 1, y, z + 1)$, $^{\mathrm{iii}}(x - 1, y, z)$, $^{\mathrm{iv}}(-x, 1 - y, -z)$, $^{\mathrm{v}}(1 - x, 1 - y, -z)$, $^{\mathrm{vi}}(1 - x, 1 - y, 1 - z)$, $^{\mathrm{vii}}(x, \frac{1}{2} - y, \frac{1}{2} + z)$, $^{\mathrm{viii}}(x + 1, \frac{1}{2} - y, \frac{1}{2} + z)$, $^{\mathrm{ix}}(-x, \frac{1}{2} + y, \frac{1}{2} - z)$, $^{\mathrm{x}}(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, $^{\mathrm{xi}}(1 - x, -y - 1, \frac{1}{2} - z)$.

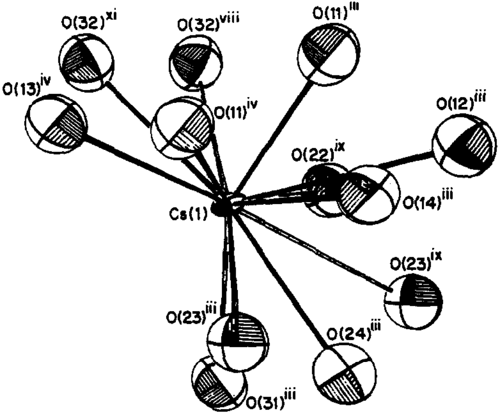

FIG. 2. The coordination polyhedron about Cs(1) in $Cs_3Fe_4(PO_4)_5$.

TABLE VII

BOND ANGLES (°) FOR $Cs_7Fe_7(PO_4)_8O_2$ WITH e.s.d.'s IN PARENTHESES

Atom A	Atom B	Atom C	Angle ABC
O(11)	Fe(1)	O(21)	94.2(4)
O(11)	Fe(1)	O(41)	94.1(5)
O(21)	Fe(1)	O(41)	90.6(4)
O^{iii}	Fe(2)	O(24)	98.4(5)
O^{iii}	Fe(2)	O(32)^{ix}	87.6(5)
O^{iii}	Fe(2)	O(42)^{iii}	88.5(5)
O^{iii}	Fe(2)	O(43)^{vi}	167.6(4)
O(24)	Fe(2)	O(32)^{ix}	105.2(5)
O(24)	Fe(2)	O(42)^{iii}	105.4(5)
O(24)	Fe(2)	O(43)^{vi}	93.6(5)
O(32)^{ix}	Fe(2)	O(42)^{iii}	149.4(4)
O(32)^{ix}	Fe(2)	O(43)^{vi}	86.4(5)
O(42)^{iii}	Fe(2)	O(43)^{vi}	91.2(5)
O	Fe(3)	O(12)^{v}	92.7(4)
O	Fe(3)	O(13)^{v}	78.3(4)
O	Fe(3)	O(23)^{i}	90.3(5)
O	Fe(3)	O(33)^{v}	174.2(5)
O	Fe(3)	O(34)^{x}	87.3(5)
O(12)^{v}	Fe(3)	O(13)^{v}	67.6(4)
O(12)^{v}	Fe(3)	O(23)^{i}	94.9(4)
O(12)^{v}	Fe(3)	O(33)^{v}	92.5(5)
O(12)^{v}	Fe(3)	O(34)^{x}	156.3(4)
O(13)^{v}	Fe(3)	O(23)^{i}	158.3(5)
O(13)^{v}	Fe(3)	O(33)^{v}	101.7(4)
O(13)^{v}	Fe(3)	O(34)^{x}	89.2(4)
O(23)^{i}	Fe(3)	O(33)^{v}	91.5(5)
O(23)^{i}	Fe(3)	O(34)^{x}	108.8(5)
O(33)^{v}	Fe(3)	O(34)^{x}	87.0(5)
O^{xi}	Fe(4)	O(11)^{vii}	87.8(4)
O^{xi}	Fe(4)	O(13)^{vii}	82.8(4)
O^{xi}	Fe(4)	O(22)^{xi}	177.0(5)
O^{xi}	Fe(4)	O(31)	91.7(5)
O^{xi}	Fe(4)	O(44)^{xi}	88.6(5)
O(11)^{vii}	Fe(4)	O(13)^{vii}	67.8(5)
O(11)^{vii}	Fe(4)	O(22)^{xi}	90.2(4)
O(11)^{vii}	Fe(4)	O(31)	154.7(5)
O(11)^{vii}	Fe(4)	O(44)^{xi}	104.0(5)
O(13)^{vii}	Fe(4)	O(22)^{xi}	98.5(4)
O(13)^{vii}	Fe(4)	O(31)	87.2(5)
O(13)^{vii}	Fe(4)	O(44)^{xi}	168.2(5)
O(22)^{xi}	Fe(4)	O(31)	91.2(5)
O(22)^{xi}	Fe(4)	O(44)^{xi}	89.8(5)
O(31)	Fe(4)	O(44)^{xi}	101.2(6)
O(11)	P(1)	O(12)	110.6(6)
O(11)	P(1)	O(13)	98.0(6)
O(11)	P(1)	O(14)	112.8(7)
O(12)	P(1)	O(13)	102.5(6)
O(12)	P(1)	O(14)	115.3(6)
O(13)	P(1)	O(14)	116.1(7)
O(21)	P(2)	O(22)	112.8(6)
O(21)	P(2)	O(23)	110.8(7)
O(21)	P(2)	O(24)	105.8(7)
O(22)	P(2)	O(23)	107.6(6)
O(22)	P(2)	O(24)	109.5(6)
O(23)	P(2)	O(24)	110.5(6)
O(31)	P(3)	O(32)	108.9(7)
O(31)	P(3)	O(33)	109.3(6)
O(31)	P(3)	O(34)	111.7(7)
O(32)	P(3)	O(33)	109.0(7)
O(32)	P(3)	O(34)	110.9(6)
O(33)	P(3)	O(34)	107.0(7)
O(41)	P(4)	O(42)	109.0(6)
O(41)	P(4)	O(43)	108.1(7)
O(41)	P(4)	O(44)	111.4(7)
O(42)	P(4)	O(43)	110.5(6)
O(42)	P(4)	O(44)	107.7(7)
O(43)	P(4)	O(44)	110.1(6)

Note. Symmetry transformations: $^{i}(x+1, y, z)$, $^{ii}(x+1, y, z+1)$, $^{iii}(x-1, y, z)$, $^{iv}(-x, 1-y, -z)$, $^{v}(1-x, 1-y, -z)$, $^{vi}(1-x, 1-y, 1-z)$, $^{vii}(x, \frac{1}{2}-y, \frac{1}{2}+z)$, $^{viii}(x+1, \frac{1}{2}-y, \frac{1}{2}+z)$, $^{ix}(-x, \frac{1}{2}+y, \frac{1}{2}-z)$, $^{x}(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$, $^{xi}(1-x, -\frac{1}{2}-y, \frac{1}{2}-z)$.

between a trigonal bipyramid and a square pyramid. The distortion is seen in the intermediate size, 147.4(7)°, of the O(32)–Fe(2)–O(42) angle. If this angle were about 30° larger, then the O, O(32), O(42), and O(43) oxygen atoms would form the base of square pyramid with the O(24) atom in an axial position. If it were about 30° smaller, then the O, Fe(2), and O(43) atoms would lie on the axis of a trigonal bipyramid with the O(24), O(32), and O(42) atoms in the equatorial plane. The average Fe(2)–O distance is 1.966 Å.

Fe(3) is coordinated to five oxygen atoms in a square pyramidal arrangement with an average Fe–O distance of 2.000 Å. A sixth oxygen atom located at a slightly longer distance (2.241 Å) forms an octahedron. Like Fe(3), Fe(4) is coordinated to five oxygen atoms in a square pyramidal geometry (Fe–O av = 1.976 Å) with a sixth oxygen atom

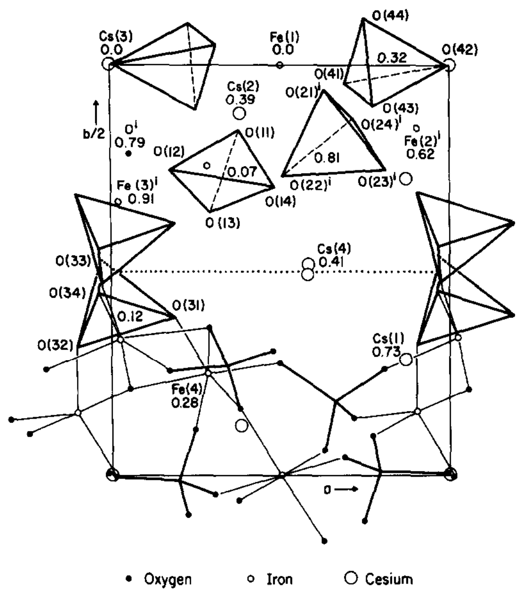

FIG. 3. One-half of the unit cell of $Cs_7Fe_7(PO_4)_8O_2$ ($0 \le b \le \frac{1}{2}$). The top portion of the figure shows the location of the Cs, Fe, and O atoms and the phosphate tetrahedra. The bottom portion shows the network of P–O and Fe–O bonds. The dotted line is a *c* glide at $b = \frac{1}{4}$. The *z* coordinates of selected Cs, Fe, and O atoms are indicated. Numbers within the tetrahedra indicate the *z* coordinates of the P atoms. A superscript i indicates atoms related to those in Table III by the symmetry operation $1 - x$, $1 - y$, $1 - z$.

located at longer distance of 2.198 Å forming an octahedron.

An interesting feature of this structure is the oxide ion bridge which joins Fe(2), Fe(3), and Fe(4) with a trigonal pyramidal geometry about the oxide.

All four unique phosphorous atoms are located in general positions and are within a distorted tetrahedral geometry. All oxygen atoms in the phosphate groups except O(14) bridge a phosphorus atom to one or two iron atoms. Not surprisingly, the P(1)–O(14) distance is the shortest P–O distance in the structure.

The four unique cesium atoms in this structure are located in tunnels. Figure 3 shows one set of tunnels; others occur parallel to the *a* and *b* axes. Cs(1), Cs(2), and Cs(4) are located in general positions and Cs(3) is located on a center of symmetry.

Discussion

The frameworks of $Cs_3Fe_4(PO_4)_5$ and $Cs_7Fe_7(PO_4)_8O_2$, have two important features: (a) the 6- to 10-coordinated cesium ions positions in holes in a $FePO_4$ framework and (b) the 5- and 6-coordinated Fe atoms. In addition, $Cs_7Fe_7(PO_4)_8O_2$ has an oxide ion bridge joining three iron atoms.

The coordination of Cs is often irregular. For example, Averbuch-Pouchot and Durif (*5*) report two different Cs coordination polyhedra in $BaCs_4(PO_3)_6$. One Cs is 9-coordinated with three different Cs–O distances; three each of 3.198, 3.228, and 3.424 Å. The second is 7-coordinated with shorter distances ranging from 2.988 to 3.337 Å. The same authors report an 11-coordinated Cs with oxygen distances from 3.160 to 3.567 Å in $CsCdP_3O_9$ (*18*). Raveau *et al.* (*6*) describe $CsP_8W_8O_{40}$ as having a Cs with five close oxygen neighbors at distances of 3.04 to 3.33 Å with six other oxygen neighbors at approximately 3.7 Å.

In $Cs_3Fe_4(PO_4)_5$, there are 12 oxygen atoms within 3.63 Å of Cs(1). If one takes 3.34 Å as the cutoff for a Cs–O bond, seven of the oxygen atoms form Cs–O bonds. With this cutoff Cs(1) is nearly planar coordinated. There are 10 oxygen atoms located in a ring around Cs(2). Six of the 10 oxygen

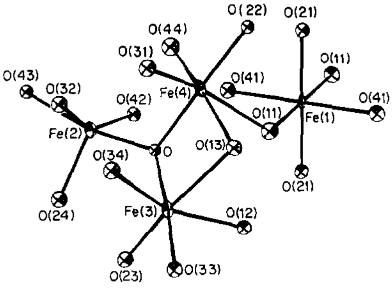

FIG. 4. The coordination polyhedra about the Fe atoms in $Cs_7Fe_7(PO_4)_8O_2$.

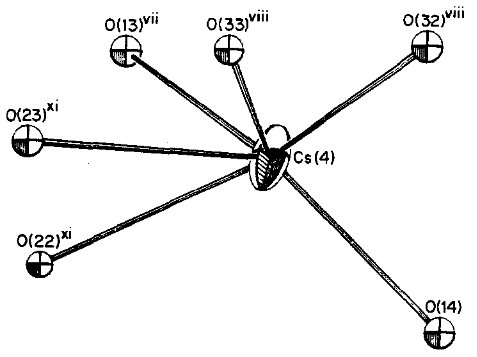

FIG. 5. The coordination polyhedron about Cs(4) in $Cs_7Fe_7(PO_4)_8O_2$.

atoms are located at a distance less than 3.34 Å; the other four are at distances of 3.40 and 3.58 Å.

The cesium coordination polyhedra in $Cs_7Fe_7(PO_4)_8O_2$ are not spherical but tubelike. Cs(1) has eight nearest oxygen neighbors within 3.34 Å and one second nearest neighbor at 3.42 Å. Six of the nine nearest oxygen atoms are within 3.34 Å of Cs(2); the other three are located at distances between 3.34 and 3.62 Å. Cs(3) has eight neighbors within 3.34 Å, 2 at 3.35 Å, and six from 3.35 to 3.80 Å. Cs(4) has only six oxygen atoms within 3.480 Å in an almost planar arrangement (Fig. 5). Considering all nearest neighbors, the coordination of Cs varies from 6 to 10.

The cesium atoms can be regarded as guests in the $FePO_4$ array. Using Pauling's definition of bond strength (*19*), the ionic bond strengths of the Cs–O bonds vary, to a first approximation, from 0.10–0.17. This small bond strength, compared to the average Fe–O bond strength of 0.5–0.6, is consistent with the idea that the cesium atoms are not part of the iron–phosphorus–oxygen array, but essentially act as templates about which the structure is built.

The Fe atoms in the $Cs_3Fe_4(PO_4)_5$ and $Cs_7Fe_7(PO_4)_8O_2$ structures are five- and six-coordinated. In $Cs_3Fe_4(PO_4)_5$, both Fe polyhedra have a distorted trigonal bipyramidal geometry, which is not a common stereochemistry for Fe(III). In $Cs_7Fe_7(PO_4)_8O_2$, the geometry of the Fe atoms are regular octahedral, intermediate between a trigonal bipyramid and a square pyramid, and square pyramidal with a longer sixth ligand making a distorted octahedron. The Fe–O distances in the Fe polyhedra in $Cs_3Fe_4(PO_4)_5$ and $Cs_7Fe_7(PO_4)_8O_2$ are comparable.

Several salt-like iron oxyphosphate structures have been reported. Of these, the $Fe_4(PO_4)_2O$ structure contains Fe(II) atoms in trigonal bipyramidal and octahedral geometries (*20*), with three of the Fe atoms linked by an oxide ion. The average Fe–O distances in the oxide ion bridge in $Cs_7Fe_7(PO_4)_8O_2$ and $Fe_4(PO_4)_2O$ are comparable. Comparison of the average Fe–O distance in the bridge with the other Fe–O distances in the Fe polyhedra shows the bridge to have slightly shorter distances in both the $Cs_7Fe_7(PO_4)_8O_2$ and $Fe_4(PO_4)_2O$ structures.

The pronounced distortions in several of the Fe polyhedra can be attributed to the difficulty of accommodating common atoms in the iron polyhedra and the phosphate tetrahedra. The Fe–O bonds are longer and weaker than the P–O bonds, and so are more easily distorted from their ideal distances and angles than the P–O bonds.

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