

OCTAHEDRAL TETRAMER IN THE CRYSTAL STRUCTURE OF LEUCOPHOSPHITE, $K_2[Fe^{3+}_4(OH)_2(H_2O)_2(PO_4)_4] \cdot 2H_2O$.

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ABSTRACT

Leucophosphate, $K_2[Fe^{3+}_4(OH)_2(H_2O)_2(PO_4)_4] \cdot 2H_2O$, possesses an atomic arrangement based on a discrete octahedral tetramer. The crystal cell criteria are 9.782(9), 9.658(9), 9.751(9) Å, $\beta = 102.24(12)^\circ$, space group $P2_1/n$. The crystal structure was solved by Patterson techniques and includes one K^+ , two P^{5+} , two Fe^{3+} , eight O^{2-} , one $(OH)^-$, and two (H_2O) in the asymmetric unit. $R(hkl) = 0.074$ for 3900 independent $F(obs)$.

The octahedral tetramer involves an edge-sharing dimer which further links at the shared corners to two more octahedra, resulting a center: vertex ratio = 1:5. A topologically identical cluster exists in amaranthite, although the two structures differ in the ligand groupings and their relative amounts. In leucophosphate, the tetramer is joined to symmetry equivalent tetramers by bridging $(PO_4)^{3-}$ tetrahedra. The K^+ ions reside in constricted channels in the structure. Half of the total water occurs in a structural cavity and probably possesses a tetrahedral grouping of hydrogen bonds.

Average polyhedral interatomic distances are $K^{VI}-O$ 2.927, $Fe(1)-O$ 2.028, $Fe(2)-O$ 2.012, $P(1)-O$ 1.540, and $P(2)-O$ 1.537 Å. The $(OH)^-$ group is bonded to three Fe^{3+} cations, resulting in a long $Fe^{3+}-(OH)^-$ 2.159 Å average because of extreme cation oversaturation.

The deep red color of amaranthite, in contradistinction to the pale-colored leucophosphate and the corner-sharing octahedral chain structures, suggests possible spin coupling on account of the short 2.90 Å Fe-Fe separation in the former compound.

INTRODUCTION

Systematic investigation of the interrelationships between atomic arrangement and paragenesis requires intimate knowledge of the mineral structures which crystallize together over a range of temperature, pressure, oxidations, and hydrogen ion concentrations. Among the highly complicated transition metal phosphate hydrates, structure analysis is necessary for establishing the correct chemical formula and for elucidation of the role of water in the crystal as well.

Leucophosphate was originally described by Simpson (1932) as chalk-like material from Weelhamby Lake, Western Australia, where it occurs with variscite and chalcedony in serpentine fractures. It was derived from the reaction of bird guano leachings with the serpentine. Admixtures with the variscite did not allow a simple composition for the obviously contaminated analyzed material.

A detailed account of leucophosphate chemistry by Axelrod, Car-

ron, Milton, and Thayer (1952) derived from their study of phosphate mineralization at Bomi Hill and Bambuta, Liberia, where the species occurs as a constituent of phosphate rock cementing cracks in boulders of high grade iron ore. With wet chemical analyses on the leucophosphite, and on bird and bat feces and guanos, they proposed an origin for the phosphates based on the interaction of bat dung leachings with the iron oxides. The leucophosphite occurs as fine-grained cherty masses and ranges optically from isotropic to weakly birefringent material. Their X-ray powder studies on the Australian material showed a range of crystallinities from essentially amorphous to crystalline materials, the latter revealing spotty powder patterns before crushing. They proposed the formula $KFe^{3+}_2(OH)(PO_4)_2 \cdot 2H_2O$.

A distinctly different paragenetic setting was reported by Lindberg (1957). The mineral occurs with avelinoite (cyrilovite) and metastrengite implanted upon frondelite from the Sapucaia pegmatite, Minas Gerais district, Brazil. Superior single crystals permitted a detailed crystal-chemical study. Recently, leucophosphite has been identified from several pegmatites in the Black Hills, South Dakota. With the guidance of Mr. W. L. Roberts and Dr. D. H. Garske, I collected exceptional specimens on the dumps of the Tip Top pegmatite, near Custer, South Dakota. The mineral occurs as columnar aggregates and clusters of monoclinic prismatic crystals up to 1 mm in length with morphology identical to the Sapucaia material described by Lindberg. It is among the latest minerals to form in open pockets in rockbridgeite, which derives from the hydrothermal reworking of triphylite giant crystals. I have also collected the species in a similar paragenesis at the Palermo No. 1 pegmatite, North Groton, New Hampshire. The leucophosphite from these pegmatites is green in daylight but purplish-grey in incandescent light.

Haseman, Lehr, and Smith (1950) synthesized and characterized at least nineteen hydrated potassium (ammonium) ferric (aluminum) phosphates, of which their Group 4 product I corresponds to the leucophosphite. Possible solid solution of $(NH_4)^+$ for K^+ and Al^{3+} for Fe^{3+} was inferred, but the series was not studied in complete detail. Leucophosphite appears at temperatures between 75° to 145°C at pH ranges of 2.5 to 6.0 and phosphate concentrations from 1.0 to 3.5 M.

The occurrence of leucophosphite in two distinct paragenetic settings adds interest to the species and provokes inquiry about its atomic arrangement, with especial emphasis on the nature of the transition metal clustering in the crystal. The two paragenetic types of leucophosphite are reminiscent of the basic ferrous-ferric phosphate occurrences described by Moore (1970). Minerals such as dufrenite, rock-

bridegite, strengite, etc. occur as fibrous masses replacing goethite beds in bog ores and were derived by phosphatic solutions acting upon these ores. Paragenetic sequences of these phases also occur with remarkable duplication from hydrothermally reworked triphylite ponds in complex giant crystal pegmatites.

EXPERIMENTAL

A superior single crystal of prismatic shape, showing $\{\bar{1}01\}$, $\{\bar{1}11\}$, and $\{011\}$ and measuring $0.10 \times 0.12 \times 0.16$ mm, was selected from a Tip Top pegmatite sample. 4200 symmetry independent reflections were gathered on a PICKER automated diffractometer utilizing a molybdenum target and graphite monochromator. Cell parameters were refined by an on-line least-squares fit of fifteen indexed monitor reflections, initially using the cell data in primitive setting of Lindberg (1957) and the results appear in Table 1 along with the cell contents. For moderately intense reflections, the mosaic spread at half-peak height was less than 0.6° at intermediate Bragg angles. Intensities were collected to maximum $2\theta = 70^\circ$ with individual scan widths of 1.8° , scan rates of $1^\circ/\text{minute}$, and 10 second background counting times. The systematic absences confirmed the uniquely determined $P2_1/n$ space group. Elimination of the extinct reflections left 3900 independent data which were processed by conventional computational procedures to obtain $|F(\text{obs})|$. Examination of several reflections by ω -rotation revealed that differential absorption amounted to at most ± 6 percent of the mean intensity and a correction was not applied.

SOLUTION OF THE STRUCTURE

The three-dimensional Patterson function, $P(uvw)$, was prepared and satellite vectors with coordinates $(1/2, 1/2 \pm 2y, 1/2)$ and $(1/2 \pm 2x, 1/2, 1/2 \pm 2z)$ were systematically tabulated. Combinations of these vectors were prepared in the form $(2x, 2y, 2z)$ and the inversion vectors were sought in $P(uvw)$. Inversion peaks of approximately half the maxima of the corresponding satellite vectors were accepted as possible solutions.

The asymmetric unit includes five heavy atoms: Fe(1), Fe(2), P(1), P(2), and K. Consequently, there are $4\text{Fe}(1) \rightarrow \text{Fe}(1)' + 4\text{Fe}(2) \rightarrow \text{Fe}(2)' + 4\text{Fe}(1) \rightarrow \text{Fe}(2) + 4\text{Fe}(1) \rightarrow \text{P}(1) + 4\text{Fe}(1) \rightarrow \text{P}(2) + 4\text{Fe}(2) \rightarrow \text{P}(1) + 4\text{Fe}(2) \rightarrow \text{P}(2) + 4\text{Fe}(1) \rightarrow \text{K} + 4\text{Fe}(2) \rightarrow \text{K} = 36$ prominent vectors, with approximate relative densities of Fe-Fe 525, Fe-P 345, and Fe-K 430. Peeling the Patterson onion proceeded with solutions from the Fe-Fe vectors, then the Fe-P and Fe-K vectors, the latter selected on the basis of the positional solutions of the Fe atoms. The metal atomic positions were unambiguously obtained in this fashion with no difficulty, and all 36 vectors could be derived from these solutions.

Least-squares refinements of the Fe, P, and K coordinates thus obtained converged to

$$R(hkl) = [\Sigma | |F(obs)| - |F(calc)| | / \Sigma |F(obs)|] = 0.32.$$

A difference synthesis revealed all eleven oxygen atoms remaining in the asymmetric unit.

REFINEMENT

The coordinates of two iron, two phosphorus, one K, and eleven independent oxygen atoms in general positions were refined by a locally modified version of the ORFLS full-matrix least-squares program for IBM 7094 computer of Busing, Martin, and Levy (1962). Scattering curves for Fe^{2+} , P^{3+} , and O^{2-} were obtained from MacGillavry and Rieck (1962). The first three cycles included scale and atomic parameter refinement followed by three cycles of scale, atomic parameter, and isotropic thermal vibration parameter refinement whereupon convergence was reached at $R(hkl) = 0.074$ for all 3900 reflections. Reasonable B -values (0.3 \AA^2 for Fe, 0.4 for P, $0.6\text{--}0.9$ for O^{2-} , $1.6\text{--}1.8$ for H_2O) and very low estimated standard errors ($\pm 0.005 \text{ \AA}$ for oxygen atoms) attest to a well-refined crystal structure and a chemical composition akin to the Sapucaia material, that is, a hydrated basic ferric phosphate.

TABLE 1. LEUCOPHOSPHITE. CRYSTAL CELL DATA.

<u>a</u>	9.782 (9) Å
<u>b</u>	9.658 (9)
<u>c</u>	9.751 (9)
<u>β</u>	102.24 (12) ^o
<u>space group</u>	$P2_1/n$
<u>specific gravity</u> ¹	2.948
<u>density (computed)</u>	2.911
<u>formula</u>	$KFe^{3+}_2(OH)(H_2O)(PO_4)_2 \cdot H_2O$
<u>Z</u>	4

¹Lindberg (1957). On crystals from the Sapucaia pegmatite.

TABLE 2. LEUCOPHOSPHITE. ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS (Estimated standard errors in parentheses).

	\bar{x}	\bar{y}	\bar{z}	$B(\text{\AA}^2)$
K	.1010 (2)	0.1958 (2)	0.5171 (2)	1.88 (2)
Fe(1)	.3695 (1)	.5512 (1)	.3919 (1)	.26 (1)
Fe(2)	.3097 (1)	.2278 (1)	.5969 (1)	.28 (1)
P(1)	.3548 (1)	.5285 (1)	.7094 (1)	.42 (1)
P(2)	.1287 (1)	.3221 (1)	.2894 (1)	.43 (1)
O(1)	.3009 (4)	.5935 (4)	.5632 (4)	.69 (4)
O(2)	.1753 (4)	.1207 (4)	.6744 (4)	.74 (4)
O(3)	.4845 (4)	.4929 (4)	.2609 (4)	.68 (4)
O(4)	.2838 (4)	.3864 (4)	.7162 (4)	.77 (4)
O(5)	.1553 (4)	.2687 (4)	.4399 (4)	.95 (5)
O(6)	.1952 (4)	.4679 (4)	.2854 (4)	.69 (5)
O(7)	.3050 (4)	.7275 (4)	.3054 (4)	.88 (5)
O(8)	.4710 (4)	.1623 (4)	.7351 (4)	.85 (4)
O(9) = (OH) ⁻	.4386 (4)	.3568 (4)	.4966 (4)	.55 (4)
O(10) = H ₂ O	.3432 (5)	.0464 (5)	.4891 (5)	1.53 (6)
O(11) = H ₂ O	.5335 (5)	.1531 (5)	.3100 (5)	1.81 (6)

The final atomic coordinates and isotropic thermal vibration parameters appears in Table 2. The $|F(\text{obs})| - F(\text{calc})$ data are listed in Table 3¹.

DISCUSSION OF THE STRUCTURE

Architecture and bonding in the octahedral tetramer

The most remarkable feature of the leucophosphate atomic arrangement is the octahedral cluster which consists of an edge-sharing doublet whose two common corners each fuse by corner-sharing to two other octahedra forming a tetramer. The tetramer is an insular octahedral cluster and is joined to surrounding symmetry equivalent tetramers by the bridging phosphate ligands, resulting in a three-dimensional

¹To obtain a copy of Table 3, order NAPS Document No. 01709 from ASIS National Auxiliary Publications Service, c/o CCM Information Corporation, 866 Third Avenue, New York, New York, 10022; remitting \$2.00 for microfiche or \$6.80 for photocopies, payable, in advance, to CCMIC-NAPS.

linkage of $\cdots \text{Fe-O-P-O} \cdots$ bonds. Setting $O_P =$ oxygen associated with the $(\text{PO}_4)^{3-}$ group, the cluster formula is $[\text{Fe}^{3+}_4(\text{OH})_2(\text{H}_2\text{O})_2(O_P)_{16}]$. Thus, the crystal-chemical formula for leucophosphite is $\text{K}_2[\text{Fe}^{3+}_4(\text{OH})_2(\text{H}_2\text{O})_2(\text{PO}_4)_4] \cdot 2\text{H}_2\text{O}$. The two symmetry independent phosphate tetrahedra are tetradentate and half the total water bonds directly to Fe^{3+} as ligands while the remaining half resides in a cavity in the structure. A sketch of the geometrically idealized tetramer topologically equivalent to the cluster in leucophosphite appears in Figure 1. The octahedral center to vertex ratio in the cluster is 1:5, which is compositionally isomorphous to the edge-sharing dimer and the infinite corner-sharing octahedral chain. The three-dimensional linkage of octahedra and tetrahedra is rather complicated. The actual distorted tetramer and its associated surrounding $(\text{PO}_4)^{3-}$ tetrahedra are featured in Figure 2.

Also noteworthy is the occurrence of a topologically identical tetramer in the crystal structure of amarantite, as revealed by Süssé (1968). Although both tetramers possess the same $\bar{1}$ point symmetry located at the midpoint of the shared edge, the ligand groupings and relative ligand proportions are quite different. The cluster in amarantite has the composition $[\text{Fe}^{3+}_4(\text{O})_2(\text{H}_2\text{O})_8(\text{O}_8)_{10}]$ and the crystal-chemical formula is $[\text{Fe}^{3+}_4(\text{O})_2(\text{H}_2\text{O})_8(\text{SO}_4)_4] \cdot 6\text{H}_2\text{O}$. In this formula, six of the sixteen sulfate oxygens do not participate as vertices of the octahedral cluster, but are hydrogen bonded only. According to Bandy (1938), amarantite is found in oxidized quartz-pyrite veins at Chuquicamata and Quetena, Chile, invariably associated with hohmannite and fibroferite, and is the latest mineral in the assemblage to appear, indicating a very low temperature of formation. Fewer bridging tetrahedra occur in the amarantite structure than in leucophosphite and the result is a chain of $\cdots \text{Fe-O-S-O} \cdots$ bonds which are joined to symmetry equivalent chains only through hydrogen bonds.

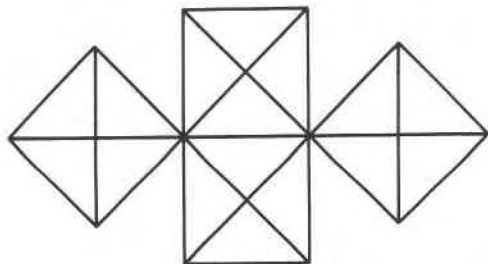


FIG. 1. Geometrically idealized octahedral tetramer which is topologically equivalent to the arrangements in leucophosphite and amarantite.

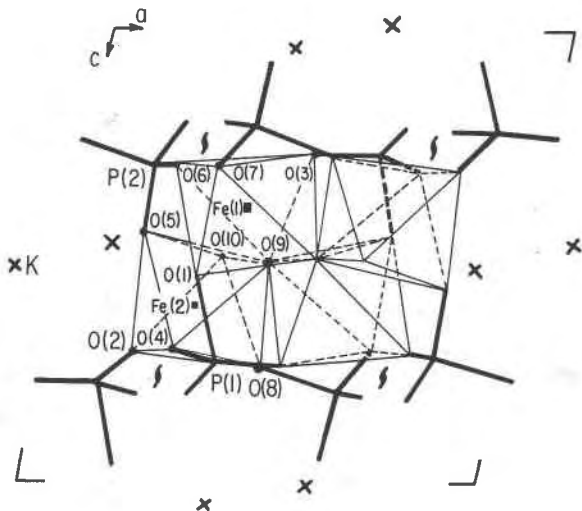


FIG. 2. The octahedral tetramer and its surrounding $(\text{PO}_4)^{3-}$ ligands in the leucophosphite crystal structure. Potassium atoms are located at the crosses in the cavities surrounding the tetramer. Atomic positions are labelled to conform with Table 2. Symmetry equivalent tetramers are centered at $(0, 0)$; $(0, 1)$; $(1, 0)$; and $(1, 1)$, and are generated by the screw operation.

Bond distances associated with the octahedra and the $(\text{PO}_4)^{3-}$ tetrahedra are presented in Figures 3 and 4 as Schlegel diagrams which are compared with the data published by Süsse. Despite the fact that the tetramers in the two structures are topologically identical and do not link directly to other octahedral entities, the individual distances differ considerably between the two structures. Factors contributing to major differences include the different relative proportions of ligands between the two structures, the differences in the bond strengths (ζ) of the P-O ($\zeta = 5/4$) and S-O ($\zeta = 6/4$) bonds, and the nature of the O(9) atom which is bonded to three Fe^{3+} cations in both structures.

This last difference is rather curious, but is substantiated by the average Fe-O(9) distances in the two accurately refined structures. In amarantite, the Fe^{3+} -O(9) 1.930 Å average is unusually short and is explicable only if an oxide (O^{2-}) anion is assumed, which, with $\Delta\Sigma = -.50$, is severely undersaturated electrostatically with respect to the coordinating cations. The corresponding Fe^{3+} -O(9) 2.159 Å average distance in leucophosphite is unusually long and a charge balanced crystal requires that $\text{O}(9) = (\text{OH})^-$. With $\Delta\Sigma = +.50$ for the $(\text{OH})^-$ group treated as a univalent anion, extreme oversaturation results in distances which are considerably longer than average. This

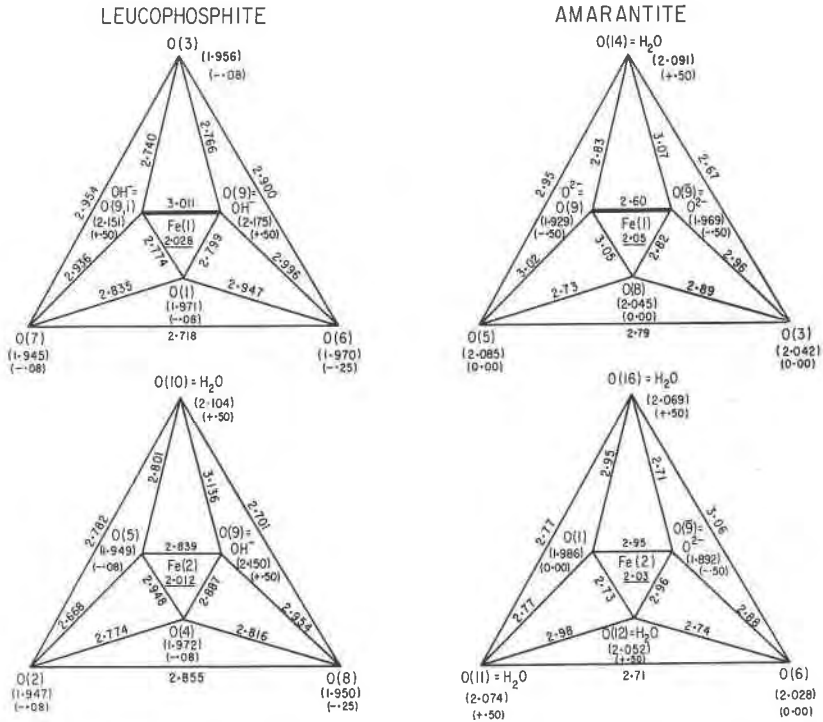


FIG. 3. Interatomic distances and anionic deviations from electrostatic neutrality in the leucophosphite octahedra and the amarantite octahedra. The tabulations are presented as Schlegel diagrams, which can be directly compared by super-position. Shared edges are drawn bold; Me-O distances and $\Delta\Sigma$ are listed parenthetically. The average Me-O distance is underlined. Estimated standard errors are Me-O \pm 0.005 and O-O' \pm 0.007 Å. The amarantite data are from Süsse (1968). *i* = inversion, *s* = screw operations applied to the atomic coordinates in Table 2.

interpretation is also substantiated by the O(9)-O(9)' shared edge distances, which are 2.60 and 3.011 Å in amarantite and leucophosphite respectively.

Average Fe³⁺-O and P⁵⁺-O distances in leucophosphite are typical for their polyhedra, with Fe(1)-O 2.028, Fe(2)-O 2.012, P(1)-O 1.540, and P(2)-O 1.537 Å. The two long Fe(1)-O(9, *i*) 2.151 and Fe(1)-O(9) 2.175 Å distances impose compensatory effects upon the remaining Fe(1)-O distances, all of which are shorter than average. In this connection, it is important to note that the electrostatic valence balances for the remaining anions about Fe(1) shown in Figure 3 indicate slight undersaturation which, when combined with the severely

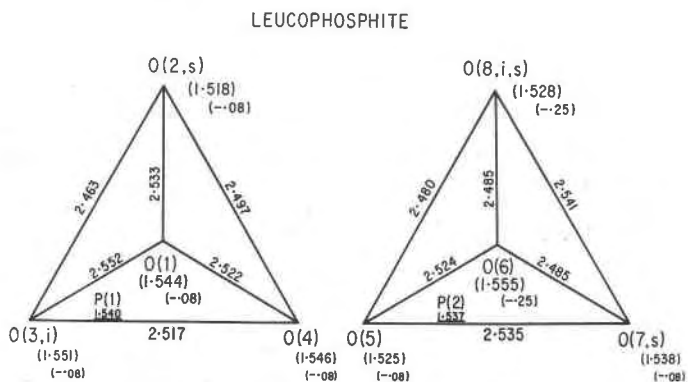


FIG. 4. Schlegel diagrams of tetrahedra in leucophosphate. See Fig. 3 legend for further remarks.

oversaturated O(9), results in an overall electrostatically neutral polyhedron.

Role of the potassium ions

The three-dimensional framework of linked octahedral tetramers and $(\text{PO}_4)^{3-}$ tetrahedra results in constricted channels which run parallel to the b -axis and which are centered at $(x, z) = (1/2, 0)$ and $(0, 1/2)$. These channels are occupied by ordered K^+ cations located across the inversion centers whose inner sphere of coordination includes six oxygen atoms. The location of the K^+ cations is shown in Figure 2 and their coordinating anions appear in Figure 5. The KO_6 polyhedron is highly irregular, with average K-O distances of 2.927 Å. It shares an edge with the $\text{Fe}(2)\text{O}_6$ octahedron and an edge with the $\text{P}(1)\text{O}_4$ tetrahedron. Although the KO_6 polyhedra do not appear essential to the rigidity of the crystal structure, the presence of a univalent cation is necessary for charge balance. Table 4 shows that electrostatic valence balance of cations about anions is assured when six-fold coordination of oxygens about K^+ is selected.

Hydrogen bonding

A final difference synthesis failed to yield conclusive information about the location of hydrogen atoms on account of the matrix of rather heavy metal atoms. A hydrogen bonding scheme is proposed which is based on simple geometrical arguments and it is shown diagrammatically in Figure 6. The atoms which can donate hydrogen bonds include $\text{O}(9) = (\text{OH})^-$ and $\text{O}(10)$, $\text{O}(11) = (\text{H}_2\text{O})$. Since $\text{O}(9)$ is coordinated to three octahedra and since the fourth octahedron is lo-

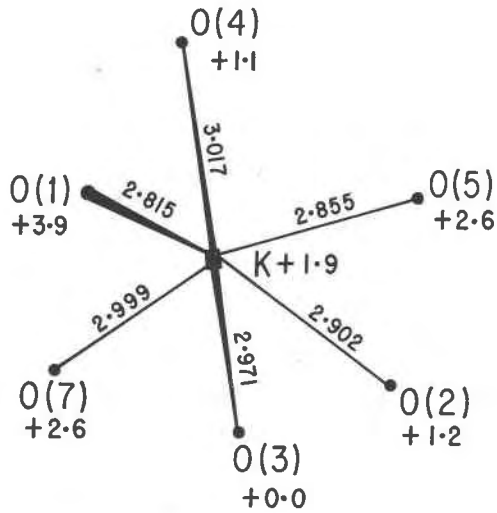


FIG. 5. Anionic environment about the potassium cation labelled in Fig. 2. Interatomic distances and elevations (in Å units) are presented.

TABLE 4. LEUCOPHOSPHITE. ELECTROSTATIC VALENCE BALANCES
(Σ) OF CATIONS ABOUT ANIONS.

			Σ	$\Delta \Sigma$
O(1)	P(1)+Fe(1)+K	5/4+3/6+1/6	1.92	-0.08
O(2)	P(1)+Fe(2)+K	5/4+3/6+1/6	1.92	- .08
O(3)	P(1)+Fe(1)+K	5/4+3/6+1/6	1.92	- .08
O(4)	P(1)+Fe(2)+K	5/4+3/6+1/6	1.92	- .08
O(5)	P(2)+Fe(2)+K	5/4+3/6+1/6	1.92	- .08
O(6)	P(2)+Fe(1)	5/4+3/6	1.75	- .25
O(7)	P(2)+Fe(1)+K	5/4+3/6+1/6	1.92	- .08
O(8)	P(2)+Fe(2)	5/4+3/6	1.75	- .25
O(9)=(OH) ⁻	Fe(1)+Fe(1)+Fe(2)	3/6+3/6+3/6	1.50	+0.50
O(10)=H ₂ O	Fe(2)	3/6	0.50	+0.50
O(11)=H ₂ O	-	-	0.00	0.00
			17.02	+0.02

cated too far away for any reasonable O \cdots O distance admissible for hydrogen bonding, it must bond to O(11), the water molecule in the cavity. Indeed, the O(9) \cdots O(11) 2.960 Å distance is acceptable.

The O(11) water molecule probably forms bonds with O(4) and O(6, s), with distances O(11) \cdots O(4) 2.816 and O(11) \cdots O(6, s) 2.861 Å. O(10) is also a donor of hydrogen bonds and the distances O(10) \cdots O(11, i) 2.828 and O(10) \cdots O(6, s) 2.730 Å are acceptable. Thus, O(6) and O(11) each receive two bonds. The O(6, s)–O(10)–O(11, i) 116°5', and O(6, s)–O(11)–O(4) 118°54' angles are not severely out of range from the ideal tetrahedral angle. Finally, I remark that O(11), which receives two bonds and donates two bonds in this model, defines a distorted tetrahedron with O(6, s), O(4), O(9), and O(10, i) at the vertices. This would suggest that O(11) is firmly held in the cavity and, unlike zeolitic water, would be fairly resistant to removal by mild thermal activation.

OBSERVATIONS CONCERNING COLOR AND Fe^{3+} –(O, OH) OCTAHEDRAL CLUSTERING

Since both leucophosphite and amaranthite have formed in different paragenetic settings but at similar temperatures and since both possess topologically the same isomer, it is reasonable to assume that at least the tightly bound octahedral edge-sharing dimer existed in

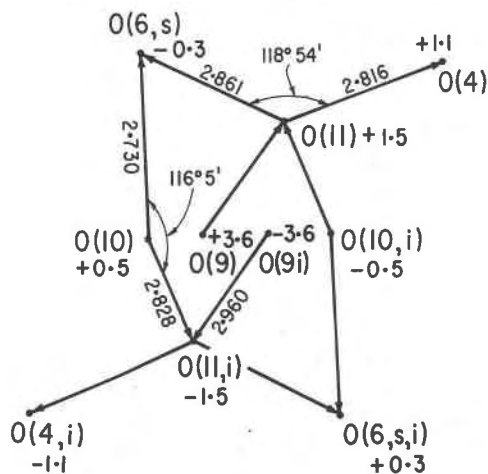


FIG. 6. Proposed hydrogen bonding scheme with distances and angles in the leucophosphite structure. The tails of the arrows are located at the donors and the heads at the acceptors. The scheme is located at the inversion center of the tetramer in Fig. 2.

solution during their crystallization. Although the octahedral tetramers are insular in both structures with respect to other octahedral clusters, continuous polyhedral polymerization exists as a result of the $(\text{PO}_4)^{3-}$ and $(\text{SO}_4)^{2-}$ bridging ligands. However, the varying degree of crystallinities observed for leucophosphite implies that polymerization is not complete in the amorphous material and that amorphous leucophosphite is incompletely condensed gel material.

The dimer involving an edge-sharing octahedral pair has received considerable attention in the chemical literature. Mulay and Selwood (1955), on the basis of magnetic susceptibility measurements, reported a diamagnetic dimer, written $[\text{Fe}_2(\text{OH})_2]^{4+}$, which evidently increases in stability with increasing temperature, at least in the region of 15 to 51°C. They proposed that exchange effects across the short $\text{Fe}(\text{OH})_2\text{-Fe}$ bridge induce subnormal magnetic moments and add that a similar explanation may account for low magnetic moments observed for red-brown ferric hydroxide gels. Schugar *et al.* (1967), in a detailed magnetic and spectral examination on a dimeric species formed by the action of the ferric cation and the trianion of N-hydroxyethylenediaminetriacetic acid with equimolar amounts of NaOH, noted a reduction of the 5.79 Bohr magneton number for high spin Fe^{3+} at low and high pH values to 2.9 BM at intermediate values. At the intermediate pH range (between approximately 4 to 9), the color of the solution was red, whereas the color was yellow at the two pH extremes. They interpreted the results as the formation of a red dimeric species, which, on account of the short $\text{Fe}^{3+}\text{-Fe}^{3+}$ contact across the hydroxyl edge-sharing bridge, possesses spin coupling and a reduction from five unpaired electrons in the yellow monomer to approximately two unpaired electrons for Fe^{3+} in the dimer.

Both leucophosphite and amarantite appear to be good crystalline examples which add new information about the nature of the dimers studied in solution. It is necessary to add here that the corner-sharing dimer has also been proposed in chemical studies. The two important dimeric species believed to exist in solution are the corner-sharing $[\text{Fe}^{3+}\text{-(OH)-Fe}]^{5+}$ and the edge-sharing $[\text{Fe}(\text{OH})_2\text{-Fe}]^{4+}$ species. Some investigators suggest the presence of *oxo* (*i.e.*, O^{2-}) bridges, but such an arrangement is implausible on the grounds of electrostatic valence balances for octahedral coordination and must involve at least one more coordinating cation of similar charge and coordination number.

Several recently determined crystal structures beg magnetic susceptibility measurements on their crystals. The $\text{Fe}\text{-Fe}$ distance between the edge-sharing *oxo* bridge in amarantite is 2.90 Å; in leuco-

phosphite, the corresponding distance between the *hydroxyl* bridge is 3.11 Å, a difference of 0.20 Å, which is explicable on the basis of the electrostatic valence balances of the cations about the bridging O(9) anions discussed earlier. Amaranthite exhibits a brilliant amaranth crimson color (whence its name) while leucophosphite is pale-colored (whence its name). In the structures of basic ferric phosphates involving corner-sharing $\cdots \text{Fe-OH-Fe} \cdots$ chains such as laueite, $\text{Mn}^{2+}\text{Fe}_2^{3+}(\text{H}_2\text{O})_6(\text{OH})_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Moore, 1965) and butlerite, $\text{Fe}^{3+}(\text{OH})(\text{H}_2\text{O})_2(\text{SO}_4)$ (Fanfani *et al.*, 1971), the Fe-Fe distances are greater than 3.4 Å but less than 4.0 Å. These latter compounds are all pale orange-yellow in color. From these observations, it is tempting to infer that spin coupling between the shared edge exists in amaranthite and that it is induced in structures where the Fe-Fe separation lies somewhere below 3.1 Å, the distance found in the pale-colored leucophosphite. Pursuant to this speculation, Gouy balance measurements are in progress for amaranthite, leucophosphite and the structures with corner-sharing octahedral chains.

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