Crystal structure of vanadium(III) tris(metaphosphate)

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Vanadium(III) tris(metaphosphate), $V(PO_3)_3$, crystallizes in the monoclinic space group *Ic* with lattice parameters $a = 10.615(2)$, $b = 19.095(4)$, $c = 9.432(1)$ Å, $\beta = 97.94(1)°$ with $Z = 12$. The equivalent parameters in the standard space group *Cc* are $a = 13.189(1)$, $b = 19.095(4)$, $c = 9.432(1)$ Å, and $\beta = 127.15(1)°$. The structure was refined by full-matrix least-squares to an $R = 0.091$ ($R_\omega = 0.065$) utilizing 2467 reflections with the atomic positions and their isotropic vibration amplitudes as parameters. The structure consists of infinite chains of PO_4 tetrahedra sharing corners with each other and bridged by VO_6 octahedra. All oxygen atoms are shared between just two cations. The average P—O⟨—P⟩ bond is 1.581 Å while the average of those shared with vanadium is 1.483 Å. The VO_6 group is moderately distorted, with differences of less than 0.06 Å between the longest and shortest V—O bond lengths in any of the three distinct VO_6 groups. The average V—O bond lengths for the three VO_6 groups are 1.995, 1.991, and 1.987 Å. A marked superlattice effect based on a cell with $b/3$ is noted.

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Le tris(métaphosphate) de vanadium(III), $V(PO_3)_3$, cristallise dans le groupe d'espace monoclinique *Ic* avec des paramètres de maille $a = 10.615(2)$, $b = 19.095(4)$, $c = 9.432(1)$ Å, $\beta = 97.94(1)°$ avec $Z = 12$. Les paramètres équivalents dans le groupe d'espace standard *Cc* sont $a = 13.189(1)$, $b = 19.095(4)$, $c = 9.432(1)$ Å et $\beta = 127.15(1)°$. On a affiné la structure par la méthode des moindres carrés (matrice complète) jusqu'à une valeur de $R = 0.091$ ($R_\omega = 0.065$) utilisant 2467 réflexions et les positions atomiques et leurs amplitudes de vibration isotrope comme paramètres. La structure consiste de chaînes infinies de tétraèdres de PO_4 partageant des coins les uns avec les autres et reliées par un octaèdre de VO_6. Tous les atomes d'oxygène sont partagés uniquement entre deux cations. La longueur moyenne du lien P—O⟨—P⟩ est de 1.581 Å alors que la moyenne des longueurs partagées avec le vanadium est de 1.483 Å. Le groupe VO_6 est modérément déformé; il existe des différences de moins que 0.06 Å entre les longueurs des distances V—O les plus courtes et des plus longues dans chacun des trois groupes VO_6 distincts. Les longueurs moyennes des liens V—O pour les trois groupes VO_6 sont 1.995, 1.991 et 1.987 Å. On note un effet marqué de superstructure basé sur une maille avec $b/3$.

[Traduit par le journal]

Introduction

The systematic study of various solid vanadium oxides has shown that a wide variety can be prepared. In addition to the oxides with vanadium having integral valences, *i.e.* V_2O_3, VO_2, and V_2O_5, series with variable valency for the cation have been prepared. Two well characterized series correspond to V_nO_{2n-1} (1, 2) with $3 \leq n \leq 8$ and V_nO_{2n+1} (3, 4) with $n = 3, 4, 6$. Polymorphic transformations and a variety of changes in physical properties have been noted (2, 4). These structures are characterized by octahedral and/or five-fold coordinate V.

Adding P_2O_5, thus forcing some of the cations into tetrahedral coordination, has to date resulted in a substantially diminished number of phases and variety of solid state properties. This may be due to the instability of stable shear structures based upon tetrahedrally coordinated cations. Among the compositions which do occur are $V(PO_3)_3$, $VO(PO_3)_2$ (5, 6), and VPO_5 (7) with the oxidation state of vanadium progressively increasing in integral steps from 3 to 5. Polymorphs have been reported for only VPO_5 to date and the structures of these have been determined (8, 9). A second tetravalent vanadium compound, $(VO)_2P_2O_7$, whose structure is being studied in this series, has not been reported generally.[1] Surprisingly, only one mixed valency vanadium phosphate system is presently known. This system consists of glasses whose conductivities indicate that polaronic hopping involves an electron hopping from V^{4+} to V^{5+} (11). The structure of these glasses is based upon a

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[1] P. Courtine and E. Bordes, private communication.

perturbed α-VPO_5 structure (12). Substitution of phosphorus into metavanadate chains and vanadium into trimetaphosphate rings has been reported (13). However, substitution of V for P in $VO(P_2SiO_8)$ (14, 15), where one might logically expect it, has not been substantiated nor has phosphorus been substituted for tetrahedral V^{5+} in $K_2V_3O_8$ (16). In each case the structure suggests that such substitution, leading to a mixed valency state vanadium in a vanadium phosphate system, should be possible.

The general conclusion available from the details of the preparation of these vanadium phosphorus compounds is that at fixed partial pressure of oxygen the fraction of vanadium reduced increases with temperature (17) as it does with an increased P/V ratio (5, 6, 18) at fixed temperature. The structural studies indicate that as the P/V ratio increases the degree of condensation of the phosphate increases. That is, VPO_5 has non-condensed phosphate groups, and infinite chains of corner sharing PO_4 groups were found (in this laboratory)[2] in $VO(PO_3)_2$ and $V(PO_3)_3$. $VPO_{4.5}$ has both condensed VO_6 groups and P_2O_7 groupings, according to our incomplete studies, while in the vanadium phosphate glasses, prepared from a mixture of $(1 + x)V_2O_5$ and $(1 - x)P_2O_5$, for $x \geq 0$ condensed vanadium polyhedra are proposed to account for the oxygen lost. Although many structures based upon condensed VO_6 groups are possible, in the vanadium phosphate system only a few have been realized. The dearth of mixed valency crystalline vanadium phosphates is worthy of note.

Trivalent metal ion trimetaphosphates have been reported for Al, Ti, Fe, Cr, Mo in addition to V (20–25). The structure of the cubic polymorph, as $Al_4(P_4O_{12})_3$, was reported by Pauling and Sherman (26). Six polymorphs have been reported for $Cr(PO_3)_3$ (25) thus presenting an interesting challenge in both preparing and determining these structures.

Experimental

Crystals of $V(PO_3)_3$ were prepared by reacting a V_2O_5–P_2O_5 mix in an evacuated sealed quartz tube at temperatures near 900°C. The product was found to contain small crystals of $VO(SiP_2O_8)$, $VO(P_2O_7)$, $V(PO_3)_3$ plus at least one additional phase. All the diffraction studies were performed on a crystal from this batch. Crystals with the same lattice parameters and symmetry as reported here were also prepared following the procedure of Lavrov *et al.* (5) and Tofield *et al.* (6).

A small equi-dimensional crystal with a radius of about 0.1 mm was used for the crystallographic study. Unit cell parameters were obtained by measuring both $\pm 2\theta$ values on a Suntex $P2_1$ automatic diffractometer using 2θ values in the range 20 to 30°. Graphite monochromatized MoKα radiation ($\lambda_{\alpha_1} = 0.70926$ Å) was used. The parameters were determined by least-squares refinement methods. Crystal data are as follows:

$V(PO_3)_3$ fw = 287.85
Monoclinic $a = 10.615(2)$, $b = 19.095(4)$, $c = 9.432(1)$ Å, $\beta = 97.94(1)°$, $Z = 12$, $D_m = 3.0 \pm 0.1$ g cm^{-3}, $D_{calcd} = 3.03$ g cm^{-3}. Space group: *Ic* or *I*2/*c*. Absences: $h+k+l$ odd in general and $h0l$ with l odd.

Data were collected with a scintillation counter up to $2\theta = 60°$ using a scan of 2° plus the α_1–α_2 separation. Backgrounds were measured on either side and one degree removed from each peak. The scan rate depended upon the peak intensity. A total of 2847 symmetry independent peaks were scanned and 2467 of these had intensity of positive measure after correcting the peak intensities for background. The latter set was used to determine the structure. All the data were corrected for Lorentz and polarization effects and for absorption based upon a spherical crystal with a radius of 0.1 mm.

At lower 2θ values the diffraction pattern showed reflections indexed with $k \neq 0$ (mod 3) to be substantially weaker than those with $k = 0$ (mod 3). Thus a Patterson function with these latter reflections was used to determine the average atomic positions assuming that the space group of this smaller cell was *I*2/*c*. The structure model at this point showed some P—O bond lengths that were unacceptable and an *R* value near 0.20. Tofield *et al.* (6) on the basis of a second-harmonic generation signal selected *Cc* as the space group for the standard cell. The final structure was derived in this space group by arbitrarily displacing the atoms sequentially from the average position in conjunction with a decreasing *R* value.[3] Although the model obtained seemed satisfactory the possibility of a false minimum exists. Therefore, the Patterson function, without the vanadium contribution and a β synthesis (27) based upon the vanadium and phosphorus positions of the model were examined for an alternative structure. None was found. Finally, the structure of $Al(PO_3)_3$ (28), reported recently, is isostructural.

The final atomic parameters, with isotropic thermal parameters, derived by full-matrix least-squares methods, are in Table 1. (The cell has been transformed to one with *Ic* symmetry.) The refinement used scattering curves for neutral atoms (29) and a weighting scheme, ω, so that $\omega(F_o - F_c)^2$ was substantially independent of F_o, *i.e.* $\omega = (46 - 0.53F + 0.0023F^2 + 1000\,(\sigma/F)^2)^{-1}$, where σ is the standard deviation based on counting statistics. (The final R and R_ω were 0.091 and 0.065 respectively considering all reflections and 0.134 and 0.094 considering the $k \neq 0$ (mod 3) reflections only.) Scattering curves were corrected for anomalous dispersion but this

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[2] N. Middlemiss and C. Calvo, unpublished results.

[3] A table of calculated and observed structure factors is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

TABLE 1. Atomic parameters for $V(PO_3)_3$ with estimated standard deviations in parentheses (values are multiplied by 10^4)

Atom	*x*	*y*	*z*	U (Å^2)*
V(*a*)	1/4	0798(2)	1/4	0057(5)
V(*b*)	2529(5)	4115(2)	2479(6)	0049(5)
V(*c*)	2308(3)	7549(2)	2631(4)	0056(6)
P(1)	9756(6)	1442(3)	7657(7)	0059(8)
P(2)	0156(5)	4803(2)	7409(6)	0063(8)
P(3)	0027(5)	8142(2)	7476(6)	0043(7)
P(4)	1026(5)	3018(2)	4494(6)	0051(8)
P(5)	0967(5)	6370(2)	4420(6)	0050(8)
P(6)	1168(6)	9681(3)	4363(7)	0073(9)
P(7)	8791(6)	6965(2)	5748(7)	0056(9)
P(8)	8809(6)	3629(2)	5710(6)	0036(8)
P(9)	8961(5)	0267(3)	5561(6)	0056(8)
O(*a*,2)	9033(10)	5190(6)	7784(13)	0106(21)
O(*a*,3)	0884(10)	1321(5)	2012(12)	0062(19)
O(*a*,6)	1501(12)	9981(6)	2994(14)	0068(22)
O(6,*a*)	2262(13)	0544(7)	0417(16)	0120(26)
O(*a*,7)	8502(11)	6635(6)	7091(13)	0092(20)
O(*a*,8)	7808(10)	6097(6)	9585(13)	0051(20)
O(*b*,2)	1211(11)	4803(7)	1862(13)	0114(22)
O(*b*,3)	8865(12)	8371(7)	8006(15)	0145(24)
O(*b*,4)	1266(12)	3577(6)	3473(15)	0159(24)
O(*b*,5)	2044(11)	3651(6)	0631(13)	0083(20)
O(*b*,9)	8769(11)	9686(6)	6562(13)	0049(19)
O(9,*b*)	8011(11)	9652(6)	9295(13)	0045(20)
O(*c*,1)	0930(13)	8251(7)	2191(15)	0112(24)
O(1,*c*)	8775(11)	1913(6)	8121(13)	0057(21)
O(*c*,4)	2022(12)	7099(7)	0734(15)	0130(24)
O(*c*,5)	1070(10)	6876(5)	3255(12)	0086(19)
O(*c*,7)	7683(11)	2840(6)	9689(14)	0083(21)
O(*c*,8)	8414(10)	3298(6)	6975(13)	0106(21)
O(4,3)	0835(10)	2294(6)	3723(12)	0068(19)
O(4,8)	9695(10)	6892(6)	0056(13)	0091(20)
O(5,2)	0776(10)	5603(5)	3814(11)	0058(18)
O(5,7)	9679(11)	3545(6)	0103(14)	0136(22)
O(6,1)	0125(13)	9079(7)	3906(16)	0091(25)
O(6,9)	0360(11)	9765(6)	0181(13)	0062(21)
O(7,3)	9673(11)	7633(6)	6137(13)	0095(21)
O(8,2)	9770(12)	4235(7)	6178(15)	0138(24)
O(9,1)	9072(12)	0973(7)	6453(15)	0115(25)

*The temperature factor expression is exp $(-8\pi^2 U \sin^2 \theta/\lambda^2)$.

effect was not large enough to distinguish the absolute configuration.

Description

The structure is an example of polyhedral packing with three tetrahedra for every octahedron and with each corner shared between two polyhedra. The general bonding motif can be discussed by considering the average structure, shown in projection in Fig. 1, since no new major features arise in the extended structure.

The VO_6 octahedra lie in pseudo-hexagonal arrays with $[10\bar{1}]$ as the normal. Adjacent layers are related by the glide plane. One of the three-fold axes of the octahedra nearly parallels the *b* axis and another nearly parallels the layer direction. Each VO_6 group is bridged to six neighbouring VO_6 groups by phosphate groups. These lie in one of the two adjacent layers and lead to the three dimensional bonding.

The $(PO_3)_n$ chains snake their way between these octahedra while running parallel to *c*. Three distinct PO_4 groups form links in this chain. Although all the PO_4 groups are oriented with a two-fold axis roughly parallel to *b*, the configuration of the central PO_4 group is inverted with respect to the end members of the link. This permits the central PO_4 group to share oxygen atoms with VO_6 groups at the same *y* level and one such bridging occurs between a given VO_6

TABLE 2. Average bond geometry in $V(PO_3)_3$*

Bond	Length (Å)		
	Maximum	Minimum	Average
V—O	2.030(12)	1.949(13)	1.991
P—O—(P)	1.623(13)	1.538(13)	1.581
P—O—(V)	1.501(12)	1.461(14)	1.483

Bonds	Angle (deg)		
	Maximum	Minimum	Average
O—V—O (axial)	177.5(5)	170.0(5)	175.2
O—V—O	95.8(5)	84.2(5)	90.0
(P)—O—P—O—(P)	108.1(6)	98.7(7)	102.6
(P)—O—P—O—(V)	114.7(8)	102.6(8)	108.8
(V)—O—P—O—(V)	119.6(7)	115.6(8)	117.7

*A complete table of bond lengths and bond angles is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

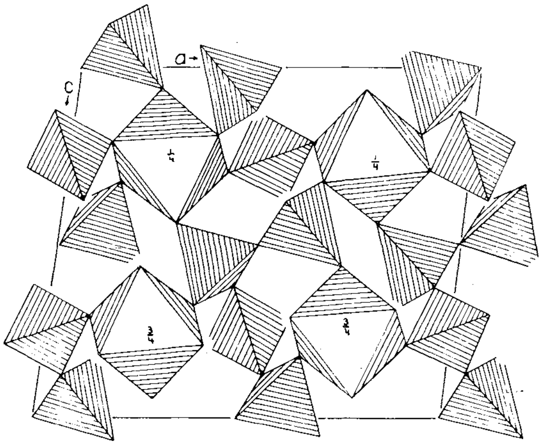

FIG. 1. The average structure of $V(PO_3)_3$ projected down the *b* axis. The vanadium ion lies within the octahedra and the phosphorus atom within the tetrahedra. The approximate *y* coordinates of the V^{3+} are shown. Oxygen atoms lie at the corners of the polyhedra.

group and each of its two VO_6 neighbours at the same *y* level. The remaining phosphate groups are shared between VO_6 groups whose *y* values differ by $\frac{1}{2}$ of the *b* axis of the average structure. Each VO_6 has four neighbouring metaphosphate chains. One oxygen is shared with each of the two chains connected to VO_6 at the central phosphate and two oxygens are shared with the other chains. The chains are rectangularly arranged about VO_6, with the rectangle defined by the vectors $\frac{1}{2}a$ and $\frac{1}{2}b$. Adjacent links in the chain have the configurations of the PO_4 groups inverted as required by the glide plane.

In the true structure all the tetrahedra are distorted with the P—O(—V) bond consistently shorter than the P—O(—P). The average values of these are 1.483 and 1.581 Å respectively (Table 2). Although the (V—)O—P—O(—V) bond angles are always the largest within a given tetrahedron, averaging 117.7 ± 0.8°, the deviation from ideality is not solely related to a displacement of the P from the center of the tetrahedron away from the P ions of the nearest neighbouring PO_4 groups. If the deviations, as measured by this angle, are to be considered random, the standard errors would have to increase by a factor of three. Even then, the deviations of the (P—)O—P—O(—P) angle would be significant since they range from 98.7 to 108.1°. Further, this angle is not always the smallest in the congruent PO_4 group. Thus the tetrahedra are not congruent and the deviations, perhaps examined with 3σ in mind, must be related to the angles of the polyhedra at the bridging oxygen. Since the distortions of the PO_4 are thus postulated to be related to the configuration of the four surrounding polyhedra the systematics of the effect is not apparent.

The angle subtended at the oxygen atom by the cations to which it is bonded ranges from 135 to 151° (9 values) when both cations are phosphorus and from 133 to 158° (18 values) otherwise. No strong correlation exists between these angles and the distortions of the polyhedra.

It is conceivable that V^{5+} could substitute for P^{5+} in the PO_4 groups, and this could be the source of some of the polyhedral distortions. The site populations of the tetrahedral cations were

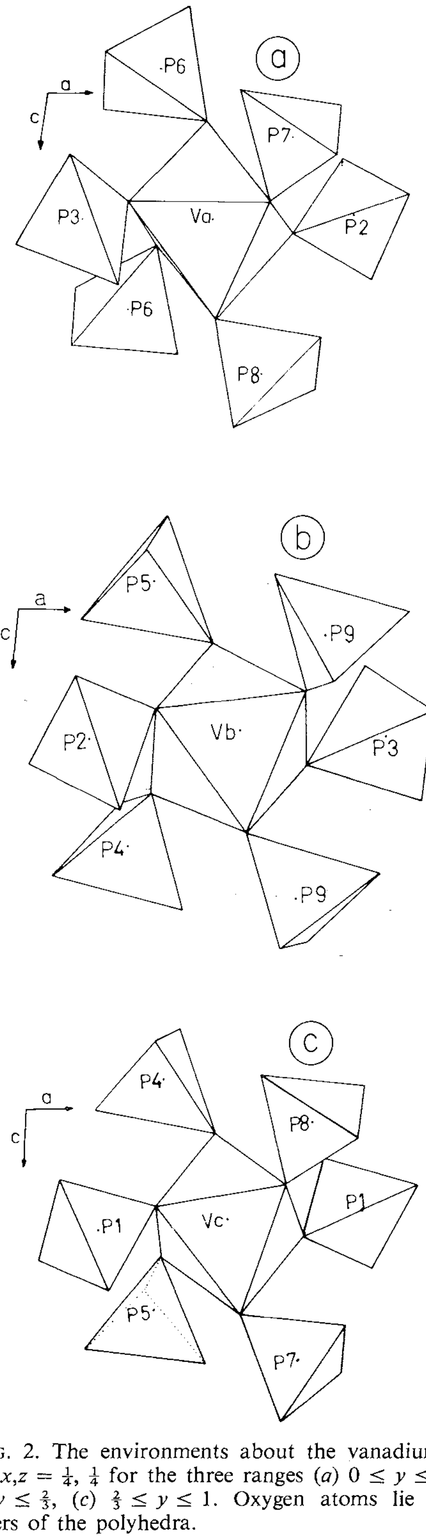

FIG. 2. The environments about the vanadium ions near $x,z = \frac{1}{4}, \frac{1}{4}$ for the three ranges (*a*) $0 \leq y \leq \frac{1}{3}$, (*b*) $\frac{1}{3} \leq y \leq \frac{2}{3}$, (*c*) $\frac{2}{3} \leq y \leq 1$. Oxygen atoms lie at the corners of the polyhedra.

varied. Changes at the 2σ level were found but not considered significant.

The displacement of the atoms from translational equivalence by $b/3$ was calculated. Two of the vanadium ions nearly superimpose, with the third displaced by about $\frac{1}{3}$ Å equatorial to b. A similar result applies to the P atoms in the set P(7), P(8), and P(9). The maximum displacement from superposition amongst the set P(4), P(5), and P(6) is $\frac{1}{4}$ Å whereas the set P(1), P(2), and P(3) has the largest set of displacements ranging from 0.16 to 0.51 Å. The major changes occur among the oxygen atoms. This results in a rotation of the polyhedra as shown in Fig. 2 *a*, *b*, *c*. Here the vanadium ions differing by about $\frac{1}{3}b$ and their nearest neighbour PO_4 environments are shown. In every case the phosphate groups sharing oxygen atoms with the upper faces of the VO_6 groups are inverted with respect to those sharing the oxygen atoms of the lower faces. Although the groups in Fig. 2*b* and Fig. 2*c* are substantially nearer to superposing with each other than with those in Fig. 2*a*, the displacements needed for superposition are large. In fact, the largest displacement from superposition of the oxygen atoms is over 1 Å with the average over 0.6 Å. Although it is possible to discuss the mutual angular displacements of each of the polyhedra it is not apparent that this will result in an understanding of the enlarged cell.

The intensities of five strong $k = 0 \pmod 3$ reflections and the 25 strongest $k \neq 0 \pmod 3$ reflections were measured at room temperature, 300°C, and 500°C. The higher temperature intensities were compared to the room temperature ones. The results shown in Fig. 3, indicate that, although the errors are large, the $k \neq 0 \pmod 3$ reflections become substantially weaker with increasing temperature while the $k = 0 \pmod 3$ reflections only weaken slightly. This suggests that the structure tends towards becoming the average structure at high temperatures. This average structure may be modified slightly, possibly through differential axis changes, from the room temperature one since there are some unacceptable bond lengths at room temperature. No evidence of a phase transition at higher temperatures was found by DTA in this laboratory confirming the results of Lavrov *et al.* (5).

Discussion

In light of the many distinct polymorphs of

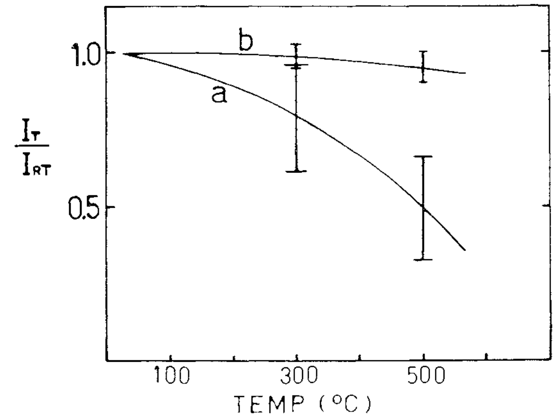

FIG. 3. The ratio of the intensity at various temperatures compared to room temperature for (*a*) 25 strongest reflections with $k \neq 0 \pmod 3$ and (*b*) 5 strong reflections with $k = 0 \pmod 3$.

$Cr(PO_3)_3$ (25) it is surprising that $V(PO_3)_3$ crystallizes as only one of these. The present structure is one common to one of the polymorphs of Al, Cr, Ti, and Mo trimetaphosphate. The structure of the cubic modification, found for Cr, Al, and Fe as cations, is based upon rings of four tetrahedra and thus bears no direct relationship to the present structure.

Unit cell dimensions of a hexagonal form are known for $Cr(PO_3)_3$ (25) and $Fe(PO_3)_3$. Although the present structure has some features of hexagonal packing, the structure is not easily transformed to a hexagonal or trigonal one. The direction of the chain should lie in a plane perpendicular or parallel to the unique axis of the hexagonal cell. In the present structure these chains are arrayed at the corners of a rectangle normal to the *c* axis and thus a substantial change will be needed to bond the VO_6 with two phosphate groups in each of three chains, as would be required for the hexagonal phase.

Deviations in the bond lengths of the two types of P—O bonds are expected based upon Baur's (30) correlation between bond length and bond strength. Thus the P—O(—P) bond with a bond strength at the oxygen atom of 2.5 will show a longer bond than the P—O(—V) where the bond strength is 1.75. The predicted bond length difference of 0.08 Å is comparable to 0.10 Å as found here.

The V^{3+}—O bond lengths and VO_6 geometry are as found in V_2O_3 (31) and other V_nO_{2n-1} structures (19, 31, 32), as well as for Al^{3+} in $Al(PO_3)_3$ (28). The higher valent vanadium systems are characterized by the short vanadyl bond and as a result, for these systems, the vanadium analogue of structures with the same stoichiometry can often differ. A case in point is MP_2O_7 where for M = Hf, Zr, Sn, Ti, and Si (10) the structures are isostructural and based upon a binary condensation of PO_4 groups. In the vanadium system the structure is written as $VO(PO_3)_2$ to emphasize the vanadyl bond and the infinite chain of corner sharing PO_4 groups.

$V(PO_3)_3$ is one of many structures and structure-types having each oxygen atom shared between only two cations. These structures involve cations with large charges in order to maintain reasonable bond orders on the oxygen atoms. Another structure where the ratio of the numbers of octahedra to tetrahedra is the same as in the present case is $VO(P_2SiO_8)$. This latter structure consists of chains of VO_6 groups containing tetravalent V and bridged by vanadyl groups (14, 15). The PO_4 groups form four membered rings bridged in the chain direction by SiO_4 groups. If P^{5+} were to fully substitute for Si^{4+}, the vanadium would be reduced yielding the same stoichiometry as in the present crystal. This form is unstable presumably because of the instability of the vanadyl bond for trivalent vanadium. Without these bonds the oxygen atom bridging the octahedra would be too underbonded.

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