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Determination of the Structure of $(VO)_3(PO_4)_2 \cdot 9H_2O$ by Powder X-ray Diffraction Analysis

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The structure of a novel vanadyl (IV) orthophosphate hydrate $(VO)_3(PO_4)_2 \cdot 9H_2O$ has been solved and refined with the use of high resolution X-ray powder diffraction data taken on Beamline X7A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The unit cell is monoclinic, $P2_1/n$, $Z = 2$, $a = 7.4315(1)$, $b = 16.6256(2)$, $c = 6.2954(1)$ Å, $\beta = 92.388°(1)$). The structure consists of large "squares" of $(VO_6–PO_4–)_4$ moieties linked together by bridging PO_4 tetrahedra and VO_6 octahedra forming a corrugated layered structure in three dimensions with water molecules located within the open cells.

Introduction

A number of vanadyl (IV) orthophosphate hydrates have been synthesized and characterized primarily by single crystal X-ray diffraction. These structures have illustrated the diverse manners in which phosphate tetrahedra and vanadyl octahedra can be linked together to form three dimensional networks. Most of these structures are layered materials in which hydrogen bonding between sheets of strongly covalently bonded VO_6 octahedra and PO_4 tetrahedra yield materials that undergo facile cleavage in the hydrogen bonded direction. The first such material described, $VO(PO_4) \cdot 2H_2O$ (*1*), consists of a two dimensional checkerboard arrangement of $VO_5(OH_2)$ and PO_4 moieties held together by hydrogen bonds to a water molecule in the third direction (stacking distance ca. 7.4 Å (*2*)). In $VO(HPO_4) \cdot \frac{1}{2}H_2O$ (*3*) and β-$VO(HPO_4) \cdot 2H_2O$ (*4*) the two dimensional, strongly covalently bonded framework is more complex. In the former compound, face-sharing vanadyl octahedra $(O_3V\text{-}[O_2][H_2O]\text{-}VO_3)$ are bridged by HPO_4 tetrahedra in the *ab* plane and are hydrogen bonded in the *c* di-

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rection with a stacking distance ca. 5.7 Å. The latter compound displays a rather complex series of strongly covalently bound tetrameric and octameric rings of alternating $VO_4(OH_2)_2$ and HPO_4 octahedral and tetrahedral fragments. These layers are held together in the *a* direction by hydrogen bonds with a stacking distance of 5.7 Å. In a departure from the layered materials just described, the structure of $VO(HPO_4) \cdot 4H_2O$ consists of double chains of alternating linked VO_6 and HPO_4 fragments running in the *a* direction, with hydrogen bonding between these chains and interchain water molecules completing the three dimensional structure.

The structure of $(VO)_3(PO_4)_2 \cdot 9H_2O$ is completely novel in two respects to the structures described above. The V/P ratio of the title compound is 3/2 and instead of a being low dimensional (one or two) layered or chain-like structure held together by hydrogen bonds in the remaining two or one directions, respectively, the title material consists of a three dimensional strongly covalently bonded network of vanadium octahedra and orthophosphate tetrahedra.

In each of the materials described above, precise control of temperature and hydration parameters are required in order to reproducibly synthesize the solid state structures produced. Because such control is a requirement, this suggests that a myriad of structure types, utilizing an almost infinite variety of linkages between VO_6 octahedra and PO_4 tetrahedra, is possible to produce, and the only limiting criteria is that of adequately characterizing the material after synthesis (i.e., structure solution based on diffraction data). In the past, the necessity of isolating single crystals of adequate size for single crystal data collection, structure solution, and refinement probably represented the greatest challenge to extending the number and variety of known vanadyl (IV) orthophosphate hydrate structure types. Recent advances in powder diffraction technology and analysis now make it possible, in principle, to solve and refine structures on the basis of powder diffraction data. The first such structure in this field appeared in 1989 (*4*), in which the structure of β-$VO(PO_4) \cdot 2H_2O$ was solved from powder data collected on a laboratory based powder diffractometer. In the work presented herein, we report the solution and refinement of the title structure based on ultra-high resolution powder diffraction data collected on the X7A beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL).

Experimental

Preparation of $VO(HPO_4) \cdot \frac{1}{2}H_2O$

Procedures for preparing $VO(HPO_4) \cdot \frac{1}{2}H_2O$ have been widely reported in the literature (*5–9*). The following procedure is convenient: 65.5 g of V_2O_5 (0.5 moles) was placed in a flask containing 1.5 L of isobutanol and 114.2 g of 85% phosphoric acid was added to the flask. The mixture was refluxed for 6–10 hr until a uniform blue solid and colorless supernatant liquid were obtained. The blue solid, $VO(HPO_4) \cdot \frac{1}{2}H_2O$, was recovered by filtration.

Preparation of $(VO)_3(PO_4)_2 \cdot 9H_2O$

$VO(HPO_4) \cdot \frac{1}{2}H_2O$ (15 g) was placed in a Soxhlet extraction thimble, which was then placed in a Soxhlet extraction apparatus. Distilled water (200 ml) was placed in the flask attached to the extraction apparatus. The entire apparatus and water were thoroughly flushed with argon to remove all air. The water was refluxed for 18 hr. A bright blue solid (0.8 g) was recovered from the water by filtration. The filtrate was returned to the extraction apparatus, and the extraction was continued for three more days. At the end of this time an additional 2.7 g of the bright blue solid were recovered by filtration. The two portions of bright blue solid exhibited identical XRD patterns. *Analysis:* 11 wt% P, 28 wt% V; TGA = 26.5 wt% lost (40–410°C); *Calcd. Empirical Formula:* $(VO)_3(PO_4)_2 \cdot 8H_2O$.

X-ray Diffraction Data

Powder data were initially collected at the synchrotron at Daresbury (U.K.). The powder was packed in a capillary and was continuously rotated throughout data collection. A wavelength of 1.5400 Å was selected by use of a double GE [220] crystal monochrometer. Data were collected from 3.0° to 60.0° with a step size of 0.002°. The unit cell was determined with the use of autoindexing software (*10*) and the pattern was decomposed to yield 107 integrated intensities. Based on these intensity data, structure solution was attempted by direct and Patterson methods. These attempts were not successful and it was determined that insufficient data were available for structure solution (d_{min} = 1.43). For this reason a more extensive data set was collected at beamline X7A at the NSLS at BNL.

TABLE I

CRYSTAL DATA FOR $(VO)_3(PO_4)_2 \cdot 9H_2O$

Lattice constants (P 2_1/n, no. 14, MW = 552.74, Z = 2)	
a(Å)	7.4316(1)
b	16.6256(2)
c	6.2954(1)
β (°)	92.388(1)
Powder data collection	
scan type	7°–75° (λ = 1.1967 Å)
2Θ limits	0.005 (13601 data points)
step size	12.9%
R_{prof}	13.5%
$R_{\mathrm{w\ prof}}$	10.2%
R_{exp}	6.9%
R_{Bragg}	
Halfwidth parameters[a]	
U	0.0141(3)
V	−0.0038(1)
W	0.0003(1)
K	0.0176(1)

[a] A Voigt function was used to model the Bragg peak profiles. The FWHM of the Gaussian portion varied with theta according to $(U \tan^2\Theta + V \tan\Theta + W)^{1/2}$, while the FWHM of the Lorentzian portion varied according to $K \sec \Theta$).

Diffraction data from 7° to 75° 2Θ (d_{min} = 0.98) were collected on a flat plate sample with a wavelength of 1.1967 Å (selected by use of a Si[111] double crystal monochromater). The trial unit cell from the earlier data set was utilized and 674 integrated intensities in the range 7° < 2Θ < 65° (d_{min} = 1.07) were extracted in space group $P2/m$. The extraction was performed with a local program based on the work of Le Bail *et al.* (*11*) and is more fully described in the discussion section. Systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$) suggested space group $P2_1/n$, $Z = 2$ (later confirmed by structure solution). Elimination of suspected systematic absences and reflections separated in two theta by less than ½ of the FWHM yielded a final data set of 450 reflections. Direct methods were used for structure solution; all heavy atoms and ½ of the oxygens were found in a MULTAN phased Fourier map. Straightforward application of full matrix least squares and difference Fourier maps (*12*) revealed the remaining atoms and confirmed the choice of unit cell and space group. No attempt was made to locate hydrogen atoms in the structure. Rietveld refinement of this model with a locally modified profile refinement package (*13*) utilizing the original powder data ($2\Theta_{\mathrm{max}}$ = 75°) has also confirmed the structure. In the final Rietveld refinement, a scale factor, two theta zero, four unit cell parameters, four profile, and an asymmetry parameter were varied. A Voigt function was used to model the diffraction profiles; U, V, W, and K parameters were varied (see Table I for a description of these parameters). The background was estimated by interpolation. In addition to these nonstructural parameters, all x, y, and z positional parameters (with the exception of V(2), situated on a center of symmetry) and thermal parameters were varied. The vanadium atoms were allowed to vibrate anisotropically, and at one point thermal parameters of O(7) and O(8) were also varied anisotropically to test a disordered model discussed below. This latter refinement converged to give R_p, R_{wp},

TABLE II

FINAL POSITIONAL[a] AND THERMAL PARAMETERS FOR $(VO)_3(PO_4)_2 \cdot 9H_2O$

Atom	x	y	z	B_{iso}
V(1)	0.1534(2)	0.2222(1)	0.5170(3)	[b]
V(2)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	[b]
P	0.5518(4)	0.3041(2)	0.5171(5)	1.81(7)
O(1)	0.2716(8)	0.1395(4)	0.5452(10)	3.3(2)
O(2)	0.3391(8)	0.3018(3)	0.5528(8)	2.0(2)
O(3)	0.1002(8)	0.2405(4)	0.8053(9)	2.9(2)
O(4)	0.1544(7)	0.2362(4)	0.2085(9)	1.6(1)
O(5)	−0.0031(7)	0.3413(3)	0.4632(9)	2.0(2)
O(6)	−0.1013(7)	0.1756(3)	0.4928(9)	1.1(1)
O(7)	0.3969(8)	0.4866(4)	0.7969(8)	3.5(2)
O(8)	0.7349(7)	0.5417(4)	0.6391(8)	2.8(2)
O(9)	0.6070(8)	0.3984(3)	0.5084(10)	3.9(2)
O(10)	0.9901(7)	0.5489(3)	0.1965(8)	3.2(2)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
V(1)	0.0070(5)	0.0014(1)	0.0038(5)	−.0003(2)	0.0021(4)	0.0004(2)
V(2)	0.0190(9)	0.0004(1)	0.0511(14)	0.0032(3)	−.0119(9)	0.0008(4)

[a] Fractional coordinates, the coordinates for V(2) were not refined.

[b] Anisotropic thermal parameters of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + B_{23}kl)]$ were employed for the V atoms.

and R_{Bragg} factors which were reduced significantly. However, one of the oxygen anisotropic thermal parameters converged to nonpositive definite values. This model was no longer pursued. Details of data collection and profile refinement are given in Table I, while final atomic positional and thermal parameters are listed in Table II. Plots of raw, calculated, and difference data are given in Fig. 1. Examination of Fig. 1 reveals that the major source of error in the Rietveld analysis is the misfit of the diffraction profiles. Prior work (*14*) has indicated that while the profile agreement factors are sensitive to experimental conditions, the Bragg or structure factor agreement factor is a better indicator of the quality of the refinement and resultant model.

Discussion

A local version of the Rietveld program (*15*), which had been adapted for synchrotron X-ray powder data with a Voigtain or pseudo-Voigtain peak shape function, was further modified to estimate observed intensities using the method of Le Bail *et al.* (*11*). During the extraction only the profile parameters (i.e., the unit cell, peak shape, and zero-point) are refined and the intensities are estimated based on the following iterative procedure. Initially, all of the observed structure factors are set to be equal to some arbitrary value, and then better estimates are obtained by Rietveld's algorithm for determining "observed" intensities. In this, the observed counts are allocated to the contributing reflections in the ratio of their calculated values. This method is much faster than those which include the intensities as least-square variables (*16*) since the maximum number of refined parameters is 13 (6 unit cell, 5 profile, asymmetry, and zero-point parameters) and is much better conditioned since there are no correlations between overlapping reflections. In general,

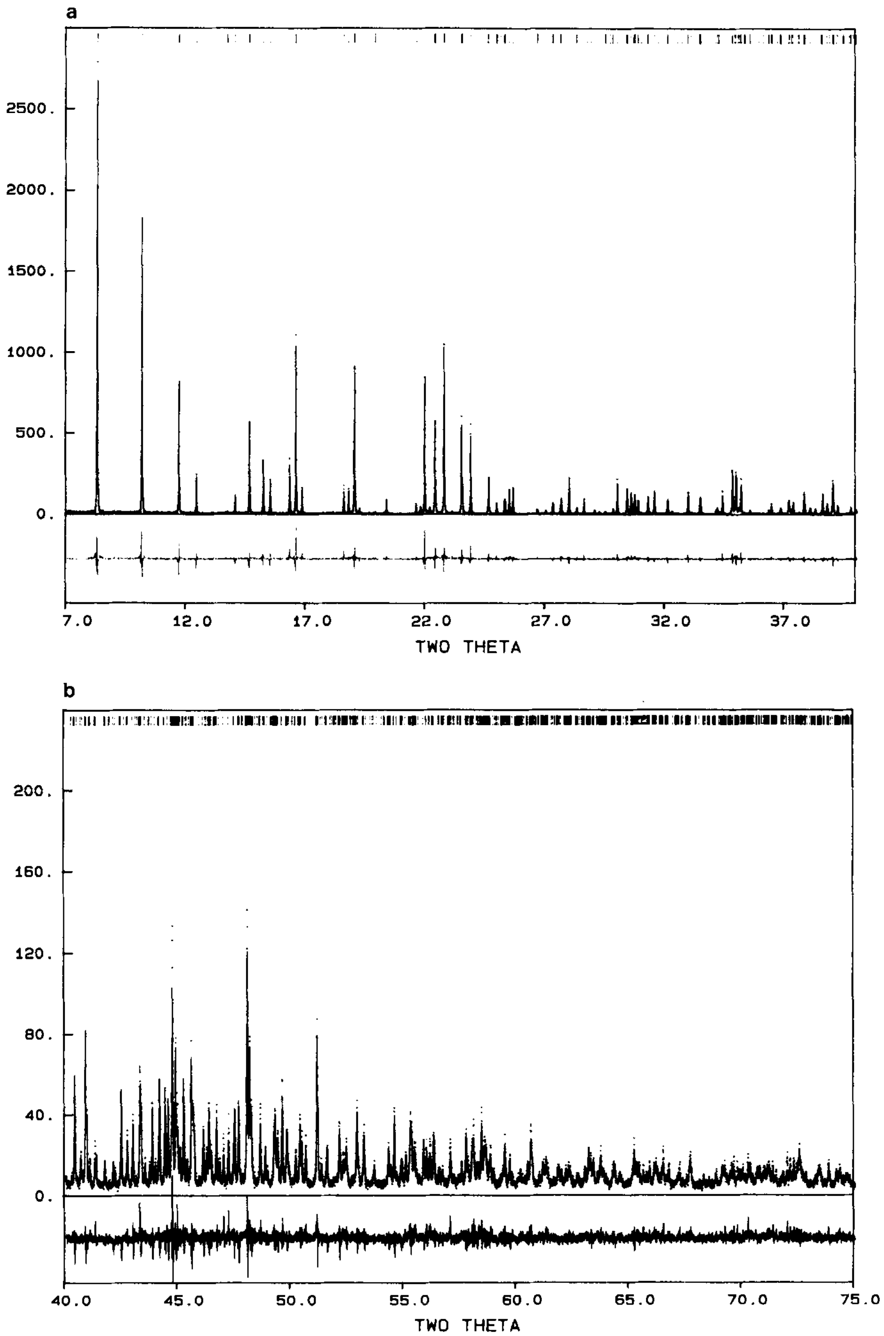

FIG. 1. Powder diffraction data (NSLS, August 1990) for $(VO)_3(PO_4)_2 \cdot 9H_2O$. Raw data are represented by points and calculated data by a continuous line. A difference plot is presented at the bottom of the figure. Marks at the top of the figure indicate Bragg peak locations.

it appears to give equally good estimates of the observed intensities. However, this procedure will tend to assign roughly equal intensities to closely overlapping peaks and, of course, exactly equal intensities to coincident peaks. Therefore, it is questionable whether these data should be included in the structure solution process. The criterion used in the present example stipulated that only peaks separated in two theta by at least ½ the FWHM (SEP > 0.5 FWHM) were used in the subsequent structure solution. A post mortem comparison of calculated intensities to intensities rejected on this basis, showed that this criteria was more stringent than necessary and that SEP > 0.4 FWHM would have been satisfactory.

The ultimate application of the method clearly depends on the instrumental resolution; with a well crystallized material it should be feasible to extract at least 2000 intensities from data collected at beamline X7A. For example, in the present material the resolution is degraded by a factor of 2–3 because of sample broadening effects.

Description of the 3-Dimensional Structure

The three dimensional structure of $(VO)_3(PO_4)_2 \cdot 9H_2O$ can be thought of as being built from a single unit, this unit being a corrugated 8-ring of four alternating VO_6 octahedra and four PO_4 tetrahedra in a chair-like conformation (shown in Fig. 2). This basic building block unit is inclined at a slight angle with respect to the bc crystallographic plane. Linkages of this building block with its symmetry related equivalents (generated by the *n* glide plane, that is, reflection and translation in the *ac* plane) via PO_4 tetrahedra and VO_6 octahedra in three dimensions produce the open structure illustrated in Fig. 3. The elongated hexagonally shaped open channels that run in the *a* and *c* directions are filled with two types of water molecules. The first type of water molecule (O(7), O(8)) is directly bound to V(2) atoms and the second type (O(10)) is not directly bound to either vanadium or phosphorus atoms, but is undoubtedly involved in a complex pattern of hydrogen bonding to vanadyl oxygens of V(2) and V(1).

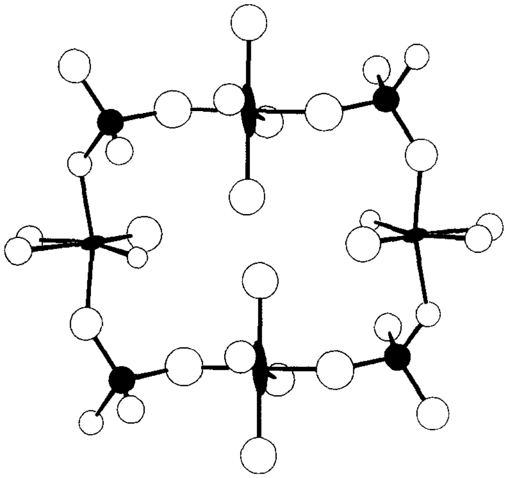

FIG. 2. A representation of the "eight ring" of four (PO_4) (shaded spheres) and four (VO_6) (darkened ellipsoids) groups arranged in a chair-like configuration. Linking these units together in three dimensions produces the overall structure.

Coordination about the Vanadium Atoms

The coordination geometry (see Table III and Fig. 4a) of $V(1)^{IV}$ is typical of that found for six coordinate V^{IV} with one short (1.637(5) Å) V–O(1) bond denoting the vanadyl oxygen trans to a rather long (2.313(5) Å) V–O(5) bond. This latter oxygen atom is identified as an oxygen of a water molecule. The planar coordination of V(1) to O(2), O(3), O(4) (bridging to phosphorus atoms), and O(6) round out the distorted octahedral coordination observed in V^{IV} octahedra. Due to its lack of apparent bonding to any other identified atom, O(6) is identified as an oxygen atom of a water molecule. In contrast to V(1), the coordination geometry about $V(2)^{IV}$ (Table III and Fig. 4b), situated on a crystallographic center of symmetry,

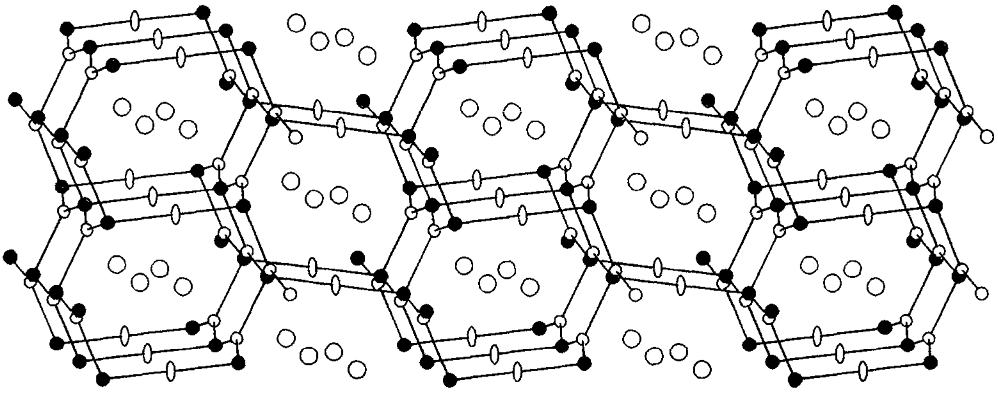

FIG. 3. A representation of the three dimensional structure of $(VO)_3(PO_4)_2 \cdot 9H_2O$. A framework of (PO_4) tetrahedra (filled spheres) and (VO_6) octahedra (open ellipsoids) encapsulate water molecules (large, unconnected open spheres). The water molecules are held in place via hydrogen bonding to water molecules within the $-(PO_4)-(VO_6)-$ framework.

TABLE III

Interatomic Distances (in Å) and Angles (in degrees) for $(VO)_3(PO_4)_2 \cdot 9H_2O$

		Distances[a]	
V(1)–O(1)	1.637	V(2)–O(7)	2.062 (×2)
V(1)–O(2)	1.918	V(2)–O(8)	2.041 (×2)
V(1)–O(3)	1.897	V(2)–O(9)	1.867 (×2)
V(1)–O(4)	1.957	P–O(2)	1.606
V(1)–O(5)	2.313	P–O(3)	1.581
V(1)–O(6)	2.043	P–O(4)	1.552
		P–O(9)	1.621
		Angles[b]	
O(1)–V(1)–O(2)	98.5	O(7)–V(2)–O(8)	90.0
O(1)–V(1)–O(3)	100.3	O(7)–V(2)–O(9)	92.6
O(1)–V(1)–O(4)	99.4	O(8)–V(2)–O(9)	89.1
O(1)–V(1)–O(5)	175.1		
O(1)–V(1)–O(6)	101.4	O(2)–P–O(3)	112.3
O(2)–V(1)–O(3)	86.3	O(2)–P–O(4)	107.5
O(2)–V(1)–O(4)	91.5	O(2)–P–O(9)	107.8
O(2)–V(1)–O(5)	77.9	O(3)–P–O(4)	107.4
O(2)–V(1)–O(6)	159.3	O(3)–P–O(9)	111.9
O(3)–V(1)–O(4)	160.3	O(4)–P–O(9)	109.9
O(3)–V(1)–O(5)	82.9		
O(3)–V(1)–O(6)	82.4		

[a] Estimated standard deviations for V–O and P–O distances is 0.005.

[b] Symmetry constraints require O–V(2)–O′ to be 180°, and the angles O(*a*)–V(2)–O(*b*) and O(*a*)–V(2)–O(*b*)′ to be complementary, where primes denote oxygen atoms related by a center of inversion. Estimated standard deviations for angles are 0.5°.

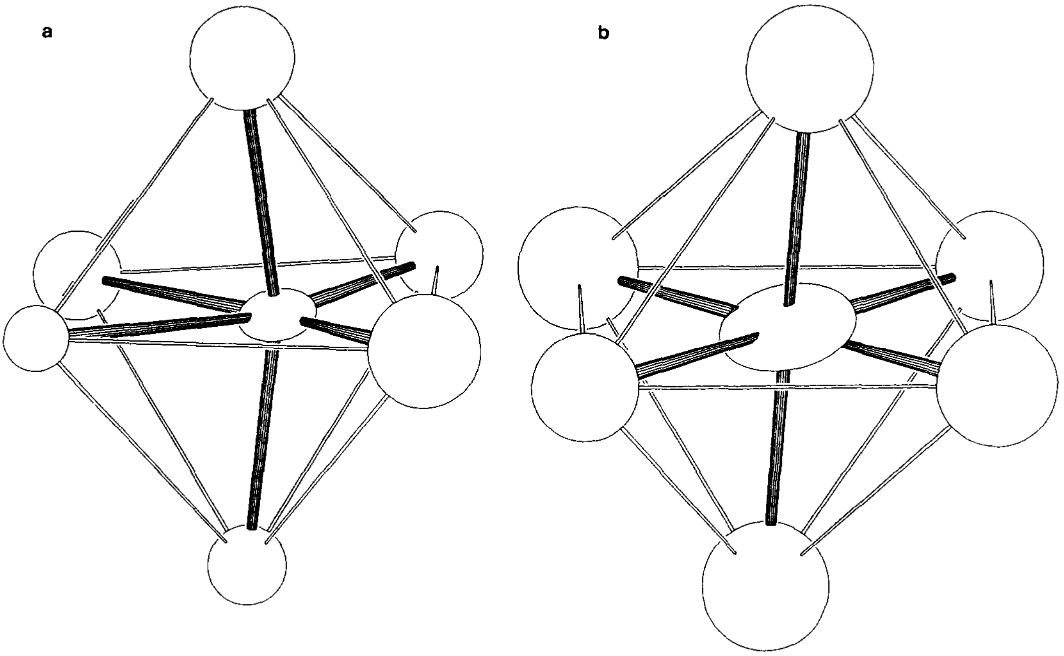

FIG. 4. (a) The coordination geometry of V(1) is "normal" (i.e., quite asymmetric) owing to the vanadyl (V=O) oxygen. (b) The coordination geometry of V(2) appears to be very symmetric but is actually symtomatic of the disorder in the V(2) positional parameters. The V(2) atom is believed to be disordered in the *X–Y* plane (of the figure), alternately forming vanadyl groups with each of the oxygens in the *x–y* plane.

appears to be quite different. The VO_6 vanadium octahedron of V(2) is held in the three-dimensional $-VO_6-PO_4-$network via two (O(9)) oxygen atoms to two orthophosphate groups. The remaining oxygen atoms in the $V(2)O_6$ coordination sphere are not orthophosphate oxygens. Additionally, the coordination geometry is quite regular, as is required by the center of symmetry. If the average V(2)–O distances recorded in Table II were an accurate representation of the coordination geometry, this would be quite unusual, as V^{IV} species are well known to form vanadyl groups (*17*) (V=O) as is the case for V(1). An examination of the anisotropic thermal parameters for V(2), however, give a clear indication of the true nature of the coordination geometry of this vanadium atom. As illustrated in Fig. 4b, the thermal ellipsoid describing V(2) is pancake-like with the large basal plane approximately defined by O(7)–O(8)–O(7′)–O(8′) (the primes denoting atoms related by a center of symmetry). Rather than representing thermal vibration, this flat thermal ellipsoid is more likely due to disorder in the V(2) atomic position. The true V(2) positions are probably best described by a fourfold disordered model in which four $\frac{1}{4}$-weighted vanadium atoms are situated off the center of symmetry toward the four oxygen atoms. This model also requires that each of the four basal oxygens be a vanadyl oxygen $\frac{1}{4}$ of the time, and oxygens of water molecules $\frac{3}{4}$ of the time. If this were the case, the thermal vibrations of O(7) and O(8) would also display similar anisotropies. A structure refinement based on powder data allowing anisotropic thermal motion for these atoms, did converge to similarly shaped, albeit physically unrealistic, thermal ellipsoids.

Acknowledgments

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