

LETTERS TO THE EDITOR

Crystal Structure of β -VO(HPO₄) · 2H₂O Solved from X-Ray Powder Diffraction

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The crystal structure of β -VO(HPO₄) · 2H₂O has been determined from X-ray powder diffraction data. The cell is triclinic (space group $P\bar{1}$, $Z = 4$) with $a = 5.659(2)$ Å, $b = 7.578(4)$ Å, $c = 12.623(5)$ Å, $\alpha = 89.66(2)^\circ$, $\beta = 102.14(2)^\circ$, and $\gamma = 92.23(2)^\circ$. Starting positional parameters were obtained by direct methods applied to 640 reflections which are derived from a modified Rietveld analysis working without structural model. The structure was refined using Rietveld profile refinement principles. The final reliability factors were $R_1 = 0.039$, $R_p = 0.076$, and $R_{wp} = 0.092$. The structure is built up of chains of corner-shared VO₄(H₂O)₂ octahedra and (HPO₄) tetrahedra alternated along the c crystallographic axis. These chains are interconnected through HPO₄ groups forming layers stacked in the [100] direction. In contrast to α -VO(HPO₄) · 2H₂O, there are no isolated water molecules between the layers.

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Introduction

The oxovanadium(V) phosphate dihydrate can be considered as a chemical precursor of a wide family of oxovanadium(IV) or (V) derivatives (1-4). Among them, several oxovanadium(IV) compounds having the general stoichiometry VO(H₂PO₄)_x · nH₂O have been studied in detail owing to their catalytic relevance (5, 6). The

oxovanadium(IV) hydrogenphosphates, which can be considered derivatives of the VOPO₄ · 2H₂O obtained by redox intercalation of protons (7), are the most widely used precursors of the active phase for n -butane oxidation.

These materials display a large variety of crystal structures owing to the great number of possible connectivity patterns among VO₆ octahedra and PO₄ tetrahedra (8-13).

Such a diversity of patterns results in a wide set of vanadium–vanadium bridging modes suitable to support magnetic interactions (14, 15).

The synthesis of some new oxovanadium(IV) hydrogenphosphates has been recently reported (7). It seems clear that the knowledge of their crystal structures would allow one to clarify both the catalytic activity of the vanadium–phosphate system and the relationship between the magnetic behavior and the topology of the bridges in the $\text{VO}_6\text{-PO}_4$ entities.

The application of new powder diffraction methodologies when single crystals are not available, as occurs with $\beta\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$, has now proved its capacity for crystal structure determination. The structures of several phosphates, including that of $\alpha\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ (12), have been recently solved in this way (16). We present here the full crystal structure determination of another form of the latter compound, $\beta\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$, from its X-ray powder pattern. It is to be noted that a wrong formulation was previously proposed for this material, i.e., $\text{VO}(\text{HPO}_4) \cdot 1.5\text{H}_2\text{O}$ (3).

Experimental

Sample preparation. We described elsewhere the synthetic strategy of all $\text{VO}(\text{HPO}_4) \cdot n\text{H}_2\text{O}$ known compounds (3, 7). The obtention of a given phase depends drastically on the solvent composition and on the reaction time.

The $\beta\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ was prepared by heating to reflux (at 50°C) for 50 hr a mixture of 4.17 g of V_2O_5 , 24 cm^3 of H_3PO_4 85%, and 4 cm^3 of HI 57% in an acetone water mixture in the ratio 27:1. The reaction time of the process may be reduced to 24 hr by using a lower acetone–water ratio (ca. 16). However, in this case, a more prolonged reflux time leads to the $\alpha\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ phase (7, 12).

Data collection. The powder diffraction

pattern was scanned in steps of 0.02° (2θ) over the angular range $10\text{--}95^\circ$ (2θ) during 35 sec per step, using a Siemens D 501 diffractometer. The $\text{CuK}\alpha$ radiation was selected by a graphite monochromator in the reflected beam. In order to minimize the orientation effects, the sample holder described by MacMurdie *et al.* (17) was used. Two impurities were detected: $\alpha\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ and $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$; the integrated intensities of the most intense reflections of these phases were less than 1% that of the major phase.

Data Analysis

Indexing was realized using the program TREOR (18). The most probable solution was triclinic. After reduction of the cell to a pseudomonoclinic one, the refined parameters were $a = 5.660(3)\text{ \AA}$, $b = 7.578(4)\text{ \AA}$, $c = 12.623(5)\text{ \AA}$, $\alpha = 89.66(2)^\circ$, $\beta = 102.14(2)^\circ$, and $\gamma = 92.23(2)^\circ$. The calculated density for $Z = 4$ was 2.50 g cm^{-3} .

In order to obtain the maximum number of individual intensities, the profile fitting procedure with cell constraints described in (19) was applied. When possible, excluded zones were used in order to eliminate some contributions of the two impurities. The refinement without structural model, already described elsewhere (12), led to the conventional Rietveld profile reliability factors $R_p = 7.5\%$ and $R_{wp} = 9.4\%$ for 967 reflections up to 95° (2θ). Intensities were then converted into structure factors and used as input data for the SHELX program (20). Atomic scattering factors and anomalous dispersion correction were obtained from the "International Tables for X-ray Crystallography" (21). The application of the fast automatic centrosymmetric direct methods facilities of the SHELX76 program, using the 640 first reflections of the powder pattern, gave a first set of coordinates of 2 vanadium, 2 phosphorus, and 10 oxygen atoms. A new profile Rietveld re-

TABLE I
DETAILS OF RIETVELD REFINEMENT

Lattice constants	a (Å),	b (Å)	c (Å)	α (°),	β (°),	γ (°)
	5.659(2),	7.578(4),	12.623(5),	89.66(2),	102.14(2),	92.23(2),
Volume (Å ³)	528.86					
Density (g cm ⁻³)	2.50					
Space group	$P\bar{1}$					
2θ range (°)	10–95					
Step scan increment (2θ)	0.02					
No. of reflections	967					
No. of structural parameters	54					
Profile parameters (definition in (19)):						
	$U_1 = 0.79(4)$,	$V_1 = -0.53(3)$,	$W_1 = 0.258(6)$			
	$U_2 = 0$,	$V_2 = 0$,	$W_2 = 1.204(9)$			
	$C = 0.082(2)$,	$D = -0.427(7)$				
Zero point (2θ)	0.068(2)					
Reliability factors (%)	$R_1 = 3.89$, $R_p = 7.64$, $R_{wp} = 9.18$, $R_E = 2.39$					

finement using this set of atomic positions as structural model, followed by Fourier difference syntheses, yielded the position of the remaining oxygen atoms. Hydrogen atoms were not detected. Details of the final refinements are given in Table I and final atomic coordinates of nonhydrogen at-

oms in Table II. Figure 1 shows the observed and calculated patterns.

Description of the Structure

Projections of the structure along the [100] and [010] directions are shown in Figs. 2 and 3. The crystal structure consists of vanadyl hydrogen phosphate layers stacked along the a axis and held together by hydrogen bonding. Contrary to the α -VO(HPO₄) · 2H₂O (12), there is no isolated water molecules between the layers. The layer organization may be described in two ways:

—Chains of alternating VO₆ octahedra and PO₄ tetrahedra sharing corners and running along the c direction. In each chain, both the apical hydroxyl oxygen of the HPO₄ groups and the oxygen of the VO²⁺ groups are pointing toward the same adjacent layer. This direction is just the opposite in the neighboring chains. The HPO₄ groups in a chain are alternatively connected to the two neighboring chains in the b direction. This network generates two kinds of rings in the layer: a classical tetrameric small one built up from two VO₆ octahedra *cis*-connected through two PO₄ tetra-

TABLE II
POSITIONAL AND THERMAL PARAMETERS FOR
 β -VO(HPO₄) · 2H₂O

Atom	x/a	y/b	z/c	β (Å ²)
V(1)	0.8860(7)	0.2762(5)	0.3628(3)	0.38(4)
V(2)	0.9087(7)	0.2197(5)	0.8621(3)	0.38(4)
P(1)	0.831(1)	0.3440(8)	0.6101(5)	1.66(9)
P(2)	0.847(1)	0.1605(7)	0.1070(5)	1.66(9)
O(1)	0.963(2)	0.269(1)	0.713(1)	2.74(9)
O(2)	0.958(2)	0.267(1)	0.219(1)	2.74(9)
O(3)	0.959(2)	0.237(1)	0.023(1)	2.74(9)
O(4)	0.882(2)	0.229(1)	0.509(1)	2.74(9)
O(5)	0.265(2)	0.382(1)	0.903(1)	2.74(9)
O(6)	0.224(2)	0.112(1)	0.406(1)	2.74(9)
O(7)	0.860(2)	0.543(2)	0.5976(9)	2.74(9)
O(8)	0.858(2)	0.962(2)	0.1211(9)	2.74(9)
O(9)	0.646(2)	0.400(1)	0.3312(8)	2.74(9)
O(10)	0.671(2)	0.099(1)	0.8364(9)	2.74(9)
O(11)	0.550(2)	0.3136(9)	0.603(1)	2.74(9)
O(12)	0.548(2)	0.197(1)	0.0805(9)	2.74(9)
O(13)	0.726(2)	0.019(1)	0.3417(9)	2.74(9)
O(14)	0.765(2)	0.466(1)	0.860(1)	2.74(9)

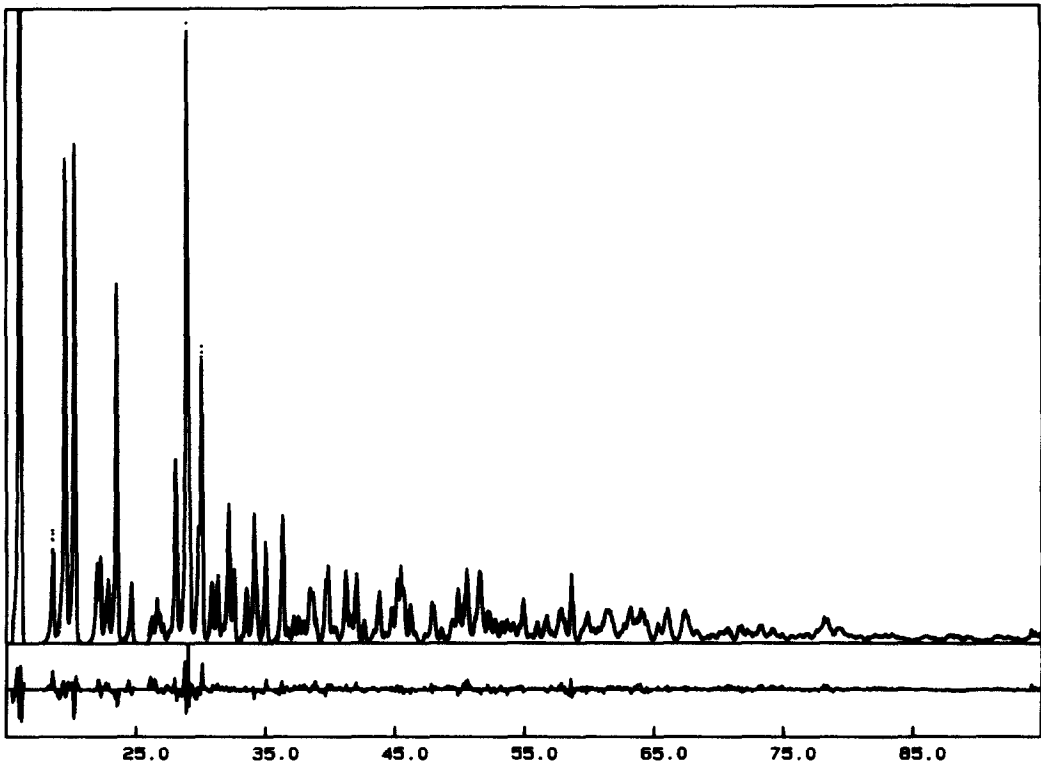


FIG. 1. Observed (···) and calculated (—) patterns of $\beta\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$. The difference pattern is at the same scale.

hedra, and a larger one elongated in the c direction and formed by four VO_6 octahedra interconnected through PO_4 tetrahedra. This way, piling up of the layers gives rise to channels along the a axis.

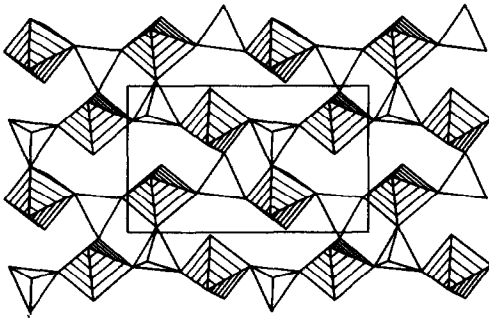


FIG. 2. Projection of the structure of $\beta\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ along [100].

—Two nearly identical but independent units of two octahedra share corners with two tetrahedra related by the centers of inversion of the cell. These units share four corners with four other similar units. One can note that the two independent units are *quasi*-related by the symmetry operation $x, 1/2 - y, 1/2 + z$. So, if the α and γ angles

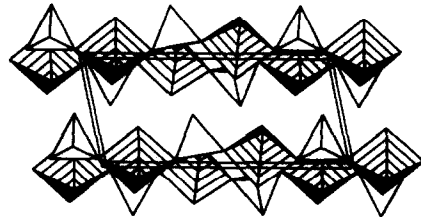


FIG. 3. Projection of the structure of $\beta\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ along [010].

were 90° the space group would be $P2_1/c$. The atomic coordinates in Table II are arranged in order to demonstrate this fact, which justifies the final choice of the cell. Refinement attempted with the strict constraint cited above led to $R_1 = 7\%$ instead of 3% for the real cell.

At this stage of the description, a valence bond analysis (VBA) using Brown's data (22, 24) provides a better understanding of the structure (Table IV) concerning the details of the cationic coordination, the location of OH groups and H_2O molecules, and the hydrogen bonds. Indeed, for the last two points, it must be recalled (22) that in H_2O molecules or OH ions, the O–H bond strength corresponds approximately to 0.8 valence unit. Therefore, if the oxygen of OH or H_2O is also bonded to one (or several) cations (including H of another water molecule, which can give $1 - 0.8 = 0.2$ v.u.), it must receive from this cation $2.0 - 0.8 = 1.2$ v.u. (if OH) or $2.0 - (2 * 0.8) = 0.4$ v.u. (if H_2O) to complete its base strength to 2.0. The difference between 2.0 and the calculated bond valence of oxygen gives information on the nature of the ligands around V and P, and on the oxygens involved in hydrogen bonding.

The vanadium atoms are coordinated in a *pseudo- C_{4v}* distorted octahedral environment (really C_1). Both V(1) and V(2) atoms show a short V–O distance ($d(V(1)–O(9)) = 1.66 \text{ \AA}$, and $d(V(2)–O(10)) = 1.57 \text{ \AA}$) corresponding to the double bond of the oxovanadium(IV) group. The first water molecule of these octahedral, corresponding to O6 and O5 for V1 and V2, respectively, is in *trans* position to the double bond ($d(V–OH_2) = 2.3 \text{ \AA}$) and weakly bonded to vanadium (0.2 v.u.). Therefore, it may be expected that O–H bonds within this type of water molecule will be shorter (0.90 \AA) than the common O–H distance (0.96 \AA). The equatorial plane of the VO_6 octahedra is defined by the four remaining oxygen atoms.

Three of them link the octahedra to hydrogenphosphate groups and the fourth, pointing alternatively to the positive and negative sense of the *b* axis along each chain, corresponds to a water molecule as it appears for O13 and O14 in the VBA analysis of Table IV. These water molecules are normally bounded to vanadium atoms (0.40 v.u.); this precludes normal O–H bond lengths in this H_2O molecule (0.90–0.93 \AA). This kind of polyhedron, very similar to that observed in $VO(HPO_4) \cdot 4H_2O$ (9), is characteristic of oxovanadium(IV) in other phosphate systems. One must note however the slight difference between V1 and V2 octahedra concerning the double bond. Whereas V(2)–O(10) (bond length 1.57 \AA) completely saturates the base strength of O10, it is not the case for V(1)–O(9) (1.66 \AA) for which 0.5 v.u. are available on O9 for further weak hydrogen bonding.

From Table III, it is clear that the PO_4

TABLE III
SELECTED INTERATOMIC DISTANCES (\AA) AND
ANGLES ($^\circ$) IN $\beta\text{-VO}(HPO_4) \cdot 2H_2O$

VO_6 groups			
V(1)–O(9)	1.66(1)	V(2)–O(10)	1.57(1)
V(1)–O(4)	1.88(1)	V(2)–O(8)	1.93(1)
V(1)–O(7)	1.94(1)	V(2)–O(3)	1.99(1)
V(1)–O(2)	1.95(1)	V(2)–O(1)	2.01(2)
V(1)–O(13)	2.11(1)	V(2)–O(14)	2.06(1)
V(1)–O(6)	2.29(1)	V(2)–O(5)	2.29(1)
O(9)–V(1)–O(4)	99.7(9)	O(10)–V(2)–O(8)	98.6(9)
O(9)–V(1)–O(7)	100.3(9)	O(10)–V(2)–O(3)	100.3(9)
O(9)–V(1)–O(2)	97.2(9)	O(10)–V(2)–O(1)	101.2(9)
O(9)–V(1)–O(13)	101.7(9)	O(10)–V(2)–O(14)	100.8(9)
O(9)–V(1)–O(6)	178.4(9)	O(10)–V(2)–O(5)	176(1)
O(4)–V(1)–O(7)	91.9(9)	O(8)–V(2)–O(3)	89.3(9)
O(4)–V(1)–O(2)	162.7(9)	O(8)–V(2)–O(1)	89.9(9)
O(4)–V(1)–O(13)	82.2(9)	O(8)–V(2)–O(14)	160.5(9)
PO_4 groups			
P(1)–O(1)	1.47(1)	P(2)–O(3)	1.46(2)
P(1)–O(7)	1.52(1)	P(2)–O(8)	1.52(1)
P(1)–O(11)	1.58(1)	P(2)–O(2)	1.63(1)
P(1)–O(4)	1.63(1)	P(2)–O(12)	1.58(1)
O(1)–P(1)–O(7)	116.1(9)	O(3)–P(2)–O(8)	116.5(9)
O(1)–P(1)–O(11)	108(1)	O(3)–P(2)–O(2)	107.6(9)
O(1)–P(1)–O(4)	109(1)	O(3)–P(2)–O(12)	110.5(9)
O(7)–P(1)–O(11)	103(1)	O(8)–P(2)–O(2)	112.5(9)
O(7)–P(1)–O(4)	114.5(9)	O(8)–P(2)–O(12)	104(1)
O(11)–P(1)–O(4)	103.9(9)	O(2)–P(2)–O(12)	105(1)

TABLE IV
 VALANCE BOND ANALYSIS OF β -VO(HPO₄) · 2H₂O USING THE ZACHARIASEN LAW (23)

	V(1)	V(2)	P(1)	P(2)	Σ ($\Sigma_{\text{exp}} = 2$)	Comments ^a
O(1)		2.01(1) <u>0.50(2)</u>	1.47(1) <u>1.51(4)</u>		<u>2.01</u>	s
O(2)	1.95(1) <u>0.60(2)</u>			1.63(1) <u>0.97(3)</u>	<u>1.57</u>	h.b.
O(3)		1.99(1) <u>0.53(2)</u>		1.46(1) <u>1.56(3)</u>	<u>2.09</u>	s
O(4)	1.88(1) <u>0.75(3)</u>		1.63(1) <u>0.97(3)</u>		<u>1.72</u>	h.b.
O(5)		2.29(1) <u>0.20(1)</u>			<u>0.20</u>	w
O(6)	2.29(1) <u>0.20(1)</u>				<u>0.20</u>	w
O(7)	1.94(1) <u>0.62(2)</u>		1.52(1) <u>1.32(4)</u>		<u>1.97</u>	s
O(8)		1.93(1) <u>0.65(2)</u>		1.52(1) <u>1.32(4)</u>	<u>1.94</u>	s
O(9)	1.66(1) <u>1.50(5)</u>				<u>1.50</u>	h.b.
O(10)		1.57(1) <u>1.99(2)</u>			<u>1.99</u>	s
O(11)			1.58(1) <u>1.11(4)</u>		<u>1.11</u>	hy
O(12)				1.58(1) <u>1.11(4)</u>	<u>1.11</u>	hy
O(13)	2.11(1) <u>0.36(2)</u>				<u>0.36</u>	w
O(14)		2.06(1) <u>0.43(2)</u>			<u>0.43</u>	w
Σ	<u>4.03</u>	<u>4.30</u>	<u>4.91</u>	<u>4.96</u>		
Σ_{expected}	4	4	5	5		

Note. $s = \exp[(R_0 - R)/B]$ with $R_0 = 1.62$, $B = 0.36$ for P and $R_0 = 1.79$, $B = 0.319$ for V. In each case of this table, the first line corresponds to the distance (\AA) and the second line to the bond strength in valence units (underlined).

^a s, saturated; h.b., hydrogen bonding on the concerned atom; hy, the oxygen corresponds to the OH group bonded to P; w, the oxygen corresponds to a water molecule.

tetrahedra are slightly distorted, as in other oxovanadium(IV) phosphates (9, 12, 13). Obviously (Table IV), O11 and O12 apical oxygens correspond to the O-H group of the hydrogenphosphate. As 0.90 v.u. are

missing to these oxygens, they would be provided by H at $R = 0.91 \text{ \AA}$, using the power law $s_H = (R/R_0)^{-N}$ with $R_0 = 0.87 \text{ \AA}$ and $N = 2.2$ (24). Finally, the intra- and interlayer hydrogen bonding involves O2,

O4, O5, O6, O9, O11–O14, as indicated in Table IV. The hydrogen bond framework involves very likely $\text{PO}-\text{H}\cdots\text{O}=\text{V}$ and *trans*- $\text{OH}_2-(\text{OH})\text{P}$ networks. In any case the hydrogen bonds would be weak, as predicted from the analysis of the IR spectrum of this compound (7).

In a recent work (7), it has been proposed that the known monohydrogenphosphate phases can be classified in three different structural types, namely Type I, $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$; Type II, $\alpha\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$; Type III, $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$ and $\beta\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$. Particularly, the β -dihydrate appears as intermediate in the thermal treatment of the tetrahydrate from both thermogravimetric and thermodiffraction experiments. Moreover, the structure of $\beta\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ is closely related with that of $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$ (9). Both compounds present a similar arrangement of VO_6 octahedra and PO_4 tetrahedra forming alternating chains which lie along the *c* direction in the β -dihydrate and along the *a* direction in the tetrahydrate (Fig. 4). The coordination geometry around both vanadium and phosphorus atoms is similar in both structures. Each phosphate group contains three oxygen atoms (shared with three different vanadium atoms) and a hydroxyl group. The vanadium atoms show very similar coordination polyhedra, having a water molecule *trans*-coordinated to the axial $\text{V}=\text{O}$ group and a second coordinated water molecule in the equatorial plane of the VO_6 octahedra. The similarity of these structures suggests that the dehydration of the tetrahydrate into the dihydrate may proceed topotactically. However, several ways for the reorganization of the infinite double chains that lie parallel to the *a* axis (6.379 Å) of the tetrahydrate may be imagined to give the interconnected single chains running in the *c* direction (12.623 Å = 2 * 6.379 Å) of the β -dihydrate. All the possible models that we imagined need to break some bonds (at least two or four per unit cell), to rotate some polyhedra, and to reconstruct the bonds. Only a careful study of the orientational relation (if any) between the two phases when dehydrating a single crystal of the tetrahydrate could give us some arguments, but fragmentation of the crystal will probably occur, owing to the large volume variation. A neutron thermodiffraction (powder) experiment is planned at ILL, which could also be informative.

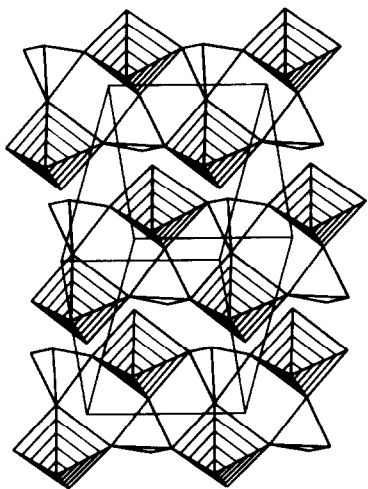


FIG. 4. View of the infinite double chains of VO_6 octahedra and PO_4 tetrahedra running along the [100] direction in $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$.

dium and phosphorus atoms is similar in both structures. Each phosphate group contains three oxygen atoms (shared with three different vanadium atoms) and a hydroxyl group. The vanadium atoms show very similar coordination polyhedra, having a water molecule *trans*-coordinated to the axial $\text{V}=\text{O}$ group and a second coordinated water molecule in the equatorial plane of the VO_6 octahedra. The similarity of these structures suggests that the dehydration of the tetrahydrate into the dihydrate may proceed topotactically. However, several ways for the reorganization of the infinite double chains that lie parallel to the *a* axis (6.379 Å) of the tetrahydrate may be imagined to give the interconnected single chains running in the *c* direction (12.623 Å = 2 * 6.379 Å) of the β -dihydrate. All the possible models that we imagined need to break some bonds (at least two or four per unit cell), to rotate some polyhedra, and to reconstruct the bonds. Only a careful study of the orientational relation (if any) between the two phases when dehydrating a single crystal of the tetrahydrate could give us some arguments, but fragmentation of the crystal will probably occur, owing to the large volume variation. A neutron thermodiffraction (powder) experiment is planned at ILL, which could also be informative.

Conclusion

An interesting feature concerning the crystal structures of all the known oxovanadium(IV) phosphates is the presence of a simple structural unit built up of two VO_6 octahedra *cis*-bridged through two $\mu(\text{OO}')$ -phosphate tetrahedra (3). Both the inner topology of these tetrameric units and the nature of their connectivity are characteristic for each crystalline phase. Thus, the degree of coplanarity of the equatorial planes of the VO_6 octahedra, the possible

existence of an inversion center, and the relative orientation of the HPO_4 and VO_6 units are significant as topological parameters. On the other hand, there exists a correlation between the connectivity and the hydration degree. In fact, the number of connections between the tetrameric units decreases as the hydration degree increases (12 for the $(\text{VO})_2\text{P}_2\text{O}_7$, 8 or 10 for the $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$, 8 for the $\alpha\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$, and 4 for $\beta\text{-VO}(\text{HPO}_4) \cdot 2\text{H}_2\text{O}$ and $\text{VO}(\text{HPO}_4) \cdot 4\text{H}_2\text{O}$). A detailed crystal-chemistry comparative analysis of all these structures will be published later.

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