Na$_5$V$_2$P$_3$O$_{14}$ · H$_2$O, a Tetravalent Vanadium Phosphate with a Layer Structure and a Pure Pyramidal Coordination of V(IV)

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A new sodium vanadium IV phosphate, Na$_5$V$_2$P$_3$O$_{14}$ · H$_2$O, has been prepared at 973 K under 2.3 Kbar hydrothermal pressure. Its structure was determined from single-crystal X-ray diffraction data. It crystallizes in the monoclinic space group *Cm* with $a = 6.3089(4)$ Å, $b = 20.1038(8)$ Å, $c = 5.1172(5)$ Å, $\beta = 91.134(6)°$, $V = 648.9$ Å^3, $Z = 2$, $R = 0.049$, and $R_w = 0.060$ for 703 unique reflections with $I > 3\sigma(I)$. The structure of this phase consists of [V$_2$P$_3$O$_{14}$]$_x$ layers interleaved with sodium cations and water molecules. The latter layers are built up from corner-sharing VO$_5$ pyramids and PO$_4$ tetrahedra. They are described in terms of [V$_2$P$_2$O$_{12}$]$_x$ double chains running along **a** connected by single PO$_4$ tetrahedra and forming large nine-sided windows. The distribution of the sodium cations and water molecules intercalated between the layers is discussed. The tetravalent state of vanadium is confirmed by magnetic measurements, whereas the presence of the H$_2$O molecule is confirmed by TG and IR measurements. © 1992 Academic Press, Inc.

Introduction

Vanadium phosphates exhibit an extraordinarily rich chemistry owing to the various oxidation states and to the flexible coordination of vanadium. In this respect, the crystal chemistry of tetravalent vanadium phosphates is mainly governed by the ability to form vanadyl groups, leading most of the time to a pseudo-octahedral coordination of this element, i.e., "5 + 1" coordination, in which the tendency of V(IV) to adopt a pyramidal coordination is clearly visible. This is indeed the case of V$_2$P$_2$O$_9$ (*1*) and of alkaline phosphates such as *A*VPO$_5$ (*A* = Li, K) (*2, 3*). This type of coordination is also observed in hydrogen-ophosphates, such as the different forms of hydrated vanadyl hydrogenophosphates VO(HPO$_4$) · nH$_2$O (*4, 7*), anhydra hydrogenophosphates (VO)$_2$H$_4$P$_2$O$_9$ (*8*) and VO(H$_2$PO$_4$)$_2$ (*9*), and in the potassium hydrogen phosphate hydrate K$_2$(VO)$_2$ P$_3$O$_9$(OH)$_3$ 1.125H$_2$O (*10*). In spite of this tendency of V(IV) to exhibit a fivefold coordination, very few phosphates involving only pure VO$_5$ pyramids have been isolated up to now. The phosphates *A*$_2$V$_3$P$_4$O$_{17}$ (*11, 12*) and K$_2$(VO)$_3$(P$_2$O$_7$)$_2$ (*13*) are characterized by the coexistence in their structure of VO$_6$ octahedra and pure VO$_5$ pyramids, whereas the phosphate Zn$_2$VO(PO$_4$)$_2$ (*14*), described as built up from VO$_6$ octahedra, is not far from giving an example of pure pyramidal vanadium structure, since one of the V–O distances is very large (2.95 Å) and can be

considered as nonexistent. Up to now the vanadyl diphosphates $A_2VP_2O_8$ (A = K, Rb, Cs) (15, 16), which are characterized by a layer structure, seem to be the only examples of structure built up from pure VO_5 pyramids and PO_4 tetrahedra. Such a feature might be related to the bidimensional character of the structure, which allows the VO_6 octahedra to be disconnected and consequently broken along the perpendicular to the layers. In order to enhance this lamellar character, water can be introduced simultaneously with univalent cations in the structure. We report here on the crystal structure of a new layered vanadium (IV) phosphate $Na_5V_2P_3O_{14} \cdot H_2O$ isolated by hydrothermal synthesis, whose layers are built up from corner-sharing VO_5 pyramids and PO_4 tetrahedra.

Synthesis

Single crystals of $Na_5V_2P_3O_{14} \cdot H_2O$ were grown by a hydrothermal technique. A mixture of 0.08 g of VO_2 and 0.895 g of $Na_2HPO_4 \cdot 12H_2O$ was added to 0.5 ml of water and sealed in a 6-cm-long, 0.4-cm-diameter gold tube. This mixture was heated to 973 K for 36 hr under an external air atmosphere of 2.3 Kbar. Subsequent cooling to room temperature at a rate of 20 K hr^{-1} produced well-formed bright green crystals in a mixture with some black and yellow crystals. They were filtered, washed with water, and dried in air at room temperature.

Structure Determination

A green crystal with dimensions 0.077 × 0.077 × 0.019 mm was selected for the structure determination. The cell parameters reported in Table I were determined and refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections with $36° < \theta < 44°$. The data were collected on a CAD-4 Enraf–Nonius diffractometer with the data collection parameters reported in Table I. The reflections were corrected for Lorentz and polarization effects, extinction, and absorption.

The Patterson function shows only the Harker's peaks $0 \, u \, 0$ and $\frac{1}{2} \, u \, 0$ characteristic of the Cm space group.

Atomic coordinates of the vanadium atom were obtained by the direct method procedure (program multan). Subsequent Fourier series allowed the formula $Na_5V_2P_3O_{14}$ to be obtained. After refinements of the coordinates of the atoms corresponding to the formula $Na_5V_2P_3O_{14}$ with anisotropic thermal factors, a difference synthesis showed a peak whose height was consistent with a sodium or an oxygen atom. The infrared spectra measurements performed with a Nicolet 60 SX spectrometer indicate the presence of water instead of hydroxyl groups, and the thermogravimetric analysis shows a water loss at 630 K of 3.15%, consistent with the formula $Na_5V_2P_3O_{14} \cdot H_2O$ (3.26%). Moreover, X-ray diffraction analysis of the anhydrous product shows that the structure has been destroyed after dehydration, in agreement with the fact that the dehydration is not reversible. Refinement of the atomic coordinates and their anisotropic thermal parameters led to $R = 0.049$ and $R_w = 0.060$, and to the atomic parameters of the Table II. The quality of crystallization of those lamellar crystals does not allow lower R values. All the calculations were performed on a Microvax II with the SDP system (17).

Magnetic susceptibility was measured with a Faraday microbalance on a small quantity of powder. This preliminary measurement shows that the reciprocal susceptibility varies linearly with temperature between 50 and 150 K. From the slope of this curve one obtains an effective magnetic moment $\mu_{eff} = 2.44 \, \mu B$ close to the value expected for two isolated V^{4+} ions ($S = \frac{1}{2}$) per formula unit.

TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND
STRUCTURE REFINEMENT PARAMETERS FOR $Na_5V_2P_3O_{14} \cdot H_2O$

Crystal data	
Space group	Cm
Cell dimensions	$a = 6.3089(4)$ Å
	$b = 20.1038(8)$ Å; $\beta = 91.134(6)°$
	$c = 5.1172(5)$ Å
Volume	648.9 Å^3
Z	2

Intensity measurements	
$\lambda(CuK\alpha)$	1.54056 Å
Scan mode	$\omega - 2/3\theta$
Scan with	$1 + 0.14 \tan \theta$
Slit aperture (mm)	$1 + \tan \theta$
Reflections measured	792
Max $\theta(°)$	78
Reflections with $I > 3\sigma$	703
Standard reflections	3 measured every 3000 s
μ	18.426 mm^{-1}

Structure solution and refinement	
Parameters refined	120
Agreement factors	$R = 0.049$
	$R_w = 0.060$
Weighting scheme	$w = f(\sin \theta/\lambda)$
Δ/σ max	0.004

Description of the Structure and Discussion

The projection of the structure along **a** (Fig. 1) and **b** (Fig. 2) shows its bidimensional character. It can indeed be described as $[V_2P_3O_{14}]_\infty$ layers interleaved with Na$^+$ ions and water molecules. As shown from these projections, the PO$_4$ tetrahedra and the VO$_5$ pyramids all have one free apex pointing toward the same direction along **c**. Moreover, these polyhedra form infinite $[VPO_7]_\infty$ chains running along **a**, in which one PO$_4$ tetrahedron alternates with one VO$_5$ pyramid.

The $[V_2P_3O_{14}]_\infty$ layers exhibit a very simple geometry as shown from the projection of the structure along **c** (Fig. 3). In these layers, two $[VPO_7]_\infty$ chains share the corners of their polyhedra, in such a way that the apex of VO$_5$ pyramid of one chain be shared with the apex of the PO$_4$ tetrahedron of the other chain, forming double ribbons $[V_2P_2O_{12}]_\infty$ running along **a**. Such double ribbons are to be compared to $[V_2P_2O_{14}]_\infty$ ribbons often observed in V(V) phosphates such as αVPO_5 (18), in V(IV) phosphates such as VO(HPO$_4$) $\cdot$ 4H$_2$O (5), or in mixed valence phosphates such as $Na_{2.44}V_4P_4O_{17}OH$ (19). The second ribbons are deduced from the first ones by replacing the VO$_5$ pyramids by VO$_6$ octahedra. Laterally, along **b**, the double $[V_2P_2O_{12}]_\infty$ ribbons are connected through single PO$_4$ tetrahedra which share their corners with the VO$_5$ pyramids, forming nine-sided windows where Na$^+$ cations are located.

Each P(1) tetrahedron of the $[V_2P_2O_{12}]_\infty$ ribbons shares three apices with VO$_5$ pyra-

TABLE II

POSITIONAL PARAMETERS AND THEIR ESTIMATED
STANDARD DEVIATIONS

Atom	x	y	z	B (Å^2)
V	0.500	0.15103(9)	0.500	0.69(3)
P1	−0.0030(6)	0.1856(1)	0.5153(8)	0.61(4)
P2	−0.3493(7)	0.000	0.558(1)	0.70(6)
Na1	−0.168(1)	0.0858(3)	0.028(1)	2.2(1)
Na2	0.2546(9)	0.2401(3)	−0.004(1)	1.5(1)
Na3	0.179(1)	0.000	−0.386(2)	4.0(2)
O1	0.244(3)	0.000	0.115(4)	8.8(9)
O2	−0.015(1)	0.1887(5)	0.224(2)	1.2(2)
O3	0.501(1)	0.1542(4)	0.210(2)	1.2(1)
O4	0.196(1)	0.1476(4)	0.622(2)	1.0(2)
O5	0.502(1)	0.2441(4)	0.644(2)	0.9(1)
O6	0.803(1)	0.1492(4)	0.634(2)	1.0(1)
O7	0.503(1)	0.0599(4)	0.632(2)	1.1(1)
O8	−0.153(2)	0.000	0.734(3)	1.3(2)
O9	−0.301(2)	0.000	0.273(3)	1.8(3)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as

$$B = \frac{4}{3}\sum_i \sum_j \mathbf{a}_i \cdot \mathbf{a}_j \cdot \beta_{ij}.$$

mids and has one free apex, consequently exhibiting three equal distances of 1.56 Å and a shorter one (1.49 Å) corresponding to the free corner (Table III). The P(2) tetrahedron, which ensures the junction between [V$_2$P$_2$O$_{12}$]$_\infty$ ribbons, shares two of its corners with VO$_5$ pyramids and has two free corners, leading to two long P–O distances and two shorter ones, respectively (Table III).
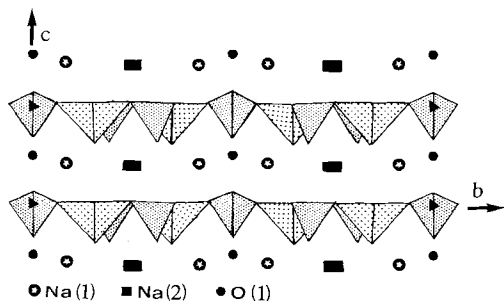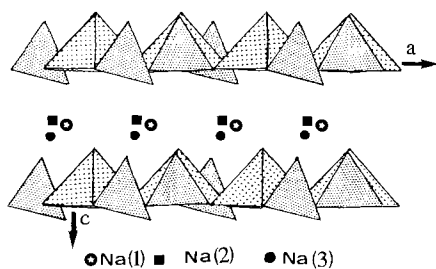

FIG. 2. Projection of the structure along **b**.

The geometry of the VO$_5$ pyramid is similar to that observed for the two-layered structure Rb$_2$VP$_2$O$_8$ (*16*) and K$_2$VP$_2$O$_8$ (*15*). The four equatorial distances are almost equal (1.95 to 2.01 Å) and close to those observed for Rb$_2$VP$_2$O$_8$ (1.967 to 1.993 Å) and K$_2$VP$_2$O$_8$ (1.97 Å). One also observes, as for the two other phases, a much shorter V–O apical bond characteristic of the vanadyl ion (Table III). This V–O distance of 1.49 Å is significantly smaller than that observed for Rb$_2$VP$_2$O$_8$ and K$_2$VP$_2$O$_8$ (1.597–1.604 Å). Such an abnormally short V–O bond has previously been observed for PbV$_2$O$_6$ (*20*). As pointed out above, all the free apices of V pyramids and P(1) tetrahedra are located on the same side of the layer. In spite of this configuration, one can note that the distance between the apical oxygen of one layer and the
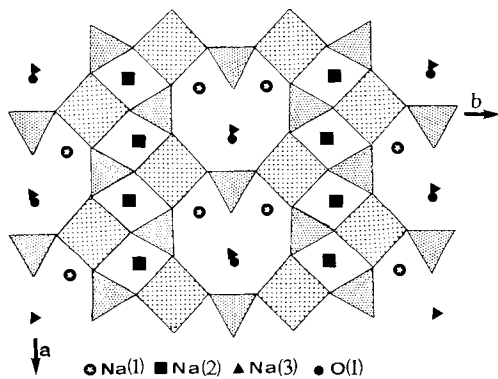

FIG. 1. Projection of the structure along **a**.

FIG. 3. Projection of the structure along **c**.

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TABLE III

DISTANCES (Å) AND ANGLES (°) IN THE PO_4
TETRAHEDRA AND IN THE VO_5 SQUARE PYRAMID

P(1)	O(2)	PO_4 tetrahedra[a] O(4)	O(5^i)	O(6^{ii})
O(2)	1.490(8)	2.548(10)	2.537(10)	2.537(10)
O(4)	113.4(5)	1.558(7)	2.501(10)	2.481(8)
O(5^i)	112.7(5)	106.8(4)	1.558(7)	2.483(10)
O(6^{ii})	112.5(5)	105.4(4)	105.5(4)	1.561(8)

P(2)	O(7^{ii})	O(7^{iii})	O(8)	O(9)
O(7^{ii})	1.577(7)	2.409(12)	2.534(10)	2.537(12)
O(7^{iii})	99.6(6)	1.577(7)	2.534(10)	2.537(12)
O(8)	109.7(4)	109.7(4)	1.522(10)	2.523(16)
O(9)	111.6(4)	111.6(4)	113.7(7)	1.491(12)

V	O(3)	VO_5 square pyramid[b] O(4) O(5)		O(6)	O(7)
O(3)	1.490(8)	2.893(10)	2.869(10)	2.862(10)	2.876(10)
O(4)	109.5(3)	2.032(7)	2.739(10)	3.830(10)	2.617(10)
O(5)	109.1(4)	85.3(3)	2.013(7)	2.694(10)	3.704(10)
O(6)	108.4(3)	142.1(3)	83.9(3)	2.017(7)	2.609(10)
O(7)	112.7(4)	82.1(3)	138.2(3)	82.2(3)	1.952(7)

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

[a] The diagonal terms are the P–O(i) distances, the terms above the diagonal are the O(i)–O(j) distances, and the terms below the diagonal are the O(i)–P–O(j) angles.

[b] The diagonal terms are the V–O(i) distances, the terms above the diagonal are the O(i)–O(j) distances, and the terms below the diagonal are the O(i)–V–O(j) angles.

V atom of the adjacent layer is 3.60 Å so that one can consider that these VO_6 octahedra do not exist in this structure, whereas they are highly elongated in $Zn_2VO(PO_4)_2$ *(14)*, with a V–O distance of 2.95 Å.

The Na(1) and Na(2) cations are all located almost at the same level between the $[V_2P_3O_{14}]_\infty$ layers, forming an almost close-packed arrangement with the H_2O molecules (O(1)) which sit also approximately in the same plane. It results in short a Na(2)–Na(2) distance of 3.18 Å, and Na(1)–Na(1) and Na(1)–Na(2) distances of 3.45 and 3.54 Å, respectively, which are

rather close to those observed in close-packed stackings of sodium cations. In this plane, each H_2O molecule is surrounded by two Na(1) cations located at 3.14 Å (Table IV); moreover, each H_2O molecule has also two nearest neighbors Na(3) at 2.597 Å along **c**.

The Na(2) cations form close-packed rows running along **a** and are located between two $[V_2P_2O_{12}]_\infty$ ribbons (Figs. 1 and 3). They exhibit an eightfold coordination, built up from four oxygens belonging to the basal plane of one layer and four apical oxygens of the next layer which delimit a square

TABLE IV

SURROUNDING OF Na$^+$ WITH
Na–O < 3.25 Å

Na(1)–O(1)	=	3.14(1)
Na(1)–O(2)	=	2.485(9)
Na(1)–O(3^{ii})	=	2.682(9)
Na(1)–O(6^{iv})	=	2.388(9)
Na(1)–O(7^{iv})	=	2.922(9)
Na(1)–O(8^v)	=	2.289(9)
Na(1)–O(9)	=	2.306(9)
Na(2)–O(2)	=	2.325(9)
Na(2)–O(2^{vi})	=	2.336(9)
Na(2)–O(3)	=	2.555(9)
Na(2)–O(3^i)	=	2.888(9)
Na(2)–O(4^v)	=	2.688(9)
Na(2)–O(5^v)	=	2.405(9)
Na(2)–O(5^{vi})	=	2.403(9)
Na(2)–O(6^{vii})	=	2.916(9)
Na(3)–O(1^v)	=	2.60(2)
Na(3)–O(1)	=	2.59(2)
Na(3)–O(4^v)	=	2.968(8)
Na(3)–O(4^{viii})	=	2.968(8)
Na(3)–O(7^v)	=	2.37(1)
Na(3)–O(7^{viii})	=	2.37(1)
Na(3)–O(8^v)	=	2.19(1)

Note. See symmetry code in the footnote to Table III.

antiprism. It is worth pointing out that four of these bonds are rather short, ranging from 2.32 to 2.40 Å (Table IV).

The Na(1) cations are located between nine-sided windows formed by the [V$_2$P$_3$O$_{14}$]$_\infty$ layers at about the same level as the Na(2) cations (Figs. 2 and 3). These cations have a sevenfold coordination with distances ranging from 2.289 to 3.14 Å (Table IV). Note that each Na(1) ion exhibits also four shorter distances ranging from 2.29 to 2.485 Å, and that the H$_2$O molecule (O(1)) is far away (3.14 Å). The corresponding NaO$_6$(H$_2$O) polyhedron is a mono-capped distorted trigonal prism.

Like the Na(1) cations, the Na(3) cations are also located in the nine-sided windows (Fig. 3), but at a different level along **c**, i.e., just between two H$_2$O molecules along **c** forming two Na(3)–O(1) bonds of 2.60 Å

(Table IV). These ions exhibit a sevenfold coordination with three shorter Na–O distances. The oxygen atoms delimit a pentagonal bipyramid. The short Na(3)–O(8) distance (2.19 Å) is similar to that observed in Na$_3$SbO(PO$_4$)$_2$ (*21*).

The *B* values of O(1) and especially of Na(3) are particularly high. This can be interpreted by the fact that the cage, where the sodium ion Na(3) and the water molecule are located, is very large, allowing a rather great mobility of these species, which tend to move toward the walls of the cage. Another possibility could be a statistical occupancy of splitted sites, e.g., 4*b* sites instead of 2*a* sites for Na(3). However, attempts to refine the positional parameters and *B* factors, starting from such positions, were unsuccessful.

Concluding Remarks

These results confirm the ability of tetravalent vanadium to exhibit a pure pyramidal coordination. They suggest, together with the previous results obtained for A_2VP$_2$O$_8$ phosphates, that such a coordination is favored in layered structures. Consequently such compounds can be obtained by introducing either large ions, such as Rb$^+$, Cs$^+$, K$^+$, or Ba^{2+}, or large amounts of smaller cations, like Na$^+$, together with water using hydrothermal synthesis. The layered character of the structure suggests possible ion-exchange properties. The latter will be studied, as well as the eventual mobility of sodium cations.

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