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Synthesis and Crystal Structure of $Na_{1+x}V_4P_4O_{17}(OH)$ ($x \approx 1.44$)

A. LE BAIL AND M. LEBLANC

Laboratoire des Fluorures, URA CNRS 449, Faculté des Sciences, Université du Maine, 72017 Le Mans Cedex, France

AND P. AMOROS

UIBCM, Departament de Quimica Inorganica, Facultat de Ciencies Quimiques, Universitat de Valencia, Dr Moliner 50, 46100 Burjassot, Valencia, Spain

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Hydrothermal synthesis starting from $Na_{0.46}VOPO_4 \cdot 1.58H_2O$ leads to a new mixed-valence sodium vanadium phosphate: $Na_{2.44}V_4P_4O_{17}(OH)$ (orthorhombic, space group *Pnma; Z* = 4; a = 13.723(5) Å, b = 6.314(2) Å, c = 16.139(4) Å; R = 0.032 for 2659 reflections). In this phase, the interconnection of three complex types of infinite chains, built from VO_6 octahedra and PO_4 tetrahedra, sometimes edge-shared, defines tunnels partly occupied by a portion of the sodium atoms. © 1990 Academic Press, Inc.

Introduction

Few sodium vanadium phosphates are known at present. Only two were recently characterized by a single crystal structure determination: $NaV^{II}V_2^{III}P_3O_{12}$ (*1*), a stuffed structure of α-$CrPO_4$ (*2, 3*), and $NaVP_2O_7$ (*4*), which is isostructural with $NaFeP_2O_7$ (*5*). The mixed-valence sodium-containing intercalates $Na_x(V_x^{IV}V_{1-x}^{V}O)PO_4 \cdot nH_2O$ are the subject of some controversy and only tentatives of indexation from X-ray powder diffraction are reported (*6, 7*); hypotheses on the organization derive from the structure of the parent phase $VOPO_4 \cdot 2H_2O$ (*8, 9*). Other phases were claimed to occur from the thermal treatment of $Na_xVOPO_4 \cdot nH_2O$: a monohydrate and two polymorphic anhydrous phases are cited in Ref. (*10*) but remain structurally uncharacterized. All contain vanadium in mixed-valence states, their mixed framework of octahedra and tetrahedra generates cage or tunnel structures in which the Na^+ ion, one of the best candidates for ionic conduction, is inserted. Abnormally high anisotropic thermal motion was observed for Na^+ in $NaV_3P_3O_{12}$ (*1*).

We report here on the synthesis and the structural study of a new mixed-valence vanadium phosphate $Na_{1+x}V_4P_4O_{17}(OH)$.

Synthesis

$Na_{0.46}VOPO_4 \cdot 1.58H_2O$ (0.197 g; ≈ 1 mmol) in 0.40 cm³ of water were inserted in a gold bucket and treated hydrothermally at 620°C, 2300 bar, for 24 hr. The result was a

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TABLE I

CRYSTALLOGRAPHIC DATA FOR $Na_{2.44}V_4P_4O_{17}(OH)$

Formula weight		672.75
Space group		*Pnma*
Z		4
Density (calcd g · cm^{-3})		3.195
Radiation		Mo$K\alpha$
μ (cm^{-1}), Mo$K\alpha$		31.6
Crystal dimensions (mm)		0.106 × 0.399 × 0.023
Lattice constants		
	a(Å)	13.723(5)
	b(Å)	6.314(2)
	c(Å)	16.139(4)
	V(Å^3)	1398(2)
Scan type		$\omega - 2\theta$
T		20°C
Angular range (°2θ)		2.52–70.00
Learn profile data collection		
Isotropic line width (°)		$A = 0.80$
$w = (A + B\,\mathrm{Tg}\theta)°$		$B = 0.15$
Maximum h, k, l		22, 10, 26
Data examined		3516
Merged data retained $I > 3\sigma(I)$		2659
Absorption correction		Gauss method
Min and max transmission factors		0.6935 0.9303
Refinement	R	0.032
	R_w	0.032
Weight: $k/(\sigma^2(F) + G \times F^2)$,	$k =$	1.9101
	$G =$	0.000047
Extinction parameter		0.00069(6)
No. of variables		169

mixture of crystals with various shapes and colors. They were filtered-out and washed with small portions of cold water and acetone.

The small amount of each crystalline variety explains that the compositions are given from the structure determinations only. One phase was identified as being $NaVP_2O_7$, the structure of which was recently determined (*4*), another one is the subject of this paper.

Structure Determination of $Na_{2.44}V_4P_4O_{17}(OH)$

A dark-green platelet crystal was selected and examined on a Siemens AED2 four-circle diffractometer, experimental details are given in Table I. The cell parameters were refined from 36 reflections well distributed in the reciprocal space at $2\theta \approx 30°$. The conditions limiting reflections were consistent with the space groups *Pnma* and $Pn2_1a$. Application of the direct method facilities of the SHELX-76 program (*11*), using the centric *Pnma* space group, gives starting coordinates for all nonhydrogen atoms. The scattering factors and the anomalous dispersion parameters were taken from "International Tables for X-Ray Crystallography" (*12*). Refinements with anisotropic thermal motions, in the hypothesis of a full site occupancy, corresponding to the formula $Na_3V_4P_4O_{18}$, lead to the residuals $R = 0.047$ and $R_w = 0.054$. At this stage, the thermal motion of the Na(2) atom in general position was abnormally high. Further refinements allowing the occupation factor of the Na(2) atom to vary lead to $R = 0.039$ and $R_w = 0.042$ with 65(1)% of sodium atom in this (8*d*) site. Then the Fourier difference map clearly revealed two peaks: one in the immediate vicinity of the V(2) atom, also affected by an abnormally high anisotropic thermal motion ($U_{33} \approx 0.0190 \approx 3\ U_{11} \approx 3\ U_{22}$); the second peak could correspond to a third site of sodium atoms although at a distance of 2.1 Å from Na(2). Crystallochemical arguments inclined us to consider seriously the two peaks on the Fourier difference map, they will be discussed in the structure description. Introducing the Na(2′) atom in a 4*c* site leads to $R = 0.034$, $R_w = 0.035$ with 27(1)% occupation; then, the final residual values $R = 0.032$, $R_w = 0.032$ were obtained with the V(2) atom placed statistically on two near positions in its octahedron.

At this stage, a valence bond analysis (VBA) using Brown's data (*13–15*) clearly indicates the necessity to replace the oxygen atom O(5) by an hydroxyl group (The formula used was $s = \exp[-(R - R_0)/B]$ with $R_0 = 1.790$; 1.620; 1.661 and $B = 0.319$; 0.36; 0.44, respectively, for V,P, and Na (*13*)). A Fourier difference map from data limited to $\sin\theta = 0.4$ seems to confirm the presence of the hydrogen atom; however, its coordinates could not be re-

TABLE IIa

ATOMIC COORDINATES ($\times 10^4$), THERMAL PARAMETERS B_{eq}, AND CALCULATED VALENCES s FOR $Na_{2.44}V_4P_4O_{17}(OH)$

Atom	x	y	z	$B_{eq}(A^2)$	s(calcd)
Na(1)	2946(1)	2500	8895(1)	1.68(7)	0.95
Na(2)[a]	2650(2)	9898(5)	1700(2)	3.96(14)	0.84
Na(2')[b]	2004(9)	2500	1102(7)	6.66(80)	0.83
V(1)	6399(0)	2500	9796(0)	0.41(2)	3.21
V(2)[c]	5443(1)	2500	2000(3)	0.53(4)[e]	3.13
V(2')[d]	5435(7)	2500	1786(13)	0.53(4)[e]	3.06
V(3)	9367(0)	15(1)	1291(0)	0.50(1)	2.94
P(1)	5132(1)	2500	8025(1)	0.45(3)	4.99
P(2)	8880(1)	2500	9531(1)	0.43(3)	5.03
P(3)	7412(1)	2500	1746(1)	0.50(3)	5.00
P(4)	4058(1)	2500	477(1)	0.57(3)	5.13
O(1)	4476(1)	566(3)	8162(1)	0.82(6)	1.96
O(2)	3457(1)	4410(3)	187(1)	0.80(6)	2.06
O(3)	1972(1)	−466(3)	8280(1)	0.86(6)	2.02
O(4)	4318(1)	469(3)	5840(1)	0.76(6)	1.85
O(5)	1147(2)	2500	9359(2)	0.73(8)	1.07
O(6)	2791(2)	2500	5623(2)	0.85(9)	2.07
O(7)	6632(2)	2500	1058(2)	0.73(8)	1.97
O(8)	1053(2)	2500	6449(2)	0.84(9)	1.99
O(9)	4146(2)	2500	1425(2)	1.29(10)	1.92
O(10)	5054(2)	2500	65(2)	1.73(12)	2.04
O(11)	6790(2)	2500	2541(2)	0.68(8)	1.96
O(12)	4848(2)	2500	3056(2)	0.85(9)	1.76
O(13)	466(2)	2500	7909(2)	0.59(8)	1.99
O(14)	9115(2)	2500	478(2)	0.76(9)	1.99
H	1105(47)	2500	9977(7)	3.95[f]	

Site occupancy (%): [a]65(1), [b]27(1), [c]88(2), [d]12(2).
[e] Tied values.
[f] Fixed value.

fined without a constrained O–H distance. The influence of the addition of the hydrogen atom on the residuals was negligible, so its position cannot really be considered as established. However, IR spectroscopy confirms the presence of OH groups.

Test in the $Pn2_1a$ acentric space group does not improve these results, so the estimated final formulation is $Na_{2.44}V_4P_4O_{17}(OH)$.

The atomic coordinates and thermal parameters are gathered in Tables IIa and IIb; selected bond lengths and angles are listed in Table III. A list of observed and calculated structure factors can be obtained upon request from the authors.

Description of the Structure and Discussion

A general view of the structure of $Na_{2.44}V_4P_4O_{17}(OH)$ is shown in Fig. 1. This rather complex structure may be described as formed by the interconnection of three types of infinite chains (which will be denoted I, II, III) running along the b direction. They delimit tunnels where the Na(2) atoms are inserted.

The first type of chains (I) is represented in Fig. 2. It is common to a large variety of phosphate compounds; for instance, they are found isolated in $VO(HPO_4) \cdot 4H_2O$ (*16*). The V(1) octahedron shares

TABLE IIb

ANISOTROPIC TEMPERATURE FACTORS $U_{ij} \times 10^4$ RELATING TO THE EXPRESSION $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots 2klb^*c^*U_{23})]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na(1)	214(8)	207(9)	219(9)		−76(7)	
Na(2)	330(13)	749(24)	425(16)	−434(16)	22(10)	97(13)
Na(2′)	603(80)	1586(165)	340(61)		218(54)	
V(1)	54(2)	37(2)	65(2)		−1(2)	
V(2)	71(2)	40(2)	92(11)		−16(3)	
V(3)	63(2)	64(2)	63(2)	7(1)	9(1)	11(1)
P(1)	69(3)	43(3)	58(3)		3(3)	
P(2)	48(3)	57(3)	59(3)		7(3)	
P(3)	60(3)	57(3)	72(3)		15(3)	
P(4)	68(3)	48(3)	100(4)		−24(3)	
O(1)	118(7)	49(7)	144(8)	0(6)	24(6)	−12(6)
O(2)	115(7)	36(7)	154(8)	9(6)	−35(6)	16(6)
O(3)	85(7)	58(7)	185(9)	12(7)	28(6)	21(6)
O(4)	91(7)	79(8)	119(8)	31(6)	−32(6)	10(6)
O(5)	120(11)	81(11)	77(10)		−11(9)	
O(6)	60(10)	118(12)	144(12)		−5(9)	
O(7)	119(11)	97(11)	59(10)		−16(9)	
O(8)	119(11)	102(11)	96(11)		38(9)	
O(9)	246(14)	136(13)	108(12)		−94(11)	
O(10)	95(12)	160(14)	404(19)		57(12)	
O(11)	80(10)	108(11)	70(10)		22(8)	
O(12)	149(11)	75(11)	99(11)		12(9)	
O(13)	105(10)	54(10)	64(10)		−11(8)	
O(14)	168(12)	55(11)	68(10)		−4(9)	

Notes. Numbers in parentheses indicate esd's; thermal factors of V(2′) were fixed to the same values as V(2).

trans oxygen atoms O(2) with the phosphate P(4) tetrahedra, forming an infinite single chain of alternating octahedra and tetrahedra. Each octahedron also shares the O(10) atom with a phosphate tetrahedron in a parallel identical chain, giving rise to the infinite double chain shown in Fig. 2.

The second type of chains (II), represented in Fig. 3, is built up from infinite single chains of alternating P(1) tetrahedra and V(2) octahedra sharing *trans* oxygen atom O(1). The P(3) tetrahedron shares an edge (O(7),O(11)) with the V(2) octahedron. Such an unusual feature has been encountered for the α-$CrPO_4$ structure type (*2*); the O(7)–O(11) contact is 2.403(4) Å, the shortest of the O–O distances. An analogous arrangement exists also as a part of the $Na_4Ni_7(PO_4)_6$ structure (*17*).

The V(3) octahedra share opposite edges (O(5),O(12) and O(13),O(14)), in order to form infinite rutile-type chains. A single chain is connected to a parallel one through the P(2) tetrahedra, thus giving rise to the infinite double chain of type III (Fig. 4). The P(2) tetrahedra share two O(4) with a group of two edge-shared V(3) octahedra and the O(14) oxygen atom with an adjacent chain of V(3) octahedra. Chains of this third type are encountered in the crystal structure of silver chromate Ag_2CrO_4 (*18*) where the octahedral sites are occupied by half of the silver atoms (Ag(1) in Ref. (*18*)); the role of $P(2)O_4$ is ensured by the CrO_4 tetrahedra, the whole framework is built from these in-

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR $Na_{2.44}V_4P_4O_{17}(OH)$

	V(1) Octahedron			⟨V(1)–O⟩ = 1.995		
V(1)	O(10)	O(2)	O(2)	O(6)	O(7)	O(8)
O(10)	1.896(3)	2.854(2)	2.854(2)	3.917(3)	2.694(4)	2.802(4)
O(2)	95.4(2)	1.961(1)	3.902(3)	2.690(2)	2.803(2)	2.899(2)
O(2)	95.4(2)	168.3(2)	1.961(1)	2.690(2)	2.803(2)	2.899(2)
O(6)	173.7(2)	84.8(2)	84.8(2)	2.026(3)	3.145(4)	2.732(4)
O(7)	85.7(3)	88.3(2)	88.3(2)	100.6(3)	2.062(3)	4.123(4)
O(8)	89.9(3)	92.1(2)	92.1(2)	83.8(3)	175.6(3)	2.065(3)

	V(2) Octahedron			⟨V(2)–O⟩ = 2.014		
V(2)	O(12)	O(1)	O(1)	O(9)	O(11)	O(7)
O(12)	1.890(5)	2.911(2)	2.911(2)	2.803(4)	2.792(3)	4.049(4)
O(1)	98.3(3)	1.957(6)	3.872(3)	2.787(2)	2.838(2)	2.765(2)
O(1)	98.3(3)	163.3(3)	1.957(4)	2.787(2)	2.838(2)	2.765(2)
O(9)	91.9(4)	89.3(2)	89.3(2)	2.007(3)	4.051(4)	3.463(3)
O(11)	90.3(3)	90.3(2)	90.3(2)	177.7(3)	2.044(3)	2.403(4)
O(7)	58.6(3)	82.4(2)	82.4(2)	109.5(3)	68.3(3)	2.230(4)

	V(3) Octahedron			⟨V(3)–O⟩ = 2.020		
V(3)	O(4)	O(3)	O(12)	O(5)	O(13)	O(14)
O(4)	1.970(2)	3.954(1)	2.828(2)	2.837(2)	2.864(3)	2.912(2)
O(3)	178.5(1)	1.984(2)	2.832(2)	2.797(2)	2.853(2)	2.809(3)
O(12)	90.8(2)	90.5(2)	2.002(2)	4.032(1)	3.195(0)	2.571(4)
O(5)	90.3(2)	88.3(2)	178.8(1)	2.030(2)	2.520(4)	3.188(0)
O(13)	90.6(2)	89.7(2)	103.7(1)	76.1(3)	2.059(1)	4.132(0)
O(14)	92.1(2)	87.6(2)	78.2(3)	101.9(1)	176.7(0)	2.074(1)

	P(1) Tetrahedron			⟨P(1)–0⟩ = 1.541
P(1)	O(8)	O(1)	O(1)	O(13)
O(8)	1.523(3)	2.563(2)	2.563(2)	2.490(4)
O(1)	114.0(3)	1.533(3)	2.442(2)	2.515(2)
O(1)	114.0(3)	105.6(2)	1.533(2)	2.515(2)
O(13)	107.0(4)	108.0(3)	108.0(3)	1.576(3)

Na(1) Polyedron	
2x –O(3)	2.506(2)
2x –O(2)	2.509(2)
–O(5)	2.580(3)
2x –O(1)	2.702(2)
⟨Na(1)–O⟩ 2.573	

	P(2) Tetrahedron		⟨P(2)–O⟩ = 1.538	
P(2)	O(6)	O(4)	O(4)	O(14)
O(6)	1.515(3)	2.482(2)	2.482(2)	2.541(4)
O(4)	108.8(2)	1.538(1)	2.565(2)	2.499(2)
O(4)	108.8(2)	113.0(2)	1.538(2)	2.499(2)
O(14)	111.4(3)	107.5(3)	107.5(3)	1.562(3)

	P(3) Tetrahedron		⟨P(3)–O⟩ = 1.540	
P(3)	O(3)	O(3)	O(11)	O(7)
O(3)	1.538(2)	2.569(2)	2.508(2)	2.542(2)
O(3)	113.2(2)	1.538(1)	2.508(2)	2.542(2)
O(11)	109.1(3)	109.1(3)	1.541(3)	2.403(4)
O(7)	111.2(3)	111.2(3)	102.4(4)	1.542(3)

Na(2) Polyedron	
–O(11)	2.365(4)
–O(8)	2.372(4)
–O(6)	2.383(4)
–O(3)	2.627(4)
–O(9)	2.667(4)
–O(2)	2.717(4)
–O(4)	3.045(3)
⟨Na(2)–O⟩	2.597

TABLE III—*Continued*

P(4)	P(4) Tetrahedron O(10)	O(2)	⟨P(4)–O⟩ = 1.531 O(2)	O(9)
O(10)	1.520(3)	2.509(2)	2.509(2)	2.524(4)
O(2)	110.5(2)	1.534(2)	2.412(2)	2.518(2)
O(2)	110.5(2)	103.6(2)	1.534(1)	2.518(2)
O(9)	111.4(4)	110.3(3)	110.3(3)	1.535(3)

Bridging Angles and Intercationic Distances (V, P, Na)

V(2)–O(1)–P(1)	137.3(2)	V(2)–P(1)	3.254(3)	Na(1)–P(4)	2.975(2)
V(1)–O(2)–P(4)	136.3(2)	V(1)–P(4)	3.249(1)	Na(1)–P(1)	3.312(2)
V(3)–O(3)–P(3)	129.7(2)	V(3)–P(3)	3.194(1)	Na(1)–P(3)	3.358(1)
V(3)–O(4)–P(2)	129.2(1)	V(3)–P(2)	3.173(1)	Na(2)–P(3)	3.016(4)
V(3)–O(5)–V(3)	103.0(1)	V(3)–V(3)	3.176(1)	Na(2)–Na(2)	3.028(5)
V(1)–O(6)–P(2)	151.1(2)	V(1)–P(2)	3.431(1)	Na(2)–V(1)	3.135(3)
V(1)–O(7)–P(3)	145.0(3)	V(1)–P(3)	3.440(2)	Na(2)–P(4)	3.214(3)
V(2)–O(7)–P(3)	91.0(3)	V(2)–P(3)	2.733(2)	Na(2)–P(2)	3.263(3)
V(2)–O(7)–V(1)	124.1(3)	V(2)–V(1)	3.791(4)	Na(2)–Na(2)	3.286(5)
V(1)–O(8)–P(1)	137.2(3)	V(1)–P(1)	3.346(2)	Na(2)–P(1)	3.428(4)
V(2)–O(9)–P(4)	122.0(3)	V(2)–P(4)	3.107(4)		
V(1)–O(10)–P(4)	167.3(2)	V(1)–P(4)	3.395(1)		
V(2)–O(11)–P(3)	98.4(3)	V(2)–P(3)	2.733(2)		
V(3)–O(12)–V(2)	128.1(2)	V(3)–V(2)	3.500(2)		
V(3)–O(12)–V(3)	103.2(1)	V(3)–V(3)	3.138(1)		
V(3)–O(13)–P(1)	129.2(2)	V(3)–P(1)	3.290(1)		
V(3)–O(13)–V(3)	100.9(1)	V(3)–V(3)	3.176(1)		
V(3)–O(14)–P(2)	130.8(2)	V(3)–P(2)	3.313(1)		
V(3)–O(14)–V(3)	98.3(1)	V(3)–V(3)	3.138(1)		

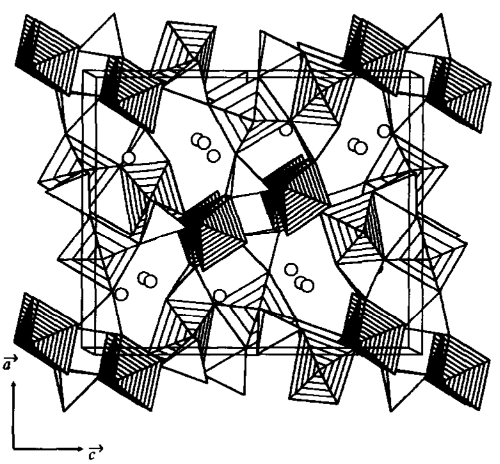

FIG. 1. Perspective view of the $Na_{2.44}V_4P_4O_{17}(OH)$ structure nearly along [010]. For the VO_6 octahedra, $V(3)O_6$ is the most shaded and $V(1)O_6$, the least (STRUPL084 (*20*)).

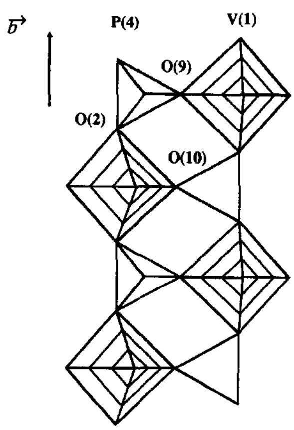

FIG. 2. View of the infinite double chains of type I developed along the *b*-axis and situated near the inversion centers at 1/2,0,0 and 0,1,/2,0. ($V(1)O_6$ octahedra and $P(4)O_4$ tetrahedra.) (STRUPL084 (*20*)).

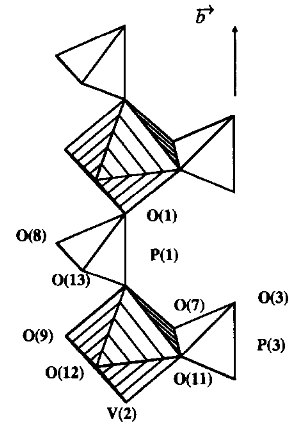

FIG. 3. View of the infinite chains of type II alternating $V(2)O_6$ octahedron and $P(1)O_4$ tetrahedron along the *b*-axis, showing edge-sharing between $P(3)O_4$ and $V(2)O_6$ (STRUPL084 (*20*)).

terconnected chains of the third type, the other half of the silver atoms occupies strongly distorted tetrahedra within the chains. More paradoxical is the isotypic high-temperature $NaAgMoO_4$ polymorph (*19*), where sodium atoms occupy the octahedral sites. In $Na_{2.44}V_4P_4O_{17}(OH)$ the $V(3)O_6$ octahedra are strongly elongated in the chain direction, leading to some large O–O distances (≈3.2 Å, half the *b* parameter), the comparable long distances in Ag_2CrO_4 and $NaAgMoO_4$ (≈3.5 Å) are obtained with cations of much larger size.

Type I and III chains are connected through the remaining fourth oxygen of P(2) in common with V(1), namely O(6).

The Na(1) polyhedron is a well-defined monocapped trigonal prism (TP). When considering that there could be two oxygen atom vacancies, the undefined Na(2) polyhedron becomes a very acceptable defective tricapped TP as shown in Fig. 5. The two vacancies, denoted Vac1 and Vac2, are in *trans*-position; their coordinates are simply estimated from those of O(11) and O(6), respectively, by adding 1/2 to the *y* coordinate. Vac1 would be a second cap for the Na(1) TP, while Vac2 points toward Na(1) through the oxygen atoms triangle constituted by the O(2)–O(2) TP edge (parallel to the *b* axis) and the O(5) cap. The Na(2′) atom is in the immediate vicinity of Vac2; however, we have not attributed this site to an oxygen atom for the two following reasons: first, the cationic environment of Vac1 and Vac2 is constituted by only

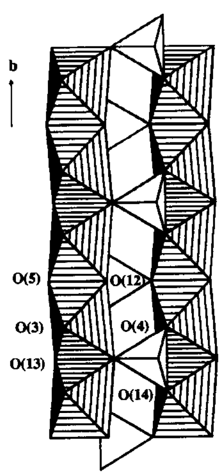

FIG. 4. View of the infinite double chains of the third type: $V(3)O_6$ octahedra sharing edges along the *b*-axis; single chains being connected through the $P(2)O_4$ tetrahedra (STRUPL084 (*20*)).

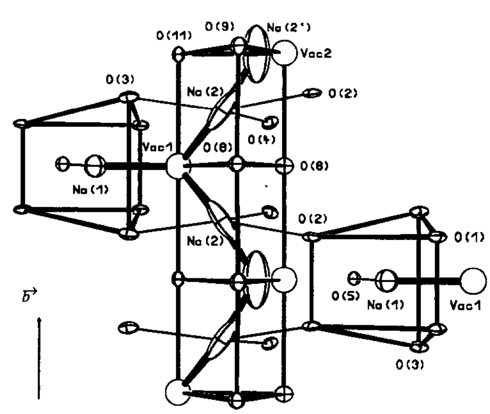

FIG. 5. ORTEP drawing (*21*) of the sodium atoms trigonal prisms. Ellipsoids are scaled to include 75% probability, the vacancies Vac1 and Vac2 are represented as spheres.

two Na(2) and one Na(1) atoms, then an oxygen atom valence would not have been compensated and this is probably the reason why there are two vacancies (all the oxygen atoms in this structure are bonded at least to one vanadium and one phosphorus atom or to two vanadium atoms). The second reason comes from the highly anisotropic thermal motion of the Na(2) atom; the ellipsoid main elongation axis points clearly from Vac1 to Vac2 (Fig. 5). Moreover, when ellipsoids are scaled to include 90% probability, Na(2) and Na(2′) interpenetrate so Na(2′) clearly indicates a possible conduction pathway.

If the site occupancy factors of Na(2) and Na(2′) are considered seriously, they represent 1.44 sodium atoms per formula; the VBA indicates (Table IIa) that V(3) is a V^{3+} ion, the shortest V(3)–O distance is very comparable with that observed in $NaVP_2O_7$—1.964(2) Å in Ref. (*4*). This and the fact the Na(1) site is fully occupied led us to propose the general formulation $Na_{1+x}V^{III}_{2+x}V^{IV}_{2-x}P_4O_{17}(OH)$, with $x \approx 1.44$ for the selected crystal.

Let us define now the limits suggested by this formulation. When the Na(2) site is fully occupied, the Na(2′) site must be empty and then $x = 2$ with only V^{3+}; the other limit is obtained for $x = 0$ and a ratio V^{III}/V^{IV} equal to 1. A value $x = 1.44$ implies a repartition of nearly 25% of V^{IV} on the V(1) and V(2) sites, i.e., a mean valence of ≈3.25. This seems to be overestimated when looking at the calculated valences whose accuracy is however relatively low in such a case (i.e., mixed valence implies that oxygens are found on mean positions, the short characteristic V^{+4}–O distance (≈1.6 Å) is not observed here but could exist locally, the abnormally high U_{33} value of the oxygen O(10) could be the consequence of a static disorder rather than a dynamic one).

Work is in progress to test the possible ionic conduction of this material; hydrothermal synthesis, under more or less reducing conditions, appears as a promising and powerful tool for the growth of new mixed-valence phases.

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