

# Synthesis and Crystal Structure of $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$

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Two new nickel metavanadate hydrates,  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ , have been synthesized using a “chimie douce” process; their crystal structures have been solved from single-crystal X-ray diffraction data. The tetrahydrate  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  crystallizes in the monoclinic space group  $C2/c$  with a unit cell of dimensions  $a = 12.969(5) \text{ \AA}$ ,  $b = 9.817(3) \text{ \AA}$ ,  $c = 6.880(2) \text{ \AA}$ ,  $\beta = 112.14(3)^\circ$ ;  $Z = 4$ ; the structure was determined from 1055 independent reflections and refined until  $R = 0.024$  and  $R_w = 0.034$ . An orthorhombic cell has been found for the dihydrate  $\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ :  $a = 5.530(1) \text{ \AA}$ ,  $b = 10.621(10) \text{ \AA}$ ,  $c = 11.756(5) \text{ \AA}$ ,  $Z = 4$ , space group  $Pnma$ ; the structure was determined from 1201 independent reflections until  $R = 0.017$  and  $R_w = 0.018$ . The structures of the two materials mainly differ in the vanadium environment in the  $(\text{VO}_3)_n^{n-}$  metavanadate chains. They are constituted of edge-linked  $\text{VO}_5$  square pyramids in the tetrahydrate and from vertex-linked  $\text{VO}_4$  tetrahedra in the dihydrate. As the hydrogen atoms were localized in these two compounds, all the hydrogen bonds existing in these structures were clearly evidenced. © 2000 Academic Press

## INTRODUCTION

Commercial lithium-ion batteries are currently made with a lithium metal oxide as cathode ( $\text{LiCoO}_2$ ,  $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$ , or  $\text{LiMn}_2\text{O}_4$ ) and carbon as anode. To increase the performance of the batteries in terms of energy densities, many research groups worldwide are trying to improve the performances of these materials by cationic or anionic substitutions (1). A few years ago, researchers from Fuji proposed the use of oxides ( $\text{SnO}_x$  or  $\text{LiMVO}_4$  with  $M = \text{Ni}, \text{Co}, \dots$ ) to replace the carbon anode (2, 3). These oxides present large electrochemical capacities at low potential. Since then, several groups have worked on vanadates for application as anodes in lithium-ion batteries. The preparation methods used were either the ceramic route or the ozonolysis of hydrated precursors (4, 5). Our approach used

a “chimie douce” process to prepare such vanadates. Indeed, several years ago, one of us developed a method for the preparation of amorphous trivalent element vanadates (6). These materials presented interesting properties as anodes in lithium-ion batteries and reacted with lithium ions by unusual mechanisms (7). These results stimulated our interest in the search for new electrode materials among the divalent-element vanadates. The synthesis process was adapted (8) and led to a substantial number of compounds giving electroactive vanadates, either new or previously prepared by other methods (9, 10). Some of the new materials were obtained as single crystals. Therefore, in this paper we present the crystal structures of two of them, namely,  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ .

## EXPERIMENTAL PROCEDURES

To obtain  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ , a solution of ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ , 0.05 M) was mixed with a nickel nitrate solution with a concentration ratio Ni/V equal to  $\frac{1}{2}$ . After about 1 h of stirring at  $50^\circ\text{C}$  under ambient pressure, a green precipitate formed,  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ . The precipitate was recovered, and the filtrate was left to age for several months, leading to the formation of green single crystals of  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ . Green single crystals of  $\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$  were obtained by keeping the same solution mixture (ammonium metavanadate and nickel nitrate) in an autoclave for 24 h at  $150^\circ\text{C}$  and under 20 bar of argon. The X-ray measurement conditions for the two vanadates are summarized in Table 1.

## STRUCTURAL STUDY

The structure of  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  was resolved using the atomic coordinates of the isostructural solid  $\text{Co}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  (13). First, the refinement of the atomic coordinates of nickel, vanadium, and oxygen atoms led to  $R = 0.043$  and  $R_w = 0.062$ . The refinement of these coordinates and the anisotropic thermal coefficients  $\beta_{ij}$  gave

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**TABLE 1**  
Crystal Data and Intensity Collection Conditions for  
 $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$

	$\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$
Formula weight (g/mol)	328.64	292.62
Space group	$C2/c$ (No. 15)	$Pnma$ (No. 62)
Unit cell parameters	$a = 12.969(5) \text{ \AA}$ $b = 9.817(3) \text{ \AA}$ $c = 6.880(2) \text{ \AA}$ $\beta = 112.14(3)^\circ$	$a = 5.530(1) \text{ \AA}$ $b = 10.621(10) \text{ \AA}$ $c = 11.756(5) \text{ \AA}$
$V; Z$	$811.4(5) \text{ \AA}^3; 4$	$690.5(7) \text{ \AA}^3; 4$
Density (g/cm <sup>3</sup> )	$D_x = 2.69(1)$	$D_x = 2.82(1)$
Faces limiting the crystal and distances (mm) <sup>a</sup>	$(1\bar{1}0): 0.100$ $(\bar{1}10): 0.100$ $(110): 0.100$ $(\bar{1}\bar{1}0): 0.100$ $(\bar{3}\bar{1}3): 0.160$ $(1\bar{1}\bar{6}): 0.170$	$(011): 0.025$ $(0\bar{1}\bar{1}): 0.030$ $(01\bar{1}): 0.080$ $(0\bar{1}1): 0.085$ $(\bar{1}02): 0.080$ $(12\bar{2}): 0.100$ $(301): 0.120$
Diffractometer	CAD4 (Enraf-Nonius)	
Temperature	298 K	
Radiation	MoK $\alpha$ , graphite monochromated ( $\lambda = 0.71069 \text{ \AA}$ )	
Scattering factors	Neutral atoms (11)	
Scan type	$\theta-2\theta$	
$\theta$ range (deg)	2–30	
Standard reflections	$(\bar{3}\bar{1}1); (021); (3\bar{1}\bar{2})$	$(\bar{1}3\bar{1}); (30\bar{3}); (321)$
Range in $h, k, l$	$-18 \leq h \leq 18;$ $-13 \leq k \leq 13;$ $0 \leq l \leq 9$	$-8 \leq h \leq 8;$ $-16 \leq k \leq 16;$ $0 \leq l \leq 9$
Maximum scan time (s)	60	60
Period of intensity control (s)	7200	7200
No. of reflections collected	2524	4285
No. of reflections with $I > 3\sigma(I)$	2256	3150
$R_{\text{int}}$ before absorption correction	0.0691	0.1037
Linear absorption coefficient (cm <sup>-1</sup> )	47.07	54.94
Transmission factors <sup>b</sup>	0.218–0.454	0.409–0.736
$R_{\text{int}}$ after absorption correction	0.0265	0.0255
Averaged reflections ( $I > 3\sigma(I)$ )	1055	1201
Weighting scheme		$1/\sigma^2(F)$
No. of variables	74	63
$R$	0.024	0.017
$R_w$	0.034	0.018

<sup>a</sup> The dimensions given are the distances from the center of the crystal to the faces of the trapezoidal platelet.

<sup>b</sup> Absorption corrections according to the method of De Meulenaer and Tompa (12) were applied.

$R = 0.027$  and  $R_w = 0.044$ . The hydrogen atoms were localized on Fourier-difference maps and were refined, being assigned isotropic thermal parameters equal to those for the oxygen atoms to which they are bound. The final reliability factors were  $R = 0.024$  and  $R_w = 0.034$ . The atomic coordinates and the isotropic thermal parameters are given in Table 2. Table 3 gives the anisotropic thermal factors for all the nonhydrogen atoms.

**TABLE 2**  
Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters  $B_{\text{eq}}$  ( $\text{Å}^2$ ) and  $B_{\text{iso}}$  ( $\text{Å}^2$ ) for Hydrogen Atoms of  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  with E.s.d. Values in Parentheses

Atom	$x$	$y$	$z$	$B_{\text{eq}}/B_{\text{iso}}$
Ni	0.25	0.25	0.5	0.73(1)
V	0.10378(3)	0.97207(3)	0.19563(5)	0.59(1)
O(1)	0.5607(1)	0.4536(2)	0.4249(2)	1.02(3)
O(2)	0.3372(1)	0.3248(1)	0.3297(3)	1.06(4)
O(3)	0.2907(1)	0.4194(2)	0.6848(2)	1.11(3)
O <sub>w</sub> (1)	0.6135(1)	0.1522(2)	0.7915(3)	1.43(4)
O <sub>w</sub> (2)	0.6064(2)	0.1204(2)	0.3959(4)	2.22(5)
H(1)	0.628(4)	0.044(5)	0.373(8)	2.2
H(2)	0.629(5)	0.163(6)	0.385(9)	2.2
H(3)	0.617(4)	0.142(4)	0.683(7)	1.4
H(4)	0.607(4)	0.088(5)	0.803(7)	1.4

The positions of nickel and vanadium atoms in  $\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$  were found by direct methods. The refinement gave  $R = 0.245$  and  $R_w = 0.309$ . Absorption correction was performed ( $R_{\text{int}} = 0.0255$ ). Successive Fourier-difference synthesis located the oxygen atoms and then the hydrogen atoms; these latter were refined, being assigned isotropic thermal parameters equal to those for the oxygen atoms to which they are bound. Finally, by considering the secondary extinction, the values of  $R = 0.017$  and  $R_w = 0.018$  were obtained. The atomic coordinates and the isotropic thermal parameters and the anisotropic thermal parameters are gathered in Tables 4 and 5, respectively.

## STRUCTURE DESCRIPTION

The structure of the nickel metavanadate tetrahydrate,  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ , is formed of metavanadate chains  $(\text{VO}_3)_n^{n-}$ ,  $\text{NiO}_4(\text{H}_2\text{O})_2$  octahedra, and isolated water molecules (Fig. 1). The metavanadate chains are formed from square-pyramidal polyhedra ( $\text{VO}_5$ ), zigzag edge-linked and aligned in the  $[001]$  direction (Fig. 2). The square-pyramidal polyhedra are very distorted, and two V–O distance

**TABLE 3**  
Anisotropic Thermal Parameters ( $\times 10^4$ ) (E.s.d. Values in Parentheses) for All Nonhydrogen Atoms of  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ni	11.7(2)	21.4(4)	46.2(9)	– 2.7(2)	11.7(4)	0.3(4)
V	8.8(2)	20.2(4)	32.5(9)	1.5(2)	8.4(3)	– 2.7(3)
O(1)	12.1(8)	47(1)	38(3)	0.6(8)	11(1)	– 8(2)
O(2)	22.1(9)	26(1)	75(3)	– 5.5(8)	27(1)	0(2)
O(3)	21.2(9)	31(1)	60(3)	– 9.4(9)	17(1)	– 9(2)
O <sub>w</sub> (1)	20(1)	47(2)	78(4)	– 6.7(9)	12(2)	– 11(2)
O <sub>w</sub> (2)	48(2)	50(2)	133(5)	4(1)	39(2)	18(2)

TABLE 4

Final Atomic Coordinates and Equivalent Isotropic Thermal Parameters  $B_{\text{eq}}$  ( $\text{\AA}^2$ ) and  $B_{\text{iso}}$  ( $\text{\AA}^2$ ) for Hydrogen Atoms of  $\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$  with E.s.d. Values in Parentheses

Atom	x	y	z	$B_{\text{eq}}/B_{\text{iso}}$
Ni	0.01947(6)	0.25	0.45960(3)	0.806(6)
V	0.19614(5)	0.53160(3)	0.32656(3)	0.697(5)
O(1)	0.1177(3)	0.6144(1)	0.4367(1)	1.51(3)
O(2)	0.1667(3)	0.3806(1)	0.3546(1)	1.38(3)
O(3)	0.0039(3)	0.5713(1)	0.2082(1)	1.26(3)
O <sub>w</sub> (1)	0.3381(4)	0.25	0.5501(2)	1.34(4)
O <sub>w</sub> (2)	0.2949(4)	0.25	0.3708(2)	1.99(5)
H(1)	0.365(5)	0.314(2)	0.586(3)	1.3
H(2)	-0.420(8)	0.25	0.406(4)	2
H(3)	-0.312(9)	0.25	0.309(4)	2

groups are found (Table 6): for each vanadium atom, three oxygen atoms (type O(1)) are common to three pyramids with a 1.9–2 Å distance, whereas the two other oxygen atoms (O(2) and O(3)), which have two neighboring vanadium atoms with shorter V–O distances (1.65 Å), link the VO<sub>5</sub> pyramids to the NiO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> groups. These latter groups are almost regular with Ni–O distances ranging from 2.038(2) to 2.049(2) Å and a mean value of 2.045(2) Å. Each octahedron is linked to two metavanadate chains by means of four oxygen atoms in equatorial positions, whereas the axial positions are occupied by oxygen atoms from two water molecules. Thus the structure contains channels parallel to the *c* axis (Fig. 1). The water molecules coordinated to the nickel atoms, corresponding to O<sub>w</sub>(1), point toward the center of these channels. Finally, the remaining water molecules (corresponding to O<sub>w</sub>(2)), linked by hydrogen bonds, are located in the channels. The establishment of the hydrogen bonds is based on the parameters used by Evans (14), which are the following for the O–H...O bond: (i) the O–O distances, which must be less than 3 Å; (ii) the H...O distances, where O correspond to an oxygen atom from another group; (iii) the angle between O–H and H...O

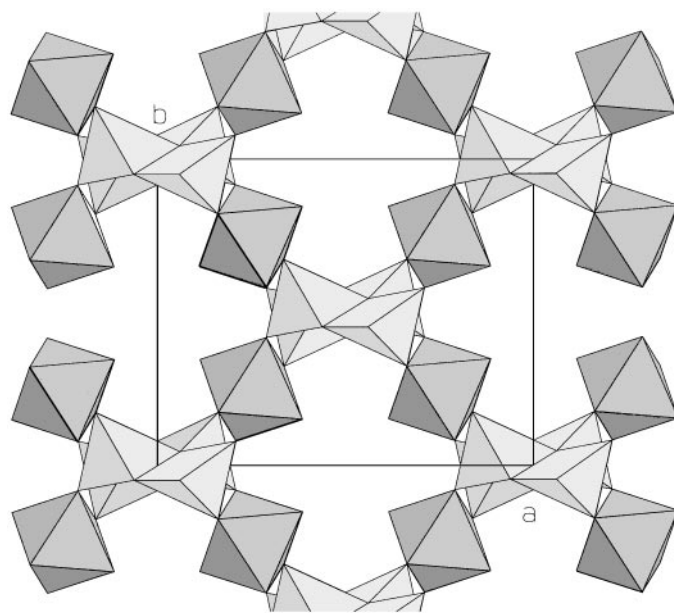


FIG. 1. Structure of  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  in projection on the (001) plane; the metavanadate chains are white, and the  $\text{NiO}_4(\text{H}_2\text{O})_2$  octahedra are darker.

bonds. These parameters are listed in Table 6. The effect of the hydrogen bonds on the molecular angle of the water molecules for O<sub>w</sub>(1) (93(7)°) and for O<sub>w</sub>(2) (116(10)°) (Table 6) compared to the value existing in the gaseous water molecule (105°) is pronounced. However, in the isolated water molecules (O<sub>w</sub>(2)) as well as in the water molecules coordinated to the nickel atoms (O<sub>w</sub>(1)), there are differences in the O<sub>w</sub>–H distances: the O<sub>w</sub>(1)–H(4) and O<sub>w</sub>(2)–H(2) distances are short compared to O<sub>w</sub>(1)–H(3) and O<sub>w</sub>(2)–H(1) (Table 6); that shows the difficulty of determining the position of hydrogen atoms in solid hydrates by X-ray methods, e.g., from difference Fourier analyses (15). Therefore, the variation of H...O distances is substantial (between 1.94 and 2.32 Å), while the O–O distances are almost the same (between 2.706 and 2.798 Å).

TABLE 5

Anisotropic Thermal Parameters ( $\times 10^4$ ) (E.s.d. Values in Parentheses) for All Nonhydrogen Atoms of  $\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ni	75.2(9)	16.0(2)	14.0(2)	0	3.8(3)	0
V	56.0(7)	15.2(2)	13.2(2)	-0.9(3)	3.2(3)	0.6(2)
O(1)	139(4)	31(1)	26(1)	4(2)	16(2)	-11(1)
O(2)	146(4)	19(1)	27(1)	-6(2)	14(2)	5(1)
O(3)	72(4)	35(1)	24(1)	11(2)	10(2)	7(1)
O <sub>w</sub> (1)	101(5)	30(2)	26(2)	0	-16(2)	0
O <sub>w</sub> (2)	93(6)	79(3)	23(2)	0	7(3)	0

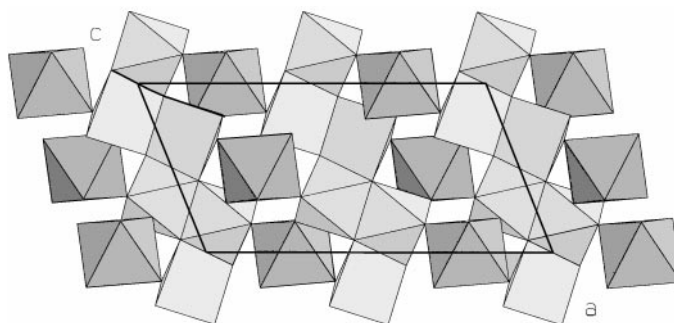


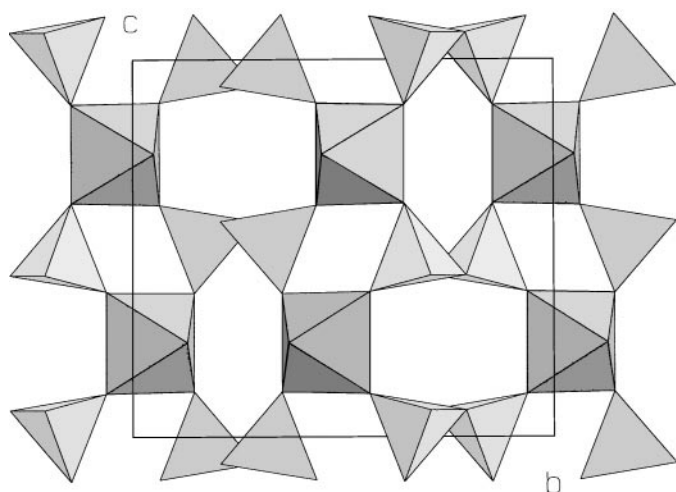
FIG. 2. Structure of  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  in projection on the (010) plane; the metavanadate chains are white, and the  $\text{NiO}_4(\text{H}_2\text{O})_2$  octahedra are darker.

**TABLE 6**  
**Interatomic Distances (Å) and Angles (Deg) in Ni(VO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O**

VO <sub>5</sub> square pyramid			
V–O(1 <sup>i</sup> )	1.899(2)	O(1 <sup>i</sup> )–V–O(1 <sup>ii</sup> )	72.60(9)
–O(1 <sup>ii</sup> )	2.027(1)	O(1 <sup>i</sup> )–V–O(1 <sup>iii</sup> )	141.01(10)
–O(1 <sup>iii</sup> )	1.876(2)	O(1 <sup>i</sup> )–V–O(2 <sup>ii</sup> )	106.95(11)
–O(2 <sup>ii</sup> )	1.653(2)	O(1 <sup>i</sup> )–V–O(3 <sup>iv</sup> )	95.36(10)
–O(3 <sup>iv</sup> )	1.655(2)	O(1 <sup>ii</sup> )–V–O(1 <sup>iii</sup> )	74.56(9)
Mean	1.822(2)	O(1 <sup>ii</sup> )–V–O(2 <sup>ii</sup> )	108.78(10)
		O(1 <sup>iii</sup> )–V–O(3 <sup>iv</sup> )	142.66(12)
		O(1 <sup>iii</sup> )–V–O(2 <sup>ii</sup> )	103.06(11)
		O(1 <sup>iii</sup> )–V–O(3 <sup>iv</sup> )	98.14(11)
		O(2 <sup>ii</sup> )–V–O(3 <sup>iv</sup> )	108.54(12)
NiO <sub>6</sub> octahedron			
Ni–O(2)	2.047(2)	O(2 <sup>v</sup> )–Ni–O(2 <sup>v</sup> )	180.00(0)
–O(2 <sup>v</sup> )	2.047(2)	–Ni–O(3)	89.73(9)
–O(3)	2.038(2)	–Ni–O(3 <sup>v</sup> )	90.27(9)
–O(3 <sup>v</sup> )	2.038(2)	–Ni–O <sub>w</sub> (1 <sup>vi</sup> )	92.92(10)
–O <sub>w</sub> (1 <sup>vi</sup> )	2.049(2)	–Ni–O <sub>w</sub> (1 <sup>vii</sup> )	87.08(10)
–O <sub>w</sub> (1 <sup>vii</sup> )	2.049(2)	O(2 <sup>v</sup> )–Ni–O(3)	90.27(9)
Mean	2.045(2)	–Ni–O(3 <sup>v</sup> )	89.73(9)
		–Ni–O <sub>w</sub> (1 <sup>vi</sup> )	87.08(10)
		–Ni–O <sub>w</sub> (1 <sup>vii</sup> )	92.92(10)
		O(3 <sup>v</sup> )–Ni–O(3 <sup>v</sup> )	180.00(0)
		–Ni–O <sub>w</sub> (1 <sup>vi</sup> )	89.62(9)
		–Ni–O <sub>w</sub> (1 <sup>vii</sup> )	90.38(9)
		O(3 <sup>v</sup> )–Ni–O <sub>w</sub> (1 <sup>vi</sup> )	90.38(9)
		–Ni–O <sub>w</sub> (1 <sup>vii</sup> )	89.62(9)
		O <sub>w</sub> (1 <sup>vi</sup> )–Ni–O <sub>w</sub> (1 <sup>vii</sup> )	180.00(0)
Hydrogen bonds and angles			
–O <sub>w</sub> (1)–H(3)	0.77(5)	O <sub>w</sub> (1)–H(4)	0.65(5)
H(3)–O <sub>w</sub> (1)–H(4)			93(7)
–O <sub>w</sub> (2)–H(1)	0.84(5)	O <sub>w</sub> (2)–H(2)	0.53(6)
H(1)–O <sub>w</sub> (2)–H(2)			116(10)
–O <sub>w</sub> (1)–O <sub>w</sub> (2)	2.706(4);	H(3)---O <sub>w</sub> (2)	1.94(5);
O <sub>w</sub> (1)–H(3)–O <sub>w</sub> (2)			173(4)
–O <sub>w</sub> (1)–O <sub>w</sub> (2 <sup>viii</sup> )	2.781(3)	H(4)---O <sub>w</sub> (2 <sup>viii</sup> )	2.14(5)
–O <sub>w</sub> (1)–H(4)–O <sub>w</sub> (2 <sup>viii</sup> )			170(4)
–O <sub>w</sub> (2)–O <sub>w</sub> (1 <sup>ix</sup> )	2.781(3)	H(1)---O <sub>w</sub> (1 <sup>ix</sup> )	2.00(5)
O <sub>w</sub> (2)–H(1)–O <sub>w</sub> (1 <sup>ix</sup> )			156(2)
–O <sub>w</sub> (2)–O(2 <sup>x</sup> )	2.798(3)	H(2)---O(2 <sup>x</sup> )	2.32(7)
O <sub>w</sub> (2)–H(2)–O(2 <sup>x</sup> )			151(1)

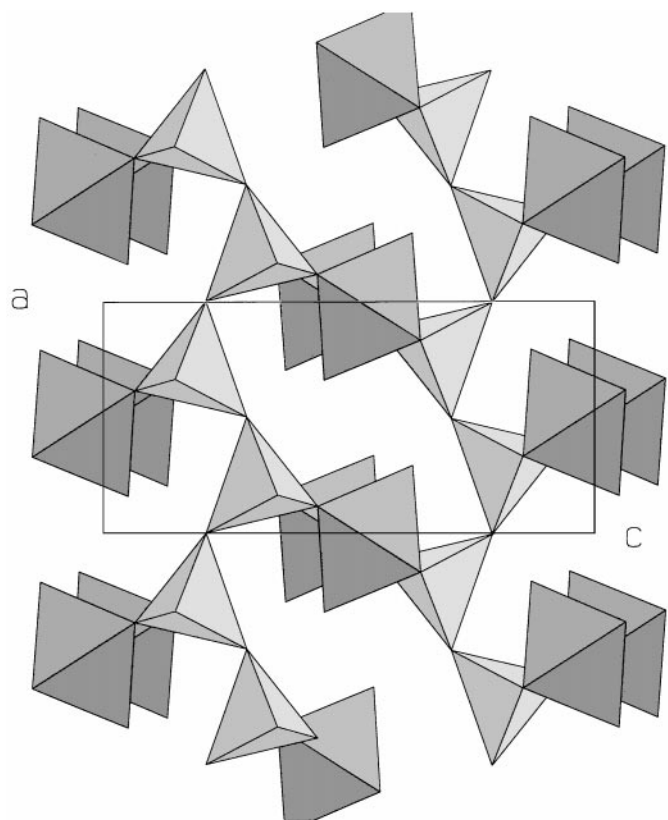
Note. Symmetry codes: (i)  $x - \frac{1}{2}, \frac{1}{2} + y, z$ ; (ii)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $x - \frac{1}{2}, 1.5 - y, z - \frac{1}{2}$ ; (iv)  $\frac{1}{2} - x, 1.5 - y, 1 - z$ ; (v)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (vi)  $1 - x, y, 1.5 - z$ ; (vii)  $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$ ; (viii)  $x, -y, z - \frac{1}{2}$ ; (ix)  $x, -y, \frac{1}{2} - z$ ; (x)  $1 - x, y, \frac{1}{2} - z$ .

The structure of the nickel metavanadate dihydrate  $\alpha$ -Ni(VO<sub>3</sub>)<sub>2</sub> · 2H<sub>2</sub>O is shown in Fig. 3. It is composed of metavanadate chains (VO<sub>3</sub>)<sub>n</sub><sup>–</sup> parallel to the [100] direction, and is formed of vertex-linked VO<sub>4</sub> tetrahedra (Fig. 4). As in the structure of Ni(VO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O, the chains are linked together by means of NiO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> octahedra. Thus a channel network is formed in the [100] direction (Fig. 3). The largest, formed from two chains and two octahedra, has the following dimensions: 5.18 × 2.88 Å. The interatomic distances and the angles between the different atoms are given in Table 7. The NiO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> octahedra are quite regular with



**FIG. 3.** Structure of  $\alpha$ -Ni(VO<sub>3</sub>)<sub>2</sub> · 2H<sub>2</sub>O in projection on the (100) plane; the metavanadate chains are white, and the NiO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> octahedra are darker.

a mean Ni–O distance of 2.035(2) Å. The four equatorial oxygen atoms are bridging atoms between nickel atoms and metavanadate chains. In these chains, two types of oxygen atoms are present: the ones that are also linked to the nickel



**FIG. 4.** Structure of  $\alpha$ -Ni(VO<sub>3</sub>)<sub>2</sub> · 2H<sub>2</sub>O in projection on the (010) plane; the metavanadate chains are white, and the NiO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> octahedra are darker.

**TABLE 7**  
**Interatomic Distances (Å) and Angles (Deg)**  
**in  $\alpha$ -Ni(VO<sub>3</sub>)<sub>2</sub> · 2H<sub>2</sub>O**

VO <sub>4</sub> tetrahedron			
V–O(1)	1.625(1)	O(1)–V–O(2)	109.96(8)
–O(2)	1.645(1)	O(1)–V–O(3)	109.38(8)
–O(3)	1.801(1)	O(1)–V–O(3 <sup>i</sup> )	107.86(8)
–O(3 <sup>i</sup> )	1.800(2)	O(2)–V–O(3)	108.94(7)
		O(2)–V–O(3 <sup>i</sup> )	111.55(8)
Mean	1.718(1)	O(3)–V–O(3 <sup>i</sup> )	109.12(8)
NiO <sub>6</sub> octahedron			
Ni–O(1 <sup>ii</sup> )	2.034(1)	O(1 <sup>ii</sup> )–Ni–O(1 <sup>iii</sup> )	90.16(6)
–O(1 <sup>iii</sup> )	2.034(1)	–Ni–O(2)	177.79(6)
–O(2)	2.028(1)	–Ni–O(2 <sup>iv</sup> )	91.75(6)
–O(2 <sup>iv</sup> )	2.028(1)	–Ni–O <sub>w</sub> (1)	90.53(7)
–O <sub>w</sub> (1)	2.058(2)	–Ni–O <sub>w</sub> (2)	89.37(7)
–O <sub>w</sub> (2)	2.028(2)	O(1 <sup>iii</sup> )–Ni–O(2)	91.75(6)
Mean	2.035(1)	–Ni–O(2 <sup>iv</sup> )	177.79(6)
		–Ni–O <sub>w</sub> (1)	90.53(7)
		–Ni–O <sub>w</sub> (2)	89.37(2)
		O(2)–Ni–O(2 <sup>iv</sup> )	86.32(6)
		–Ni–O <sub>w</sub> (1)	88.35(7)
		–Ni–O <sub>w</sub> (2)	91.76(7)
		O(2 <sup>iv</sup> )–Ni–O <sub>w</sub> (1)	88.35(7)
		–Ni–O <sub>w</sub> (2)	91.76(7)
		O <sub>w</sub> (1)–Ni–O <sub>w</sub> (2)	179.86(11)
Hydrogen bonds and angles			
–O <sub>w</sub> (1)–H(1)	0.81(3)	O <sub>w</sub> (1)–H(1 <sup>iv</sup> )	0.81(3)
H(1)–O <sub>w</sub> (1)–H(1 <sup>iv</sup> )			113(4)
–O <sub>w</sub> (2)–H(2)	0.81(5)	O <sub>w</sub> (2)–H(3)	0.73(5)
H(2)–O <sub>w</sub> (2)–H(3)			113(7)
–O <sub>w</sub> (1)–O(3 <sup>v</sup> )	2.797(2)	H(1)–O(3 <sup>v</sup> )	2.02(3)
O <sub>w</sub> (1)–H(1)–O(3 <sup>v</sup> )			160(1)
–O <sub>w</sub> (2)–O <sub>w</sub> (1 <sup>vi</sup> )	2.927(3)	H(2)–O <sub>w</sub> (1 <sup>vi</sup> )	2.16(5)
O <sub>w</sub> (2)–H(2)–O <sub>w</sub> (1 <sup>vi</sup> )			159(1)
–O <sub>w</sub> (2)–O(2 <sup>vii</sup> )	2.999(2)	H(3)–O(2 <sup>vii</sup> )	2.38(4)
O <sub>w</sub> (2)–H(3)–O(2 <sup>vii</sup> )			144.1(2)
–O <sub>w</sub> (2)–O(2 <sup>viii</sup> )	2.999(2)	H(3)–O(2 <sup>viii</sup> )	2.38(4)
O <sub>w</sub> (2)–H(3)–O(2 <sup>viii</sup> )			144.1(2)

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

atoms lead to V–O distances of 1.6 Å, and the others are located midway ( $d_{V-O} = 1.8$  Å) between two vanadium atoms. Finally, the water molecules, which belong to the first nickel coordination sphere, form hydrogen bonds with the O(2), O(3), and O<sub>w</sub>(1) atoms (Table 7). For example, the H(3) hydrogen atom forms two hydrogen bonds with the O(2) oxygen atoms from two different metavanadate chains. It is interesting to note that the O–H bonds calculated in  $\alpha$ -Ni(VO<sub>3</sub>)<sub>2</sub> · 2H<sub>2</sub>O (0.73 and 0.81 Å, Table 7) are more realistic than those found in Ni(VO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O (0.53–0.84 Å, Table 6).

For hydrogen-bond determination, the valence bond model has been used. The valence bond model (16, 17) is

generally used to check the validity of structure resolutions. However, the application of this model to solids presenting hydrogen bonds is not easy. Indeed, the formula  $s = \exp(r_0 - r)/B$  (where  $s$  is the bond valence,  $r_0$  an empirical value tabulated for each type of bond,  $B$  a constant equal to 0.37, and  $r$  the real bond length) does not give good results with hydrogen atoms. For instance, if the valence of hydrogen for the O<sub>w</sub>–H bonds in the Ni(VO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O compound is calculated with the formula ( $r_0 = 0.882$  Å), then the values obtained for the sum of the bond valences are 3.56 for O<sub>w</sub>(1) (including the Ni–O<sub>w</sub>(1) bond) and 3.70 for O<sub>w</sub>(2) instead of 2, without consideration of hydrogen bonds. The discrepancy is due to the uncertainty in the hydrogen atom positions (16). To solve this problem for a hydrogen bond of O–H---O type, one solution is to calculate the O–H valence indirectly by subtracting the H---O valence from 1. This latter value is graphically obtained from the scheme given in (16). The results obtained for Ni(VO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O are shown in Table 8a. They are in agreement with the valences +2 and +5 for nickel and vanadium, respectively. Moreover, a valence of around 2 is found for all the oxygen atoms. Finally, the method also allows one to check that all hydrogen bonds are considered and the obtained results are consistent with those presented in Table 6. The same reasoning was followed for  $\alpha$ -Ni(VO<sub>3</sub>)<sub>2</sub> · 2H<sub>2</sub>O (Tables 7 and 8b), and it also confirmed the valences of vanadium, oxygen, and nickel and the presence of hydrogen bonds.

**TABLE 8**  
**Bond Valence Calculations Using  $s = \exp(r_0 - r)/B$  with  $r_0(V^{5+}-O) = 1.803$  Å,  $r_0(Ni^{2+}-O) = 1.654$  Å, and  $B = 0.37$  (16) in Ni(VO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O and  $\alpha$ -Ni(VO<sub>3</sub>)<sub>2</sub> · 2H<sub>2</sub>O**

	(a) Ni(VO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O					$\Sigma_{cal}$	$\Sigma_{theo}$
	O(1)	O(2)	O(3)	O <sub>w</sub> (1)	O <sub>w</sub> (2)		
Ni		0.35 (×2)	0.35(×2)	0.34(×2)		2.08	2
V	0.77; 0.55; 1.50		1.49			5.13	5
						0.82	
H(1)				0.125	0.875		1
H(2)		0.075			0.925		1
H(3)				0.875	0.125		1
H(4)				0.9	0.1		1
$\Sigma_{cal}$	2.14	1.93	1.84	2.2	2.03		
$\Sigma_{theo}$	2	2	2	2	2		
	(b) $\alpha$ -Ni(VO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O					$\Sigma_{cal}$	$\Sigma_{theo}$
	O(1)	O(2)	O(3)	O <sub>w</sub> (1)	O <sub>w</sub> (2)		
Ni	0.36(×2)	0.36(×2)		0.34	0.36	2.14	2
V	1.62	1.53	1.01(×2)			5.17	5
H(1)			0.125	0.875(×2)			1
H(2)				0.09	0.91		1
H(3)		0.065(×2)			0.87		1
$\Sigma_{cal}$	1.98	1.96	2.15	2.18	2.14		
$\Sigma_{theo}$	2	2	2	2	2		

## DISCUSSION

The structure of  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  can be compared with those obtained previously for  $\text{Co}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  (13) and  $\text{Mn}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  (18). The most important discrepancy arises from the counting and positioning of the hydrogen atoms. In the case of manganese metavanadate, seven hydrogen atoms were localized in a general position by Fourier-difference synthesis; they were affected by orientation disorder, but their positions were not refined (18). Similarly, five hydrogen atoms were found for  $\text{Co}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ . They were located in general position. Three had an occupation factor of 1, while the two others had an occupation factor of  $\frac{1}{2}$ . Here, for the nickel metavanadate  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$ , we have located without ambiguity the four hydrogen atoms that belong to the two water molecules in general position. In the same way, the structure resolution of  $\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$  allowed the position of the hydrogen atoms which were not obtained for the isostructural  $\alpha\text{-Co}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$  (19) and  $\alpha\text{-Mn}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$  (18) materials to be found. For this last compound, the position of hydrogen atoms was reported in a recently published paper (20).

The two hydrates  $M(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\alpha\text{-}M(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$  (with  $M = \text{Co}$ ,  $\text{Ni}$ , and  $\text{Mn}$ ) mainly differ in the vanadium environment, which is square pyramidal and tetrahedral, respectively. The mean V–O distances are 1.82 Å in  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 1.72 Å in  $\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ . In these structures, the divalent cations ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Mn}^{2+}$ ) are in an octahedral environment with two water molecules in axial positions and four oxygen atoms in equatorial positions. The latter link the divalent cations to the metavanadate chains. The mean  $M^{2+}$ –O bond length values increase in the two types of structure from  $\text{Ni}^{2+}$  to  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  in agreement with the evolution of their ionic radii in octahedral oxygenated environments ( $\text{Ni}^{2+}$ , 0.690 Å;  $\text{Co}^{2+}$ , 0.745 Å;  $\text{Mn}^{2+}$ , 0.830 Å (21)). The main difference is observed in the distortion of the  $\text{MO}_4(\text{H}_2\text{O})_2$  octahedra. For the nickel metavanadates these octahedra are nearly perfect since the axial distances are only 0.3% and 0.6% higher than the equatorial distances for  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ , respectively. The distortion increases with the size of the cation: 0.9% for  $\text{CoO}_4(\text{H}_2\text{O})_2$  in  $\text{Co}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  (2.6% in  $\alpha\text{-Co}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ ) and 1.8% in  $\text{Mn}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  (2% in  $\alpha\text{-Mn}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ ). For cobalt metavanadates we observe a large differ-

ence in the values of this ratio, probably due to a Jahn–Teller distortion of the octahedral environment of the high-spin cation  $\text{Co}^{2+}$  ( $d^7$ ).

## CONCLUSION

The nickel metavanadates  $\text{Ni}(\text{VO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\alpha\text{-Ni}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$  have been synthesized and their structures resolved. In these two materials the vanadium coordination is different: it is 5 in the tetrahydrate and 4 in the dihydrate. The hydrogen atoms were located by Fourier difference synthesis, which allowed us to show that the valence bond model can be useful for the description of hydrogen bonds in hydrates. Studies of their thermal and electrochemical properties are now in progress.

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