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Hydrothermal Synthesis and Structure of Nickel(II) Metavanadate Monohydrate, NiV₂O₆·H₂O

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Abstract

The structure of NiV₂O₆·H₂O consists of infinite chains of [VO₄] tetrahedra running along the [100] direction connected by isolated [Ni₂O₈(H₂O)₂] dimeric entities to build up a three-dimensional network. A valence-bond analysis allows the identification of the O atoms of the water molecules.

Comment

From the theoretical point of view, the understanding of the magnetic interactions in solids containing metallic centres connected through more or less symmetrical diamagnetic anions is a challenging task. Some correlations leading to guidelines for the rationalization of the magnetic properties have been proposed which deal with transition metal oxophosphorus derivatives (Beltrán *et al.*, 1991; Amorós, Beltrán & Beltrán, 1992). However, it seems clear that both structural and magnetic data on these types of materials are as yet insufficient to substantiate the role of the group orbitals of the anions in the propagation of the exchange interactions (Marcos, Amorós, Beltrán & Beltrán, 1993a). Therefore, in the search for new magnetic systems, we have undertaken a systematic study of other transition metal derivatives in which the oxophosphorus species are replaced by other related anionic entities (Marcos, Amorós, Beltrán & Beltrán, 1993b), such as vanadate in the title compound. Whereas inorganic phosphate materials have been studied extensively because of their fundamental and applied interest (Umegaki, 1989), the solid-state chemistry of vanadates is, comparatively, unknown. In fact, the number of transition metal vanadate derivatives whose struc-

tures have been determined is very limited (see, for example, Mocała & Ziółkowski, 1987; Leblanc & Ferey, 1990; Lafontaine, Ferey & Rodríguez, 1990), and, in particular, only one transition metal metavanadate compound, CuV₂O₆(H₂O)₂, has been structurally characterized.

We report here the synthesis and crystal structure of a new nickel(II) metavanadate hydrate, NiV₂O₆·H₂O.

To an aqueous solution (7 ml) containing 3.948 g (16.6 mmol) of NiCl₂·6H₂O, a concentrated solution of KOH (6 ml, 1.4 M) was added dropwise while stirring until a pale green suspension (pH *ca* 6) was obtained. Then, a solution (11 ml) containing 3.048 g (25.0 mmol) of NaVO₃ was dripped over the nickel suspension with stirring. The pH of the final suspension increased until it reached *ca* 10. The mixture was placed in a steel-covered teflon container filled to 80% of its volume (23 ml). The reaction vessel was maintained at 473 K and autogenous pressure for a week before cooling at 30 K h⁻¹ to room temperature. The resulting solid was separated by filtration, washed with water, rinsed with acetone and dried in a desiccator at room temperature. Well formed orange crystals of the title compound were obtained together with another major polycrystalline green product identified by X-ray powder diffraction as Ni_{12+x}H_{6-2x}(VO₄)₈(OH)₆ (Marcos, Amorós, Beltrán & Beltrán, 1993b). Separation of crystals of the title compound was easily performed because of the differences in colour, crystal habit and size.

Condensation of metallic centres *via* oxolation with the formation of *M—O—M* oxo bridges requires high pH values, *i.e.* the presence of OH⁻ groups in the coordination sphere of the metallic ions, and is favoured by using elevated pressures and high metal-ion concentrations (Marcos, Amorós, Beltrán & Beltrán, 1993a). In practice, solids showing different degrees of condensation of the cationic aggregates can be obtained by adjusting these main variables. Under our pH working conditions and using a relatively soft hydrothermal procedure, condensation of the prevalent vanadium ionic species, the tetrahedral [VO₂(OH)₂] entity (Livage, Henry & Sanchez, 1989), allows the formation of the infinite chains built up of VO₄³⁻ tetrahedra characteristic of metavanadates and observed in the structure of NiV₂O₆·H₂O (see below). At the same time, dimerization of the Ni^{II} species to give [Ni₂O₈(H₂O)₂] is observed. This fact, although favoured in basic media (Livage, Henry & Sánchez, 1989), results in rather unusual solid derivatives.

Figs. 1 and 2 show views of the crystal structure of the title compound along the [010], [001] and [100] directions. NiV₂O₆·H₂O has a quite open three-dimensional structure built up from two different motifs. The anionic moiety consists of infinite metavanadate [VO₃⁻]_∞ chains running along the [100] direction. Within these chains, each VO₄ tetrahedron shares two corners with two other metavanadate groups. However,

the cationic counterpart consists of isolated units formed by two edge-sharing fused Ni^{II} octahedra. In this way, the structure of the title compound might be described as consisting of isolated metavanadate chains connected only through [Ni₂O₈(H₂O)₂] dimers, in such a way that each dimer is surrounded by four different metavanadate chains.

Two different VO₄ groups alternate along the metavanadate chains, —V(1)—O(5)—V(2)—O(6)—. Each V atom is connected to the adjacent V atoms through O-atom bridges and the other two positions of the tetrahedral coordination sphere are occupied by O atoms shared by Ni²⁺ ions. However, while V(2) tetrahedra merely act as μ-(O,O') bridges between two different Ni₂O₈(H₂O)₂ dimers, V(1) tetrahedra act as μ-(O) intradimeric bridges and μ-(O,O') interdimeric bridges.

The V—O bond distances are, in both cases, in good agreement with the data reported in the literature for CuV₂O₆(H₂O)₂ (Leblanc & Ferey, 1990). As in the copper derivative, the longest V—O distances [V(1)—O5, V(1)—O6; see Table 2] correspond to the intrachain shared O atoms. This type of linear single vanadate chain is similar, although more corrugated, than that observed in the copper derivative (Leblanc & Ferey, 1990). This, in turn, is a characteristic of pyroxenes, MM'Si₂O₆ (Liebau, 1981), and also appears in several polyphosphates, such as (LiPO₃)_n, (KPO₃)_n and (MPO₃)_n, where M = Rb and Cs (Umegaki, 1989). The Ni octahedra defining the dimers are equivalent and related by a centre of symmetry. The coordination sphere of each Ni atom consists of five O atoms from metavanadate groups and another O atom belonging to a water molecule. The Ni—O bond distances range from 1.997 (6) to 2.111 (6) Å, with the longest one involving the water molecule.

This last assertion derives from the valence-bond analysis of the title compound based on Brese's data (Brese & O'Keeffe, 1991). Such an analysis (see Table 3) provides a better understanding of the metavanadate structure with respect to details of the cationic coordination, the location of water molecules and the hydrogen-bonding network. The results of the structure analysis using the equations of Brown (1992),

$$V_i = \sum_j S_{ij}$$

$$S_{ij} = \exp(R_o - R_{ij}/B),$$

where R_o values were taken from Brese & O'Keeffe (1991), B was set equal to 0.37 Å and R_{ij} is the interatomic distance, show reasonable agreement with the expected atomic valences for Ni and V atoms [2.09, 5.05 and 5.07 v.u. for Ni, V(1) and V(2), respectively]. The calculated values for the O atoms are also close to those expected, except for the O(1) atoms (0.29 v.u.). It is reasonable, therefore, to assume that these are the O atoms of the water molecules. Such a low calculated value must be related to the fact that it has not been possible to locate protons and

consequently the valence of the O atom used in the OH bonds has not been included in Table 3. On the other hand, the relatively low valence value shown by O(4) (1.75 v.u.) is typical of a hydrogen-bond acceptor. Both the spatial arrangement of the O(1) and O(4) atoms and the calculated valence values suggest that the orientation of the protons of the water molecules forms a hydrogen-

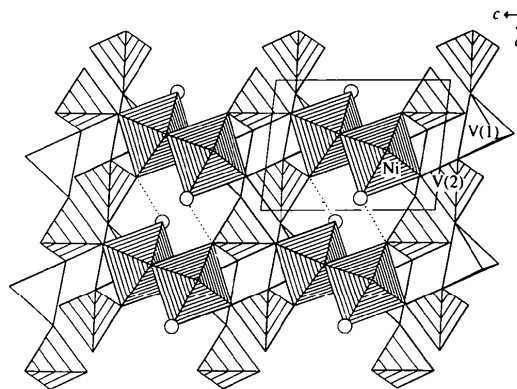


Fig. 1. View of the crystal structure of NiV₂O₆.H₂O along the [010] direction. Open circles represent the O atoms [O(1)] of the water molecules and dotted lines correspond to hydrogen bonds.

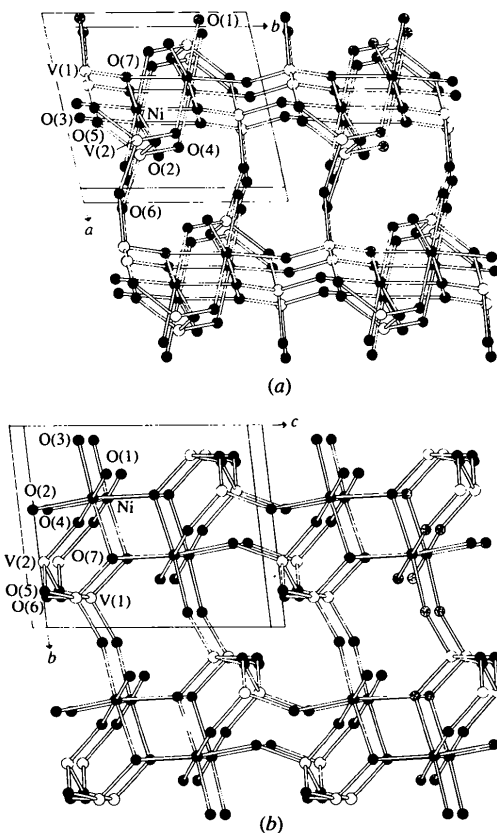


Fig. 2. Views of the structure of the title compound along (a) the [001] and (b) the [100] directions showing the intercrossing channel system.

bonding network providing strong interactions between O(1) and O(4) [O(1)··O(4) 2.867 (9) Å; see Fig. 1].

The final result is that NiV₂O₆·H₂O exhibits an open framework in which different types of intercrossing channels appear running along the [001] and [100] directions (Fig. 2). It is throughout these channels that the hydrogen-bonding network extends. It should be noted that the structure of NiV₂O₆·H₂O differs markedly from that of the anhydrous vanadate, NiV₂O₆, which involves both octahedrally and tetrahedrally coordinated V atoms arranged by means of edge-sharing in a ramsdellite-type double chain (Le Bail & Lafontaine, 1990). In order to elucidate the involvement of the VO₄³⁻ groups in the transmission of the magnetic interactions, a magnetic study, including ⁵¹V solid-state NMR, is currently in progress.

Experimental

Crystal data

NiV₂O₆·H₂O

M_r = 549.21

Triclinic

P $\bar{1}$

a = 5.833 (2) Å

b = 6.593 (3) Å

c = 7.730 (3) Å

α = 80.97 (3)°

β = 81.11 (3)°

γ = 76.43 (3)°

V = 283.2 (2) Å³

Z = 1

D_x = 3.220 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 30 reflections

θ = 10–12.5°

μ = 6.495 mm⁻¹

T = 293 (2) K

Plate

0.44 × 0.10 × 0.04 mm

Yellow

Data collection

Siemens R3m/V diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scan

T_{min} = 0.062, *T_{max}* =

0.120

980 measured reflections

851 independent reflections

744 observed reflections

[*I* > 2σ(*I*)]

R_{int} = 0.0334

θ_{\max} = 23.52°

h = 1 → 6

k = -7 → 7

l = -8 → 8

3 standard reflections

monitored every 100

reflections

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.0487

wR(*F*²) = 0.1284

S = 1.108

851 reflections

92 parameters

w = 1/[σ²(*F_o*²) + (0.0943*P*)²

+ 1.5608*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 1.237 e Å⁻³

Δρ_{min} = -1.298 e Å⁻³

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Ni	0.4242 (2)	0.6411 (2)	0.65246 (14)	0.0085 (4)
V(1)	0.3937 (2)	1.1484 (2)	0.7692 (2)	0.0070 (5)
V(2)	0.1964 (2)	0.6737 (2)	1.0909 (2)	0.0081 (5)
O(1)	0.0886 (11)	0.7597 (10)	0.5627 (9)	0.023 (2)
O(2)	0.2550 (11)	0.5847 (10)	0.8965 (8)	0.0152 (14)
O(3)	0.4581 (11)	0.9269 (9)	0.6845 (9)	0.0174 (14)
O(4)	0.2490 (10)	0.4793 (9)	1.2568 (8)	0.0148 (14)
O(5)	0.6146 (10)	1.1539 (9)	0.9039 (8)	0.0130 (13)
O(6)	-0.1014 (10)	0.8181 (10)	1.1231 (8)	0.0173 (14)
O(7)	0.4162 (10)	1.3437 (9)	0.5982 (7)	0.0105 (13)

Table 2. Selected geometric parameters (Å, °)

Ni—O(3)	1.997 (6)	V(1)—O(7)	1.707 (6)
Ni—O(2)	2.012 (6)	V(1)—O(6 ^{iv})	1.759 (6)
Ni—O(7 ⁱ)	2.014 (6)	V(1)—O(5)	1.787 (6)
Ni—O(4 ⁱⁱ)	2.070 (6)	V(2)—O(2)	1.656 (6)
Ni—O(7 ⁱⁱⁱ)	2.081 (6)	V(2)—O(4)	1.674 (6)
Ni—O(1)	2.111 (6)	V(2)—O(5 ^v)	1.768 (6)
V(1)—O(3)	1.633 (6)	V(2)—O(6)	1.775 (6)
O(3)—Ni—O(2)	94.5 (3)	O(7 ⁱⁱⁱ)—Ni—O(1)	89.5 (2)
O(3)—Ni—O(7 ⁱ)	94.0 (3)	O(3)—V(1)—O(7)	107.0 (3)
O(2)—Ni—O(7 ⁱ)	171.4 (2)	O(3)—V(1)—O(6 ^{iv})	108.2 (3)
O(3)—Ni—O(4 ⁱⁱ)	88.2 (3)	O(7)—V(1)—O(6 ^{iv})	110.7 (3)
O(2)—Ni—O(4 ⁱⁱ)	91.0 (3)	O(3)—V(1)—O(5)	110.1 (3)
O(7 ⁱ)—Ni—O(4 ⁱⁱ)	90.1 (2)	O(7)—V(1)—O(5)	105.4 (3)
O(3)—Ni—O(7 ⁱⁱⁱ)	174.2 (3)	O(6 ^{iv})—V(1)—O(5)	115.2 (3)
O(2)—Ni—O(7 ⁱⁱⁱ)	90.9 (2)	O(2)—V(2)—O(4)	111.9 (3)
O(7 ⁱ)—Ni—O(7 ⁱⁱⁱ)	80.6 (2)	O(2)—V(2)—O(5 ^v)	108.7 (3)
O(4 ⁱⁱ)—Ni—O(7 ⁱⁱⁱ)	89.8 (2)	O(4)—V(2)—O(5 ^v)	107.2 (3)
O(3)—Ni—O(1)	92.5 (3)	O(2)—V(2)—O(6)	110.7 (3)
O(2)—Ni—O(1)	88.2 (3)	O(4)—V(2)—O(6)	110.4 (3)
O(7 ⁱ)—Ni—O(1)	90.5 (3)	O(5 ^v)—V(2)—O(6)	107.8 (3)
O(4 ⁱⁱ)—Ni—O(1)	179.0 (2)		

Symmetry codes: (i) 1 - *x*, 2 - *y*, 1 - *z*; (ii) 1 - *x*, 1 - *y*, 2 - *z*; (iii) *x*, *y* - 1, *z*; (iv) -*x*, 2 - *y*, 2 - *z*; (v) 1 - *x*, 2 - *y*, 2 - *z*.

Table 3. Bond-valence analysis (v.u.) for NiV₂O₆·H₂O

	Ni	V(1)	V(2)	Σ
O(1)	0.29	—	—	0.29
O(2)	0.38	—	1.49	1.87
O(3)	0.40	1.58	—	1.98
O(4)	0.33	—	1.42	1.75
O(5)	—	1.04	1.09	2.13
O(6)	—	1.13	1.07	2.20
O(7)	0.37	1.30	—	1.99
	0.32	—	—	—
Σ	2.09	5.05	5.07	—

Data collection and cell refinement: Siemens *P3* software. Data reduction: *XDISK*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL92* (Sheldrick, 1992). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL92*.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1075). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cu-Bearing Tourmaline from Paraiba, Brazil

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Abstract

Crystal structure refinement of copper-bearing tourmaline from Paraiba, Brazil, rim composition $\{\text{Na}_{0.54}\text{Ca}_{0.05}\}\{\text{Li}_{1.21}\text{Mn}_{0.04}\text{Cu}_{0.10}\text{Al}_{1.66}\}\text{Al}_6\{\text{Si}_{5.92}\text{Al}_{0.08}\}\text{O}_{18}\{\text{BO}_3\}_3\{(\text{OH})_{3.56}\text{F}_{0.44}\}$, core composition $\{\text{Na}_{0.55}\text{Ca}_{0.01}\}\{\text{Li}_{1.16}\text{Mn}_{0.08}\text{Cu}_{0.05}\text{Al}_{1.71}\}\text{Al}_6\{\text{Si}_{5.88}\text{Al}_{0.12}\}\text{O}_{18}\{\text{BO}_3\}_3\{(\text{OH})_{3.70}\text{F}_{0.30}\}$, shows the octahedrally coordinated Z site to be completely occupied by Al, and Li to occur only at the octahedrally coordinated

Y site. The high displacement factors at the O1 and O2 positions indicate significant positional disorder that is induced by occupancy of the X [$\approx 0.57\text{Na} + 0.43\Box$ (vacancy)] and Y [$\approx 1.2\text{Li} + 1.8(\text{Al} + \text{Mn}^{3+})$] sites by cations of very different size and charge.

Comment

Bank, Henn, Bank, von Platen & Hofmeister (1990) reported the occurrence of Cu-rich tourmaline from the state of Paraiba, Brazil. Their samples were Mn-rich elbaite containing up to 2.1 wt% CuO and 0.11 wt% FeO, and are thus unusual in that Cu had only been reported previously in the p.p.m. range in tourmaline (Bassett, 1953; Power, 1968). Henn & Bank (1990) and Rossman, Fritsch & Shigley (1991) examined the colouration mechanisms in Cu-bearing tourmaline, and showed that Cu is solely responsible for the blue colour. Optical-absorption maxima in the 695–940 nm region were assigned to *d-d* transitions in Cu^{2+} , and maxima at 700 and 520 nm are due to *d-d* transitions in Mn^{3+} .

Two specimens were studied in the present work; a sample from the rim (T54) and a sample from the core (T55). Site occupancies were refined in the following manner. The X and Y sites contain more than two scattering species [(Na, Ca, vacancy) and (Li, Mn, Cu, Al), respectively]; hence, the chemical site occupancies cannot be refined directly. However, the total scattering at each of these sites may be derived from the refinement and then compared with the chemical species assigned to these sites from the chemical analysis and calculation of the formula unit. The scattering at the X, Y and Z sites was considered as variable and represented by a single scattering species: $X = \text{Na}$, $Y = \text{Mg}$ and $Z = \text{Al}$. The occupancies at the Z sites refined to within one standard deviation (0.004) of unity; these values were fixed at 1.0 for the final cycles of refinement. The occupancy of the X site refined to 0.65 (2) Na for both crystals. When the scattering from the minor Ca at the X site is considered, there is reasonably good agreement between the refined scattering and the chemical species assigned to the X site from the chemical analyses. The occupancy at the Y site refined to 0.822 (6) and 0.831 (6) Mg for T54 and T55, respectively. This gives an effective Y-site scattering of 9.86 and 9.97 equivalent electrons per site for T54 and T55, respectively, and can be compared with an effective scattering of 9.70 and 9.72 equivalent electrons calculated from the site assignments from the unit formulae. Thus there is close agreement between the results of the site-occupancy refinement and the site assignments for the unit formulae calculated from the chemical analyses.

There is significant positional disorder at the O1 and O2 positions in Cu-bearing tourmaline, as indicated by the relatively high U_{eq} values at the O1 and O2 positions. This is a common feature in many tourmaline structures, and Burns, MacDonald & Hawthorne (1994)