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BRIEF COMMUNICATIONS

Hydrothermal Synthesis and Structural Characterization of a Nickel(II) Vanadyl(IV) Phosphate Hydrate: $Ni_{0.5}VOPO_4 \cdot 1.5H_2O$

K. H. LII AND L. F. MAO

Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan, Republic of China

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A new phosphate hydrate, $Ni_{0.5}VOPO_4 \cdot 1.5H_2O$, was synthesized hydrothermally and characterized by single-crystal X-ray diffraction, thermogravimetric analysis, and magnetic susceptibility. The title compound crystallizes in the orthorhombic space group *Pnma* with a = 10.344(1), b = 9.350(3), c = 9.731(1) Å, Z = 8, and R = 0.025. The structure consists of units of one NiO_6 and two VO_6 octahedra sharing a common oxygen. Units are linked through either V–O–Ni bonds or phosphate groups to form a three-dimensional architecture with a channel parallel to the b-axis. The aquo ligands are located in the channel. The structure is markedly different from that prepared by the redox intercalation reaction method. © 1992 Academic Press, Inc.

Introduction

We have recently reported hydrothermal synthesis and structural characterization of several new compounds in the alkali-metal vanadium phosphate system (*1–3*). Among these phosphates the layered mixed-valence compounds $A_{0.5}VOPO_4 \cdot xH_2O$ (A = Na, x = 2.0; A = K, x = 1.5) are particularly interesting, since they were originally prepared by redox intercalation reactions of $VOPO_4 \cdot 2.0H_2O$ with iodides in aqueous solution, and they are the first intercalation reactions in which the charge transfer proceeds chemically (*4, 5*). The layered oxide hydrate $VOPO_4 \cdot 2H_2O$ also undergoes redox intercalation reactions with alkaline-earth and transition-metal cations in the presence of reducing agents. On the basis of powder X-ray diffraction, it was reported that the basic tetragonal structure of $VOPO_4 \cdot 2H_2O$ was essentially maintained and cations were incorporated into the interlayer spaces. Since intercalation reaction often yields a polycrystalline product difficult to characterize and the hydrothermal method is useful for growth of single crystals, the synthesis from cations in place of Na^+ or K^+ has been performed. In this report, we describe an extension of our previous work to the compound $Ni_{0.5}VOPO_4 \cdot 1.5H_2O$. The structure is markedly different from that of the corresponding sodium or potassium compound.

Experimental

Green crystals of the title compound were obtained by heating a mixture of 0.609 g V_2O_5, 0.502 g V_2O_3, 0.500 g NiO, 1.16 ml

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TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND REFINED PARAMETERS FOR $Ni_{0.5}VOPO_4 \cdot 1.5H_2O$

Crystal data	
Space group	*Pnma* (No. 62)
Cell constants	a = 10.344(1), b = 9.350(3), c = 9.731(1) Å, V = 941.2(3) Å^3
Z	8
Density (calcd)	3.081 g/cm^3
Abs. coeff. (Mo$K\alpha$)	42.9 cm^{-1}
Intensity measurements	
λ(Mo$K\alpha$)	0.70930 Å
Scan mode	$\theta/2\theta$
Scan speed	8.24°/min
Scan width	0.65° + 0.35° tan θ
Maximum 2θ	55°
Unique reflections measured	1140
Structure solution and refinement	
Reflections included	955 ($I > 2.5\,\sigma(I)$)
Parameters refined	106
Agreement factors	R = 0.025, R_w = 0.024
GOF	1.78
$(\Delta\rho)_{max}$; $(\Delta\rho)_{min}$	0.35 e/Å^3; −0.28 eÅ^3

85% H_3PO_4 (molar ratio Ni : V : P = 1 : 2 : 2.5), and 12 ml H_2O in a 23-ml Teflon lined autoclave at 230°C and autogenous pressure for 84 hr before slow cooling to room temperature. The product was filtered, washed with water, rinsed with ethanol, and dried under vacuum at ambient temperature. The X-ray powder pattern of the product compared well with that calculated from the single-crystal data. The contents of Ni, V, and P were analyzed by using an ICP-AE spectrometer after dissolving the sample in dilute aqua regia. Anal. Calcd for $Ni_{0.5}VOPO_4 \cdot 1.5H_2O$: Ni, 13.45%; V, 23.34%; P, 14.19%. Found: Ni, 13.8%; V, 23.2%; P, 14.5%.

A crystal having the dimensions 0.10 × 0.10 × 0.25 mm was selected for indexing and intensity data collection on an Enraf–Nonius CAD4 diffractometer with graphite-monochromated Mo$K\alpha$ radiation. The intensities of three reflections were monitored and no significant decay was detected. The reflections were corrected for Lp and absorption effects. Corrections for absorption effects were based on ψ scans of a few suitable reflections with χ values close to 90° (T_{max}, T_{min} = 0.999, 0.893). Based on the systematic absences and statistical distribution of the intensity data, and successful solution and refinement of the structure, the space group was determined to be *Pnma* (No. 62). Direct methods (NRCVAX) were used to locate the metal atoms, with the remaining atoms being found from successive difference Fourier maps (*6*). Bond-strength calculations were carried out to help locate hydrogen atoms. The structure was refined by full-matrix least-squares refinement based on F values. All of the non-hydrogen atoms were refined with anisotropic temperature factors. Neutral-atom scattering factors and corrections for anamolous dispersion were taken from "International Tables for X-Ray Crystallography" (*7*). Data collection and refined parameters are collected in Table I.

Thermogravimetric analysis (TG), using a Du Pont 951 thermogravimetric analyzer, was performed on a powder sample of the title compound in flowing N_2 with a heating rate of 5°C/min. A 161.17-mg polycrystalline sample was used to collect variable-

TABLE II

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR $Ni_{0.5}VOPO_4 \cdot 1.5H_2O$

Atom	x	y	z	B_{iso} (Å^2)[a]
Ni	0.24853(6)	0.25	0.62234(7)	0.62(2)
V(1)	0.15368(9)	0.25	0.27382(9)	0.45(3)
V(2)	−0.03450(8)	0.25	0.59372(9)	0.47(3)
P	0.09614(8)	0.5508(1)	0.67758(9)	0.43(3)
O(1)	−0.0986(2)	0.3951(3)	0.4696(2)	0.83(9)
O(2)	0.0968(2)	0.3839(2)	0.6772(2)	0.53(9)
O(3)	−0.0252(2)	0.5971(3)	0.7555(2)	0.71(9)
O(4)	0.1461(3)	0.25	0.4416(4)	0.7(1)
O(5)	0.3483(3)	0.25	0.7960(4)	0.8(1)
O(6)	0.2164(2)	0.5972(3)	0.7549(3)	0.87(9)
O(7)	0.3717(3)	0.4010(3)	0.5491(3)	1.4(1)
O(8)	0.1396(5)	0.25	0.0435(4)	1.6(2)
H(1)	0.403(5)	0.470(6)	0.608(5)	5.7(16)
H(2)	0.357(5)	0.415(6)	0.485(5)	2.2(14)
H(3)	0.192(8)	0.25	0.004(9)	4.5(26)
H(4)	0.080(8)	0.25	0.012(9)	5.2(28)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

TABLE III

SELECTED BOND DISTANCES (Å), BOND ANGLES (°), AND BOND–VALENCE SUMS (Σs) FOR $Ni_{0.5}VOPO_4 \cdot 1.5H_2O$

	Bond distances		
Ni–O(2)	2.078(2) (2×)[a]	Ni–O(4)	2.053(3)
Ni–O(5)	1.980(3)	Ni–O(7)	2.031(3) (2×)
Σs(Ni–O) = 2.11			
V(1)–O(3)	1.973(2) (2×)	V(1)–O(4)	1.635(4)
V(1)–O(6)	1.970(2) (2×)	V(1)–O(8)	2.246(5)
Σs(V(1)–O) = 4.19			
V(2)–O(1)	1.933(3) (2×)	V(2)–O(2)	2.018(2) (2×)
V(2)–O(4)	2.383(4)	V(2)–O(5)	1.619(4)
Σs(V(2)–O) = 4.16			
P–O(1)	1.519(3)	P–O(2)	1.561(2)
P–O(3)	1.529(2)	P–O(6)	1.517(2)
Σs(P–O) = 5.05			
O(7)–H(1)	0.92(6)	O(7)–H(2)	0.66(5)
O(8)–H(3)	0.67(8)	O(8)–H(4)	0.69(8)
	Bond angles		
Ni–O(4)–V(1)	146.2(2)	Ni–O(4)–V(2)	82.7(1)
V(1)–O(4)–V(2)	131.2(2)	H(1)–O(7)–H(2)	122(5)
H(3)–O(8)–H(4)	117(11)		

[a] Number of times the distance occurs.

temperature magnetic susceptibility $\chi(T)$ data from 4 to 300 K in a magnetic field of 5 kG using a Quantum Design SQUID magnetometer. The measured susceptibility was corrected for core diamagnetism (*8*).

Results and Discussion

Final positional and thermal parameters are listed in Table II. Selected bond distances, bond angles, and bond-valence sums (*9*) are given in Table III. Bond-order sums of the cations are in good accordance with their formal oxidation states. The VO_6 octahedron is distorted as a result from the displacement of the V atom towards one of the apical oxygen atoms. This kind of deformation is characteristic of most vanadyl(IV) compounds. As shown in Fig. 1(a), each vanadium octahedron shares its four equatorial oxygen atoms with four different PO_4 groups. The remaining two ligands of V(1) consist of a vanadyl oxygen, O(4), and a water molecule, H_2O(8), coordinated *trans* to it. Atom O(4) is also weakly bonded to V(2) in a position *trans* to the vanadyl group V(2)=O(5). The NiO_6 octahedron is considerably more regular with an average Ni–O bond length of 2.042 Å, which agrees quite well with the sum of ionic radii, 2.05 Å, for 6-coordinated Ni^{2+} and 3-coordinated O^{2-}. The Ni coordination sphere consists of two water molecules in *cis* positions, two oxygen atoms belonging to two phosphate groups, and two vanadyl oxygens in *trans* positions. Each NiO_6 octahedron shares a face with a neighboring V(2)O_6 octahedron. It is also observed that the coordination around O(4) is planar, i.e., the oxygen atom lies in the plane formed by V(1), V(2), and Ni atoms. The NiV_2O units are linked through either V(2)–O(5)–Ni bonds or phosphate groups to form a three-dimensional architecture with a channel parallel to the *b*-axis (Fig. 1(b)). The aquo ligands are located in the channel.

The TG analysis shows water loss in several steps (Fig. 2). The first weight loss

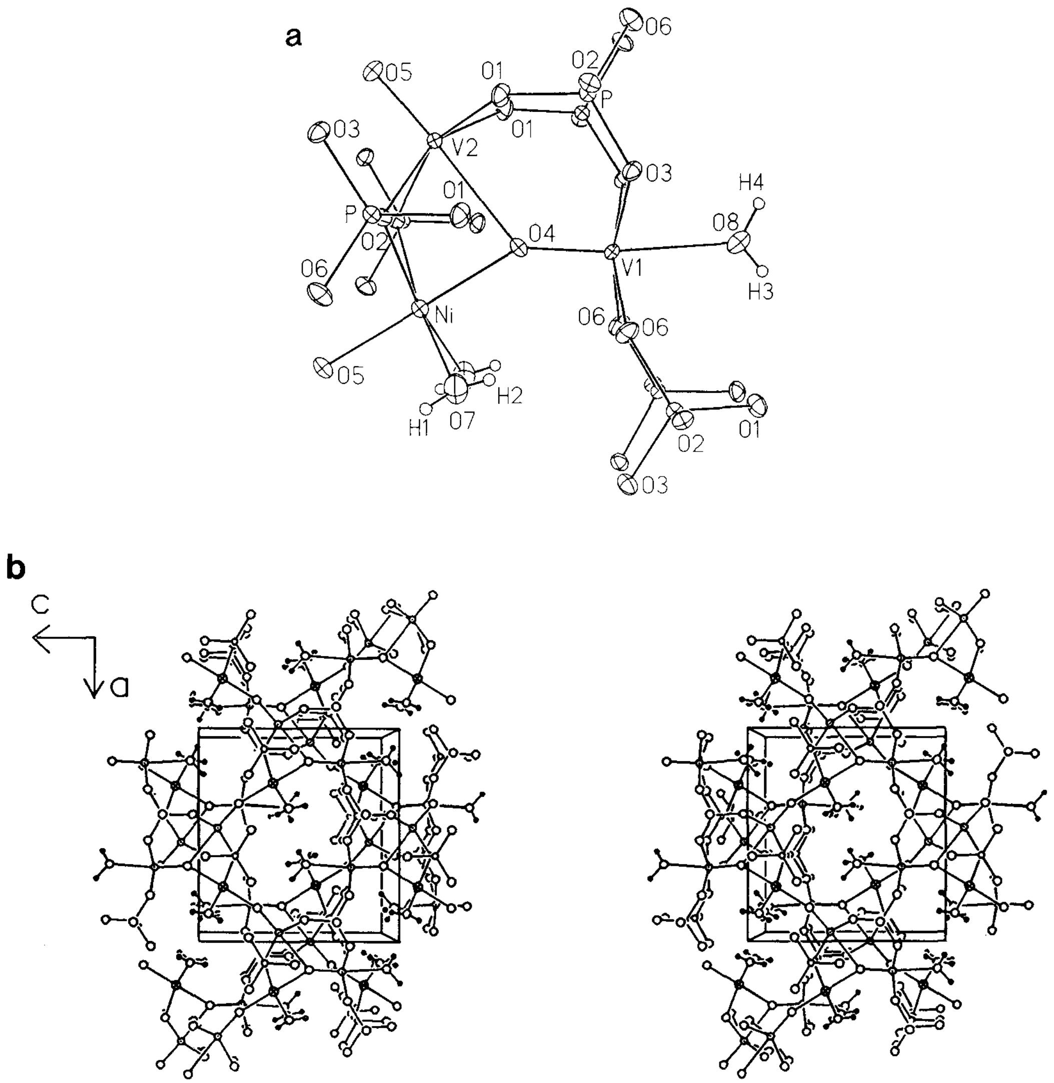

FIG. 1. Views of the structure of $Ni_{0.5}VOPO_4 \cdot 1.5H_2O$. (a) The unit containing $V(1)O_6$, $V(2)O_6$, and NiO_6 octahedra. Thermal ellipsoids are shown at the 60% probability level. Hydrogen atoms are represented by small open circles. (b) Stereoscopic view along the *b*-axis. Cross-hatched circles, Ni atoms; dotted circles, V atoms; large open circles, O atoms; medium open circles, P atoms; small open circles, H atoms.

(~4.2%, ~270°C) may be rationalized by the loss of $H_2O(8)$ and can be compared with the calculated value of 4.12%. Beyond ~270°C the sample decomposes in a manner which is not clear to us. However, the observed total weight loss of 12.45% between room temperature and 850°C agrees well with that calculated for the loss of all the aquo molecules (12.37%).

At higher temperatures, $\chi_M T$ remains es-

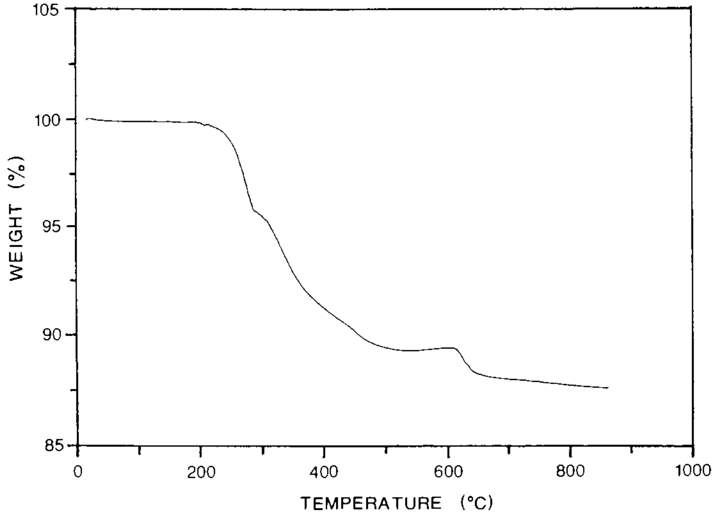

FIG. 2. Thermogravimetric analysis of $Ni_{0.5}VOPO_4 \cdot 1.5H_2O$ in flowing N_2 at 5°C/min.

sentially constant (Fig. 3). The deviation of $\chi_M T$ to smaller values with decreasing temperature may arise from antiferromagnetic interaction. The higher temperature data could be better illustrated in a plot of the inverse susceptibility vs temperature. The data over the interval 100 to 300 K were least-squares fitted to the relation $\chi_M = C/(T - \theta)$. The solid line is the fit where the Curie constant $C = 1.126$ $cm^3 \cdot K/mol$ and the Weiss constant $\theta = -7.67$ K. From the relation $C = N\mu_{eff}^2/3k_B$ one obtains the effective magnetic moment $\mu_{eff} = 3.00$ μ_B per formula unit. The measured value is considerably greater than the spin-only value of 2.65 μ_B and requires that the Ni(II) atom has a μ_{eff} of 3.46 μ_B if one assumes that the V(IV) atoms have μ_{eff} values of 1.73 μ_B. This

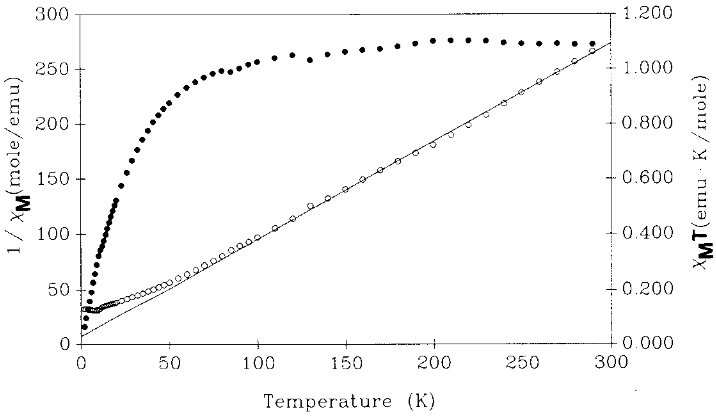

FIG. 3. $\chi_M T$ (solid circles) and $1/\chi_M$ (open circles) plotted as a function of temperature. The solid line represents a least-squares fit to the data from 100 to 300 K according to $\chi = C/(T - \theta)$.

seems quite high for an octahedral Ni(II). Although octahedral Ni(II) complexes generally have magnetic moments greater than the spin-only value of 2.83 μ_B, and a large number of nickel(II) complexes of the form *trans*-NiA_2X_2, where A is an amine and X a halogen, commonly have moments between 3.3 and 3.5 μ_B (*10*), the magnetic properties of the title compound are clearly more complicated than can be described by the Curie–Weiss equation.

We have shown that single crystals of the title compound can be readily obtained by the hydrothermal method, and its structure is characterized through a combination of techniques including single-crystal X-ray diffraction, thermal analysis, and magnetic susceptibility measurements. The compound reported herein crystallizes in a new structural type, and has different nickel and water contents from those of the previous work (*5*). Interestingly, the phases $A_{0.5}VOPO_4 \cdot xH_2O$ (A = Na or K) prepared by the hydrothermal method crystallize in a lower symmetry than that from the redox intercalation reaction (triclinic vs tetragonal), although they have similar alkali metal and water contents and the basic structure of the parent $VOPO_4 \cdot 2H_2O$ is essentially maintained (*3*). Since the hydrothermal method is a useful and convenient technique for crystal growth of these interesting compounds, it is likely that many additional phases containing divalent metals will be synthesized in the future.

Supplementary Material Available

Tables of anisotropic thermal parameters and bond angles; tables of observed and calculated structure factors.

Acknowledgments

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