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Crystal Structure of $Ni_{0.5}VOPO_4\cdot 2H_2O$, a Layered Vanadyl(IV) Phosphate Hydrate with Tetragonal Symmetry

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Introduction

It has been reported that $VOPO_2\cdot 2H_2O$ undergoes redox intercalation reactions with alkali-, alkaline-earth-, and transition-metal iodides in aqueous solution at room temperature to form compounds with the general composition $M_xVOPO_4\cdot nH_2O$, where M is the cation and $x \leq 1$.[1–4] The phase relations as x is varied are complex. On the basis of powder X-ray diffraction, the basic tetragonal structure of $VOPO_4\cdot 2H_2O$ was maintained and cations were incorporated into the interlayer spaces. However, detailed structural information has been unavailable due to the lack of suitable single crystals for X-ray analysis. As the hydrothermal method is particularly suited for the synthesis of low-temperature phases and for growth of single crystals, crystal growth of $M_xVOPO_4\cdot nH_2O$ by the hydrothermal method has been performed. Crystals of $M_{0.5}VOPO_4\cdot nH_2O$ (M = Na, K, Ca, Sr, Pb, Co, Ni; n = 2, 1.5) have been grown at 230 °C using Teflon-lined pressure vessel.[5–8] All compounds except $Pb_{0.5}VOPO_4\cdot 1.5H_2O$ and $Ni_{0.5}VOPO_4\cdot 1.5H_2O$ consist of layers of vanadium phosphorus oxide with metal cations and water molecules between the layers. Crystals of mixed-valence compounds $Na_{0.5}VOPO_4\cdot 2H_2O$ and $K_{0.5}VOPO_4\cdot 3H_2O$ are black. The other compounds are green since all vanadium(V) is reduced to vanadium(IV). Interestingly, most phases crystallize in a crystal symmetry lower than those prepared from redox intercalation reactions. $Na_{0.5}VOPO_4\cdot 2H_2O$, $K_{0.5}VOPO_4\cdot 1.5H_2O$, and $Ca_{0.5}VOPO_4\cdot 2H_2O$ are triclinic, $Sr_{0.5}VOPO_4\cdot 2H_2O$ and $Pb_{0.5}VOPO_4\cdot 2H_2O$ are monoclinic, $Ni_{0.5}VOPO_4\cdot 1.5H_2O$ is orthorhombic, and $Co_{0.5}VOPO_4\cdot 2H_2O$ is tetragonal. All the structures except that of $Ni_{0.5}VOPO_4\cdot 1.5H_2O$ can be derived topologically from the parent $VOPO_4\cdot 2H_2O$. The crystal structure of the tetragonal phase, $Co_{0.5}VOPO_4\cdot 2H_2O$, is particularly interesting because it can be used to infer the orientation and steric relationships between interlayer ions and host lattice in the intercalation compounds. The structures in the immediate vicinity of the transition-metal ion intercalants (Fe, Co, Ni) in the intercalation compounds $Fe_{0.4}VOPO_4\cdot 2H_2O$, $Co_{0.2}VOPO_4\cdot 2H_2O$, and $Ni_{0.2}VOPO_4\cdot 2H_2O$ have been studied by use of EXAFS.[9] The results indicate that Fe^{3+} and Co^{2+} ions have four oxygen nearest neighbors at 1.95 and 2.03 Å, respectively, whereas Ni^{2+} ions have six oxygen nearest neighbors at 2.05 Å. The Co content of the intercalation compound is lower than that of the compound prepared by the hydrothermal technique. In addition, the Co^{2+} ions in $Co_{0.5}VOPO_4\cdot 2H_2O$ are coordinated by six oxygen atoms instead of four as in $Co_{0.2}VOPO_4\cdot 2H_2O$. We have now prepared another tetragonal phase $Ni_{0.5}VOPO_4\cdot 2H_2O$, the structure of which is analogous to that of $Co_{0.5}VOPO_4\cdot 2H_2O$. The Ni^{2+} ions in both $Ni_{0.5}VOPO_4\cdot 2H_2O$ and $Ni_{0.2}VOPO_4\cdot 2H_2O$ have six oxygen nearest neighbors. We report herein single-crystal X-ray structure of the layered vanadyl(IV) phosphate hydrate $Ni_{0.5}VOPO_4\cdot 2H_2O$, which contains units of linear V=O—Ni—O=V.

Table I. Crystallographic Data of $Ni_{0.5}VOPO_4\cdot 2H_2O$

formula	$H_4O_7PVNi_{0.5}$	Z	4
fw	227.3	μ(Mo Kα), cm^{-1}	39.35
space group	$I4/m$	ρ(calcd), g cm^{-3}	2.898
a, Å	6.251	T, °C	24
c, Å	13.334(3)	R[a]	0.0260
V, Å^3	521.0(3)	R_w[b]	0.0305

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$, $w = [\sigma^2(F) + 0.0010F^2]^{-1}$.

Table II. Atomic Coordinates and Thermal Parameters for $Ni_{0.5}VOPO_4\cdot 2H_2O$

	x	y	z	10^2U_{eq},[a] Å^2
Ni	0	0	0	1.56(2)
V	0	0	0.27687(5)	0.95(2)
P	$^1/_2$	0	$^1/4$	1.00(3)
O(1)	0.3026(2)	−0.0213(2)	0.3181(1)	1.32(4)
O(2)	0	0	0.1568(2)	1.72(6)
O(3)[b]	0.2645(4)	0.1900(4)	0	2.34(7)
H	0.319(8)	0.174(7)	−0.060(3)	5.0

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The thermal parameter for the H atom is fixed. [b] Water oxygen atom.

Experimental Section

Synthesis. Hydrothermal treatment of NiO (0.075 g), VO_2 (0.25 g), V_2O_5 (0.183 g), 3.75 mol dm^{-3} H_3PO_4 (3.5 mL) (molar ratio Ni:V:P = 1:5:13), and H_2O (10 mL) for 2 days at 230 °C gives green square plate crystals of $Ni_{0.5}VOPO_4\cdot 2H_2O$ as the minor product. The optimized synthetic conditions have not been determined, although reactions with different starting materials or with different mole ratios have been performed. The major product of these reactions is $Ni_{0.5}VOPO_4\cdot 1.5H_2O$.

Crystallographic Analysis. A green plate crystal with the dimensions 0.25 × 0.25 × 0.037 mm was selected for indexing and intensity data collection on a Nicolet R3m/V four-circle diffractometer using graphite-monochromated Mo Kα radiation. Unit cell parameters and orientation matrix were determined by a least-squares fit of 20 peak maximuma (2θ = 20–30°). Axial oscillation photographs were taken to check the unit cell parameters and the symmetry $4/m$. Of the 1411 reflections measured (maximum 2θ = 55°, octants collected $\pm h,+k,\pm l$, scan mode ω–2θ), 315 were unique (R_{int} = 0.0245) and 299 reflections were considered observed ($I > 3.0\sigma(I)$) after Lp and absorption corrections. Correction for absorption was based on ψ scans of a few suitable reflections with χ values close to 90° using the program XEMP of the SHELXTL PLUS program package ($T_{min,max}$ = 0.462, 0.799). On the basis of the systematic absences, statistics of intensity distribution, and successful solution and refinement of the structure, the space group was determined to be $I4/m$. Direct methods (SHELXTL PLUS) were used to locate the metal and phosphorus atoms with the remaining oxygen and hydrogen atoms being found from successive difference Fourier maps. Subsequent refinement, including the atomic coordinates for all atoms, anisotropic thermal parameters for all non-hydrogen atoms, and a fixed isotropic thermal parameter for the H atom, converged at R = 0.0260 and R_w = 0.0305. The highest peak in the final difference map was 0.58 e/Å^3. Neutral-atom scattering factors for all atoms were used. Anomalous dispersion and secondary extinction corrections were applied. All calculations were performed on a DEC MicroVAX computer system using SHELXTL PLUS programs. Crystallographic data are summarized in Table I. Atomic coordinates and thermal parameters are included in Table II. Motifs of mutual adjunction, bond lengths, and bond-valence sums are

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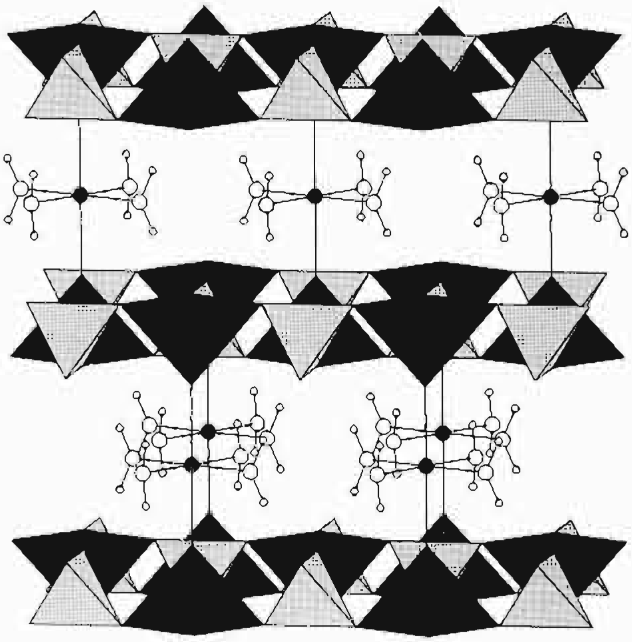

Figure 1. Polyhedral view (*c* vertical) of $Ni_{0.5}VOPO_4{\cdot}2H_2O$ with the nickel, water oxygen, and hydrogen atoms shown as solid, large open, and small open circles, respectively.

Table III. Motifs of Mutual Adjunction, Bond Lengths (Å) Coordination Numbers (C.N.), and Bond-Valence Sums (Σs) for $Ni_{0.5}VOPO_4{\cdot}2H_2O$

	O(1)	O(2)	O(3)	C.N.	Σs
Ni		2/1 2.090(3)	4/1 2.036(2)	6	2.04
V	4/1 1.975(1)	1/1 1.602(3)		5	4.02
P	4/1 1.538(1)			4	4.95
H	1/1 1.91(5)		1/2 0.88(4)	2	1.07
C.N.	3	2	3		

listed in Table III. Bond-valence sums for all cations are in good accordance with their formal oxidation states.

Results and Discussion

The structure of $Ni_{0.5}VOPO_4{\cdot}2H_2O$ consists of layers of vanadium phosphorus oxide with the Ni^{2+} ions and water molecules between the layers (Figure 1). The hydrogen atoms were located from difference Fourier maps and were incuded in the refinement. In contrast, the hydrogen atoms of the cobalt analogue $Co_{0.5}VOPO_4{\cdot}2H_2O$ could not be located, since the water molecule is disordered. The bonding scheme of the V atom is five-coordinate in which the stereochemistry is square pyramidal. A short vanadium-to-oxygen bond defines the vanadyl group V═O, and four equatorial V–O bonds are equivalent. In $M_{0.5}VOPO_4{\cdot}nH_2O$ (M = Na, K, Ca, Sr, Pb; *n* = 1.5, 2), the water molecule as the sixth ligand is weakly bonded trans to V═O to produce a distorted octahedron. Few phosphates involving only VO_5 square pyramids have been reported. $A_2VOP_2O_7$ (A = K, Rb, Cs),[10,11] $Na_5V_2P_3O_{14}{\cdot}H_2O$,[12] and $AVOPO_4$ (A = Rb, Cs)[13] are the only instances of structures composed of pure VO_5 pyramids and PO_4 tetrahedra. The layer in $Ni_{0.5}VOPO_4{\cdot}2H_2O$ is a 4-connected net in which corner-sharing vanadium and phosphorus polyhedra alternate. Each VO_5 pyramid shares its four equatorial oxygen atoms with four different PO_4 groups. Along the [110] direction the vanadyl oxygens alternately point up and down relative to a layer. The interlayer separation for $Ni_{0.5}VOPO_4{\cdot}2H_2O$ is 6.667 Å, which is considerably shorter than that in the parent $VOPO_4{\cdot}2H_2O$ (7.40 Å). On incorporation of the cations, the layers become negatively charged and are brought closer together by electrostatic interaction with the interlayer metal cations. The interlayer separation in $Ni_{0.5}VOPO_4{\cdot}2H_2O$ is comparable to that in $Co_{0.5}VOPO_4{\cdot}2H_2O$ (6.714 Å) but significantly longer than those in $M_{0.5}VOPO_4{\cdot}nH_2O$ (M = Na, K, Ca, Sr, Pb; *n* = 1.5, 2) (6.30–6.53 Å). The Ni^{2+} ion in $Ni_{0.5}VOPO_4{\cdot}2H_2O$ is coordinated by six oxygen atoms including two *trans* vanadyl oxygens from adjacent layers and four equatorial water oxygens such that linear V═O—Ni—O═V chains are formed. The hydrogen atom is also weakly bonded to a basal oxygen of a VO_5 pyramid at 1.91 Å. The coordination octahedron around each Ni atom has D_{4h} symmetry. The layer stacking in $Ni_{0.5}VOPO_4{\cdot}2H_2O$ can be generated from the parent $VOPO_4{\cdot}2H_2O$ by a relative displacement of adjacent layers along the diagonal direction by 4.42 Å (=$(a + b)/2$). The EXAFS data suggest that Ni^{2+} ions in the intercalation compound $Ni_{0.2}VOPO_4{\cdot}2H_2O$ are also six-coordinate with a first shell of oxygen neighbors at 2.05 Å and a second, distant shell of approximately 8 ± 1 oxygen atoms at 3.02 Å. An intercalation site was proposed for the Ni ion occupancy between the layers. In contrast, the crystallographic data on $Ni_{0.5}VOPO_4{\cdot}2H_2O$ indicate that the second, distant shell about Ni has 16 oxygen atoms at ~4.15 Å. The structure of $Ni_{0.5}VOPO_4{\cdot}2H_2O$ differs from that of $Ni_{0.2}VOPO_4{\cdot}2H_2O$ not only in the Ni content but also in the intercalation site. Preparations under moderate hydrothermal conditions result in different modifications of the intercalation compounds $M_xVOPO_4{\cdot}nH_2O$.

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Supplementary Material Available: Tables giving anisotropic thermal parameters and complete bond lengths and angles (2 pages). Ordering information is given on any current masthead page.

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