The Formation of Striped Phases by Charge Localization in Vanadium Phosphates

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ABSTRACT

The compound \((\text{H}_3\text{O})_{1.5}[[\text{VO(H}_2\text{O})]\text{PO}_4]_3\cdot 2.5\text{H}_2\text{O}\) is a new member of a series of vanadium phosphates containing vanadium in both plus four and five oxidation states. Charge ordering occurs in these mixed vanadium phosphate layered compounds forming striped phases with different periodicities. The VOPO_4 layers undulate as a consequence of differences in the O-O atom distances in the ordered V(V)O_6 and V(IV)O_6 octahedra.

INTRODUCTION

Many aspects of the chemistry of layered vanadium phosphates have been studied since Ladwig’s early work on the synthesis and properties of VOPO_4·2H_2O [1]. The structure of VOPO_4·2H_2O was determined by Tietze using single crystal X-ray diffraction [2]. Layers are formed by connecting distorted VO_5(H_2O) octahedra with PO_4 tetrahedra. Adjacent VO_5(H_2O) octahedra are related by an inversion center within the layer so that the orientation of the vanadyl V=O groups alternates above and below the layer (see Figure 1). The interlayer space is occupied by an additional water molecule that is hydrogen bonded to the coordinated water molecule. Intercalation reactions of both neutral molecules and ions have been reported [3-7]. Mixed valence compounds are formed by insertion of cations into the interlayer space and reduction of V(V) to V(IV) [3,5]. A large number of compounds based on VOPO_4 layers were subsequently synthesized in single crystal form by using mild hydrothermal conditions [8-12]. The crystal chemistry, including the interlayer cation and solvent molecule locations, are now well understood from the detailed structural studies. Here we note only that phases are known with a water molecule coordinated to the vanadium atom (distorted octahedral) [8,12] and without (square pyramidal) [8-10] and that only a small number of mixed valence systems have been characterized by single crystal X-ray diffraction [13-17]. The known mixed valence systems are summarized in Table I. A small number of mixed valence compounds in which the layers are cross linked by an additional phosphate group are also included [18].

Here we discuss the evidence for charge ordering in the mixed valence compounds and describe a new example with the composition \((\text{H}_3\text{O})_{1.5}[[\text{VO(H}_2\text{O})]\text{PO}_4]_3\cdot 2.5\text{H}_2\text{O}\).

EXPERIMENTAL

Synthesis: a) The compound Na[VO(H_2O)PO_4]_2·2 H_2O (1) was prepared by hydrothermal synthesis in a Teflon lined steel autoclave at 130°C for 3 days: NaVO_3 (0.122 g, 1 mmol), BPO_4 (0.317 g, 3 mmol) and 3 mL H_2O. The reaction products were prismatic dark green crystals of (1), average size 0.1-0.3 mm, yield approximately 80% based on vanadium, together with some unidentified brownish powder. b) (H_3O)_{1.5}[[\text{VO(H}_2\text{O})]\text{PO}_4]_3\cdot 2.5\text{H}_2\text{O} (2): \text{V}_2\text{O}_5 (1.819 g, 10 mmol), \text{H}_2\text{C}_2\text{O}_4 (0.480 g, 5 mmol), 1.20 mL \text{H}_3\text{PO}_4 (85 wt% solution in H}_2\text{O, 20 mmol}) and 30 mL H_2O were mixed in a 100 mL flask and refluxed for 10 h at 70°C in air. After cooling the pH
was adjusted to 1.33 by adding dropwise HNO₃ and the resulting blue solution was left at room temperature in air. Dark green plate-like crystals began forming after several days and the crystallization process was completed within a week, yield approximately 80% based on vanadium.

**Table I. Mixed valence layered vanadium phosphates.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>BVS [20]</th>
<th>Fig. No.</th>
<th>o × d*</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>Na₀.₅VOPO₄·₂H₂O</td>
<td>4.55, 4.56</td>
<td>Fig. 3c</td>
<td>0 × 1</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>4.59, 4.69</td>
<td></td>
<td></td>
<td>[14]</td>
</tr>
<tr>
<td>1</td>
<td>4.57</td>
<td>Fig. 3c</td>
<td>0 × 1</td>
<td>this work</td>
</tr>
<tr>
<td>K₀.₅VOPO₄·₁.₅H₂O</td>
<td>4.57</td>
<td>Fig. 3c</td>
<td>0 × 1</td>
<td>[15, 13]</td>
</tr>
<tr>
<td>Rb₀.₅VOPO₄·₁.₅H₂O</td>
<td>4.51</td>
<td>Fig. 3c</td>
<td>0 × 1</td>
<td>[15]</td>
</tr>
<tr>
<td>N₂C₂H₁₀(VO)₂(PO₄)₂·H₂PO₄</td>
<td>4.97, 5.15</td>
<td>Fig. 3d</td>
<td>1 × 0</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>4.04, 4.08</td>
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<td></td>
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<tr>
<td>(C₄H₁₂N₂)(H₃O)[(VOPO₄)₄(H₂O)H₂PO₄]·₃H₂O</td>
<td>4.07</td>
<td>Fig. 3d</td>
<td>1 × 0</td>
<td>[18]</td>
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<tr>
<td></td>
<td>5.09</td>
<td></td>
<td></td>
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<tr>
<td>(NH₄)₀.₅VOPO₄·₁.₅H₂O</td>
<td>3.94</td>
<td>Fig. 3b</td>
<td>1 × 1</td>
<td>[17, 16]</td>
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<tr>
<td></td>
<td>5.27</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>4.55</td>
<td></td>
<td></td>
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<tr>
<td>(H₃O)₁.₅[[VO(H₂O)]PO₄]₃·₂.₅H₂O</td>
<td>4.07</td>
<td>Fig. 3a</td>
<td>2 × 1</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>5.04</td>
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<td></td>
<td>4.46</td>
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</table>

* o × d refer to the numbers of ordered (o) and disordered (d) ‘stripes’, BVS ≡ Bond Valence Sum.

**Structure Determination:** Single crystal X-ray diffraction data were obtained using a Bruker SMART 1K CCD diffractometer with Mo-Kα radiation and a graphite monochromator.

a) Na[VO(H₂O)PO₄]₂·₂.₅ H₂O (1) at T = 293K: triclinic, space group P-1 (#2), a = 6.2883(10), b = 6.2901(10), c = 6.8465(11) Å, α = 107.199(2), β = 92.453(3), γ = 90.102(3)°, V = 258.43(7) Å³, Z = 1, ρ_calcd = 2.685 gcm⁻³; µ = 2.069 mm⁻¹, θ_max = 39.96°, 831 measured reflections, 472 independent reflections; corrections for Lorentz factor, polarization, air absorption and absorption due to variations in the path length through the detector faceplate, Psi-scan absorption correction. The structure was solved by direct methods and refined by full matrix least squares on F² (SHELXTL)[21], all non-H atoms anisotropic; GOF = 1.278, R values (I > 2σ(I)): R1 = 0.0218, wR2 = 0.0635; max./min. residual electron density 0.211 and -0.202 e Å⁻³.

b) (H₃O)₁.₅[[VO(H₂O)]PO₄]₃·₂.₅H₂O (2) at T = 293K; orthorhombic, space group Pbca (#61), a = 8.8453(6), b = 14.1484(9), c = 26.401(2) Å, V = 3304.0(4) Å³, Z = 8, ρ_calcd = 2.403 gcm⁻³; µ = 2.069 mm⁻¹; θ_max = 35.98°, 7169 measured reflections, 1138 independent reflections; corrections as above. The structure was solved by direct methods and refined by full matrix least squares on F² (SHELXTL)[21], all non-H atoms anisotropic; GOF = 0.961, R values (I > 2σ(I)): R1 = 0.0709, wR2 = 0.1315; max./min. residual electron density 0.497 and -0.487 e Å⁻³.
RESULTS

The mixed valent vanadium phosphates form an interesting series of systems with respect to the distribution of V(V) and V(IV) ions within the layers. All of the compounds in Table 1 have close to equal amounts of V(V) and V(IV) but have very different structures. In the alkali metal series, the structures of K$_{0.5}$VOPO$_4$·1.5H$_2$O and Rb$_{0.5}$VOPO$_4$·1.5H$_2$O are well determined and contain a single inequivalent vanadium atom. Some disagreement, however, exists in the literature concerning the structure of Na$_{0.5}$VOPO$_4$·2H$_2$O. Wang et al. solved the structure in space group P-1 with Z=4 [13], whereas Yamase and Makino [14] solved the structure in P1 with Z=1. We have synthesized and redetermined the structure of this phase (1) and obtained an excellent refinement in P-1 with Z=1 with only one inequivalent vanadium atom. All of the reported structure solutions for Na$_{0.5}$VOPO$_4$·2H$_2$O are similar and it is possible that small composition variations are responsible for the differences. The bond valence sum values have been calculated for each structure and are given in Table I. The values indicate that the V(IV) and V(V) sites are disordered in (1). The structure of (1) is shown in Figure 1.

![Figure 1. The structure of Na[VO(H$_2$O)PO$_4$] 2H$_2$O (1) Selected bond lengths (Å): V(1)-O(1) = 1.578(3), V(1)-O(6) = 1.957(3), V(1)-O(5) = 1.958(3), V(1)-O(4) = 1.961(3), V(1)-O(3) = 1.962(3), V(1)-O(2) = 2.357(4). Bond valence sum (BVS): V(1) = 4.45.](image)

Single crystal X-ray diffraction studies revealed that the structure of (2) is also based on VOPO$_4$·H$_2$O layers and contains vanadium in both V(V) and V(IV) oxidation states. The unit cell contents of the structure are shown in Figure 2. The bond distances and angles are typical for hydrated oxovanadium phosphates. In contrast to the parent VOPO$_4$·2H$_2$O and the mixed valence alkali metal phases, the structure contains three crystallographically distinct vanadium atoms, which bond valence sums indicate have different oxidation states. The atoms V1 and V2 are V(IV) and V(V) respectively and V3 is a disordered mixture of V(IV) and V(V). As a consequence of the vanadium charge ordering the layers are no longer flat but undulate periodically along the c axis. Similar behavior was observed previously in (NH$_4$)$_{0.5}$VOPO$_4$·1.5H$_2$O [16,17] and is discussed below. Hydronium cations and water molecules occupy interlayer sites in a complex and disordered arrangement.
Figure 2. Two projections of the unit of cell contents of \((H_2O)_3[VO(H_2O)PO_4]_3\cdot2.5H_2O\). Selected bond lengths (Å): V(1)-O(1) = 1.602(10), V(1)-O(4) =1.946(10), V(1)-O(6) =1.957(10), V(1)-O(11) =1.984(11), V(1)-O(12) =1.999(13), V(1)-Ow1 =2.273(12), V(2)-O(2) =1.546(11), V(2)-O(5) =1.873(10), V(2)-O(7) =1.884(10), V(2)-O(9) =1.930(11), V(2)-O(8) =1.935(11), V(2)-Ow2 =2.305(11), V(3)-O(3) =1.598(12), V(3)-O(10) =1.899(13), V(3)-O(14) =1.912(11), V(3)-O(13) =1.926(12), V(3)-O(15) =1.923(12), V(3)-Ow3 =2.315(13). Bond valence sums (BVS): V(1) = 4.07, V(2) = 5.04, V(3) = 4.46.

DISCUSSION

The structures of the compounds in Table 1 other than those of the alkali metal compounds contain ordered arrangements of all or some of the V(IV) and V(V) atoms. The ordering is apparent on inspection of the bond lengths or by calculation of bond valence sums [20]. The ordering is shown schematically in Figure 3. In the horizontal direction in the figure, not only do the oxidation states alternate but the V(IV) and V(V) octahedra alternate up and down so that all the V(V) octahedra are on one side of the layer and the V(IV) octahedra are on the other. A consequence of the charge ordering is that the VOPO_4.H_2O layers must bend to accommodate the larger and smaller V(IV) and V(V) octahedra on opposite sides of the layer. The relative number of the ordered and disordered rows (‘stripes’) is also indicated in Table I.

The origin of the undulation can be seen in more detail by inspection of the edge-on view of the VOPO_4 layer in \((NH_4)_{0.5}VOPO_4\cdotH_2O\) (Figure 4). The V1 and V2 octahedra are V(V) and V(IV) respectively, and the V3 octahedra are disordered. In the V1O_6 octahedron the O1-O1 and O2-O2 distances are 2.851 and 2.858 Å and in the V2O_6 octahedron the O5-O5 and O3-O3 separations are 2.653 and 2.614 Å. Because V1, V2, and V3 share oxygen atoms from a common tetrahedron, the consequence of the difference in oxygen-oxygen distances is to force the V3O_6 octahedra to tilt. In the V3O_6 octahedra the O-O distances are similar (O7-O9 is 2.694 Å and O6-O8 is 2.739 Å). The orientation of the next pair of V1 and V2 octahedra in the horizontal
direction in Figure 4 is inverted and consequently along this direction the layers undulate in a regular way. Similar behavior is observed for the other ordered structures.

\textbf{Figure 3.} Ordered arrangements of V(IV) and V(V) in vanadium phosphate layered compounds. Phosphate tetrahedra are grey, V(V), V(IV) and disordered V(IV,V) octahedra are hatched, lightly hatched, and open, respectively. The arrangements correspond to different numbers of ordered(o) and disordered rows (d) and are represented by the symbol (o \times d). Figures 3a, b, c, d, correspond to the arrangements 2 \times 1, 1 \times 1, 0 \times 1, 1 \times 0.

\textbf{Figure 4.} Edge on view of the layer in (NH\textsubscript{4})\textsubscript{0.5}VOPO\textsubscript{4}1.5H\textsubscript{2}O.

GG1.7.5
The origin of the charge localization is more difficult to describe. Most likely it arises from the distribution of the interlayer ammonium and/or hydronium cations in the interlayer space and the hydrogen bonds that they form with the oxygen atoms in the layers. A detailed discussion of this is beyond the scope of this paper. We note here only that very strong hydrogen bonds (O-O distances 2.7 Å) are formed with the water molecules coordinated to the V(V) atoms and that analysis of the hydrogen bonding is difficult because of the disorder of the interlayer species.

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REFERENCES