Hydrothermal Synthesis and Structural Characterization of $(VO)_2(PO_4)_2H_2PO_4\cdot N_2C_2H_{10}$, a New Three-Dimensional, Organically Templated Mixed-Valence Vanadium Phosphate Related to the $2VOSO_4\cdot H_2SO_4$ Structure

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Several new open-framework organovanadium phosphates have recently been reported[1−6] in which organic cations play a key structural role in "templating" the extended, three-dimensional V/P/O frameworks of these structures. All of these syntheses employed moderate-condition hydrothermal reactions in order to prepare the new phase as single crystals. In this paper, we report the hydrothermal synthesis and structural characterization of $(VO)_2(PO_4)_2H_2PO_4\cdot N_2C_2H_{10}$, a new organically templated open-framework mixed-valence vanadophosphate, containing discrete V^{IV} and V^{V} atomic sites. Structurally, $(VO)_2(PO_4)_2H_2PO_4\cdot N_2C_2H_{10}$ is closely related to the $2VOSO_4\cdot H_2SO_4$ family of phases (vide infra).

Pleochroic midgreen/very dark green blocks (up to 0.5 mm) of the title material were produced as a minor (<5%) component from the reaction of V_2O_5, H_3PO_4, ethylenediamine, HF, and water.[7] The majority phase (>90% by visual inspection) of deep purple rods is $V_2PO_8F\cdot N_2C_2H_{12}$.[4] Infrared measurements (KBr pellet method) on a pure sample of $(VO)_2(PO_4)_2H_2PO_4\cdot N_2C_2H_{10}$ (Figure 1), prepared from a stoichiometric starting mixture, revealed bands due to N−H and C−H stretches, as well as HPO_4, PO_4, and VO_6 modes.[8]

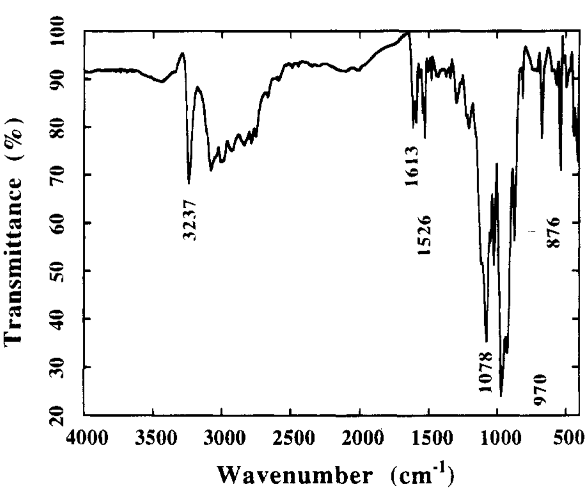

Figure 1. IR spectrum of $(VO)_2(PO_4)_2H_2PO_4\cdot N_2C_2H_{10}$.

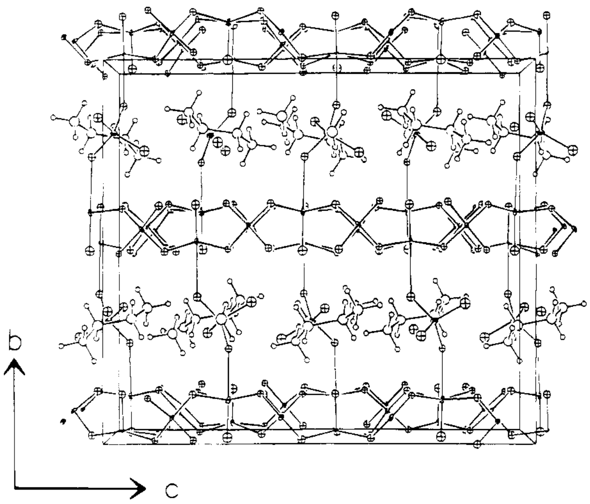

Figure 2. ORTEP view approximately down [100] of the $(VO)_2(PO_4)_2H_2PO_4\cdot N_2C_2H_{10}$ crystal structure, showing the [101] $VOPO_4$ layers linked *via* bridging H_2PO_4 groups, and interlayer doubly protonated ethylenediamine cations.

Single-crystal X-ray diffraction measurements[9] on the green phase indicated a complex three-dimensional structure (Figure 2) built up from vertex-linked vanadium-centered octahedra and phosphate tetrahedra, connected via V−O−P bonds ($\theta_{\min} = 127.6°$, $\theta_{\max} = 141.7°$, $\theta_{av} = 134.5°$). There are no V−O−V bonds in this structure. There are two formula units in the asymmetric unit of this structure (four independent VO_6, four PO_4, and two H_2PO_4 centers in the framework). Two doubly protonated ethylenediamine molecules make up the rest of the unit-cell contents.

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(7) The initial synthesis was carried out by heating a mixture of 0.6821 g of V_2O_5 (3.75 mmol, Aldrich, 99.6+%), 0.42 mL of ethylenediamine (6.28 mmol, Aldrich, 99%), 0.43 mL of 49% HF (12.4 mmol, Fisher), 0.86 mL of 85% H_3PO_4 (12.6 mmol, EM Science), and 10 mL of distilled water (555.6 mmol) in a Teflon-lined 23-mL capacity Parr 4749 bomb at 60 °C for 12 h and then 160 °C for 48 h. The bomb was cooled to ambient over 6 h (final pH = 3.2), and two phases were recovered by vacuum filtration. The major phase of this first synthesis was $V_2PO_8F\cdot enH_2$,[4] with a minor component of $(VO)_2(PO_4)_2H_2PO_4\cdot N_2C_2H_{10}$. A second stoichiometric synthesis with respect to the title compound proceeded as follows: 0.6821 g of V_2O_5, 10 mL of H_2O, and 0.42 mL of ethylenediamine were mixed in a 23-mL Teflon cup, and stirred for 6 h. 1.17 mL of 85% H_3PO_4 solution was then added to the mixture, and the bomb was sealed immediately. The bomb was heated to 60 °C for 14 h and then 160 °C for 48 h. Product recovery after cooling to ambient (final pH of filtrate = 3.3) resulted in a mass of thin dark green plates (to 0.5 × 0.5 × 0.02 mm) and green powder. The powder pattern of a mixture of ground plates and powder matched a LAZY-PULVERIX simulation based on the $(VO)_2(PO_4)_2H_2PO_4\cdot N_2C_2H_{10}$ single-crystal parameters, indicating phase purity for the second synthesis.

(8) Infrared data for $(VO)_2(PO_4)_2H_2PO_4\cdot N_2C_2H_{10}$ (cm^{-1}): 3237(m), 3079(m), 3000(m), 2928(m), 2833(m), 2750(m), 2666(w), 1613(m), 1526(m), 1296(w), 1206(w), 1078(s), 970(vs), 876(m), 671(m), 534(m). The peak at 3237 cm^{-1} is characteristic of bound −OH (dihydrogen phosphate group).

(9) Crystal data: $(VO)_2(PO_4)_2H_2PO_4\cdot N_2C_2H_{10}$, green block 0.4 × 0.4 × 0.3 mm, $M_r = 514.92$, orthorhombic, space group $Pc2_1n$ (No. 33) based on well-defined systematic absences of $0kl$; $l \neq 2n$; $hk0$, $h + k \neq 2n$, $a = 8.891$ (3) Å, $b = 15.971$ (4) Å, $c = 18.037$ (5) Å, $V = 2561$ (2) Å^3, $Z = 8$, $R(F) = 4.04\%$, $R_w(F) = 3.76\%$ [236 parameters; 3059 reflections with $I > 3\sigma(I)$]. Significant pseudosymmetry was apparent in the refinement, especially among the vanadium species. Anisotropic refinement of the oxygen atoms species led to some nonpositive definite thermal factors, and the O atoms were modeled as isotropic. A symmetry check of the final $(VO)_2(PO_4)_2H_2PO_4\cdot N_2C_2H_{10}$ coordinates (program *MISSYM*) revealed no additional symmetry. Attempts to model the $(VO)_2(PO_4)_2H_2PO_4\cdot N_2C_2H_{10}$ structure in space group *Pcmn*, which is also consistent with the absence conditions, were not successful.

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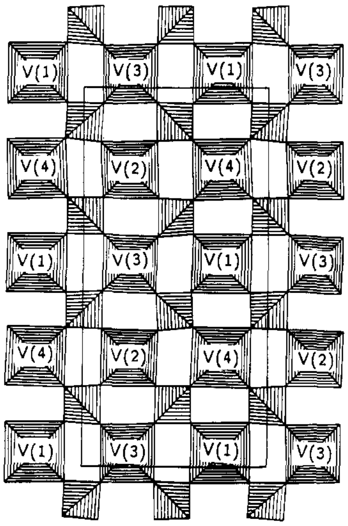

Figure 3. STRUPLO polyhedral view of one α-$VOPO_4$-type layer of the $(VO)_2(PO_4)_2H_2PO_4{\cdot}N_2C_2H_{10}$ structure, viewed down [010]. The vanadium centers are labeled to show the segregation of the vanadium(IV) [V(1) and V(4)] and vanadium(V) [V(2) and V(3)] centers.

Each octahedrally coordinated vanadium cation makes one short "vanadyl" terminal V=O bond (d < 1.62 Å), and five V−O−P links, each to a different, adjacent phosphorus atom (as a phosphate group). This type of coordination is characteristic of both vanadium(IV) and vanadium(V).[10] Four of the six phosphate groups [P(1)−P(4)] make four P−O−V bonds to nearby V atoms. This V/P/O configuration results in puckered, "checkerboard" vertex-sharing VO_6/PO_4 layers orientated in the [101] plane (Figure 3), of nominal stoichiometry $VOPO_4$, similar to those found in the vanadium(V)-containing phase α-$VOPO_4$.[11,12] The remaining two phosphorus-centered entities [P(5), P(6)] each make two P−O−V bonds, and serve as "pillars" to connect the puckered [101] VO_6/PO_4 layers into a three-dimensional network, in the b direction (Figure 2). These bonds connect these P atoms to the long V−O bond trans to the vanadyl V=O link in each case. The two uncoordinated P−O bonds of each of these two phosphate anions are long (d > 1.56 Å), indicating that they are all protonated[13] (i.e., as H_2PO_4 dihydrogen phosphate groups), as confirmed by the IR data (vide supra).

The charge-balancing criterion requires that the vanadium be present half as V^{IV} and half as V^{V}. This is strongly supported by bond valence sum (BVS) calculations,[14] which indicate that two of the vanadium atoms [V(1) and V(4)] are present as vanadium(IV), and two [V(2) and V(3)] as vanadium(V). Using parameters appropriate[14] to V^{IV}, BVS values of 4.08, 4.89, 4.71, and 4.04 were obtained for V(1), V(2), V(3), and V(4), respectively. BVS parameters[14] for V^{V} yielded the following: BVS[V(1)] = 4.30, BVS[V(2)] = 5.15, BVS[V(3)] = 4.97, and BVS[V(4)] = 4.25. These BVS results indicate that the V(1) and V(4) species have V^{IV} character, and the V(2) and V(3) species have V^{V} character. Magnetic susceptibility data (vide infra) support this valence assignment for the vanadium species. This V^{IV}/V^{V} valence segregation has interesting consequences with respect to the infinite $VOPO_4$ layers in this structure: in the a crystallographic direction, the $V^{IV}O_6$ and $V^{V}O_6$ groups *alternate*. However, in the c direction the V^{IV}- and V^{V}-centered groups *segregate* into alternate strings (Figure 3).

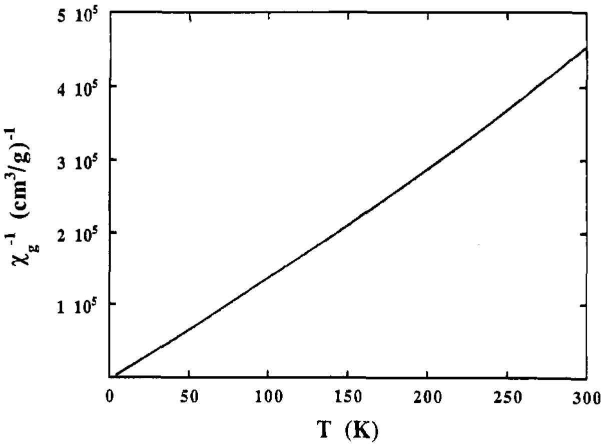

Figure 4. Plot of inverse molar susceptibility *versus* temperature for $(VO)_2(PO_4)_2H_2PO_4{\cdot}N_2C_2H_{10}$.

Both $[H_3N(CH_2)_2NH_3]^{2+}$ ethylenediamine dications occupy the interlayer region of the structure (Figure 2). Octahedral/tetrahedral 12-rings effectively surround the organic entities. Guest−framework H-bonding is significant in this structure, and 11 N−H···O H-bonds are formed. These link to various framework oxygen atoms involved in V=O, V−O−P, and P−OH bonds. On heating $(VO)_2(PO_4)_2H_2PO_4{\cdot}N_2C_2H_{10}$, TGA (ramp under oxygen) indicates that the organic entities and water are lost in a clean, one-step process beginning at ~250 °C (obs 19.9%, calc 20.6%). This results in structural transformation to unidentified products (X-ray powder diffraction measurements on the green residue of nominal stoichiometry $V_2P_3O_{12}$).

Magnetic susceptibility data for $(VO)_2(PO_4)_2H_2PO_4{\cdot}N_2C_2H_{10}$ (Figure 4) revealed paramagnetic behavior over the temperature range 4.2−300 K. The data were modeled by the function $\chi = \chi_0 + C/(T - \theta)$, where χ is the measured magnetic susceptibility, C the Curie constant, T the temperature (K), and θ the Weiss constant, with $\chi_0 = -3.02 \times 10^{-7}$ emu/g, $C = 7.452 \times 10^{-4}$ emu K/g, and $\theta = 2.5$ K. This corresponds to a μ_{eff} of 1.70 μ_B, in good agreement with the predicted spin-only value of 1.73 μ_B, assuming that half the vanadium species are present as d^1 vanadium(IV).

Some materials built up from pillared MO_6/XO_4 checkerboard sheets, which are closely related to $(VO)_2(PO_4)_2H_2PO_4{\cdot}N_2C_2H_{10}$, have been reported previously. $2VOSO_4{\cdot}H_2SO_4$ [or $(VO)_2(SO_4)_2H_2SO_4$][15] serves as the prototype material for this class of structures, with dihydrogen sulfate bridges between the infinite $VOSO_4$ layers. $Na_2(MoOPO_4)_2(HPO_4){\cdot}2H_2O$[16] contains $Mo^{V}O_6/PO_4$ layers, pillared by disordered hydrogen phosphate groups. $Cs(H_3O)[Mo_2O_2(PO_4)_2(HPO_4)]$[17] is a cesium

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analogue of the sodium phase and shows reversible sorption/desorption of water. Organically templatedanalogues of this structure type, such as $CH_3NH_3[Mo_2O_2(PO_4)_2(HPO_4)]$,[18] may also be prepared. Other reactions in the organovanadophosphate phase space[19] lead to more complex, two-dimensional "defect" checkerboard structures.

In summary, the hydrothermal synthesis and single-crystal structure of $(VO)_2(PO_4)_2H_2PO_4{\cdot}N_2C_2H_{10}$, which is built up from a three-dimensional network of $V^{IV}O_6$, $V^{V}O_6$, PO_4, and H_2PO_4 polyhedra, are reported. The V^{IV} and V^{V} valence distribution is well defined in this compound. This phase complements other open-framework organovanadium phosphates[1-6] and the $2VOSO_4{\cdot}H_2SO_4$-type materials[15-18] noted above.

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Supporting Information Available: Tables of crystal data (9 pages); tables of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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