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Hydrothermal Synthesis and Characterization of Two- and Three-Dimensional Solids of the Oxovanadium(IV)−Phosphite System. The Structures of $[HN(Me)(CH_2CH_2)_2N(Me)H][(VO)_4(OH)_2(HPO_3)_4]$, $[H_2N(CH_2CH_2)_2NH_2][(VO)_3(HPO_3)_4(H_2O)_2]$, and $[VO(HPO_3)(H_2O)]$

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Contemporary interest in the chemistry of the oxovanadium phosphate system, $V-O-PO_4^{3-}$, stems from its practical applications to catalysis[1,2] and the unusually diverse structural chemistry associated with the solid phases.[3-7] Similarly, the related oxovanadium organophosphonate system, $V-O-RPO_3^{2-}$, has witnessed an extensive development, reflecting applications to catalysis, as hosts in intercalation compounds and as protonic conductors.[8-10] We have recently demonstrated that by exploiting the structure directing properties of organoammonium cationic templates, the chemistry of both the $V-O-PO_4^{3-}$ system and the $V-O-RPO_3^{2-}$ system can be dramatically expanded.[11-18] While phosphite, HPO_3^{2-}, represents a member of the phosphorus oxoanions, which may also be considered as the simplest example of the phosphonate class, RPO_3^{2-} with R = H, the chemistry of the oxovanadium phosphite system, $V-O-HPO_3^{2-}$, remains relatively unexplored. Since the structural chemistry of phosphite with d-block elements, such as Co, Ni, and Zn, reveals complex 2-D and 3-D phases,[19-20] we sought to investigate the oxovanadium phosphite system, exploiting the templating influence of organoammonium cations. Pursuing this strategy, the two-dimensional phase, $[HN(Me)(CH_2CH_2)N(Me)H][(VO)_4(OH)_2(HPO_3)_4]$ (**1**), and two three-dimensional phosphites, $[H_2N(CH_2CH_2)_2NH_2][(VO)_3(HPO_3)_4]$ (**2**) and the template-free $[VO(HPO_3)(H_2O)]$ (**3**), were synthesized and structurally characterized.

The hydrothermal reaction of VCl_4, H_3PO_3, 1,4-dimethylpiperazine, and H_2O in the mole ratio 1:6.17:4.11:1835 at 150 °C under autogenous pressure for 6 days provided blue crystals of $[HN(Me)(CH_2CH_2)_2N(Me)H][(VO)_4(OH)_2(HPO_3)_4]$ (**1**) in 45% yield.[21] The infrared spectrum of **1** exhibited a broad medium intensity band at 3435 cm^{-1} associated with $v(N-H)$ of the organoammonium cation and two strong absorbances at 1100 cm^{-1} characteristic of $v(P{=}O)$. The strong band at 955 cm^{-1} is assigned to $v(V{=}O)$.

As shown in Figure 1, the structure of **1** consists of V−O−P layers, constructed from V(IV) square pyramids and HPO_3^{2-} tetrahedra, with the interlamellar space occupied by the $[HN(Me)(CH_2CH_2)_2N(Me)H]^{2+}$ cations.[22] The coordination about the V sites is defined by the terminal oxo group, a bridging −OH group, and the oxygen donors from each of three adjacent $(HPO_3)^{2-}$ groups. The vanadium sites are paired into corner-sharing binuclear units via the bridging hydroxy group. The pattern of polyhedral connectivity generates four distinct cyclic motifs within the layers: large eight polyhedral or 16-membered $(V_4P_4O_8)$ rings, five polyhedral or 10-membered $(V_3P_2O_5)$ rings which include the {V−O(H)−V} units, four polyhedral 8-membered $(V_2P_2O_4)$ rings, and three polyhedral 6-membered (V_2PO_3) rings which result from the symmetrical bridging of a binuclear vanadium site by a phosphite group. The terminal oxo groups of the vanadium centers and the {P−H} units of the phosphites are directed above and below the planes into the interlamellar space. The organoammonium cations are oriented with the nitrogen

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(21) The vanadium(IV) source VCl_4 was **carefully** hydrolyzed in H_2O to give a 1.80 M solution. A mixture of VCl_4, H_3PO_3, 1,4-dimethylpiperazine, and H_2O in the mole ratio 1:6.17:4.11:1835 was placed in a 23 mL Teflon-lined Parr acid digestion bomb (35% fill volume) and heated at 150 °C for 6 days. After cooling to room temperature over a 5 h period, blue rods of **1** were filtered from the yellow mother liquor, washed with water, and air dried. Yield: 45% based on vanadium. Anal. Calcd for $C_6H_{22}N_2O_{18}P_4V_4$: C, 9.76; H, 2.98; N, 3.79. Found: C, 9.67; H, 2.91; N, 3.99. IR (KBr pellet, cm^{-1}) 3435(m), 3008(m), 2736(m), 1624(m), 1465(m), 1100(vs), 1023(vs), 955(s), 618(m).

(22) Crystal data: $C_6H_{22}N_2O_{18}P_4V_4$; monoclinic $C2/c$, $a = 12.978(3)$ Å, $b = 10.130(2)$ Å, $c = 19.130(4)$ Å, $\beta = 91.40(3)°$, $V = 2514.2(9)$ Å^3, $Z = 4$, $D_{calc} = 1.949$ g cm^{-3}; structure solution and refinement based on 1647 reflections with $I_o \geq 3\sigma(I_o)$ (Mo Kα, $\lambda = 0.710\,73$ Å) converged at $R = 0.0512$. The {V═O} unit of V2 is disordered along the V═O vector so as to exhibit equal populations with the V=O vector directed above and below the V−P−O plane.

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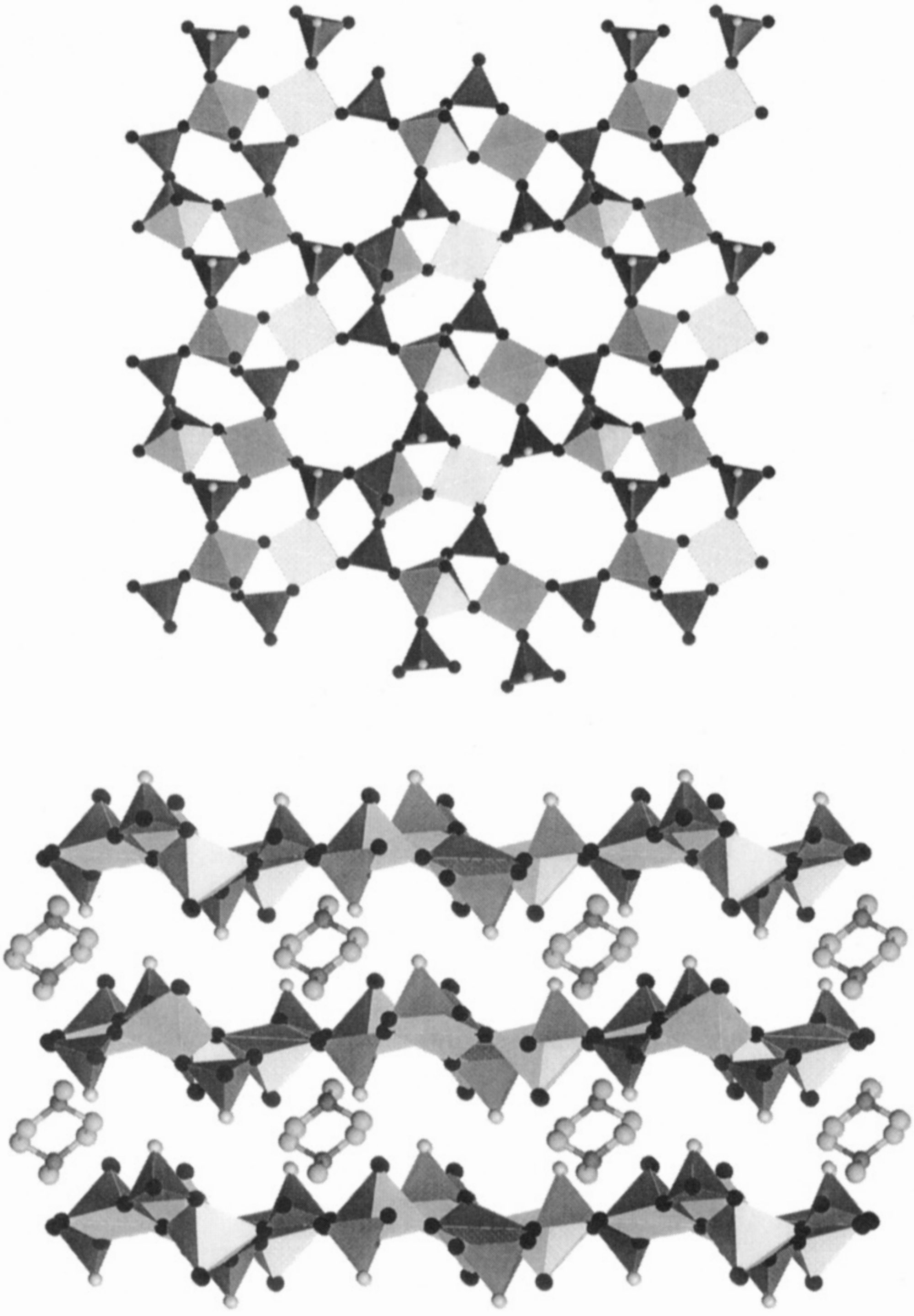

Figure 1. (a, top) Polyhedral representation of the V–P–O layer of **1**. (b, bottom) View of the structure of **1** along the *c* direction showing the alternation of inorganic anionic layers and organic cationic units. Selected bond lengths (Å) and angles (deg): V–O(phosphite), 1.987(9) (av); V–O(H), 1.963(7) (av); V–O(H)–V, 141.4(4).

centers directed toward the large cavities of two adjacent planes.

The dramatic influence of the organic template in determining structure is illustrated by the 3-dimensional phase $[H_2N(CH_2CH_2)_2NH_2][(VO)_3(HPO_3)_4(H_2O)_2]$ (**2**), which was prepared in the reaction of VCl_4, H_3PO_3, piperazine, and H_2O in the mole ratio 1:5.61:2.35:1668 at 150 °C for 6 days.[23] The infrared spectrum of **2** exhibits characteristic bands for υ(N–H) (3419 cm^{-1}), υ(V=O) (961 cm^{-1}) and υ(P–O) (1091 cm^{-1}).

As illustrated in Figure 2, the structure of **2** consists of a 3-D V–P–O network constructed from vanadium(IV) octahedra and square pyramids and phosphite tetrahedra, with the organic cations occupying well-defined channels.[24] In contrast to the structure of **1**, the vanadium sites of **2** are isolated, that is, linked through phosphite groups exclusively, with no V–O–V

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[23] A mixture of VCl_4, H_3PO_3, piperazine, and H_2O in the mole ratio 1:5.61:2.35:1668 was heated for 6 days at 150 °C and autogenous pressure. After ramped cooling to room temperature over a 14 h period, blue crystals of **2** were collected, washed with water, and ethanol and air-dried. Yield: 30% based on vanadium. Anal. Calcd for $C_4H_{20}N_2O_{17}P_4V_3$: C, 7.44; H, 3.10; N, 4.34. Found: C, 7.35; H, 3.22; N, 4.52. IR (KBr pellet, cm^{-1}): 3419(m), 2998(m), 1606(vs), 1091(vs), 961(s), 593(s).

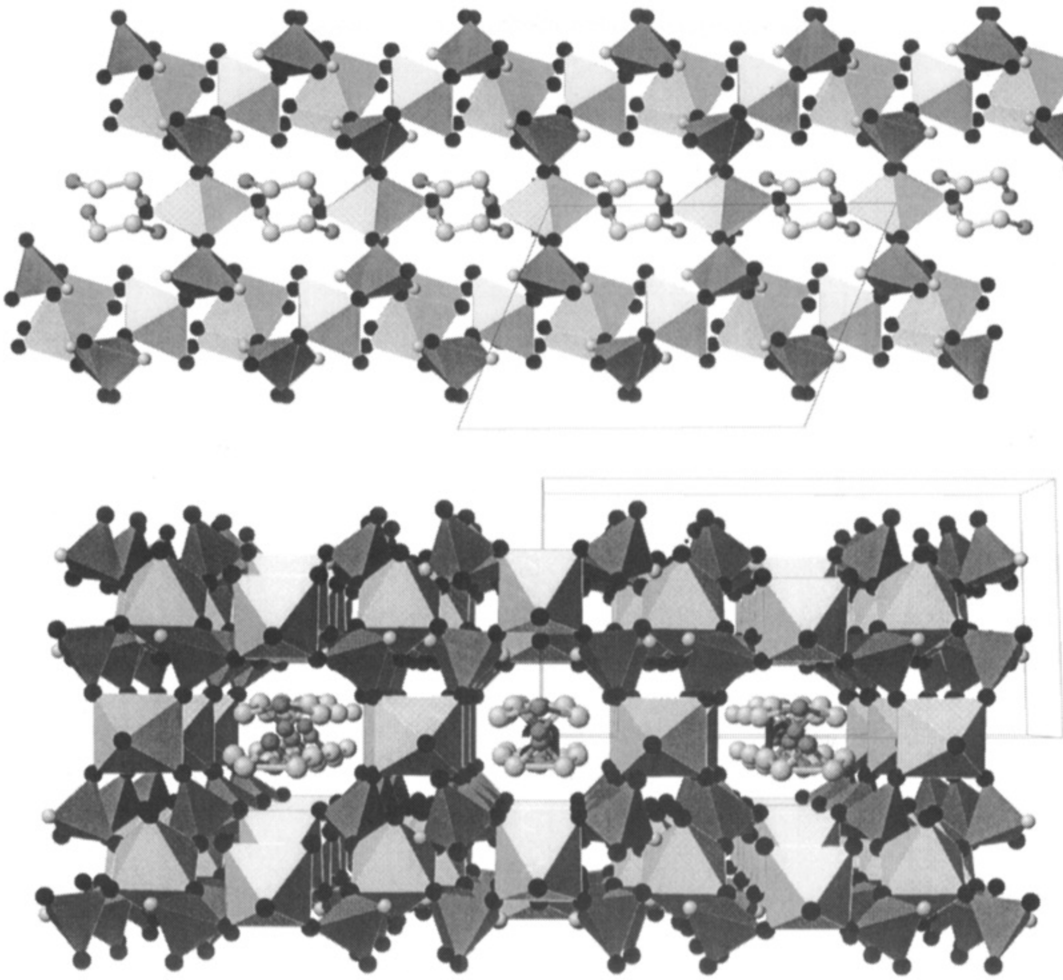

Figure 2. (a, top) View of the structure of **2**, parallel to the *b* axis, showing the linking of V−P−O layers by $\{VO_6\}$ octahedra and the location of the cations. (b, bottom) View of the structure of **2** parallel to the *a* axis, showing the channels occupied by the organoammonium cations. Selected bond lengths (Å) and angles (deg). Octahedral V site in the V−P−O plane: V−O(phosphite), 2.006(4) (av); V−O(aquo), 2.411(5); O_t−V−O(aquo), 178.4(2). Square-pyramidal site: V−O(phosphite), 1.970(3). Octahedral V site linking V−P−O planes: V−O(phosphite), 1.954 (8); V−O(aquo), 2.18(1); O_t−V−O(aquo), 164.7 (5).

interactions. The 3-D network may be described as V−P−O layers linked through $\{VO_6\}$ octahedra into a "pillared" motif with a 9.2 Å repeat between the layer midpoints. The layers are constructed from eight polyhedral 16-atom ($V_4P_4O_8$) rings, exhibiting corner-sharing of polyhedra exclusively. The rings contain two octahedral and two square-pyramidal V(IV) centers. The square-pyramidal geometry is defined by the terminal oxo group and four oxygen donors from each of four adjacent phosphite groups. The octahedral geometry is generated by a terminal oxo group, an aquo ligand, and four phosphite oxygen donors. The aquo group adopts the characteristic *trans* orientation with respect to the oxo group. The layers are linked through octahedral vanadium site which coordinate to pairs of phosphite donors from rings on each of two adjacent layers. The terminal oxo group and the aquo ligand of this exoplanar site also adopt the trans orientation. The vanadyl oxygens and the aquo groups of the layers are directed toward the interlamellar space to provide a channel lined with groups participating in hydrogen bonding to the organoammonium cation.

While organic cationic templates are often not incorporated into the product solid framework, their presence may be essential to product formation and crystallization.[25] This observation is pertinent to the synthesis of $[VO(HPO_3)(H_2O)]$ (**3**), prepared in the reaction of VCl_4, H_3PO_3, 1,2-diaminopropane, and H_2O in the mole ratio 1:4.46:2.36:1325 at 150 °C for 6 days.[26] The requirement of the organoamine in the synthesis of **3** may reflect its role in adjusting the pH of the solution and in providing a reducing environment for the reaction, thus maintaining the vanadium in the +4 oxidation state. The infrared spectrum of **3** exhibited promi-

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(24) Crystal data: $C_4H_{20}N_2O_{17}P_4V_3$; *C2/m*, $a = 13.419(3)$ Å, $b = 17.125(3)$ Å, $c = 9.252(2)$ Å, $\beta = 112.79(1)°$, $V = 1960.1(7)$ Å^3, $Z = 4$, $D_{calc} = 2.171$ g cm^{-3}; structure solution and refinement based on 2427 reflections converged at $R = 0.0467$. The square pyramidal vanadium site V3 is disordered about the mirror plane through $y = 0$, resulting in equal populations of the $\{V{=}O\}$ grouping above and below the plane generated by the four basal oxygen donors. Similarly, 2-fold disorder about the octahedral V2 site results in disorder of the terminal oxo group and one of the phosphate oxygen donors. Each site was adequately modeled at 0.5 site occupancy.

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(26) A mixture of VCl_4, H_3PO_3, 1,2-diaminopropane, and H_2O in the mole ratio 1:4.46:2.36:1325 was heated in a 23 mL Parr acid digestion bomb (35% fill volume) for 6 days at 150 °C. After cooling to room temperature, blue rods of **3** were isolated in 50% yield. Anal. Calcd for H_3O_5PV: H, 1.82; V, 30.9. Found: H, 1.67; V, 30.6. IR (KBr pellet, cm^{-1}) 3428(m, br), 1654(w), 1137(s), 956(s), 753(m).

(27) Crystal data: H_3O_5PV; tetragonal, $I4_1/a$, $a = 17.633(2)$ Å, $c = 5.331(1)$ Å, $V = 1657.3(6)$ Å^3, $Z = 16$, $D_{calc} = 2.644$ g cm^{-3}; structure solution and refinement based on 361 reflections converged at $R = 0.0573$.

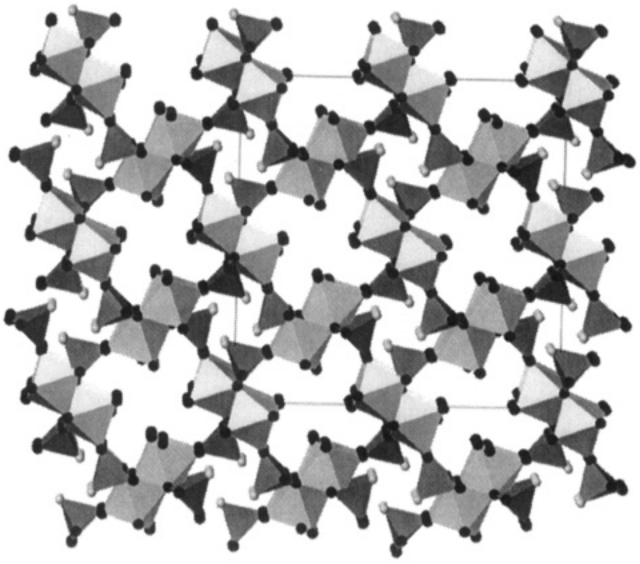

Figure 3. View of the structure of **3** parallel to the *c* axis, illustrating the major and minor channels described in the text. Selected bond lengths (Å) and angles (deg): V−O(phosphite), 1.935(9), 2.031(9), 2.001(9), 2.293(9) (trans to O_t); V−O(aquo), 2.107 (9); O_t−V−O(aquo), 93.0(4); O_t−V−O1, 172.9(4).

nent bands associated with υ(O−H) for the aquo ligand (3428 cm^{-1}), υ(V=O) (956 cm^{-1}) and υ(P−O) (1137 cm^{-1}).

The 3-D V−P−O network of **3** is illustrated in Figure 3. The polyhedral connectivity produces a framework characterized by two types of channels, a larger tunnel into which project the terminal oxo groups and aquo ligands of the V(IV) centers, and a smaller tunnel occupied by the hydrogen atoms of the phosphite groups. In contrast to the structure of **2**, the vanadium sites of **3** assume a motif based on edge-sharing of pairs of $\{VO_6\}$ octahedra. However, this binuclear structural unit is quite distinct from that of **1**, which consists of binuclear $\{VO_5\}$ square pyramids, corner-sharing through hydroxide {V−O(H)−V} interactions. In the case of **3**, the vanadium pairs are linked through doubly bridging phosphite oxygen donors from each of two phosphite groups. Each phosphite center in this manner serves to link two vanadium centers of a single ring unit and a third vanadium site from a neighboring ring. Each vanadium site coordinates to a terminal oxo group, an aquo ligand, and four phosphite oxygen donors. Curiously, the aquo group is cis to the terminal oxo group, allowing both unshared vertexes of the $\{VO_6\}$ octahedra to project into the larger channel of the framework. Aquo groups are oriented so as to hydrogen bond to oxo groups in adjacent vanadium sites in the channel. It is instructive to compare the structure of **3** to the $VO(HPO_4)\cdot xH_2O$ family of structures, as these materials serve as precursors for the catalyst employed in butane oxidation to maleic anhydride. In contrast to the structural motif of edge-sharing pairs of $\{VO_6\}$ octahedra linked by $\{HPO_3\}$ tetrahedra into a three-dimensional framework adopted by **3**, the structure of $VO(HPO_4)\cdot 0.5\ H_2O$ consists of V−P−O layers constructed from binuclear units of face-sharing $\{VO_6\}$ octahedra.[28] Likewise, the structure of α-$VO(HPO_4)\cdot 2H_2O$[29] is a layered V−P−O network exhibiting chains of corner-sharing $\{VO_6\}$ octahedra. The two-dimensional structures of β-$VO(HPO_4)\cdot 2H_2O$[30] and $VO(HPO_4)\cdot 4H_2O$[31] are constructed from isolated $\{VO_6\}$ octahedra linked through $\{PO_4\}$ tetrahedra.

The preliminary investigation described in this work reveals a rich structural chemistry for the oxovanadium phosphite system, perhaps rivaling that of the oxovanadium phosphate system. By exploitation of the significantly different coordination requirements of HPO_3^{2-} and PO_4^{3-}, solid-phase materials exhibiting significant microporous properties may be accessible and structural variations in the size and shapes of the cavities may be introduced. While attempts to tailor the structures of 2-D and 3-D materials are in their infancy,[32] structural variations are clearly possible through manipulation of reaction conditions and precursors.

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Supporting Information Available: Tables of atomic positional parameters, bond lengths and angles, and anisotropic temperature factors for **1−3** (16 pages).

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