Hydrothermal Synthesis and Structural Characterization of an Organically Templated Layered Oxovanadium(IV) Organophosphonate: $(C_2H_5NH_3)_2[V_3O_3(H_2O)(PhPO_3)_4]$

M. Ishaque Khan,† Young-Sook Lee,‡ Charles J. O'Connor,‡ Robert C. Haushalter,*,§ and Jon Zubieta*,†

Departments of Chemistry, Syracuse University, Syracuse, New York 13244–4100, and University of New Orleans, New Orleans, Louisiana 70148

Received February 18, 1994

The metal organophosphonate system exhibits a rich coordination chemistry, including mononuclear[1,2] and binuclear coordination compounds,[3] polyoxoanion cluster frameworks,[4–9] linear one-dimensional complexes,[9] and layered solid phases.[10–16] The layered solid materials consist of alternating organic and inorganic domains and exhibit useful sorptive and catalytic properties.[17–21] The structurally well-defined internal void spaces and coordination sites characteristic of the oxovanadium organophosphonate solids allow these materials to intercalate alcohols by coordination of the substrate molecule to the vanadium sites of the V/P/O layer. Furthermore, the $VO(RPO_3)\cdot H_2O$ phases recognize primary alcohols in preference to secondary and tertiary alcohols. The combination of such substrate-specific recognition with the incipient and/or actual coordinative unsaturation of the metal sites, with the thermal stability and reactivity of metal–oxide functionalities, and with the interplay of hydrophobic and hydrophilic domains provides desirable properties for the design of highly selective oxidation catalysts.[22,23]

Despite such attractive features, the chemistry of the $V/O/RPO_3^{2-}$ solid phases remains relatively undeveloped and restricted to the $VO(RPO_3)\cdot H_2O\cdot R'OH$ materials[14] and the structurally characterized $[VO(PhPO_3)(H_2O)]$[15] and $[(VO)_2\{CH_2(PO_3)_2\}(H_2O)_4]$.[16] However, for the analogous inorganic oxovanadium phosphate phases, we recently demonstrated that incorporation of organic templates results in a dramatic expansion of the structural and compositional range of the materials and provides a general methodology for the preparation of open-framework materials.[24–27] Although oxovanadium organophosphonate molecular clusters organized about organic templates have been prepared,[4] no examples of organically templated $V/O/RPO_3^{2-}$ solid phases have been structurally characterized. We reported the hydrothermal synthesis and single-crystal X-ray structure of

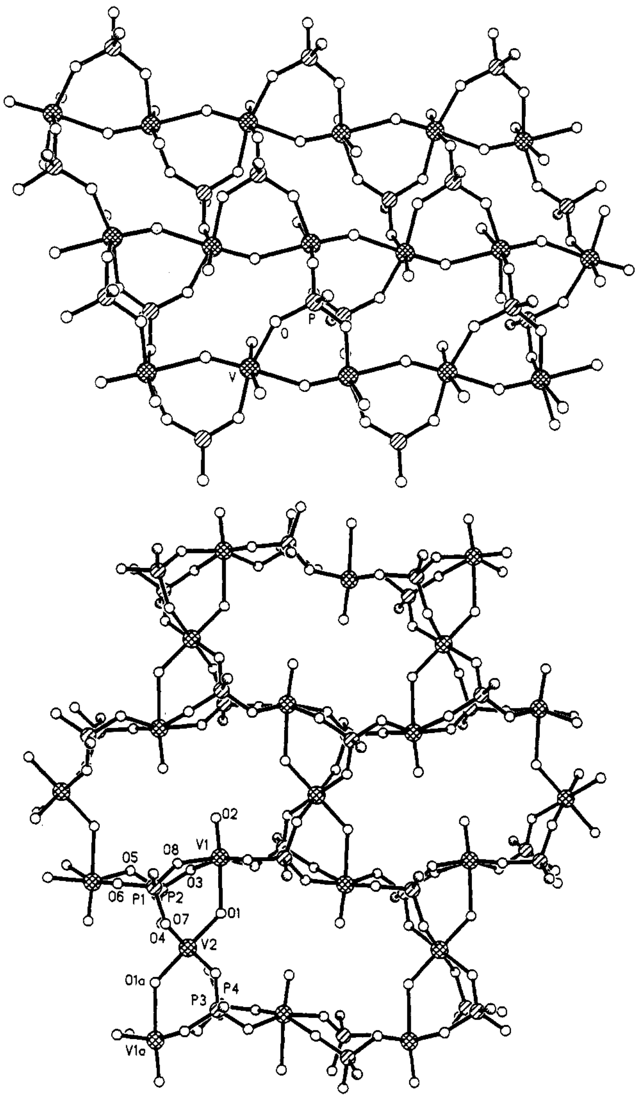

Figure 1. A comparison of the *bc* planes of $[VO(C_6H_5PO_3)(H_2O)]$ and **1**. (a) Top: The infinite {–V=O—V–} chains of the V/P/O layer of $[VO(C_6H_5PO_3)(H_2O)]$ are evident. (b) Bottom: The discrete $\{V_3O_3(H_2O)\}$ zigzag units of **1** terminate with {V=O} or {V—OH₂} groups projecting into the cavity generated by edge-sharing of six vanadium octahedra and four phosphonate tetrahedra.

---

† Syracuse University.

‡ University of New Orleans.

§ NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540.

(1) Clark, E. T.; Rudolf, P. R.; Martell, A. E.; Clearfield, A. *Inorg. Chim. Acta* **1989,** *164,* 59.
(2) Rudolf, P. R.; Clark, E. T.; Martell, A. E.; Clearfield, A. *J. Coord. Chem.* **1985,** *14,* 139.
(3) Chen, Q.; Salta, J.; Zubieta, J. *Inorg. Chem.* **1993,** *32,* 4485.
(4) Huan, G. H.; Jacobson, A. J.; Day, V. W. *Angew. Chem.* **1991,** *103,* 426; *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 422.
(5) Huan, G.; Day, V. W.; Jacobson, A. J.; Goshorn, D. P. *J. Am. Chem. Soc.* **1991,** *113,* 3188.
(6) Müller, A.; Hovemeier, K.; Rohlfing, R. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 1192.
(7) Chen, Q.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 261.
(8) Chang, Y.-D.; Salta, J.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* in press.
(9) Sergienko, V. S.; Tolkacheva, E. O.; Ilyukhin, A. B.; Starikova, Z. A.; Krol, I. A. *J. Chem. Soc., Chem. Commun.* **1992,** 144.
(10) Bujoli, B.; Palvadeau, P.; Rouxel, J. *Chim. Mater.* **1990,** *2,* 582.
(11) Cao, G.; Lee, H.; Lynch, V.; Mallouk, T. E. *Inorg. Chem.* **1988,** *27,* 2781.
(12) Zhang, Y.; Clearfield, A. *Inorg. Chem.* **1992,** *31,* 2821.
(13) Bhardwaj, C.; Hu, H.; Clearfield, A. *Inorg. Chem.* **1993,** *32,* 4294.
(14) Johnson, J. W.; Jacobson, A. J.; Butler, W. M.; Rosenthal, S. E.; Brody, J. F.; Lewandowski, J. T. *J. Am. Chem. Soc.* **1989,** *111,* 381.
(15) Huan, G. H.; Jacobson, A. J.; Johnson, J. W.; Corcoran, E. W., Jr. *Chem. Mater.* **1990,** *2,* 2.
(16) Huan, G. H.; Johnson, J. W.; Jacobson, A. J.; Merola, J. S. *J. Solid State Chem.* **1990,** *89,* 220.
(17) Dines, M. B.; Cooksey, R. E.; Griffith, P. C. *Inorg. Chem.* **1983,** *22,* 567.
(18) Cao, G.; Mallouk, T. E. *Inorg. Chem.* **1991,** *30,* 1434.
(19) Rosenthal, G. L.; Caruso, J. *Inorg. Chem.* **1992,** *31,* 3104.
(20) Burwell, D. A.; Valentine, K. G.; Timmermans, J. H.; Thompson, M. E. *J. Am. Chem. Soc.* **1992,** *114,* 4144.
(21) Clearfield, A. *Chem. Rev.* **1988,** *88,* 125.
(22) Mallouk, T. E.; Lee, H. *J. Chem. Educ.* **1990,** *67,* 829.
(23) Haushalter, R. C.; Mundi, L. A. *Chem. Mater.* **1992,** *4,* 31.
(24) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J. *Science* **1993,** *259,* 1596.
(25) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 610.
(26) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1993,** *5,* 1595.
(27) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, C. J. *Chem. Mater.* **1993,** *5,* 1690.

0020-1669/94/1333-3855$04.50/0

$(C_2H_5NH_3)_2[V_3O_3(H_2O)(PhPO_3)_4]$ (**1**), a layered solid which is constructed from organophosphonate-bridged trinuclear $\{V_3O_3(H_2O)\}^{6+}$ units bridged by $(C_6H_5PO_3)^{2-}$ groups and which adopts an open V/P/O layer structure to accommodate the organic cation.

The hydrothermal reaction of a mixture of NH_4VO_3, $C_6H_5PO_3H_2$, NH_4Cl, $C_2H_5NH_3Cl$, and H_2O in the mole ratio 0.3:6:3:6:200 at 160 °C and autogenous pressure for 48 h yielded light-green plates of **1** in 64% yield.[28] The infrared spectrum of **1** exhibits four bands in the 925–1200-cm^{-1} range associated with PO_3 vibrations and a feature at 991 cm^{-1} assigned to $\mu(V^{IV}{=}O)$. Thermal gravimetric analysis of **1** exhibits an initial weight loss between 130 and 160 °C corresponding to one H_2O molecule per unit formula. A second weight change associated with loss of the organic templates and decomposition of the phosphonate occurs between 340 and 430 °C.

The structure of $(C_2H_5NH_3)_2[V_3O_3(H_2O)(C_6H_5PO_3)_4]$ (**1**)[29] consists of layers of corner-sharing $\{VO_6\}$ octahedra and $\{PO_3C\}$ tetrahedra, with the phenyl groups extending from both sides of the V/P/O layer. The pattern of alternating organic and inorganic layers is reminiscent of the structure of $[VO(C_6H_5PO_3)(H_2O)]$.[15] However, the structural similarities do not extend to the detailed structure of the oxide layers, which distort in **1** to accommodate the presence of the organic cationic templates. Whereas the structure of $[VO(C_6H_5PO_3)(H_2O)]$ exhibits an oxide layer having a vanadium–oxo to phenylphosphonate composition of 1:1 and exhibiting infinite $\{-V{=}O{-}V-\}$ chains with alternating short and long V—O bonds, **1** features a $\{VO\}:RPO_3^{2-}$ composition of 3:4 with discrete trinuclear $\{V_3O_3(H_2O)\}$ units bridged through $\{C_6H_5PO_3\}^{2-}$ groups (Figure 1). The $\{V_3O_3(H_2O)\}$ trinuclear units exhibit zigzag $\{-V{=}O{-}V-\}$ chains with short–long alternation of V—O bonds, such that each $\{V_3O_3(H_2O)\}$ chain terminates in an oxo atom at one end and an aquo ligand at the other.[29] The kinks in the $\{-V{=}O{-}V-\}$ chains are a consequence of edge sharing between the three vanadium octahedra of the trinuclear unit and four bridging $(RPO_3)^{2-}$ groups. Thus, the central vanadium octahedron of the unit coordinates to four bridging organophosphonates, while each terminal vanadium octahedron shares two of these bridging $(RPO_3)^{2-}$ tetrahedra with the central vanadium and forms two additional edge-sharing interactions with phosphate tetrahedra which bridge to an adjacent trinuclear unit.

The trinuclear structural motifs shown in Figure 1 fuse in such a fashion as to generate cavities in the V/P/O layer, defined by rings constructed from the edge sharing of six vanadium octahedra and four $(RPO_3)^{2-}$ tetrahedra. These cavities are polar with aquo groups and vanadyl oxygens projecting into the void space. The V/P/O layers are stacked to produce tunnels parallel to the cell *a* axis, which are occupied by the $(C_2H_5NH_3)^+$ cations. The walls of these tunnels are defined by the organophosphonate phenyl groups which project above and below the V/P/O planes. The organic cations are oriented in the cavities with the ammonium group, $-NH_3^+$, directed toward the hydrophilic holes in the V/P/O layer, while the $-C_2H_5$ group trails into the hydrophobic region generated by the phenyl substituents. The incorporation of the organic template into the $V/O/C_6H_5PO_3^{2-}$ system results in dramatic structural rearrangement within the V/P/O layer of **1** as compared to $[VO(C_6H_5PO_3)(H_2O)]$, in contrast to a relatively minor distortion of the gross alternating pattern of inorganic and organic layers. The structure may be described as amphiphilic and rationalized on the basis of partitioning into hydrophilic and hydrophobic domains. While the templating mechanism remains enigmatic, it is clear that charge-compensating and space-filling effects contribute to the process and that different template molecules will provide different distortions of the V/P/O layer, as in $[(C_2H_5)_4N][(VO)_3(OH)(C_2H_5PO_3)_3]\cdot H_2O$.[31]

The high-temperature magnetic susceptibility data ($T > 20$ K) exhibit Curie–Weiss paramagnetism

$$\chi = \frac{C}{T-\Theta} + \mathrm{TIP} = \frac{Ng^2\mu_B^2S(S+1)}{k(T-\Theta)} + \mathrm{TIP}$$

with $C = 1.075$ emu K/mol, $\Theta = -14$ K, and TIP = 0.000 361 emu/mol. The electron structure of **1** corresponds to one unpaired electron per vanadium(IV) ion[30] with spin $S = {}^1/_2$. This results in an average Curie–Weiss *g* value 1.95 for each of the V(IV) ions. The large negative Weiss constant indicates that there is a substantial amount of antiferromagnetic exchange in this complex. At lower temperatures, the magnetic susceptibility begins to deviate from Curie–Weiss law behavior, but there is no characteristic magnetic anomaly to allow a precise determination of the strength of the magnetic coupling.

Acknowledgment. This work was supported by NSF Grant No. CHE9318824. C.J.O. acknowledges a grant from the Louisiana Education Quality Support Fund [LEQSF(RF/1994–94)-ENH-TR-60] administered by the Board of Regents of the State of Louisiana.

Supplementary Material Available: Tables giving a structure determination summary, atomic positional parameters and isotropic thermal parameters, anisotropic thermal parameters, bond lengths, bond angles, and calculated hydrogen atom positions for **1**, Figure S1, illustrating the alternating organic and inorganic planes of **1**, and Figure S2, showing the susceptibility of **1** plotted as a function of temperature (12 pages). Ordering information is given on any current masthead page.

---

(28) A mixture of NH_4VO_3 (1.36 g, 11.6 mmol), $C_6H_5PO_3H_2$, NH_4Cl, $C_2H_5NH_3Cl$, and H_2O in the mole ratio 0.3:6:3:6:200 was placed in a 23-mL Teflon-lined autoclave which was heated at 160 °C and autogenous pressure for 48 h. The reaction vessel and its contents were slowly cooled to room temperature over a period of 72 h. Light green crystals of **1** were filtered from the colorless mother liquor and mechanically separated from a small amount of amorphous yellow impurity. Yield of crystalline **1**: 0.6 g, 64% based on vanadium. While a range of reactant stoichiometries were tried, the reported values represent the optimal ratio. Anal. Calcd for $C_{28}H_{38}N_2O_{16}V_3$: C, 41.4; H, 4.69; N, 3.45. Found: C, 41.2; H, 4.55; N, 3.52. IR (KBr pellet, cm^{-1}): 3433 (m), 3057 (m), 1608 (m), 1433 (m), 1258 (w), 1138 (s), 1051 (vs, br), 1012 (sh), 928 (m), 799 (w), 746 (m), 718 (w), 694 (m), 590 (m).

(29) Crystal data for $(C_2H_5NH_3)_2[V_3O_3(H_2O)(C_6H_5PO_3)_4]$ (**1**): monoclinic space group $P2_1/c$ with $a = 14.708(3)$ Å, $b = 12.406(2)$ Å, $c = 10.275(2)$ Å, $\beta = 93.66°$, $V = 1871.0(6)$ Å^3, $Z = 2$, $D_{calc} = 1.657$ g cm^{-3}; data collected at 213 K on a crystal of dimensions 0.25 × 0.29 × 0.11 mm^3 on a Rigaku AFC5S diffractometer using a $2\theta-\omega$ scan mode with a 2θ range of 0–45°; structure solution and refinement based on 2327 reflections with $I_o \geq 3\sigma(I_o)$ (4286 reflections total; graphite crystal monochromated Mo Kα radiation, $\lambda = 0.710\,73$ Å) converged at a conventional discrepancy factor of 0.072. Disorder of the vanadium atoms over two equally populated sites results from the $\{H_2O{-}V{=}O{-}V{=}O{-}V{=}O\}$ chain ordering in the two possible orientations about the center of symmetry. Thus, the V2 site does not rest on the center of symmetry of 0, $^1/_2$, 0 but is displaced to 0.0013, 0.5138, –0.0193. The presence of the center of symmetry produces a second half-occupancy V2A site at –0.0013, 0.4862, 0.0193. Consequently, the long–short alternation of {V—O} bonds within the $\{V_3O_3(H_2O)\}$ linkages requires the equal population of two V1 sites with displacements along the O—V—O axis from the average position. This disorder model gave satisfactory refinement of thermal parameters and consistent values for the bond valences of all vanadium sites.[30] The formulation of **1** as a V(IV) material is consistent with the magnetic and electronic properties and with the bond valences cited above. Attempts to refine the structure in the noncentrosymmetric space group *Pc* gave unreasonable anisotropic temperature factors and a hopelessly correlated matrix.

(30) Brown, I. D. In *Structure and Bonding in Crystals*; O'Keefe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; Vol. II, p 1.

(31) Khan, M. I.; Lee, Y.-S.; O'Connor, C. J.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.*, in press.