Chem. Mater. **1994**, *6*, 721-723

Hydrothermal Synthesis and Structure of $[(C_2H_5)_4N][(VO)_3(OH)(H_2O)(C_2H_5PO_3)_3]\cdot H_2O$. An Inorganic–Organic Polymer Exhibiting Undulating V/P/O Layers and Interlamellar Organic Templates

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Received February 18, 1994
Revised Manuscript Received April 15, 1994

The considerable interest in the chemistry of layered materials stems from their practical applications as catalysts, hosts in intercalation compounds, and protonic conductors.[1-4] Intercalative reactions of layered solids provide a means for preparing new materials with tailored solid-state structures and properties.[5-10] The vanadyl organophosphonates, $VO(RPO_3)\cdot xH_2O$,[11-14] a class of materials exhibiting well-defined void spaces and coordination sites, as well as readily modified organic substituents, can recognize primary alcohol molecules and selectively discriminate among various branched isomers. While this combination of substrate-specific recognition and coordinative unsaturation of the transition metal sites offers an approach to the design of highly selective oxidation catalysts,[8,9] the intercalative chemistry of the solid phases of the $V/O/RPO_3^{2-}$ system remains largely undeveloped. To extend the chemistry of this system, we have exploited the techniques of hydrothermal synthesis which afford low-temperature routes to metastable phases and allow the introduction of organic cations to modify the structures of the solid assemblies.[15,16] In this fashion, a novel layered vanadium(IV) organophosphonate $(Et_4N)[(VO)_3(OH)(H_2O)(EtPO_3)_3]\cdot H_2O$ ($1\cdot H_2O$) incorporating templating organic cations and exhibiting undulating inorganic V/P/O layers has been prepared.

The reaction of $NaVO_3$, $C_2H_5PO_3H_2$, $(C_2H_5)_4NCl$ and H_2O in the mole ratio 3:4:6:300 at 140 °C for 5 days yields green plates of $(Et_4N)[(VO)_3(OH)(H_2O)(C_2H_5PO_3)_3]\cdot H_2O$ ($1\cdot H_2O$) in 40% yield.[17] The infrared spectrum of $1\cdot H_2O$ exhibits intense bands at 1120, 1062, and 1025 cm^{-1} associated with the PO_3 group and a sharp band at 998 cm^{-1} assigned to $\nu(V{=}O)$.

The structure of 1[18] consists of layers of corner-sharing vanadium(IV) square pyramids and $\{PO_3C\}$ tetraheda, with the phosphate $-C_2H_5$ groups and the vanadyl $\{V{=}O\}$ moieties projecting from both surfaces of the V/P/O layer, as shown in Figure 1. In contrast to the prototypical structure of $[VO(C_6H_5PO_3)(H_2O)]$, which exhibits planar V/P/O layers and alternating inorganic layers and phenyl bilayers, the V/P/O layers of 1 undulate in such a fashion as to produce interlamellar cavities occupied by the organic cationic templates. The organic cations populate channels defined by the crests and troughs of adjacent V/P/O layers, which exhibit an interlayer repeat distance of 10.73 Å. These channels are bounded on two flanks by the $-C_2H_5$ substituents of the organophosphonate groups, on a third side by the concave surface of the V/P/O layer which projects both $-C_2H_5$ groups and $\{V{=}O\}$ units into the interlamellar region, and on the remaining side by the convex surface of the adjacent layer which projects vanadyl groups exclusively. Thus, through the interplay of hydrophobic–hydrophilic interactions, nonpolar interlamellar regions bounded by organic substituents and relatively nonpolar vanadyl groups[9] have been created.

As shown in Figure 2, there are two distinct vanadium environments associated with the V/P/O planes of 1. The V1 and V2 centers form a hydroxy-bridged binuclear unit with the terminal oxo groups adopting the anticonfiguration relative to the $\{V_2O_7\}$ plane. On the other hand, the V3 sites consist of isolated $\{VO_5\}$ square pyramids with the coordination geometry at the vanadium defined by a terminal oxo group, three oxygen donors from each of three phosphonate units and an aquo ligand. The geometries adopted by the vanadium centers of 1 may be contrasted to those observed for $[VO(C_6H_5PO_3)(H_2O)]$ which contains infinite one-dimensional $\{{-}V{=}O{-}V{=}O{-}\}$ chains and for $[VO(C_6H_5PO_3)(H_2O)_2]$ which is characterized by isolated $\{VO_6\}$ octahedra and $\{RPO_3\}$ tetrahedra in a corner-sharing array.

Ethylphosphonate groups in three distinct environments serve to bridge the vanadium centers and to link the structure into its unique two dimensional array. Each organophosphonate group associated with the P1 and P4 sites adopts the symmetrical bridging mode between V

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(17) A mixture of $NaVO_3$, $C_2H_5PO_3H_2$, $(C_2H_5)_4NCl$, and H_2O in the mole ratio 3:4:6:300 was placed in a 23-mL Teflon-lined Parr acid digestion bomb (35% fill volume) and heated at 140 °C for 5 days. After the resultant mixture was allowed to cool slowly to room temperature, light green plates of $1\cdot 2H_2O$ were filtered from the light green mother liquor. Yield: 40% based on V. Anal. Calcd for $C_{28}H_{80}N_2O_{30}P_6V_6$: C, 23.7; H, 5.65; N, 1.98. Found: C, 24.0; H, 5.87; N, 1.72.

(18) Crystal data for $C_{14}H_{40}NO_{15}P_3V_3$: orthorhombic space group $Pca2_1$ with $a = 21.461(4)$ Å, $b = 13.912(3)$ Å, $c = 19.247(4)$ Å, $V = 5749(3)$ Å^3, $Z = 4$, $D_{calc} = 1.636$ g cm^{-3}; structure solution and refinement based on 2413 reflections with $F_o \geq 4\sigma(F_o)$ (Mo Kα radiation, $\lambda = 0.710\,73$ Å) converged at $R = 0.0563$.

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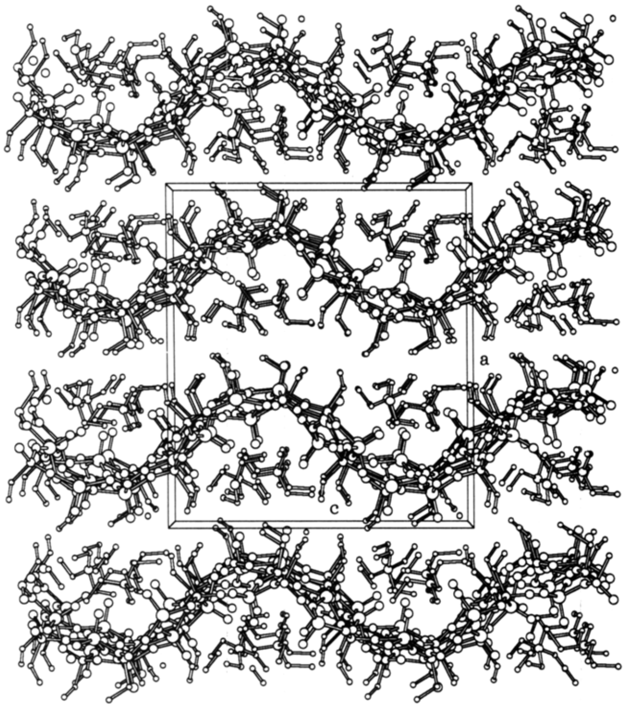

Figure 1. View of the *ac* plane of $(Et_4N)[(VO)_3(OH)(H_2O)(EtPO_3)_3]$ (1), showing the undulating V/P/O layers and the interlamellar channels occupied by the Et_4N^+ cations.

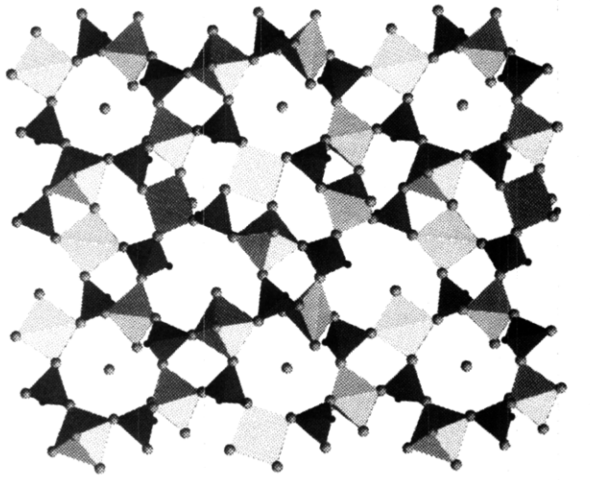

Figure 2. View of the *bc* plane of 1, highlighting the coordination about the vanadium centers. Average bond lengths (Å) and angles (deg): (a) for the binuclear vanadium sites V–O(terminal), 1.58(2); V–O(phosphonate), 1.97(2); V–O(μ-OH), 1.98(2); V–(μ-OH)–V, 140(1); (b) for the mononuclear sites V–O(terminal), 1.52(2); V–O(phosphonate), 1.96(2); V–O(aquo), 2.02(2).

atoms of the $\{V_2(\mu^2\text{-}OH)(\mu^2\text{-}O_2P(Et)O)\}$ binuclear units, as well as serving as a monodentate ligand to an adjacent binuclear unit. The second type of organophosphonate group bridges vanadium centers from each of two adjacent binuclear units to a mononuclear vanadium site, which the third type links a vanadium site of a binuclear unit to two adjacent mononuclear vanadium centers. The complexity of the connectivity pattern is reflected in the presence of 6-membered $\{V_2PO_3\}$ rings, 8-membered $\{V_2P_2O_4\}$ rings, 10-membered $\{V_3P_2O_5\}$ rings, and 16-membered $\{V_4P_4O_8\}$ rings formed by the corner-sharing of the $\{VO_5\}$ square pyramids and the $\{O_3PC\}$ tetrahedra.

The calculated bond valences[19] of the vanadium centers are between 3.90 and 4.10, indicating that all sites are formally V(IV), an observation confirmed by the magnetic properties of the material. The high-temperature magnetic susceptibility data ($T > 20$ K) exhibits Curie–Weiss paramagnetism:

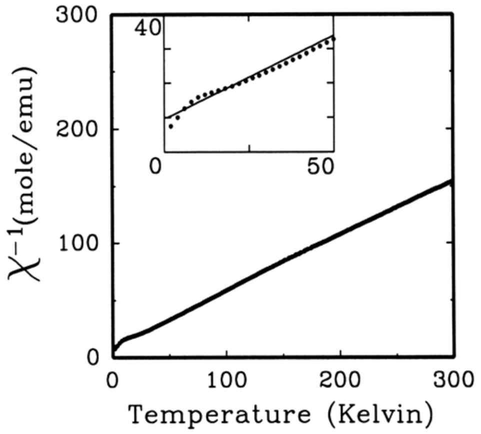

Figure 3. Magnetic susceptibility of 1 plotted as a function of temperature over the 1.7–300 K temperature region. The curve drawn through the data is the fit to the theoretical model as described in the text. The inset shows an expansion of the inverse magnetic susceptibility data at the lowest temperatures where the data begins to deviate from Curie–Weiss law.

$$X = \frac{C}{T-\theta} = \frac{N_g{}^2\mu_B{}^2S(S+1)}{k(T-\theta)}$$

with $C = 2.04$ emu K/mol and $\Theta = -19$ K. The electron structure of 1 corresponds to one unpaired electron per vanadium(IV) center with spin $S = {}^1/_2$. This results in an average Curie–Weiss g value of $g = 1.91$ for each of the V(IV) ions. The large negative Weiss constant indicates that there is a substantial amount of antiferromagnetic exchange in this material. At lower temperatures the magnetic susceptibility begins to deviate from Curie–Weiss law, but there is not characteristic magnetic anomaly to allow a precise determination of the magnetic coupling.

The isolation and characterization of 1 confirm not only that organic templates may be employed to direct the organization of layered solids but also that the identity of the templates may have profound influence on the structural characteristics of the phase. While it is not unexpected that the structure of 1 should contrast with those of the template-free prototypes $[VO(PhPO_3)(H_2O)]$ and $[VO(PhPO_3)(H_2O)_2]$, it is noteworthy that 1 is also structurally distinct from the two other examples of organic cation templated $V/O/RPO_3{}^{2-}$ phases isolated to date, $(EtNH_3)_2[(VO)_3(PhPO_3)_4(H_2O)]$ (**2**)[20] and $(Et_2NH_2)(Me_2NH_2)[(VO)_4(PhPO_3)_4(OH)_2]$ (**3**).[21] The former exhibits the gross structural features of the $[VO(PhPO_3)(H_2O)]$ prototype with alternating V/P/O layers and organic bilayers, but with the template intercalated into the projecting organic domain; in contrast, the latter features a unique modification of the layer registry such that the phenyl groups project from one surface only of the V/P/O layers to give an alternation of phenyl bilayers–V/P/O layer–cation layer–V/P/O layer–phenyl bilayer– and so on. Furthermore, the details of polyhedral connectivity within the V/P/O layers are also distinct: **2** exhibits

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trinuclear $\{V_3O_3(H_2O)\}$ zigzag units, while **3** exhibits hydroxy-bridged binuclear sites exclusively.

Acknowledgment. This work was supported by NSF Grant No. CHE 9318824.

Supplementary Material Available: Tables of atomic positional parameters and isotropic thermal parameters, anisotropic thermal parameters, bond lengths, bond angles, and calculated hydrogen atom portions for 1 (10 pages). Ordering information is given on any current masthead page.