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Organically Templated Layered Vanadium(IV)–Oxo–Organophosphonate Exhibiting Intercalated Organic Cations and Open-Framework V/P/O Layers: $[(C_2H_5)_2NH_2][(CH_3)_2NH_2][V_4O_4(OH)_2(C_6H_5PO_3)_4]$

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The chemistry of the layered metal organophosphonates[1-10] has witnessed dramatic development in recent years because of the potential applications of such materials as sorbents, catalysts, and ion exchangers.[11-15] Since these materials exhibit well-defined void spaces and coordination sites, as well as readily modified organic substituents, both intercalative chemistry and modification of organic functionalities by either pre- or postsynthesis reactions may be exploited to prepare materials with tailored solid-state structures and properties.[16-18] The vanadyl organophosphonates, $VO(RPO_3)\cdot xH_2O$,[6-9] are of particular interest as a consequence of their shape-selective intercalative chemistry with alcohols. This combination of substrate-specific recognition with the incipient and/or actual coordinative unsaturation of the transition metal sites and with the thermal stability of the vanadium oxide framework provides intriguing possibilities for the design of highly selective oxidation catalysts.[17] However, the chemistry of the $V/O/RPO_3^{2-}$ solid phases remains relatively unexplored, with the notable exception of Jacobson's work on the $[VO(RPO_3)(H_2O)]$ class of materials and their alcohol intercalative derivatives.[6-8] In an effort to extend the chemistry of the $V/O/RPO_3^{2-}$ system, we have attempted to exploit solvothermal synthesis to assemble simple molecular units into larger assemblies, an approach which has proved successful in the preparation of the polyoxovanadium–organophosphonate clusters $[V_4O_4\{PhP(O)_2OP(O)_2Ph\}_4Cl]^-$, $[V_6O_6(C_4H_9PO_3)_8Cl]$, $[V_7O_{12}(PhPO_3)_6]^{2-}$,[19] $[V_{12}O_{20}(H_2O)_{12}(PhPO_3)_8Cl]^{2-}$,[20] and $[V_{18}O_{25}(H_2O)_2(PhPO_3)_{20}Cl_4]^{4-}$.[21] The hydrothermal technique not only affords a route to low-temperature metastable phases but also allows the introduction of organic templates to direct the synthesis of open framework solids and materials with defined hydrophilic and hydrophobic domains. In this paper, we report the synthesis and structure of a novel layered vanadium(IV) organophosphonate incorporating templating organic cations at two distinct sites to produce a triple-layer material with open framework V/P/O inorganic layers, $[(C_2H_5)_2NH_2][(CH_3)_2NH_2][V_4O_4(OH)_2(C_6H_5PO_3)_4]$ (**1**).

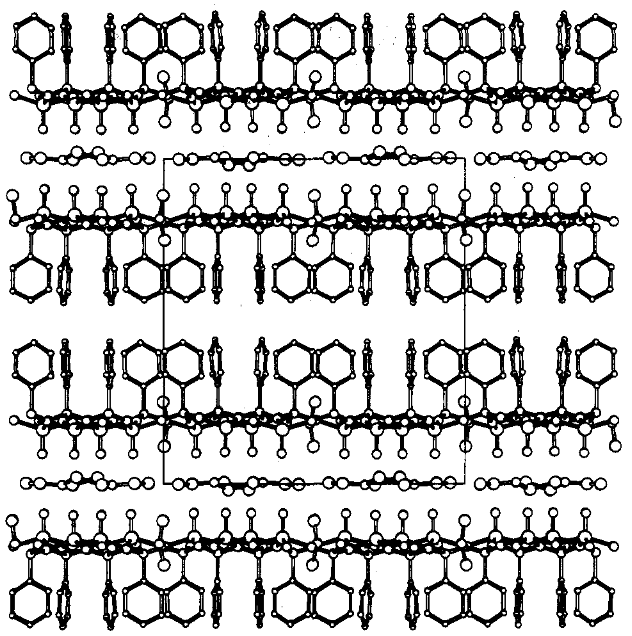

Figure 1. View of the *ac* plane of $[(C_2H_5)_2NH_2][(CH_3)_2NH_2][V_4O_4(OH)_2(C_6H_5PO_3)_4]$ (**1**), showing the layer of $(C_2H_5)_2NH_2^+$ cations intercalated between inorganic V/P/O layers, which are in turn separated by bilayers of phenyl groups. The positions of the $(CH_3)_2NH_2^+$ are also highlighted and shown to penetrate the V/P/O layers.

The hydrothermal reaction of $RbVO_3$, $C_6H_5PO_3H_2$, $(C_2H_5)_2NH_2Cl$, $(CH_3)_2NH_2Cl$, and H_2O at 160 °C for 4 days yields green plates of **1** in 20–25% yield.[22] The infrared spectrum of **1** exhibited three bands in the 1050-1200-cm^{-1} range associated with PO_3 group vibrations and a strong sharp band at 1016 cm^{-1} assigned to $\nu(V^{IV}{=}O)$. The compound is insoluble in all common solvents, although it may be digested over a 5-day period into a refluxing solution of $(C_2H_5)_4NOH$ in dimethylformamide. This results in a mixture of as yet unidentified $V/O/PhPO_3^{2-}$ species which may be related to the molecular clusters previously described.[19-21]

As shown in Figure 1, the structure of $[(C_2H_5)_2NH_2][(CH_3)_2NH_2][V_4O_4(OH)_2(C_6H_5PO_3)_4]$ (**1**) is dramatically different from that of $[VO(C_6H_5PO_3)(H_2O)]$, which consists of alternating inorganic layers and organic bilayers. The introduction of the

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(1) Alberti, G.; Costantino, U.; Allulli, S.; Tomassini, N. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113.

(2) (a) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Solid State Ionics* **1988**, *26*, 63. (b) Cao, G.; Lee, H.-J.; Lynch, V.; Mallouk, T. E. *Inorg. Chem.* **1988**, *27*, 2781.

(3) (a) Martin, K. J.; Squattrito, P. J.; Clearfield, A. *Inorg. Chim. Acta* **1989**, *155*, 7. (b) Zhang, Y.; Clearfield, A. *Inorg. Chem.* **1992**, *31*, 2821.

(4) Bujoli, B.; Palvadeau, P.; Rouxel, J. *Chem. Mater.* **1990**, *2*, 582.

(5) 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.

(6) Huan, G. H.; Jacobson, A. J.; Johnson, J. W.; Corcoran, E. W., Jr. *Chem. Mater.* **1990**, *2*, 2.

(7) Huan, G. H.; Johnson, J. W.; Jacobson, A. J.; Merola, J. S. *J. Solid State Chem.* **1990**, *89*, 220.

(8) Huan, G.; Jacobson, A. J.; Johnson, J. W.; Goshorn, D. P. *Chem. Mater.* **1992**, *4*, 661.

(9) Alberti, G.; Costantino, U.; Marmottini, F.; Vivani, R.; Zappelli, P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1357.

(10) Bhardwaj, C.; Hu, H.; Clearfield, A. *Inorg. Chem.* **1993**, *32*, 4294.

(11) Dines, M. B.; Cooksey, R. E.; Griffith, P. C. *Inorg. Chem.* **1983**, *22*, 567.

(12) Cao, G.; Mallouk, T. E. *Inorg. Chem.* **1991**, *30*, 1434.

(13) Rosenthal, G. L.; Caruso, J. *Inorg. Chem.* **1992**, *31*, 3104.

(14) Burwell, D. A.; Valentine, K. G.; Timmermans, J. H.; Thompson, M. E. *J. Am. Chem. Soc.* **1992**, *114*, 4144.

(15) Clearfield, A. *Chem. Rev.* **1988**, *88*, 125.

(16) Mallouk, T. E.; Lee, H. *J. Chem. Educ.* **1990**, *67*, 829.

(17) Haushalter, R. C.; Mundi, L. A. *Chem. Mater.* **1992**, *4*, 31.

(18) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* **1993**, *259*, 1558.

(19) Chang, Y.-D.; Salta, J.; Zubieta, J. *Angew. Chem.*, in press.

(20) Chen, Q.; Zubieta, J. Unpublished results.

(21) Salta, J.; Chang, Y.-D.; Chen, Q.; Zubieta, J. *Angew. Chem.*, in press.

(22) A mixture of $RbVO_3$, $C_6H_5PO_3H_2$, $(C_2H_5)_2NH_2Cl$, $(CH_3)_2NH_2Cl$, and H_2O in the mole ratio 4:6:4:4:300 was placed in a 23 mL capacity Teflon-lined autoclave and heated at 160 °C and autogenous pressure for 4 days. After cooling to room temperature, green plates of **1** were filtered from the nearly colorless mother liquor, washed with water, and air dried. Yield: 0.11 g of crystalline material (25% based V). Anal. Calcd for $C_{30}H_{42}N_2O_{18}P_4V_4$: C, 34.4; H, 4.02; N, 2.68. Found: C, 34.2; H, 4.12; N, 2.49. IR (KBr pellet, cm^{-1}): 1184 (m), 1143 (m), 1077 (broad, vs), 1016 (s), 814 (w), 745 (s), 722 (s), 692 (vs), 574 (s), 425 (s).

(23) Crystal data for $C_{30}H_{42}N_2O_{18}P_4V_4$ (**1**): monoclinic space group $P2_1/c$ with $a = 21.022(4)$ Å, $b = 19.034(3)$ Å, $c = 10.771(2)$ Å, $\beta = 99.63(2)°$, $V = 4249.1(11)$ Å^3, $Z = 4$, $D_{calc} = 1.635$ g cm^{-3}; structure solution and refinement based on 3067 reflections with $I_o \geq 3\sigma(I_o)$ (Mo K$_\alpha$ radiation, $\lambda = 0.710\,73$ Å) converged at $R = 0.0602$.

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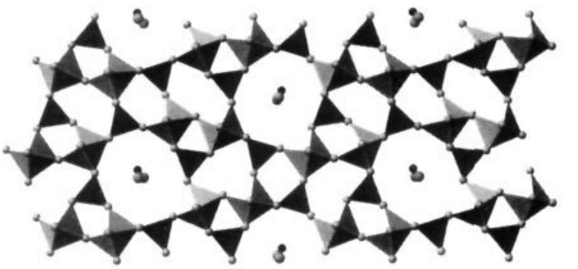

Figure 2. View of the *bc* plane of **1** illustratine the $\{V_2O_2(\mu\text{-OH})\}$ binuclear units and the rings constructed from corner-sharing of four vanadium square pyramids and four organophosphonate tetrahedra.

intercalating organic cations has disrupted the registry of layers such that the structure of **1** exhibits a trilayer repeat represented by a layer of $(C_2H_5)_2NH_2{}^+$ cations sandwiched between inorganic V/P/O layers which are in turn bounded by organic bilayers consisting of phenyl group from adjacent $V/O/C_6H_5PO_3$ slabs. The structure of $[VO(C_6H_5PO_3)(H_2O)]$ is constructed from layers of corner-sharing $\{VO_6\}$ octahedra and $\{CPO_3\}$ tetrahedra, with *phenyl groups extending from both sides of the metal oxide layers*. In contrast, the structure of **1** consists of corner-sharing $\{VO_5\}$ square pyramids and $\{CPO_3\}$ tetrahedra, with *phenyl groups directed exclusively to one face of the layer* while the $\{V{=}O\}$ groups are directed to the other. Since the $\{V{=}O\}$ groups of the adjacent layer are directed toward the vanadyl face of the neighboring layer, a highly hydrophilic region is produced which accommodates the layer of $(C_2H_5)_2NH_2{}^+$ cationic templates. Whereas the structure of $[VO(C_6H_5PO_3)(H_2O)]$ is defined by an interlayer repeat of 14.14 Å, the registry of layers in **1** is such as to produce two repeat distances: 8.89 Å between V/P/O layers sandwiching the $(C_2H_5)_2NH_2{}^+$ intercalators and 12.29 Å between V/P/O layers sandwiching phenyl group bilayers. The partitioning of the structure into polar and nonpolar domains is evident, and **1** appears to be amphiphilic with hydrophobic–hydrophilic interactions determining the layer packing.

The structural differences between $[VO(C_6H_5PO_3)(H_2O)]$ and **1** are further accentuated in the oxide layer, shown in Figure 2. The vanadium octahedra of $[VO(C_6H_5PO_3)(H_2O)]$ share axial oxygens, forming infinite $\{{-}V{=}O{-}V{=}O{-}\}$ chains with alternating short–long interactions. In **1**, however, discrete $\{V_2O_2(OH)\}^{3+}$ binuclear units are bridged through phosphonate tetrahedra to form the layer motif. The vanadium centers of each binuclear unit are bridged by a phosphonate group which directs the third oxygen donor to an adjacent binuclear unit. The coordination at each vanadium site of the binuclear unit is completed by bonding to two oxygen donors from two phosphonate groups, each of which in turn bridges to an adjacent binuclear unit. Thus, while the largest cavity in the V/P/O layer of $[VO(C_6H_5PO_3)(H_2O)]$ is constructed from the corner-sharing of four vanadium octahedra and two phosphonate tetrahedra, producing a 12-membered ring, the cavity size in **1** is expanded by corner-sharing of four vanadium square pyramids and four phosphonate tetrahedra, resulting in a 16–membered ring with a V–V diagonal distance of *ca.* 10.5 Å. The distortion of the V/P/O layer in **1** from that in $[VO(C_6H_5PO_3)(H_2O)]$ reflects the necessity of accommodating the $(CH_3)_2NH_2{}^+$ cation, which projects through the V/P/O inorganic layer. The structure of **1** demonstrates the dramatic topological flexibility of vanadium polyhedra and phosphonate tetrahedra in incorporating a variety of substrates. The structure of **1** is thus able to accommodate intercalation of organic cations both between layers and within layers, by suitable modification of the $[VO(C_6H_5PO_3)(H_2O)]$ parent structure.

Valence sum calculations[24] identify the vanadium sites as V(IV). This requires that the bridging oxygen be assigned as a hydroxo ligand, feature consistent with the $\{V{-}O(H){-}V\}$ bond distances of 1.96(1) Å (average), a value *ca.* 0.15 Å longer than a $\{V{-}O{-}V\}$ bond for a bridging oxo group.

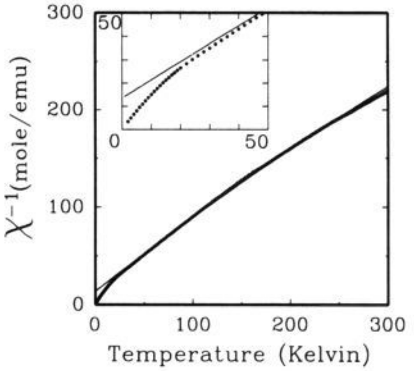

Figure 3. The magnetic susceptibility of **1** plotted as a function of temperature over the 1.7-300 K temperature region. The curve drawn through the data is the fit to the theoretical model as described in the text. The inset shows an expansion of the inverse magnetic susceptibility data at the lowest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

The temperature dependent magnetic susceptibility of **1** is shown in Figure 3. The high-temperature magnetic susceptibility data ($T > 20$ K) exhibits Curie–Weiss paramagnetism,

$$\chi = \frac{C}{T-\theta} + \text{TIP} = \frac{4Ng^2\mu_B{}^2S(S+1)}{3k(T-\theta)} + \text{TIP}$$

with $C = 1.246$ emu K/mol, $\theta = -17$ K, and TIP = 0.000 534 emu/mol. The electron structure of $(Et_2NH_2)(Me_2NH_2)[V_4O_4(OH)_2(C_6H_5PO_3)_4]$ corresponds to one unpaired electron per vanadium(IV) ion with spin $S = {}^1/_2$. This results in an average Curie–Weiss g value of 1.82 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, but there is no characteristic magnetic anomaly to allow a precise determination of the strength of the magnetic coupling.

The isolation and characterization of **1** demonstrate not only that organic templates intercalate into layered structures of the $V/O/RPO_3{}^{2-}$ system but also that both the registry of the layers and the detailed structure of inorganic V/P/O layers may be dramatically influenced. The layered structure of **1** together with the presence of coordinatively unsaturated V(IV) sites which may become accessible upon removal of the intercalated $Et_2NH_2{}^+$ cations suggests that the ultimate goal of preparing 2-D solids capable of selectively sorbing substrate molecules and selectively catalyzing reactions at the transition metal site has been partially realized. While considerable structural modification may be attained by exploiting template organization of the solid, one problem remains the removal of template without concomitant structural collapse. Although we have yet to measure the sorptive properties of **1**, absorption into layered solids with vacant coordination sites and exhibiting aromatic bilayers separating the inorganic domains has been observed in structurally related materials.[5] Investigations are in progress comparing the sorptive properties of the template-containing solids of type **1** to those of the prototype solids, $[VO(RPO_3)(H_2O)]$.

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Supplementary Material Available: Tables of atomic positional parameters and isotropic thermal parameters, anisotropic thermal parameters, bond lengths, bond angles, and calculated hydrogen atom positions for **1** (10 pages); observed and calculated structure factors (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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