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An Octahedral−Tetrahedral Vanadium Phosphate One-Dimensional Chain Incorporating 1-Aminoethane-2-ammonium Cations as Ligands

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The cooperative assembly of molecular precursors into one-, two-, or three-dimensional solids of designed structure, while of intense interest in the preparation of materials with applications to molecular electronics, optical systems, and heterogeneous catalysis,[1,2] remains a significant synthetic challenge. One approach to the preparation of solid-state materials which preserve in the product the inorganic and organic structural elements of the precursors adopts low-temperature hydrothermal techniques,[3,4] which favor the kinetic trapping of metastable materials, often of unprecedented structures. By combining hydrothermal synthesis with the introduction of organic templates or cations which serve to direct the organization of the phase, the structural chemistry of the system may be vastly expanded. The applications of these approaches to the synthesis of new phases of the V−P−O system demonstrate their value.

The intense interest in the chemistry of the vanadium oxide phosphate (V−P−O) compounds reflects the catalytic relevance of the system[5,6] and the structural diversity of the networks of connected vanadium and phosphorus polyhedra formed in these compounds.[7−12] Vanadium−oxo sites not only form tetrahedral, square-pyramidal, trigonal-bipyramidal, and octahedral coordination sites but may also link polyhedra through shared oxygen atoms to form larger aggregates which are in turn connected through phosphate tetrahedra into elaborate two-or three-dimensional structures. We have recently demonstrated that the introduction of organic substrates results in two-dimensional networks, such as $(H_2NC_4H_8NH_2)[(VO)_2(PO_4)_2]$ and $(H_2NC_4H_8NH_2)[(VO)_3(PO_4)_2(HPO_4)_2]\cdot H_2O$,[13] and three-dimensional frameworks, represented by $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7]\cdot 4H_2O$,[14] $(H_3NCH_2CH_2NH_3)_{5/2}[V(H_2O)_2(VO)_8(OH)_4(PO_4)_4(HPO_4)_4]\cdot 2H_2O$,[15] $(H_3NCH_2CH_2CH_2NH_3)K[(VO)_3(PO_4)_3]$,[16] and $[H_3NCH_2CH_2CH_2NH_3][(VO)_3$-

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$(OH)_2(H_2O)_2(PO_4)_2]$.[17] While charge-compensating and space-filling effects contribute to the structure-directing properties of the organic cation, the templating mechanism remains unclear, and the same template may produce radically different structures under marginally different reaction conditions. This observation is illustrated by the isolation in the hydrothermal reaction of V_2O_5, H_3PO_4, and ethylenediamine of the unique one-dimensional phase $[VO(PO_4)(H_2NCH_2CH_2NH_3)]$ (**1**), a material containing the 1-aminoethane-2-ammonium group acting as both nitrogen donor ligand and cation.

The hydrothermal reaction of KVO_3, $C_6H_5PO_3H_2$, H_3PO_4, $H_2NCH_2CH_2NH_2$, $(C_2H_5)_2NH_2Cl$, and H_2O in the mole ratio 1:1:2:3.3:1.7:100 at 160 °C under autogenous pressure for 4.5 days yielded blue-green needles of **1** in 80% yield.[18] While neither $C_6H_5PO_3H_2$ nor $(C_2H_5)_2NH_2^+$ appear in the product, both are essential for the isolation and crystallization of **1**. The requirement of organophosphonates RPO_3H_2 in the preparation of purely $V{-}O{-}PO_4^{3-}$ phases has been noted previously.[19] While the role of the organophosphonate remains enigmatic, it has been established that clusters of the $V(IV){-}O{-}RPO_3^{2-}$ class form readily under hydrothermal conditions,[20] suggesting that the organophosphonate serves to provide a repository of reduced vanadium in some as-yet uncharacterized anionic cluster. The dialkylammonium salt serves as a reducing agent, a common observation in the preparations of $V{-}O{-}PO_4^{3-}$ and $V{-}O{-}RPO_3^{2-}$ phases.[21] The infrared spectrum exhibited medium intensity bands in the 3000–3200 cm^{-1} range associated with $\nu(N{-}H)$ of the 1-aminoethane-2-ammonium group and a series of three strong absorbances in the 980–1200 cm^{-1} characteristic of $\nu(P{-}O)$ stretching frequencies of the PO_4^{3-} group. A feature at 943 cm^{-1} is assigned to $\nu(V{=}O)$.

As shown in Figure 1, the structure of **1** consists of one-dimensional ribbons constructed from V(IV) octahedra and PO_4^{3-} tetrahedra.[22] The coordination about the vanadium centers is defined by a terminal oxo group, four phosphate oxygen donors from three PO_4^{3-} groups, and a monodentate $(H_2NCH_2CH_2NH_3)^+$ ligand. Each vanadium octahedron shares corners in a cis disposition with two adjacent vanadium octahedra to produce a zig–zag polyhedral chain, which when viewed down the direction of propagation, the crystallographic *a* axis, reveals a ribbon two octahedra in width. A phosphate group bridges three vanadium centers through three of the four oxygen donors. While two of the coordinated phosphate oxygen bond to a single vanadium site, the third bridges two vanadium centers, resulting in an unusual edge-sharing interaction between the phosphate tetrahedron and one vanadium octahedron. The fourth oxygen of each phosphate group is pendant and unprotonated, the short P–O distance of 1.498(6) Å and the valence sums[23] confirming the multiply bonded {P=O} description of this moiety. While pendant P–O units in the V–P–O system are most commonly protonated,[12,24] the unprotonated form has also been observed in the V/O/organophosphonate system.[25] As shown in Figure 2a, the uncoordinated {P=O} groups in **1** project from both faces of the one-dimensional ribbon, so as to form strong hydrogen-bonded contacts to the $-NH_3^+$ moieties projecting from an adjacent ribbon into the interchain void space ($N_2 \cdots O4$, 2.87 Å). The result of these interactions is the alignment of the $\{VO(PO_4)(H_2NCH_2CH_2NH_3)\}_n$ strands into an incipient layer motif, shown in Figure 2b. Intrastrand hydrogen bonding of the amine terminus of the ligand to the oxygen atoms of the V–P–O network is also significant (N1··O1, 2.72 Å).

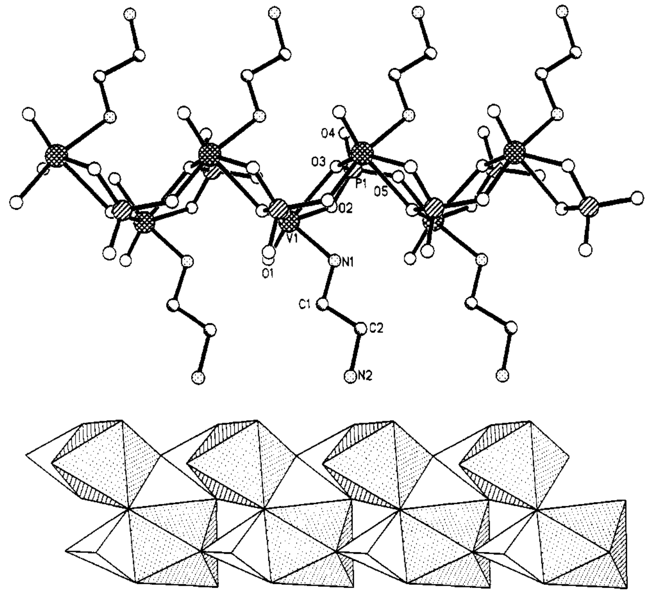

Figure 1. (a, top) View of the chain structure of $[VO(PO_4)(H_2NCH_2CH_2NH_3)]$ (**1**) along the crystallographic *c* axis, showing the atomic-labeling scheme. (b, bottom) Polyhedral representation of the structure of **1**, showing the zig-zag chain of corner-sharing $\{VO_5N\}$ octahedra.

The most curious feature of the structure is the presence of the organic template as both nitrogen-donor ligand and charge-compensating cation. One end of the 1-aminoethane-2-ammonium cation coordinates to a V(IV) site while the other terminus is protonated; the ethylene backbones of the ligand cations extend outward from either face of the inorganic ribbon and penetrate the interchain region. Adjacent ribbons orient so as to maximize hydrogen bonding interactions between $-NH_3^+$ groups and pendant {P=O} moieties on neighboring strands, producing an incipient layer structure. The

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(18) A mixture of KVO_3, $C_6H_5PO_3H_2$, H_3PO_4, ethylenediamine, $(C_2H_5)_2NH_2Cl$, and H_2O in the mole ratio 1:1:2:3.3:1.7:100 was placed in a 23-mL Teflon-lined Parr acid digestion bomb (40% fill volume) and heated at 160 °C for 4.5 days. After cooling to room temperature over a 5 h period, blue-green needles were filtered from the orange-red mother liquor, washed with water, and air dried. Yield: 80% based on vanadium. Anal. Calcd for $C_2H_9N_2O_5PV$: C, 10.8; H, 4.06; N, 12.6. Found: C, 10.6; H, 4.12; N, 12.5. IR (K Br pellet, cm^{-1}) 1640(m); 1593(vs); 1533(s); 1483(w); 1353(m); 1226(w); 1163(w); 1122(vs); 1087(w); 1056(w); 1015(s); 981(s); 963(s); 943(s); 920(sh); 660(s); 640(m); 628(w); 582(m); 538(vs); 480(m).

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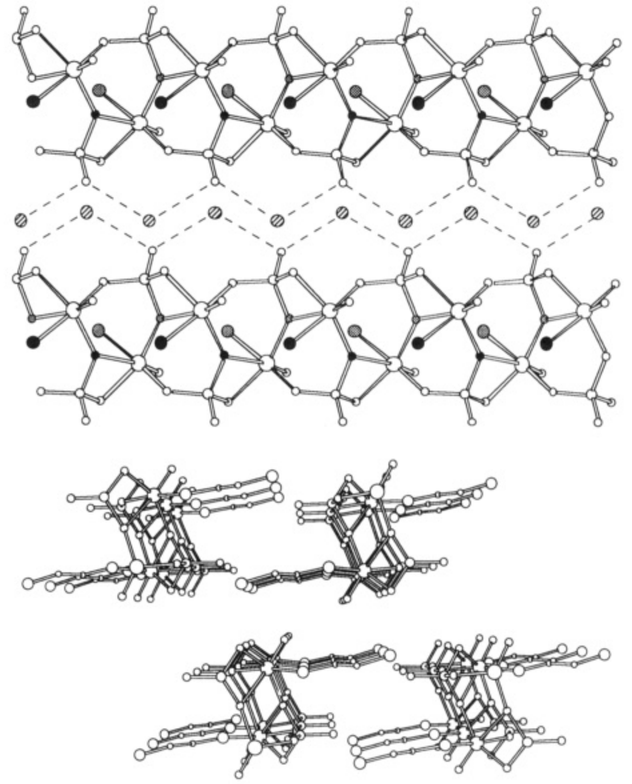

Figure 2. (a, top) Schematic representation of the hydrogen-bonding between $\{VO(PO_4)(NH_2CH_2CH_2NH_3)\}_n$ strands and within each individual strand. Striped atoms are $-NH_3^+$ nitrogen sites hydrogen-bonded to the pendant {P=O} groups of an adjacent strand. Larger black and gray spheres represent N atoms above and below the plane of the projection, respectively, while smaller black and gray spheres represent oxygen atoms above and below the plane, respectively. The intrastrand H bonding occurs between these amine nitrogen centers ($-NH_2$) and phosphate oxygen sites. (b, bottom) View of the structure of **1** along the crystallographic *a* axis, illustrating the incipient layer structure.

vanadyl groups of the ribbons project into this "interlamellar" region.

The temperature dependent magnetic susceptibility of **1** exhibits Curie–Weiss paramagnetism:

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

where $C = 0.370$ emu K/mol, $\theta = 1.8$ K, and TIP = 0.000 06 emu/mol. The electron structure of **1** corresponds to V(IV), a $3d^1$ electron structure with one unpaired election per metal ion and spin $S = {}^1/_2$, to give a *g* value of 1.98 for the compound. The positive Weiss constant indicates that there is ferromagnetic exchange. At lower temperatures, the magnetic moment begins to increase, but there is no characteristic magnetic anomaly to allow a precise determination of the nature and strength of the magnetic coupling. Since the material is a linear chain, the magnetic data were fit to the $S = {}^1/_2$ Heisenberg linear chain model developed by Bonner and Fisher,[26] to give $g = 1.95$, $J/k = 3.2$ K, TIP = 0.000 11 emu/mol, values consistent with a ferromagnetic linear chain. The inverse magnetic susceptibility of **1** plotted on function of temperature is shown in Figure 3.

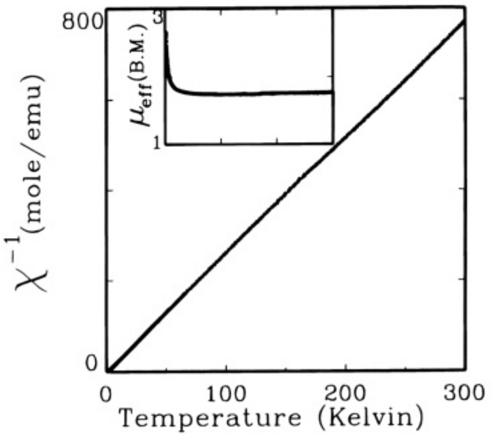

Figure 3. Inverse magnetic susceptibility of **1** plotted as a function of temperature over the 2–300 K region. The line drawn through the data is the fit to the Curie–Weiss model as described in the text. The inset shows the effective magnetic moment plotted as a function of temperature over the 2–300 K region. The line drawn through the points is the best fit to the Bonner–Fisher model to the data.

The isolation of **1** demonstrates that while organoamines are generally incorporated into V/O/phosphate phases as isolated cations, the ligating potential of the group may also be expressed under appropriate conditions, an observation which may allow a significant expansion of the structural chemistry of such phases by utilizing covalent organic structural elements in the construction of the extended phase. Such covalent linkage of organic groups to the V–P–O network may influence the dimensionality of the material.[27] While V–P–O phases incorporating organodiammonium cations are generally two- or three-dimensional materials,[13–17] compound **1** assumes a ribbonlike one-dimensional structure. Furthermore, under appropriate conditions, such organodiamine ligands should incorporate into V/O/phosphate phases as neutral bidentate ligands, allowing the introduction of covalent tethers of varying lengths, geometries, and steric requirements as elements for the design of solid materials. In this regard it is noteworthy that 2,2′-bipyridine incorporates into the phase $[V_9O_{21}(bipy)_4]^{28}$ as a neutral chelating ligand and that the phase exhibits a one-dimensional chain structure.

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Supplementary Material Available: Tables of structure determination summary, atomic positional parameters and isotropic temperature factors, anisotropic thermal parameters, bond lengths, bond angles, and calculated hydrogen atom positions for **1** and a complete discussion of the experimental conditions employed in the magnetism study (7 pages). Ordering information is given on any current masthead page.

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