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An Organically Templated Layered Vanadium Oxide: Hydrothermal Synthesis, Single-Crystal Structure, and Magnetic Properties of $(H_3N(CH_2)_3NH_3)[V_4O_{10}]$

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The utilization of the hydrothermal technique in combination with cationic organic templates has been extensively used in the synthesis of zeolites and molecular sieves.[1−3] The extension of the hydrothermal techniques and the use of organic templates to the exploratory synthesis of reduced molybdenum and vanadium phosphates and vanadium phosphonates have allowed us to isolate a series of novel organically templated vanadium phosphates and vanadium phosphonates with molecular, 1-D, 2-D, and 3-D open-framework structures.[4−9] Several studies[10] have been recently reported on the hydrothermal synthesis of surfactants/transition metal oxides composite materials since the synthesis of the silica-based mesoporous molecular sieves MCM-41 was described.[11] The hydrothermal synthesis of vanadium oxides using aromatic amines as templates have been described in two brief communications.[12] The vanadium oxide chains or layers contain, in both cases, vanadium coordination complexes with the aromatic amines. Lamellar vanadium oxides containing organic molecules or polymers in the interlayer regions have been prepared via intercalation reactions with $V_2O_5{\cdot}nH_2O$ xerogel.[13] Here we report the hydrothermal synthesis and single-crystal structure of $(H_3N(CH_2)_3NH_3)[V_4O_{10}]$ (**1**), a layered mixed-valence vanadium oxide with organic ammonium cations between the layers.

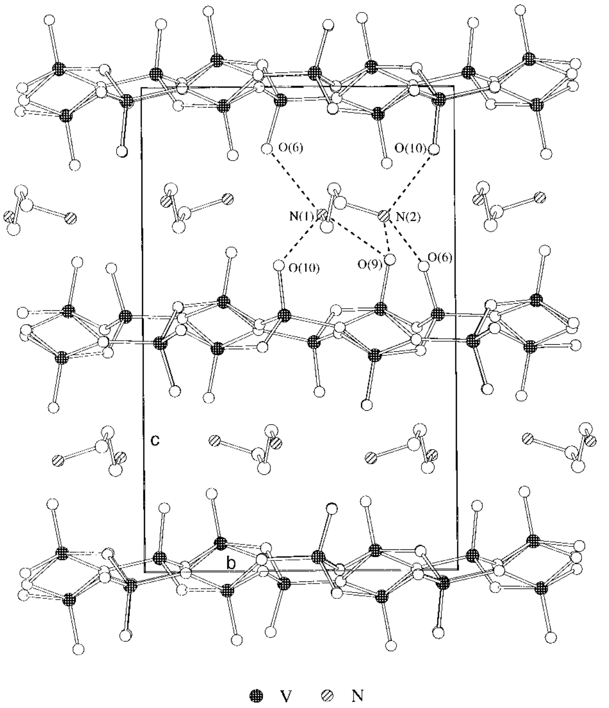

Figure 1. View of the structure of **1** down the *a* axis showing the layers of vanadium oxide and the propanediammonium dications in the interlayer space. Dashed lines indicate hydrogen bonds.

Black platelike crystals of 1 were prepared from the hydrothermal reaction of $V_2O_5{:}H_2NCH_2CH_2CH_2NH_2{:}HCl{:}H_2O$ in a molar ratio of 1:1.5:12.3:341 at 170 °C for 66 h.[14] The solid was filtered, washed with water, and air-dried (yield 57% based on vanadium). Comparison of the measured powder X-ray pattern of 1 to the pattern calculated from the atomic coordinates of the single-crystal study indicates a monophasic material. A single-crystal X-ray diffraction study[15] of **1** revealed novel vanadium oxide layers with propanediammonium dications occupying the interlamellar space as depicted in Figure 1. A view perpendicular to the vanadium oxide layer is shown in Figure 2. The layers are constructed from equal number of $\{VO_4\}$ tetrahedra and $\{VO_5\}$ square pyramids. While the $\{VO_4\}$ tetrahedra

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(14) A mixture of V_2O_5 (0.296 g), HCl (1.0 M, 2.0 mL), 1,3-diaminopropane (0.2 mL), and H_2O (10 mL) in a molar ratio of 1:12.3:1.5:341 heated in a 23-mL acid digestion bomb at 170 °C for 66 h gave 0.20 g black plates of 1.

(15) Crystal data for (1), $V_4O_{10}N_2C_3H_{12}$, FW = 439.90, monoclinic, space group $P2_1/n$, $a = 7.971(2)$Å, $b = 9.977(2)$Å, $c = 15.651(3)$Å, $\beta = 100.47(2)°$, $V = 1224.0(4)$ Å^3, and $Z = 4$. Data were collected on an AFC7R diffractometer with Mo Ka radiation ($\lambda = 0.7106$ Å) and a 18 kW rotating anode generator at room temperature. Structure solution and refinement by full-matrix least-squares using *teXsan* program package based on 1977 reflections with $I \geq 3\sigma(I)$ and 172 variables gave $R(Rw) = 0.040$ (0.043). All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located from difference Fourier maps and included in the refinement with fixed positional and thermal parameters.

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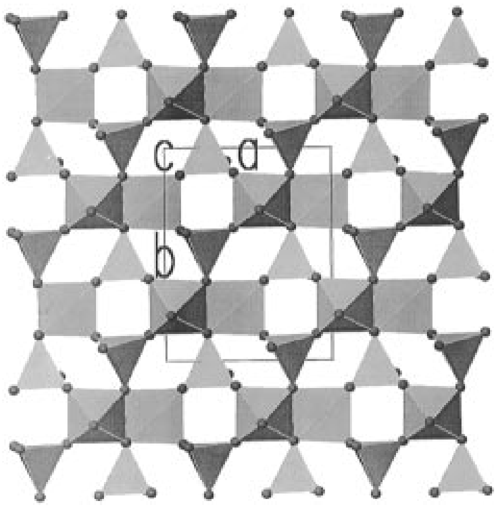

Figure 2. View perpendicular to one of the vanadium oxide layers in **1**.

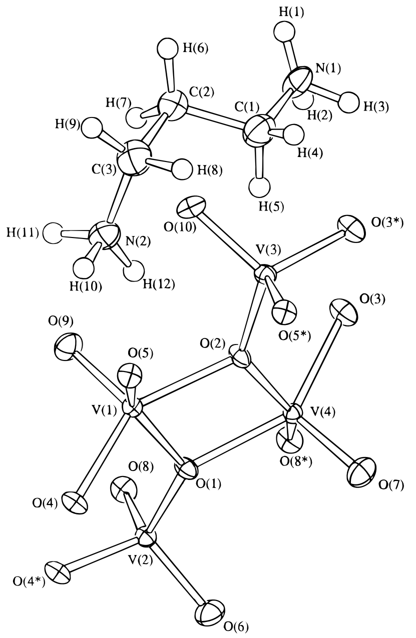

Figure 3. ORTEP drawing of the asymmetric unit in the structure of **1** showing the coordination environments around the vanadium atoms. Thermal ellipsoids are at the 50% level. The atoms with asterisks represent symmetry-related atoms.

are isolated from each other, the $\{VO_5\}$ square pyramids exist in pairs sharing one edge. Within a pair of square pyramids, the two apical oxygen atoms are oriented toward opposite sides of the plane of the layer. Each pair of the pyramids is linked to six $\{VO_4\}$ tetrahedra via corner-sharing, forming two dimensional layers. There are four independent V sites in the structure. While the atoms V(1) and V(4) have a distorted square-pyramidal configuration, the atoms V(2) and V(3) are in a fairly regular tetrahedral coordination environment (Figure 3). The V−O bond distances of $\{V(2)O_4\}$ tetrahedron are in the range 1.648(4)−1.826(4) Å, and bond angles in the range 106.0(2)−113.2(2)°. The $\{V(3)O_4\}$ tetrahedron has bond distances in the range 1.643(5)−1.834(4) Å, and bond angles in the range 107.6(2)−111.3(2)°. The $\{V(1)O_5\}$ square pyramid has the shortest bond distance of 1.612(4) Å formed with the vanadyl oxygen O(9), and the rest of the four V−O bond distances in the range of 1.912 (4)−1.967 (4) Å. The {V(4)O5}square pyramid has its vanadyl oxygen O(7) at a distance of 1.603(4) Å , and the other four oxygen atoms at distances in the range 1.924(4)−1.974 (4) Å. While the square pyramidal vanadium has an oxidation state of +4, the tetrahedral vanadium is indicative of an oxidation state of +5. This assignment of oxidation state is consistent with the overall charge balance of the compound and confirmed by the valence sum calculations[16] which gave a value of 4.1 for V(1) and V(4), and 4.8 for V(2) and V(3). There is an extensive hydrogen bonding network formed among the $-NH_3^+$ groups of the propanediammonium cations and the terminal oxygen atoms (O(6), O(7), O(9), O(10)) from the adjacent oxide layers above and below with N−O distances in the range 2.813(7)−2.995(7) Å as indicated by the dashed lines in Figure 1. This extensive hydrogen-bonding motif causes the organic components in **1** to be released only at elevated temperatures. Thermogravimetric analysis (TGA) of **1** at a heating rate of 10 °C/min under N_2 showed no weight loss until ca. 300 °C, where the release of the organic component commences.

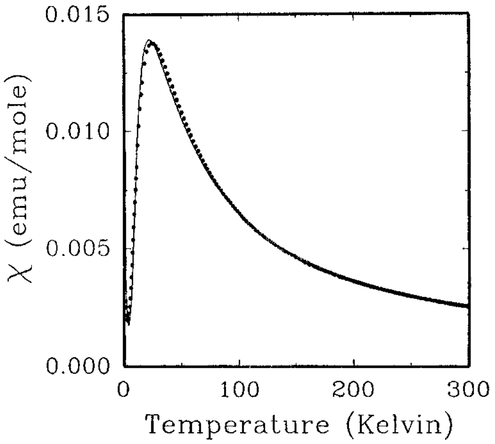

Figure 4. Magnetic susceptibility of **1** plotted as a function of temperature over the 2−300 K temperature region. The solid curve drawn through the data is the fit to the binuclear model as described in the text.

Shown in Figure 4 is the magnetic susceptibility data which were recorded on a 54 mg polycrystalline sample of 1 over the temperature range 2−300 K at a magnetic field of 1000 G using a Quantum Design MPMS-5S SQUID susceptometer. Measurement and calibration techniques have been reported elsewhere.[17] The high-temperature magnetic susceptibility data ($T > 75$ K) exhibits Curie−Weiss paramagnetism with $C = 0.973$ emu/mol, $\theta = -48$ K, and TIP (temperature independent paramagnetism) = 0.0003 emu/mol. The electronic structure of 1 corresponds to two paramagnetic V(IV) ($S = {}^1/_2$) units per formula unit. There is a maximum in the low-temperature magnetic susceptibility at 25 K. This indicates a moderate amount of antiferromagnetic coupling in 1. Although compound 1 contains four vanadium ions, two of them are V(IV) ions, the other two diamagnetic V(V) ions. Therefore, the magnetic exchange in the analog may be analyzed as for a binuclear compound with two V(IV) units ($S_1 = S_2 = {}^1/_2$). The effect of the spin Hamiltonian, $H = -2JS_1S_2$, on the behavior of a pair of magnetically interacting electrons can be expressed as follows:

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$$\chi = (Ng^2\mu_B{}^2/kT)\{e^{2J/kT}/(1 + 3e^{2J/kT})\} \quad (1)$$

The correction for secondary magnetic exchange interactions using the molecular exchange field approximation is also required to fit the data. The equation that describes the effect of a molecular exchange field on the magnetic susceptibility is

$$\chi = \chi'/\{1 - (zJ'/Ng^2\mu_B{}^2)\chi'\} + \text{TIP} \quad (2)$$

where χ' is the magnetic susceptibility of the material in the absence of the exchange field, and χ is the molecular exchange field influenced magnetic susceptibility that is actually measured. The magnetic susceptibility data of **1** were analyzed with these equations, and the results of a least-squares fit of eq 1 corrected with eq 2 yields the parameters $g = 2.043$, $J/k = -18$ K, $zJ'/k = -12$ K, and TIP = 0.0021 emu/mol. In addition, the data were corrected for the presence of a 1.5% paramagnetic (monomeric) impurity. The result of this fit is illustrated in Figure 4.

There has been a great deal of interest in vanadium bronzes $M_xV_2O_5$, especially lithium vanadium bronzes $Li_xV_2O_5$, because of their interesting electronic properties and potential applications in high-energy batteries.[18] Molecular and polymer vanadium bronzes have also been the subject of many studies.[13] These molecular or polymer vanadium bronzes are a class of materials containing lamellar vanadium oxides with organic molecules or organic polymers in the interlayer regions. These materials are prepared by intercalation reactions with V_2O_5 xerogels, and are usually poorly crystalline solids. The oxide layers in the structures of 1 are similar to those in the structure of CsV_2O_5[19] where the Cs^+ cations lie between the vanadium oxide layers. A layered compound with the composition of $N(CH_3)_4$-$[V_4O_{10}]$ has been recently reported.[20] Unfortunately, neither the experimental nor the structural data are given for this compound. Oxide **1** discussed here represents a new class of organically based vanadium bronzes which are different from those obtained from intercalation reactions. In similar ways, we have isolated several new layered vanadium oxides containing different organic cations including α- and β-$(H_3N(CH_2)_2NH_3)[V_4O_{10}]$, $(HN(C_2H_4)_3NH)[V_6O_{14}]\cdot H_2O$, $(H_3CNH(C_2H_4)_2NHCH_3)[V_6O_{14}]$, and α- and β-$(H_2N(C_2H_4)_2NH_2)[V_4O_{10}]$.[21] Thermal removal of the organic templates from these compounds may lead to new vanadium oxide materials. The characterization of the thermal decomposition products is in progress. The study of their crystal structures, magnetic properties, and structural transformation upon removal of the templates will be presented in future publications.

Note added in proof: The title compound was recently reported (Riou, D.; Férey, G. *J. Solid State Chem.* **1995**, *120*, 137) as well as two additional layered vanadium oxides with interlayer organic cations (Riou, D.; Férey, G. *Inorg. Chem.* **1995**, *34*, 6520). The two compounds reported in the latter paper, will also be described by us (*Inorg. Chem.*, in press).

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Supporting Information Available: Tables listing crystallographic parameters, atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters for the non-hydrogen atoms, and bond lengths and angles (15 pages); observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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