$[HN(C_2H_4)_3NH][V_6O_{14}]\cdot H_2O$: A mixed-valence layered vanadium oxide with interlamellar organic cations

Yiping Zhang,[a,b] **Robert C. Haushalter***[a] **and Abraham Clearfield***[b]

[a] *NEC Research Institute, 4 Independence Way, Princeton, NJ 08540, USA*
[b] *Department of Chemistry, Texas A&M University, College Station, TX 77843, USA*

The new mixed-valence vanadium oxide $[(HN(C_2H_4)_3NH)][V_6O_{14}]\cdot H_2O$ contains layers of composition $[(V^{5+})_2(V^{4+})_4O_{14}]^{2-}$ with protonated $[HN(C_2H_4)_3NH]^{2+}$ dications and water molecules in the interlayer region.

It is well known that vanadium pentoxide xerogels, $V_2O_5{\cdot}nH_2O$, possessing a porous layered structure, are capable of intercalating a variety of neutral and charged guest species such as alkali-metal ions,[1] alkylamines,[2] alcohols,[3] pyridine,[4] benzidine,[5] *etc*. The resulting intercalation compounds usually retain the lamellar structure with the guest species occupying the interlayer regions. The intercalation mechanism, however, can involve cation exchange, acid–base, or redox chemistry depending on the nature of the guest species. Partial reduction of V^{5+} to V^{4+} has been observed upon intercalation with alkylamines, ammonia,[4] pyridine, and benzidine. In the cases of aniline[6] and thiophene,[7] the reduction of the vanadium oxide host and the simultaneous oxidative polymerization of the guest molecules in the interlayer regions have been observed. These intercalation compounds with reduced vanadium sites constitute an interesting class of organic–inorganic composite materials that can be viewed as organic molecular or polymer vanadium bronzes by analogy to alkali-metal bronzes.[8] However, the structural information about these intercalation compounds is very limited due to the lack of good quality single crystals. It has been recently demonstrated that hydrothermal techniques are well suited for the preparation and crystal growth of novel two- and three-dimensional reduced vanadium phosphates containing various organic or inorganic cations.[9] In this communication we report the application of these techniques to the V–O system which has resulted in the hydrothermal synthesis and single-crystal structure of $[HN(C_2H_4)_3NH][V_6O_{14}]\cdot H_2O$ **1**, a mixed-valence vanadium oxide with interlamellar organic cations.

Compound **1** was prepared as a single-phase material by a hydrothermal reaction. A mixture of V_2O_5 (0.225 g), 1,4-diazabicyclo[2.2.2]octane (DABCO, 0.201 g) and H_2O (10 ml) in the mole ratio of 1.0 : 1.44 : 448 was sealed in a 23 ml poly(tetrafluoroethylene) lined acid-digestion bomb which was kept at 170 °C for 45 h. Thin black plates and a black crystalline solid were isolated (0.127 g, yield 47% based on V) after filtration, washing with water, and air-drying. The X-ray powder pattern of both the black plates and the crystalline solid matched the calculated pattern generated from the single-crystal structure data. The single-crystal X-ray analysis[†] of the black thin plates revealed **1** as a layered structure containing vanadium oxide layers running parallel to the (100) plane, with protonated DABCO dications and water molecules in the interlayer region, as shown in Fig. 1(*a*). The DABCO dications are separated from each other by a distance of 6.66 Å along the *b* axis and 7.57 Å along the *c* axis. The water molecules fill the empty space between the DABCO dications. The DABCO dications between the layers are oriented with their N atoms pointing toward the oxide layers, forming hydrogen bonds with the adjacent oxide layers above and below. The N atoms are in short contact with the bridging oxygen atom O(6) at an N···O distance of 2.855(7) Å, and two terminal oxygens O(4) and O(7) at N···O distances of 3.109(6) and 3.056(7) Å, respectively. The water molecule O(8), on the other hand, is not involved in any strong hydrogen-bonding interactions with the oxide layers. The shortest O(8)···O distance is 3.17(1) Å. The vanadium oxide layers [Fig. 1(*b*)] contain infinite zigzag chains of edge-sharing distorted $V^{4+}O_5$ square pyramids running parallel to the *b* axis, with their terminal vanadyl groups oriented in pairs toward opposite sides of the layers. These infinite chains are connected together by $V^{5+}O_4$ tetrahedra along the direction of the *c* axis giving a layer composition of $[(V^{5+})_2(V^{4+})_4O_{14}]^{2-}$. The assignment of the oxidation states for the vanadium atoms is consistent with their coordination geometries and is confirmed by valence sum calculations[10] which give values of 4.2 for V(1), 4.1 for V(2), and 4.8 for V(3). The $V^{4+}O_5$ square pyramids have bond distances in the range 1.586(4)–2.010(4) Å. The distorted $V^{5+}O_4$ tetrahedron has bond distances in the range 1.590(4)–1.806(5) Å, and bond angles in the range 108.3(2)–111.8(2)°. Surprisingly, in spite of the fact that oxide **1** contains two thirds of the vanadium atoms in the 4+ oxidation state, an EPR (electron paramagnetic resonance) signal was not

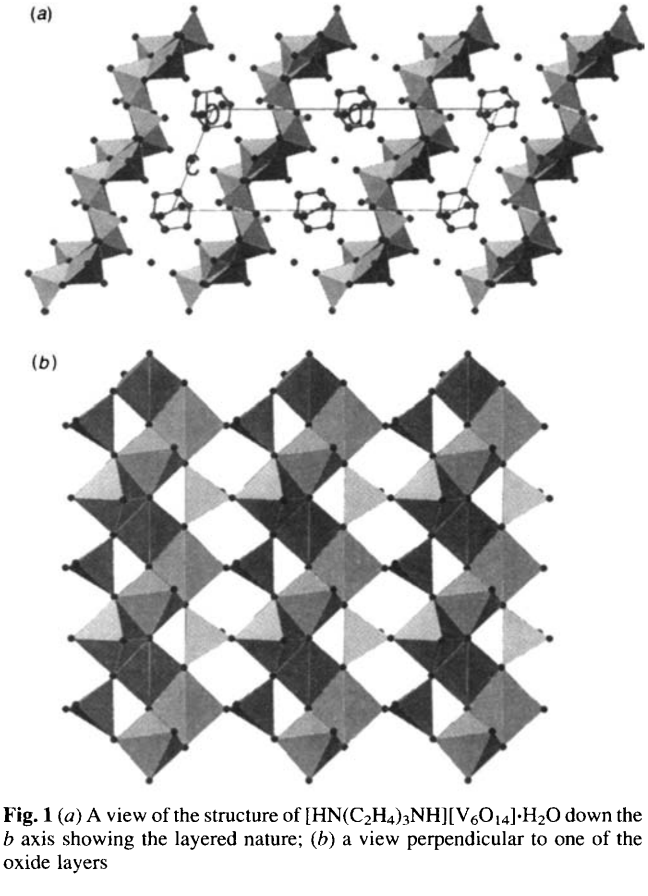

Fig. 1 (*a*) A view of the structure of $[HN(C_2H_4)_3NH][V_6O_{14}]\cdot H_2O$ down the *b* axis showing the layered nature; (*b*) a view perpendicular to one of the oxide layers

observed for oxide **1**. Preliminary magnetization measurements in the temperature range 5–300 K show that oxide **1** has a suppressed magnetic moment of 0.9 μ_B at 300 K compared to *ca.* 5.5 μ_B which would be expected for four unpaired electrons. The magnetic behaviour is non Curie–Weiss type in the temperature range of 5–300 K and the magnetic susceptibility χ increases with increasing temperature in the range of $150 < T < 300$ K. Since the unpaired spin in each V^{4+} (d^1) resides in an $d_{x^2-y^2}$ orbital, which is oriented toward the centre of the shared edge, the suppressed moment (relative to the spin-only values expected from V^{4+} d^1) reflects the partial pairing of the spins from the edge-sharing vanadium square pyramids. The magnetic properties of oxide **1** above room temperature are under investigation. Several other layered vanadium oxides prepared in our laboratories also have magnetic moments far below the expected spin-only values.

Thermogravimetric analysis (TGA) of **1**, carried out under N_2 with a heating rate of 10 °C min^{-1} showed a first mass loss of 3% at a temperature of 260 °C, and a second mass loss of *ca.* 19% in the temperature range 400–450 °C. These two mass losses correspond to the release of the water molecules (calculated value of 2.7%) and the DABCO molecules (calculated value 16.9%), respectively. Oxide **1** continued to lose mass gradually up to 800 °C, the highest temperature measured. The characterization of the final thermal decomposition product is in progress.

In summary, a novel layered organic-based vanadium oxide, $[HN(C_2H_4)_3NH][V_6O_{14}]\cdot H_2O$, has been hydrothermally synthesized and its single-crystal structure determined, which represents the first structurally characterized example of an organic-based layered vanadium oxide.

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Footnote

[†] *X-ray structure data for* **1**. Monoclinic, space group *C*2, $a = 19.302(4)$, $b = 6.661(1)$, $c = 7.574(1)$ Å, $\beta = 111.29(1)°$, $U = 907.4(3)$ Å^3, $Z = 4$. A black plate crystal with dimensions of 0.32 × 0.20 × 0.02 mm was mounted on a glass fibre. Data were collected on a Rigaku AFC7R four-circle diffractometer at 20 °C in the range $5 < 2\theta < 60°$ using the ω–2θ scan technique. No decay of the crystal was observed throughout the data collection. A total of 1483 reflections was collected of which 1093 reflections with $I_o > 3\sigma(I_o)$ were used. An empirical absorption correction based on Ψ scans was applied. The structure was solved by direct methods (MITHRILL) and refined using the TEXSAN crystallographic software package of Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps and were included in the refinement with fixed positional and thermal parameters. Structure solution and refinement based on 1093 reflections with $I_o > 3\sigma(I_o)$ and 131 parameters gave $R(R_w) = 0.027$ (0.027). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/30.

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