

Hydrothermal Synthesis and Crystal Structure of a Novel Layered Vanadate with 1,4-Diazabicyclo[2.2.2]octane as the Structure-Directing Agent: $(C_6H_{14}N_2)V_6O_{14} \cdot H_2O$

Linda F. Nazar,* Bryan E. Koene, and James F. Britten†

Department of Chemistry, University of Waterloo
Guelph-Waterloo Centre for Graduate
Work in Chemistry
Waterloo, Ontario, Canada N2L 3G1

Received September 13, 1995

Revised Manuscript Received October 23, 1995

Hydrothermal synthesis at relatively low temperatures (120–250 °C) and pressure using organic cations as templating agents has proved to be an extremely prolific method for the preparation of novel 2D and 3D “open-framework” main-group oxides and phosphates.¹ Recently, the technique has also been extended to the synthesis of an impressive range of transition-metal phosphates.² The number of transition-metal oxides prepared by this route, however, is extremely small. The use of inorganic cations as templates has resulted in open-framework structures in a few cases for W³ and Mn oxides.⁴ The only reported example of the use of an organic cation as a template, however, is layered $(NMe_4)Mo_{4-6}O_{12}$,⁵ whose structure was deduced from Rietveld refinement of powder XRD data. To our knowledge, similar chemistry has not been reported for vanadates, perhaps owing to the propensity of this system to form oxyvanadium clusters. In some cases, the use of an organic molecule as an intended template in hydrothermal syntheses of vanadium oxides has resulted in the formation of an infinite-lattice structure, but exclusion of the organic component from the lattice.⁶ This has led some to speculate that the organic component, though necessary, may sometimes act simply as a reducing agent.^{6b}

Vanadium oxides are of particular interest as candidates for active cathode materials in reversible lithium ion batteries or electrochromic devices. This results from their favorable electrochemical characteristics, including mixed ionic and electronic conduction properties.^{7,8} Traditional high-temperature solid-state synthesis has provided a wealth of binary and ternary

phases,^{9,10} most of which possess a large capacity for reversible lithium insertion but have somewhat restricted pathways for lithium diffusion due to their fairly dense structure. There is considerable desire for new synthetic approaches¹¹ and new structural types, especially those with more “open-framework” structures that have the potential for less-hindered Li ion mobility.

Here, we report the first single-crystal structure of an organic cation-templated infinite-lattice transition-metal oxide resulting from hydrothermal synthesis. It possesses a unique structure composed of a new arrangement of edge-shared VO_5 square pyramids that are corner-shared with VO_4 tetrahedra to form highly puckered layers, between which the DABCO cations are sandwiched. We have also examined electrochemical Li insertion into this host material. The results show that although Li insertion is hindered in the DABCO-filled host, after removal of the DABCO the lattice can reversibly intercalate up to at least 8 Li/mol of V_6O_{14} .

The title material was synthesized under hydrothermal conditions using 1,4-diazabicyclo[2.2.2]octane (DABCO, or $C_6H_{12}N_2$) as the templating agent and $NaVO_3$ as the source of vanadium. Typically, the reaction mixture of molar composition 2:1 DABCO:V (0.06 M in V) was stirred to homogeneity, and the pH of the mixture was adjusted to about 2 by the dropwise addition of 6 M nitric acid. The slurry was then sealed in a Teflon-lined stainless steel autoclave and heated to 180 °C for 3 days under autogenous pressure. The resulting monophasic product, consisting of small black prismatic single crystals with a metallic luster was filtered, washed with water, and dried in air at ambient temperature. The yield was at least 85% based on V.

Suitable plate-shaped crystals were obtained for X-ray analysis. The monoclinic unit cell (Figure 1) shows the protonated DABCO cations located between the $V_6O_{14}^{2-}$ layers. The inorganic framework sheets are composed of edge-sharing square pyramids (SP) that form pairs of alternating “up” and “down” orientations joined to form zigzag ribbons (Figure 2). This unique characteristic of the polyhedral arrangement has not been reported for any other single-layer vanadium oxide, and it has even been suggested that this arrangement of two edge-shared vanadium SPs oriented in the same direction is not possible.¹² We have also observed this structural feature in one other organically templated vanadium oxide to date, although the framework structure is not the same as the title compound.¹³ The repulsion of the adjacent square-pyramidal vanadium cations (in both cases) is partially compensated by a substantial tilt of the polyhedra. In this case it yields layers that are highly puckered along the [010] direction. The bases of the square pyramids are not perfectly flat but have a substantial dihedral angle com-

† Department of Chemistry, McMaster University, Hamilton, Ontario.

(1) Davis, M. E. *Acc. Chem. Res.* **1993**, *26*, 111.

(2) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, Z. *Chem. Mater.* **1993**, *5*, 1595. Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, Z.; Connor, C. J. *Science* **1993**, *259*, 1595. Riou, D.; Férey, G. *J. Solid State Chem.* **1994**, *111*, 422. Cavellec, M.; Riou, D.; Férey, G. *J. Solid State Chem.* **1994**, *112*, 441. Loiseau, T.; Férey, G. *J. Solid State Chem.* **1994**, *112*, 416. Li, Y. J.; Whittingham, M. S. *Solid State Ionics* **1993**, *63*, 391.

(3) Guo, J.; Reis, K. P.; Whittingham, M. S. *Solid State Ionics* **1992**, *53*, 305.

(4) Golden, G. C.; Chen, C. C.; Dixon, J. B. *Science* **1986**, *231*, 717. Shen, Y.-F.; Zenger, R. P.; Suib, S. L.; McCurdy, L.; Potter, D. I.; O'Young, C. L. *Science* **1993**, *260*, 511.

(5) Guo, J.; Whittingham, M. S.; Zavalij, P. *Chem. Mater.* **1994**, *6*, 357.

(6) (a) Whittingham, M. S.; Guo, J.; Chen, R.; Chirayil, T.; Janauer, G.; Zavalij, P. *Solid State Ionics* **1995**, *75*, 257. (b) Leroux, F.; Mar, A.; Guyomard, D.; Piffard, Y. C. *R. Acad. Sci. Paris* **1995**, *320* (IIb), 147.

(7) Walk, C. R. In *Lithium Batteries*; Gabana, J. P., Ed.; Academic Press: New York, 1983. Garcia-Alvarado, F.; Tarascon, J. M.; Wilkens, B. *J. Electrochem. Soc.* **1992**, *139*, 3206.

(8) Li, W.; Dahn, J. R.; Wainwright, D. S. *Science* **1994**, *264*, 1115.

(9) Galy, J. *J. Solid State Chem.* **1992**, *100*, 229.

(10) Cocciantelli, J. M.; Menetrier, M.; Delmas, C.; Doumerc, J. P.; Puchard, M.; Hagenmuller, P. *Solid State Ionics* **1992**, *50*, 99. Garcia-Alvarado, F.; Tarascon, J. M. *Solid State Ionics* **1994**, *73*, 247.

(11) Maingot, S.; Baddour, R.; Pereira-Ramos, J. P.; Baffier, N.; Willmann, P. *J. Electrochem. Soc.* **1993**, *140*, L158. Pereira-Ramos, J. P.; Bach, S.; Farcy, J.; Baffier, N. *Proc. MRS Symp.* **1995**, *369*, 191.

(12) Enjalbert, R.; Galy, J. *Acta Crystallogr.* **1986**, *C42*, 1467.

(13) Nazar, L. F.; Taylor, N.; Koene, B. E., submitted.

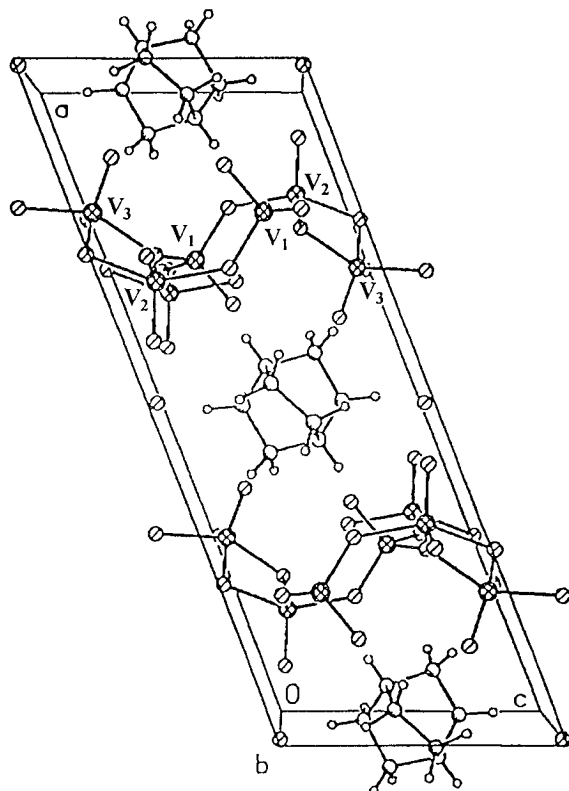


Figure 1. Unit cell of $(\text{C}_6\text{H}_{14}\text{N}_2)\text{V}_6\text{O}_{14}\cdot\text{H}_2\text{O}$, showing inequivalent vanadium sites and DABCO interlayer cations.

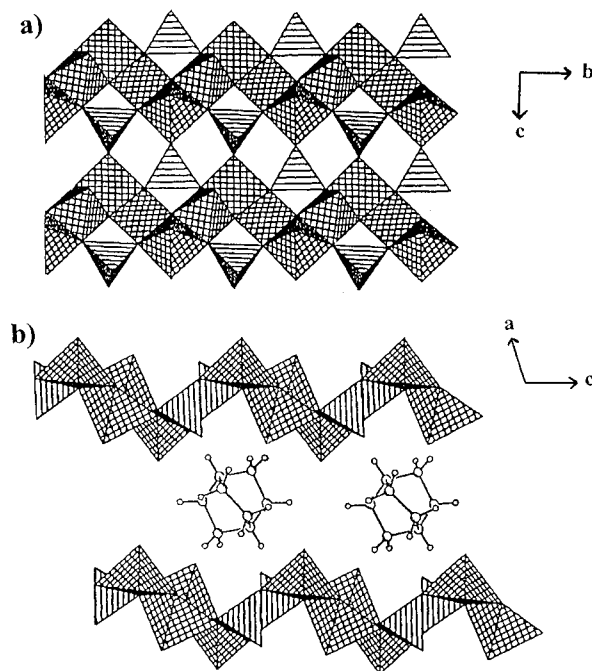


Figure 2. (a) Portion of the crystal structure of $(\text{C}_6\text{H}_{14}\text{N}_2)\text{V}_6\text{O}_{14}\cdot\text{H}_2\text{O}$ (along [100]) that depicts four square-pyramidal VO_5 units linked to form a single layer: Note the pairs of edge-sharing square pyramids that have the same relative orientation. (b) the structure shown along [010].

pared to other known vanadates.¹⁴ The structure is furthermore unique and unusual, since double-layered structures with six coordinate vanadium are generally formed for cations with either a large diameter

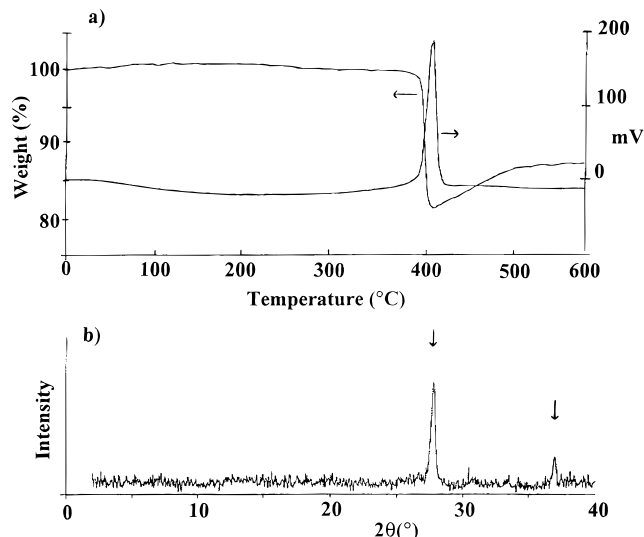


Figure 3. (a) TGA-DTA curves for $(\text{C}_6\text{H}_{14}\text{N}_2)\text{V}_6\text{O}_{14}\cdot(\text{dehydrated})$ obtained in flowing air. (b) powder XRD pattern of $(\text{C}_6\text{H}_{14}\text{N}_2)\text{V}_6\text{O}_{14}\cdot\text{H}_2\text{O}$ calcined in air at 400 °C.

$(\text{NH}_4^+, \text{K}^+)$ or high charge (Ca^{2+}).⁹ Single layers of mixed four- and five-coordinate vanadium have not been previously reported for vanadium oxide bronzes and appear to be the result of DABCO cations in the synthesis. Galy theorized that the formation of the double layers was a result of distortions at the edge of the lattice occurring during the intercalation of large or highly charged ions into every other layer of V_2O_5 .⁹ The templating route that we employ results in a different host lattice since the framework is constructed in the presence of the organic cations.

The fact that $(\text{DABCO})\text{V}_6\text{O}_{14}$ contains one four-coordinate and two five-coordinate V sites in the unit cell implies that the electron density is localized in this structure, giving rise to isolated V^{4+} and V^{5+} sites, respectively, and an average oxidation state of $\text{V}^{4.33}$. This is the first example of a mixed coordination geometry in such a material. Many other vanadium oxide bronzes, such as $\gamma\text{-LiV}_2\text{O}_5$ ¹⁴ or $\alpha'\text{-Na}_x\text{V}_2\text{O}_5$,¹⁵ also appear to contain discrete V^{5+} and V^{4+} ions, although both sites maintain square-pyramidal geometry in these cases. Not surprisingly, the V–O bond lengths in the 5-coordinate sites are comparable to those found for V_2O_5 and common vanadium oxide bronzes.^{9,12} The shortest bond, an average of 1.583 Å, corresponds to the axial $\text{V}=\text{O}$ or vanadyl bond in either the square-pyramidal (SP) ($\text{V}_2\text{-O}_2$ or $\text{V}_3\text{-O}_3$) or tetrahedral site ($\text{V}_1\text{-O}_1$). The remaining bond lengths in the tetrahedral site are similar, on average 1.76 Å. The two SP sites both possess, on average, equatorial V–O bond lengths of 1.945 Å, although the SP site that is corner-shared with three tetrahedral sites is more highly distorted, with bond lengths ranging from 1.859 to 2.010 Å.

The electrochemical properties of this material as a host for reversible lithium insertion were examined using a cell comprised of a lithium counter electrode, 1.0 M LiClO_4 /propylene carbonate as the electrolyte, and glass-fiber mesh as the separator. The working electrode consisted of approximately 2 mg of $(\text{DABCO})\text{V}_6\text{O}_{14}$ mixed with 90 wt % carbon black and 2% EPDM binder. This mixture was pressed onto a 1 cm² fine stainless

(14) Galy, J.; Darriet, J.; Hagenmuller, P. *Rev. Chim. Miner.* **1971**, 8, 509.

(15) Carpy, A.; Galy, J. *Acta. Crystallogr.* **1975**, B31, 1481.

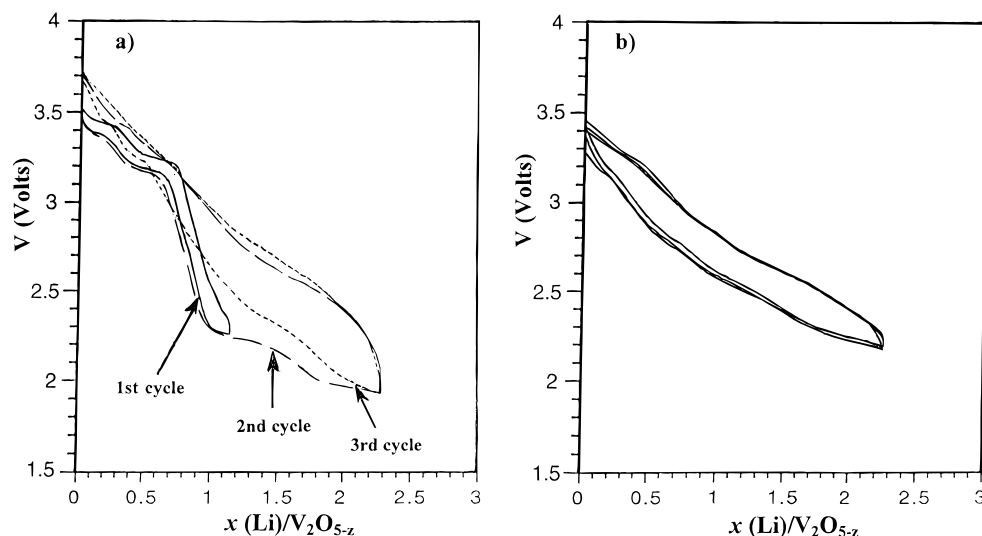


Figure 4. Discharge-charge curves for lithium insertion in the calcined vanadium oxide ($(\text{C}_6\text{H}_{14}\text{N}_2)\text{V}_6\text{O}_{14}$) at 0.1 mA/cm^2 oxide for (a) cycles 1 \rightarrow 3 and (b) cycles 7 \rightarrow 10.

steel mesh, and the cell assembly was then compressed in a battery casing using a screw-thread fitting. The cell was cycled under galvanostatic conditions at current densities ranging from 0.05 to 0.2 mA/cm^2 between preset voltage (or charge) limits using a MACPILE system. The results for the pristine $(\text{DABCO})\text{V}_6\text{O}_{14}$ showed that only 0.9 mol of Li could be intercalated per $(\text{DABCO})\text{V}_6\text{O}_{14}$ (equivalent to 0.3 mol of $\text{Li}/\text{V}_2\text{O}_{5.67}$) when the reduction potential was limited to 1.9 V . We ascribe this low lithium capacity to the presence of the DABCO dication between the layers, which appears to hinder the Li insertion process by a combination of steric and electrostatic effects. The DABCO could be readily removed from the lattice, however, by calcination. TGA/DTA carried out in flowing air (Figure 3) showed that the DABCO is combusted from the lattice at 405°C , corresponding to a sharply defined weight loss of 16% . This is followed by a gradual weight gain of approximately 3% between 405 and 500°C , consistent with oxidation of the $\text{V}_6\text{O}_{14}^{2-}$ framework from $\text{V}^{4.33+}$ to $\text{V}^{5.0+}$. The loss of DABCO from the material was therefore monitored in the thermal balance during isothermal treatment at 400°C , and care was taken not to attain the temperature at which complete oxidation occurred. The black appearance of the resultant material suggested that this was successful; however, the XRD pattern showed that the product was very poorly crystalline, as only two diffraction peaks at high angle ($d = 3.20 \text{ \AA}$, $d = 2.43 \text{ \AA}$) were evident. This is suggestive of remanent short-range order in the material, typical of many vanadium oxides, including VO_2 .

Li insertion in the material after removal of the DABCO was more facile and showed interesting behavior (Figure 4a). The moles of Li inserted are expressed per mole of V_2O_{5-z} ($0.33 > z > 0$) to facilitate comparison. During the first discharge under a constant current of $100 \mu\text{A/cm}^2$, despite the relatively amorphous nature of the material, several well-defined plateaus are evident which are recovered on the subsequent charge cycle when the limiting voltage is 2.25 V . The overall curve and features are unlike those of "semicrystalline" V_2O_5 xerogels¹⁶ but bear remarkable similarity to that observed for lithium insertion in polycrystalline V_2O_5 .¹⁷

In the latter, each plateau corresponds to formation of an ordered $\text{Li}_x\text{V}_2\text{O}_5$ phase (a series of bronzes, $\text{Li}_x\text{V}_2\text{O}_5$ ($0 < x < 1.0$) can also be formed by treatment of V_2O_5 with LiI in acetonitrile¹⁸). We conclude that similar sites are available for insertion in the heat-treated $\text{V}_6\text{O}_{14}^{2-}$ (" V_2O_{5-z} ") although no long-range order is evident by XRD. Upon deeper discharge to 1.9 V (cycle 2), the plateaus are lost on reoxidation, and the following cycle (3) shows a featureless curve suggesting a different disordered phase has been formed by this process. Lithium insertion in this phase is completely reversible, as illustrated by cycling curves 7 \rightarrow 10 (Figure 4b). This behavior has also been noted for deep discharge of crystalline V_2O_5 for which the disordered phase $\omega\text{-Li}_3\text{V}_2\text{O}_5$ is formed at $x = 3$, although this results in a material with a different XRD pattern (reflections with d spacings at 2.04 and 1.45 \AA).¹⁹ The latter process also corresponds to a transition from crystalline to amorphous on deep discharge; here, the reduction process corresponds to a transition between two different amorphous phases with short-range order.

Work is currently in progress to remove and/or replace the interlayer cation by ion exchange and to examine methods of "pinning" the layers together to form tunnel structures.

Acknowledgment. We thank the NSERC (Canada) for financial support through a research grant to L.F.N.

Supporting Information Available: X-ray crystallographic data (8 pages). Ordering information is given on any current masthead page.

CM9504302

(16) Baddour, R.; Pereira-Ramos, J. P.; Messina, R.; Perichon, J. *J. Electroanal. Chem.* **1990**, *277*, 359.

(17) Murphy, D. W.; Christian, P. A. *Science* **1979**, *205*, 651. Crouch-Baker, S.; Huang, C. K.; Huggins, R. A. *Proc. Electrochem. Soc.* **1988**, *88*, 44. West, K.; Zachau-Christiansen, B.; Jacobsen, T. *J. Power Sources* **1993**, *43/44*, 127.

(18) Murphy, D. W.; Christian, P. A.; DiSalvo, F. J.; Waszczak, J. V. *Inorg. Chem.* **1979**, *18*, 2800.

(19) Delmas, C.; Br  thes, S.; Menetrier, M. *J. Power Sources*, **1991**, *34*, 113.