Nickel Vanadate Nanotubes: Synthesis and Crystal Structure of $[Ni(C_8H_{22}N_4)](VO_3)_2{\cdot}3H_2O$

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The assembly of molecular building blocks into network structures is of interest as a route to microporous compounds with intracrystalline reactivity and sorption properties. Efforts have been made to design solid structures with specific porosity by a rational choice of combinations of molecular building blocks, for example, by coordination of metal cations with suitable multidentate organic ligands.[1−10] These organic−inorganic materials have various intracrystalline functional groups and pore sizes, and several show significant thermal stability with respect to removal of the organic guest species.

As part of a more general study of the combination of coordination polymers with metavanadate chains as a route to stable porous structures,[11,12] we have synthesized and characterized an unusual nickel vanadate with a tubular structure. The reaction of VO_3^- with $Ni[(C_8H_{22}N_4)(H_2O)_2]^{2+}$ in aqueous solution results in the formation of the neutral framework $[Ni(C_8H_{22}N_4)](VO_3)_2$ with tubular pores that have free diameters that vary from ∼3 to ∼5.4 Å. As synthesized, water molecules occupy the channels and can be removed and reabsorbed without destruction of the framework. The framework is stable to ∼200 °C without water molecules in the channels.

$Ni[(C_8H_{22}N_4)(H_2O)_2]Cl_2{\cdot}3H_2O$ was first synthesized by adding a solution of $NiCl_2{\cdot}6H_2O$ (2.377 g, 10 mmol, Aldrich) in H_2O (10 mL) to a solution of *N,N′*-bis(3-aminopropyl)ethylenediamine (1.854 g, 10 mmol) in H_2O (5 mL). Transparent purple crystals were isolated on standing at room temperature for 2 days.

The single-crystal structure determination[13] of $Ni[(C_8H_{22}N_4)(H_2O)_2]Cl_2{\cdot}3H_2O$ shows the presence of discrete octahedral $Ni[(C_8H_{22}N_4)(H_2O)_2]^{2+}$ cations, Cl^- anions, and lattice water molecules. The $Ni[(C_8H_{22}N_4)(H_2O)_2]^{2+}$ octahedron contains two water molecules coordinated to the nickel atom in a trans configuration. Four other nitrogen atoms from *N,N′*-bis(3-aminopropyl)ethylenediamine complete the octahedron.

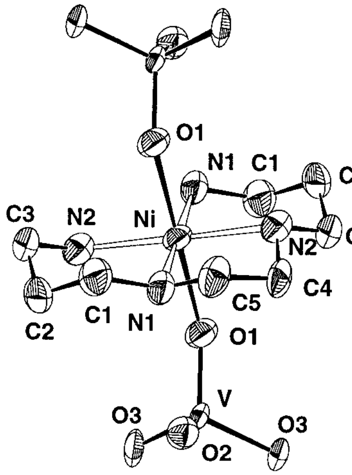

Figure 1. Local geometry of VO_4 and $Ni(C_8H_{22}N_4)O_2$ units. The C(4) and C(5) atoms are disordered over two positions with 50% probability (only one position is shown for each). The thermal ellipsoids are shown at 30% probability. Selected bond distances (Å): V−O(1) 1.641(4), V−O(2) 1.637(4), V−O(3) 1.796(4), 1.800(4), Ni−O(1) 2.096(4), Ni−N(1) 2.091(5), Ni−N(2) 2.093(5).

An immediate precipitate of $[Ni(C_8H_{22}N_4)](VO_3)_2{\cdot}3H_2O$ is formed on mixing aqueous solutions of NH_4VO_3 (0.117 g, 1.0 mmol, Aldrich) in 20 mL of water and $Ni[(C_8H_{22}N_4)(H_2O)_2]Cl_2{\cdot}3H_2O$ (0.197 g, 0.5 mmol) in 20 mL of water at room temperature. Subsequent slow interdiffusion of the two solutions gave rod-shaped yellow crystals of $[Ni(C_8H_{22}N_4)](VO_3)_2{\cdot}3H_2O$ suitable for single-crystal X-ray diffraction. The compound is stable in air, and its composition by elemental analysis and infrared spectrum are given in ref 14.

The structure of $[Ni(C_8H_{22}N_4)](VO_3)_2{\cdot}3H_2O$ as determined by single-crystal X-ray diffraction[15] is composed of one crystallographically distinct VO_4 tetrahedron and one $Ni(C_8H_{22}N_4)O_2$ octahedron (Figure 1). In the $Ni(C_8H_{22}N_4)O_2$ octahedron, the C(4) and C(5) atoms are disordered over two positions (50% probability) about an inversion center. The VO_4 tetrahedra share corners to complete VO_3 chains, O(3)−V−O(3)−V, that extend

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(13) $Ni[(C_8H_{22}N_4)(H_2O)_2]Cl_2{\cdot}3H_2O$: purple polyhedral crystal, $T = 293$ K, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.643(9)$ Å, $b = 8.019(9)$ Å, $c = 15.65(2)$ Å, $\alpha = 95.30(2)°$, $\beta = 95.011(8)°$, $\gamma = 97.752(9)°$, $V = 941.4(17)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.390$ g/cm^3, $\mu = 1.334$ mm^{-1}, $5° \leq 2\theta$ (Mo Kα) $\leq 47°$, R(int) = 0.0463, GOF = 1.181, $R_w(F^2) = 0.0941$ (all data), and $R(F) = 0.0386$ [based on $F_o^2 > 2\sigma(F_o^2)$]. Diffractometer: Siemens SMART 1 K CCD (Mo Kα radiation, graphite monochromator). Structure refinement: *SHELXTL* (Sheldrick, G. M., Version 5.03, Siemens Analytical X-ray Instruments, Madison, WI, 1995). Absorption correction: *SADABS* (Sheldrick, G. M., University of Göttingen, 1995).

(14) Elemental analysis: C (obsd 19.30%, calcd 19.80%), H (obsd 5.93%, calcd 5.82%), N (obsd 11.36%, calcd 11.55%), Ni (obsd 11.43%, calcd 12.11%), V (obsd 21.00%, calcd 21.01%). The infrared spectrum (KBr pellet method) was recorded on a Galaxy FTIR 5000 series spectrometer: $\bar{\nu}$ = 3318m, 3254m, 3198m, 2930m, 2870m, 1634w, 1597w, 1460w, 1436w, 1400w, 1285w, 1150m, 1065m, 1032w, 922s, 862m, 814s, 648s.

(15) $[Ni(C_8H_{22}N_4)](VO_3)_2{\cdot}3H_2O$: yellow polyhedral crystal, $T = 293$ K, rhombohedral, space group $R\bar{3}$ (No. 148), $a = 14.4133$ (6) Å, $\alpha = 116.236(1)°$, $V = 1469.75(11)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.644$ g/cm^3, $\mu = 1.929$ mm^{-1}, $3° \leq 2\theta$ (Mo Kα) $\leq 47°$; R(int) = 0.0251, GOF = 1.248, $R_w(F^2) = 0.1441$ (all data), and $R(F) = 0.046$ [$F_o^2 > 2\sigma(F_o^2)$].

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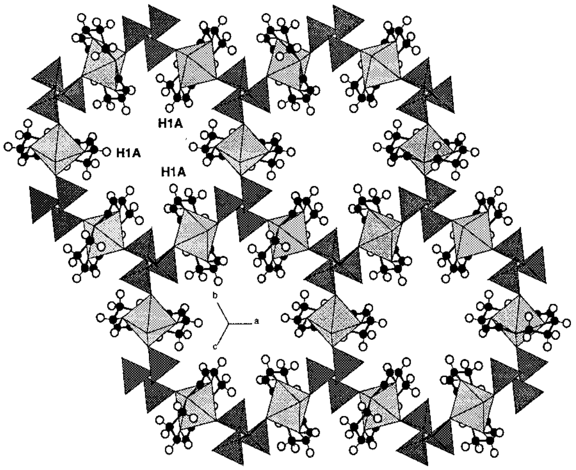

Figure 2. View in the [111] direction showing the channels. The VO_4 tetrahedra and $Ni(C_8H_{22}N_4)O_2$ octahedra are shown dark and light shaded and C and H atoms as filled and open circles, respectively. The H atoms labeled H1A define the narrowest point of the channels.

along the 3-fold screw axis. The O(1) oxygen atom of the VO_4 tetrahedron is coordinated to $Ni(C_8H_{22}N_4)O_2$, and the other oxygen atom, O(2), is terminal. Each $Ni(C_8H_{22}N_4)O_2$ octahedron connects two VO_3 chains by sharing oxygen atoms (Figure 1) to build up a neutral $[Ni(C_8H_{22}N_4)](VO_3)_2$ framework. The framework has 12-ring channels in the [111] direction counting the number of VO_3 chains and $Ni(C_8H_{22}N_4)O_2$ cations (Figure 2). The distances between neighboring *N*,*N*′-bis(3-aminopropyl)ethylenediamine ligands coordinated to Ni atoms along the [111] direction are 3.505 Å (C(3)···C(3)) and 3.610 Å (C(3)···C(4)). The bond valence sum values calculated are 5.14 and 2.19, in agreement with the expected values of 5.00 and 2.00 for V(V) and Ni(II), respectively.[16] In the channel, water molecules partially occupy seven distinct sites and are highly disordered.

Due to the arrangement of the *N*,*N*′-bis(3-aminopropyl)ethylenediamine ligands, the channels have variable free diameter. The narrowest dimension is defined by the three hydrogen atoms (H1A) that are shown in Figure 2. These hydrogen atoms that are related by the 3_1 screw axis form an equilateral triangle with a H−H distance of 7.71 Å that is at an angle to the [111] direction. Assuming 1 Å for the van der Waals radius of the H atom, the minimum free diameter of the channel is 2.94 Å. Three oxygen atoms that are bonded only to vanadium atoms define the largest free diameter along the channel, 5.6 Å.

Thermogravimetric analysis (TGA) shows that all of the water molecules in the channels are removed on heating from room temperature to ~100 °C. The X-ray structure refinement results gives a composition of $[Ni(C_8H_{22}N_4)](VO_3)_2{\cdot}xH_2O$ ($x = \sim 3.4$), which is in good agreement with TGA results (obsd weight loss, 10.8%, calcd weight loss, 11.1%) for the composition $[Ni(C_8H_{22}N_4)](VO_3)_2{\cdot}3H_2O$. No weight loss is observed between ~100 and ~200 °C. The structure collapses on loss of *N*,*N*′-bis(3-aminopropyl)ethylenediamine above ~200 °C. Between ~200 and ~500 °C the compound decomposes to form a glassy residue of nickel and vanadium oxides (weight loss, calcd 36.13%, obsd 36.05%).

When the sample is heated at a pressure of $\sim 10^{-2}$ Torr at ~100 °C, the porous structure is retained on removal of the water molecules from the channels. This dehydrated sample spontaneously reabsorbs water near room temperature and ambient pressure. TGA measurements confirmed the full readsorption of water molecules at room temperature though some hysteresis is observed. The structural integrity of the sample on removal of water was established by high-temperature X-ray diffraction. Little change in the relative intensities of the diffraction peaks is observed on heating, and the initial powder pattern is recovered on cooling. At 50 °C, a dehydrated sample gave lattice parameters (hexagonal setting) $a = 24.152$ Å, $c = 8.045$ Å compared with values of $a = 24.478$ Å, $c = 8.498$ Å. The dehydration produces a large reduction in the unit cell volume (342 Å^2) from 4410 Å^2 at ambient temperature to 4064 Å^2 at 50 °C; apparently the framework is very flexible. The change in unit cell dimensions is 4 times greater along the hexagonal *c* direction than along *a*. This anisotropic contraction reduces the minimum free diameter of the channels and is likely responsible for the hysteresis observed in the water absorption data.

Finally, we note that other vanadates with tubelike structures have been reported. For example, the high-temperature phase NaV_3O_{10} contains isolated tubes based on square pyramidal vanadium oxygen coordination and containing sodium cations.[17] Similarly, in the vanadium organophosphonate $(H_3O)[(V_3O_4)(H_2O)(C_6H_5PO_3)_3]{\cdot}xH_2O$, prepared hydrothermally at 180 °C, VO_5 pyramids and phenylphosphonate groups define tubes containing hydronium cations and water molecules.[18] The direct reaction of vanadate with complex cations in solution reported here, however, may be a more generally useful approach to the synthesis of tubular frameworks with larger pores.

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Supporting Information Available: A view of a part of one channel perpendicular to the [111] direction emphasizing the VO_3 chains (Figure S1) and TGA data showing the weight changes (%) as a function of temperature for water desorption and readsorption (Figure S2). Crystallographic data for $[Ni(C_8H_{22}N_4)](VO_3)_2{\cdot}3H_2O$ and $Ni[(C_8H_{22}N_4)(H_2O)_2]Cl_2{\cdot}3H_2O$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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