Inorg. Chem. **2002**, *41*, 5638–5640

Inorganic Chemistry
Communication

Novel Oxovanadium Phosphate Tubule Incorporating 2,2-Bipyridine Ligands: Hydrothermal Synthesis and Crystal Structure of $[(V^{IV}O)_3(\mu_5\text{-}PO_4)_2(2,2'\text{-bpy})(\mu\text{-}OH_2)]\cdot 1/3H_2O$

Wenbin Yang and Canzhong Lu*

The State Key Laboratory of Structural Chemistry,
Fujian Institute of Research on the Structure of Matter,
The Chinese Academy of Sciences, Fuzhou, Fujian 350002, P.R. China

Received June 12, 2002

The novel tubular framework of $[(V^{IV}O)_3(\mu_4\text{-}PO_4)_2(2,2'\text{-bpy})(\mu\text{-}OH_2)]\cdot 1/3H_2O$, which was synthesized from hydrothermal reaction, possesses some attractive structural features: (i) $O{=}V^{IV}O_4(OH_2)$ octahedra and PO_4 tetrahedra linked together by corner-sharing and face-sharing into a cylinder-shaped channel including 6 water molecules per cell unit, and (ii) (VO)(2,2′-bpy) groups regularly arranged around the tube, so that the 2,2-bpy ligands constitute an organic shell around an aqueous polar channel.

The widespread contemporary interest in metal (particularly transition metal) phosphates has been dominated by their diverse compositions, various structural aesthetics, and potentially useful catalytic, electrical, optical, and magnetic properties.[1] Recently, hydrothermal or solvothermal synthetic methods using organic amines as templates have been extensively devoted to the exploration of new open frameworks with elements other than Al, Si, and P, resulting in many new classes, such as gallophosphates[2] and transition metal phosphates, as reviewed by Prof. Férey et al.[1] In these materials, the amines are usually introduced as compensating charges and/or space filler;[3] on the other hand, they may act as a ligand directly coordinated to the metal centers within the framework rather than as a countercation. As an example of the latter, a microporous gallophosphate, $[Ga_2(DETA)(PO_4)_2]\cdot 2H_2O$, has been reported,[4] in which the diethylenetriamine (DETA) binds in a tridentate fashion to half of the Ga centers within the framework. One may expect that such open framework metal phosphates incorporating organic ligands exhibit novel potential shape-selective and catalytic activities. However, only a few examples are known.[5−8] On the basis of these findings, we attempted using 2,2′-bpy to synthesize new metal phosphates and have produced a novel oxovanadium phosphate tubule, $[(V^{IV}O)_3(\mu_4\text{-}PO_4)_2(2,2'\text{-bpy})(\mu\text{-}OH_2)]\cdot 1/3H_2O$ (**1**).

Complex **1** was originally synthesized from the hydrothermal reaction of V_2O_5, $VOSO_4$, 2,2′-bpy, H_3PO_4, and H_2O in a molar ratio of 0.75:1.5:2.6:4.5:1000 at 195 °C for 3 days and isolated as sapphire-colored hexangular columns (~40% yield based on V) by hand from light green crystals, which proved to be $[(V^{IV}O_2)_2(HPO_4)(2,2'\text{-bpy})_2]\cdot H_2O$[9] by X-ray structural analysis. Monophasic crystals of **1** in high yield (90−95% based on V) were obtained in the presence of excessive 2,2′-bpy, or by addition of a certain amount of reducing reagent $NH_2OH\cdot HCl$ into the reaction system.[10] However, when using $VOSO_4$ as the single vanadium source, various reactions with different stoichiometry, temperatures, and reaction times only produced shallow blue amorphous powder of **1**. The coloration of the crystals indicated that all vanadium atoms in **1** are tetravalent with valence sums of 3.894−4.034.[11] The assignment of oxidation states for vanadium atoms is consistent with their coordination geom-

---

* To whom correspondence should be addressed. E-mail: czlu@ms.fjirsm.ac.cn. Fax: 0086-0591-3714946.

(1) Cheetham, A. K.; Férey, G..; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268.

(2) (a) Huang, L. C.; Kao, H. M.; Lii, K. H. *Chem. Mater.* **2000**, *12*, 2411−2417. (b) Lin, C. H.; Wang, S. L. *Chem. Mater.* **2000**, *12*, 3717. (c) Walton, R. I.; Millange, F.; O'Hare, D. *Chem. Mater.* **2000**, *12*, 1977. (d) Wragg, D. S.; Bull, I.; Hix, G. B.; Morris, R. E. *Chem. Commun.* **1999**, 2037.

(3) (a) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 610. (b) Khan, M. I.; Meyer, L. M.; Haushalter, R. C.; Schweitzer, A. L.; Zubieta, J.; Dye, J. L. *Chem. Mater.* **1996**, *8*, 43. (c) Soghomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J.; O'Connor, J. *Science* **1993**, *259*, 1596.

(4) Lin, C. H.; Wang, S. L.; Lii, K. H. *J. Am. Chem. Soc.* **2001**, *123*, 4649.

(5) (a) Vaidhyanathan, R.; Natarajan, S.; Rao, C. R. R. *J. Mater. Chem.* **1999**, *9*, 2789. (b) Neeraj, S.; Natarajan, S.; Rao, C. R. R. *New J. Chem.* **1999**, *23*, 303. (c) Wessels, T.; McCusker, L. B.; Baerlocher, C.; Reinert, P.; Patarin, J. *Microporous Mesoporous Mater.* **1998**, *23*, 67. (d) Reinert, P.; Patarin, J.; Marler, B. *Eur. J. Solid State Inorg. Chem.* **1998**, *35*, 389.

(6) Helliwell, M.; Gallois, B.; Kariuki, B. M.; Kaucic, V.; Helliwell, J. R. *Acta Crystallogr.* **1993**, *B49*, 420.

(7) Meyer, L. M.; Haushalter, R. C.; Zubieta, J. *J. Solid State Chem.* **1996**, *125*, 200.

(8) (a) Harrison, W. T. A.; Phillips, M. L. F.; Stanchfield J.; Nenoff, T. M. *Inorg. Chem.* **2001**, *40*, 895. (b) Halasyamani, P. S.; Drewitt, M. J; O'Hare, D. *Chem. Commun.* **1997**, 867. (c) Rodgers, J. A.; Harrison, W. T. A. *Chem. Commun.* **2000**, 2385.

(9) Zhang, Y. P.; Haushalter, R. C.; Zubieta, J. *Inorg. Chem. Acta* **1997**, *260*, 105.

10.1021/ic0257874 CCC: $22.00

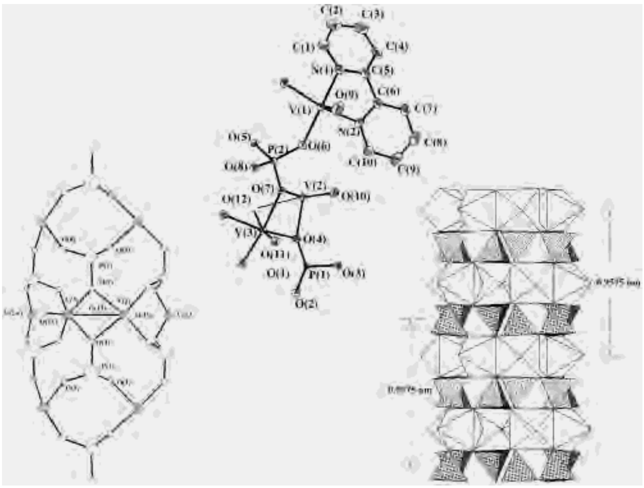

Figure 1. (a) Neutral structural unit for **1** with atom labeling (symmetry modes: #1 $x, y, z + 1$; #2 $x - y + {}^{1}/_{3}, x - {}^{1}/_{3}, -z - {}^{1}/_{3}$; #3 $x - y + {}^{1}/_{3}, x - {}^{1}/_{3}, -z - {}^{4}/_{3}$; #4 $y + {}^{1}/_{3}, -x + y + {}^{2}/_{3}, -z - {}^{1}/_{3}$; #5 $y + {}^{1}/_{3}, -x + y + {}^{2}/_{3}, -z - {}^{4}/_{3}$; #6 $x, y, z - 1$). (b) Cutaway view showing that the wall of the tube consists of $\{V_2P_2O_4\}$ 8-membered rings. (c) Assembly model of the proposed tubule (P(1) tetrahedra crossed pattern, P(2) tetrahedra dashed line pattern, and vanadium octahedra blank).

etries and the overall charge balance of the compound, and it is confirmed by the ESR spectrum. The ESR spectrum at room temperature exhibits a paramagnetic center with $g = 1.9611$, which is divided into two signals ($g = 1.9617$ and 1.9636, respectively) at 77 K, attributed to the two different coordination environments of vanadium atoms (Figure 1a). The IR spectrum exhibits a strong bond at 897 cm^{-1} assigned to $\nu(V{=}O)$ and a series of characteristic bands for both the phosphate group (964−1146 cm^{-1}) and 2,2′-bpy (1317−1614 cm^{-1}).

The X-ray diffraction analysis[12] of a single crystal of **1** revealed that the one-dimensional tubule is constructed from the neutral $[(V^{IV}O)_3(PO_4)_2(2,2'\text{-bpy})(OH_2)]$ unit (Figure 1a). There are three crystallographically distinct vanadium sites. V(1) is coordinated by one terminal oxygen and two nitrogen atoms from a 2,2-bpy ligand and by two corner-sharing oxygen atoms that are connected to two phosphate groups. V(2) and V(3) possess a distorted octahedral coordination geometry with one terminal oxygen atom [V−(t-O), ca. 1.585 Å] opposite to one bridging H_2O group [$V-(\mu_2\text{-}OH_2)$, ca. 2.458 Å] and four equatorial oxygens (V−O, 1.958−2.089 Å) that are connected to four phosphate groups. The V−N distances (ca. 2.121 Å) are clearly in the range observed for a formal V−N single bond. The presence of direct V−N (ligand) bonds is uncommon, but not unprecedented, in some vanadophosphate structures.[13] Two crystallographically distinct PO_4 groups exhibit similar coordination modes: both are connected to five vanadium atoms via oxygen atoms and have one μ_3- and three μ_2-oxygen atoms.

From bond valence analysis, it is clear that O(12) is a water molecule, as well as O(13) and O(14). Although V(2)−O(12) and V(3)−O(12) bonds are abnormally long, it is really important to include O(12) in the coordination of V(2) and V(3) because the water molecule is responsible of the curvature which leads to the tubule. The neutral $[(V^{IV}O)_3(PO_4)_2(2,2'\text{-bpy})]$ unit can be divided into two parts, namely, the $(VO)_2(PO_4)_2(\mu\text{-}OH_2)$ subunit and $(VO)(2,2\text{-bpy})$ group. The former contains a $\{V_2\}$ cluster of face-sharing octahedra ($V^{IV}-V^{IV}$, 3.0711(9) Å) and is linked by corners into a 1-D tube. If we take into account the radius of the oxygen atoms, the external and internal diameters of the tube are 11.05 and 3.53 Å, respectively. The view illustrated in Figure 1c shows that the tube consists of $\{P(1)_6\}$, $\{V_6\}$, and $\{P(2)_6\}$ cross sections arranged alternately in an ABCBABCB manner along the *c* axis direction. The A···A or C···C intercept is 9.575 Å, a value equal to the cell parameter of $c = 9.5745(2)$ Å. The wall of the tube is composed of 8-membered rings defined by two V, two P, and four O atoms. As shown in Figure 1b, three of four oxygens of each PO_4 tetrahedron bond three $\{V_2\}$ clusters, so that each $\{V_2\}$ cluster forms six eight-membered rings and three rings for each P center. These rings display interesting bending with various O−P−O and O−V−O angles subtended at the apex. The degree of curvature favors the formation of the tube. The fourth oxygen of each phosphate group is opposite to the wall of the tubule links a VO(2,2′-bpy) group, so that 2,2-bpy ligands constitute an organic shell around the polar tube (Figure 2). There are six channel water molecules with two crystallographically distinct positions per cell unit, a number that is consistent with the result from thermogravimetric analysis (TGA). Channel water molecules are loosely bound to the inner tube via weak hydrogen bonding (O···O distances of 3.03−3.17 Å).

---

(10) Synthesis of $[(V^{IV}O)_3(\mu_4\text{-}PO_4)_2(2,2'\text{-bpy})(\mu\text{-}OH_2)]\cdot 1/3H_2O$ (**1**). Reagents were purchased from Aldrich Chemical Co. and used without further purification. Method 1: A mixture of V_2O_5 (0.136 g), $VOSO_4$ (0.245 g), 2,2′-bpy (0.234 g), H_3PO_4 (wt 85%, 0.519 g), and H_2O (18 mL) in a molar ratio of 0.75:1.5:1.5:4.5:1000 was heated at 195 °C for 3 days. After slowly cooling, sapphire hexagonal column crystals of $[(V^{IV}O)_3(PO_4)_2(2,2'\text{-bpy})]\cdot 4/3H_2O$ (**1**) (~40% yield based on V) isolated by mechanical separation from light green crystals proved to be $[(VO_2)_2(HPO_4)(2,2'\text{-bpy})_2]\cdot H_2O$[11a] by X-ray structural analysis. Method 2: A mixture of V_2O_5 (0.136 g), $VOSO_4$ (0.245 g), 2,2-bpy (0.547 g), H_3PO_4 (wt 85%, 0.519 g), and H_2O (18 mL) in a molar ratio of 0.75:1.5:3.5:4.5:1000 was heated at 200 °C for 5 days. After slowly cooling, monophasic crystals of **1** were obtained in 95% yield. Method 3: Monophasic crystals of **1** were also obtained in high yield (90%) from the hydrothermal reaction of V_2O_5, $NaVO_3\cdot H_2O$, 2,2-bpy, $NH_2OH\cdot HCl$, H_3PO_4, and H_2O in a molar ratio of 0.55:1.5:1.5:5.0:6.5:1000 at 200 °C for 4 days. Anal. Calcd for **1**: C, 21.04; H, 1.88; N, 4.91; P, 10.85; V, 26.77%. Found: C, 19.97; H, 1.92; N, 4.93; P, 10. 78; V, 26.72%. IR (KBr, cm^{-1}) for **1**: 3450b, 3138m, 3076m, 1647w, 1614m, 1606s. 1576w, 1502w, 1473s, 1448s, 1317m, 1254w, 1146vs, 1105vs, 1049s, 1001vs, 964s, 897vs, 810w, 777s, 733m, 654m, 644m, 607w, 552m, 467s, 411vs.

(11) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

(12) Crystallographic data for **1**: trigonal space group $R\bar{3}$ (No. 148), $M_r = 570.97$, $a = 29.7600(3)$ Å, $c = 9.5745(2)$ Å, $V = 7343.66(19)$ $Å^3$, $Z = 18$, $\rho_{calcd} = 2.324$ g cm^{-3}, 8422 reflections collected ($1.37° \leq \theta \leq 25.02°$, $\lambda = 0.71073$ Å), 2882 ($R_{int} = 0.0289$) unique. Data collection was performed at room temperature on a Siemens SMART CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). SADABS absorptions were applied. The structure was solved by direct methods (SHELXS-97) and successive Fourier difference synthesis and refined by full-matrix least-squares (SHELXL-97) with anisotropic thermal parameters for all non-hydrogen atoms. A Fourier difference synthesis revealed the positions of all hydrogen atoms, which were introduced in the refinement as fixed isotropic contributors. Final refinement (299 least-squares parameters) converged to R1 = 0.0370 and wR2 = 0.0976 ($I > 2\sigma(I)$), and GOF = 1.148 with highest residual electron density 1.233 e $Å^{-3}$.

(13) (a) Mokry, L. M.; Thompson, J.; Bond, M. R.; Otieno, T.; Mohan, M.; Carrano, C. J. *Inorg. Chem.* **1994**, *33*, 2705. (b) Otieno, T.; Mokry, L. M.; Bond, M. R.; Carrano, C. J.; Dean, N. S. *Inorg. Chem.* **1996**, *35*, 850.

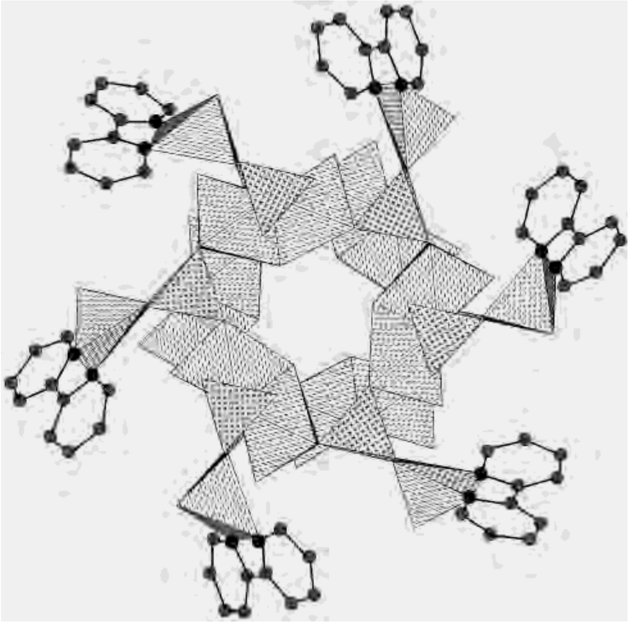

Figure 2. Polyhedral diagram showing the tubular channel orthogonal to the paper plane, which can accommodate solvent (V−O polyhedra dashed lines, PO_4 parallel lines).

Although the extensive exploration of hydrothermal synthesis of the V−O−P system has generated numerous oxovanadium phosphates possessing interesting structures,[3] few example of inorganic−organic hybrid open-famework oxovanadium phosphates was reported. Compound **1** is of very interest not only because of the presence of an unprecedented neutral structural unit but also because of 2,2-bpy ligands directly coordinating to vanadium sites within the framework and constituting an organic shell around the polar tubule.

TGA studies of **1** were performed under N_2 from 50 to 850 °C using a 10 °C/min rate. From the structural result, we expected to observe two steps in the dehydration: one for $O(13)H_2$ and $O(14)H_2$, which are loosely bound to the inner tube, and the other for $O(12)H_2$, which belongs to the vanadium octahedra. Although such a difference cannot be seen in the TGA curve, the TGA result displays 4.17% total weight loss from 50 to 175 °C, which is consistent with the removal of $^4/_3$ water molecules per $[(V^{IV}O)_3(\mu_4\text{-}PO_4)_2(2,2'\text{-bpy})(\mu\text{-}OH_2)]\cdot 1/3H_2O$ unit (calculated: 4.20%). There is no significant weight loss within the temperature range 175−310 °C. Interestingly, when crystals of **1** were heated at 250 ° for 5 h, cooled to room temperature, and exposed to moist air for 12 h, the broad absorption band of $\nu(H_2O)$, 3365 cm^{-1}, similar to that of the original solid (3450 cm^{-1}), reappeared in the IR spectrum of the sample. However, the X-ray powder diffraction patterns do not quite match before and after thermal treatments (250 °C) (there are a few intense peaks missing in the high angle region), indicating that the hydration/dehydration process is not fully reversible. Over the range 310−663 °C, the mass loss should correspond to the removal of 2,2-bpy. However, the observed mass loss (14.36%) was much lower that the expected value (calcd 27.32%). The lower reduction in mass loss was likely due to the retention of carbon in the solid residue. Beyond 663 °C, the residual carbon was slowly removed from the solid residue, resulting in $(VO)_3(PO_4)_2$ as the final product with a residual weight of 68.72% (calcd 68.48%).

In summary, we described here the hydrothermal synthesis and structure of a novel organic−inorganic hybrid tubular oxovanadium phosphate. The successful synthesis of **1** provides an interesting example of the use of chelating organic ligands to construct new open framework materials incorporating organic ligands. Given the large variety of organic chelate reagents that can be used in this synthetic system, and the range of elements observed in metal phosphates, the scope for the further synthesis of other novel metal phosphates in this class appears to be very inspiring.

Acknowledgment. The authors thank the 973 Program (001CB108q) of the Ministry of Science and Technology, the National Science Foundation of China (20073048), the Chinese Academy of Sciences, and the NSF of Fujian for financial support.

Supporting Information Available: Tables of crystal data and refinement, atomic coordinates, thermal parameters, bond distances, bond angles (also CIF format), BVS calculations. Figures of TGA curves, powder X-ray diffraction patterns, IR spectra of **1** before and after thermal trements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC0257874