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$NH_4VOPO_4{\cdot}H_2O$, a New One-Dimensional Ammonium Vanadium(IV) Phosphate Hydrate

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Introduction

Vanadium phosphates (VPOs) and related phases are of significant current interest as potential catalysts, ion exchangers, and molecular sieves[1−4] as well as in bioinorganic chemistry.[5] A number of ammonium VPOs have been structurally characterized, including α-$NH_4V^{III}(HPO_4)_2$,[6] β-$NH_4V^{III}(HPO_4)_2$,[7] $NH_4V^{IV}OPO_4$,[8] α-$NH_4V^{V}O_2HPO_4$,[9] β-$NH_4V^{V}O_2HPO_4$,[10] $NH_4V^{III}P_2O_7$,[11] $(NH_4)_2V^{IV}OP_2O_7$,[11] α-$(NH_4)_2(V^{IV}O)_3(P_2O_7)_2$,[11] and the novel peroxo-phase $(NH_4)_5(V^{V}O)_2(O_2)_4PO_4{\cdot}H_2O$.[12] In this note, we report the synthesis and characterization of $NH_4VOPO_4{\cdot}H_2O$, a new ammonium vanadium(IV) phosphate hydrate with strong one-dimensional character.

Experimental Section

Synthesis. $NH_4VOPO_4{\cdot}H_2O$ was prepared from a mixture of VCl_3 (0.22 g), ZnO (0.23 g), 85% H_3PO_4 (0.64 g), and 28% NH_4OH solution (5.11 g) (starting molar ratio N:V:P = 3:1:4). The components were mixed, sealed in a 23-mL Parr Teflon-lined hydrothermal bomb, and heated to 180 °C for 96 h. After slow cooling, the bomb was opened to reveal aqua blue rods of $NH_4VOPO_4{\cdot}H_2O$ and a white solid, each in ∼50% yield. The white product, presumably a zinc phosphate, could not be identified on the basis of X-ray powder diffraction measurements.

Characterization. The infrared spectrum of $NH_4VOPO_4{\cdot}H_2O$ (KBr disk method) is shown in Figure 1.[13] TGA (Rigaku Thermoflex instrument, heating rate: 5 °C/min under N_2) showed a 17.5% weight loss over a broad range (160−420 °C) possibly corresponding to loss of NH_3 and H_2O (calc 17.7%). X-ray powder data[14] for well-ground, pale blue $NH_4VOPO_4{\cdot}H_2O$ [Siemens D5000 automated powder diffractometer, Cu Kα (radiation, $\lambda = 1.54178$ Å, $T = 25(2)$ °C] are presented in Table 1. Magnetic susceptibility data were collected on a Quantum Design MPMS-7 SQUID magnetometer over the temperature range 5−300 K, using an applied field of 1.2 kG. $NH_4VOPO_4{\cdot}H_2O$ displays Curie−Weiss paramagnetism between 4 and 300 K, with no evidence for any cooperative magnetic phenomena.

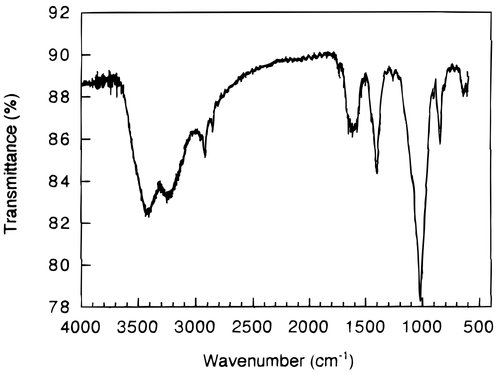

Figure 1. Infrared spectrum of $NH_4VOPO_4{\cdot}H_2O$.

Table 1. Powder X-ray Diffraction Data for $NH_4VOPO_4{\cdot}H_2O$

h	k	l	d_{obs}(Å)	d_{calc}(Å)	Δd	I_{rel}
0	0	1	8.446	8.450	−0.004	12
1	0	0	6.769	6.775	−0.006	100
1	0	−1	5.330	5.334	−0.004	10
1	0	1	5.236	5.239	−0.003	8
0	0	2	4.228	4.225	0.003	10
1	1	0	3.981	3.977	0.003	12
1	0	−2	3.616	3.615	0.001	21
2	0	0	3.387	3.387	0.000	5
0	1	2	3.202	3.203	−0.002	2
1	1	−2	2.911	2.912	0.000	3
1	1	2	2.882	2.881	0.002	10
2	1	0	2.790	2.789	0.001	10
2	1	−1	2.658	2.660	−0.002	3
2	1	1	2.636	2.636	0.000	4
0	2	0	2.457	2.457	0.001	2
2	1	−2	2.345	2.344	0.001	3
1	1	3	2.287	2.287	0.000	1
3	0	−1	2.192	2.192	0.001	2
3	0	1	2.172	2.172	0.000	3
3	1	0	2.052	2.052	0.000	1
0	1	4	1.941	1.941	0.001	2
3	1	−2	1.858	1.858	0.000	2
3	0	3	1.746	1.746	0.000	2
4	0	0	1.694	1.694	0.000	4
4	0	1	1.655	1.655	0.000	2
0	2	4	1.601	1.602	−0.001	1

Structure Determination. Single-crystal diffraction [Siemens P4 diffractometer, Mo Kα radiation, $\lambda = 0.710\,73$ Å, $T = 25(2)$ °C] was carried out on an aqua blue rod of $NH_4VOPO_4{\cdot}H_2O$. After data reduction [3297 measured intensities merged to 1649 unique observations, with 1590 of these with $I > 3\sigma(I)$ considered observed], the systematic absence condition ($0k0$, k) indicated space group $P2_1$ or $P2_1/m$. The structure was solved in space group $P2_1$ (No. 4) by direct methods[15] and refined to convergence.[16] No model could be established in $P2_1/m$. Five H atoms were located from Fourier difference maps, and one ammonium H atom was placed by geometrical means. H atoms were refined by riding on their respective N or O atoms. Crystallographic data are summarized in Table 2.

Results and Discussion

A fundamental step in the formation of $NH_4VOPO_4{\cdot}H_2O$ is the oxidation of vanadium(III) to vanadium(IV) during the

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(1) Centi, G.; Trifiro, F.; Ebner, J. R.; Franchetti, V. M. *Chem. Rev.* **1988**, *88*, 55.

(2) Clearfield, A. *Chem. Rev.* **1988**, *88*, 125.

(3) Jacobson, A. J.; Johnson, J. W.; Brody, J. F.; Scanlon, J. C.; Lewandowski, J. T. *Inorg. Chem.* **1985**, *24*, 1782.

(4) Khan, M. I.; Meyer, L. M.; Haushalter, R. C.; Schweizer, A. L.; Zubieta, J.; Dye, J. L. *Chem. Mater.* **1996**, *8*, 43.

(5) Toney, J. H.; Brock, C. P.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7263.

(6) Bircsak, Z.; Harrison, W. T. A. *Acta Crystallogr.* **1998**, *C54*, 1195.

(7) Haushalter, R. C.; Wang, Z.; Thompson, M. E.; Zubieta, J. *Inorg. Chim. Acta* **1995**, *232*, 83.

(8) Haushalter, R. C.; Chen, Q.; Soghomonian, V.; Zubieta, J.; O'Connor, C. *J. Solid State Chem.* **1994**, *108*, 128.

(9) Amorós, P.; Le Bail, A. *J. Solid State Chem.* **1992**, *97*, 283.

(10) Amorós, P.; Beltran-Porter, D.; Le Bail, A.; Férey, G.; Villeneuve, G. *Eur. J. Solid State Inorg. Chem.* **1988**, *25*, 599.

(11) Trommer, J.; Worzala, H.; Rabe, S.; Schneider, M. *J. Solid State Chem.* **1998**, *136*, 181.

(12) Schwendt, P.; Tyrselova, J.; Pavelcik, F. *Inorg. Chem.* **1995**, *34*, 1964.

(13) Infrared data (cm^{-1}): 970 (vs), 1380 (m), 1490 (m), 1680 (m), 2800−3500 (b, s). This last region is attributable to N−H and bound H_2O modes.

(14) Refined cell parameters: $a = 6.776(2)$ Å, $b = 4.913(2)$ Å, $c = 8.452(3)$, and $\beta = 91.05(2)°$ ($V = 281.3$ Å^3), based on peak positions established relative to the Cu Kα_1 wavelength ($\lambda = 1.540\,56$ Å).

(15) Sheldrick, G. M. *SHELXS86 User Guide*; University of Göttingen: Göttingen, Germany, 1985.

(16) Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS User Guide*; Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 1997.

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Table 2. Crystallographic Parameters for $NH_4VOPO_4{\cdot}H_2O$

formula VPO_6NH_6	fw 197.97
cryst syst monoclinic	space group $P2_1$ (No. 4)
$a = 6.7756(5)$ Å	$b = 4.9147(7)$ Å
$c = 8.4539(8)$ Å	$\beta = 91.092(7)°$
$V = 281.46(5)$ Å^3	$Z = 2$
$\lambda = 0.710\,73$ Å	$\rho_{calc} = 2.34$ g/cm^3
$\mu = 20.1$ cm^{-1}	$R(F)^a = 0.0305$
$R_w(F)^b = 0.0396$	

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 3. Atomic Positional/Thermal Parameters for $NH_4VOPO_4{\cdot}H_2O$

atom	*x*	*y*	*z*	U_{eq} (Å^2)
N(1)	0.1765(4)	0.1741(5)	0.5110(3)	0.0181
V(1)	0.64041(7)	0.1106(1)	0.84025(5)	0.0115
P(1)	0.6332(1)	0.1585(2)	1.22278(8)	0.0100
O(1)	0.6264(3)	0.2792(4)	1.0517(2)	0.0162
O(2)	0.4191(3)	0.3559(4)	0.7777(2)	0.0156
O(3)	0.8331(4)	−0.1980(5)	0.9378(3)	0.0282
O(4)	0.5275(3)	−0.1698(4)	0.6947(2)	0.0150
O(5)	0.8167(3)	0.2486(5)	0.7475(3)	0.0225
O(6)	0.8339(3)	0.1950(4)	1.3015(2)	0.0165

hydrothermal reaction. Similar oxidation reactions[17] have been ascribed to the O_2 present in the bomb, both in the void space and in solution. Reactions starting from vanadium(IV)-containing precursors were not successful in preparing $NH_4VOPO_4{\cdot}H_2O$, resulting in $VO(HPO_4){\cdot}{}^1/_2H_2O$,[18] NH_4VOPO_4,[8] or unidentified phases. The presence of zinc oxide is required to form $NH_4VOPO_4{\cdot}H_2O$. The role of this additive is obscure at present, although it has precedence in the hydrothermal syntheses of $Ba_2V^{IV}O(PO_4)_2{\cdot}H_2O$[19] and $(CN_3H_6)_2(V^VO_2)_3(PO_4)(HPO_4)$.[20] It may act to regulate pH by hydrolysis[17] or control the quantity of phosphate anions in solution. A similar role[17] has been suggested for "structure-directing" organic bases which are not incorporated into the final product.[21] The synthesis reported here shares the problems of low yields/mixed products which plague many hydrothermal reactions,[22] although a full analysis of the reacting species[17] allows a much more systematic approach in this area of synthetic chemistry.

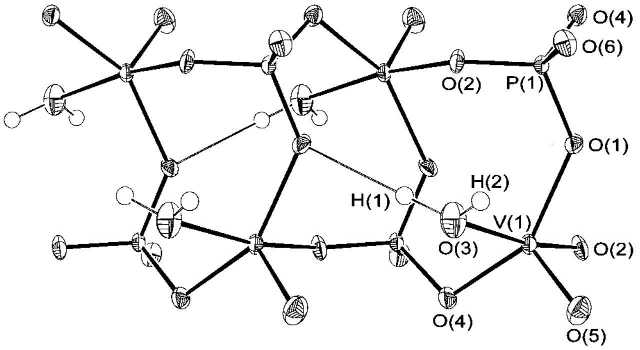

Figure 2. Details of the [010] chain in $NH_4VOPO_4{\cdot}H_2O$ showing the intrachain H bond as a thin line (50% thermal ellipsoids for the non-hydrogen atoms). Selected geometrical data (Å; deg) with esd's in parentheses: V(1)−O(1) 1.974(2), V(1)−O(2) 1.988(2), V(1)−O(3) 2.155(3), V(1)−O(4) 1.990(2), V(1)−O(5) 1.593(2), P(1)−O(1) 1.563(2), P(1)−O(2) 1.529(2), P(1)−O(4) 1.553(2), P(1)−O(6) 1.514(2); V(1)−O(1)−P(1) 132.7(1), V(1)−O(2)−P(1) 139.9(1), V(1)−O(4)−P(1) 111.3(1).

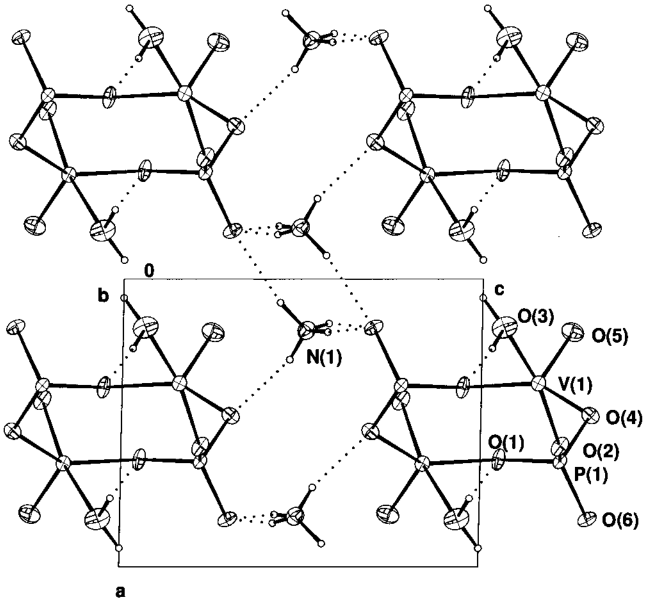

Figure 3. View down [010] of the $NH_4VOPO_4{\cdot}H_2O$ structure, with hydrogen bonds indicated by dotted lines.

Atomic positional and thermal parameters for $NH_4VOPO_4{\cdot}H_2O$ are listed in Table 3. Pure vanadium(IV) character is strongly supported by its color and by crystallochemical considerations. The vanadium cation adopts a distorted square pyramidal coordination with respect to its O atom neighbors. Other vanadium(IV) phosphates show a similar VO_5 geometry,[23] although distorted octahedral coordination is more common.[24] In $NH_4VOPO_4{\cdot}H_2O$, one of the basal V−O vertexes is to a water molecule, with this bond showing a slight lengthening, compared to the other three basal V−O−P bridges formed by this unit. The axial V=O vanadyl link is typically short, indicating strong multiple-bond character.[24] A bond valence sum (BVS) calculation[25] for V yielded a value of 3.79 (expected 4.00). The phosphate group is a typical tetrahedron, with d_{av}(P−O) = 1.540 Å, and BVS(P) = 4.94 (expected 5.00). Three P−O−V links are formed by this group (θ_{av} = 128°). The terminal P−O(6) vertex is short [1.514(2) Å], indicating that this O atom is not protonated.

The polyhedral connectivity in $NH_4VOPO_4{\cdot}H_2O$ results in infinite anionic chains of stoichiometry $[VOPO_4{\cdot}H_2O]^-$ which propagate along the polar [010] direction. These chains (Figure 2) are built up from four rings (four nodal V/P atoms, or eight atoms in total) of alternating VO_5 and PO_4 moieties. These four rings are fused edgeways into infinite ladderlike chains. One of the water molecule H atoms is involved in an intrachain hydrogen bond, as V−O(3)−H(1)···O(1) [d(H···O) = 2.12 Å]. The $[VOPO_4{\cdot}H_2O]^-$ chains and NH_4^+ cations form a layerlike arrangement in the *c* direction (Figure 3). The ammonium cation forms four N−H···O hydrogen bonds. Three of these H bonds are to terminal P−O(6) acceptors, and one is to a V−O(4)−P bridge.

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(17) (a) Roca, M.; Marcos, M. D.; Amorós, P.; Beltrán-Porter, A.; Edwards, A. J.; Beltrán-Porter, D. *Inorg. Chem.* **1996**, *35*, 5613. (b) Roca, M.; Marcos, M. D.; Amorós, P.; Alamo, J.; Beltrán-Porter, A.; Beltrán-Porter, D. *Inorg. Chem.* **1997**, *36*, 3414.

(18) Torardi, C. C.; Calabrese, J. C. *Inorg. Chem.* **1984**, *23*, 1308.

(19) Harrison, W. T. A.; Lim, S. C.; Vaughey, J. T.; Jacobson, A. J.; Goshorn, D. P.; Johnson, J. W. *J. Solid State Chem.* **1994**, *113*, 444.

(20) Bircsak, Z.; Harrison, W. T. A. *Inorg. Chem.* **1998**, *37*, 3204.

(21) Zhang, Y.; Clearfield, A.; Haushalter, R. C. *J. Solid State Chem.* **1995**, *117*, 157.

(22) Zubieta, J. *Comments Inorg. Chem.* **1994**, *16*, 153.

(23) Haushalter, R. C.; Soghomonian, V.; Chen, Q.; Zubieta, J. *J. Solid State Chem.* **1993**, *105*, 572.

(24) Le Bail, A.; Férey, G.; Amorós, P.; Beltran-Porter, D.; Villeneuve, G. *J. Solid State Chem.* **1989**, *79*, 169.

(25) Brown, I. D. *J. Appl. Crystallogr.* **1996**, *29*, 479.

$NH_4VOPO_4 \cdot H_2O$ bears essentially no relation to the burgundy red $NH_4V^{IV}OPO_4$,[8] which consists of a three-dimensional network of VO_6 and PO_4 groups, connected via V−O−V and V−O−P bonds. $NH_4VOPO_4 \cdot H_2O$ shows some resemblance to $V^{IV}O(HPO_4) \cdot 4H_2O$.[26] In this latter phase, ladderlike, edge-shared four-ring chains akin to those in $NH_4VOPO_4 \cdot H_2O$ are formed from $VO_4(OH_2)_2$ octahedra and HPO_4 tetrahedra as the polyhedral building units.

Acknowledgment. We thank the Australian Research Council for financial support.

Supporting Information Available: An X-ray crystallographic file, in CIF format, for $NH_4VOPO_4 \cdot H_2O$ is available on the Internet only. Access information is given on any current masthead page.

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(26) Leonowicz, M. E.; Johnson, J. W.; Brody, J. F.; Shannon, H. F.; Newsam, J. M. *J. Solid State Chem.* **1985**, *56*, 370.