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$H_2N(CH_2CH_2)_2NH_2[(VO)_4(H_2O)_4(HPO_4)_2(PO_4)_2]$: An Organically Templated Vanadium Phosphate with One Dimensional $\{-\mathrm{V}-\mathrm{O}{=}\mathrm{V}-\mathrm{O}-\}$ Chains

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The new vanadium phosphate $H_2N(CH_2CH_2)_2NH_2[(VO)_4(H_2O)_4(HPO_4)_2(PO_4)_2]$, **(1)**, was prepared from the reaction of VCl_4:H_3PO_4:1,4-diaminopiperazine hydrochloride:tetra-*n*-buytlammonium hydroxide:H_2O in a mole ratio of 1:8.9:4.4:5.2:2268 in a sealed glass tube for 3 h at 200 °C. Phosphate **1** crystallizes in the acentric monoclinic space group *Im* with $a = 7.025(1)$, $b = 9.470(2)$, and $c = 16.570(3)$Å, $\beta = 96.03(3)°$, $V = 1096.3\ (6)$ Å^3, $Z = 2$, and $R\ (R_w) = 0.0517\ (0.0595)$ and possesses a three dimensional (3-D) covalently bonded structure comprised of a vanadium phosphate net with occluded organic cations occupying tunnels within the oxide framework. The structure can be qualitatively described as a severely defected $VOPO_4$ structure type, with phosphate **1** displaying several different VO_6 environments that can be envisioned as related to the infinite $\{O{=}V\cdots O\}_n$ strings present in $VOPO_4$: (a) infinite 1-D chains of VO_6 octahedra sharing opposite vertices with the remaining four vertices connected to $\{PO_4\}$ tetrahedra just as in $VOPO_4$; (b) 1-D chains as in point a but with every other octahedron missing with the distorted octahedral coordination requirements satisfied by the addition of an aquo ligand *trans* to the V═O group; (c) 1-D chains as in point a but with every other one missing and each V atom coordinated to three aquo ligands; (d) a region that would be occupied by a 1-D chain in $VOPO_4$ but is totally missing and is occupied by the organic dication. As a result, some of the $\{PO_4\}$ tetrahedra are either absent or possess P−OH groups to compensate for the missing V atoms.

Introduction

The field of open framework and microporous solids has been dominated, in terms of both number of structure types and technological importance, by the all tetrahedral framework aluminosilicate[1] and aluminophosphate[2] materials. While octahedral−tetrahedral framework structures are known for many minerals, substantial numbers of synthetic open framework materials incorporating octahedral framework constituents have been discovered only recently. For example, in the molybdenum phosphate system, many octahedral−tetrahedral framework solids with alkali and alkaline earth cations have been prepared and structurally characterized.[3] In addition, a large number of molybdenum phosphate frameworks encapsulating occluded organic cations have been prepared via hydrothermal synthesis techniques.[3] Several of these molybdenum phosphates have been demostrated to be microporous and to possess very large internal void volumes.[4−8] The vanadium phosphates also form a large number of framework structures both without a template[9] and with alkali and alkaline earth cations.[10−16] Vanadium phosphates, arsenates, and phosphonates with templating organic cations have yielded a surprisingly large number of new connectivity patterns, with the vanadium-centered octahedral and square pyramidal polyhedra combining with the $\{PO_4\}$ and $\{RPO_3\}$ tetrahedra, to form materials with molecular,[17] one-dimensional (1-D),[18] 2-D,[19,20] and 3-D[21−24] structures. In this

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Table 1. Crystallographic Data for $H_2N(CH_2CH_2)_2NH_2[(VO)_4(H_2O)_4(HPO_4)_2(PO_4)_2]$

chem formula: $C_4H_{22}N_2O_{24}P_4V_4$
$a = 7.0250(10)$ Å
$b = 9.470(2)$ Å
$c = 16.570(3)$ Å
$\beta = 96.08(3)°$
$V = 1096.3(6)$ Å^3
$Z = 2$
fw = 809.6
space group: *Im* (No. 8)
$T = 20$ °C
$\lambda = 0.710\,73$ Å
$\mu = 20.43$ cm^{-1}
$\rho_{calcd} = 2.452$ g·cm^{-3}
$R^a = 0.0517$
$R_w{}^b = 0.0595$

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

paper, the synthesis and structural characterization of the new vanadium phosphate $H_2N(CH_2CH_2)_2NH_2[(VO)_4(H_2O)_4(HPO_4)_2(PO_4)_2]$ (**1**), which possesses a 3-D framework structure with tunnels occupied by piperazinium dications that are hydrogen bonded to certain framework oxygen atoms, is discussed. The structure will be compared to a highly defected $VOPO_4$ type structure as well as to other organically templated vanadium phosphates.[25] The synthetic conditions used to prepare **1** will be contrasted to other vanadium phosphates that contain piperazine cations.

Experimental Section

General Data. The reactions were performed in thick wall glass tubes. The vanadium starting material was obtained from the careful dropwise addition of VCl_4 to an appropriate volume of ice and water. ***Caution***! the hydrolysis, which evolves copious amounts of HCl, should be performed within a well-ventilated fume hood behind adequate shielding. The resultant blue solution was 1.47 M in vanadium. The 1,4-diaminopiperazine hydrochloride was purchased from Aldrich (quoted purity ca. 85%) and used as received.

$H_2N(CH_2CH_2)_2NH_2[(VO)_4(H_2O)_4(HPO_4)_2(PO_4)_2]$ (1). Phosphate **1** was prepared from the reaction of VCl_4:H_3PO_4:1,4-diaminopiperazine hydrochloride:tetra-n-buytlammonium hydroxide:H_2O in mole ratios of 1:8.9:4.4:5.2:2268 in a sealed thick walled glass tube (11 mm i.d., 15 mm o.d., and 250 mm long, fill factor = 40%) for 5 h at 200 °C. A brown side product begins to appear if the reaction proceeds beyond this point. The product consists of a 40% yield (based on V) of monophasic blue rectangular plates of **1** which were isolated by washing with water and air drying.

Crystallography. The data was collected on a Rigaku AFC7R diffractometer equipped with an 18kW RU300 rotating anode. The structure were solved and refined with the *teXsan* crystallographic package from Molecular Structure Corp. All non-hydrogen atoms were refined anisotropically, and the H atoms were included in their calculated positions with a fixed isotropic *U* value. Attempts to solve and refine the structure in the centrosymmetric space group *I2/m* were unsuccessful. The crystallographic data are summarized in Table 1, the positional and isotropic thermal parameters are found in Table 2 while selected distances and angles are collected in Table 3.

Magnetic Susceptibility. The magnetic data was collected using a Quantum Design MPMS-5S SQUID susceptometer. Measurement and calibration techniques are reported elsewhere.[26] The temperature dependent data were obtained at a field of 1000 G.

Results and Discussion

In the vanadium phosphate, vanadium arsenate, and vanadium phosphonate systems, a very large number of new solids with organic templates have recently been prepared.[18-24] One general trend that has been observed is that there is a relatively narrow range of size and positive charge per volume requirements for the occluded organic templates. This contrasts with, for example, the silicoaluminate zeolites which often tend to form with occluded nonpolar tetraalkylammonium cations. Most of the observed framework compositions in the V−O−P or V−O−RPO_3 (R = alkyl or aryl group) systems do not contain cationic templates possessing larger alkyl groups and a relatively low positive charge per volume, e.g. tetrabutylammonium cations, but rather small alkyl ammonimum cations (e.g. methylammonium) or diammonium cations (e.g ethylenediammonium) tend to be entrained. In fact, we have taken advantage of the fact that these nonpolar cations are not incorporated into the frameworks by using, for example, Bu_4NOH, to adjust the pH of the reaction mixture. However, one of the most favorable situations for crystallization appears to be the presence of both small, highly charged alkylammonium cations combined with alkali metal cations or hydronium cations as has also been found in the molybdenum phosphate system.[3] Under the synthetic conditions investigated so far, many of the stucturally characterized vanadium phosphates have been found to have framework V:P ratios near 1:1. If the ratio of V:P tends toward the higher values and the vanadium is nearly fully oxidized, one observes the formation of Keggin type $M_{12}P$ clusters as well as polyoxometallate species.

Table 2. Atomic Coordinates ($\times 10^4$) and Isotropic Temperature Factors (Å^2 $\times$ 10^3) for $H_2N(CH_2CH_2)_2NH_2[(VO)_4(H_2O)_4(HPO_4)_2(PO_4)_2]$ (**1**)

	x	*y*	*z*	*U*(eq)[a]
V(1)	5874	0	6832	16(1)
V(2)	5967(5)	5000	4254(2)	15(1)
V(3)	8285(5)	0	4056(2)	8(1)
V(4)	13224(5)	0	3834(2)	10(1)
P(1)	5613(6)	1988(3)	5113(2)	12(1)
P(2)	10084(6)	2051(3)	2758(2)	14(1)
O(1)	8120(25)	0	7005(8)	77(9)
O(2)	5632(16)	1541(9)	6011(5)	31(3)
O(3)	5206(16)	1355(10)	7683(5)	35(3)
O(4)	8213(16)	5000	4249(7)	27(4)
O(5)	5601(13)	3621(8)	5125(5)	17(2)
O(6)	5570(14)	3476(10)	3349(5)	27(3)
O(7)	2698(17)	5000	4029(8)	39(5)
O(8)	10551(14)	0	4360(7)	37(3)
O(9)	8463(12)	1573(9)	3233(5)	20(2)
O(10)	7374(11)	1454(8)	4763(5)	15(2)
O(11)	5334(15)	0	3491(7)	41(4)
O(12)	11989(14)	1496(15)	3113(8)	62(5)
O(13)	13789(13)	1477(13)	4639(7)	45(4)
O(14)	4641(19)	3533(10)	6871(6)	48(4)
O(15)	2399(27)	0	6424(14)	76(9)
C(1)	5738(19)	1332(14)	761(8)	28(3)
C(2)	4717(21)	1309(16)	1489(8)	33(3)
N(1)	3433(25)	0	1499(11)	31(4)
N(2)	11931(20)	5000	5742(9)	19(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The synthesis of phosphate **1** resembles previous syntheses in that a vanadium source (in this case the hydrolyzate of VCl_4) is combined with phosphoric acid and the template and treated hydrothermally in the 200 °C range. It has been observed that the large number of variables present for the synthesis of solids in the vanadium phosphate system, such as reaction time, molar ratio of reactants, temperature, pH, absolute concentration, type of template, and the nature of the vanadium source all have an effect on the product obtained. The fact that the outcome of the reaction can be greatly altered by relatively small perturbations of these variables is dramatically illustrated by the following fact. While a 40% yield of monophasic **(1)** is obtained upon reaction of VCl_4:H_3PO_4:1,4-diaminopiperazine hydrochloride:tetra-*n*-buytlammonium hydroxide:H_2O in a mole ratio of

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $H_2N(CH_2CH_2)_2NH_2[(VO)_4(H_2O)_4(HPO_4)_2(PO_4)_2]$ (**1**)

V(1)−O(1)	1.574(17)	V(1)−O(2)	1.990(9)
V(1)−O(3)	1.999(10)	V(1)−O(15)	2.464(19)
V(1)−O(2A)	1.990(9)	V(1)−O(3A)	1.999(10)
V(2)−O(4)	1.579(12)	V(2)−O(5)	1.984(9)
V(2)−O(6)	2.079(9)	V(2)−O(7)	2.287(12)
V(2)−O(5A)	1.984(9)	V(2)−O(6A)	2.079(9)
V(3)−O(8)	1.619(10)	V(3)−O(9)	2.033(9)
V(3)−O(10)	1.958(8)	V(3)−O(11)	2.183(11)
V(3)−O(9A)	2.033(9)	V(3)−O(10A)	1.958(8)
V(4)−O(8)	2.152(11)	V(4)−O(12)	1.993(13)
V(4)−O(13)	1.944(12)	V(4)−O(11A)	1.642(12)
V(4)−O(12A)	1.993(13)	V(4)−O(13B)	1.944(12)
P(1)−O(2)	1.546(9)	P(1)−O(5)	1.547(8)
P(1)−O(10)	1.507(9)	P(1)−O(13A)	1.511(10)
P(2)−O(9)	1.520(10)	P(2)−O(12)	1.499(11)
P(2)−O(3B)	1.518(10)	P(2)−O(14A)	1.569(10)
O(1)−V(1)−O(2)	97.8(5)	O(1)−V(1)−O(3)	100.2(5)
O(2)−V(1)−O(3)	90.1(4)	O(1)−V(1)−O(15)	174.6(7)
O(2)−V(1)−O(15)	78.5(5)	O(3)−V(1)−O(15)	83.9(5)
O(1)−V(1)−O(2A)	97.8(5)	O(2)−V(1)−O(2A)	94.3(5)
O(3)−V(1)−O(2A)	160.6(5)	O(15)−V(1)−O(2A)	78.5(5)
O(1)−V(1)−O(3A)	100.2(5)	O(2)−V(1)−O(3A)	160.6(5)
O(3)−V(1)−O(3A)	79.9(6)	O(15)−V(1)−O(3A)	83.9(5)
O(2A)−V(1)−O(3A)	90.1(4)	O(4)−V(2)−O(5)	102.1(4)
O(4)−V(2)−O(6)	93.1(4)	O(5)−V(2)−O(6)	92.9(3)
O(4)−V(2)−O(7)	170.4(6)	O(5)−V(2)−O(7)	85.0(4)
O(6)−V(2)−O(7)	80.0(4)	O(4)−V(2)−O(5A)	102.1(4)
O(5)−V(2)−O(5A)	82.3(5)	O(6)−V(2)−O(5A)	164.6(4)
O(7)−V(2)−O(5A)	85.0(4)	O(4)−V(2)−O(6A)	93.1(4)
O(5)−V(2)−O(6A)	164.6(4)	O(6)−V(2)−O(6A)	87.9(5)
O(7)−V(2)−O(6A)	80.0(4)	O(5A)−V(2)−O(6A)	92.9(3)
O(8)−V(3)−O(9)	94.6(4)	O(8)−V(3)−O(10)	100.8(4)
O(9)−V(3)−O(10)	86.2(3)	O(8)−V(3)−O(11)	172.7(6)
O(9)−V(3)−O(11)	80.5(3)	O(10)−V(3)−O(11)	84.3(3)
O(8)−V(3)−O(9A)	94.6(4)	O(9)−V(3)−O(9A)	94.2(5)
O(10)−V(3)−O(9A)	164.5(4)	O(11)−V(3)−O(9A)	80.5(3)
O(8)−V(3)−O(10A)	100.8(4)	O(9)−V(3)−O(10A)	164.5(4)
O(10)−V(3)−O(10A)	89.4(5)	O(11)−V(3)−O(10A)	84.3(3)
O(9A)−V(3)−O(10A)	86.2(3)	O(8)−V(4)−O(12)	84.2(4)
O(8)−V(4)−O(13)	81.2(4)	O(12)−V(4)−O(13)	86.8(5)
O(8)−V(4)−O(11A)	176.4(5)	O(12)−V(4)−O(11A)	98.3(4)
O(13)−V(4)−O(11A)	96.4(4)	O(8)−V(4)−O(12A)	84.2(4)
O(12)−V(4)−O(12A)	90.6(8)	O(13)−V(4)−O(12A)	165.3(5)
O(11A)−V(4)−O(12A)	98.3(4)	O(8)−V(4)−O(13B)	81.2(4)
O(12)−V(4)−O(13B)	165.3(5)	O(13)−V(4)−O(13B)	92.0(7)
O(11A)−V(4)−O(13B)	96.4(4)	O(12A)−V(4)−O(13B)	86.8(5)

1:8.9:4.4:5.2:2268, changing the relative ratios of the starting materials to 1:2.2:1.7:1.2:2830 and substituting piperazine for 1,4-diaminopiperazine give an entirely different product, namely, the layered material $H_2N(CH_2CH_2)_2NH_2[(VO)_4(OH)_4(PO_4)_2]$[20] **(2)**. While the mechanistic details remain obscure for the synthesis of **1**, N−N bond cleavage of organohydrazines in reactions with metal−oxo species is not uncommon.[27] In addition, we recently reported two other layered vanadium phosphates containing interlamellar piperazinium dications, $H_2N(CH_2CH_2)_2NH_2[(VO)_2(PO_4)_2]$[19] **(3)** and $(H_2N(CH_2CH_2)_2NH_2)_2[(VO)_3(HPO_4)_2\,(PO_4)_2]\cdot H_2O$[19] **(4)**, that possess defected or distorted $VOPO_4$-like layers.

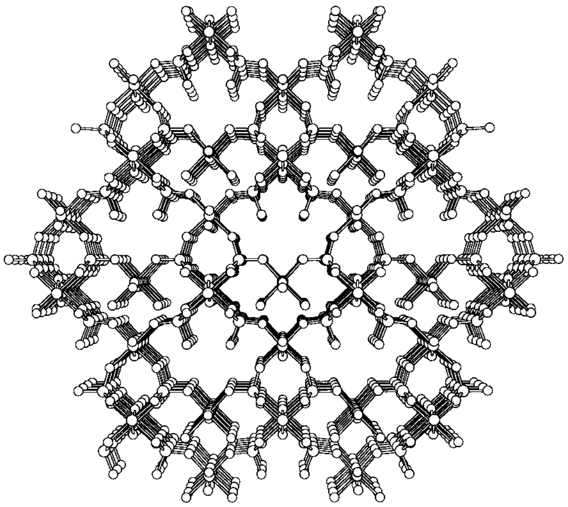

Figure 1. Perspective view of the structure of **1** down the crystallographic [100] direction where the polar nature of the structure is evident. Piperazinium dications are not shown.

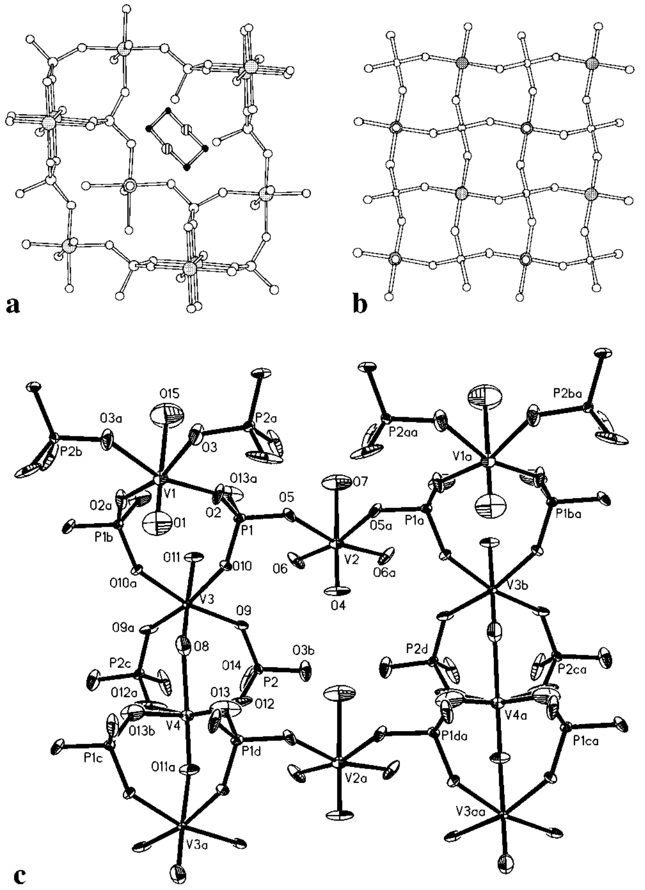

Figure 2. Section of the structure of **(1)** (a) projected down [100] emphasizing the similarities to the $VOPO_4$ structure type (b) and an ORTEP view of a section of the structure of (**1**), showing the atom-labeling scheme and 50% thermal ellipsoids (c).

The structure of phosphate **1** was solved and refined in the acentric space group *Im* which is a nonstandard setting of *Cm*. The framework is built up from distorted V(IV) octahedra combined with PO_4 or HPO_4 tetrahedra with a V:P ratio of one. As might be expected from this ratio, the structure has certain structural motifs related to those of the $VOPO_4$ structure type. A projection of the structure down the crystallographic [100] direction is shown in Figure 1 where the polar nature of the structure is apparent. The [100] direction is parallel to the 1-D ···O−V−O−V··· chains. In order to facilitate the comparison of the structure of phosphate **1** with that of $VOPO_4$, a small section of **(1)** projected down [100] along with a corresponding structure of $VOPO_4$ is shown in parts a and b of Figure 2 which corresponds to the [001] direction in tetragonal $VOPO_4$. While a basic alteration of the $\{VO_6\}$ octahedron and $\{PO_4\}$ tetrahedron on a square net is apparent in Figure 2, the most obvious difference in the structures is that one of what was an octahedral location in $VOPO_4$, has been occupied by the piperazinium cation. As can be seen in Figure 2, phosphate

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[27] Abrams, M. J.; Larsen, S. K.; Shaikh, S. N.; Zubieta, J. *Inorg. Chim. Acta* **1991**, *185,* 7.

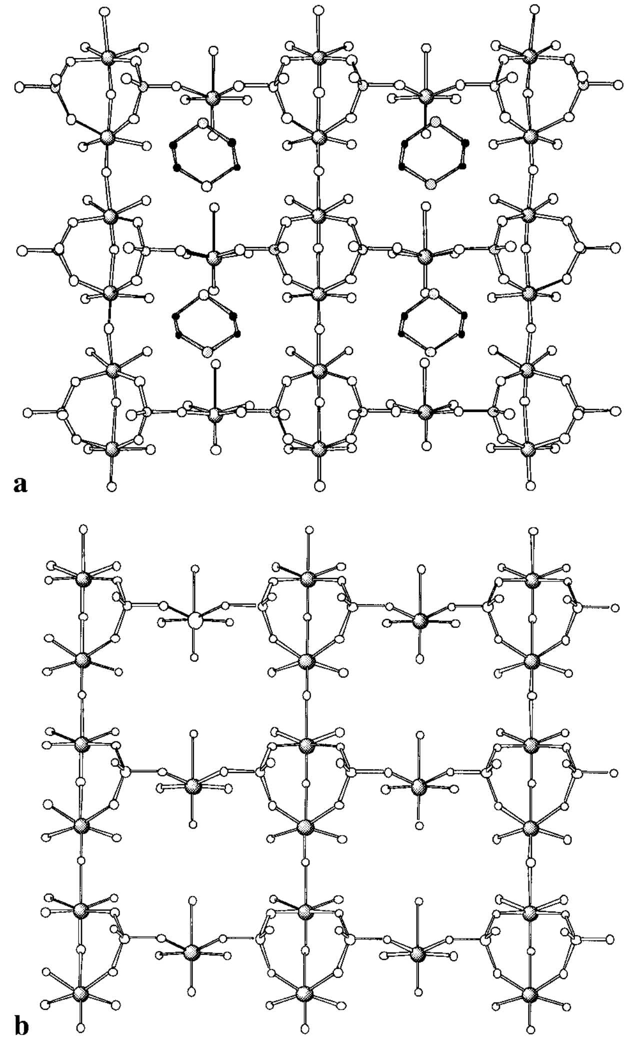

Figure 3. View of how the two VO_6 octahedra that contain aquo ligands bridge between the infinite 1-D $\{-O{=}V{\cdots}O{=}V-\}_n$. Part a shows the connection provided by the $(H_2O)VO_5$ octahedron while part b depicts the bonding of the $(H_2O)_3VO_3$ octahedron to the 1-D chains.

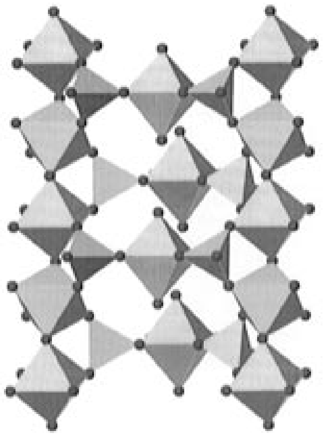

Figure 4. Illustration of how the defected octahedral chains bridge the infinite $\{-O{=}V{\cdots}O{=}V-\}$ chains.

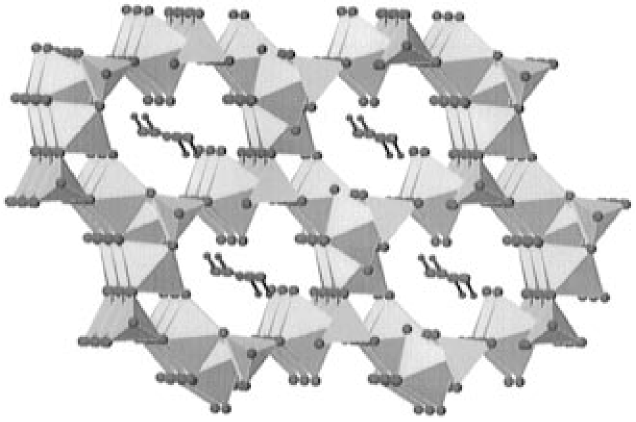

Figure 5. Polyhedral representation of the structure nearly parallel to [010] showing the tunnels in which the piperazinium dications reside.

1 appears to display a similar motif in projection but actually possesses vacancies of both the VO_6 octahedra and PO_4 tetrahedra.

The basic $VOPO_4$ structure type and its variants are a recurring theme in the V−P−O system. The structure (Figure 2b) results from the interaction of the four equidistant equatorial oxygen ligands on vanadium with the four bonds of the phosphate tetrahedron forming a layer which directs the short vanadyl V=O, and the long V−O contact *trans* to it, perpendicular to the plane. In the structure of $VOPO_4$, there are V=O groups arranged in 1-D chains such that the oxygen atom of the vanadyl group (V=O distance ca. 1.6 Å) contacts the vacant coordintion site on the next adjacent vanadium atom (V−O distance >2.3 Å) along the tetragonal *c* axis to give infinite 1-D $\{{\cdot\cdot}O{=}V{\cdots}O{=}V{\cdot\cdot}\}$ chains. In $VOPO_4$, these 1-D chains are bonded to adjacent parallel chains via 4/2 PO_4 tetrahedra. Similar 1-D chains exist in **1** which run parallel to [100] and, as in $VOPO_4$, are bonded to 4/2 $\{PO_4\}$ groups. Unlike $VOPO_4$, however, the 1-D chains are bonded to two PO_4 and two HPO_4 tetrahedra. Two vertices of the PO_4 groups are bound to adjacent octahedra in the 1-D chain, and one vertex is coordinated to the vanadium which bears an oxo group *trans* to an aquo ligand while the remaing vertex is bonded to the vanadium with an oxo group and three water ligands. Two vertices of the HPO_4 tetrahedra bridge adjacent octahedra in the 1-D chain, in a fashion similar to the PO_4 tetrahedra, and a third vertex forms an equatorial contact to the monoaquated vanadium while the remaining oxygen is present as a P-OH group.

Examination of the section of the structure of **1** depicted in Figure 2a shows that there are regions of the structure which would correspond to the location of the infinite $\{{\cdot\cdot}O{=}V{\cdots}O{=}V{\cdot\cdot}\}$ chains in comparison to the $VOPO_4$ structure type (Figure 2b). The four regions can be described as follows. (a) The first is chains of infinite corner sharing octahedra with $\{{\cdot\cdot}O{=}V{\cdots}O{=}V{\cdot\cdot}\}$ bonds very similar to those found in $VOPO_4$ itself. Two of the four crystallographically independent V atoms, V3 and V4 of Figure 2c, are in this coordination environment. (b) The second is 1-D "chains" as in part a but with every other V(1) octahedron missing with the distorted octahedral coordination requirements satisfied by the addition of an aquo ligand *trans* to the V=O group. The manner in which these monoaquated distorted VO_6 octahedra connect the two crystallographically independent 1-D infinite chains, via two of its equatorial oxygen ligands, is shown in Figure 3a. This figure also illustrates how the piperazinium dication is located in the position created by the "missing" VO_6 octahedron. (c) The third is 1-D "chains" as in part a with every other V(2) octahedron missing, as in part b, and three aquo ligands coordianted to the V atoms that remain. Like the monoaquated VO_6 in (b), the $O_3V(H_2O)_3$ octahedra bridge the two types of infinite chain together as depicted in Figure 3b. The manner in which these two types of defected chain bridge the infinite $\{{\cdot\cdot}O{=}V{\cdots}O{=}V{\cdot\cdot}\}$ together is illustrated in Figure 4; (d) The fourth is a region consisting of a vacancy whose location would correspond to a missing octahedon in the $VOPO_4$ structure

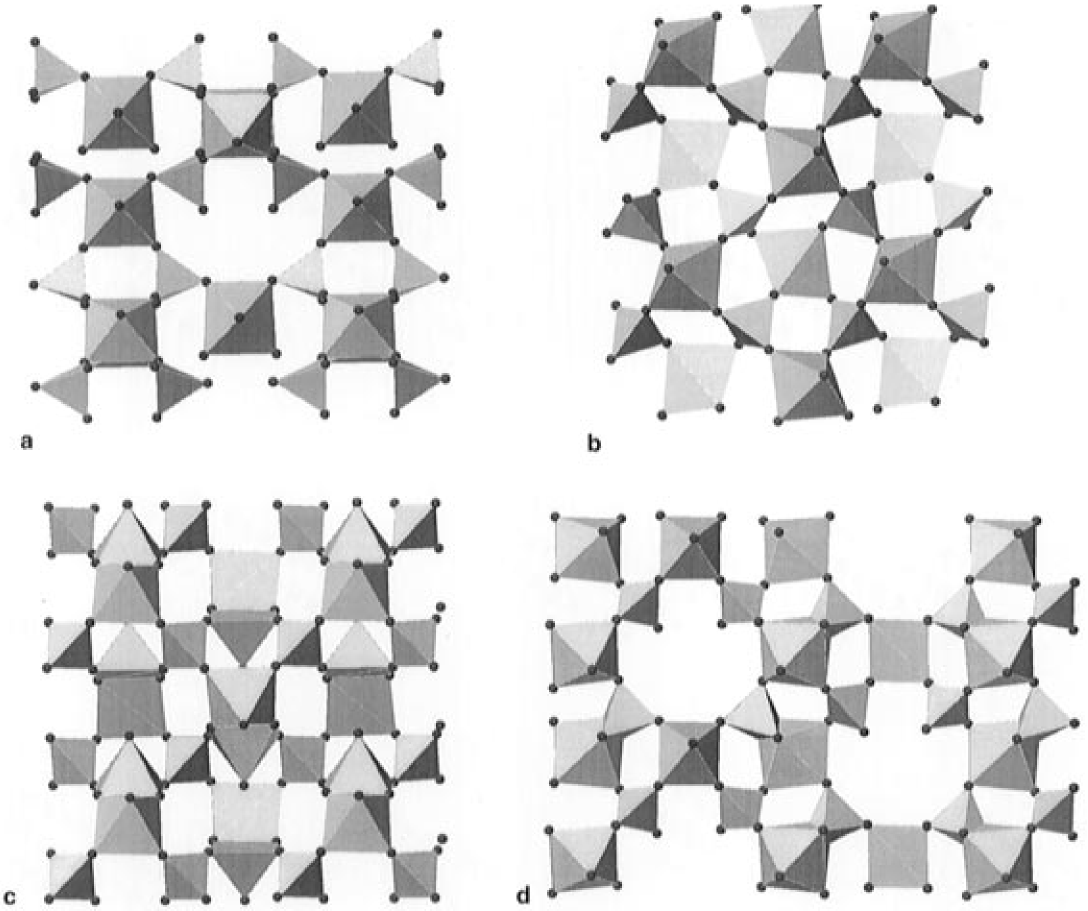

Figure 6. Comparison of the structures of the four vanadium phosphates (**1**−**4**) shown in parts a, c, b, and d, respectively, highlighting the similarities between them and $VOPO_4$. Phosphates **1** and **3** have the same ratio V:P as $VOPO_4$ while compounds **2** and **4** possess structures that are defected and stuffed versions of the $VOPO_4$ structure, respectively.

which is filled by the piperazinium dication. All four of these regions are shown viewed parallel to chain direction in Figure 2a.

In addition to the structural features of the covalent framework discussed above, phosphate **1** contains a very large number of H-bonded interactions between the hydrogen, oxygen, and nitrogen atoms of the framework, aquo ligands, template, and P−OH groups. The framework-template hydrogen-bonded interactions result in the framework encapsulating the piperazinium dication in a manner such that the template resides in large tunnels that run parallel to the *b* axis of the unit cell as shown in Figure 5.

The magnetic susceptibility for **1** was measured over the 2−300 K temperature range. The high temperature data displayed Curie-Weiss paramagnetism and was fit to the equation $\chi = C/(T - \Theta) + \mathrm{TIP}$ with $C = 1.58$ emu K mol^{-1}, $\Theta = -19$ K, and TIP $= 3.76 \times 10^{-4}$ emu mol^{-1}. With one unpaired electron per vanadium, the fitted parameters predict an average g value of $g = 2.05$ for **1**.

Conclusions

Reaction of piperazine or piperazine precursors in reaction mixtures containining phosphoric acid and the hydrolyzate of VCl_4 has allowed the isolation of three structurally distinct layered vanadium phosphates, $H_2N(CH_2CH_2)_2NH_2[(VO)_4(OH)_4(PO_4)_2]$ **(2)**, $H_2N(CH_2CH_2)_2NH_2[(VO)_2(PO_4)_2]$ **(3)** and $(H_2N(CH_2CH_2)_2NH_2)_2[(VO)_3(HPO_4)_2(PO_4)_2]\cdot H_2O$ **(4)**, in addition to the 3-D framework material **(1)**. With the exception of compound **4**, all can be prepared as single phase materials. All four compounds are related in a general way to the parent structure of $VOPO_4$. This is illustrated in Figure 6 in which all four structures are projected along appropriate directions to emphasize their relationship to the $VOPO_4$ structure type. Layered materials **2**−**4** represent nearly equidimensional examples of “stuffed”, stoichiometrically equivalent, and defected versions of the $VOPO_4$ layer, respectively. These results serve to indicate the exquisite sensititvity of the structure of the final products on the numerous interacting reaction parameters such as time, temperature, mole ratio of reactants, pH, concentration, and nature of the template. While the syntheses discussed here are reproducible, the *a priori* design of a given framework structure and composition remains a goal for future work.

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Supporting Information Available: Tables of crystallographic data including additional experimental procedures, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** (8 pages). Ordering information is given on any current masthead page.

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