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Hydrothermal Synthesis and Crystal Structure of an Organically Templated Open-Framework Vanadium Phosphate: $(H_3NCH_2CH_2NH_3)_4[V^{III}(H_2O)_2(V^{IV}O)_6(OH)_2(HPO_4)_3(PO_4)_5]\cdot 3H_2O$

Yiping Zhang,[†,‡] Abraham Clearfield,[*,†] and Robert C. Haushalter[*,‡]

NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540, and Department of Chemistry, Texas A&M University, College Station, Texas 77843

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An ethylenediamine encapsulated open-framework vanadium phosphate, $(H_3NCH_2CH_2NH_3)_4[V^{III}(H_2O)_2(V^{IV}O)_6(OH)_2(HPO_4)_3(PO_4)_5]\cdot 3H_2O$ (**1**) has been synthesized from the hydrothermal reaction of V_2O_5:H_3PO_4:$H_2NCH_2CH_2NH_2$:H_2O in a mole ratio of 1:6.9:3.6:265 at 170 °C for 5 days, and its structure determined by single-crystal X-ray crystallography. Phosphate **1** is monoclinic, space group $C2/c$, $a = 20.674$ (2) Å, $b = 9.956$ (2) Å, $c = 23.694$ (1) Å, $\beta = 101.154$ (5) Å. $Z = 4$, $V = 4784.8$ (10) Å^3. Refinement with 3757 observed reflections for which $I \geq 3\sigma(I)$ gave $R = 0.039$ and $R_w = 0.040$. The structure consists of layers built from V(IV) square pyramids and μ_2-OH bridged V(IV) pyramids with $(HPO_4)^{2-}$ and $(PO_4)^{3-}$ tetrahedra connected together by V(III) octahedra to give rise to the formation of very large interconnected tunnels parallel to the b axis and [101] direction. The tunnels are occupied by ethylenediammonium and water molecules.

Introduction

There has been intense interest for decades in the chemistry of silicoaluminates and aluminophosphates known as zeolites and molecular sieves.[1–3] Their most interesting properties result from their unique open-framework structures.[4] While the number of synthetic aluminophosphate (AlPO) based microporous solids continue to grow,[5] recently, progress has been made toward preparing microporous solids containing transition-metal elements as in the molybdenum phosphate system[6] and titanium silicate system.[7] Their open frameworks are built from octahedral MO_6 and tetrahedral PO_4 or SiO_4, in contrast to the all tetrahedral framework of zeolites and AlPO molecular sieves. One of the more famous examples of an open-framework structure with an octahedral–tetrahedral framework is phosphate cacoxenite,[8] $AlFe_{24}O_6(OH)_{12}(PO_4)_{17}(H_2O)_{17}\cdot 51H_2O$, which contains the largest microporous openings ever observed in a solid at 14.2 Å. As compared to the Si- or Al-containing materials, these transition-metal-containing materials could have enhanced catalytic, redox, and photochemical reactivities. In addition, it would likely be easier to generate a vacant site on an octahedrally coordinated transition metal to facilitate the sorption of small molecules. We have recently extended the synthesis of organically templated open-framework materials containing transition elements to the V–P–O system. The V–P–O system has received considerable attention because of not only its application to catalysis[9] but also its rich and impressive structural chemistry associated with the ability of vanadium to have tetrahedral, square-pyramidal, and octahedral coordination environments in various oxidation states. Introduction of other inorganic and organic cations into this system leads to rather interesting and complicated structures[10–13] in which the second inorganic cations adopt a variety of coordination environments. In addition to those with 1-D polymeric chains[14,15] and 2-D layered structures,[16,17] we have been able to make compounds with three-dimensional open-framework structures by judicious choice of inorganic and organic cations. Examples include $(H_3N(CH_2)_3NH_3)K[(VO)_3(PO_4)_3]$,[18] $(H_3N(CH_2)_3NH_2)[(VO)_3(OH)_2(H_2O)_2(PO_4)_2]$,[19] chiral intertwined double helices in $(CH_3)_2NH_2K_4[(VO)_{10}$-

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[†] Texas A&M University.

[‡] NEC Research Institute.

[*] To whom all correspondence should be addressed.

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Table 1. Crystallographic Data for 1

empirical formula	$V_7P_8O_{45}N_8C_8H_{55}$
FW	1587.94
a, Å	20.674(2)
b, Å	9.956(2)
c, Å	23.694(1)
β, deg	101.154(6)
V, Å^3	4784.8(10)
Z	4
space group	$C2/c$
D_c, g/cm^3	2.20
T, °C	20 ± 1
λ(Mo Kα), Å	0.7107
trans coeff	0.94−0.99
no. of reflections ($I \geq 3\sigma(I)$)	3757
no. of variables	345
R	0.039
R_w	0.040
goodness of fit	1.60
max shift/error	0.01
max peak in final diff map	0.48 e$^-$/Å^3
min peak in final diff map	−0.50 e$^-$/Å^3

$(H_2O)_2(OH)_4(PO_4)_7]\cdot 4H_2O$,[20] and very large ethylenediamine-filled tunnels in $(H_3N(CH_2)_2NH_3)_2(NH_3(CH_2)_2NH_2)[V(H_2O)_2(VO)_8(OH)_4(HPO_4)_4(PO_4)_4]\cdot 2H_2O$.[21] We report here the synthesis and structural characterization of another ethylenediammonium encapsulated vanadium phosphate, $(H_3NCH_2CH_2NH_3)_4[V^{III}(H_2O)_2(V^{IV}O)_6(OH)_2(HPO_4)_3(PO_4)_5]\cdot 3H_2O$ (**1**) which contains the largest fraction of organic material of any known open-framework vanadium phosphate.

Experimental Section

Synthesis. Blue bipyramidal-shaped crystals of compound **1** were obtained in 57% yield from hydrothermal reaction of V_2O_5:H_3PO_4:$H_2NCH_2CH_2NH_2$:H_2O in the mole ratio of 1:6.9:3.6:265 at 170 °C for 5 days. Reactions under different conditions with other vanadium sources also yielded compound 1 with minor impurity phases. Large good-quality crystals were obtained as the major product from hydrothermal reaction of VO_2:CuO:H_3PO_4:$H_2NCH_2CH_2NH_2$:H_2O in a mole ratio of 1:0.7:6.9:3.6:265 at 160 °C for 4 days.

X-ray Crystallographic Study. A blue crystal of **1** having approximate dimensions of 0.2 × 0.2 × 0.4 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation and a 18 *kW* rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 reflections in the range $20.49° \leq 2\theta \leq 29.91°$ corresponded to a monoclinic cell. On the basis of the systematic absences (hkl: $h + k \neq 2n$; $h0l$: $l \neq 2n$) and the successful solution and refinement of the structure, the space group was determined to be $C2/c$. The data were collected out to 60° in 2θ using the $\omega - 2\theta$ scan technique at a speed of 16°/min in ω. A total of 7532 reflections were measured of which 7336 were unique (R_{int} for averaging equivalent reflections is 0.041). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection. An empirical absorption correction based on ψ scans was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.[22] The non-hydrogen atoms were refined anisotropically. Most of the hydrogen atoms were located from difference Fourier maps and included in the refinement with fixed positional and thermal parameters. The final cycle of full-matrix least-squares refinement was based on 3757 observed reflections ($I \geq 3\sigma(I)$) and 345 variable parameters and converged with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.039$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.040$. Detailed crystallographic data are listed in Table 1.

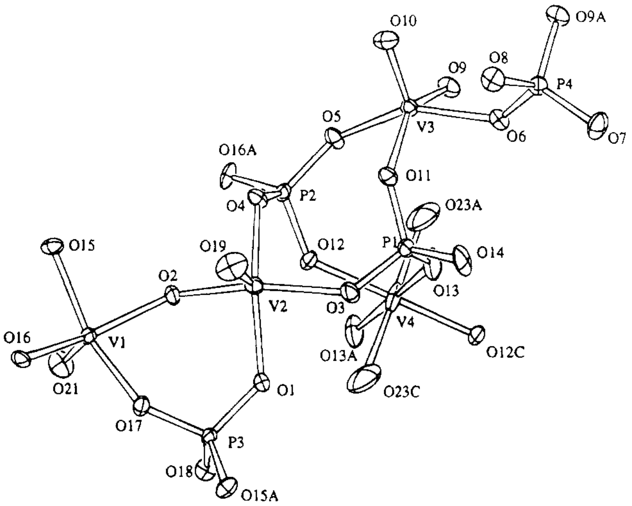

Figure 1. ORTEP drawing of the asymmetric unit in the structure of **1** showing the coordination environment of the metals and the numbering scheme used in tables. Thermal ellipsoids are at the 50% probability level.

Results

An ORTEP drawing of the asymmetric unit of the structure is shown in Figure 1. Atomic positions and thermal parameters are provided in Table 2. Selected bond distances and angles are listed in Tables 3 and 4, respectively. The V(3) atom has a typical square-pyramidal configuration consisting of four phosphate oxygens at distances in the range 1.942(3)−2.013(3) Å, and one apical vanadyl oxygen (O(10)) at a distance of 1.584(3) Å. The V(1) and V(2) atoms have a similar square pyramidal coordination environment as that of V(3), except that these two vanadium pyramids share an OH group (O(2)). This μ_2-OH group is at an equal distance of 1.977(3) Å to both of the vanadium centers. The V(4) atom which sits on the inversion center, however, is in a fairly regular octahedral configuration (as indicated by the bond distances and angles in Tables 3 and 4) consisting of four phosphate oxygen atoms and two water molecules with all six V−O distances in the range 1.967(3)−2.004(4) Å. Such a regular octahedral coordination is usually preferred by V(III) and is consistent with the valence sum calculation.[23] There are four types of phosphate groups in terms of bonding

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Table 2. Positional Parameters and *B*(eq) for 1

atom	x	y	z	B(eq)
V(1)	0.77857(4)	0.09001(8)	0.72247(3)	0.97(1)
V(2)	0.67397(4)	0.09421(8)	0.82721(3)	1.19(2)
V(3)	0.56010(4)	0.42283(8)	0.93582(3)	1.08(2)
V(4)	0.25	0.25	0.5	1.93(3)
P(1)	0.60686(6)	0.1282(1)	0.93943(5)	1.25(2)
P(2)	0.68951(6)	0.3841(1)	0.87628(5)	1.03(2)
P(3)	0.78557(6)	0.1253(1)	0.82501(5)	0.97(2)
P(4)	0.44246(6)	0.3142(1)	0.99566(5)	1.14(2)
O(1)	0.7346(2)	−0.0541(4)	0.8545(1)	1.72(7)
O(2)	0.7426(2)	0.1634(3)	0.7874(1)	1.43(7)
O(3)	0.6398(2)	0.0483(3)	0.8980(2)	1.87(8)
O(4)	0.6514(1)	0.2895(3)	0.8298(1)	1.26(7)
O(5)	0.6420(2)	0.4627(3)	0.9060(1)	1.40(7)
O(6)	0.5148(2)	0.3413(3)	0.9956(1)	1.32(7)
O(7)	0.4340(2)	0.2131(4)	1.0415(1)	2.04(8)
O(8)	0.4081(2)	0.2524(3)	0.9361(1)	1.66(7)
O(9)	0.5946(2)	0.5560(3)	0.9966(1)	1.48(7)
O(10)	0.5032(2)	0.4938(4)	0.8916(1)	1.86(7)
O(11)	0.5652(2)	0.2399(3)	0.9086(1)	1.37(7)
O(12)	0.7385(2)	0.2987(4)	0.9182(1)	2.10(8)
O(13)	0.6568(2)	0.1854(4)	0.9903(1)	2.44(9)
O(14)	0.5612(2)	0.0331(4)	0.9669(2)	2.71(9)
O(15)	0.7253(2)	0.2228(3)	0.6713(1)	1.37(7)
O(16)	0.7687(2)	−0.0142(3)	0.6500(1)	1.46(7)
O(17)	0.7760(2)	−0.0842(3)	0.7612(1)	1.24(6)
O(18)	0.8548(2)	−0.0893(3)	0.8562(1)	1.47(7)
O(19)	0.6177(2)	0.0355(4)	0.7772(2)	2.68(9)
O(20)	0.5	0.3771(6)	0.25	3.1(1)
O(21)	0.8531(2)	0.1392(4)	0.7340(2)	2.09(8)
O(22)	0.4524(3)	0.1932(6)	0.1664(2)	6.6(2)
O(23)	0.2781(2)	0.4271(5)	0.4760(2)	4.3(1)
N(1)	0.1364(2)	0.4803(5)	0.5893(2)	2.1(1)
N(2)	0.1188(2)	0.1730(5)	0.5964(2)	2.5(1)
N(3)	0.0663(2)	0.1130(5)	0.2286(2)	2.1(1)
N(4)	0.8070(2)	0.2385(5)	0.5726(2)	2.4(1)
C(1)	0.0864(3)	0.4070(6)	0.6166(3)	2.8(1)
C(2)	0.1103(3)	0.2723(6)	0.6411(2)	2.4(1)
C(3)	0.0168(3)	0.2213(6)	0.2241(2)	2.0(1)
C(4)	0.7462(3)	0.2189(7)	0.5277(2)	3.2(1)

[a] $B_{eq} = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

Table 3. Selected Bond Distances (Å)

V(1)–O(2)	1.973(3)	V(1)–O(15)	1.977(3)
V(1)–O(16)	1.982(3)	V(1)–O(17)	1.967(3)
V(1)–O(21)	1.589(3)	V(2)–O(1)	1.963(3)
V(2)–O(2)	1.974(3)	V(2)–O(3)	1.995(3)
V(2)–O(4)	2.003(3)	V(2)–O(19)	1.601(4)
V(3)–O(5)	1.998(3)	V(3)–O(6)	2.013(3)
V(3)–O(9)	1.985(3)	V(3)–O(10)	1.583(3)
V(3)–O(11)	1.942(3)	V(4)–O(12)	1.967(3)
V(4)–O(12)C	1.967(3)	V(4)–O(13)	2.003(3)
V(4)–O(13)A	2.003(3)	V(4)–O(23)A	1.974(5)
V(4)–O(23)C	1.974(5)	P(1)–O(3)	1.523(3)
P(1)–O(11)	1.507(3)	P(1)–O(13)	1.537(4)
P(1)–O(14)	1.565(4)	P(2)–O(4)	1.544(3)
P(2)–O(5)	1.529(3)	P(2)–O(12)	1.532(3)
P(2)–O(16)A	1.539(3)	P(3)–O(1)	1.544(3)
P(3)–O(15)A	1.534(3)	P(3)–O(17)	1.542(3)
P(3)–O(18)	1.522(3)	P(4)–O(6)	1.520(3)
P(4)–O(7)	1.515(4)	P(4)–O(8)	1.577(3)
P(4)–O(9)A	1.532(3)	N(1)–C(1)	1.511(7)
N(2)–C(2)	1.483(7)	N(3)–C(3)	1.477(7)
N(4)–C(4)	1.495(7)	C(1)–C(2)	1.506(8)
C(3)–C(3)A	1.52(1)	C(4)–C(4)A	1.49(1)

Table 4. Selected Bond Angles Involving the Non-Hydrogen Atoms of 1

O(2)–V(1)–O(15)	88.9(1)	O(2)–V(1)–O(16)	151.3(1)
O(2)–V(1)–O(17)	85.1(1)	O(2)–V(1)–O(21)	104.6(2)
O(15)–V(1)–O(16)	82.4(1)	O(15)–V(1)–O(17)	144.4(1)
O(15)–V(1)–O(21)	107.8(2)	O(16)–V(1)–O(17)	86.3(1)
O(16)–V(1)–O(21)	104.1(2)	O(17)–V(1)–O(21)	107.7(2)
O(1)–V(2)–O(2)	87.0(1)	O(1)–V(2)–O(3)	81.8(1)
O(1)–V(2)–O(4)	149.0(1)	O(1)–V(2)–O(19)	107.1(2)
O(2)–V(2)–O(3)	152.4(2)	O(2)–V(2)–O(4)	82.5(1)
O(2)–V(2)–O(19)	105.1(2)	O(3)–V(2)–O(4)	94.2(1)
O(3)–V(2)–O(19)	102.4(2)	O(4)–V(2)–O(19)	103.7(2)
O(5)–V(3)–O(6)	150.6(1)	O(5)–V(3)–O(9)	85.0(1)
O(5)–V(3)–O(10)	104.5(2)	O(5)–V(3)–O(11)	88.0(1)
O(6)–V(3)–O(9)	84.9(1)	O(6)–V(3)–O(10)	104.9(2)
O(6)–V(3)–O(11)	85.3(1)	O(9)–V(3)–O(10)	107.4(2)
O(9)–V(3)–O(11)	146.3(1)	O(10)–V(3)–O(11)	106.3(2)
O(12)–V(4)–O(12)C	180.00	O(12)–V(4)–O(13)	92.1(1)
O(12)–V(4)–O(13)A	87.9(1)	O(12)–V(4)–O(23)A	85.6(2)
O(12)–V(4)–O(23)C	94.4(2)	O(12)–V(4)–O(13)	87.9(1)
O(12)–V(4)–O(13)A	92.1(1)	O(12)–V(4)–O(23)A	94.4(2)
O(12)–V(4)–O(23)C	85.6(2)	O(13)–V(4)–O(13)A	180.00
O(13)–V(4)–O(23)A	90.6(2)	O(13)–V(4)–O(23)C	89.4(2)
O(13)A–V(4)–O(23)A	89.4(2)	O(13)A–V(4)–O(23)C	90.6(2)
O(23)–V(4)–O(23)	180.00	O(3)–P(1)–O(11)	111.0(2)
O(3)–P(1)–O(13)	112.5(2)	O(3)–P(1)–O(14)	109.5(2)
O(11)–P(1)–O(13)	110.0(2)	O(11)–P(1)–O(14)	108.2(2)
O(13)–P(1)–O(14)	105.4(2)	O(4)–P(2)–O(5)	110.8(2)
O(4)–P(2)–O(12)	107.9(2)	O(4)–P(2)–O(16)A	111.2(2)
O(5)–P(2)–O(12)	112.8(2)	O(5)–P(2)–O(16)A	108.1(2)
O(12)–P(2)–O(16)A	106.0(2)	O(1)–P(3)–O(15)A	107.8(2)
O(1)–P(3)–O(17)	110.6(2)	O(1)–P(3)–O(18)	109.4(2)
O(15)A–P(3)–O(17)	109.0(2)	O(15)A–P(3)–O(18)	109.9(2)
O(17)–P(3)–O(18)	110.1(2)	O(6)–P(4)–O(7)	111.7(2)
O(6)–P(4)–O(8)	109.9(2)	O(6)–P(4)–O(9)A	111.4(2)
O(7)–P(4)–O(8)	107.0(2)	O(7)–P(4)–O(9)A	110.1(2)
O(8)–P(4)–O(9)A	106.7(2)	N(1)–C(1)–C(2)	113.2(4)
N(2)–C(2)–C(1)	113.3(5)	N(3)–C(3)–C(3)A	111.1(4)
N(4)–C(4)–C(4)A	110.8(6)		

modes. The atom P(1) has its two oxygens (O(3) and O(11)) bridging V(2) and V(3) and one oxygen atom (O(13)) bonded to V(4). The atom O(14) is terminal and not bonded to any metal centers. The atom P(2) has its four oxygen atoms bonded to V(1), V(2), V(3), and V(4). The atom P(3) connects three vanadium atoms through its three phosphate oxygen atoms, O(1), O(15)A, and O(17). The atom P(4) has only two oxygen atoms (O(6) and O(9)A) bonded to two vanadium atoms. The other two oxygens (O(7) and O(8)) are not involved in bonding with any vanadium atoms. Thus the infinite 3-D structure is constructed from these V(IV) pyramids, corner-sharing V(IV) pyramids, and V(III) octahedra, $(PO_4)^{3-}$ and $(HPO_4)^{2-}$ tetrahedra. A view of the structure down the *b* axis is provided in Figure 2. The overall structure can be described as layers parallel to the [101] plane, constructed from V(IV) square pyramids and phosphate tetrahedra, linked into a three-dimensional network by V(III) octahedra. A view perpendicular to the plane of the layer is shown in Figure 3. The layer is built from the intergrowth of two kinds of chains: one of them contains two μ_2-OH bridged vanadium pyramids connected through phosphate tetrahedra into infinite chains running along the *b* axis. The other kind of chain involves separated vanadium pyramids bridged through phosphate oxygen atoms. The two kinds of chains are interconnected in such a way to give rise to the formation of rectangular-shaped 16-member rings containing eight vanadium pyramids and eight phosphate tetrahedra. There are four polar P–OH groups protruding into the center region of the rings. In fact, these P–OH groups are strongly hydrogen bonded with an O- -O contact of 2.463(5) Å as indicated by dashed lines in Figure 3, whereas the side regions of the rings possess less polar V=O vanadyl groups and P–O moieties. The V- -V distance of the two vanadyl pyramids at two long sides of the ring is 17.29 Å. These rings run in a zigzag fashion with each of the rings surrounded by six neighboring rings.

These layers containing the large holes are connected together by the V(III) centers to form a three-dimensional network structure. These V(III) octahedra serve

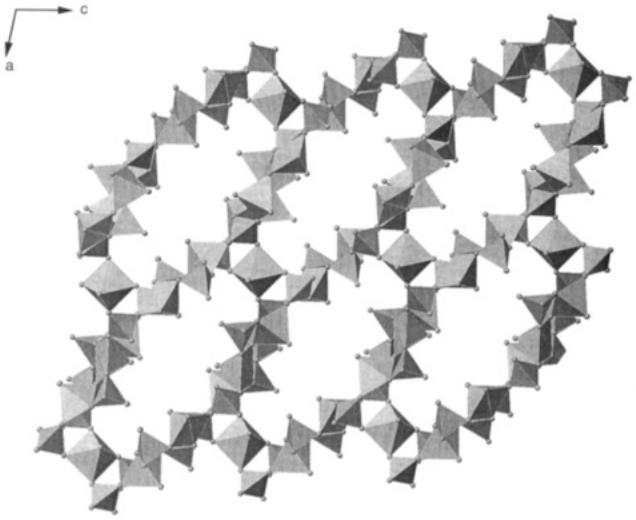

Figure 2. View down the crystallographic *b* axis showing the large tunnels running through the *b* axis. Ethylenediamine and water molecules in the tunnels are omitted for clarity.

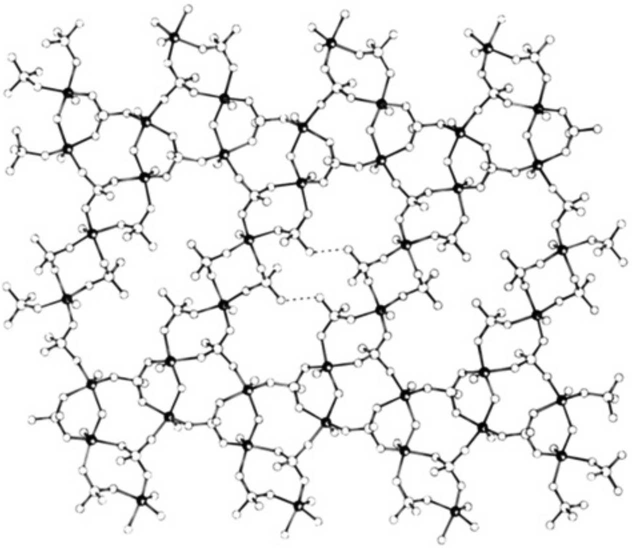

Figure 3. Top view of one layer of compound **1** showing 16-member rings containing eight vanadium pyramids and eight phosphate tetrahedra as the basic building blocks of the layers. Dashed lines indicate hydrogen bonds.

as tether points to hold the layers together. The V(III) centers are separated from each other by a distance of 17.3 Å along the [101] direction and 9.96 Å along the *b* axis to give rise to the formation of interconnected large tunnels running along both the *b* axis and the [101] direction. These tunnels are occupied by ethylenediammonium cations and water molecules as shown in Figure 4. The tunnels running along the [101] directions are filled with one-quarter of the amines, whereas three-quarters of the amines and the water molecules occupy the larger tunnels along the *b* axis. The amine molecules are surprisingly well ordered in these tunnels. This stands in contrast to those organic molecules in the open-framework structures in the Al−P−O system, where the organic molecules are usually severely disordered. The ordering of the organic amine molecules in this structure can be, to a great extent, attributed to the formation of extensive hydrogen bonds among the P−OH groups, the framework oxygens, and the amine molecules. A list of short O- -O and O- -N contacts provided in Table 5 indicates possible hydrogen bonds.

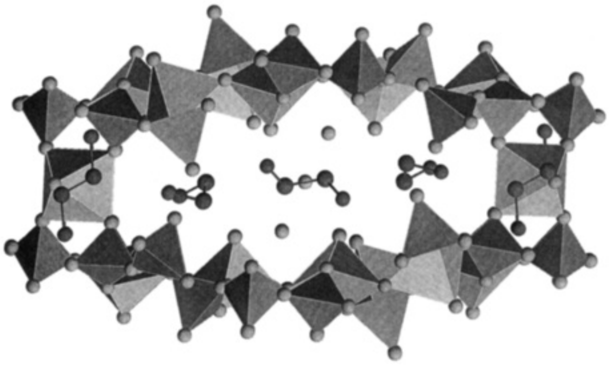

Figure 4. View down one of the tunnels showing possible hydrogen bonds among the template, water molecules, and the oxide framework.

Table 5. List of Short O- -O and O- -N Contacts (Å) Indicating Possible Hydrogen Bonds

O(1)	N(4)[a]	2.927(6)	O(5)	N(4)[b]	2.950(6)
O(8)	N(1)[c]	2.888(5)	O(7)	O(14)[d]	2.463(5)
O(8)	O(18)[e]	2.544(5)	O(16)	N(1)[f]	2.832(5)
O(18)	N(3)[g]	2.833(5)	O(20)	O(22)	2.737(6)
O(18)	N(2)[h]	2.853(6)	O(20)	N(3)[i]	2.814(7)
O(6)	N(2)[i]	2.894(5)	O(7)	N(4)[k]	2.900(6)
O(4)	N(3)[j]	2.856(5)	O(13)	N(1)[j]	2.963(6)

[a] Atom related by $1.5 - x, -0.5 + y, 1.5 - z$. [b] Atom related by $1.5 - x, 0.5 + y, 1.5 - z$. [c] Atom related by $0.5 - x, -0.5 + y, 1.5 - z$. [d] Atom related by $1 - x, y, 2 - z$. [e] Atom related by $-0.5 + x, 0.5 + y, z$. [f] Atom related by $0.5 + x, -0.5 + y, z$. [g] Atom related by $2 - x, -y, 2 - z$. [h] Atom related by $1 - x, y, 1.5 - z$. [i] Atom related by $0.5 + x, 0.5 + y, z$. [j] Atom related by $0.5 + x, 0.5 - y, 0.5 + z$. [k] Atom related by $-0.5 + x, 0.5 - y, 0.5 + z$.

Thermogravimetric analysis (TGA), carried out at a heating rate of 10 °C/min, of compound **1** shows a weight loss of 4% in the temperature range 150−300 °C, a second weight loss of 15% in the temperature range 300−500 °C with maximum rate of loss around 350 °C. These two weight losses correspond to the release of the water molecules (calculated value of 3.9%) and organic amines (calculated value of 17.4%), respectively. The compound continues to lose weight gradually until 750 °C where a third major loss (ca. 8%) occurs. Powder X-ray diffraction study on the dark green sample obtained from calcination of compound 1 at 400 °C for 10 h indicated that the framework structure had collapsed upon loss of the water molecules and diammonium cations.

Discussion

The compound described here is a second example of ethylenediamine encapsulated open-framework structures of vanadium phosphates. The other example, $(H_3N(CH_2)_2NH_3)_2(NH_3(CH_2)_2NH_2)[V(H_2O)_2(VO)_8(OH)_4(HPO_4)_4(PO_4)_4]\cdot H_2O$,[21] V_9P_8-en, synthesized from the hydrothermal reaction of V_2O_5, V metal, ethylenediamine, $H_2O_3PCH_3$, and H_3PO_4, has similar structural features. While there are structural similarities between these two phosphates, the detailed polyhedral connectivity with the V(IV) layers differs substantially. Compound **1** has a V:P ratio of 7:8, whereas V_9P_8-en has a value of 9:8. The layers in the structure of V_9P_8-en are built from domed 8-member rings which contain four vanadium pyramids and four phosphate tetrahedra (Figure 5). In compound **1**, however, the layers are built from rectangular-shaped 16-member rings containing eight vanadium pyramids and eight phosphate tetra-

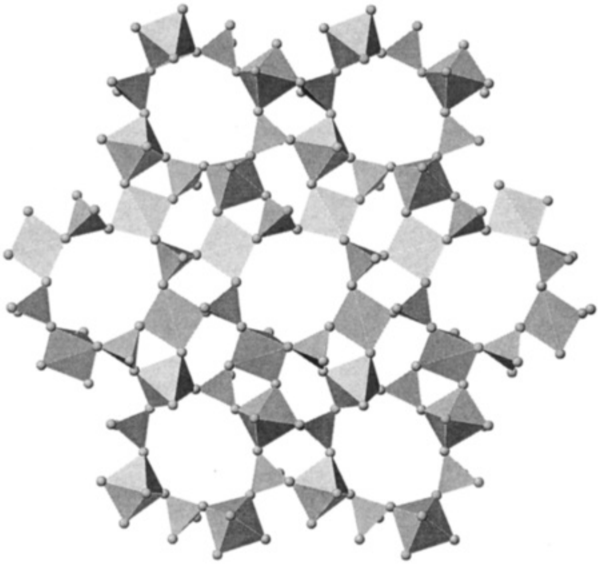

Figure 5. Top view of one layer of compound V_9P_8-en showing the domed 8-member rings containing four vanadium pyramids and four phosphate tetrahedra as the basic building blocks of the layers.

hedra. If two more vanadium pyramids are inserted in the middle region of each 16-member ring, two domed 8-member rings are formed. Compound **1** has a more open framework and contains a larger fraction of organic material than V_9P_8-en. It has been found that monophasic V_9P_8-en can also be synthesized from reactions of V_2O_5, H_3PO_4, and ethylenediamine under hydrothermal conditions.[24]

The introduction of different organic and inorganic templates into the V−P−O system leads to different structures which are very sensitive not only to the nature of the templates incorporated but also to reaction conditions. When diaminopropane is used for replacement of ethylenediamine, there is evidence that a compound with similar composition and open-framework to those of V_9P_8-en can be made. However, in most cases, a different compound with composition of $(H_3N(CH_2)_3NH_2)[(VO)_3(OH)_2(H_2O)(PO_4)_2]$ is formed.[19] The use of piperazine as the organic temperate often leads to layered vanadium phosphates with the organic cations in between the layers.[16] The reaction pathways of self-assembly of these small inorganic and organic precursors into solid-state materials remains unclear at this point. However, by judicious choice of inorganic and organic cations, we have been able to make 1-D, 2-D, and 3-D materials from simple small molecules in V−P−O system by hydrothermal reactions. By using the same ethylenediamine template, but a minor change in the reaction conditions, a new one-dimensional chain type compound of composition $(H_3NCH_2CH_2NH_3)[V(OH)(HPO_4)_2]\cdot H_2O$ has been made. Its synthesis, structure, and magnetic properties will be presented in a future publication.

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Supplementary Material Available: Tables listing of atomic coordinates including H atoms and anisotropical thermal parameters for the non-hydrogen atoms (25 pages); listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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(24) Zhang, Y.; Haushalter, R. C.; Clearfield, A., unpublished results.