Crystal Growth, Structure, and Properties, of a new Oxovanadium(IV) Phosphate Material,
[H₂en]₄[V₇P₈O₃₅(OH)₆(H₂O)]·3H₂O Prepared via a Mild One Step Hydrothermal Route

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ABSTRACT

One new oxovanadium(IV) phosphate material, $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ was prepared utilizing a one step, mild hydrothermal route involving ethylenediamine as the reducing agent. The compound was structurally characterized by single crystal and powder X-ray diffraction methods and found to crystallize in the monoclinic space group $C2/c$. The temperature dependence of the magnetic susceptibility of was measured and found to be paramagnetic down to 2K. The compound was further characterized by IR and UV-Vis spectroscopies.

INTRODUCTION

Vanadium containing compounds have been investigated for a variety of applications, including as magnetic materials¹⁻⁴, for catalysts⁵⁻⁸, and as cathode materials⁹⁻¹². In these applications the oxidation state of vanadium can range from fully oxidized to reduced. The chemistry of vanadium is rich with many accessible oxidation states, including +5, +4, +3, and +2, where color can be utilized to distinguish and confirm the oxidation states of the vanadium species. In an aqueous solution, vanadium can exist in oxidation states from +2 to +5 with colors ranging from yellow (V^{5+}), blue (V^{4+}), green (V^{3+}), and lilac (V^{2+}).¹³⁻¹⁸ It is possible to reduce aqueous vanadium species using organic reducing agents, where the combination of organic reagent and temperature determine the final vanadium oxidation state. We have recently reported on a convenient two-step hydrothermal method that facilitates the formation of hybrid materials containing metal cations in reduced states.¹⁹⁻²⁴ In the case of those reactions, the rate of metal reduction is slow relative to the crystallization of an unwanted species, and the use of the two-step approach is extremely effective for obtaining the desired reduced products.

To create the title compound, $[H_2en]_4[V_7P_8O_{35}(OH)_6(H_2O)] \cdot 3H_2O$, we wanted to explore use of more soluble vanadium precursors and stronger reducing agents to perform a one step reaction involving an *in situ* reduction followed by product crystallization. To that end, reactions were devised using ethylenediamine, a well known, strong reducing agent.²⁵ Ethylenediamine has also been shown to be an effective templating agent for porous structures, often residing in channels as protonated ions.^{26, 27} Concentrated phosphoric acid can be used to help solubilize vanadium precursors and as a source of phosphate ligands for the formation of a three dimensional inorganic framework. Several oxovanadium(IV) phosphates have been prepared using similar methods, including $(C_2H_{10}N_2)_4[H_2Ni(H_2O)_2(VO)_8(OH)_4(PO_4)_8]$ ²⁸,

$(\text{C}_2\text{H}_8\text{N}_2)[(\text{VO})(\text{VOH})(\text{PO}(\text{OH})_3)](\text{PO}_4)_2$ ²⁹, $(\text{C}_2\text{H}_{10}\text{N}_2)(\text{C}_2\text{H}_9\text{N}_2)_2[(\text{VO})_4(\text{PO}_4)_4(\text{H}_2\text{O})]$ ³⁰, and $(\text{C}_2\text{H}_{10}\text{N}_2)[(\text{HVO}_3)(\text{HVO}_2)(\text{PO}_4)]$.³¹ Herein we report the synthesis, structural characterization, optical spectroscopy, and magnetic properties of the title compound.

EXPERIMENTAL SECTION

Reagents. NaVO_3 (96%, Alfa Aesar), 85% H_3PO_4 (ACS grade, Fisher), and ethylenediamine (en) (99% min, Sigma-Aldrich) were used as received.

Synthesis. Bright blue single crystals of $[\text{C}_2\text{H}_{10}\text{N}_2]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$, $\text{C}_2\text{H}_{10}\text{N}_2 = \text{H}_2\text{en}^{2+}$, were grown via a one step hydrothermal route. In a fume hood, 3 mmol of NaVO_3 , 1 mL of 85% H_3PO_4 , 2.4 mL of H_2O , and 1 mL of ethylenediamine were placed in a thick walled pyrex tube and sealed with a polytetrafluoroethylene (PTFE) stopper. The tube was placed inside a programmable oven and heated to 170°C at a rate of 10°C/min, held for 5 days, and slowly cooled to room temperature at a rate of 0.1°C/min. The mother liquor was decanted yielding a phase pure product in approximately 82% yield based on V_2O_5 . A powder X-Ray diffraction pattern (PXRD) of ground crystals demonstrates the phase purity of the product crystals. (See Figure S1.)

Single Crystal X-ray Diffraction. X-ray intensity data from a bright blue crystal were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$).³² The raw area detector frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.³² Final unit cell parameters were determined by least-squares refinement of 9951 reflections from the data set. Direct methods structure solution, difference Fourier calculations and full-matrix least –squares refinements against F^2 were performed with SHELXL-2014 using OLEX2.³³

The compound crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data was consistent with the space groups *Cc* and *C2/c*. The centrosymmetric group *C2/c* was confirmed by structure solution. The complex asymmetric unit consists of 3.5 vanadium atoms, four phosphorus atoms, 17 oxo oxygen atoms, three hydroxyl groups (O5, O17, O20), a disordered set of oxygen atoms bonded to V4 which were modeled as 0.5 oxo oxygen atoms and 0.5 water molecules, one interstitial water (O23), half of another interstitial water located on a crystallographic two-fold axis of rotation (O24), one complete ethylenediammonium (H_2en^{2+}) cation (C1,C2,N1,N2), and half each of two additional H_2en^{2+} cations, one located on an inversion center (C3,N3) and one located on a two-fold axis of rotation (C4,N4). There is crystallographically imposed two-fold disorder of the pseudo-octahedral $\text{V}(\text{O})\text{O}_4(\text{H}_2\text{O})$ grouping (V4) as follows. Vanadium V4 is disordered across an inversion center and only half is present per asymmetric unit. Initial refinements with V4 located on the inversion center resulted in a highly elongated displacement parameter ($U_3/U_1 = 15.6$); displacing the V4 position just off the center (0.14 Å) gave an acceptably spherical ellipsoid ($U_3/U_1 = 3.5$). The inversion symmetry also imposes disorder on the atoms coordinated axially to V4: O21 (V4-O21 = 1.604(7) Å) and water molecule O22 (V4-O22 = 2.320(7) Å), but does not disorder the equatorial oxygen atoms O16 and O18, which are consistent with inversion symmetry. V4, O21 and O22 were refined with fixed occupancy values of 0.5; the nearly superimposed O21/O22 atoms were assigned common displacement parameters. Identical 50/50 oxo/water scrambling was observed upon trial refinements in the acentric space group *Cc*, which lacks inversion symmetry, and therefore *C2/c* was retained as the proper space group. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon and nitrogen (H_2en^{2+} hydrogens) were located in difference maps before being included as riding atoms with refined isotropic

displacement parameters. Water and hydroxyl hydrogen atoms were located in difference maps and refined isotropically. All O-H distances were restrained to be approximately equal using a SHELX SADI restraint. The largest residual electron density peak in the final difference map is $0.50 \text{ e}^-/\text{\AA}^3$, located $0.76 \text{ \AA}$ from C4. Crystallographic data, selected interatomic distances, and select hydrogen bonding distances are listed in Tables 1, 2, and 3 respectively.

Powder X-ray diffraction (PXRD). Powder X-ray diffraction data were collected on a Rigaku D/Max-2100 powder X-ray diffractometer using Cu K α radiation. The step scan covered the angular range $5\text{-}45^\circ 2\theta$ in steps of 0.04° . No impurities were observed and the calculated and experimental PXRD patterns are in excellent agreement (See Figure S1).

Energy-Dispersive Spectroscopy (EDS). Elemental analysis was performed on the single crystals using a TESCAN Vega-3 SBU scanning electron microscope (SEM) with EDS capabilities. The crystals were mounted on carbon tape and analyzed using a 20 kV accelerating voltage and an accumulation time of 1 minute. As a qualitative measure, EDS confirmed the presence of each reported element in the title compounds.

Infrared Spectroscopy. The IR spectrum of ground crystals of $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ was recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer fitted with an ATR accessory in the range of $650\text{-}4000 \text{ cm}^{-1}$.

UV-Vis Spectroscopy. UV-Vis diffuse reflectance spectroscopy data of ground crystals of $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ was obtained using a PerkinElmer Lambda 35 UV-Vis scanning spectrophotometer equipped with an integrating sphere accessory in the range of $200\text{-}900 \text{ nm}$. Reflectance data were transformed to absorbance via the Kubelka-Munk function.³⁴

Magnetic Susceptibility. The magnetic susceptibility of $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ was measured using a Quantum Design MPMS SQUID VSM Evercool magnetometer. The zero-field cooled magnetic susceptibility was measured as a function of temperature between 2-300K in an applied field of 1000 Oe. The measured magnetic data were corrected for shape and radial offset effects using methods reported by Morrison et. al.³⁵

RESULTS AND DISCUSSION

Synthesis. A number of reduced oxovanadium(IV) phosphate materials have been synthesized under acidic mild hydrothermal conditions using ethylenediamine as an *in situ* reducing agent and templating agent. Crystals of $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ were obtained via such a method. Initial reactions using vanadium(V) oxide as a vanadium source resulted in an amorphous brown powder. Reactions using sodium metavanadate resulted in single crystals of $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$, most likely due to the superior solubility of sodium metavanadate at elevated temperatures when compared with vanadium(V) oxide. An increased dwell time was found to dramatically improve the product yield, with dwells of 5 days yielding a phase pure product in approximately 82% yield.

Structure. $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ crystallizes in the monoclinic space group $C2/c$ and exhibits a porous three-dimensional crystal structure consisting of distorted $\text{VO}_4(\text{OH})$ and VO_5 square pyramids linked via bridging phosphate ligands that form 2D sheets which are linked via $\text{VO}_5(\text{H}_2\text{O})$ octahedra. Channels that form in the (010) and (101) directions are filled with hydrogen bonded interstitial waters and H_2en^{2+} ions. The extended structure of $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ viewed down the b -axis and (101) direction is shown in Figures 1 and 2. V(1) and V(2) are located in distorted $\text{VO}_4(\text{OH})$ square pyramids with four

equatorial V-O bonds of roughly the same length and one exceptionally short V-O axial bond. Three out of five oxygens bonded to V(1), O2, O3, and O4, originate from bridging phosphate ligands; one, O5, from a bridging hydroxide; and one, O1, is a monodentate oxo atom. Three out of five oxygens bonded to V(2), O7, O8, and O9, originate from bridging phosphate ligands; one, O5, from a bridging hydroxide; and one, O6, is a monodentate oxo atom. The V-O bond distances of V(1) and V(2) range from 1.5870(12) Å – 2.0111(12) Å. Polyhedral representations of V(1) and V(2) are shown in Figure 3. V(3) is located in a distorted VO₅ distorted square pyramid with four equatorial V-O bonds of roughly the same length and one exceptionally short V-O axial bond. Four out of five oxygens bonded to V(3), O(11), O(12), O(13), and O(14), originate from bridging phosphate ligands. The remaining oxygen, O(10), is a monodentate oxo atom. V(4) is located in a distorted VO₅(OH) octahedron with four equatorial V-O bonds of roughly the same length and one exceptionally long and one exceptionally short V-O axial bond. Four out of six oxygens bonded to V(4), two O(16) and two O(18), originate from bridging phosphate ligands; one, O(22), from a monodentate water; and one, O21, is a monodentate oxo atom. Polyhedral representations of V(3) and V(4) are shown in Figure 4. Channels that form in the (010) and (101) directions are filled with interstitial waters and H₂en²⁺ ions that are held by hydrogen bonds with distances ranging from 1.722(19) Å – 2.31(3) Å. V(1), V(2), and V(3) form 2D sheets via bridging phosphate ligands shown in Figure 5. Select hydrogen bond distances are given in Table 3. Bond valence sums for each vanadium site were calculated found to be 4.07 for V(1), 3.98 for V(2), 4.02 for V(3), and 4.15 for V(4),^{36, 37} confirming the oxidation state of V as +4 and being consistent with the compositions obtained by single crystal X-ray diffraction.

Infrared Spectroscopy. The IR spectrum for [H₂en]₄[V₇P₈O₃₅(OH)₆(H₂O)]·3H₂O which is shown in Figure S2, was collected between 650 – 4000 cm⁻¹. The broad band observed in the

3200 – 3600 cm^{-1} region is characteristic for O-H vibrations of water molecules and hydroxyl groups. The presence of phosphate groups produces P-O vibrations. The expected bending mode of water at around 1600 cm^{-1} is observed. Bands between 1600 cm^{-1} and 100 cm^{-1} are attributed to bending and stretching modes of ethylenediamine.³⁸ The intense band around 1000 cm^{-1} is attributed to the asymmetric stretching and bending modes of the phosphate P-O bonds.³⁹

UV-VIS. UV-Vis absorbance data shown in Figure 6 was collected using ground crystals of $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$. Vanadium in the +4 oxidation state has a d^1 electron configuration and a transition from the $^2\text{T}_{2g}$ ground state to the $^2\text{E}_g$ excited state is expected. Three absorption maxima are observed for each compound approximately located at 401 nm, 627 nm, and 775 nm and can be assigned to $d_{xy} \rightarrow d_z^2$, $d_{xy} \rightarrow d_{x^2-y^2}$, and $d_{xy} \rightarrow d_{xz}/d_{yz}$ transitions of V(4), respectively.^{40, 41}

Magnetism. The unpaired electrons in $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ can be observed in magnetic susceptibility measurements. The temperature dependences of the magnetic susceptibilities measured in an applied field of 1000 Oe, are shown in Figure 7. As the vanadium polyhedra are separated by bridging phosphate ligands, due to the long V-V separation, no magnetic coupling is expected or observed. Down to 2K, the data do not reveal any long-range magnetic order and follow the Curie-Weiss (C-W) law as expected for simple paramagnetic species. The magnetic moment calculated from the inverse susceptibility is 1.72 μ_B , which is in good agreement with the expected value of 1.73 μ_B for a $3d^1$ spin-only system.⁴²

CONCLUSION

We have successfully synthesized and characterized the new oxovanadium(IV) phosphate material, $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ utilizing a one step, mild hydrothermal technique.

Vanadium in this structures is in the +4 oxidation state. The structure exhibits phosphate bridged vanadium(IV) polyhedra and exhibits simple paramagnetic behavior due to long V-V distances.

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Table 1. Crystallographic Data for [H₂en]₄[V₇P₈O₃₅(OH)₆(H₂O)]·3H₂O

formula weight	1586.93
temperature (K)	100(2)
crystal system	monoclinic
space group	<i>C2/c</i>
<i>a</i> (Å)	20.6241(9)
<i>b</i> (Å)	9.9553(5)
<i>c</i> (Å)	23.6628(11)
β (°)	101.1608(16)
volume Å ³	4766.5(4)
<i>Z</i>	4
density (g/cm ³)	2.211
abs coeff (mm ⁻¹)	1.714
<i>R</i> (int)	0.0400
<i>R</i> (<i>F</i>) ^a	0.0217
<i>R</i> _w (<i>F</i> _o ²) ^b	0.0534
^a <i>R</i> (<i>F</i>) = $\Sigma F_o - F_c /\Sigma F_o $	
^b <i>R</i> _w (<i>F</i> _o ²) = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$	

Table 2. Selected Interatomic distances (Å) for [H₂en]₄[V₇P₈O₃₅(OH)₆(H₂O)]·3H₂O

V(1)–O(1)	1.5870(12)	V(2)–O(9)	2.0111(12)	V(4)–O(18)	1.984(9)	P(2)–O(17)	1.5565(13)
V(1)–O(2)	1.9700(11)	V(3)–O(10)	1.5916(12)	V(4)–O(21)	1.863(7)	P(3)–O(3)	1.5410(12)
V(1)–O(3)	1.9834(12)	V(3)–O(11)	1.9408(12)	V(4)–O(22)	2.070(7)	P(3)–O(9)	1.5391(12)
V(1)–O(4)	1.9788(11)	V(3)–O(12)	1.9970(12)	P(1)–O(2)	1.5437(11)	P(3)–O(12)	1.5296(12)
V(1)–O(5)	1.9748(11)	V(3)–O(13)	1.9820(11)	P(1)–O(4)	1.5349(12)	P(3)–O(18)	1.5304(12)
V(2)–O(5)	1.9778(12)	V(3)–O(14)	2.0170(11)	P(1)–O(7)	1.5457(12)	P(4)–O(13)	1.5337(12)
V(2)–O(6)	1.5918(12)	V(4)–O(16)	2.071(8)	P(2)–O(8)	1.5224(12)	P(4)–O(14)	1.5272(12)
V(2)–O(7)	1.9735(12)	V(4)–O(16)	1.955(9)	P(2)–O(11)	1.5103(12)	P(4)–O(19)	1.5196(12)
V(2)–O(8)	1.9955(12)	V(4)–O(18)	1.965(9)	P(2)–O(16)	1.5396(14)	P(4)–O(20)	1.5766(12)

Table 3. Hydrogen Bond distances (Å) for [H₂en]₄[V₇P₈O₃₅(OH)₆(H₂O)]·3H₂O

H(5)–O(2)	1.974(18)	H(23B)–O(19)	2.04(2)	H(2A)–O(15)	1.91	H(3B)–O(19)	1.96
H(17)–O(19)	1.698(19)	H(24)–O(23)	1.953(19)	H(2B)–O(14)	1.99	H(3C)–O(7)	2.01
H(20)–O(15)	1.71(3)	H(1A)–O(3)	1.93	H(2C)–O(16)	2.46	H(4A)–O(9)	1.98
H(22A)–O(7)	2.10(2)	H(1B)–O(16)	2.01	H(2C)–O(21)	2.43	H(4B)–O(15)	1.93
H(22B)–O(13)	1.96(2)	H(1B)–O(17)	2.48	H(2C)–O(22)	2.40	H(4C)–O(24)	1.89
H(23A)–O(6)	2.37(2)	H(1C)–O(20)	1.98	H(3A)–O(12)	2.23		

FIGURES

Figure 1. $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ viewed down the b -axis. V, P, N, O, C, and H shown in blue, grey, light blue, red, black, and white, respectively.

Figure 2. $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ viewed down the (101) direction. V, P, N, O, C, and H shown in blue, grey, light blue, red, black, and white, respectively.

Figure 3. Polyhedral representations of V(1) and V(1). V, P, O, and H shown in blue, grey, red, and white, respectively.

Figure 4. Polyhedral representations of V(3) and V(4). V, P, O, and H shown in blue, grey, red, and white, respectively.

Figure 5. 2D sheets formed by the connectivity of V(1), V(2), V(3), and phosphate ligands. V, P, O, and H shown in blue, grey, red, and white, respectively.

Figure 6. UV/Vis absorbance spectrum of $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$. Three absorption maxima at 401 nm, 627 nm, and 775 nm can be assigned to $d_{xy} \rightarrow d_z^2$, $d_{xy} \rightarrow d_{x^2-y^2}$, and $d_{xy} \rightarrow d_{xz}/d_{yz}$ transitions, respectively.

Figure 7. Magnetic susceptibility plot of $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$. χ and $1/\chi$ are shown in red and blue, respectively.

Graphical Abstract

A new oxovanadium(IV) phosphate material, $[\text{H}_2\text{en}]_4[\text{V}_7\text{P}_8\text{O}_{35}(\text{OH})_6(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$, was prepared utilizing a one step hydrothermal route with an ethylenediamine reducing agent.