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Synthesis and crystal structures of $(NH_3CH_2CH_2NH_3)_{1.5}[(VO)_2(HPO_4)_2(PO_4)]$ and $(C_4H_{12}N_2)_2[V_4O_6H(HPO_4)_2(PO_4)_2]$, two layered vanadium phosphates templated with organic diamines

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Abstract

Two new layered vanadium phosphates templated by ethylenediamine, $(NH_3CH_2CH_2NH_3)_{1.5}[(VO)_2(HPO_4)_2(PO_4)]$ (**1**), and piperazine, $(C_4H_{12}N_2)_2[V_4O_6H(HPO_4)_2(PO_4)_2]$ (**2**), have been synthesized hydrothermally and their structures determined by single-crystal X-ray diffraction. Compound **1** crystallizes in the monoclinic space group $C2/c$ (no. 15) with $a = 18.6051(5)$, $b = 7.1193(1)$, $c=23.4597(7)$ Å, $\beta = 96.558(2)^\circ$, $V = 3087.03$ Å^3, $Z = 8$, and $R1 = 0.0583$. The structure consists of infinite chains of *trans*-corner-shared VO_6 octahedra, which are bridged by phosphate groups. The infinite chains are connected by VO_5 square pyramids via V–O–P bonds to form layers with 10-sided windows. Adjacent layers are aligned such that infinite tunnels along the [001] direction are generated. Ethylenediammonium cations are located at sites both in the interlayer space and in the windows within the layers. Crystal data for **2**: orthorhombic, space group $Pna2_1$ (no. 33), $a = 13.1812(6)$, $b = 15.2918(8)$, $c = 6.2821(3)$ Å, $V = 1266.25$ Å^3, $Z = 2$, and $R1 = 0.0367$. Compound **2** is a mixed-valence V^{IV}/V^{V} vanadium phosphate as was confirmed by magnetic susceptibility measurements. $V^{IV}O_6$ octahedra connected via HPO_4 groups form a double chain, which alternates with a chain of *trans*-corner-shared square pyramids containing an infinite V^{IV}–O–V^{V}–O motif. Both chains are connected through phosphate groups to form a layer, which contains 14-membered empty windows. Piperazinium dications are anchored in the interlayer space.

Keywords: Vanadium phosphate; Ethylenediamine; Piperazine; Hydrothermal synthesis; Structure

1. Introduction

The vanadium–oxo–phosphate systems are under extensive study not only due to their catalytic importance [1] but also due to rich structural chemistry, which they exhibit. This is evidenced by a growing number of these systems with incorporated inorganic [2] and organic [3] species. Application of organic amines as structural directing agents or templates in the synthesis of V/P/O phases has become a convenient way for preparing new compounds with chain, layered or framework structures. The templates with the greatest versatility appear to be ethylenediamine and piperazine. With ethylenediamine as a template, six three-dimensional [4–9] and one one-dimensional [10] vanadium phosphates have been prepared. Nevertheless, to the best of our knowledge, no layered vanadium phosphate containing ethylenediamine as a template has been reported.

Two organically templated mixed-valence V^{IV}/V^{V} phosphates have been described recently: in $[H_3N(CH_2)_3NH_3][V^{IV}V^{V}_2P_2O_{13}(H_2O)_2]$ [11], two VO_6 and one VO_5 polyhedra share corners to form a trimer in which both V^{IV} and V^{V} are randomly distributed among the vanadium sites; in $(NH_3CH_2CH_2NH_3)[(VO)_2(H_2PO_4)(PO_4)_2]$ [7], $V^{IV}O_6$ and $V^{V}O_6$ octahedra are separated by PO_4 groups.

We present two new layered vanadium phosphates in this paper. One is a V^{IV} phosphate templated with ethylenediamine, and the other one is a mixed-valence V^{IV}/V^{V} phosphate with piperazine.

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2. Experimental

2.1. Synthesis and initial characterization

Synthesis was carried out in Teflon-lined acid digestion bombs with an internal volume of 23 cm^3 under autogenous pressure by heating the starting mixture at 180°C for 3 days. Compound **1**, $(NH_3CH_2CH_2NH_3)_{1.5}[(VO)_2(HPO_4)_2(PO_4)]$, was prepared from a reaction mixture of V_2O_5 (2 mmol), V (1 mmol), ethylenediamine (7.5 mmol), H_3PO_4 (15 mmol) in 9 mL of water. Immediately after mixing a voluminous precipitate was formed with pH of the reaction mixture at around 5. The hydrothermal treatment produced a mixture of blue crystals of $(H_3NCH_2CH_2NH_3)_2(H_3NCH_2CH_2NH_2)[V(H_2O)_2(VO)_8(OH)_4(HPO_4)_4(PO_4)_4(H_2O)_2]\cdot 2H_2O$ [4] and light green needles of **1**. Sufficient amount of green needles was manually separated and used for the single-crystal X-ray structure determination, and thermogravimetric and elemental analyses.

The amount of ethylenediamine in **1** determined by elemental analysis of the sample agrees well with the proposed formula. Found: C, 7.06; H, 3.15; N, 7.96%. Theoretical: C, 7.00, H, 3.31; N, 8.17%. Energy-dispersive X-ray fluorescence analysis using a JEOL analytical electron microscope confirmed the presence of V and P (39 and 61 at%, respectively).

Compound **2**, $(C_4H_{12}N_2)_2[V_4O_6H(HPO_4)_2(PO_4)_2]$, was prepared from a reaction mixture of V_2O_5 (3 mmol), piperazine (7.5 mmol), H_3PO_4 (15 mmol) in 9 mL of water. The pH value of the suspension formed was around 4. The product was a mixture of green crystals and brown plates. The green crystals were the known compound $(C_4H_{12}N_2)_2[(VO)_3(HPO_4)_2(PO_4)_2]\cdot H_2O$ [12], the brown plates were separated and used for further study. Based on the results of the structural study, the synthesis was optimized so that pure compound **2** was obtained as a mixture of powder and irregularly shaped crystals. The product was prepared from V_2O_5 (2 mmol), piperazine (3.75 mmol), H_3PO_4 (8 mmol), and 9 mL of water. The digestion bomb was filled with pure oxygen before sealing, heated at 180°C for 10 h at autogenous pressure, and then cooled to room temperature within another 10 h.

The amount of piperazine in **2** found by elemental analysis corresponds to that proposed in the formula. Found: C, 11.20; H, 3.03; N, 6.66%. Theoretical: C, 11.17, H, 3.14; N, 6.52%. The presence of V and P (48 and 52 at%, respectively) was also confirmed by EDX analysis.

Thermogravimetric analysis was performed on a Perkin-Elmer TGA 7 thermal analyzer: the samples were heated to 950°C at 10°C min^{-1} in nitrogen.

2.2. Single-crystal X-ray diffraction

Crystals of dimensions $0.05\times0.05\times0.4$ mm^3 (compound **1**) and $0.05\times0.1\times0.3$ mm^3 (**2**) were used for indexing and intensity data collection on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source. Intensity data were collected in 1271 frames for both **1** and **2** with increasing ω (width of 0.3° per frame). Number of measured and observed reflections ($F_o > 4\sigma(F_o)$): 17 219, 2209 for **1**; 7536, 2774 for **2**. Agreement between equivalent reflections (R_{int}): 0.0706 for **1** and 0.0338 for **2**. Empirical absorption corrections were applied by using the SADABS program for Siemens area detector ($T_{min,\,max} = 0.724$, 0.963 for **1**; 0.732, 0.956 for **2**). On the basis of systematic absences, statistics of intensity distribution and the successful solution and refinement of the structures, the space groups were determined to be *C*2/*c* (no. 15) for **1** and *Pna*2$_1$ (no. 33) for **2**. The structures were solved by direct methods: the V and P atoms were first located and all the O, C, and N atoms were found in different Fourier maps. The H atoms were not located. The final cycles of least-squares refinement including the atomic coordinates and anisotropic thermal parameters converged to $R1 = 0.0583$, w$R2 =$ 0.1574 and GOF = 1.049 for **1** and to $R1 = 0.0367$, w$R2 = 0.0934$ and GOF = 1.037 for **2**. Structure solution and refinement were performed by using SHELXTL Version 5 [13]. Crystallographic data are given in Table 1.

2.3. Magnetic susceptibility measurements

Variable-temperature magnetic susceptibility $\chi(T)$ data were obtained on 30 mg of polycrystalline sample of **2** from 2 to 300 K in a magnetic field of 5 kG after

Table 1
Crystallographic data for $(NH_3CH_2CH_2NH_3)_{1.5}[(VO)_2(HPO_4)_2(PO_4)]$ (**1**) and $(C_4H_{12}N_2)_2[V_4O_6H(HPO_4)_2(PO_4)_2]$ (**2**)

	1	**2**
Chemical formula	$C_3H_{17}N_3O_{14}P_3V_2$	$C_8H_{27}N_4O_{22}P_4V_4$
fw	513.99	858.97
Space group	*C*2/*c* (no. 15)	*Pna*2$_1$ (no. 33)
a (Å)	18.6051(5)	13.1812(6)
b (Å)	7.1193(1)	15.2918(8)
c (Å)	23.4597(7)	6.2821(3)
β (deg)	96.558(2)	
V (Å)^3	3087.0(2)	1266.2(2)
Z	8	2
μ(Mo$K\alpha$) (cm^{-1})	16.0	17.9
ρ_{calcd} (g cm^{-3})	2.212	2.253
λ (Å)	0.71073	0.71073
T (°C)	23	23
$R1$[a]	0.0583	0.0367
w$R2$[b]	0.1574	0.0934

[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o| \text{for} F_o > 4\sigma(F_o)$.

[b] $wR2 = \sum w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$ for all unique reflections. $w = 1/[\sigma^2(F_o^2) + (a * P)^2 + b * P]$, $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$, where $a = 0.0706$, $b = 1.77$ for **1** and $a = 0.0338$, $b = 2.66$ for **2**.

zero-field cooling on a Quantum Design SQUID magnetometer. Experimental susceptibility data were corrected for diamagnetic contributions [14] and the molar susceptibilities χ_M were then calculated. The Curie constant C and the Weiss constant θ were obtained by a least-squares fitting to the relation $\chi_M = C/(T - \theta)$ in the temperature range from 25 to 300 K.

3. Results and discussion

3.1. Thermogravimetric analysis

The decomposition of both compounds is a two-step process, which starts at 300°C and finishes at 750°C. The TGA curve for **1** showed weight loss of 26.8%, which is in a good agreement with the theoretical value of 26.3% calculated for the release of 1.5 molecules of ethylenediamine and 2.5 molecules of water from one molecule of **1**. Based on the powder X-ray diffraction, the intermediate obtained by heating **1** to 500°C is amorphous. The major product of heating to 950°C was found to be VOP_2O_6 [15]. Vanadium oxides are present probably as a mixture of amorphous V_xO_y.

A steep decrease of weight begins at 300°C during heating of **2**. A slightly slower decrease of the sample weight continues above 400°C up to 700°C. The total weight loss of 28.6% for thermal decomposition of **2** corresponds to the theoretical one of 27.4% calculated for the release of water and piperazine molecules according to the above given formula. The product of heating is amorphous.

3.2. Structure

The atomic coordinates, thermal parameters, bond lengths, and valence sums are given in Tables 2 and 3.

Compound **1***:* Both vanadium atoms are tetravalent with V(1) being five coordinated and V(2) six coordinated. Both $V(1)O_5$ square pyramid and $V(2)O_6$ octahedron are strongly distorted and have a very short V=O bond which is characteristic of the vanadyl ion VO^{2+}. Bond valence sums for O(1) and O(6) are 1.15 and 1.02, respectively, indicating that they are hydroxo oxygens of HPO_4 groups.

The structure consists of vanadium–phosphate layers in the *ab*-plane with both the intralayer space and interlamellar region filled with ethylenediammonium cations, as illustrated in the projection along *b*-axis (Fig. 1). There are two vanadium–phosphate layers within the repeat distance *c*. Each layer consists of infinite chains of *trans*-corner-sharing $V(2)O_6$ octahedra running parallel to the [010] direction (Fig. 2). These chains have alternating short and long V–O bonds. The bond angle at the shared oxygen atom, O(13), between two V(2) atoms is 134°. Adjacent octahedra within a chain are bridged by $HP(1)O_4$ and $P(3)O_4$ groups in the same way as that in one-dimensional $Na_3M(OH)(HPO_4)(PO_4)$ (M = Al, Ga) [16], $[H_2N(CH_2CH_2)_2NH_2][(VO)_2(HAsO_4)_2(H_2AsO4)_2]$ [17], and $[H_2N(CH_2CH_2)_2NH_2][(VO)(O_3P(CH_2)PO_3)]$ [18] and in three-dimensional $(H_3O)_2[(VO)V_2(OH)_2(O_3PCH_2CH_2PO_3)_2]\cdot H_2O$ [19].

Table 2
Atomic coordinates and thermal parameters (Å^2 × 100) for $(NH_3CH_2CH_2NH_3)_{1.5}[(VO)_2(HPO_4)_2(PO_4)]$ (**1**) and $(C_4H_{12}N_2)_2[V_4O_6H(HPO_4)_2(PO_4)_2]$ (**2**)

Atom	x	y	z	U_{eq}[a]
Compound **1**				
V(1)	0.48182(5)	0.4021(1)	0.35944(4)	0.0201(3)
V(2)	0.25841(5)	0.1376(1)	0.24912(4)	0.0192(3)
P(1)	0.30578(8)	0.4114(2)	0.36521(6)	0.0193(4)
P(2)	0.58901(8)	0.6481(2)	0.44529(7)	0.0217(4)
P(3)	0.38677(8)	0.4253(2)	0.22633(6)	0.0189(4)
O(1)	0.2637(2)	0.3909(6)	0.4189(2)	0.030(1)
O(2)	0.3844(2)	0.4293(6)	0.3913(2)	0.0249(9)
O(3)	0.2801(2)	0.5884(6)	0.3325(2)	0.027(1)
O(4)	0.2917(2)	0.2364(5)	0.3281(2)	0.0245(9)
O(5)	0.5142(2)	0.6032(6)	0.4132(2)	0.0248(9)
O(6)	0.5694(2)	0.7226(6)	0.5062(2)	0.031(1)
O(7)	0.6363(2)	0.4767(6)	0.4545(2)	0.027(1)
O(8)	0.6234(2)	0.8164(6)	0.4187(2)	0.031(1)
O(9)	0.3411(2)	0.2462(5)	0.2147(2)	0.0249(9)
O(10)	0.3375(2)	0.5981(6)	0.2266(2)	0.030(1)
O(11)	0.4315(2)	0.4066(8)	0.2841(2)	0.040(1)
O(12)	0.4319(2)	0.4586(6)	0.1775(2)	0.028(1)
O(13)	0.2889(2)	−0.0779(5)	0.2645(2)	0.0207(9)
O(14)	0.5010(2)	0.1944(6)	0.3843(2)	0.030(1)
N(1)	0.2475(3)	0.4226(7)	0.1044(2)	0.028(1)
N(2)	0.0826(3)	0.3422(8)	−0.0028(3)	0.035(1)
N(3)	0.4198(3)	0.9091(7)	0.1919(2)	0.027(1)
C(1)	0.2010(4)	0.402(1)	0.0488(3)	0.039(2)
C(2)	0.1211(3)	0.3745(9)	0.0574(3)	0.032(2)
C(3)	0.4982(3)	0.899(1)	0.2174(3)	0.033(2)
Compound **2**				
V(1)	0.89431(5)	0.40378(4)	0.43761	0.0117(2)
V(2)	0.47706(6)	0.47903(6)	0.6144(2)	0.0258(2)
P(1)	0.09535(8)	0.53130(7)	0.4436(2)	0.0119(2)
P(2)	0.68382(8)	0.43273(7)	0.3949(2)	0.0138(2)
O(1)	0.9858(2)	0.5043(2)	0.4167(5)	0.0182(7)
O(2)	0.8895(2)	0.4000(2)	0.1151(2)	0.0139(6)
O(3)	0.8594(2)	0.4356(2)	0.7361(5)	0.0191(7)
O(4)	0.1596(3)	0.4473(2)	0.5111(5)	0.0192(7)
O(5)	0.7494(2)	0.3505(2)	0.4237(6)	0.0135(6)
O(6)	0.6162(2)	0.4395(2)	0.5940(6)	0.0237(8)
O(7)	0.7591(2)	0.5088(2)	0.3725(5)	0.0168(7)
O(8)	0.3827(2)	0.5732(2)	0.6928(6)	0.0210(7)
O(9)	0.5184(2)	0.5577(2)	0.3888(6)	0.0222(7)
O(10)	0.4099(3)	0.4082(3)	0.4930(7)	0.039(1)
O(11)	0.9603(3)	0.3193(2)	0.4781(6)	0.0252(8)
N(1)	0.2833(4)	0.8562(3)	0.6361(8)	0.040(1)
N(2)	0.2751(3)	0.7083(3)	0.3546(7)	0.028(1)
C(1)	0.1875(4)	0.8090(3)	0.5985(9)	0.032(1)
C(2)	0.3757(5)	0.7991(4)	0.603(1)	0.041(2)
C(3)	0.3733(4)	0.7557(4)	0.384(1)	0.039(1)
C(4)	0.1875(4)	0.7700(3)	0.3790(9)	0.027(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Bond lengths (Å) and valence sums (Σs) for $(NH_3CH_2CH_2NH_3)_{1.5}[(VO)_2(HPO_4)_2(PO_4)]$ (**1**) and $(C_4H_{12}N_2)_2[V_4O_6H(HPO_4)_2(PO_4)_2]$ (**2**)

Compound **1**			
V(1)–O(2)	2.048(4)	V(1)–O(5)	1.957(4)
V(1)–O(11)	1.904(4)	V(1)–O(12)	1.951(4)
V(1)–O(14)	1.615(4)		
Σs(V(1)–O) = 4.06			
V(2)–O(3)	1.997(4)	V(2)–O(4)	2.013(4)
V(2)–O(9)	1.975(4)	V(2)–O(10)	1.955(4)
V(2)–O(13)	1.661(4)	V(2)–O(13)	2.217(4)
Σs(V(2)–O) = 4.03			
P(1)–O(1)	1.564(4)	P(1)–O(2)	1.525(4)
P(1)–O(3)	1.524(4)	P(1)–O(4)	1.525(4)
Σs(P(1)–O) = 5.00			
P(2)–O(5)	1.538(4)	P(2)–O(6)	1.605(4)
P(2)–O(7)	1.505(4)	P(2)–O(8)	1.526(4)
Σs(P(2)–O) = 4.90			
P(3)–O(9)	1.539(4)	P(3)–O(10)	1.534(4)
P(3)–O(11)	1.513(5)	P(3)–O(12)	1.514(4)
Σs(P(3)–O) = 5.13			
N(1)–C(1)	1.486(8)	N(2)–C(2)	1.527(9)
N(3)–C(3)	1.514(8)	C(1)–C(2)	1.535(9)
C(3)–C(3)	1.52(1)		
Compound **2**			
V(1)–O(1)	1.958(3)	V(1)–O(2)	2.028(3)
V(1)–O(3)	1.992(3)	V(1)–O(5)	2.079(3)
V(1)–O(7)	2.434(3)	V(1)–(11)	1.578(3)
Σs(V(1)–O) = 4.08			
V(2)–O(6)	1.935(3)	V(2)–O(8)	1.965(4)
V(2)–O(9)	1.937(4)	V(2)–O(4)	1.814(4)
V(2)–O(10)	1.593(4)		
Σs(V(2)–O) = 4.54			
P(1)–O(1)	1.512(3)	P(1)–O(2)	1.518(3)
P(1)–O(3)	1.520(3)	P(1)–O(4)	1.596(3)
Σs(P(1)–O) = 5.00			
P(2)–O(5)	1.537(3)	P(2)–O(6)	1.539(4)
P(2)–O(7)	1.536(3)	P(2)–O(8)	1.546(4)
Σs(P(2)–O) = 4.93			
N(1)–C(1)	1.473(8)	N(1)–C(2)	1.513(9)
N(2)–C(3)	1.496(7)	N(2)–C(4)	1.499(7)
C(1)–C(4)	1.502(8)	C(2)–C(3)	1.53(1)

The infinite chains are linked together by $V(1)O_5$ square pyramids via –V(1)–O(12)–P(3)– bonds. The P–OH groups of $HP(1)O_4$ and $HP(2)O_4$ are directed towards the interlamellar region. The remaining corner of $HP(1)O_4$ is connected to $V(1)O_5$. $HP(2)O_4$ has only one oxygen, O(5), bonded to V(1) and extends away from the layer as a pendant group. The remaining two terminal oxygen atoms, O(7) and O(8), are hydrogen bond acceptors from ethylenediammonium cations as inferred from the O(7)$\cdots$N(1) and O(7)$\cdots$N(2) distances of 2.72 Å and the O(8) $\cdots$N(3) distance of 2.71 Å. Within the layer there are 10-sided windows formed by the edges of four VO_6 octahedra, two VO_5 square pyramids and four phosphate tetrahedra (Fig. 3). The layers are arranged in such a way that these windows create infinite tunnels along the [001] direction.

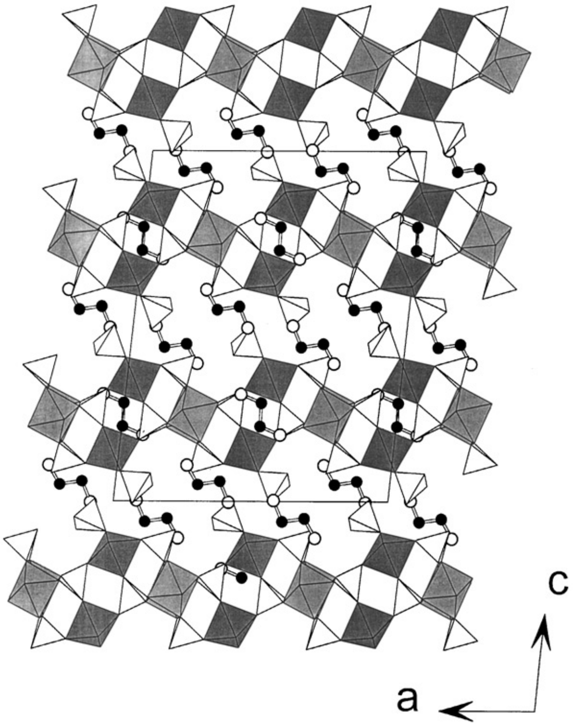

Fig. 1. Polyhedral representation of $(NH_3CH_2CH_2NNH_3)_{1.5}[(VO)_2(HPO_4)_2(PO_4)]$ viewed along the [010] direction. The light and dark gray polyhedra represent the $V(2)O_6$ and $V(1)O_6$ groups, respectively, the tetrahedra are the PO_4 groups; solid and open circles represent carbon and nitrogen atoms, respectively.

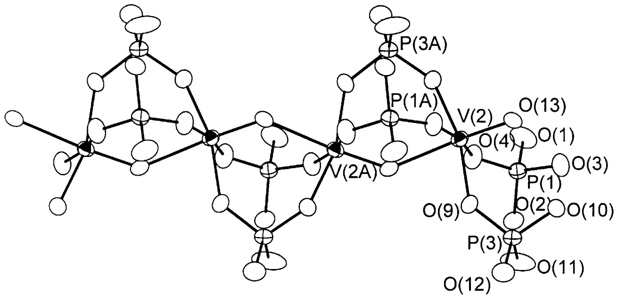

Fig. 2. Representation of *trans*-corner-sharing chain of $V(2)O_6$ octahedra bridged by $HP(1)O_4$ and $P(3)O_4$ tetrahedra in **1**. The thermal ellipsoids are shown at the 60% probability.

In these tunnels, one third of the ethylenediammonium dications are nested in the intralayer space. The rest of the cations are locked in the positions between the layers.

Compound **2**: The structure is formed of layers composed of PO_4 tetrahedra and VO_5 and VO_6 polyhedra with piperazinium dications in the interlayer space. As shown by valence sums for V(1) ($\Sigma s = 4.08$), compound **2** contains six-coordinated tetravalent vanadium atoms (Fig. 4). The valence sum of 4.48 for V(2) indicates that these five-coordinated atoms are both tetravalent and pentavalent. P(1) has a terminal OH

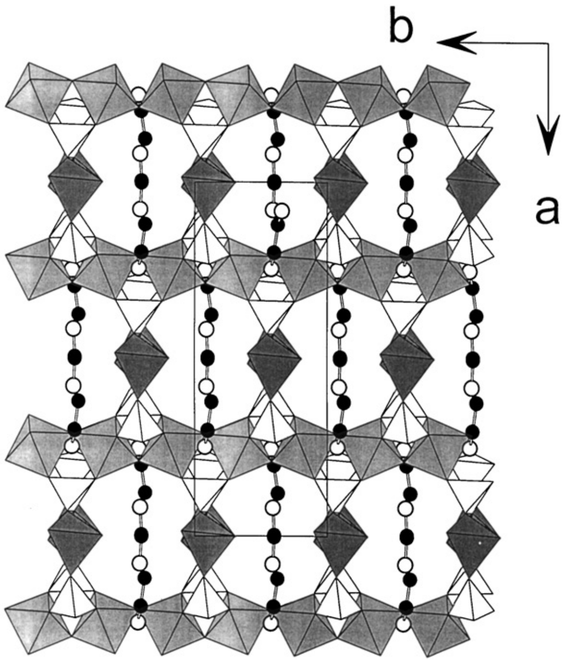

Fig. 3. The structure of $(NH_3CH_2CH_2NNH_3)_{1.5}[(VO)_2(HPO_4)_2(PO_4)]$ viewed along the [001] direction.

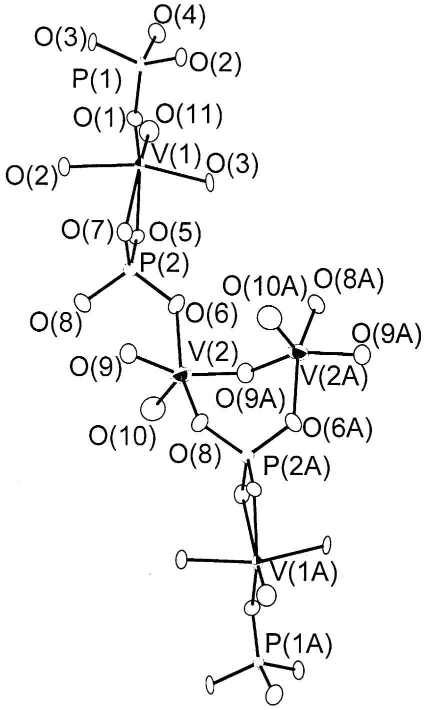

Fig. 4. The structural units of **2** viewed approximately along the [010] direction. The thermal ellipsoids are shown at the 60% probability.

group as inferred from unsatisfied valence sums for O(4) $(\Sigma s = 1.04)$. Both $V(1)O_6$ and $V(2)O_5$ polyhedra have terminal oxygens O(11) and O(10), respectively, with the $V \cdots O$ distance of about 1.6 Å indicating a $V=O$ bond.

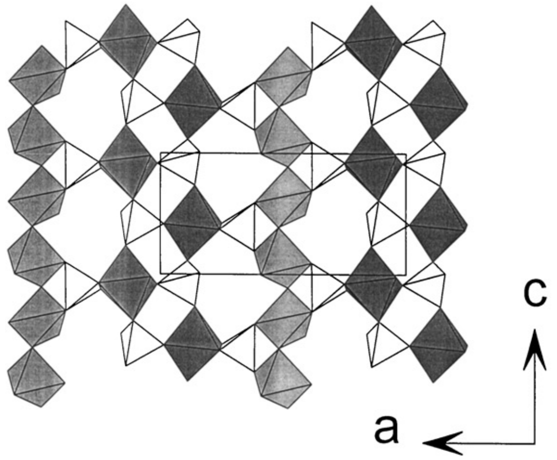

Fig. 5. A layer of **2** viewed along the [010] direction. The light and dark gray polyhedra represent the $V(1)O_6$ and $V(2)O_5$ groups, respectively, and the tetrahedra are the PO_4 groups.

The layers of **2** are composed of two types of chains running parallel to the [001] direction (Fig. 5). In the first type, $V(1)O_6$ groups share *trans* corners with $HP(1)O_4$ groups forming a chain in which VO_6 octahedra alternate with HPO_4 tetrahedra. Two such chains are connected via P(1)–O(1)–V(1) bonds and are related by a 2_1 symmetry operation along the *c*-axis. The second type of the chains, composed of *trans*-corner-shared $V(2)O_5$ tetragonal pyramids, forms a zigzag backbone with the V–O–V angle of 120°. Adjacent $V(2)O_5$ groups are bridged by $P(2)O_4$ tetrahedra, in a manner similar to that found for the chain in **1**. In **2**, the adjacent VO_5 polyhedra are bridged by one $P(2)O_4$ tetrahedron only to form an infinite chain of the $[M(T\phi_4)\phi]$ type, where M is a five or more coordinated atom, T is a three or four coordinated and ϕ is an unspecified ligand [20]. Both types of the chains are connected by an edge sharing of $V(1)O_6$ with $P(2)O_4$ via O(5) and O(7) in a similar way as in $(C_4H_{12}N_2)_2[(VO)_3(HPO_4)_2(PO_4)_2] \cdot H_2O$ [12] and $[VO(PO_4)(H_2NCH_2CH_2NH_3)]$ [10] to form sheets in the *ac*-plane. Due to this connection, seven-membered empty windows are generated within the layers.

A plot of the reciprocal magnetic susceptibility vs. temperature (Fig. 7) reveals Curie–Weiss para magnetism at temperature above 50 K with $C = 1.015\,\mathrm{emu\,K\,mol^{-1}}$ and $\theta = -13.78\,\mathrm{K}$. The effective magnetic moment, calculated from the equation $\mu_{\mathrm{eff}} = 2.828C^{1/2}$, is $2.85\,\mu_B$. This value is close to the value of $3\,\mu_B$ for three independent unpaired electrons per formula unit. There are four vanadium atoms per formula unit, two of them are V(1) from isolated VO_6 octahedra and two of them are central atoms of corner shared $V(2)O_5$ tetragonal pyramids forming the V(2)–O(9)–V(2)–O(9) infinite chain. Assuming two electrons as belonging to the $V(1)O_6$ octahedra, one unpaired electron must be present at one of two V(2) sites of the

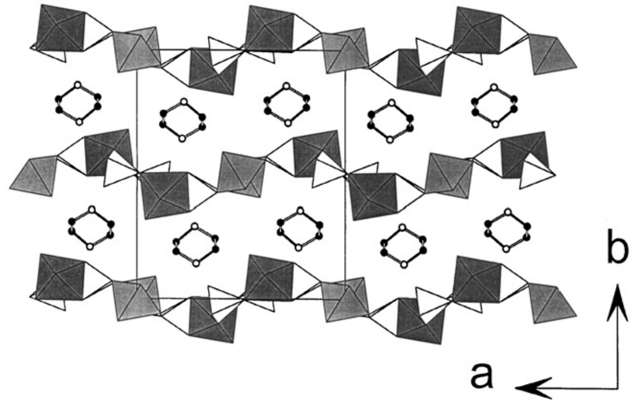

Fig. 6. The structure of **2** viewed along the [001] direction. Solid and open circles are carbon and nitrogen atoms, respectively.

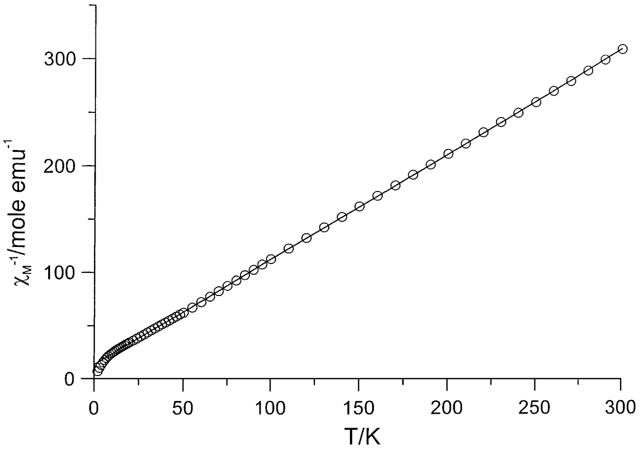

Fig. 7. Inverse molar magnetic susceptibility vs. temperature for **2**. The straight line represents a least-squares fit to the data from 50 to 300 K.

chain. Therefore, an alternation of the valence of the vanadium atoms in the chain can be expected. This is supported by the valence sum calculation (vide supra) for V(2). A ferromagnetic interaction is observed below 10 K.

To balance charge, every other O(9) atom must be a hydroxo oxygen, as inferred from the valence sum ($\Sigma s = 1.56$) and the piperazine molecules must be present as dications. These dications are anchored to the layers by H bonds to the O(4)H hydroxo groups with the O(4)$\cdots$N(1) distance of 2.83 Å and to the O(5) and O(7) atoms with the O(5)$\cdots$N(2) and O(7)$\cdots$N(1) distances of 2.87 and 2.67 Å, respectively (Fig. 6).

The presence of V^V was also tested by the reaction with sodium iodide analogously to the reaction of $VOPO_4$ reported by Jacobson et al. [21]. Due to the reduction of V^V, iodine is released and sodium is present in the solid product as confirmed by the energy-dispersive X-ray fluorescence analysis.

4. Conclusions

The distinct feature of the compound **1** is the presence of the template both in the interlayer space and in the windows within the layers. Although several layered templated vanadium phosphates are known, the compound presented in this paper, $(NH_3CH_2CH_2NH_3)_{1.5}[(VO)_2(HPO_4)_2(PO_4)]$, is the first example of layered vanadium phosphate templated with ethylenediammonium cations.

The structure of piperazine templated vanadium phosphate reported in this paper contains isolated VO_6 octahedra together with chains composed of corner-shared VO_5 tetragonal bipyramids. The compound contains a mixed-valence V^V/V^{IV} chain composed of *trans*-corner-shared tetragonal pyramids. Compounds with such mixed-valence V^V/V^{IV} chains usually have a V=O–V=O arrangement of the bonds. In this case, however, the interatomic distance between vanadium and bridging oxygen (V(2)$\cdots$O(9) of 1.946 and 1.818 Å) suggests the presence of single bonds only. The double bond is also formed in the VO_5 polyhedron but with a terminal O(10) atom. Therefore the bonds in the chain can be written as V(=O)–O–V(=O)–O–. This arrangement is observed for the first time.

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