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Synthesis and structural characterization of $(H_4APPIP)[V_3(C_2O_4)_2(HPO_4)_3(PO_4)(H_2O)] \cdot 6H_2O$ (APPIP = 1,4-bis(3-aminopropyl)piperazine), a layered vanadium oxalatophosphate containing double 6-ring units

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Abstract

A new vanadium(III) oxalatophosphate has been synthesized hydrothermally and characterized by single-crystal X-ray diffraction and thermogravimetric analysis. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.604(2)$ Å, $b = 12.391(2)$ Å, $c = 15.220(3)$ Å, $\alpha = 71.090(3)^\circ$, $\beta = 82.630(3)^\circ$, $\gamma = 62.979(3)^\circ$, $V = 1843.8(5)$ Å^3 and $Z = 2$. The structure consists of $V_6(HPO_4)_6$ double 6-ring (D6R) units connected by coordinating $C_2O_4^{2-}$ and PO_4^{3-} anions to form anionic sheets in the *ab* plane with charge-compensating quadruply protonated 1,4-bis(3-aminopropyl)piperazinium cations and water molecules between the sheets. It is one of the few compounds with 2D layer structures and the second example containing D6R units in the system of metal oxalatophosphates. The iron analogue was also synthesized.

Keywords: Vanadium; Phosphate; Oxalate; Structure

1. Introduction

The synthesis of open-framework transition metal phosphates has been a subject of intense research owing to their interesting structural chemistry and potential applications in catalysis. A large number of these materials have been synthesized in the presence of organic amines as structure-directing agents [1–3]. Recently many research activities have also focused on the synthesis of organic–inorganic hybrid compounds by incorporating organic ligands in the structures of metal phosphates. The underlying idea is to combine the robustness of inorganic phosphate frameworks with the versatility and chemical flexibility of organic ligands. A large number of oxalate-phosphates and 4,4′-bpy-phosphates of transition metals and group 13 elements have been reported [4,5]. We have also synthesized metal phosphates containing the organic ligand isonicotinate (4-pyridinecarboxylate) in which both neutral N-donor and anionic O-donor groups are present [6]. The oxalatophosphates form the largest group among these organically modified metal phosphates. Most of these oxlatophosphates adopt 3-D framework structures, while only a few have 2-D layer or 1-D chain structures. Four compounds with 2-D layer structures have been reported: $(NH_4)_2[(VO)_2(C_2O_4)(HPO_4)_2]$, which consists of $[(VO)_2(C_2O_4)]$ dimers linked by HPO_4 groups to form layers [7]; $[(R)\text{-}C_5H_{14}N_2]_2[Ga_4(C_2O_4)(HPO_4)_2(PO_4)_4] \cdot 2H_2O$, the first oxalatophosphate with a chiral amine, which consists of GaO_6 octahedra and GaO_4 tetrahedra linked by oxalate and phosphate groups to form layers that interact through the protonated chiral amine [8]. $(C_2N_2H_{10})_2[Ga_2(C_2O_4)_2(HPO_4)_3] \cdot H_2O$ and $(C_2N_2H_{10})_3[Ga_4(C_2O_4)_4(HPO_4)_4(H_2PO_4)_2]$ consist of corrugated layers of gallophosphate with the oxalate unit being coordinated to each Ga atom as a mono-bidentate ligand [9]. As part of continuing work of this

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system, we prepared a new oxalatophosphate, $(H_4APPIP)[V_3(C_2O_4)_2(HPO_4)_3(PO_4)(H_2O)]\cdot 6H_2O$ (APPIP = 1,4-bis(3-aminopropyl)piperazine), that has a new type of layer structure built of D6R units connected by phosphate and oxalate groups. There are two types of oxalate units in the structure: one type acts as a bridging ligand and chelates two metal atoms while the other oxalate unit chelates only one metal atom and has two C–O groups pendant between adjacent layers. In this paper, the synthesis and structural characterization of this new vanadium compound are presented. The iron analogue was also prepared.

2. Experimental section

2.1. Synthesis and preliminary characterization

The hydrothermal reactions were carried out in Teflon-lined stainless-steel Parr acid digestion bombs with an internal volume of 23 mL. All chemicals were purchased from Aldrich. Green tabular crystals of $(H_4APPIP)[V_3(C_2O_4)_2(HPO_4)_3(PO_4)(H_2O)]\cdot 6H_2O$ (**1**) were obtained by heating a mixture of VCl_3 (1 mmol), oxalic acid dihydrate (2 mmol), H_3PO_4 (3 mmol), APPIP (2 mmol), and H_2O (10 mL) at 165°C for 3 d followed by slow cooling at 5°C h^{-1} to room temperature. The pH values before and after reaction were 2.7 and 3.4, respectively. The yield was 22% based on vanadium. The powder X-ray diffraction pattern of the bulk product is in good agreement with the calculated pattern on the basis of the results from single-crystal X-ray diffraction (Fig. 1). Elemental analysis of the bulk product confirms the stoichiometry (Found: C, 15.95; H, 4.39; N, 5.27%. Calcd. for $C_{14}H_{45}N_4O_{31}P_4V_3$: C, 16.13; H, 4.35; N, 5.38%). Compound **1** can also be prepared in a yield of 20% by heating a mixture of V_2O_5 (0.43 mmol), V metal (0.57 mmol), oxalic acid dehydrate (3 mmol), APPIP (2 mmol), and H_2O (10 mL) under the same reaction conditions. Colorless crystals of the iron analogue $(H_4APPIP)[Fe_3(C_2O_4)_2(HPO_4)_3(PO_4)(H_2O)]\cdot xH_2O$ (**2**) were obtained by heating $FeCl_3\cdot 6H_2O$ (1.5 mmol), oxalic acid dihydrate (3 mmol), H_3PO_4 (11.5 mmol), APPIP (6 mmol), and H_2O (10 mL) at 120°C for 3 d. The yield was nearly quantitative based on iron. The initial and final pH values were 4.6. This iron compound is isostructural with **1** as indicated from powder X-ray diffraction. When the starting molar ratio of $FeCl_3\cdot 6H_2O$:oxalic acid:H_3PO_4:APPIP was 1:3:3:3, the reaction produced **2** in small crystallite size.

To test whether the organic ammonium cation can be exchanged under the same conditions as those for $[H_3N(CH_2)_3NH_3]_2[Fe_4(OH)_3(HPO_4)_2(PO_4)_3]\cdot xH_2O$ [10], a powder sample of **2** was stirred at 50°C for 12 h in a 100-fold excess aqueous solution of ammonium chloride and then washed with water and ethanol. CHN analysis results were essentially the same as those before ion exchange, indicating that the $(H_4APPIP)^{4+}$ cations were not exchanged under the conditions. In contrast to **2**, 83% of propylenediammonium cation in $[H_3N(CH_2)_3NH_3]_2[Fe_4(OH)_3(HPO_4)_2(PO_4)_3]\cdot xH_2O$ was exchanged with NH_4^+. The ion exchange reaction was performed on compound **2** only because vanadium(III) is subject to oxidation.

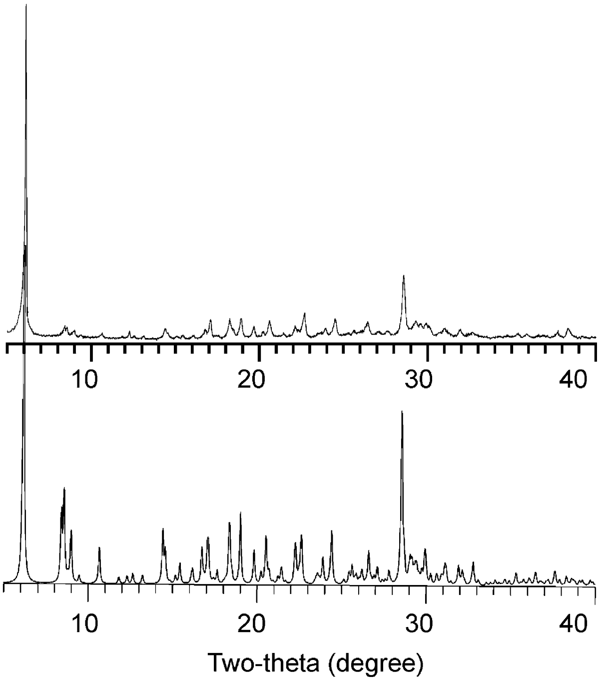

Fig. 1. Experimental X-ray powder pattern (top) and simulated powder pattern (bottom) based on the results from single-crystal X-ray diffraction for **1**.

Thermogravimetric analysis (TGA), using a Perkin Elmer TGA7 thermal analyzer, was performed on a powder sample of **1** in flowing nitrogen atmosphere in the temperature range of 30–900°C with a heating rate of 5°C min^{-1}. The TGA curve showed weight loss in several overlapping steps, which began at 30°C and was incomplete by 900°C (Fig. 2). The observed weight loss in the step between 30°C and ca. 170°C was 10% which is close to that calculated for the loss of six lattice water molecules (10.36%). The TG analysis alone does not determine the amount of lattice water molecules because there are important overlaps between different weight losses. Rather, EA, TGA and single-crystal X-ray diffraction were used in combination to determine the water content.

Powder X-ray diffraction studies of a sample of **1** that had been heated at 150°C, 160°C and 170°C for 1 h in air and then cooled to room temperature revealed that the interlayer separation did not change after loss of lattice water molecules. However, the pattern for 170°C clearly showed an additional broad weak peak at $2\theta \sim 7°$

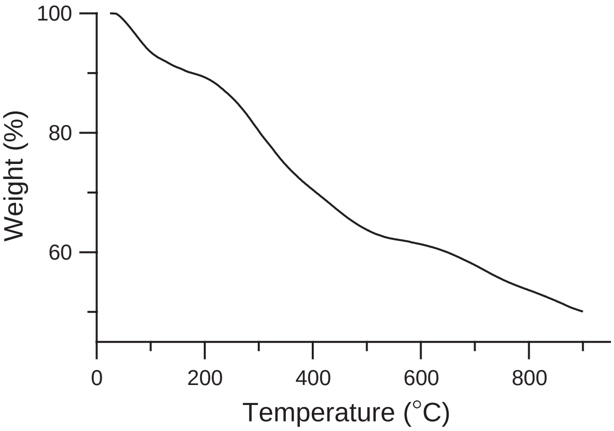

Fig. 2. TGA of **1** in flowing nitrogen at 5°C min^{-1}.

as a shoulder of the sharp strong (001) reflection at $2\theta = 6.1°$. The appearance of the additional peak may indicate the decomposition of the structure and be related to the onset of further weight loss in TGA.

2.2. Single-crystal X-ray diffraction

A suitable crystal of **1** with dimensions $0.3 \times 0.2 \times 0.08$ mm was selected 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 at room temperature in 1271 frames with ω scans (width 0.30° per frame). Empirical absorption corrections based on symmetry equivalents were applied ($T_{\min,\ \max} = 0.658$, 0.901). On the basis of statistical analysis of the intensity distributions and successful solution and refinement of the structures, the space group was determined to be $P\bar{1}$ (No. 2). The structure was solved by direct methods and difference Fourier syntheses. All atoms are at general positions. Eight water oxygen atom sites were located. We earlier refined the structure with all water oxygen sites fully occupied. Ow(4) to Ow(8) atoms showed very large thermal parameters, which are indicative of partial occupancy or positional disorder. The Ow(5)···Ow(8) and Ow(6)···Ow(7) distances are very short (1.6 and 1.0 Å), precluding simultaneous oxygen occupancy of these sites. The multiplicities of all Ow atoms were allowed to refine. The Ow(1) to Ow(3) sites were fully occupied. Ow(4) to Ow(8) positions, respectively, refined to multiplicities of 0.85(3), 0.73(2), 0.48(3), 0.74(5), and 0.33(2), which amount to 6 water oxygen atoms per formula unit. The H atoms, which are bonded to the C atoms in APPIP molecule, were positioned geometrically and refined using a riding model. The H atoms bonded to N and O atoms were not located. The final cycles of least-squares refinement including atomic coordinates and anisotropic thermal parameters for all atoms converged at $R_1 = 0.0582$ and $wR_2 = 0.1567$. The final difference electron density maps were featureless and the highest peak and deepest hole were 0.99 and $-0.96\ e\,Å^{-3}$, respectively. All calculations were performed using SHELXTL Version 5.1 software package [11]. CIF file for **1** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-223625. A crystal of **2** was also selected for indexing and intensity data collection.[1] Structural analysis results indicate that it is isotypic to **1**. But the water oxygen atom sites in **2** could not be located due to disorder.

3. Results and discussion

3.1. Description of the structure

The crystallographic data and selected bond lengths are given in Tables 1 and 2, respectively. The asymmetric unit consists of 56 distinct nonhydrogen atoms, all of which are at general positions in the unit cell. Bond-valence calculations indicate that all vanadium atoms are trivalent, O(3), O(7), O(12), O(15), O(16), and O(17) have valence sums of 1.15, 1.13, 1.11, 1.21, 1.20, and 0.43, respectively, and all other oxygen atoms have values close to 2 [12]. The valence sums of O(15) and O(16) can be satisfied by forming hydrogen bonds with hydrogen phosphate groups and $(H_4APPIP)^{4+}$ cations [O(15)···O(3) = 2.48 Å, O(15)···N(3) = 2.66 Å, O(16)···O(7) = 2.52 Å, O(16)···O(12) = 2.51 Å]. To balance charge, O(3), O(7), and O(12) are hydroxo oxygen atoms, and O(17), which is bonded to V(1) only, is a water oxygen. Therefore, P(1), P(2), and P(3) form HPO_4 groups, and P(4) is a PO_4 group. There are three independent oxalate ligands per asymmetric unit: $C(1)C(2)O_4^{2-}$ is at general position, whereas the other two oxalate anions have C_i symmetry.

A polyhedral plot of the complete crystal structure is shown in Fig. 3. It consists of anionic sheets of the formula $[V_3(C_2O_4)_2(HPO_4)_3(PO_4)(H_2O)]^{4-}$ with charge compensating quadruply protonated 1,4-bis(3-aminopropyl)piperazinium cations and water molecules between the layers. As shown in Fig. 4 each layer is constructed from $V_6(HPO_4)_6$ double 6-ring (D6R) units which are connected by oxalate ligands ($C(3)_2O_4^{2-}$ and $C(4)_2O_4^{2-}$) along the [110] direction and $P(4)O_4^{3-}$ tetrahedra along [$1\bar{1}0$]. Each D6R unit has C_i symmetry and is formed of 12 alternating V- and P-centered polyhedra (six V and six P) (Fig. 5). V(1) is coordinated by three HPO_4^{2-} tetrahedra, one water molecule, and one monobidentate $C(1)C(2)O_4^{2-}$ unit as a terminal

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[1] Crystal data for $(H_4APPIP)[Fe_3(C_2O_4)_2(HPO_4)_3(PO_4)(H_2O)] \cdot xH_2O$: triclinic, $P\bar{1}$, $a = 11.5567(9)$ Å, $b = 12.390(1)$ Å, $c = 15.281(1)$ Å, $\alpha = 70.522(1)°$, $\beta = 82.544(2)°$, $\gamma = 63.135(1)°$, $V = 1839.6(4)\ Å^3$, $R_1 = 0.0732$ and $wR_2 = 0.1969$.

Table 1
Crystallographic data for $(H_4APPIP)[V_3(C_2O_4)_2(HPO_4)_3(PO_4)(H_2O)]\cdot 6H_2O$

Chemical formula	$C_{14}H_{45}N_4O_{31}P_4V_3$
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	11.604(2)
b (Å)	12.391(2)
c (Å)	15.220(3)
α (deg)	71.090(3)
β (deg)	82.630(3)
γ (deg)	62.979(3)
V (Å^3)	1843.8(5)
Z	2
Formula weight	1042.24
T (°C)	23
λ (Mo$K\alpha$) (Å)	0.71073
D_{calc} (g cm^{-3})	1.877
μ(Mo$K\alpha$), cm^{-1}	10.3
Number of reflections collected	21,742
Unique data ($I > 2\sigma(I)$)	6780
Number of variables	528
R_1[a]	0.0582
wR_2[b]	0.1567
$(\Delta\rho)_{max,min}$	0.99, −0.96

[a] $R_1 = \sum|F_o| - |F_c||/\sum|F_o|$.

[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\mathrm{Max}(F_o, 0) + 2(F_c)^2]/3$, where $a = 0.0755$ and $b = 1.30$.

Table 2
Atomic coordinates and thermal parameters (Å^2) for $(H_4APPIP)[V_3(C_2O_4)_2(HPO_4)_3(PO_4)(H_2O)]\cdot 6H_2O$[a]

Atom	x	y	z	U_{eq}[b]
V(1)	0.54231(5)	0.93310(6)	0.22933(4)	0.0164(1)
V(2)	0.37760(5)	0.35489(5)	−0.00020(4)	0.0142(1)
V(3)	0.88274(5)	0.85326(5)	−0.00388(4)	0.0137(1)
P(1)	0.66121(8)	0.08916(8)	0.07125(6)	0.0149(2)
P(2)	0.26017(8)	0.18108(9)	0.16819(6)	0.0144(2)
P(3)	0.75978(8)	0.68989(8)	0.16019(6)	0.0143(2)
P(4)	0.14517(8)	0.64969(9)	−0.09462(6)	0.0166(2)
O(1)	0.7168(2)	0.9838(2)	0.0246(2)	0.0194(5)
O(2)	0.5410(2)	0.1985(3)	0.0180(2)	0.0280(6)
O(3)	0.7681(2)	0.1352(3)	0.0650(2)	0.0298(6)
O(4)	0.6308(2)	0.0404(3)	0.1729(2)	0.0235(6)
O(5)	0.3733(2)	0.0794(3)	0.2346(2)	0.0219(6)
O(6)	0.2184(2)	0.1237(3)	0.1113(2)	0.0224(6)
O(7)	0.1483(2)	0.2348(3)	0.2349(2)	0.0253(6)
O(8)	0.2884(3)	0.2900(3)	0.1079(2)	0.0274(6)
O(9)	0.8679(2)	0.7150(2)	0.1014(2)	0.0215(6)
O(10)	0.6997(2)	0.7760(3)	0.2222(2)	0.0209(5)
O(11)	0.6584(2)	0.7003(3)	0.0991(2)	0.0234(6)
O(12)	0.8248(3)	0.5515(3)	0.2300(2)	0.0261(6)
O(13)	0.2229(2)	0.5169(3)	−0.0291(2)	0.0256(6)
O(14)	0.0441(2)	0.7294(3)	−0.0376(2)	0.0235(6)
O(15)	0.2355(3)	0.7128(3)	−0.1400(2)	0.0241(6)
O(16)	0.0822(2)	0.6406(3)	−0.1741(2)	0.0281(6)
O(17)	0.4758(3)	0.9331(3)	0.1104(2)	0.0293(6)
O(18)	0.5976(2)	0.9170(3)	0.3566(2)	0.0247(6)
O(19)	0.4644(2)	0.8161(3)	0.3134(2)	0.0274(6)
O(20)	0.4339(2)	0.420243)	0.0909(2)	0.0225(6)
O(21)	0.4801(2)	0.4494(2)	−0.0894(2)	0.0192(5)
O(22)	0.9188(2)	0.0036(2)	−0.0904(2)	0.0190(5)
O(23)	0.9902(2)	0.8720(3)	0.0867(2)	0.0201(5)
O(24)	0.5811(4)	0.8286(4)	0.5095(2)	0.0477(9)
O(25)	0.4553(4)	0.7125(4)	0.4631(2)	0.052(1)
C(1)	0.5620(4)	0.8484(4)	0.4255(3)	0.0267(8)
C(2)	0.4880(4)	0.7847(4)	0.4007(3)	0.0303(9)
C(3)	0.4872(3)	0.4911(3)	0.0526(2)	0.0162(7)
C(4)	0.9801(3)	0.0382(3)	−0.0518(2)	0.0155(7)
Ow(1)	0.7342(3)	0.2974(4)	−0.1417(3)	0.0472(9)
Ow(2)	0.2648(7)	0.0784(7)	−0.5629(3)	0.106(2)
Ow(3)	0.823(1)	0.516(1)	0.4299(5)	0.180(4)
Ow(4)[c]	0.042(1)	0.242(2)	−0.494(1)	0.28(1)
Ow(5)	0.7062(9)	0.3790(8)	−0.4252(5)	0.089(4)
Ow(6)	0.079(1)	0.206(1)	−0.2858(6)	0.055(5)
Ow(7)	0.108(2)	0.242(4)	−0.350(5)	0.42(4)
Ow(8)	0.861(2)	0.329(2)	−0.411(2)	0.12(1)

[a] The atomic coordinates and thermal parameters of the APPIP molecule are given in supplementary materials.

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

[c] The occupancy factors for Ow(4) to Ow(8) are 0.85(3), 0.73(3), 0.48(3), 0.74(5), and 0.33(2), respectively.

ligand. The coordination environments of V(2) and V(3) are chemically similar. Each V is coordinated by four phosphate tetrahedra (three HPO_4^{2-} and one PO_4^{3-}) and one oxalate ligand ($C(3)_2O_4^{2-}$ or $C(4)_2O_4^{2-}$). These two oxalate ligands are bisbidendate chelate, which bridge vanadium atoms in adjacent D6R units. The V–O bond lengths vary from 1.944 to 2.103 Å and O–V–O bond angles lying between 78.4° and 107°. The longest bond length and smallest bond angle are associated with bonding involving the oxalate units, which are also observed in other oxalatophosphates. The quadruply protonated $(H_4APPIP)^{4+}$ cations and water molecules occupy space between the layers. Three N atoms are within 3 Å to framework oxygen atoms; this distance is indicative of N–H···O hydrogen bonding. The water molecules form hydrogen bonds among themselves, as indicated from short O···O distance. Ow(5) also participates in hydrogen bonding with the framework. TGA confirms the content of lattice water molecules (Table 3).

3.2. Comparison with known structures

D6R units are versatile and have been observed in aluminosilicate zeolites and a 3-D aluminum oxalatophosphate, $(C_4H_{12}N_2)[Al_2(PO_4)(HPO_4)(C_2O_4)]\cdot H_2O$ [13,14]. The latter consists of columns of D6R units connected by bisbidentate oxalate ligands forming 12-membered channels in which N-methylpiperazinium cations and water molecules are located. Two oxalatophosphates which were also prepared using APPIP as the structure-directing agent have been reported. $(H_4APPIP)_{0.5}[Fe_2(HPO_4)_3(C_2O_4)]$ consists of layers of iron phosphate which are bridged by oxalate units to form a 3-D framework with 12-membered channels in which the amine molecule resides [15]. (H$_4$APPIP)

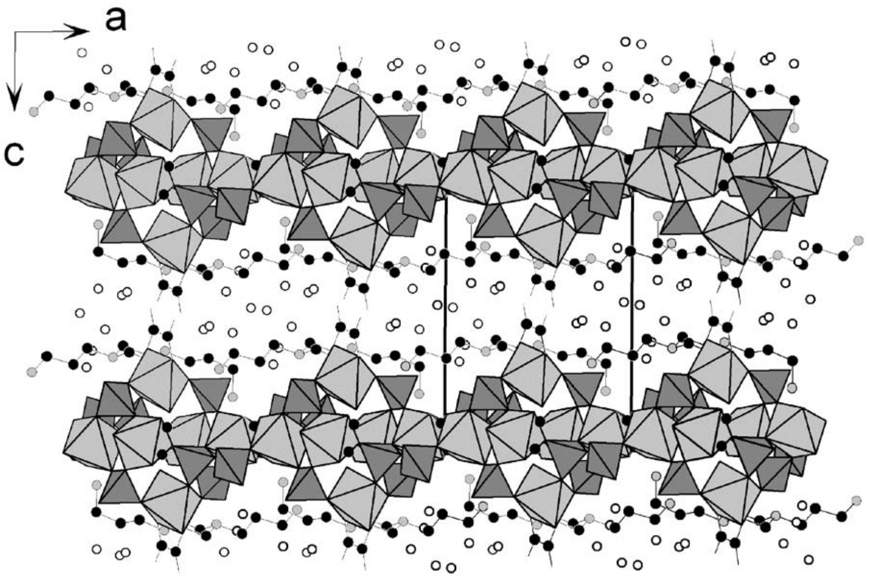

Fig. 3. Structure of **1** viewed along the *b*-axis. The light and dark gray polyhedra are VO_6 octahedra and phosphate tetrahedra, respectively. Black circles, C atoms; gray circles, N atoms; water oxygen atoms, open circles. H atoms are not shown.

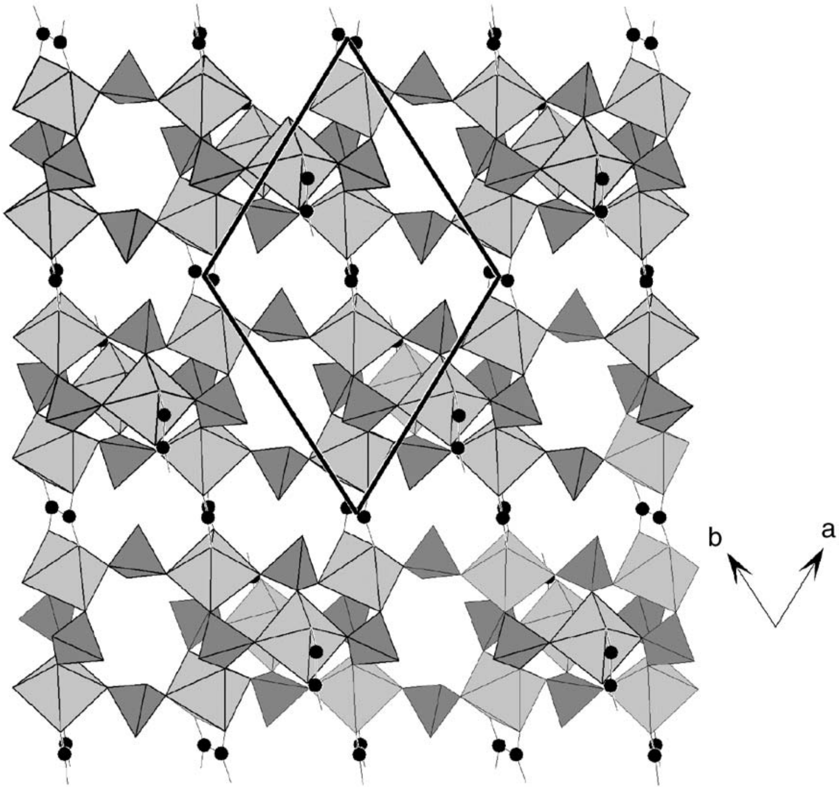

Fig. 4. Section of a vanadium oxalatophosphate layer in **1** viewed along the *c*-axis.

$[Ga_6(OH)_2(PO_4)_2(HPO_4)_4(C_2O_4)_3]\cdot 3.5H_2O$ consists of double layers of gallium phosphate which are linked by oxalate units to form a 3-D framework with intersecting channels where the amine the water molecules are located [16]. Compound **1** is also characterized by the presence of two types of oxalates,

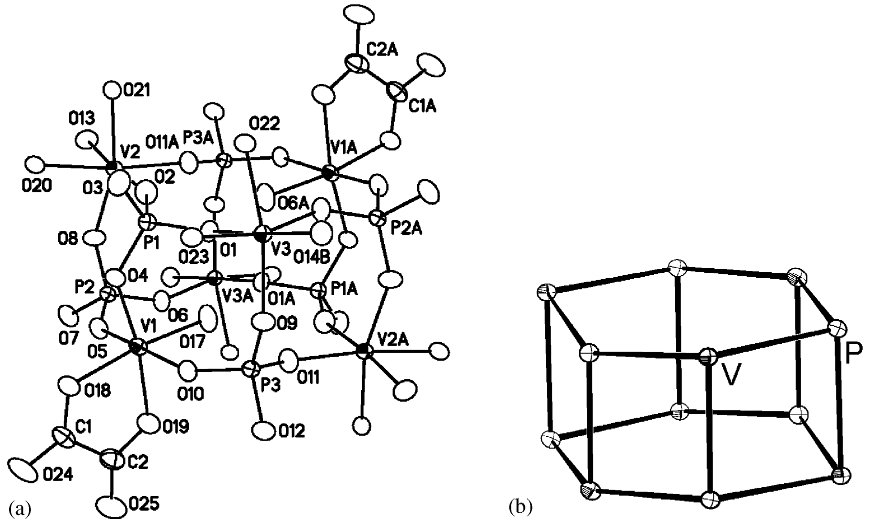

Fig. 5. (a) A D6R unit in **1** showing atom labeling scheme. Thermal ellipsoids are shown at 50% probability. (b) The network structure of a D6R unit. Only the V and P atoms are shown.

Table 3
Selected bond lengths (Å) for $(H_4APPIP)[V_3(C_2O_4)_2(HPO_4)_3(PO_4)(H_2O)]\cdot 6H_2O$[a]

V(1)–O(4)	1.957(3)	V(1)–O(5)	1.991(2)
V(1)–O(10)	1.998(2)	V(1)–O(17)	2.058(3)
V(1)–O(18)	2.039(3)	V(1)–O(19)	2.061(3)
V(2)–O(2)	1.968(3)	V(2)–O(8)	1.972(3)
V(2)–O(11)	2.000(3)	V(2)–O(13)	1.950(2)
V(2)–O(20)	2.108(3)	V(2)–O(21)	2.110(3)
V(3)–O(1)	1.980(2)	V(3)–O(6)	2.005(3)
V(3)–O(9)	1.988(3)	V(3)–O(14)	1.944(2)
V(3)–O(22)	2.087(3)	V(3)–O(23)	2.103(3)
P(1)–O(1)	1.530(3)	P(1)–O(2)	1.516(3)
P(1)–O(3)	1.565(3)	P(1)–O(4)	1.528(3)
P(2)–O(5)	1.531(2)	P(2)–O(6)	1.520(3)
P(2)–O(7)	1.572(3)	P(2)–O(8)	1.514(3)
P(3)–O(9)	1.535(2)	P(3)–O(10)	1.524(3)
P(3)–O(11)	1.526(3)	P(3)–O(12)	1.577(3)
P(4)–O(13)	1.528(3)	P(4)–O(14)	1.531(3)
P(4)–O(15)	1.548(3)	P(4)–O(16)	1.549(3)
C(1)–O(18)	1.273(5)	C(1)–O(24)	1.250(5)
C(1)–C(2)	1.548(6)	C(2)–O(19)	1.286(5)
C(2)–O(25)	1.229(5)	C(3)–O(20)	1.250(4)
C(3)–O(21)	1.256(4)	C(3)–C(3)	1.552(7)
C(4)–O(22)	1.259(4)	C(4)–O(23)	1.248(4)
C(4)–C(4)	1.555(6)		

[a] The bond lengths within the APPIP molecule are given in supplementary materials. The C–H bond lengths are 0.97 Å.

namely a monobidentate and a bisbidentate ligand. This structural characteristic is rare and there are only two examples in literature, namely $(H_4APPIP)[Ga_6(OH)_2(PO_4)_2(HPO_4)_4(C_2O_4)_3]\cdot 3.5H_2O$ and $(H_3DETA)[Fe_3(C_2O_4)_2(HPO_4)_2(PO_4)]$ [17].

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References

[1] R.C. Haushalter, L.A. Mundi, Chem. Mater. 4 (1992) 31, and references therein.
[2] K.-H. Lii, Y.-F. Huang, V. Zima, C.-Y. Huang, H.-M. Lin, Y.-C. Jiang, F.-L. Liao, S.-L. Wang, Chem. Mater. 10 (1998) 2599, and references therein.
[3] A.K. Cheetham, G. Férey, T. Loiseau, Angew. Chem. Int. Ed. 38 (1999) 3268 , and references therein.
[4] (a) H.-M. Lin, K.-H. Lii, Y.-C. Jiang, S.-L. Wang, Chem. Mater. 11 (1999) 519.
(b) C.-Y. Chen, P.P. Chu, K.-H. Lii, Chem. Commun. 16 (1999) 1473.
(c) Z.A.D. Lethbridge, P. Lightfoot, J. Solid State Chem. 143 (1999) 58.
(d) Z.A.D. Lethbridge, A.D. Hiller, R. Cywinske, P. Lightfoot, J. Chem. Soc. Dalton Trans. 10 (2000) 1595.
(e) A. Choudhury, S. Natarajan, C.N.R. Rao, J. Solid State Chem. 146 (1999) 538.
(f) A. Choudhury, S. Natarajan, C.N.R. Rao, Chem. Eur. J. 6 (2000) 1168.
(g) Y.-C. Jiang, S.-L. Wang, K.-H. Lii, N. Nguyen, A. Ducouret, Chem. Mater. 15 (2003) 1633, and references therein.
[5] (a) K.-H. Lii, Y.-F. Huang, Inorg. Chem. 38 (1999) 1348.
(b) C.-Y. Chen, F.-R. Lo, H.-M. Kao, K.-H. Lii, Chem. Commun. 12 (2000) 1061.
(c) Y.-C. Jiang, Y.-C. Lai, S.-L. Wang, K.-H. Lii, Inorg. Chem. 40 (2001) 5320.
(d) L.-H. Huang, H.-M. Kao, K.-H. Lii, Inorg. Chem. 41 (2002) 2936.

(e) Z. Shi, S. Feng, S. Gao, L. Zhang, G. Yang, J. Hua, Angew. Chem. Int. Ed. 39 (2000) 2325.

[6] C.-M. Wang, S.-T. Chuang, Y.-L. Chuang, H.-M. Kao, K.-H. Lii, J. Solid State Chem., in press.

[7] J. Do, R.P. Bontchev, A.J. Jacobson, Inorg. Chem. 39 (2000) 3230.

[8] K.-H. Lii, C.-Y. Chen, Inorg. Chem. 39 (2000) 3374.

[9] M. Mrak, U. Kolitsch, C. Lengauer, V. Kaucic, E. Tillmanns, Inorg. Chem. 42 (2003) 598.

[10] K.-H. Lii, Y.-F. Huang, V. Zima, C.-Y. Huang, H.-M. Lin, Y.-C. Jiang, F.-L. Liao, S.-L. Wang, Chem. Mater. 10 (1998) 2599.

[11] G.M. Sheldrick, SHELXTL Programs, Version 5.1, Bruker AXS GmbH: Karlsruhe, Germany, 1998.

[12] I.D. Brown, D. Altermatt, Acta Crystallogr. B 41 (1985) 244.

[13] W.H. Meier, D.H. Olson (Eds.), Atlas of Zeolite Structure Types, Butterworth-Heinemann, London, 1992.

[14] K. Kedarnath, A. Choudhury, S. Natarajan, J. Solid State Chem. 150 (2000) 324.

[15] A. Choudhury, S. Natarajan, J. Mater. Chem. 9 (1999) 3113.

[16] C.T.S. Choi, E.V. Anokhina, C.S. Day, Y. Zhao, F. Taulelle, C. Huguenard, Z. Gan, A. Lachgar, Chem. Mater. 14 (2002) 4096.

[17] Y.-C. Jiang, S.-L. Wang, K.-H. Lii, N. Nguyen, A. Ducouret, Chem. Mater. 15 (2003) 1633.