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Hydrothermal syntheses and structures of two novel vanadium selenites, $\{[\text{VO}(\text{OH})(\text{H}_2\text{O})](\text{SeO}_3)\}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)[(\text{VO})(\text{SeO}_3)_2]$

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Abstract

Two novel vanadium selenites $\{[\text{VO}(\text{OH})(\text{H}_2\text{O})](\text{SeO}_3)\}_4 \cdot 2\text{H}_2\text{O}$ **1** and $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)[(\text{VO})(\text{SeO}_3)_2]$ **2** were synthesized by hydrothermal method and their crystal structures were determined by single-crystal X-ray diffraction. It is characterized by inductively coupled plasma (ICP), thermogravimetric (TG) and elemental analyses. Compound **1** crystallizes in the monoclinic system, space group $C2/c$, $a = 21.2250(11) \text{ \AA}$, $b = 12.6309(6) \text{ \AA}$, $c = 17.0249(10) \text{ \AA}$, $\beta = 96.830(3)^\circ$, $V = 4531.8(4) \text{ \AA}^3$ and $Z = 8$, $R_1 [I > 2\sigma(I)] = 0.0344$, $wR_2 [I > 2\sigma(I)] = 0.119$; Compound **2** crystallizes in the monoclinic system, space group $P2_1/c$, $a = 9.6389(4) \text{ \AA}$, $b = 6.9922(3) \text{ \AA}$, $c = 15.0324(5) \text{ \AA}$, $\beta = 102.297(2)^\circ$, $V = 989.90(7) \text{ \AA}^3$ and $Z = 4$, $R_1 [I > 2\sigma(I)] = 0.0452$, $wR_2 [I > 2\sigma(I)] = 0.117$. $\{[\text{VO}(\text{OH})(\text{H}_2\text{O})](\text{SeO}_3)\}_4 \cdot 2\text{H}_2\text{O}$ has a 1D structure constructed from the $\{[\text{VO}(\text{OH})(\text{H}_2\text{O})](\text{SeO}_3)\}_\infty$ chains. $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)[(\text{VO})(\text{SeO}_3)_2]$ has a layered structure composed of alternating VO_5 and SeO_3 units with protonated ethylenediamine as interlayer guest.

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Keywords: Vanadium selenite; Hydrothermal synthesis; Structure; Template; Chain; Layer

1. Introduction

In the past few years, the design and synthesis of microporous solids is of great interest for their potential application and their various novel framework topologies [1–3]. The diversity in synthetic systems is derived from the great possibility of the structural construction for both variables of inorganic and organic parts. Vanadium systems have been intensively studied for the variable oxidation states and coordination geometries, which leads to a great variety of potential polyhedral connectivities [4]. A large group of vanadium phosphates and phosphonates has been synthesized and characterized. With respect to their potentially useful physical properties, the diversity of the crystal chemistry of this notable family, ranging from one- to two- or three-dimensional network types, is still interesting and attracting [5,6]. In contrast, the known chemistry of

vanadium selenites is very limited, though the lone pair on the selenium of selenite can behave similarly to corresponding phosphate.

The structures of inorganic solids containing the $[\text{Se}^{\text{IV}}\text{O}_3]^{2-}$ selenite ion are very interesting because of the nonbonded electron pair that places the cation in asymmetric coordination [7]. From a synthetic and crystal chemical perspective, it is suggested that there is rich structural chemistry in metal selenites. Recently, hydrothermal techniques have been applied to metal selenite system in order to produce diversity of the crystal chemistry [8–14]. Some vanadium selenites such as $A\text{V}_2\text{SeO}_7$ ($A = \text{K}$ and Rb), $A\text{VSeO}_5$ ($A = \text{Rb}$, Cs), $A\text{V}_3\text{Se}_2\text{O}_{12}$ ($A = \text{K}$, Rb , Cs , NH_4), $\text{K}(\text{VO})(\text{SeO}_3)_2\text{H}$, $\text{V}_2\text{Se}_2\text{O}_9$, $(\text{VO}_2)(\text{SeO}_3)$ and $\text{Cd}(\text{VO}_2)_4(\text{SeO}_3)_3 \cdot \text{H}_2\text{O}$, have been synthesized [15–21]. A general feature of these vanadium selenites is that the vanadium and the selenites groups form frameworks with alkali or alkaline earth cation. Another coordination complex-linked vanadium selenite, $[\text{Cu}(\text{phen})]_2\text{V}_2\text{Se}_2\text{O}_{11}$, has been reported by our group [22].

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To our knowledge, three organically templated selenites, $(\text{CN}_3\text{H}_6)_4[\text{Zn}_3(\text{SeO}_3)_5]$, $[\text{C}_4\text{N}_2\text{H}_{12}]_{0.5}[\text{Fe}_2\text{F}_3(\text{SeO}_3)_2]$ and $[\text{C}_2\text{N}_2\text{H}_8]_{0.5}\text{ZnSeO}_3$ have been synthesized [23,24]. However, there have been no reports on the structures of vanadium selenites templated by organic amine so far. We report here the synthesis of two organically templated vanadium selenites, $\{[\text{VO}(\text{OH})(\text{H}_2\text{O})](\text{SeO}_3)\}_4 \cdot 2\text{H}_2\text{O}$ (**1**) and $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)[\text{VO}(\text{SeO}_3)_2]$ (**2**) by using triethylamine and ethylenediamine as the structure directing agents, respectively. **1** has one-dimensional (1D) chain structure composed of VO_6 octahedra and SeO_3 pyramids. **2** has two-dimensional (2D) structure of anionic layers, resulted from the connection of VO_5 square-pyramids with SeO_3 pyramids by corner-sharing, and the organic ammonium cations $(\text{NH}_3^+\text{CH}_2\text{CH}_2\text{NH}_3^+)$ locate in the interlayer regions.

2. Experimental

2.1. Synthesis and characterization

All syntheses were carried out in 23 mL Teflon-lined stainless steel vessels under autogenous pressure with a filling capacity of $\sim 50\%$. The elemental analysis was performed on a Perkin-Elmer 2400 element analyzer, and inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300 DV ICP spectrometer. The thermal gravimetric analysis and differential thermal analysis were carried out in air on a Perkin-Elmer DTA 1700 differential thermal analyzer with a rate of $10^\circ\text{C}/\text{min}$.

A mixture of V_2O_5 (0.453 g), SeO_2 (1.100 g), triethylamine (0.3 mL) and H_2O (10 mL) in the mole ratio 1:4:2:220 was sealed in a 23 mL Teflon-lined stainless steel autoclave and heated for 10 days at 110°C . After the mixture was cooled to room temperature, green columned crystals of **1** were obtained in 55% yield based on vanadium, washed with distilled water and dried at room temperature. A mixture of V_2O_5 (0.453 g), SeO_2 (1.100 g), ethylenediamine (0.5 mL) and H_2O (10 mL) in the mole ratio 1:4:2.8:220 was sealed in a 23 mL Teflon-lined stainless steel autoclave and heated for 10 days at 110°C . After the mixture was cooled to room temperature, green prismatic crystals of **2** were obtained with a large amount of unidentified side product, washed with distilled water and dried at room temperature. Anal Calcd (found) for **1** (wt%): V, 21.40 (21.09); Se, 33.20 (34.12); Anal Calcd (found) for **2** (wt%): V, 13.13 (13.68); Se, 41.20 (41.68); C, 6.23 (6.31); H, 2.60 (2.38); N, 7.27 (7.48).

2.2. Determination of crystal structure

Crystals of **1** and **2** suitable for single-crystal X-ray diffraction with size $0.6\text{ mm} \times 0.3\text{ mm} \times 0.2\text{ mm}$ and

$0.4\text{ mm} \times 0.4\text{ mm} \times 0.3\text{ mm}$ were glued to a thin glass fiber with epoxy resin and mounted on a Siemens SMART CCD diffractometer equipped with a normal-focus, 2.4-kW sealed-tube X-ray source (graphite-monochromatic $\text{MoK}\alpha$ radiation, $\lambda(\text{MoK}\alpha) = 0.71073\text{ \AA}$) operating at 50 kV and 40 mA. Intensity data were collected at a temperature of $20 \pm 2^\circ\text{C}$. The total number of measured reflections and observed unique reflections were 4216 and 1427 for **1**, for **2** were 10923 and 3262, respectively. For compound **1**, intensity data of 1427 independent reflections ($-23 \leq h \leq 23$, $-14 \leq k \leq 14$, $-18 \leq l \leq 9$) were collected in the ω scan mode. For compound **2**, intensity data of 3262 independent reflections ($-10 \leq h \leq 10$, $-7 \leq k \leq 6$, $-16 \leq l \leq 16$) were collected in the ω scan mode. Data processing was accomplished with the SAINT processing program [25]. Direct methods were used to solve structures using the SHELXTL crystallographic software package. The structure was solved in the space group $C2/c$ for compound **1** and $P2_1/c$ for compound **2** and refined on F^2 by full-matrix least squares using SHELXT97 [26]. The selenium and vanadium atoms were located first. Carbon and nitrogen atoms were found in the difference Fourier map. Hydrogen atoms were placed geometrically. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal parameters and details of the data collection and refinement for structures **1** and **2** are listed in Table 1. Atomic coordinates and equivalent isotropic displacement parameters of compounds **1** and **2** are listed in Tables 2 and 3. Selected bond lengths of compounds **1** and **2** are listed in Table 4.

3. Results and discussion

Although solid state oxides have been conventionally prepared by high-temperature solid-state reactions,

Table 1
Crystal data and structure refinement for **1** and **2**

	1	2
Empirical formula	$\text{V}_4\text{Se}_4\text{O}_{26}\text{H}_{16}$	$\text{C}_2\text{H}_{10}\text{N}_2\text{VSe}_2\text{O}_7$
fw	951.73	382.98
T (K)	293(2)	293(2)
λ (Å)	0.7103	0.7103
Space group	$C2/c$	$P2_1/c$
a (Å)	21.2250(11)	9.6389(4)
b (Å)	12.6309(6)	6.9922(3)
c (Å)	17.0249(10)	15.0324(5)
β ($^\circ$)	96.830(3)	102.297(2)
V (Å ³)	4531.8(4)	989.90(7)
Z	8	4
ρ_{calc} (Mg m^{-3})	2.790	2.570
μ (mm^{-1})	8.137	8.371
R_1^a [$I > 2\sigma(I)$]	0.0344	0.0452
wR_2^b [$I > 2\sigma(I)$]	0.119	0.117

Note: $R_1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|$; $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]\}^{1/2}$.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
V(1)	1398(1)	5215(2)	−1131(2)	15(1)
V(2)	1103(1)	7715(2)	1134(2)	14(1)
V(3)	1399(1)	10218(2)	−1130(2)	15(1)
V(4)	1096(1)	2719(2)	1128(2)	15(1)
Se(1)	1681(1)	7663(1)	−521(1)	15(1)
Se(2)	820(1)	5162(1)	520(1)	15(1)
Se(3)	818(1)	10162(1)	520(1)	14(1)
Se(4)	1681(1)	2664(1)	−521(1)	14(1)
O(1)	1392(5)	6796(8)	−1248(6)	20(3)
O(2)	1476(5)	5381(8)	62(6)	17(3)
O(3)	1710(5)	3743(8)	−1068(7)	27(3)
O(4)	1572(5)	5119(9)	−2279(7)	31(3)
O(5)	2453(5)	5526(9)	−875(7)	25(3)
O(6)	647(5)	5055(9)	−1288(7)	29(3)
O(7)	1023(5)	7870(8)	−46(6)	19(3)
O(8)	786(5)	6263(8)	1079(7)	28(3)
O(9)	1088(5)	9285(8)	1254(6)	21(3)
O(10)	873(5)	7661(9)	2249(6)	27(3)
O(11)	28(5)	8022(9)	927(7)	28(3)
O(12)	1853(5)	7572(9)	1305(6)	28(3)
O(13)	1708(5)	8738(8)	−1088(7)	26(3)
O(14)	1484(5)	10379(8)	48(6)	19(3)
O(15)	1611(5)	10152(8)	−2271(6)	24(3)
O(16)	2447(5)	10505(9)	−907(7)	30(3)
O(17)	648(5)	10075(9)	−1274(7)	26(3)
O(18)	1091(5)	4298(8)	1248(7)	21(3)
O(19)	1020(4)	2887(8)	−46(6)	16(3)
O(20)	884(5)	2626(9)	2302(6)	27(3)
O(21)	1874(5)	2583(9)	1283(7)	27(3)
O(22)	64(4)	3030(9)	925(7)	24(3)
O(23)	803(5)	11239(8)	1107(7)	27(3)
O(24)	1402(5)	1810(8)	−1252(6)	18(3)
O(1W)	2497(6)	8698(8)	−2498(8)	27(3)
O(2W)	0	1182(12)	2500	27(4)
O(3W)	0	6209(12)	2500	25(4)

Note: U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
V(1)	7484(1)	4978(2)	2714(1)	20(1)
Se(1)	9261(1)	1345(1)	2077(1)	18(1)
Se(2)	4097(1)	4224(1)	1875(1)	21(1)
O(1)	8614(5)	3621(7)	1949(3)	25(1)
O(2)	5854(5)	3970(8)	1838(4)	35(1)
O(3)	7697(7)	3762(10)	3622(4)	54(2)
O(4)	11024(5)	1915(7)	2104(4)	32(1)
O(5)	8755(6)	517(8)	1006(4)	38(1)
O(6)	3830(6)	1967(10)	2117(7)	82(3)
O(7)	3408(6)	4392(9)	766(4)	44(2)
C(1)	5040(8)	863(12)	−297(6)	33(2)
C(2)	9965(8)	9253(10)	5365(5)	25(2)
N(1)	6146(6)	2228(9)	172(4)	28(1)
N(2)	9153(7)	7581(8)	4946(4)	26(1)

Note: U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Selected bond lengths (\AA) for compound **1** and **2**

<i>Compound 1</i>			
V(1)–O(1)	2.007(11)	V(2)–O(7)	2.006(10)
V(1)–O(2)	2.029(11)	V(2)–O(8)	1.952(10)
V(1)–O(3)	1.973(11)	V(2)–O(9)	1.993(11)
V(1)–O(4)	2.035(12)	V(2)–O(10)	2.017(11)
V(1)–O(5)	2.264(10)	V(2)–O(11)	2.299(10)
V(1)–O(6)	1.597(11)	V(2)–O(12)	1.596(11)
V(3)–O(13)	1.980(11)	V(4)–O(18)	2.005(11)
V(3)–O(14)	2.002(11)	V(4)–O(19)	1.997(10)
V(3)–O(15)	2.048(11)	V(4)–O(20)	2.104(10)
V(3)–O(16)	2.240(11)	V(4)–O(21)	1.650(10)
V(3)–O(17)	1.596(10)	V(4)–O(22)	2.213(10)
V(3)–O(24)#1	2.021(11)	V(4)–O(23)#2	1.970(11)
Se(1)–O(1)	1.711(10)	Se(2)–O(2)	1.698(10)
Se(1)–O(7)	1.714(10)	Se(2)–O(8)	1.692(11)
Se(1)–O(13)	1.671(11)	Se(2)–O(18)	1.699(10)
Se(3)–O(9)	1.717(11)	Se(4)–O(3)	1.656(11)
Se(3)–O(14)	1.730(10)	Se(4)–O(19)	1.726(10)
Se(3)–O(23)	1.690(11)	Se(4)–O(24)	1.700(10)
<i>Compound 2</i>			
V(1)–O(1)	1.985(5)	Se(2)–O(2)	1.716(5)
V(1)–O(2)	1.954(5)	Se(2)–O(6)	1.652(6)
V(1)–O(3)	1.585(6)	Se(2)–O(7)	1.662(6)
V(1)–O(4)#3	1.952(5)	C(1)–N(1)	1.491(10)
V(1)–O(6)#4	1.934(6)	C(1)–C(1)#5	1.512(16)
Se(1)–O(1)	1.705(5)	C(2)–N(2)	1.472(9)
Se(1)–O(4)	1.737(5)	C(2)–C(2)#6	1.526(14)
Se(1)–O(5)	1.682(5)		

Note: Symmetry transformations used to generate equivalent atoms (for compound **1**): 1 $x, y + 1, z$; 2 $x, y - 1, z$.

Symmetry transformations used to generate equivalent atoms (for compound **2**): 3 $-x + 2, y + 1/2, -z + 1/2$; 4 $-x + 1, y + 1/2, -z + 1/2$; 5 $-x + 1, -y, -z$; 6 $-x + 2, -y + 2, -z + 1$.

hydrothermal methods have been demonstrated to be effective in the syntheses of solid state oxides and inorganic–organic hybrid materials as well [27–30]. In a specific hydrothermal process, many factors may affect the formation and crystal growth of products, such as the type of initial reactants, pH value, reaction time and temperature. In our case, low temperature was of crucial importance for the crystallization of products, for high-temperature led the precipitation of metal Se in the presence of reductive amine. In the crystallization of **1** and **2**, reaction should be controlled under 110–120°C.

The structure of **1** consists of 1D chains constructed from VO_6 octahedra and SeO_3 pyramids which were corner shared. As shown in Fig. 1, the connectivity of the alternating VO_6 and SeO_3 units results in the infinite chains. The asymmetric unit of **1** contains four V and Se atoms, respectively. The coordination of each octahedral vanadium center is defined by a vanadyl oxygen (V(1)–O(6) 1.597(11) Å, V(2)–O(12) 1.596(11) Å, V(3)–O(17) 1.596(10) Å, V(4)–O(21) 1.650(10) Å) and three oxygen donors from SeO_3 groups, with the V–O bond distances ranging from 1.952(10) to 2.029(10) Å; two remaining positions are a hydroxyl group (V(1)–O(4) 2.035(12) Å, V(2)–O(10) 2.017(11) Å, V(3)–O(15)

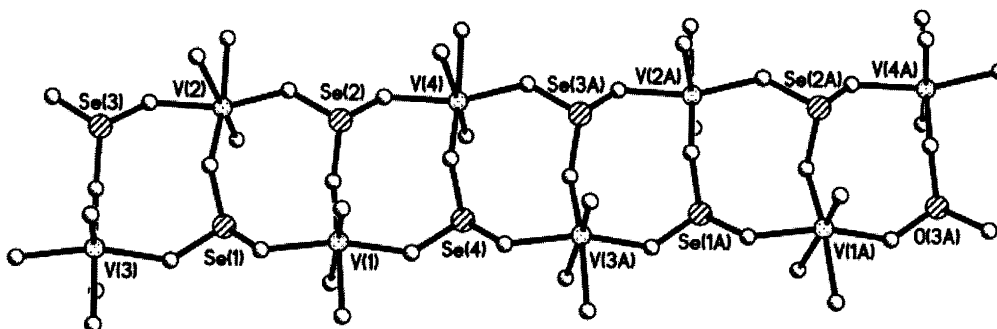


Fig. 1. View of $\{[\text{VO}(\text{OH})(\text{H}_2\text{O})](\text{SeO}_3)\}_\infty$ chains in **1**.

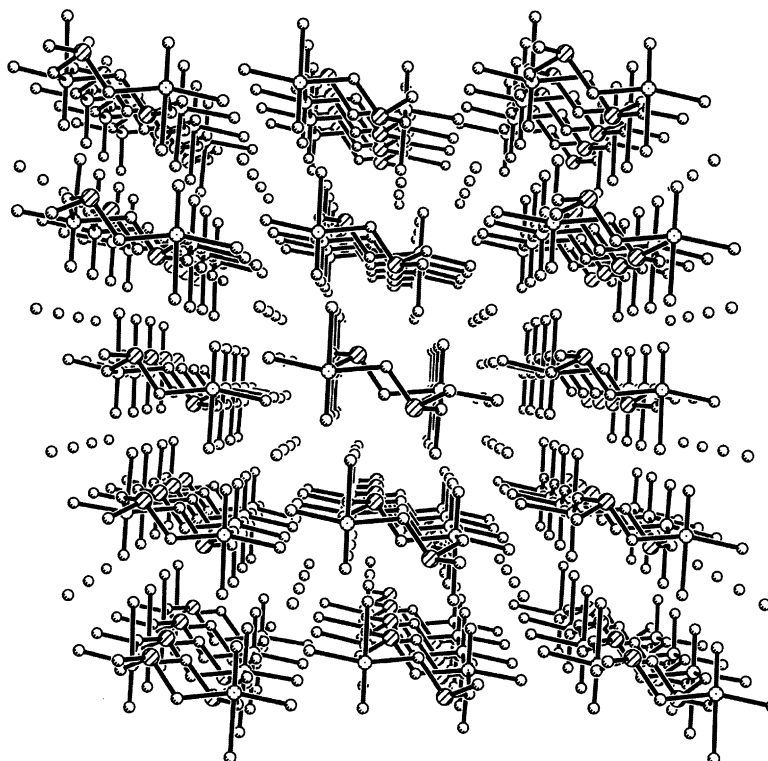


Fig. 2. The framework structure of $\{[\text{VO}(\text{OH})(\text{H}_2\text{O})](\text{SeO}_3)\}_4 \cdot 2\text{H}_2\text{O}$ **1** along $[0\ 1\ 0]$.

2.048(11) Å, V(4)–O(20) 2.104(10) Å) and a water molecule (V(1)–O(5)_w 2.264(10) Å, V(2)–O(11)_w 2.299(10) Å, V(3)–O(16)_w 2.240(11) Å, V(4)–O(22)_w 2.213(10) Å). Each of four independent Se atoms is bound to three oxygen atoms coming from three adjacent VO₆ groups to form a SeO₃ pyramid with a lone pair electron. Thus, V and Se atoms, together with their associated oxygen atoms, form the first type of polyhedral chain in $\{[\text{VO}(\text{OH})(\text{H}_2\text{O})](\text{SeO}_3)\}_4 \cdot 2\text{H}_2\text{O}$. As illustrated in Fig. 2, the lattice water residing between the chains stabilize the structure. Single-crystal structure analysis, as well as elemental analysis, shows there are no triethylamine molecules incorporated in the structure. However, triethylamine is found to be necessary for the formation of the $\{[\text{VO}(\text{OH})(\text{H}_2\text{O})]$

$(\text{SeO}_3)\}_4 \cdot 2\text{H}_2\text{O}$ (**1**) since parallel reactions with different structure-directing agents result in different networks. If ethylenediamine is used instead of triethylamine, the layered compound of $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3) \cdot [(\text{VO})(\text{SeO}_3)_2]$ (**2**) will be obtained.

The structure of **2** contains macroanionic layers $[(\text{VO})(\text{SeO}_3)_2]^{2-}$ compensated by protonated ethylenediamine. As shown in Fig. 3, there are two crystallographically independent Se atoms and one V atoms in the asymmetric unit of the compound **2**. Each VO₅ square pyramid shares four oxygen atoms with adjacent Se atoms and the V–O bond lengths vary within 1.934(6)–1.985(5) Å, while each SeO₃ trigonal pyramid shares two oxygens with adjacent V atoms and the Se–O bond lengths vary within 1.652–1.737(5) Å. Both VO₅

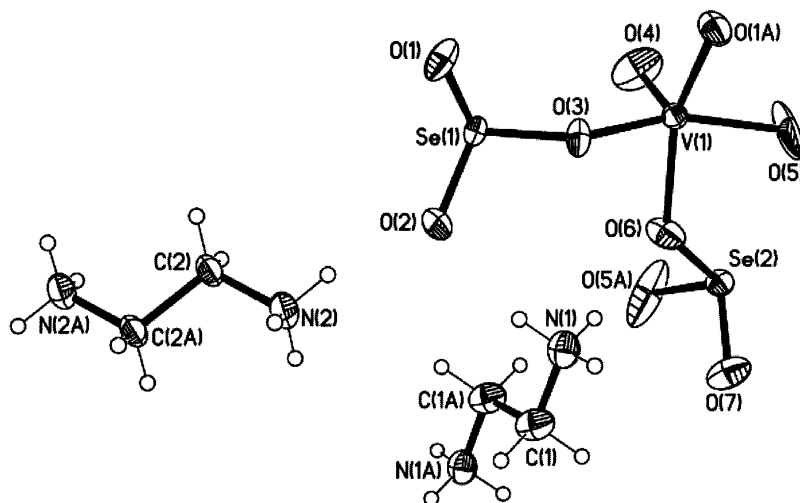


Fig. 3. ORTEP drawing of the asymmetric unit of **2** (50% thermal ellipsoids).

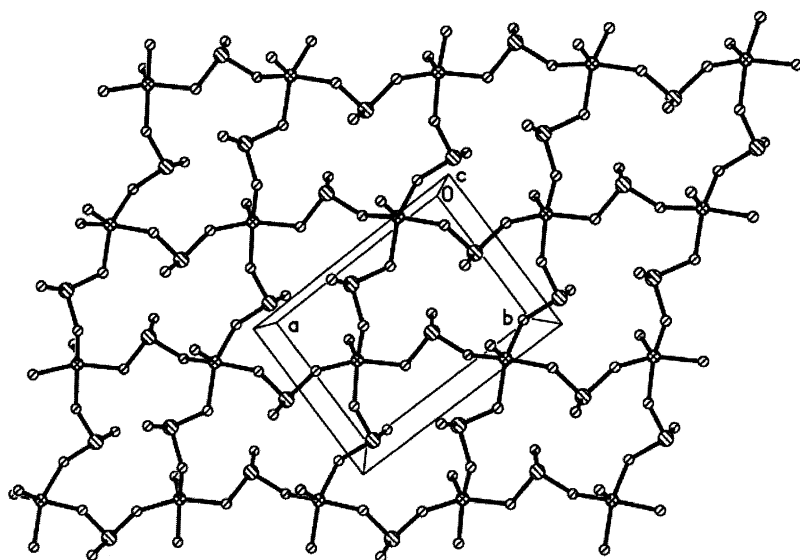


Fig. 4. View of the layered $[(VO)(SeO_3)_2]^{2-}$ along the c -axis in **2**.

and SeO_3 leave a terminal oxygen with bond length of $V(1)-O(3)$ 1.585(6) Å, $Se(1)-O(5)$ 1.682(5) Å and $Se(2)-O(7)$ 1.662(6) Å. This implies a possibility of further condensation to higher dimensionality. The +4 oxidation states of V atoms have been confirmed by valence sum calculation. The connectivity of the alternating VO_5 and SeO_3 unit results in the inorganic layers, which contain interconnected $[(VO_3)_4(SeO_3)_4]$ eight-membered rings (Fig. 4). The bridging distance between two octahedral V centers is 6.122 Å and the bridging distances between Se atoms on the eight-membered ring are 4.162 and 8.339 Å, respectively. The organic amine cations ($NH_3^+CH_2CH_2NH_3^+$) located in the interlayer regions are hydrogen bonded to the framework oxygen atoms (Fig. 5). In this reaction, ethylenediamine acts not only as a templating agent, but also as

a reducing agent, which is responsible for the reduction of V^{5+} to V^{4+} .

The TGA-DTA study was carried out from room temperature to 800°C. A weight loss of ~10.86% for **1** from 260°C to 300°C is in agreement with the calculated amount of water molecules. Another weight loss of ~49.31% in the range of 300–480°C is corresponding to the release of hydroxyl groups and selenium dioxides. The TGA curve of compound **2** shows that the protonized ethylenediamine cations decomposed in the region 240–300°C with a weight loss of 15.67%. The release of selenium dioxides are contributed to another weight loss of ~47.05% in the range of 300–480°C. A small gain between 480°C and 520°C shown in the curve was attributed to the oxidation of the V from V^{4+} to V^{5+} .

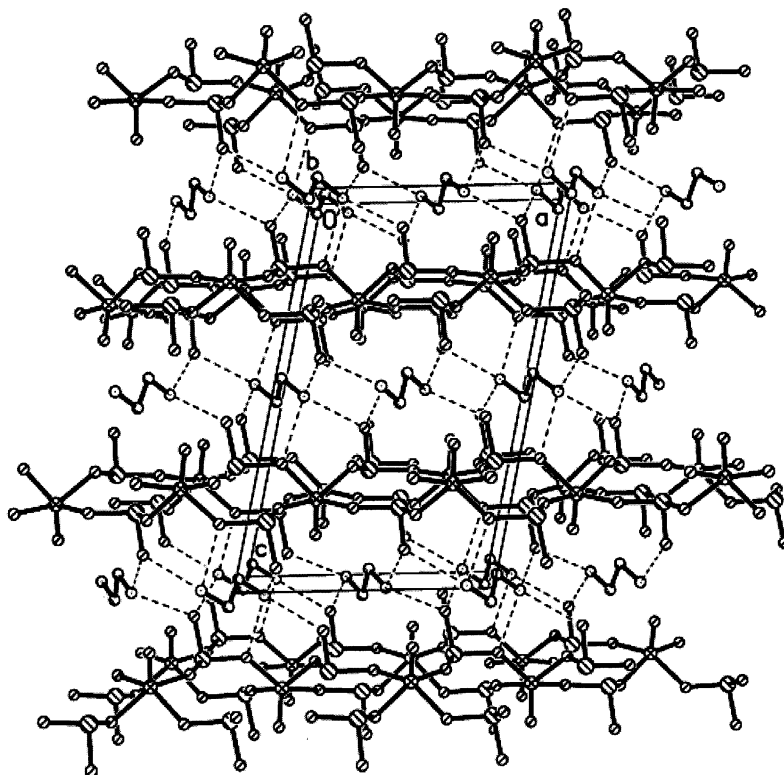


Fig. 5. View of the packing structure of **2** along the *b*-axis.

4. Conclusion

We have hydrothermally synthesized two novel vanadium selenites using triethylamine and ethylenediamine as the structure directing agents, respectively. In compound **1** the connection of the alternating VO_5 and SeO_3 units results in the infinite chains $\{[\text{VO}(\text{OH})(\text{H}_2\text{O})](\text{SeO}_3)\}$ and water molecules are trapped between the chains. The structure of compound **2** contains macroanionic layers $[(\text{VO})(\text{SeO}_3)_2]^{2-}$ that are charge-balanced by protonated ethylenediamine. The successful synthesis of compounds **1** and **2** demonstrated that it is possible to assemble open-framework of vanadium selenite with various structural architectures using organic species as the template under suitable conditions.

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