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Mild Synthesis and Structural Characterization of a Novel Vanadyl Selenite-Hydrogen Selenite Phase, Na[VO(SeO_3)($HSeO_3$)]·1,5H_2O

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Abstract: Single crystals of Na[VO(SeO_3)($HSeO_3$)]·1,5H_2O have been prepared by solvent slow evaporation from an equimolar aqueous mixture of sodium selenite and vanadyl sulfate. The overall arrangement consists of VO_6 octahedra, $[SeO_3]^{2-}$ and $[HSeO_3]^{-}$ anions forming a strong backbone with channel-like voids, while sodium cations participate in the framework, ensuring the overall charge balance. The crystal packing of the material features channels with a star-shaped section showing a mean aperture of 6.10 Å with the oxygen atoms of the V=O moieties pointing towards the interior of the cavities. Their dimensions are the narrowest reported until now in vanadium selenite compounds. Disordered sodium cations with occupancy factor of 0.5 are found in the star-shaped section cavities together with disordered water molecules, interacting with each other via hydrogen bonds.

Keywords: vanadyl selenite; vanadyl hydrogen selenite; crystal structure; crystal packing; layered structure; channels

1. Introduction

Compounds containing selenite or hydrogen selenite anions are of great interest within the scientific community, from synthetic, structural and chemical points of view.

The bridging properties of selenites for connecting to transition metal cations allow magnetic exchange between paramagnetic centers in oligonuclear transition metal selenite complexes [1]. Recently, the weakly coordinative capability of the Se(IV) electron lone pair has been found to give rise to supramolecular interactions, as observed for the polyoxoselenitepalladate anions $[Pd_{15}(\mu_3\text{-}SeO_3)_{10}(\mu_3\text{-}O)_{10}Na]^{9-}$ in the solid state [2]. Regarding the chemistry of extended solids, the stereochemically active lone pair of electrons in Se(IV) may cause the inorganic selenites to crystallize into non-centrosymmetric structures exhibiting interesting physical properties such as nonlinear optical second harmonic generation (SHG) [3,4]. Moreover, it has been observed that some selenites show a highly robust 3D open framework structure, which is retained upon the removal of guests or coordinated small molecules. Selenite and hydrogen selenite anions allow the formation of solid-state structures characterized by the presence of open channels and/or cavities able to house the selenium electron pair [5]. The porous structures of selenite derivatives open the possibility of using such compounds for the synthesis of Metal-Organic Frameworks (MOFs) or Porous Coordination Polymers (PCPs). The formation of either open-framework or non-centrosymmetric materials has been the focus of intense research for many years, since the combination of both an open-framework and non-centrosymmetry within a single compound is especially attractive. Templated vanadium selenites are considered interesting systems owing to the presence of multiple asymmetric building units. This includes the possibility of using chiral organic amines, out-of-center octahedral distortions on vanadium cations, and stereoactive lone pairs on the Se(IV) centers [6–9].

Hydrothermal techniques have been applied to metal selenite systems in order to obtain different crystal phases [6,9]. These reaction conditions are especially attractive for exploratory work because they promote the growth of large single crystals and can be tuned to accommodate nearly any metal center [10]. Metal oxides have been widely used, owing to their structural diversity and technologically advantageous properties [11].

Pursuing our interest in the chemistry of selenite transition metal complexes to be used as precursor for the preparation of the corresponding metal selenides, we reacted sodium selenite with transition metal salts in water solution at room temperature. In the case of the reaction between vanadyl sulfate and sodium selenite in acidic conditions, we observed the formation of a microcrystalline powder. This was unambiguously identified as $Na[VO(SeO_3)(HSeO_3)]\cdot1,5H_2O$. Its crystal structure is here discussed and compared with selenite and hydrogen selenite vanadyl phases reported in the literature.

2. Materials and Methods

2.1. General Techniques

All manipulations were carried out at room temperature in the air; vanadyl sulfate (97% purity), sodium selenite (98% purity), and solvents (Analytical Grade) were purchased and used as received (Aldrich, St. Louis, MO, USA). FTIR spectra (4000–400 cm^{-1}) were recorded on a Nicolet Nexus spectrophotometer equipped with a Smart Orbit HATR accessory (diamond).

2.2. X-ray Data Collection, Structure Solution, and Refinement

The intensity data of the compound were collected on a Bruker APEX II single crystal diffractometer [12,13] equipped with an area detector using a graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Crystallographic and experimental details of the reported structure are summarized in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares procedures (based on F_o^2) using SHELXL-2014/7 (version 2014/7) [14,15], first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atom of the hydrogen selenite anion was introduced into the geometrically calculated position. The sodium cation was found disordered in two positions with occupancy factor of 0.69 and 0.40 respectively. The structure has been deposited in the Inorganic Crystal Structure Database (ICSD) with CSD number 434385.

2.3. Preparation of $Na[VO(SeO_3)(HSeO_3)]\cdot1,5H_2O$

A water solution (10 mL) of Na_2SeO_3 (0.706 g, 4.1 mmol) was prepared and acidified by adding an equimolar amount of a sulfuric acid solution (96%) [d = 1.84 g/mL]. A pale blue water solution (15 mL) containing $VOSO_4$ (0.665 g, 4.1 mmol) was added dropwise to the first solution at room temperature. The clear blue solution was stirred for 20 min. Then the solvent was left to evaporate, and small amount of deep green crystals suitable for X-ray analysis were obtained. FTIR (Diamond crystal HATR): ν (SeO_3^{2-}) = 693 cm^{-1}, ν (VO^{2+}) = 958 cm^{-1}.

Table 1. Summary of crystallographic data for Na[VO(SeO_3)($HSeO_3$)]·1,5H_2O.

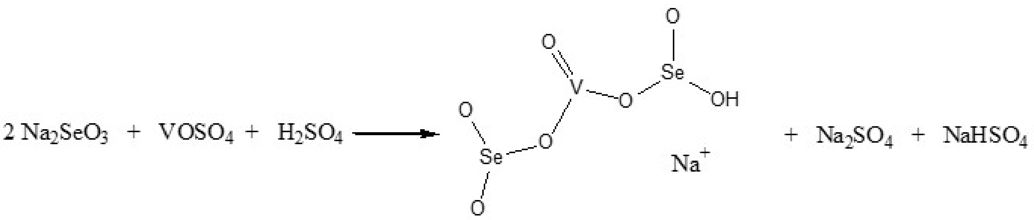
	Na[VO(SeO_3)($HSeO_3$)]·1,5H_2O
Formula	$H_4NaO_{8,5}Se_2V$
FW	371.88
crystal system	Monoclinic
space group	$C2/c$
a, Å	18.5779(16)
b, Å	7.5662(7)
c, Å	12.5844(11)
β, deg	111.612(1)
V, Å^3	1644.6(3)
Z	8
T(K)	298
D_{calcd}, g cm^{-3}	3.004
$F(000)$	1352.0
μ, cm^{-1}	10.125
rflns collected	9710
rflns unique	1697
rflns observed [$I > 2\sigma(I)$]	1365 [R_{int} = 0.0618]
Parameters	134
R indices [$I > 2\sigma(I)$]	$R1 = 0.0382$; $wR2 = 0.1001$
R indices (all data)	$R1 = 0.0504$; $wR2 = 0.1064$

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]$.

3. Results and Discussion

3.1. Chemistry and Crystal Growth

The exchange reaction between Na_2SeO_3 and $VOSO_4$ salts in water solution and at room temperature led to the formation of a vanadyl selenite hydrogen selenite phase, whose crystalline structure was fully elucidated by means of X-ray diffraction analysis on suitable single crystals obtained by slow evaporation of the solvent. A relatively small number of vanadium selenite compounds with analogous arrangement are present in the literature, although their syntheses have been carried out in hydrothermal conditions. In the phase here reported, the overall charge balance of the extended [VO(SeO_3)($HSeO_3$)] network is ensured by sodium cations. According to the study by Olshansky et al., the acidic pH environment is necessary for the attainment of similar phases, and this can be extended also to the present case [16]. The overall chemical reaction equation is reported in Scheme 1.



Scheme 1. Chemical reaction equation.

3.2. Crystal Structure Description

The asymmetric unit of Na[VO(SeO_3)($HSeO_3$)]·1,5H_2O consists of 11 non-hydrogen atoms, among them one vanadium and two crystallographically independent Se atoms, namely Se1 and Se2, as shown in Figure 1. A list of the most important bond distances and angles is reported in the caption of the figure. A sodium atom is also present, disordered in two positions (Na1 and Na2) with occupancy factor of 0.5.

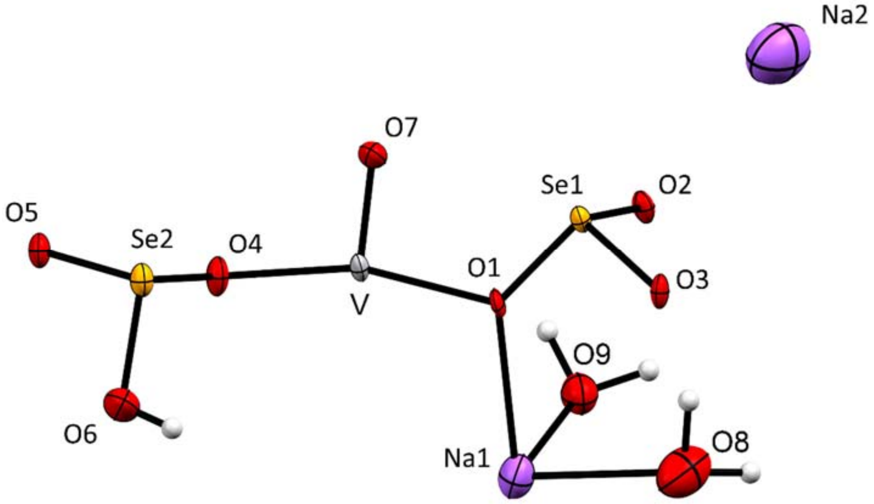


Figure 1. ORTEP view of the asymmetric unit of $Na[VO(SeO_3)(HSeO_3)]\cdot 1{,}5H_2O$. Ellipsoids are depicted at their 30% probability level. List of the most important bond distances [Å] and angles [deg]: Se1-O1 1.712(4), Se1-O3 1.698(4), Se1-O2 1.695(4), Se2-O5 1.656(4), Se2-O4 1.687(4), Se2-O6 1.7560(7), V-O1 1.993(4), V-O4 1.990(5), V-O7 1.596(5); O3-Se1-O1 99.3(2), O2-Se1-O1 100.5(2), O2-Se1-O3 97.6(2), O5-Se2-O4 100.5(2), O5-Se2-O6 97.08(17), O4-Se2-O6 98.83(19), O4-V-O1 162.2(2), O7-V-O1 97.2(2), O7V-O4 100.5(2), Se1-O1-V 120.4(2), Se2-O4-V 123.9(3).

The vanadium atom lies in a distorted octahedral environment with six oxygen atoms: the terminal V=O, two make V-O-Se2 linkages, and the remaining three form V-O-Se1 linkages. The short V=O distance of 1.596(5) Å and the V-O bond distances ranging from 1.982(4) to 2.209(5) Å are in agreement with the mean values observed in similar moieties reported in the Crystallographic Data Bank [17]. In particular, as reported in Figure 2, the distorted octahedron presents the shortest and the longest V-O distances in *trans* to one another, with the remaining four V-O bond lengths on the equatorial plane. Moreover, the vanadium atom is out of the mean plane defined by the equatorial bonded oxygen atoms of 0.297(5) Å.

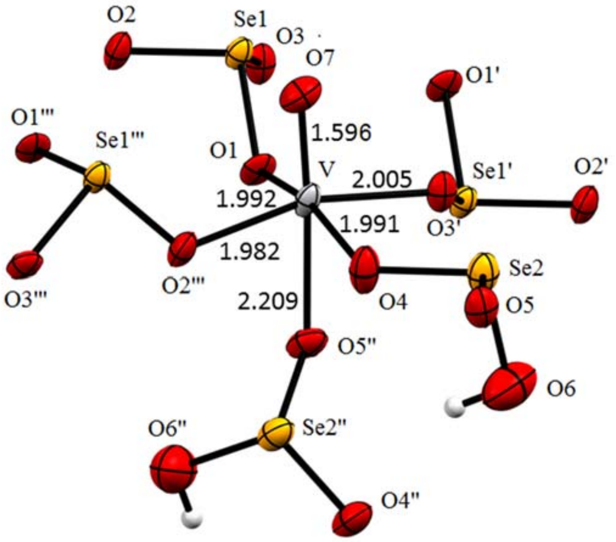


Figure 2. ORTEP diagram of the distorted vanadium octahedron, bond distances are reported in Å. Ellipsoids are depicted at their 30% probability level. Symmetry codes for atoms: ‘ = 2 − x, 2 − y, 1 − z; ′′ = 2.5 − x, −0.5 + y, 1.5 − z; ‘′′ = 2 − x, y, 1.5 − z.

The two Se atoms exhibit a trigonal pyramidal geometry with a stereoactive lone pair. The three oxygen atoms around Se1 are connected to the neighboring VO_6 octahedra with bond angles of 120.4(2), 120.3(2) and 122.7(3)° (mean value 121.1(2)°). The selenium lone pair occupies the tetrahedral site. In the case of Se2; however, only two of the oxygen atoms form such linkages, while the third is protonated. The V-O-Se2 bond angles involving the non-protonated oxygen atom are 115.8(2) and 123.9(2)°. The presence of a longer Se2-O6 bond distance of 1.756(1) Å and the absence of interactions of this oxygen with the vanadium atom are coherent the presence of a terminal OH group.

3.3. Analysis of Molecular Packing

The overall framework structure of the compound is built up of VO_6, SeO_3, and $HSeO_3$ units. All three oxygen atoms of SeO_3 are shared by three neighboring vanadium-oxygen octahedra in such a manner as to form a ladder developing along the *c*-axis, consisting of edge-shared eight membered rings, each ring composed of two Se and two V atoms and four bridging oxygen atoms, as shown in Figure 3.

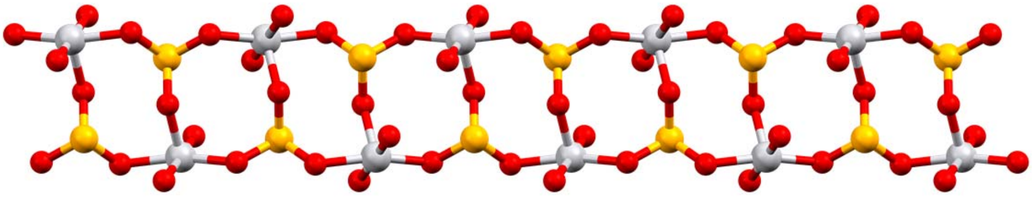


Figure 3. Partial framework structure of $Na[VO(SeO_3)(HSeO_3)]\cdot 1{,}5H_2O$ evidencing the formation of a ladder developing along the *c*-axis consisting of edge-shared eight membered rings.

These ladders are connected to one another by $HSeO_3$ groups along the *a*-axis to form a layer in the *ac*-plane as shown in Figure 4. This connectivity leads to the formation of a sixteen-membered bifurcated aperture with the dimensions 8.664 Å and 9.058 Å (vanadium to vanadium distance). The Se-O-H pendant moiety dandling above and below the aperture.

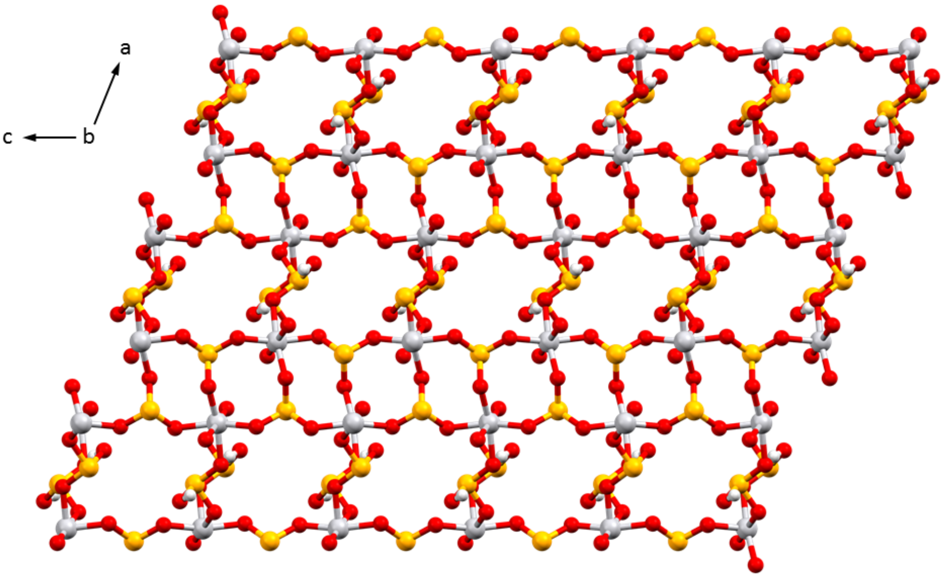


Figure 4. Extension of the ladders in $Na[VO(SeO_3)(HSeO_3)]\cdot 1{,}5H_2O$ along the *a*-axis to form a layer in the *ac*-plane. Sodium atoms and water molecules have been omitted for clarity.

3.4. Crystal Packing of Disordered Na$^+$ *Cation in the Channels*

The chain and layer motif observed in compound Na[VO(SeO$_3$)(HSeO$_3$)]·1,5H$_2$O is similar to that in earlier reported vanadium selenite compounds organically templated with nitrogen containing cations and is considered to be a building unit in the vanadium selenite, whose progressive building up process, from the one-dimensional structure to two and three-dimensional complex structures has been demonstrated [6,9].

Viewing the crystal packing along the *c*-axis, as depicted in Figure 5, it is evident to observe the formation of channels with a star-shaped section with a mean aperture of 6.10 Å (O to O distance), with the oxygen atoms of the V=O moieties pointing towards the interior of the cavities.

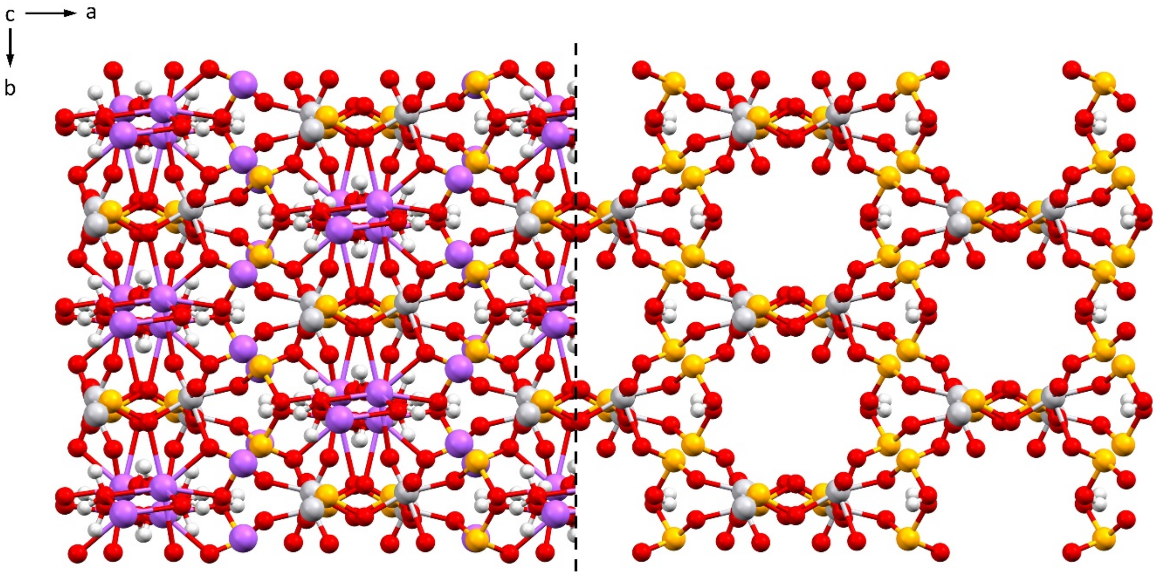


Figure 5. Crystal packing viewed along the *c*-axis, evidencing the formation of channels with a star-shaped section in which disordered Na$^+$ cations (purple) and water molecules can insert.

Both the V and Se atoms are in the +4 oxidation state, so that the framework charge is -1, [(VO)(HSeO$_3$)(SeO$_3$)]$^-$ balanced by metal cations. In fact, disordered sodium cations are found in the star-shaped section cavities (Figure 5) together with water molecules, interacting each other via hydrogen bonds.

As far as the 16-member star-shaped apertures are concerned, similar types of channels are also observed in reported vanadium selenite compounds organically templated with nitrogen-containing cations [7–9,16].

The mean dimension of the diameter of the cavities can vary depending on the size of the cationic moiety located into the channel and the presence of crystallization solvent molecules. Figure 6 shows the crystal packing of structures containing vanadium selenite hydrogen selenite compounds reported in the literature, in which channels developing along one of the crystallographic axes are present.

The dimensions of the mean diameter of the channels are reported in Table 2. All deposited structures present a dimension greater than the one observed in the case of Na[VO(SeO$_3$)(HSeO$_3$)]·1,5H$_2$O. This is due to the greater hindrance of the nitrogen-containing organic cations—sometimes cocrystallized together with solvent molecules—with respect to the dimension of the sodium atom. Moreover, the nitrogen-containing cations inserted into the channels reported in the literature are involved in a strong network of hydrogen bonds with the oxygen atoms of the selenite or hydrogen selenite anions.

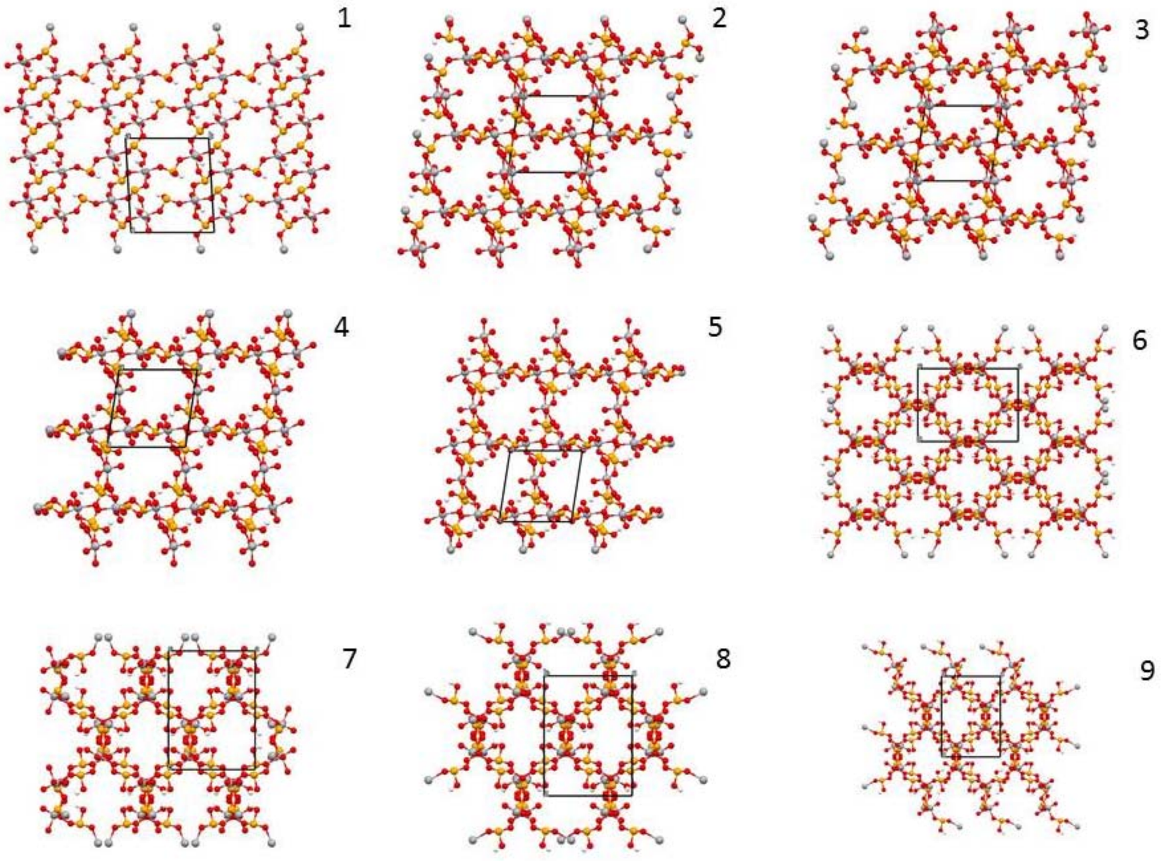


Figure 6. Channels developing in the crystal packing of reported vanadium selenite compounds organically templated with nitrogen containing cations.

Table 2. Mean diameter [Å] of the cavities found in the literature compared with the one observed in Na[VO(SeO_3)($HSeO_3$)]·1,5H_2O.

Na[VO(SeO_3)($HSeO_3$)]·1,5H_2O	1	2	3	4	5	6	7	8	9
6.10	6.50 [9]	7.83 [16]	7.38 [16]	7.89 [16]	7.95 [16]	7.83 [7]	8.27 [7]	7.57 [7]	6.40 [7]

In the crystallographic data bank of inorganic compounds, the crystal structures of the K[VO(SeO_3)($HSeO_3$)] [18] and of NH_4[VO(SeO_3)($HSeO_3$)] [19] are described. In those cases, the crystal structure and the morphology, shape and dimensions of the channels are very different from those of the presented phase. In fact, in both potassium and ammonium containing structures, very similar to one another, the overall crystal packing is composed of chains built up by VO_5 square pyramids pointing up and down alternatingly with respect to the direction of the chains and SeO_3 trigonal pyramid units. These chains are connected to one another by very strong hydrogen bonds. Moreover, each VO_5 interacts with adjacent VO_5 through the long V···O interaction. In the crystal packing of [NH_4][H(VO)(SeO_3)$_2$] and [K][H(VO)(SeO_3)$_2$], narrow channels with an average diameter of 4.35 Å are formed, and the potassium atom or NH_4^+ cations, with analogous steric hindrance, can insert. Both cations strongly interact with the oxygen atoms of the selenite and hydrogen selenite anions by hydrogen bonds.

4. Conclusions

Carrying out a reaction between vanadyl sulfate and sodium selenite with a water solvent at room temperature and under acidic conditions, a novel selenite hydrogen selenite phase was formed. The formula is Na[VO(SeO_3)($HSeO_3$)]·1,5H_2O, and its structure is composed of chain and layer crystallographic motifs, similar to those observed in previously reported vanadium selenite compounds organically templated with nitrogen-containing cations. The crystal packing of the material features channels with a star-shaped section with a mean aperture of 6.10 Å. The dimension of the cavities is, to our knowledge, the narrowest that has been reported until now for vanadium selenite compounds. Other selenite phases containing simple inorganic cations have been reported in the literature, such as with potassium or ammonium. In the present case, the overall crystal network is more similar to the one observed in reported organically templated vanadium selenite compounds than to the potassium- or ammonium-containing selenite structures. We suggest that the dimensions of the sodium cations, which are remarkably smaller than those of ammonium or potassium cations, makes it possible to keep the formation of main channels, as observed in reported vanadium selenite compounds, available to host disordered sodium cations together with disordered solvent molecules. This size effect can be exploited to obtain open framework compounds, where the structural presence of the cations does not prevent the accessibility of the cavities.

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