[VO(SeO$_3$)(H$_2$O)$_2$]·0.5H$_2$O

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In poly[[diaquaoxido[μ_3-trioxidoselenato(2−)]vanadium(IV)] hemihydrate], {[VO(SeO$_3$)(H$_2$O)$_2$]·0.5H$_2$O}$_n$, the octahedral V(H$_2$O)$_2$O$_4$ and pyramidal SeO$_3$ building units are linked by V−O−Se bonds to generate ladder-like chains propagating along the [010] direction. A network of O−H···O hydrogen bonds helps to consolidate the structure. The O atom of the uncoordinated water molecule lies on a crystallographic twofold axis. The title compound has a similar structure to those of the reported phases [VO(OH)(H$_2$O)(SeO$_3$)]$_4$·2H$_2$O and VO(H$_2$O)$_2$(HPO$_4$)·2H$_2$O.

Comment

Vanadium phosphates (VPOs) have been intensively studied for many years due to their catalytic (Hutchings, 2009) and electrochemical applications (Yang *et al.*, 2010), and their magnetic properties (Geupel *et al.*, 2002). Crystallochemically, VPOs display remarkable structural diversity due to the accessibility of different vanadium oxidation states (V^{III}, V^{IV} and V^V) with different coordination preferences to O atoms and the variety of bonding modes of the linking (hydrogen) phosphate anions (Amorós *et al.*, 1999; Whittingham *et al.*, 2005); when organic templates are employed in the synthesis, still further structural variety is possible (Finn *et al.*, 2003). Compared to phosphates, other oxo-anions such as selenite in combination with vanadium cations have been less well studied. We now describe the structure of the vanadium(IV)-containing compound poly[[diaquaoxido[μ_3-trioxidoselenato(2−)]vanadium(IV)] hemihydrate], (I). The only other well characterized vanadium selenite hydrates are V^{IV}O(H$_2$O)(SeO$_3$), (II) (Huan *et al.*, 1991), and [V^{V}O(OH)(H$_2$O)(SeO$_3$)]$_4$·2H$_2$O, (III) (Dai *et al.*, 2003).

The polyhedral building units of (I) are a vanadium(IV) atom bonded to six O atoms (two of which are from water molecules) in a distorted octahedral arrangement and a pyramidal selenite group (Fig. 1 and Table 1). An uncoordinated water molecule (O-atom site symmetry 2) completes the structure of this hemihydrate.

V1 makes a characteristic short 'vanadyl' bond to O5, which must have significant double-bond character: such short V=O

bonds are typical of both V^{IV} (Mentre *et al.*, 2009) and V^V (Yakubovich *et al.*, 2008). Sometimes the vanadyl O atom can make a weak bond to another metal ion (Duc *et al.*, 2006; Meng *et al.*, 2009), but here it is bonded only to V1, although it also acts as an acceptor for two O−H···O hydrogen bonds (see below). Water atom O6 in (I) is coordinated *trans* to O5 at a relatively long V−O distance, whereas the V−O bond lengths of the other four O atoms are clustered in a narrow range around 2.0 Å. The second water molecule (O4) is bonded to V1 in a *cis* orientation with respect to O6, and its *trans* oxygen atom (O2) also links to the Se atom. Atoms O1 and O3 complete the vanadium coordination sphere; both of these also link to Se. The bond valence sum (BVS) for V1, calculated by the Brown & Altermatt (1985) method, is 4.09 (expected value 4.00) assuming that V^{IV} is present, which is supported by the pale-blue crystal colour of (I) (Bircsak *et al.*, 1999).

Se1 shows its expected trigonal pyramidal geometry (Verma, 1999) with respect to O1, O2 and O3, which can be understood in terms of its unseen formal [Ar]3d^{10}4s^2 lone pair of electrons occupying the fourth tetrahedral vertex. The mean Se−O separation is 1.698 Å and the Se BVS of 4.08 compares well to the expected value of 4.00. Se1 is displaced from the plane of its attached O atoms by 0.7724 (11) Å, which is comparable to the situation in related compounds (Johnston & Harrison, 2007).

The polyhedral connectivity in (I) means that each V atom is linked to three Se atoms and each Se atom is linked to three V atoms, thus there are no V−O−V links. Ladder-like chains propagating along the [010] direction (Fig. 1) occur in the crystal of (I) featuring vertex sharing of the constituent V(H$_2$O)$_2$O$_4$ octahedra and SeO$_3$ pyramids, generating edge-shared 4-rings.

The water molecules in (I) form O−H···O hydrogen bonds with all their available H atoms (Table 2). O6 makes two hydrogen bonds to an adjacent chain displaced in the *c* direction. O4 makes one hydrogen bond to a chain displaced
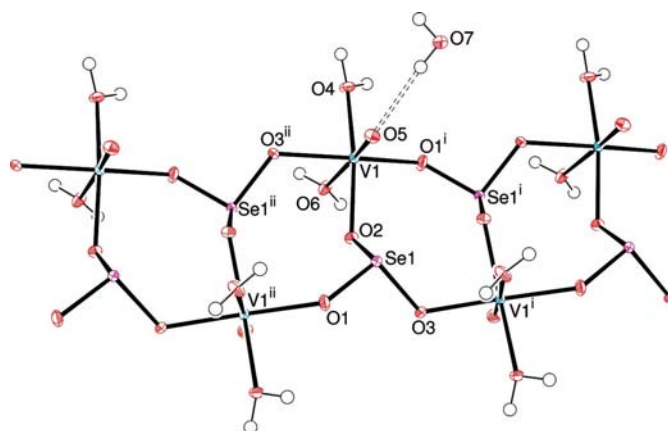

Figure 1
Fragment of an [010] chain in (I), showing the vertex-sharing connectivity of the V(H$_2$O)$_2$O$_4$ and SeO$_3$ building units and the hydrogen bond (double-dashed line) between the uncoordinated water molecule and atom O5. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.]
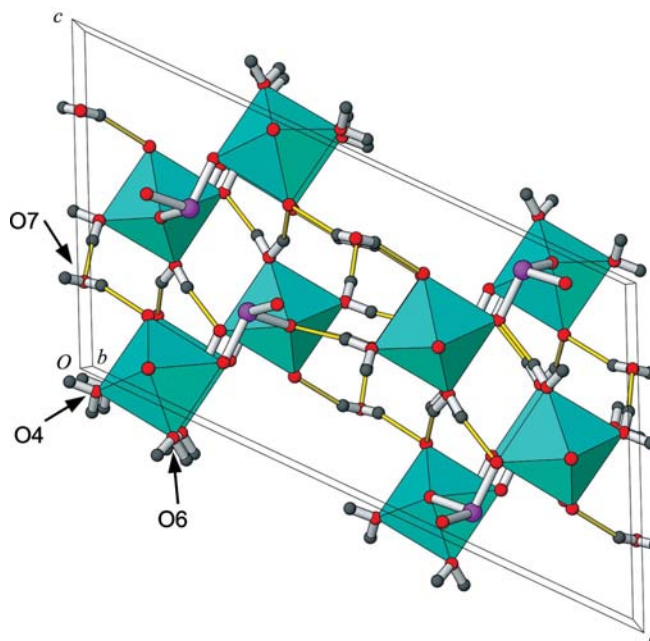
inorganic compounds

Figure 2
Unit-cell packing for (I), viewed approximately down [010]. In the electronic version of the paper, the $V(H_2O)_2O_4$ groups are shown as green polyhedra, Se atoms as purple spheres, O atoms as red spheres, H atoms as grey spheres, and hydrogen bonds as thin yellow lines.

in the a direction; its other H atom bonds to the uncoordinated water molecule (O7). Finally, O7, makes two symmetry-equivalent hydrogen bonds to the vanadyl O atom to reinforce the inter-chain connectivity in the a direction (Fig. 2).

Although they share similar polyhedral building units, the structures of (I) and (II) are completely different, with the latter adopting a layered network of vertex- and edge-sharing $V(H_2O)O_5$ and SeO_3 polyhedra akin to that in $VO(HPO_4)\cdot$ $0.5H_2O$ (Leonowicz *et al.*, 1985). The relationship of (I) and (III) deserves some comment: if the formula for (III) of $[VO(OH)(H_2O)(SeO_3)]_4\cdot2H_2O$ stated by Dai *et al.* (2003) is rewritten as $VO(OH)(H_2O)(SeO_3)\cdot0.5H_2O$, the similarity to (I) is apparent, with an OH group bonded to V^V in (III) replacing a water molecule bonded to V^{IV} in (I) to maintain charge balance. The reported unit cell of (III) is much larger than that of (I), but the structural motif of polyhedral chains is similar to that of (I). The H atoms in (III) were not located, so the hydrogen-bonding networks cannot be compared. Dai *et al.* (2003) synthesized their compound from V_2O_5 and the crystal colour of (III) was described as green. The presumed terminal V—OH bond in (III) is uncommon and perhaps unexpected, given the low-pH synthesis used. However, it is known that V^V can undergo facile reduction to V^{IV} in hydrothermal reactions (Meng *et al.*, 2009) and that some V^{IV} compounds are green in colour (Geupel *et al.*, 2002). Thus, an alternative formulation for (III) could be $V^{IV}O(H_2O)_2$- $(SeO_3)\cdot0.5H_2O$, *i.e.* a polymorph with the same formula as (I); such polymorphism is a known feature of vanadium phosphate chemistry (Le Bail *et al.*, 1989).

In terms of vanadium phosphates, (I) bears a close resemblance to $VO(H_2O)_2(HPO_4)\cdot2H_2O$, (IV) (Leonowicz *et al.*,

1985; Fratzky *et al.*, 1999), which features ladder-like chains constructed from $V(H_2O)_2O_4$ and HPO_4 building units; the hydrogen phosphate ion is topologically equivalent to selenite, as the P—OH vertex does not link to vanadium. However, the presence of two uncoordinated water molecules per chain-formula-unit in (IV) compared to half a water molecule in (I) leads to a completely different hydrogen-bonding arrangement.

Experimental

Crystal data

$[VO(SeO_3)(H_2O)_2]\cdot0.5H_2O$	$V = 1116.48\ (11)$ Å^3
$M_r = 238.9$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 18.7819\ (13)$ Å	$\mu = 8.26$ mm^{-1}
$b = 6.2881\ (4)$ Å	$T = 120$ K
$c = 10.5581\ (4)$ Å	$0.20 \times 0.10 \times 0.08$ mm
$\beta = 116.443\ (4)°$	

Data collection

Nonius KappaCCD diffractometer	6097 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)	1276 independent reflections
$T_{min} = 0.289$, $T_{max} = 0.558$	1133 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	79 parameters
$wR(F^2) = 0.054$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{max} = 0.67$ e Å^{-3}
1276 reflections	$\Delta\rho_{min} = -0.59$ e Å^{-3}

Table 1
Selected bond lengths (Å).

V1—O5	1.613 (2)	V1—O6	2.2300 (18)
V1—O1^i	1.9677 (19)	Se1—O1	1.6718 (19)
V1—O3^{ii}	2.007 (2)	Se1—O3	1.7060 (18)
V1—O2	2.0098 (19)	Se1—O2	1.7151 (18)
V1—O4	2.039 (2)		

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H1$\cdots$O7^{iii}	0.82	1.86	2.671 (3)	171
O4—H2$\cdots$O3^{iv}	0.81	1.88	2.689 (3)	174
O6—H3$\cdots$O5^v	0.82	2.16	2.906 (3)	151
O6—H4$\cdots$O2^{vi}	0.82	1.97	2.777 (3)	165
O7—H5$\cdots$O5	0.81	2.03	2.801 (3)	158

Symmetry codes: (iii) $-x, -y + 1, -z$; (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $x, -y, z - \frac{1}{2}$; (vi) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.

The H atoms were located in a difference map and regularized [O—H = 0.82 (1) Å and H—O—H = 104 (2)°], then treated as riding atoms in the final refinement cycles with the constraint $U_{iso}(H) = 1.2U_{eq}(O)$ applied.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997), *SCALEPACK* and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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