inorganic papers

[Y(HSeO$_3$)(SeO$_3$)(H$_2$O)]·H$_2$O

William T. A. Harrison

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail:
w.harrison@abdn.ac.uk

The title compound, aqua(hydrogen trioxoselenato)(trioxoselenato)yttrium(III) monohydrate, which is isostructural with its samarium(III) and neodymium(III) analogues, contains YO$_8$, SeO$_3$ and HSeO$_3$ coordination polyhedra, which fuse together by corner- and edge-sharing, resulting in a layered structure. A network of O—H···O hydrogen bonds helps to consolidate the crystal packing.

Comment

The title compound, (I) (Fig. 1), is isostructural with its samarium (Koskenlinna *et al.*, 1994) and neodymium (de Pedro *et al.*, 1994) analogues.

Compound (I) contains both (SeO$_3$)$^{2-}$ selenite and (HSeO$_3$)$^-$ hydrogen selenite anions. The unobserved lone pair of electrons of the Se^{IV} species gives rise to the characteristic pyramidal shape of these oxo-anions. As seen previously (Koskenlinna *et al.*, 1994), the Se–OH vertex [1.745 (4) Å] in (I) is longer than the Se—O bonds [mean = 1.690 (15) Å] (Table 1). The Se atoms are displaced from the planes of their three attached oxygen atoms by 0.804 (2) and 0.814 (2) Å for Se1 and Se2, respectively. In terms of bond angles, the angle of the edge-sharing (to Y) O1–Se1–O2 grouping is significantly more acute [92.37 (16)°] than the other O–Se–O sets (mean = 100.4°).

The yttrium cation in (I) is surrounded by eight oxygen atoms, one of which (O7) is part of a water molecule, with a fairly narrow spread of distances [2.258 (3)–2.419 (3) Å;
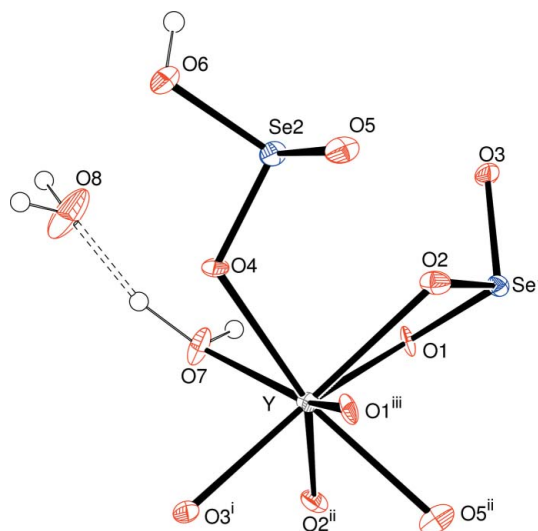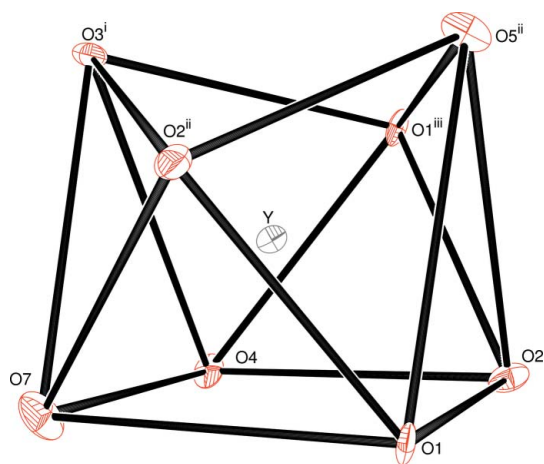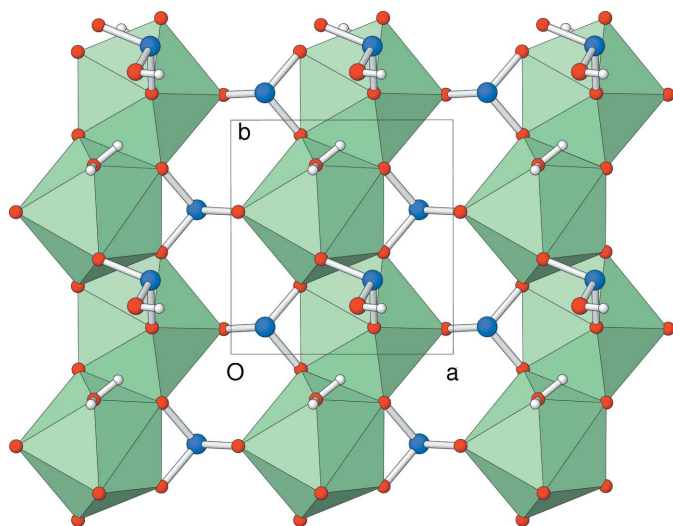

Figure 1
The asymmetric unit of (I) expanded to show the Y atom coordination (70% displacement ellipsoids; spheres of arbitrary radius for the H atoms). Symmetry codes as in Table 1.
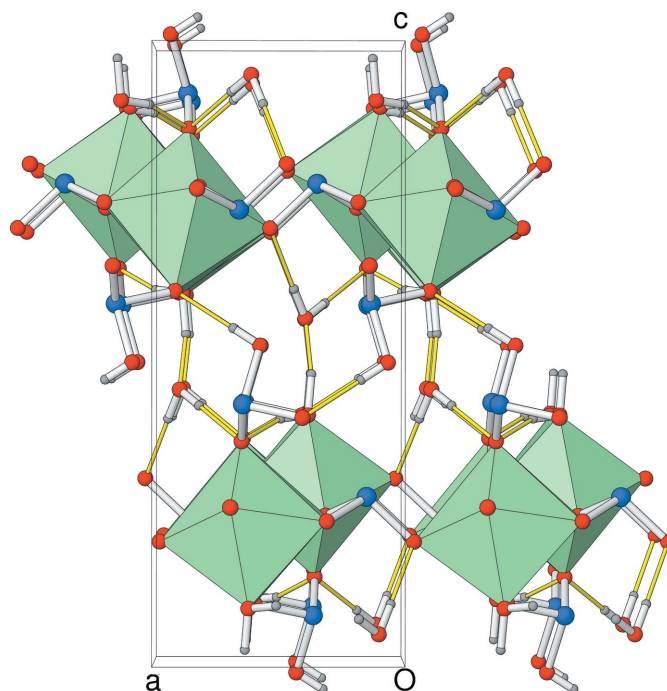
Figure 2
Detail of (I) showing the Y atom coordination with O···O contacts < 3.3 Å shown as lines (50% displacement ellipsoids). Symmetry codes as in Table 1.

Figure 3
View down [001] of a layer in (I) in polyhedral representation, showing the [010] chains of edge-sharing YO_8 groups cross-linked by the Se1 atoms. Colour key: YO_8 groups green, Se atoms blue, O atoms red, H atoms grey.

Figure 4
The packing in (I), viewed down [010]. Drawing convention as in Fig. 3, with the H···O portions of the hydrogen bonds highlighted in yellow.

mean = 2.36 (5) Å]. The next nearest O atom has a distance of Y—O4^i = 3.872 (3) Å [symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$]. The YO_8 grouping could be described as a highly distorted square antiprism (Fig. 2) or possibly as irregular. Atoms O1, O2, O4 and O7 conform well to a square [r.m.s. deviation from the mean plane = 0.041 Å; O1···O4 = 3.915 (5) Å and O2···O7 = 3.988 (5) Å], whereas the nominal O1^{iii}, O2^{ii}, O3^i and O5^{ii} (see Table 1 for symmetry codes) square is grossly distorted [r.m.s. deviation from the mean plane = 0.399 Å; O1^{iii}···O2^{ii} = 4.440 (5) Å and O3^i···O5^{ii} = 3.339 (5) Å]. The Y atom is displaced by 1.3249 (18) Å from the first plane, and 1.1900 (18) Å from the second. The interplanar dihedral angle is 1.8 (2)°. Atoms O3, O4 and O5 are bicoordinate to Y and Se (mean Y—O—Se = 124.2°), whilst O1 and O2 are tricoordinate to one Se and two Y atoms (bond angle sums = 343.5 and

349.0°, respectively). O6 is part of a terminal Se—OH vertex and O7 and O8 are parts of water molecules.

The polyhedral connectivity in (I) (Fig. 3) involves chains of YO_8 groups sharing edges, *via* O1 + O2^{ii} and O1^{iii} + O2 pairs, to result in chains propagating along [010]. The relatively acute O1—Y—O2^{ii} and O1^{iii}—Y—O2 bond angles of 67.81 (12) and 68.02 (11)° respectively, correlate with this polyhedron-fusing role. The Y···Y^{ii} separation within the chain is 3.9668 (5) Å. The Y/O chains are cross-linked in the [100] direction by the Se1O₃ groups, involving the edge-sharing motif noted above. Finally, the (HSe2O₃)⁻ groups decorate and reinforce the [010] Y/O chains, resulting in a structure with layered character.

The hydrogen-bonding scheme in (I) involves all the H atoms participating in O—H···O links (Table 2). The Y-bonded water molecule (O7) makes a hydrogen bond to an adjacent YO_8 group in the same sheet (*via* H2) and to the inter-sheet water molecule (*via* H1). The hydrogen selenite anion makes the only direct inter-sheet hydrogen bond (Fig. 4). As well as accepting an hydrogen bond, the non-coordinated water molecule (O8) makes two hydrogen bonds to the same adjacent sheet.

The average metal–oxygen distances in these isostructural phases are Y—O = 2.36 (5) Å, Sm—O = 2.42 Å and Nd—O = 2.45 Å. This pattern is exactly consistent with the differences in the eight-coordinate atomic radii (Shannon, 1976) of Y^{3+} (1.019 Å), Sm^{3+} (1.079 Å) and Nd^{3+} (1.109 Å).

Experimental

A mixture of YCl₃·6H₂O (0.83 g, 2.74 mmol), SeO₂ (0.5 g, 4.5 mmol) and water (10 ml) was sealed in a 23 ml Teflon-lined autoclave and

heated to 433 K for three days, followed by cooling to room temperature over a few hours. Product recovery by vacuum filtration and rinsing with water and acetone led to 0.173 g (16.6% based on Y) of tiny colourless bars and rods of (I).

Crystal data

[Y(HSeO$_3$)(SeO$_3$)(H$_2$O)]·H$_2$O	$Z = 4$
$M_r = 379.87$	$D_x = 3.447$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 6.5485$ (3) Å	$\mu = 17.92$ mm^{-1}
$b = 6.8987$ (2) Å	$T = 120$ (2) K
$c = 16.2022$ (7) Å	Rod, colourless
$V = 731.95$ (5) Å^3	$0.14 \times 0.03 \times 0.02$ mm

Data collection

Nonius KappaCCD diffractometer	6897 measured reflections
ω and φ scans	1667 independent reflections
Absorption correction: multi-scan	1523 reflections with $I > 2\sigma(I)$
(*SADABS*; Bruker, 1999)	$R_{int} = 0.054$
$T_{min} = 0.188$, $T_{max} = 0.716$	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + 0.7811P]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.053$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.63$ e Å^{-3}
1667 reflections	$\Delta\rho_{min} = -0.72$ e Å^{-3}
101 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	664 Friedel pairs
	Flack parameter: 0.646 (11)

Table 1
Selected geometric parameters (Å, °).

Y—O3^i	2.258 (3)	Y—O1	2.419 (3)
Y—O7	2.346 (3)	Se1—O3	1.680 (3)
Y—O5^{ii}	2.347 (3)	Se1—O1	1.701 (3)
Y—O4	2.367 (3)	Se1—O2	1.710 (3)
Y—O2^{ii}	2.372 (3)	Se2—O4	1.672 (3)
Y—O1^{iii}	2.376 (4)	Se2—O5	1.689 (3)
Y—O2	2.402 (4)	Se2—O6	1.745 (4)
Se1—O1—Y^{ii}	130.66 (18)	Y^{iii}—O2—Y	112.41 (13)
Se1—O1—Y	101.19 (15)	Se1—O3—Y^{iv}	130.39 (19)
Y^{ii}—O1—Y	111.66 (13)	Se2—O4—Y	117.18 (17)
Se1—O2—Y^{iii}	135.03 (18)	Se2—O5—Y^{iii}	124.96 (17)
Se1—O2—Y	101.58 (15)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H1···O4^v	0.82	1.92	2.712 (5)	164
O7—H2···O5^{vi}	0.92	1.93	2.806 (5)	159
O7—H3···O8	0.86	1.82	2.644 (5)	163
O8—H4···O3^{vii}	0.94	1.93	2.874 (5)	179
O8—H5···O5^{viii}	0.93	2.03	2.964 (5)	179

Symmetry codes: (v) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (vi) $x, y + 1, z$; (vii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (viii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

The crystal studied was an inversion twin with volume fractions of 0.354 (11):0.646 (11) for the component reported in the tables and its enantiomer, respectively. All the H atoms were located in difference maps and refined as riding in their as-found relative positions, with U_{iso}(H) = 1.2U_{eq} (carrier).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997), and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *ATOMS* (Shape Software, 2005); software used to prepare material for publication: *SHELXL97*.

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