Strontium manganese diselenite, SrMn(SeO$_3$)$_2$, containing unusual MnO$_{5+1}$ polyhedra

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Hydrothermally prepared SrMn(SeO$_3$)$_2$ contains infinite chains of vertex-sharing irregular MnO$_{5+1}$ polyhedra [mean Mn—O 2.226 (3) Å], which are fused into layers *via* pyramidal SeO$_3$ groups [mean Se—O 1.698 (3) Å]. Nine-coordinate Sr^{2+} cations [mean Sr—O 2.715 (4) Å] complete the layered structure.

Comment

SrMn(SeO$_3$)$_2$ (Fig. 1) is isostructural with the synthetic compound SrZn(SeO$_3$)$_2$ (Johnston & Harrison, 2001), but with subtly different divalent metal coordination. In SrZn(SeO$_3$)$_2$, the Zn atom is coordinated by six O atoms in an unusual 4+2 coordination, described as bicapped tetrahedral. In the title compound, the Mn atom has six O-atom neighbours, with one Mn—O bond distinctly longer than the other five. The average Mn—O separation for the five near-neighbour O atoms (2.180 Å) is in very good agreement with the ionic radius sum for high-spin Mn^{II} and O^{2-} (2.19 Å; Shannon, 1976). However, the bond-valence sum (BVS; Brown, 1996) of 1.76 for Mn is much lower than the expected value of 2.00. If the more distant O atom [Mn—O 2.452 (3) Å] is considered, the Mn BVS rises to 1.93. This MnO$_{5+1}$ coordination is so grossly distorted from octahedral as to be better regarded as irregular; the nominal *trans* O—Mn—O bond angles are 144.6, 149.0 and 166.9°. The variance of the *cis* O—Mn—O angles (mean 91.2°), as quantified by the method of Robinson *et al.* (1971), has the exceptionally large value of 239.5.

Both of the [SeO$_3$]$^{2-}$ groups in SrMn(SeO$_3$)$_2$ adopt the usual pyramidal coordination (Hawthorne *et al.*, 1987; Harrison, 1999), with BVS(Se1) = 4.08 and BVS(Se2) = 4.06 (expected value 4.00). The Sr^{2+} cation has irregular ninefold coordination by oxygen [mean Sr—O 2.715 Å], with BVS(Sr) = 1.98 (expected value 2.00). The next-nearest O atom is some 3.99 Å distant. As well as their Mn and Se neighbours, all of the O atoms are bonded to one or more Sr^{2+} cations. The average Sr—O separation in SrZn(SeO$_3$)$_2$ is 2.700 (5) Å.

The overall structure consists of infinite chains of vertex-linked MnO$_{5+1}$ groups orientated along the [100] direction. The SeO$_3$ units are fused on to these chains *via* edge sharing. The SeO$_3$ pyramids containing Se1 link adjacent chains in the [001] direction, forming sheets perpendicular to [010], while the SeO$_3$ pyramids containing Se2 are grafted on to the chains. The interlayer Sr^{2+} cations bind adjacent sheets in the [100] direction and provide charge balancing. In a [100] projection (Fig. 2), there appear to be small channels present at ($y = 0$, $z = 0$) and symmetry-equivalent locations. These are probably associated with the Se^{IV} lone pairs and do not represent voids accessible by other chemical species.

Other manganese selenites exhibit distorted Mn^{II}O$_6$ polyhedra. In Mn$_3$(SeO$_3$)$_3 \cdot$H$_2$O (Johnston *et al.*, 2002), one of the MnO$_6$ groups is extremely distorted, with four short bonds (Mn—O < 2.24 Å) and two longer bonds (Mn—O > 2.39 Å) in a *cis* configuration. Similarly, in the mixed-valence phase Mn^{II}Mn$_2^{III}$O(SeO$_3$)$_3$ (Wildner, 1994), the divalent species is described as an MnO$_{4+2}$ grouping, with four short and two long Mn—O bonds. These distorted Mn^{II} environments can be partly attributed to the inter-polyhedral connectivity of the MnO$_6$ and SeO$_3$ groups.
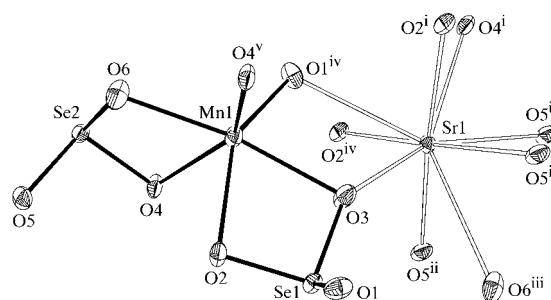

Figure 1
A fragment of SrMn(SeO$_3$)$_2$ with 50% probability displacement ellipsoids, showing the edge sharing of the SeO$_3$ and MnO$_{5+1}$ moieties. The symmetry codes are as in Table 1.
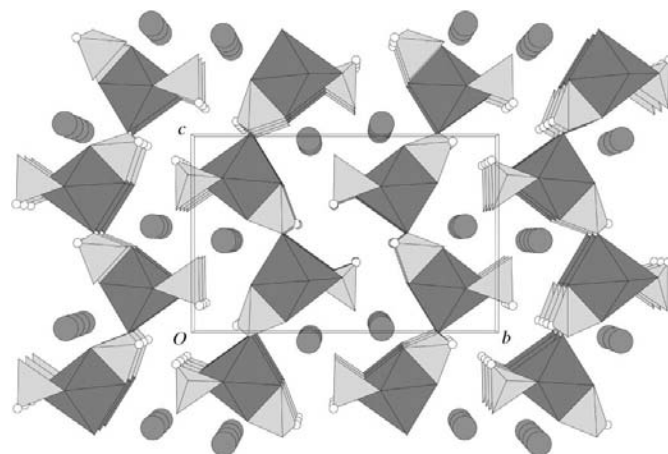

Figure 2
A packing diagram for SrMn(SeO$_3$)$_2$ viewed down [100], in polyhedral representation. The SeO$_3$ pyramids (light shading) are represented by SeO$_3$*E* tetrahedra, where the dummy atom *E*, geometrically placed 1.0 Å from Se and indicated by a small sphere, represents the Se^{IV} lone pair. Sr^{2+} cations are represented by spheres of arbitrary radii.

inorganic compounds

Experimental

$SrCO_3$ (0.154 g, 1 mmol), $MnCl_2{\cdot}4H_2O$ (0.3956 g, 2 mmol), 0.5 M H_2SeO_3 (6 ml) and 1 M LiOH (4.5 ml), at a pre-oven pH of 8.5, were hydrothermally reacted in a 23 ml-capacity sealed Teflon-lined steel bomb in an oven at 453 K. The bomb was removed after 67 h and cooled over a period of 3 h. Upon opening, the bomb contained a clear solution, unidentified white and brown powders, and colourless rod-shaped single crystals of the title compound. The products were recovered by vacuum filtration, and washed with water and then acetone.

Crystal data

$SrMn(SeO_3)_2$	$D_x = 4.184$ Mg m^{-3}
$M_r = 396.48$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 3396
$a = 4.4432\,(2)$ Å	reflections
$b = 14.8002\,(7)$ Å	$\theta = 2.5{-}32.5°$
$c = 9.5955\,(5)$ Å	$\mu = 22.01$ mm^{-1}
$\beta = 94.072\,(1)°$	$T = 298\,(2)$ K
$V = 629.41\,(5)$ Å^3	Rod, colourless
$Z = 4$	$0.34 \times 0.05 \times 0.02$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	2273 independent reflections
	1869 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.050$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$\theta_{max} = 32.5°$
	$h = -6 \rightarrow 6$
$T_{min} = 0.048$, $T_{max} = 0.640$	$k = -22 \rightarrow 21$
7110 measured reflections	$l = -13 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.090$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.01$	$\Delta\rho_{max} = 2.37$ e Å^{-3}
2273 reflections	$\Delta\rho_{min} = -1.83$ e Å^{-3}
91 parameters	

The highest difference peak is 0.83 Å from Se2 and the deepest difference hole is 0.95 Å from Sr1.

Data collection: SMART (Bruker, 1999); cell refinement: SMART; data reduction: SMART; 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 (Dowty, 1999); software used to prepare material for publication: SHELXL97.

Table 1
Selected geometric parameters (Å, °).

Sr1—O3	2.461 (4)	Mn1—O6	2.174 (3)
Sr1—O2^i	2.558 (3)	Mn1—O3	2.231 (3)
Sr1—O5^{ii}	2.607 (3)	Mn1—O2	2.235 (4)
Sr1—O5^i	2.632 (3)	Mn1—O4	2.452 (3)
Sr1—O5^{iii}	2.704 (3)	Se1—O3	1.687 (4)
Sr1—O2^{iv}	2.721 (3)	Se1—O1	1.690 (3)
Sr1—O1^{iv}	2.792 (4)	Se1—O2	1.711 (3)
Sr1—O4^i	2.927 (4)	Se2—O6	1.683 (3)
Sr1—O6^{iii}	3.033 (4)	Se2—O5	1.693 (3)
Mn1—O1^{iv}	2.104 (4)	Se2—O4	1.725 (3)
Mn1—O4^v	2.159 (3)		
O1^{iv}—Mn1—O4^v	107.57 (13)	O2—Mn1—O4	82.45 (12)
O1^{iv}—Mn1—O6	109.38 (15)	O3—Se1—O1	102.95 (18)
O4^v—Mn1—O6	84.05 (12)	O3—Se1—O2	94.75 (17)
O1^{iv}—Mn1—O3	83.70 (14)	O1—Se1—O2	99.03 (17)
O4^v—Mn1—O3	91.19 (13)	O6—Se2—O5	100.39 (18)
O6—Mn1—O3	166.89 (15)	O6—Se2—O4	96.42 (15)
O1^{iv}—Mn1—O2	144.61 (13)	O5—Se2—O4	100.58 (17)
O4^v—Mn1—O2	94.43 (13)	Se1—O1—Mn1^{vi}	123.14 (17)
O6—Mn1—O2	100.00 (14)	Se1—O2—Mn1	97.93 (16)
O3—Mn1—O2	68.11 (13)	Se1—O3—Mn1	98.81 (16)
O1^{iv}—Mn1—O4	91.48 (12)	Se2—O4—Mn1^{vii}	115.94 (16)
O4^v—Mn1—O4	148.98 (15)	Se2—O4—Mn1	92.58 (13)
O6—Mn1—O4	66.32 (11)	Mn1^{vii}—O4—Mn1	148.98 (15)
O3—Mn1—O4	115.60 (12)	Se2—O6—Mn1	104.32 (16)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1190). Services for accessing these data are described at the back of the journal.

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