

LiMn₃(SeO₃)₂(HSeO₃)₆

Magnus G. Johnston and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, Scotland
Correspondence e-mail: w.harrison@abdn.ac.uk

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The title compound, lithium trimanganese bis[trioxoselenate(IV)] hexakis[hydrogentrioxoselenate(IV)], is built up from a vertex-sharing network of distorted Mn^{III}O₆ octahedra, SeO₃ and HSeO₃ pyramids and unusual Li(OH)₆ octahedra, resulting in a dense three-dimensional structure. Mn, Li and one Se atom have site symmetries of $\bar{1}$, $\bar{3}$, and 3, respectively. An O—H···O hydrogen bond helps to establish the crystal packing.

Comment

The title compound, (I), is the second lithium manganese selenite to be characterized by single-crystal diffraction, complementing Li₅Mn₅(SeO₃)₈ (Wildner, 1993), which contains both Mn^{II} and Mn^{III} in a 4:1 ratio. In contrast, (I), which arose from an unexpected atmospheric oxidation reaction, contains only Mn^{III}.

The constituent polyhedra for (I) are shown in Fig. 1 and selected geometric data are listed in Table 1. Mn1 (site symmetry $\bar{1}$) has substantially distorted octahedral coordination to its O-atom neighbours, with four short bonds (<1.92 Å) and two long bonds [2.258 (2) Å] in a *trans* conformation. This distorted coordination polyhedron correlates with the prediction of the high-spin *d*⁴ Mn^{III} cation to undergo a Jahn–Teller distortion (Dunitz & Orgel, 1960). The bond-valence sum (BVS) for Mn1 calculated by the method of Brown (1996) is 3.23 (expected 3.00). The Jahn–Teller radius for Mn1 in (I), as defined by Ammeter *et al.* (1979), is 0.41 Å, indicating a significant degree of distortion. The mean Mn1–O distance of 2.022 Å in (I) is in fairly good agreement with the empirical linear relationship $d_{\text{calc}}(\text{Mn}^{\text{III}}-\text{O}) = (1.994 + 7.08\Delta_{\text{oct}}) \text{ \AA}$ derived by Shannon *et al.* (1975) for a series of high-spin Mn^{III}-containing materials, where Δ_{oct} is the octahedral distortion factor, as defined by these workers: for (I), $\Delta_{\text{oct}} = 6.82 \times 10^{-3}$ and $d_{\text{calc}}(\text{Mn}-\text{O}) = 2.042 \text{ \AA}$. In Li₅Mn₅(SeO₃)₈ (Wildner, 1993), the axial distortion of the Mn^{III}O₆ octahedron (Mn site symmetry $\bar{1}$) is one of the largest known, with a Δ_{oct} value of 9.02×10^{-3} .

Both Se^{IV} atoms in (I) display their characteristic pyramidal geometries, due to the unseen lone pair occupying the fourth tetrahedral vertex about selenium. Atom Se1 occupies a crystallographic threefold axis and the resulting [SeO₃]²⁻

group [displacement of Se1 from the plane of its three attached O atoms = 0.8097 (12) Å] makes three equivalent Se–O1–Mn1 links. Atom Se2 occupies a general position and has two short bonds (<1.70 Å) and one long bond [1.763 (2) Å] to its O-atom neighbours [displacement of Se2 from the O-atom plane = 0.818 (2) Å]. This bond-length distribution is characteristic of the [HSeO₃]⁻ hydrogenselenite ion (Verma, 1999) and the H atom attached to O4 could clearly be discerned in a difference map. This atom participates in an O–H···O hydrogen bond (Fig. 1 and Table 2).

Atom Li1 is surrounded by six OH groupings which are part of the Se2 hydrogenselenite groups. The Li site symmetry of $\bar{3}$ means that there is only one distinct Li–O bond length. The Li(OH)₆ octahedron is almost regular, with the *cis* O–Li–O bond angles being either 89.56 (9) or 90.44 (9)°. The resulting

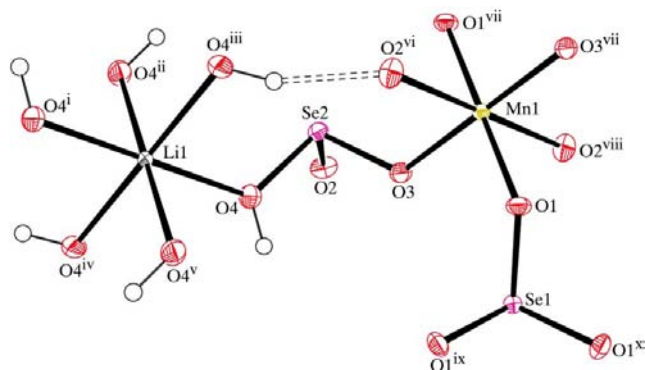


Figure 1
A fragment of (I), showing the constituent polyhedra and the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. The hydrogen bond is indicated by a dashed line. [Symmetry codes: (i) $-x, -y, -z$; (ii) $y - x, -x, z$; (iii) $y, y - x, -z$; (iv) $-y, x - y, z$; (v) $x - y, x, -z$; (vi) $\frac{1}{3} - y, x + y - \frac{1}{3}, z - \frac{1}{3}$; (vii) $1 - x, -y, -z$; (viii) $\frac{2}{3} + y, \frac{1}{3} + y - x, \frac{1}{3} - z$; (ix) $1 + y - x, 1 - x, z$; (x) $1 - y, x - y, z$.]

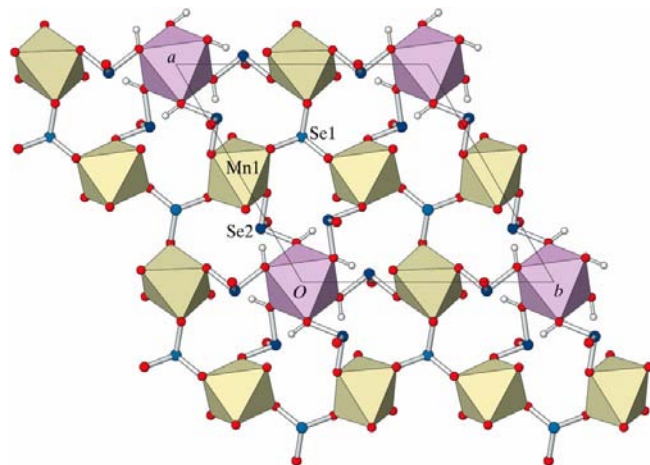


Figure 2
A polyhedral representation [for MnO₆ and Li(OH)₆] of part of an (001) layer in (I), with $-0.33 < z < 0.33$. The Li cation is at the origin and equivalent points.

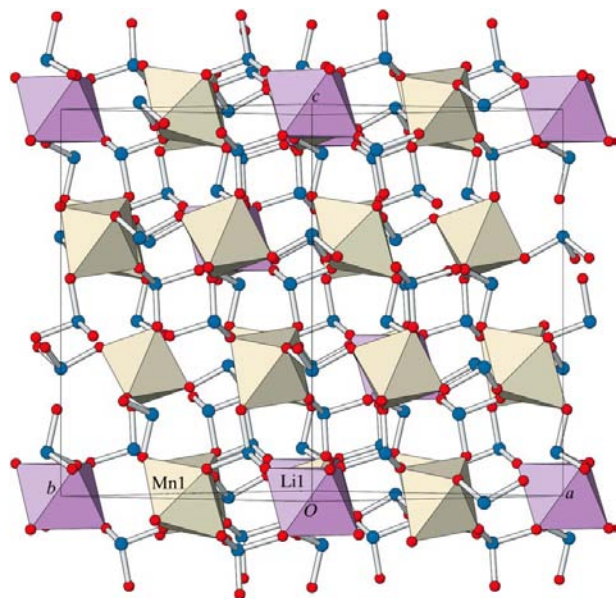


Figure 3
A polyhedral representation of the unit-cell packing in (I). The H atoms have been omitted for clarity.

Li...H separation of 2.61 Å is far too long to constitute any kind of chemical bond (Baur, 1973). Such Li(OH)₆ polyhedra have long been known to occur in layered hydroxides of the clay family (Wadsley, 1952).

The polyhedral connectivity in (I) results in pseudo-layers propagating in (001) (Fig. 2). Every Li(OH)₆ polyhedron, located at the unit-cell origin and equivalent positions, is surrounded by six MnO₆ octahedra in the layer. The Mn-centred moieties are surrounded by two Li(OH)₆ and four MnO₆ groupings. The Se1O₃ group bridges three adjacent MnO₆ groups and the HSe2O₃ group bridges between the Li- and Mn-centred octahedra. Its third vertex (O2) bridges to another MnO₆ octahedron in a layer either above or below its own layer. Thus, the four distinct O atoms in (I) are all bicoordinate bridges: three form Mn—O—Se links and one an Li—O—Se link. There are no Li—O—Mn bonds in (I).

These (0001) layers stack according to rhombohedral crystal symmetry (Fig. 3), resulting in dense polyhedral layers, bridged by the Se2-centred oxo-anions into a three-dimensional network.

Experimental

A mixture of aqueous 0.5 M 'H₂SeO₃' solution (dissolved SeO₂) (7 ml), aqueous 1 M LiCl solution (8 ml) and MnCl₂·6H₂O (0.714 g, 3 mmol) was sealed in a 23 ml Teflon-lined hydrothermal bomb and heated to 473 K for 6 d. Upon cooling over a few hours and then opening the bomb, there was no solid product. The resultant colourless liquor was placed in a Petri dish and, after several weeks, dozens of small orange hexagonal platelets and blocks of (I) were seen growing. A crystal of (I) was dredged out of the viscous liquors for data collection. The reaction was repeatable.

Crystal data

LiMn₃(SeO₃)₂(HSeO₃)₆
M_r = 1193.46
 Trigonal, *R* $\bar{3}$
a = 11.1205 (7) Å
c = 14.843 (1) Å
V = 1589.65 (18) Å³
Z = 3

D_x = 3.740 Mg m⁻³
 Mo *K*α radiation
μ = 15.61 mm⁻¹
T = 293 (2) K
 Block, orange
 0.12 × 0.11 × 0.10 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
T_{min} = 0.256, *T_{max}* = 0.304

5504 measured reflections
 1283 independent reflections
 1017 reflections with *I* > 2σ(*I*)
R_{int} = 0.030
θ_{max} = 32.5°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.024
wR (*F*²) = 0.051
S = 0.97
 1283 reflections
 57 parameters

H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0231*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.66 e Å⁻³
 Δρ_{min} = -0.62 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Li1—O4	2.155 (2)	Se1—O1	1.7005 (18)
Mn1—O3	1.8938 (19)	Se2—O2	1.664 (2)
Mn1—O1	1.9144 (18)	Se2—O3	1.6963 (19)
Mn1—O2 ⁱ	2.258 (2)	Se2—O4	1.763 (2)
Se1—O1—Mn1	125.19 (11)	Se2—O3—Mn1	122.88 (11)
Se2—O2—Mn1 ⁱⁱ	120.95 (11)	Se2—O4—Li1	124.35 (11)

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

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O4—H1...O2 ⁱⁱⁱ	0.88	1.87	2.711 (3)	159

Symmetry code: (iii) $-x + \frac{2}{3}, -y + \frac{1}{3}, -z + \frac{1}{3}$.

The H atom was located in a difference map and refined as riding in its as-found relative position, with *U*_{iso}(H) = 1.2*U*_{eq}(O). A PLATON (Spek, 2003) analysis of (I) indicated significant pseudo-symmetry corresponding to the space group *R* $\bar{3}m$. Attempts to model the structure in this space group, in which more than 20% of the atoms violate the possible higher symmetry, led to physically unreasonable Se...Se contacts and much higher residuals and so was abandoned.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; 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.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3060). Services for accessing these data are described at the back of the journal.

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