Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Lanthanum selenite, $La_2(SeO_3)_3$

William T. A. Harrison

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

Received 10 January 2000
Accepted 29 February 2000

Hydrothermally prepared $La_2(SeO_3)_3$ contains a three-dimensional network of LaO_{10} polyhedra [d_{av}(La—O) = 2.622 (3) Å] and SeO_3 pyramids [d_{av}(Se—O) = 1.691 (3) Å]. One of the SeO_3 pyramids is in a general position and the other has crystallographic *m* symmetry. There are pseudo-channels in the [010] direction which are probably associated with the Se^{IV} lone pairs.

Comment

The lanthanum cation adopts an irregular tenfold coordination, assuming a cut-off of 2.90 Å for the maximum La—O distance [d_{av}(La—O) = 2.622 (3) Å]. The bond valence sum (BVS) of 3.08, calculated by the Brown (1996) formalism, is close to the expected value of 3.00.

The two distinct selenium(IV) species adopt their characteristic pyramidal coordinations (Wildner, 1991; Harrison, 1999), with d_{av}(Se1—O) = 1.690 (3) Å, BVS(Se1) = 4.17, d_{av}(Se2—O) = 1.692 (3) Å and BVS(Se2) = 4.13 (expected BVS = 4.00). The Se2 atom has *m* symmetry.

The polyhedral connectivity in $La_2(SeO_3)_3$ results in infinite sheets of triangular-face-sharing (*via* O1, O2 and O3) and edge-sharing (*via* O3 and O4) LaO_{10} groups arrayed normal to [001]. The $Se1O_3$ group is closely associated with these layers, and the $Se2O_3$ group serves to fuse adjacent layers into a three-dimensional structure. The O5 atom also links adjacent LaO_{10} layers *via* an La—O5(Se2)—La bond. Both $Se1O_3$ and $Se2O_3$ share an edge with an LaO_{10} group (Fig. 1), which is similar to the polyhedral connectivity seen in other rare-earth selenites such as $Nd(HSeO_3)(SeO_3)\cdot H_2O$ (de Pedro *et al.*, 1994). When the structure of $La_2(SeO_3)_3$ is viewed down [010] (Fig. 2), there appears to be infinite channels of approximate dimension 3.6 × 5.5 Å (measured atom-to-atom), but these are probably associated with the stereochemically active selenium(IV) lone pairs and do not represent space accessible by other chemical species. Similar pseudo-channels associated with selenium lone pairs have been seen in phases such as $Bi_2Cu(SeO_3)_4$ (Effenberger, 1996) and $La_2Cu(SeO_3)_4$ (Harrison & Zhang, 1997).

$La_2(SeO_3)_3$ complements $La(HSeO_3)(SeO_3)$ (Morris *et al.*, 1992) which has a somewhat similar structure involving LaO_{10} and $(H)SeO_3$ polyhedra sharing edges and faces. However, the latter phase is genuinely layered, with inter-sheet bonding occurring only *via* Se—OH···O—Se hydrogen bonds and van der Waals forces.

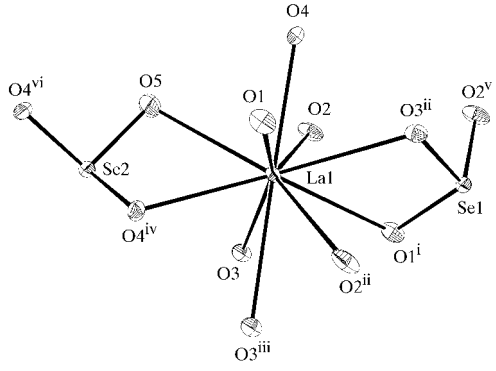

Figure 1
A fragment of the $La_2(SeO_3)_3$ structure with 50% displacement ellipsoids. Symmetry codes are as in Table 1.

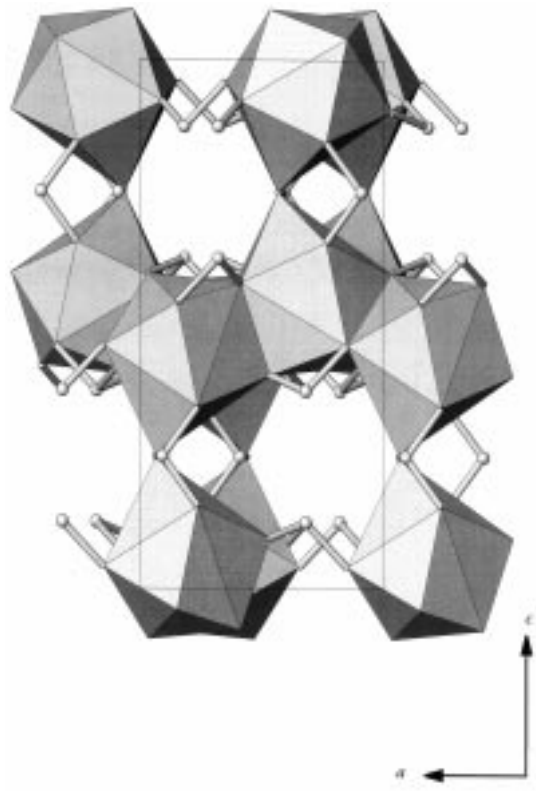

Figure 2
View down [010] of $La_2(SeO_3)_3$, with the LaO_{10} groups in polyhedral representation and the Se atoms represented by spheres of arbitrary radii.

Experimental

A starting mixture of 'H_2SeO_3' (dissolved SeO_2) (8 ml, 0.5 *M*), LiOH (4 ml, 1 *M*), H_2O (4 ml) and $La(NO_3)_3\cdot 9H_2O$ (1.732 g) (Li:La:Se ratio of 1:1:1) was heated to 423 K in a 23 ml-capacity sealed teflon-lined

 © 2000 International Union of Crystallography • Printed in Great Britain – all rights reserved

bomb for 6 d. Upon cooling the bomb to ambient temperature over 2–3 h, the resulting solids [unidentified yellowish powder and transparent plates of $La_2(SeO_3)_3$] were recovered by vacuum filtration and washing with water.

Crystal data

$La_2(SeO_3)_3$
M_r = 658.70
Orthorhombic, *Pbnm*
a = 7.0725 (5) Å
b = 8.4187 (7) Å
c = 14.2273 (11) Å
V = 847.1 (2) Å^3
Z = 4
D_x = 5.17 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3360 reflections
θ = 1–30°
μ = 22.64 mm^{-1}
T = 300 K
Plate, colourless
0.10 × 0.10 × 0.03 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
Area-detector scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.060, T_{max} = 0.424
7762 measured reflections
1271 independent reflections
1079 reflections with $I > \sigma(I)$
R_{int} = 0.05
θ_{max} = 30°
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -19 \rightarrow 19$
Intensity decay: none

Refinement

Refinement on F
R = 0.026
wR = 0.029
S = 1.08
1079 reflections
67 parameters
Chebychev polynomial with 3 parameters (Carruthers & Watkin, 1979) 0.377, 0.275, 0.230
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.19 e Å^{-3}
$\Delta\rho_{min}$ = −1.06 e Å^{-3}
Extinction correction: Larson (1967)
Extinction coefficient: 1.8 (8)

The highest difference peak is 0.72 Å from La1 and the deepest difference hole is 0.66 Å from La1.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SMART*; program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *CRYSTALS*.

Table 1
Selected geometric parameters (Å, °).

La1—O1	2.536 (4)	La1—O4^{iv}	2.561 (3)
La1—O1^{i}	2.656 (4)	La1—O5	2.7928 (19)
La1—O2	2.467 (4)	Se1—O1^{i}	1.687 (3)
La1—O2^{ii}	2.684 (4)	Se1—O2^{v}	1.669 (4)
La1—O3	2.583 (4)	Se1—O3^{ii}	1.713 (3)
La1—O3^{iii}	2.727 (3)	Se2—O4^{iv}	1.694 (3)
La1—O3^{ii}	2.718 (3)	Se2—O4^{vi}	1.694 (3)
La1—O4	2.499 (3)	Se2—O5	1.689 (5)
O1^{i}—Se1—O2^{v}	106.79 (18)	La1—O3—La1^{iii}	118.59 (13)
O1^{i}—Se1—O3^{ii}	99.71 (17)	La1—O3—La1^{i}	100.31 (11)
O2^{v}—Se1—O3^{ii}	95.11 (17)	La1^{iii}—O3—La1^{i}	105.19 (12)
O4^{iv}—Se2—O4^{vi}	104.6 (2)	La1—O3—Se1^{i}	126.46 (17)
O4^{iv}—Se2—O5	97.88 (17)	La1^{iii}—O3—Se1^{i}	103.14 (15)
O4^{vi}—Se2—O5	97.88 (17)	La1^{i}—O3—Se1^{i}	99.35 (15)
La1—O1—La1^{ii}	103.26 (13)	La1—O4—La1^{vii}	117.47 (12)
La1—O1—Se1^{ii}	130.87 (18)	La1—O4—Se2^{vii}	128.03 (17)
La1^{ii}—O1—Se1^{ii}	102.50 (16)	La1^{vii}—O4—Se2^{vii}	104.33 (15)
La1—O2—La1^{i}	104.36 (13)	La1—O5—La1^{viii}	143.1 (2)
La1—O2—Se1^{v}	148.5 (2)	La1—O5—Se2	95.63 (12)
La1^{i}—O2—Se1^{v}	106.19 (16)	La1^{viii}—O5—Se2	95.63 (12)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1284). Services for accessing these data are described at the back of the journal.

References

Brown, I. D. (1996). *J. Appl. Cryst.* **29**, 479–480.
Bruker (1999). *SADABS* and *SMART Software*. Bruker AXS Inc., Madison, Wisconsin, USA.
Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* A**35**, 698–699.
Effenberger, H. (1996). *Acta Chem. Scand.* **50**, 967–972.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Harrison, W. T. A. (1999). *Acta Cryst.* C**55**, 1980–1983.
Harrison, W. T. A. & Zhang, Z. (1997). *J. Solid State Chem.* **133**, 572–575.
Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.
Morris, R. E., Harrison, W. T. A., Stucky, G. D. & Cheetham, A. K. (1992). *Acta Cryst.* C**48**, 1182–1185.
Pedro, M. de, Enjalbert, R., Castro, A., Trombe, J.-C. & Galy, J. (1994). *J. Solid State Chem.* **108**, 87–93.
Shape Software (1999). *ATOMS*. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1997). *CRYSTALS*. University of Oxford, England.
Wildner, M. (1991). *Monatsh. Chem.* **122**, 585–594.