Dilithium selenate hydrate, $Li_2SeO_4 \cdot H_2O$

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Dilithium selenate hydrate, $Li_2SeO_4 \cdot H_2O$, is confirmed to be isostructural with its sulfate analogue. It consists of a polar arrangement of LiO_4, $LiO_3(H_2O)$, and SeO_4 tetrahedra [$d_{av}(Li-O) = 1.953\,(8)$ Å and $d_{av}(Se-O) = 1.630\,(3)$ Å], sharing vertices by way of $Li-O-Li$ and $Li-O-Se$ bonds.

Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean $\sigma(Se-O) = 0.003$ Å
R factor = 0.029
wR factor = 0.073
Data-to-parameter ratio = 15.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound is confirmed to be isostructural with dilithium sulfate hydrate, $Li_2SO_4.H_2O$. The unit cell found here matches those reported by both Bielen *et al.* (1962) and Pistorius (1967), allowing for an axis transformation in the latter case. The sulfate structure was established as long ago as 1934 (Ziegler) and has been redetermined several times since then, using both X-ray and neutron methods (Larson & Helmholz, 1954; Ozerov *et al.*, 1963; Larson, 1965; Smith *et al.*, 1968; Karppinen *et al.*, 1986). $Li_2SO_4.H_2O$ is of particular interest due to its pyroelectric properties (Lundgren *et al.*, 1984).

In $Li_2SeO_4 \cdot H_2O$ (Fig. 1), the two lithium cations are both tetrahedrally coordinated by O atoms, with $d_{av}(Li1-O) = 1.959\,(8)$ Å and $d_{av}(Li2-O) = 1.946\,(9)$ Å. Bond-valence sum (BVS) calculations, using the Brown (1996) formalism, yielded values of BVS(Li1) = 1.06 and BVS(Li2) = 1.10, in good agreement with the expected value of 1.00. The selenate group [BVS(Se) = 6.14, expected 6.00] is essentially a regular tetrahedron [$d_{av}(Se-O) = 1.630\,(3)$ Å; spread of $O-Se-O$ bond angles = $108.53\,(16)-111.42\,(19)^{\circ}$], in conformity with
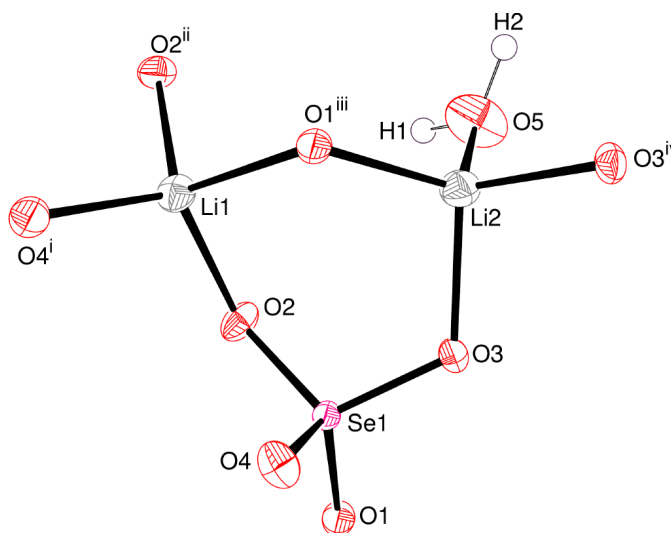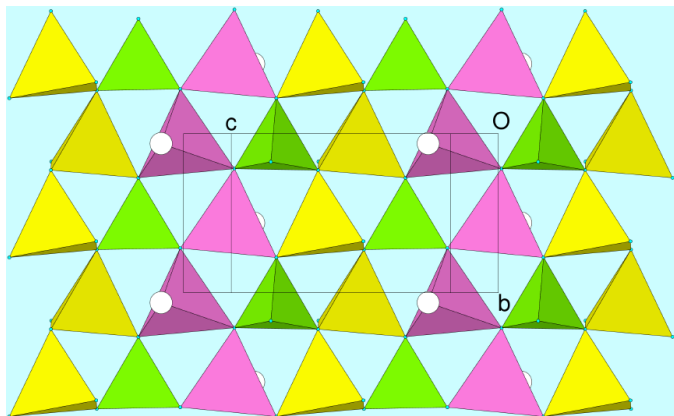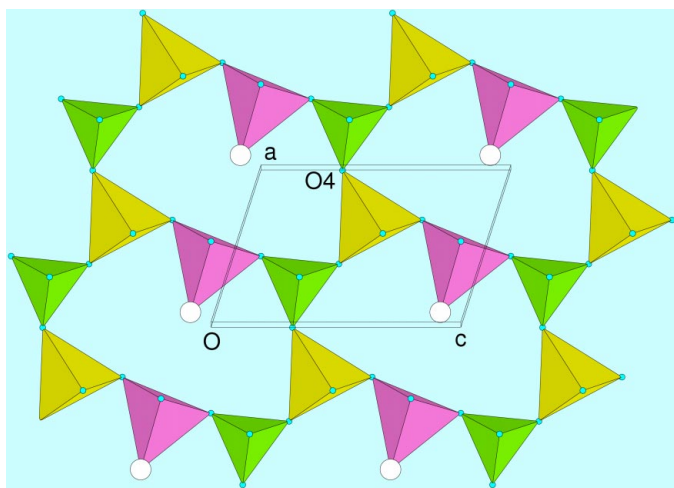

Figure 1
Fragment of $Li_2SeO_4 \cdot H_2O$ (50% displacement ellipsoids). Symmetry codes as in Table 1.

Figure 2
Side-on view, approximately normal to (100), of a curtain of tetrahedra in $Li_2SeO_4 \cdot H_2O$, showing the zigzag [010] columns of $Li1O_4$ and $Li2O_3(H_2O)$ tetrahedra forming an infinite sheet in the bc plane. The Se atoms (as selenate groups) occupy six-ring vacancies in the Li/O sheet and in turn provide crosslinking to adjacent sheets via Se1—O4—Li1 bonds. Colour key: $Li1O_4$ tetrahedra yellow, $Li2O_3(H_2O)$ tetrahedra pink, SeO_4 tetrahedra green, O5 white spheres of arbitrary radius.

Figure 3
Polyhedral representation of a tetrahedral pseudo-layer in $Li_2SeO_4 \cdot H_2O$, viewed approximately down [010] ($-0.4 < y < 0.40$), showing the polyhedral eight-ring voids associated with the water molecules. The colour key is as in Fig. 2.

previous structural studies of this anion (Giester & Wildner, 1992).

Atom O5, which is attached to Li2, must be part of a water molecule, although its attached H atoms could not be located from difference maps in the present study. A similar problem was encountered in an X-ray study of the sulfate structure, and was attributed to high thermal motion, possibly as a result of dynamic disorder, and weak hydrogen bonding of the H atoms (Larson, 1965). Thus, the H-atom positions for the present study, which should be regarded as tentative, were taken from the neutron diffraction study of $Li_2SO_4 \cdot H_2O$ (Smith $et~al.$, 1968) and refined by riding on O5. This results (Table 2) in a hydrogen-bonding scheme in which O5—H2$\cdots$O5—H2$\cdots$O5 chains propagate roughly in the polar [010] direction. The

O5—H1$\cdots$O4 bonds serve to stabilize polyhedral eight-ring voids, as described below.

The $Li1O_4$, $Li2O_3(H_2O)$, and SeO_4 groups are linked together by corner sharing: O1, O2 and O3 are each bonded to two Li and one Se (average Li—O—Li and Li—O—Se bond angles = 111.3 and 121.8°, respectively), and O4 is bicoordinate to one Li and one Se. Bond-valence sums for the O atoms are as follows: BVS(O1) = 1.99, BVS(O2) = 2.06, BVS(O3) = 2.07, BVS(O4) = 1.88 and BVS(O5) = 1.92. The last of these includes the effect of the two riding H atoms.

The resulting structure (Fig. 2) can be visualized in terms of ruffled sheets of tetrahedra propagating in the bc plane. Tetrahedral three-rings (cf Fig. 1) are a distinctive feature of the sheets. All the tetrahedra point in the polar b direction (in the individual crystal studied they point along [0$\bar{1}$0]). Cross-linking between sheets in the a direction occurs via Se1—O4—Li1 links. An alternative view of the structure (Fig. 3), looking down [010] on to one pseudo-layer of tetrahedra, emphasizes the structural role of O4 and reveals polyhedral eight-rings associated with the space requirements of the water (O5/H1/H2) molecules.

Experimental

Crystal data

$Li_2(SeO_4) \cdot H_2O$	$D_x = 2.570$ Mg m^{-3}
$M_r = 174.86$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 896
$a = 5.5798~(3)$ Å	reflections
$b = 5.0284~(3)$ Å	$\theta = 2.5$–$32.5°$
$c = 8.4521~(5)$ Å	$\mu = 8.21$ mm^{-1}
$\beta = 107.634~(2)°$	$T = 293~(2)$ K
$V = 226.00~(2)$ Å^3	Plate, colourless
$Z = 2$	$0.28 \times 0.12 \times 0.04$ mm

Data collection

Bruker SMART 1000 CCD diffractometer	1153 independent reflections
	1096 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.027$
Absorption correction: multi-scan ($SADABS$; Bruker, 1999)	$\theta_{max} = 32.5°$
	$h = -8 \rightarrow 8$
$T_{min} = 0.207$, $T_{max} = 0.735$	$k = -4 \rightarrow 7$
2324 measured reflections	$l = -11 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.073$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.98$	$\Delta\rho_{max} = 1.24$ e Å^{-3}
1153 reflections	$\Delta\rho_{min} = -1.18$ e Å^{-3}
75 parameters	Absolute structure: Flack (1983);
H-atom parameters constrained	261 Friedel pairs
	Flack parameter = 0.06 (2)

Table 1
Selected geometric parameters (Å, °).

Li1—O4^i	1.909 (6)	Li2—O3	1.951 (13)
Li1—O2	1.968 (12)	Li2—O1^{iii}	1.965 (9)
Li1—O2^{ii}	1.972 (8)	Se1—O4	1.619 (3)
Li1—O1^{iii}	1.986 (8)	Se1—O2	1.629 (3)
Li2—O5	1.919 (8)	Se1—O3	1.631 (3)
Li2—O3^{iv}	1.940 (9)	Se1—O1	1.641 (3)
Se1—O1—Li2^v	123.3 (4)	Li1—O2—Li1^{vi}	111.1 (4)
Se1—O1—Li1^v	117.5 (4)	Se1—O3—Li2^{vii}	125.9 (4)
Li2^v—O1—Li1^v	109.9 (4)	Se1—O3—Li2	117.8 (2)
Se1—O2—Li1	119.5 (2)	Li2^{vii}—O3—Li2	113.1 (4)
Se1—O2—Li1^{vi}	126.5 (3)	Se1—O4—Li1^{viii}	136.3 (3)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H1$\cdots$O4^{ix}	0.98	1.97	2.875 (6)	153
O5—H2$\cdots$O5^x	0.94	2.17	3.039 (5)	154

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

The highest difference peak and deepest difference hole are 0.74 and 0.78 Å, respectively, from Se1.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *SHELXL*97.

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