

Li₂Sn(OH)₆

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Hydrothermally prepared dilithium tin hexahydroxide crystallizes in the monoclinic system (space group $P2_1/n$), with the Sn atom at a site with $\bar{1}$ symmetry and all other atoms in general positions. The Sn coordination polyhedron is made up of six hydroxide groups. The Li atom is tetrahedrally coordinated by oxygen, with the tetrahedra sharing two corners and one edge with the adjacent Sn octahedra. Hydrogen bonds between the OH groups provide additional bonds in the framework.

Comment

Recently, there has been much interest in tin oxide compounds as anodes in high-energy-density lithium batteries (Idota *et al.*, 1997; Courtney & Dahn, 1997; Goward *et al.*, 1999). In a search for new anode materials and in an attempt to understand the reduction mechanism of tin oxides, a systematic study of lithium tin oxides has been made by our group. This work presents the crystal structure of a new lithium tin hydroxide, Li₂Sn(OH)₆, resulting from this study.

The title structure is built up from slightly distorted Li tetrahedra and Sn octahedra (Fig. 1). Each Li tetrahedron shares two corners and one edge with three Sn octahedra (Fig. 2) to form a network. On the other hand, each Sn octahedron that lies on the center of symmetry shares two coplanar edges (O1–O2) and two corners (O3) to form a chain

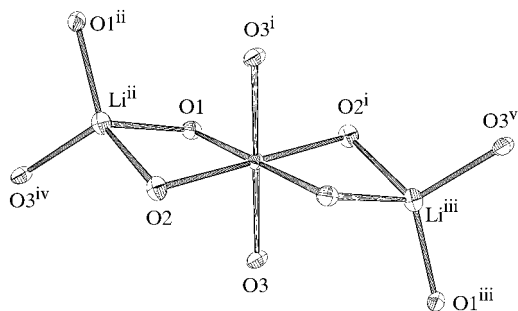


Figure 1

The structure of Li₂Sn(OH)₆, with displacement ellipsoids at the 50% probability level. Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $x - 1, y, z$.

along the a axis. Two corners (O2) of the Sn octahedron are also shared with Li tetrahedra, even though they are already involved in edge-sharing. The Sn–O2–Li-sharing links the chains into a three-dimensional network. Three hydrogen bonds (Table 2) between the OH groups form additional links in the network.

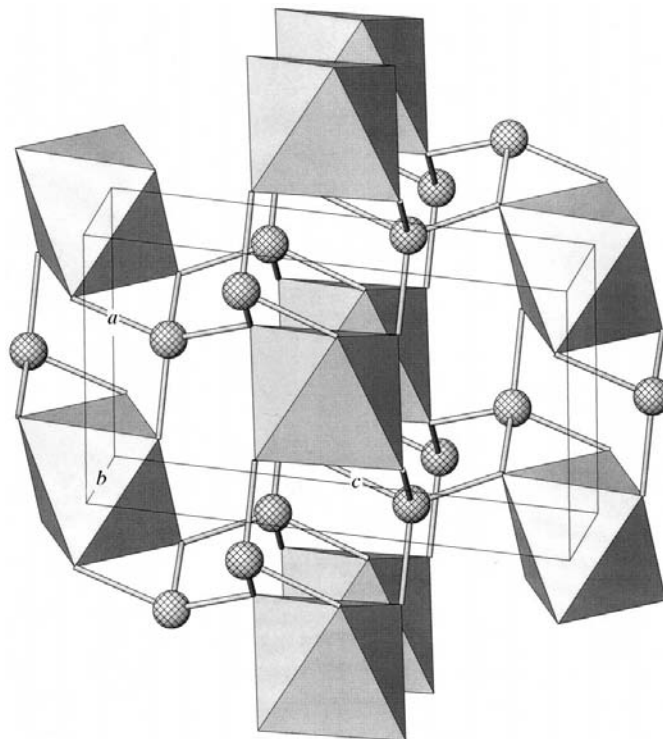


Figure 2

The three-dimensional structure of Li₂Sn(OH)₆. Sn(OH)₆ are shown as octahedra and Li atoms as balls.

This structure is related to the hydrated lithium tin hydroxide compound Li₂Sn(OH)₆·2H₂O reported previously by Reuter & Bargon (1997). It crystallizes in space group $P2_1/n$, with $a = 5.023$ (1), $b = 6.923$ (1) and $c = 10.202$ (3) Å, and $\beta = 99.78$ (1)°. In contrast with the title compound, there is no edge-sharing in the hydrate, where each Li tetrahedron shares three corners with Sn octahedra to form a three-dimensional framework. The fourth corner is occupied by a water molecule (Fig. 3). The presence of these water groups increases the unit-cell volume from 257.6 Å³ in the title compound to 349.6 Å³ in the hydrate.

An Li₂Sn(OH)₆ material reported by Nakata & Toyooka (1997) also crystallizes in space group $P2_1/n$, with $a = 10.2016$ (5), $b = 6.9246$ (3) and $c = 5.0255$ (2) Å, and $\beta = 99.764$ (3)°. Interestingly, the cell dimensions for this compound are essentially the same as those for the above-mentioned crystalhydrate (the a and c axes are switched). This structure was solved using powder diffraction data and can be converted to the previous structure. However, while Sn and three O atoms convert to the same type of atoms, Li atoms convert to the O atoms of the water molecule. Thus, the water molecule in this third structure was misinterpreted as Li.

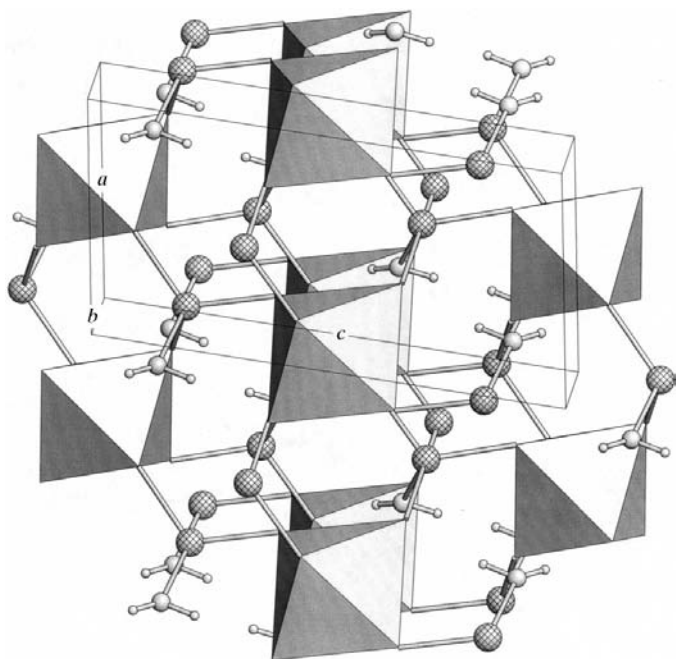


Figure 3
The structure of the hydrate $\text{Li}_2\text{Sn}(\text{OH})_6 \cdot 2\text{H}_2\text{O}$. $\text{Sn}(\text{OH})_6$ are shown as octahedra, and Li atoms (crossed) and water molecules are shown as balls.

Experimental

The title compound was prepared by hydrothermal treatment of SnO (Fisher) and LiOH (Aldrich) in a molar ratio of 1:3. The LiOH solution was prepared and then mixed with SnO powder and stirred for 5 min. The cloudy liquid was transferred to a Parr reactor and heated at 443 K for 3 d. The solution was cooled and filtered, and white crystals of $\text{Li}_2\text{Sn}(\text{OH})_6$ were separated manually from the gray powder and dried at 330 K for 5 h.

Crystal data

$\text{Li}_2\text{Sn}(\text{OH})_6$	$D_x = 3.024 \text{ Mg m}^{-3}$
$M_r = 234.62$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 929 reflections
$a = 5.1640$ (6) Å	$\theta = 8\text{--}57^\circ$
$b = 5.4013$ (7) Å	$\mu = 4.90 \text{ mm}^{-1}$
$c = 9.2982$ (11) Å	$T = 293$ (2) K
$\beta = 96.596$ (2)°	Irregular, colorless
$V = 257.63$ (5) Å ³	$0.12 \times 0.08 \times 0.06 \text{ mm}$
$Z = 2$	

Data collection

Bruker SMART Apex CCD diffractometer	617 independent reflections (92% coverage)
ω scans	$R_{\text{int}} = 0.033$
Absorption correction: ψ scan (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 28.79^\circ$
$T_{\text{min}} = 0.65$, $T_{\text{max}} = 0.75$	$h = -6 \rightarrow 6$
1511 measured reflections	$k = -5 \rightarrow 7$
	$l = -11 \rightarrow 12$
	Intensity decay: negligible

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0167P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.017$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.041$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.058$	$\Delta\rho_{\text{max}} = 0.85 \text{ e \AA}^{-3}$
617 reflections	$\Delta\rho_{\text{min}} = -0.50 \text{ e \AA}^{-3}$
56 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
All H-atom parameters refined	Extinction coefficient: 0.0132 (18)

Table 1

Selected geometric parameters (Å).

Sn—O3 × 2	2.0388 (19)	Li—O3 ⁱ	1.921 (5)
Sn—O1 × 2	2.055 (2)	Li—O2 ⁱⁱ	2.023 (5)
Sn—O2 × 2	2.063 (2)	Li—O1 ⁱⁱⁱ	2.064 (5)
Li—O1	1.920 (5)		

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O1—H1 \cdots O2 ⁱ	0.64 (4)	2.23 (4)	2.847 (3)	165 (4)
O2—H2 \cdots O3 ⁱⁱ	0.62 (3)	2.27 (3)	2.864 (3)	161 (4)
O3—H3 \cdots O2 ⁱⁱⁱ	0.72 (4)	2.34 (4)	3.020 (3)	158 (3)

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

All Sn and O atoms were located from the electron-density map. The Li and H atoms were located from difference Fourier maps.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); 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.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1309). Services for accessing these data are described at the back of the journal.

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