

## Lithium Hydrogenselenite

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**Abstract.** LiHSeO<sub>3</sub>, piezoelectric, orthorhombic,  $P2_12_12_1$ ,  $a = 5.0579$  (4),  $b = 11.1868$  (6),  $c = 5.2213$  (3) Å,  $V = 295.43$  Å<sup>3</sup>,  $Z = 4$ ,  $d_x = 3.034$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 12.347$  mm<sup>-1</sup>. The structure consists of HSeO<sub>3</sub><sup>-</sup> ions forming spiral chains of SeO<sub>3</sub> groups, interlinked by hydrogen bonds of length 2.616 Å, running in the [100] direction. Li<sup>+</sup> ions further stabilize the structure to form a three-dimensional network with Li<sup>+</sup> contacts to four O atoms in the range 1.92–2.02 Å.

**Introduction.** The alkali-metal trihydrogenselenites,  $MH_3(\text{SeO}_3)_2$ , constitute a group of materials with interesting physical and electrical properties (Shulalov, Ivanov, Gordeeva & Kirpichnikova, 1970). A corresponding group of alkali-metal hydrogenselenites,  $MH\text{SeO}_3$  (*Gmelin's Handbuch der Anorganische Chemie*, 1927) also exists. A series of studies has been started to find out whether some of these compounds may also display similar properties, e.g. ferro- or antiferroelectric. The crystal structure of LiHSeO<sub>3</sub> as determined by X-ray diffraction is reported here, and will be followed by a similar study of NaHSeO<sub>3</sub>. A preliminary report on the LiHSeO<sub>3</sub> structure has been given (Chomnilpan & Liminga, 1978).

The cell dimensions were determined from a powder photograph recorded on a Guinier–Hägg XDC-700 focusing camera with Cr  $K\alpha_1$  radiation ( $\lambda = 2.289753$  Å) and CoP<sub>3</sub> ( $a = 7.707780$  Å at 298 K) as internal standard. A least-squares refinement based on the  $\theta$  values of 37 reflexions provided the cell parameters.

Crystals of LiHSeO<sub>3</sub> were grown by slow evaporation at room temperature from an aqueous solution of H<sub>2</sub>SeO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> in stoichiometric ratio. The space group was determined from Weissenberg photographs. The diffraction symmetry and systematic absences indicated space group  $P2_12_12_1$ . Crystals of LiHSeO<sub>3</sub> must therefore be piezoelectric. Some samples were analysed by DTA and DSC to detect possible phase transitions; none was found in the temperature range 103 to 413 K, but some evidence was obtained for a minor transition starting at 415 K, followed by decomposition starting at 425 K.

The crystal used for data collection had 18 faces and measured 0.17 × 0.14 × 0.16 mm in the directions of the axes. The intensities were collected at room temperature on a PDP8/A-controlled Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation and an  $\omega/2\theta$  step-scan method. Background corrections were made with the profile-analysis method (Lehmann & Larsen, 1974). Five standard reflexions, monitored at regular intervals, indicated an average decrease in intensity of about 3% by the end of the experiment. A scaling function was derived as the average of the individual scaling functions for the different test reflexions. All intensities were corrected with this function. The intensities of all reflexions within two octants of reciprocal space ( $\bar{h}kl$  and  $h\bar{k}\bar{l}$ ) were measured out to  $\sin \theta/\lambda = 1.062$  Å<sup>-1</sup>. Standard deviations of the intensities were estimated from Poisson counting statistics, the scatter observed in the test reflexions, and the uncertainty in the scaling function (McCandlish, Stout & Andrews, 1975). The intensities were corrected for Lorentz, polarization and absorption effects. The Gaussian quadrature method was used for the absorption correction, with an 8 × 8 × 8 grid. The transmission factors were in the range 0.258–0.342.

The structure factors were assigned variances from  $\sigma^2(F^2) = \sigma_c^2(F^2) + \{[\sigma^2(\mu)/\mu^2] + [\sigma^2(t)/t^2]\}(utF^2)^2$ , where  $\sigma_c^2$  was derived as described above, and the second term accounts for errors in the absorption correction due to errors in  $\mu$  and  $t$ , the mean path-length through the crystal. The quantity  $\{[\sigma^2(\mu)/\mu^2] + [\sigma^2(t)/t^2]\}$  was estimated as 0.05. The number of reflexions measured was 3220; of these, 944 had  $F^2 < 2\sigma(F^2)$  and were excluded.

All calculations were made on IBM 1800 and IBM 370/155 computers with programs described by Lundgren (1976).

The structure was solved by the heavy-atom technique and refined by minimizing  $\sum w(|F_o|^2 - |F_c|^2)^2$  with *UPALS*, where the weights  $w = \sigma^2(F_o^2)^{-1}$ . A difference synthesis was calculated after the first series of refinements, in which the positional and anisotropic thermal parameters for the non-hydrogen atoms were refined together with a scale factor and an isotropic extinction coefficient. A peak appeared in a position consistent with a likely H atom position on the basis of Se–O bond distances; an Se–OH bond is expected to

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be about 0.1 Å longer than an Se—O bond (Chomnilpan, Tellgren & Liminga, 1978).

The parameters refined in the final refinements were: one scale factor, one isotropic extinction coefficient, 18 positional parameters, 30 anisotropic thermal parameters for the non-hydrogen atoms, and one isotropic thermal parameter for the H atom. The shifts of the refined parameters in the last cycle were all  $< 0.1\sigma$ . The final  $R(F^2) = \sum ||F_o|^2 - |F_c|^2| / \sum |F_o|^2 = 0.037$ ,  $R_w(F^2) = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)^2]^{1/2} = 0.085$ ,  $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.023$  and the standard deviation of an observation of unit weight  $S = 0.94$ .

The final extinction coefficient  $g$  was 0.59 (5) (Coppens & Hamilton, 1970), which gives a maximum correction of 25% in  $F(002)$ .

Scattering factors for H, Li<sup>+</sup>, O, Se and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates are listed in Table 1.\*

The absolute configuration was determined by reversing the signs of the Miller indices and repeating the final refinement. The resulting  $R(F^2) = 0.056$ ,  $R_w(F^2) = 0.129$  and  $R(F) = 0.038$ , and  $S = 1.429$ . The ratio  $R_w[F^2(h\bar{k}l)]/R_w[F^2(hkl)]$  is therefore 1.520. The original combination of coordinates and Miller indices thus corresponds to the correct absolute atomic arrangement.

The final fit between the observed and calculated structure factors was examined by means of a  $\delta R = [(F_o^2 - F_c^2)/\sigma(F_o^2)]$  normal probability plot (Abrahams & Keve, 1971). The resulting plot showed a marked departure from linearity, *i.e.*  $\delta R$  does not have a random-normal distribution. The source of this possible systematic error could not be traced in the data or the model. No systematic features could be found in a difference synthesis based on the final parameters.

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34721 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^5$ , for H  $\times 10^3$ ) for LiHSeO<sub>3</sub>

Numbers in parentheses here and throughout this paper give the c.s.d.'s of the least significant digits.

	<i>x</i>	<i>y</i>	<i>z</i>
Se	13182 (4)	14709 (2)	26684 (4)
O(1)	1453 (32)	28331 (13)	20826 (34)
O(2)	-10507 (42)	5713 (15)	16447 (33)
O(3)	7139 (37)	13403 (18)	60376 (32)
Li	25770 (96)	41678 (39)	18300 (90)
H	210 (15)	152 (4)	662 (13)

**Discussion.** A stereoscopic view of the atomic arrangement is presented in Fig. 1, and the details of the Li<sup>+</sup> ion environment are in Fig. 2. Selected interatomic distances and angles are given in Table 2.

The asymmetric unit consists of one independent Li<sup>+</sup> ion and one HSeO<sub>3</sub><sup>-</sup> ion. The HSeO<sub>3</sub><sup>-</sup> ions are linked together *via* O(3)—H...O(1) hydrogen bonds forming spiral chains running in the [100] direction. The Li<sup>+</sup> ions are tetrahedrally coordinated to O atoms from four different HSeO<sub>3</sub><sup>-</sup> ions which form part of three different chains (Fig. 2). The Li—O contacts thus link the HSeO<sub>3</sub><sup>-</sup> chains to form a three-dimensional network.

*The Li<sup>+</sup> ion.* The Li<sup>+</sup> ion is tetrahedrally surrounded by four O atoms with Li—O distances in the range 1.92–2.02 Å (O—Li—O angles in the range 104.1–113.7°). The average Li—O distance of 1.961 Å agrees well with the overall mean of 1.960 Å based on twelve structures with four-coordinated Li<sup>+</sup> (Hermansson, Thomas & Olovsson, 1977). In the ferroelectric

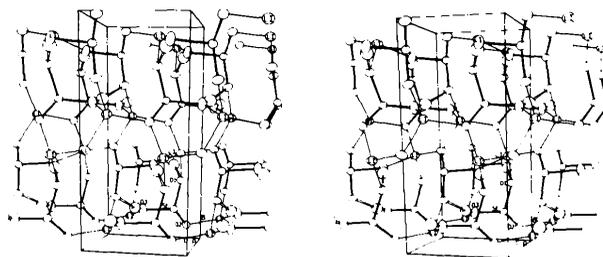


Fig. 1. Stereoscopic ORTEP (Johnson, 1965) illustration of the LiHSeO<sub>3</sub> crystal structure. Atoms belonging to the asymmetric unit and all Li atoms are labelled. Covalent bonds are filled, hydrogen bonds are open and ionic bonds are drawn as single lines. The ellipsoids are scaled to include 50% probability.

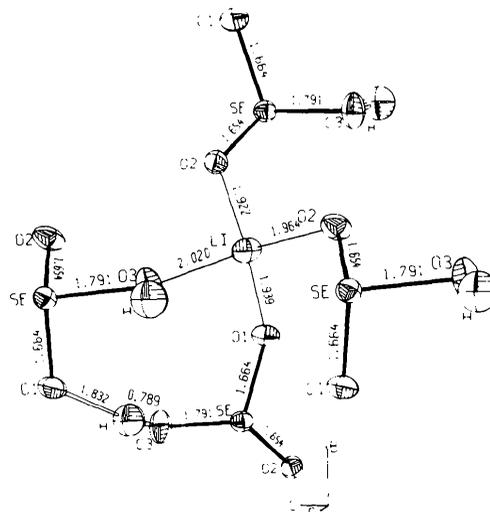


Fig. 2. The Li<sup>+</sup> ion and its environment. The hydrogen-bond scheme is also shown.

Table 2. *Interatomic distances (Å) and angles (°) in LiHSeO<sub>3</sub>*

Ionic bonds				
Li—O(1)	1.939 (5)	Li—O(2)	1.922 (5)	
Li—O(2)	1.964 (5)	Li—O(3)	2.020 (5)	
Angles				
O(1)—Li—O(2)	113.7 (2)	O(1)—Li—O(3)	104.1 (2)	
O(2)—Li—O(3)	105.9 (2)	O(2)—Li—O(2)	113.8 (2)	
O(2)'—Li—O(1)	110.2 (2)	O(2)—Li—O(3)	108.5 (2)	
Covalent bonds				
O—Se—O	O—Se	Se—O	∠O—Se—O	
O(1)—Se—O(2)	1.664 (2)	1.654 (2)	103.87 (9)	
O(1)—Se—O(3)	1.664 (2)	1.792 (2)	101.21 (9)	
O(2)—Se—O(3)	1.654 (2)	1.792 (2)	98.29 (9)	
Hydrogen bond				
O—H...O	O—H	H...O	O...O	∠O—H...O
O(3)—H...O(1)	0.79 (7)	1.83 (7)	2.616 (3)	172 (5)

LiH<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub> (Tellgren & Liminga, 1972), the Li<sup>+</sup> ion is six-coordinated with Li—O distances in the range 2.13–2.22 Å (average 2.164 Å).

*The HSeO<sub>3</sub><sup>-</sup> ion.* The HSeO<sub>3</sub><sup>-</sup> ion is pyramidal with two shorter Se—O bonds [1.654 (2), 1.664 (2) Å] and one longer Se—OH bond [1.792 (2) Å]. In the alkali trihydrogenselenites, the average value of the Se—O bonds is about 1.65 Å, and that of Se—OH about 1.75 Å (Chomnilpan, Tellgren & Liminga, 1978). The shorter bonds in the present case agree well with those in the trihydrogenselenites, whereas the Se—OH bond seems to be significantly longer, but in the same range as those found in Sc(HSeO<sub>3</sub>)<sub>3</sub> (Valkonen & Leskelä, 1978). The O—Se—O angles, 98.3–103.9°, are in the same range as those observed for the trihydrogenselenites.

The HSeO<sub>3</sub><sup>-</sup> ions are hydrogen bonded to form spiral chains. The O(3)—H...O(1) bond [O...O 2.616 (3) Å] is in the same range as the corresponding bonds in the trihydrogenselenites (2.52–2.65 Å) (Chomnilpan, Tellgren & Liminga, 1978). The observed O—H distance in the present case is 0.79 (7) Å. It is known that X-ray-determined X—H distances are systematically shorter than those determined by neutron

diffraction, whereas the direction of the X—H bond is considerably less affected (Kvick, 1974). The H atom in the present case should thus be shifted along the O—H bond by about 0.2 Å to reach the true nuclear position. The O—H distance in the present case should thus be about 0.98 Å based on the correlation of O—H vs O...O distances (Lundgren, 1974), and from a comparison with the trihydrogenselenites (Chomnilpan, Tellgren & Liminga, 1978).

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