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Hydrogen Bond Studies. 54*. A Neutron Diffraction Study of the Ferroelectric Lithium Trihydrogen Selenite, $LiH_3(SeO_3)_2$

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The crystal structure of the ferroelectric $LiH_3(SeO_3)_2$ has been studied using three-dimensional neutron diffraction data. The position of the heavy atoms are in agreement with earlier investigations, whereas the hydrogen bond network differs considerably. The present study reveals three almost linear O–H···O hydrogen bonds of length 2.518, 2.552, and 2.646 Å with O–H···O angles 176.6, 173.3, and 172.3°, respectively. The shortest bond has an O–H distance of 1.14 Å, which is longer than expected. The lithium ion is surrounded by six oxygen atoms forming an octahedron with Li–O distances in the range 2.13–2.22 Å.

Introduction

The heavy atom structure of the ferroelectric $LiH_3(SeO_3)_2$ has been determined by Vedam, Okaya, and Pepinsky (*1*) using X-rays. The hydrogen-bond network has been proposed from a preliminary neutron diffraction study using data obtained along the *b* and *c* axes by Van den Hende and Boutin (*2*). This structure is, however, in disagreement with that proposed for $LiD_3(SeO_3)_2$ from a DMR study by Soda and Chiba (*3*). In no investigation has the position of the lithium atom been found. The present investigation has been undertaken to establish the hydrogen-bond network and to determine the coordinates of the lithium atoms. In so doing, it was hoped to lay the foundation for a more rigorous explanation of the ferroelectric behavior of the compound. This study is to be followed by a neutron diffraction study of the deuterated compound $LiD_3(SeO_3)_2$.

X-Ray studies of $NH_4H_3(SeO_3)_2$, $RbH_3(SeO_3)_2$, and $CsH_3(SeO_3)_2$ are also in progress at this institute. X-Ray and neutron diffraction studies of alkali trihydrogen selenites have so far been published for $KH_3(SeO_3)_2$ (*4*, *5*) and $NaH_3(SeO_3)_2$ (*6*).

Space Group and Unit Cell

The diffraction symmetry and systematic absences confirmed the findings of Vedam, Okaya, and Pepinsky (*1*), that $LiH_3(SeO_3)_2$ has a monoclinic unit cell, space group *Pn* [equivalent positions (x,y,z); $(\frac{1}{2}+x,\bar{y},\frac{1}{2}+z)$].

The unit cell dimensions were determined from powder photographs recorded using a Guinier-Hägg XDC-700 focussing camera with $CrK\alpha_1$ radiation ($\lambda = 2.28962$ Å) and using CoP_3 ($a = 7.7073$ Å at 25°C) as an internal standard. A least-squares treatment of the observed θ-values from 38 reflexions provided the parameters given in Table I.[1] The parameters are in good agreement with those given by Berlincourt, Cook, and Rander (*7*).

TABLE I

CRYSTAL DATA

Crystal system space group	Monoclinic *Pn*
a	6.2554(3) Å
b	7.8823(5)
c	5.4339(5)
β	105.325(5)°
V	258.404 Å^3
Z	2
D_x	3.391 g cm^{-3}
μ_{calc}	1.2 cm^{-1}

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[1] Numbers in parentheses here and throughout this paper are the estimated standard deviations in the least significant digits.

* Part 53: Acta Crystallogr., in press.

Experimental

Lithium trihydrogen selenite was prepared from an aqueous solution of lithium carbonate and selenious acid in a stoichiometric ratio. Large single crystals were grown easily by slow evaporation at room temperature. A crystal with a volume of 130 mm^3, enclosed in a thin-walled quartz tube, was used for the data collection. The crystal had six boundary planes $0\bar{1}1, 01\bar{1}, 10\bar{1}, \bar{1}01, 0\bar{1}\bar{1}, 011$. The first two were 0.195 cm from the crystal center and the latter four 0.238 cm from the center point. It was mounted so that the χ and ϕ angles for the ($h00$), ($0k0$), and ($00l$) reflexions were −2.89, 129.01; −84.94, 4.27; and −4.77, −156.14 degrees, respectively [symmetrical *A* setting, Arndt and Willis (*8*)].

The room temperature intensity data were collected at the Swedish Atomic Energy reactor R2 at Studsvik, using a Hilger & Watts four-circle diffractometer controlled by a PDP-8 computer. The neutron intensity at the specimen was 5×10^4 neutron cm^{-2} sec^{-1} at a wavelength of 1.097 Å. A region of reciprocal space extending out to $\sin\theta/\lambda = 0.75$ Å^{-1} was examined and the $\omega - 2\theta$ step scan technique was employed. Two standard reflexions were measured at regular intervals to provide a check on crystal and electronic stability. No significant changes were observed in these standards. A total of 899 independent reflexions were measured of which 815 had intensities greater than $3\sigma_{\text{count}}$. The intensities were corrected for Lorentz, absorption and secondary extinction effects (cf. computer programs).

TABLE II

ATOMIC COORDINATES ($\times 10^5$)[a]

Atom	x	y	z
Se(1)	23300	39507(23)	08800
Se(2)	76690(20)	10074(21)	91095(26)
O(1)	19252(40)	22747(32)	−13341(47)
O(2)	79816(38)	27366(31)	110145(46)
O(3)	30176(43)	29114(33)	36189(49)
O(4)	70944(42)	20193(35)	61072(49)
O(5)	47888(42)	47641(32)	05452(46)
O(6)	51917(40)	02447(29)	91695(44)
Li	00241(150)	24866(146)	48066(160)
H(1)	32880(84)	14685(64)	−09938(82)
H(2)	61997(106)	38177(71)	07074(98)
H(3)	55051(60)	23084(52)	52793(75)

[a] In order to define an origin the x and z coordinates of Se(1) were fixed. The values used were those given in the X-ray study (*1*).

The linear absorption coefficient ($\mu = 1.2$ cm^{-1}) was calculated using a value of 34 barns for the incoherent scattering cross-section for hydrogen. The resulting transmission factors were in the range 0.49–0.73.

Location of the Lithium and Hydrogen Atoms

A three-dimensional difference Fourier synthesis based on the atomic positions from the X-ray work (*1*) readily provided the positions of the lithium and hydrogen atoms. However, the hydrogen atom positions from the map agreed neither with those reported in the earlier neutron diffraction study (*2*) nor with the DMR study (*3*). A refinement of the thermal and positional parameters of lithium and the heavy atoms was performed followed by a second three-dimensional difference synthesis. No significant changes were obtained in the hydrogen atom positions.

Refinement

The structure was refined by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ using the full matrix least squares program LINUS (*9*). Each reflexion was assigned a weight inversely proportional to the estimated variance of the observation $w = 1/\sigma^2(F)$ where $\sigma^2(F) = \sigma^2{}_{\text{count}}(F^2)/4F^2 + 0.0006F^2$. The first term is based on counting statistics and the second is an empirical correction term to take account of other errors in the data.

As was pointed out in the X-ray study (*1*) the heavy atom structure is near centrosymmetric. It was noticed in the present study that the correlation matrix obtained had elements in the range 0.50–0.70 for the correlation between Se(1)–Se(2), O(1)–O(2), O(3)–O(4), and O(5)–O(6). The refinement was based on the 815 reflexions with intensities $>3\sigma_{\text{count}}$. The parameters refined comprised 34 positional and 72 anisotropic thermal parameters, one over-all scale factor and one isotropic extinction parameter. The final agreement factor was

$$R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.029,$$

$$R_w = \{[\Sigma w(|F_o| - |F_c|)^2]/\Sigma w F_o{}^2\}^{1/2} = 0.039.$$

The standard deviation of an observation of unit weight $\sigma_1 = [\Sigma w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$ was $= 1.28$, where m is the total number of observations and n the number of parameters varied. The final parameters are given in Tables II and III, observed and calculated structure factors in Table IV. The

TABLE III

ANISOTROPIC THERMAL PARAMETERS ($\times 10^5$). THE FORM OF THE TEMPERATURE FACTOR IS $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. THE ROOT-MEAN-SQUARE COMPONENTS R_i ($\times 10^3$ Å) OF THERMAL DISPLACEMENT OF THE ATOMS ALONG THE ELLIPSOID AXES ARE ALSO LISTED

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Se(1)	562(30)	479(21)	793(34)	083(19)	118(26)	033(21)	096(3)	109(2)	126(3)
Se(2)	478(30)	418(19)	915(36)	−018(19)	070(25)	027(21)	092(3)	113(2)	120(2)
O(1)	917(43)	682(30)	1015(51)	−014(35)	060(40)	−195(38)	107(4)	137(3)	155(3)
O(2)	777(44)	602(29)	1221(54)	013(34)	065(40)	−206(36)	111(4)	126(4)	155(3)
O(3)	747(42)	823(35)	1017(47)	062(32)	146(39)	260(36)	107(4)	123(3)	168(3)
O(4)	797(46)	924(38)	1093(54)	−053(31)	161(42)	266(37)	115(3)	122(3)	178(3)
O(5)	774(44)	684(35)	1646(70)	−119(34)	373(48)	117(38)	110(4)	144(4)	159(3)
O(6)	756(43)	555(31)	1621(67)	−131(31)	392(47)	−17(37)	107(4)	138(4)	150(3)
Li	1207(112)	921(68)	1245(138)	33(62)	355(96)	28(78)	131(8)	149(7)	171(6)
H(1)	1903(104)	910(55)	1833(108)	−153(58)	350(83)	−139(62)	153(5)	173(5)	194(5)
H(2)	2771(150)	1408(88)	2187(126)	−1046(99)	732(111)	−187(86)	149(6)	173(5)	271(7)
H(3)	1097(85)	1270(59)	1967(114)	−025(53)	249(73)	129(65)	141(5)	168(5)	202(5)

observed F_o values are corrected for extinction using the expression

$$|F_o|_{\text{corr}} = |F_o| \times [1 + (\bar{T}\cdot 2\cdot |F_c|^2\cdot g\cdot \lambda^3/V^2\cdot \sin 2\theta)]^{1/4},$$

where λ is in Å and V is the unit cell volume in Å^3 (*9*).

The mean path length through the crystal for a particular reflexion is given by $\bar{T}$, calculated using the expression $\bar{T} \approx -\ln A^*/\mu$, where $\ln A^*$ is the natural logarithm of the transmission factor, and μ is the linear absorption coefficient in cm^{-1}. The refined value of the isotropic extinction parameter is $g = 7556(287)$. This corresponds to a mosaic spread parameter of approximately 8 sec or a domain size of 0.8 μm depending upon whether a Zachariasen (*10*) Type I or Type II description is assumed.

The extinction correction factors as given above were for the majority of the reflexions in the range 1.00–1.20 but were higher in a few cases. The maximum value was 1.77.

An anisotropic extinction correction was also attempted but gave no further improvement. The coherent scattering amplitudes used were $\bar{b}_{\text{Se}} = 0.780$, $\bar{b}_{\text{O}} = 0.577$, $\bar{b}_{\text{Li}} = -0.194$, and $\bar{b}_{\text{H}} = -0.372 \times 10^{-12}$ cm (*11*). As there has been some discussion about the scattering amplitude for selenium (*5*, *6*), a refinement including also the scattering amplitudes for the two selenium atoms was performed. It gave a mean value $\bar{b}_{\text{Se}} = 0.794(6) \times 10^{-12}$ cm. No change in the R value or significant change in any parameter was observed.

Computer Programs

The calculations were all performed on the CDC 3600 computer in Uppsala using programs briefly described by Jönsson and Liminga (*12*).

Description and Discussion of the Structure

General

The structure is illustrated in Figs. 1–4. Bond distances and angles are listed in Tables V and VI, some of them are also shown in Figs. 1 and 2.

The atomic arrangement in the asymmetric unit is illustrated in Fig. 1. It can be described formally as consisting of a Li^+ ion, a $HSeO_3^-$ ion, and a H_2SeO_3 molecule. The $HSeO_3^-$ and H_2SeO_3 groups are connected via hydrogen bonds (Fig. 2) to form S-shaped chains running in the direction of the c axis (Figs. 3 and 4). These chains are held together by $Li^+\cdots O$ bonds. The ferroelectric axis is nearly perpendicular to the (001) plane (*7*) (cf. Fig. 4).

The Lithium Ion

The lithium ion is surrounded by six oxygen atoms arranged in a nearly perfect octahedron with Li–O distances between 2.13–2.22 Å (Figs. 3 and 4, Table V). As can be seen in Fig. 3 the lithium ions form $Li^+\cdots O$ bonds with four different chains thus creating a three-dimensional network.

TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS (×100). THE FOUR COLUMNS ARE, IN ORDER, k, l, $|F_0|$ AND $|F_c|$. REFLEXIONS MARKED WITH ONE ASTERISK WERE NOT USED FOR THE REFINEMENTS

0,K,L			
0	2	134	132
0	4	603	576
0	6	330	331
1	0	24	6
1	1	216	218
1	2	271	270
1	3	102	104
1	4	288	285
1	5	72	68
1	6	67	64
1	7	78	84
2	0	26	14
2	1	215	231
2	2	238	244
2	3	331	333
2	4	308	315
2	5	52	49
2	6	106	104
2	7	185	190
3	0	50	53
3	1	105	116
3	2	182	189
3	3	87	95
3	4	112	118
3	5	211	212
3	6	27	21*
3	7	150	151
4	0	205	213
4	1	50	62
4	2	55	64
4	3	63	63
4	4	195	205
4	5	255	255
4	6	81	83
4	7	115	118
5	0	70	76
5	1	312	334
5	2	141	159
5	3	34	30*
5	4	59	60
5	5	136	136
5	6	141	144
5	7	46	56
6	0	152	147
6	1	194	208
6	2	71	86
6	3	219	226
6	4	228	233
6	5	87	98
6	6	108	104
7	0	11	4*
7	1	187	206
7	2	52	48
7	3	102	107
7	4	58	64
7	5	191	195
7	6	46	30
8	0	67	50
8	1	224	240
8	2	0	8*
8	3	233	245
8	4	40	55*
8	5	148	150
9	0	42	22*
9	1	127	125
9	2	242	256
9	3	51	50
9	4	189	200
9	5	54	48
10	0	335	320
10	1	151	162
10	2	119	126
10	3	191	205
10	4	152	170
11	0	69	74
11	1	129	143
11	2	50	53
1,K,L			
0	-7	127	133
0	-5	40	31
0	-3	233	228
0	-1	208	206
0	1	270	268
0	3	547	523
0	5	145	148
0	7	266	264
1	-7	150	148
1	-6	200	200
1	-5	108	111
1	-4	141	140
1	-3	149	151
1	-2	134	138
1	-1	284	285
1	0	96	89
1	1	178	177
1	2	198	203
1	3	81	73
1	4	190	195
1	5	249	251
1	6	332	325
1	7	186	191
2	-7	32	22*
2	-6	204	203
2	-5	207	209
2	-4	271	272
2	-3	169	171
2	-2	78	75
2	-1	185	188
2	0	451	451
2	1	306	313
2	2	250	255
2	3	113	112
2	4	226	222
2	5	61	66
2	6	316	312
2	7	64	69
3	-7	135	134
3	-6	229	226
3	-5	120	119
3	-4	240	237
3	-3	104	109
3	-2	533	546
3	-1	133	136
3	0	68	63
3	1	87	83
3	2	581	623
3	3	337	336
3	4	234	241
3	5	184	186
3	6	291	288
3	7	121	120
4	-7	344	336
4	-6	160	156
4	-5	67	66
4	-4	81	79
4	-3	458	450
4	-2	235	235
4	-1	398	404
4	0	102	101
4	1	56	56
4	2	63	64
4	3	260	262
4	4	72	75
4	5	144	151
4	6	68	76
4	7	65	61
5	-7	84	83
5	-6	204	196
5	-5	484	468
5	-4	64	67
5	-3	369	367
5	-2	326	320
5	-1	349	352
5	0	143	139
5	1	531	536
5	2	137	140
5	3	53	54
5	4	32	41*
5	5	325	320
5	6	84	84
6	-6	309	295
6	-5	37	28*
6	-4	257	243
6	-3	54	52
6	-2	77	69
6	-1	112	122
6	0	213	208
6	1	135	140
6	2	192	194
6	3	46	51
6	4	73	75
6	5	133	136
6	6	79	81
7	-6	138	132
7	-5	112	108
7	-4	149	146
7	-3	94	89
7	-2	314	297
7	-1	236	234
7	0	255	246
7	1	174	172
7	2	53	69
7	3	225	229
7	4	262	264
7	5	225	225
7	6	101	106
8	-5	124	125
8	-4	195	185
8	-3	11	32*
8	-2	144	136
8	-1	43	30
8	0	116	119
8	1	0	5*
8	2	207	211
8	3	51	44
8	4	59	51
8	5	89	89
9	-5	78	77
9	-4	56	40
9	-3	82	81
9	-2	69	76
9	-1	93	88
9	0	103	96
9	1	57	61
9	2	89	98
9	3	137	143
9	4	34	31*
10	-4	134	131
10	-3	223	211
10	-2	37	40*
10	-1	172	174
10	0	32	23*
10	1	147	147
10	2	29	27*
10	3	225	236
11	-2	38	29
11	-1	174	177
11	0	103	107
11	1	136	135
11	2	61	88
2,K,L			
0	-8	214	219
0	-6	84	82
0	-4	228	230
0	-2	203	203
0	0	505	508
0	2	140	148
0	4	485	472
0	6	150	152
1	-8	104	111
1	-7	251	246
1	-6	13	34*
1	-5	276	280
1	-4	65	59
1	-3	127	130
1	-2	52	52
1	-1	206	209
1	0	134	135
1	1	179	181
1	2	73	67
1	3	249	255
1	4	96	100
1	5	50	52
1	6	99	107
1	7	107	103
2	-7	154	156
2	-6	72	73
2	-5	46	41
2	-4	174	181
2	-3	259	256
2	-2	200	204
2	-1	160	159
2	0	512	509
2	1	261	259
2	2	146	145
2	3	318	321
2	4	221	225
2	5	92	92
2	6	60	60
2	7	192	200
3	-7	96	96
3	-6	115	112
3	-5	75	69
3	-4	341	337
3	-3	68	67
3	-2	133	136
3	-1	88	88
3	0	138	138
3	1	320	319
3	2	123	121
3	3	111	117
3	4	50	47
3	5	216	217
3	6	50	55
4	-7	35	38*
4	-6	254	250
4	-5	62	60
4	-4	73	66
4	-3	101	96
4	-2	77	75
4	-1	117	113
4	0	103	99
4	1	149	147
4	2	181	183
4	3	141	145
4	4	62	64
4	5	82	87
4	6	250	250
5	-7	31	28*
5	-6	93	93
5	-5	122	123
5	-4	111	110
5	-3	104	104
5	-2	407	415
5	-1	51	54
5	0	215	208
5	1	146	145
5	2	367	361
5	3	141	141
5	4	446	441
5	5	30	42*
5	6	34	32*
6	-6	219	212
6	-5	224	217
6	-4	192	193
6	-3	129	124
6	-2	215	220
6	-1	42	30
6	0	483	459
6	1	65	52
6	2	183	185
6	3	53	51
6	4	126	122
6	5	210	212
6	6	129	128
7	-6	29	26*
7	-5	402	385
7	-4	249	240
7	-3	141	138
7	-2	160	162
7	-1	367	360
7	0	77	73
7	1	404	384
7	2	71	70
7	3	37	33*
7	4	32	28*
7	5	270	270
8	-5	65	52
8	-4	31	41*
8	-3	484	464
8	-2	134	138
8	-1	352	354
8	0	58	55
8	1	286	268
8	2	92	84
8	3	474	457
8	4	52	45
8	5	78	82
9	-5	96	90
9	-4	232	219
9	-3	74	81
9	-2	208	200
9	-1	159	158
9	0	86	83
9	1	201	189
9	2	182	179
9	3	152	152
9	4	88	92
10	-4	200	196
10	-3	34	30*
10	-2	33	27*
10	-1	54	58
10	0	253	245
10	1	147	144
10	2	171	175
10	3	20	12*
11	-2	61	62
11	-1	32	22*
11	0	104	105
11	1	35	40
3,K,L			
0	-7	187	190
0	-5	442	431
0	-3	30	31*
0	-1	689	726
0	1	460	453
0	3	372	369
0	5	433	420
1	-8	117	111
1	-7	44	40
1	-6	73	79
1	-5	258	261
1	-4	37	38*
1	-3	298	306
1	-2	72	75
1	-1	96	100
1	0	212	212
1	1	185	180
1	2	252	251
1	3	247	244
1	4	118	119
1	5	99	99
1	6	198	196
2	-7	250	254
2	-6	92	96
2	-5	89	91
2	-4	352	354
2	-3	206	209
2	-2	241	243
2	-1	89	94
2	0	268	261
2	1	60	54
2	2	417	407
2	3	246	248
2	4	56	69
2	5	162	165
2	6	235	242
3	-7	75	78
3	-6	268	264
3	-5	60	54
3	-4	123	122
3	-3	166	167
3	-2	458	459
3	-1	76	76
3	0	164	160
3	1	34	33*
3	2	284	277
3	3	33	24*
3	4	200	199
3	5	48	47
3	6	43	47
4	-7	203	198
4	-6	262	256
4	-5	159	157
4	-4	107	114
4	-3	329	332
4	-2	138	147
4	-1	68	69
4	0	18	17*
4	1	285	280
4	2	112	110
4	3	174	170
4	4	35	29*
4	5	99	101
4	6	98	95
5	-7	51	54
5	-6	27	22*
5	-5	237	235
5	-4	98	99
5	-3	105	102
5	-2	92	91
5	-1	364	352
5	0	138	134
5	1	419	406
5	2	208	201
5	3	84	84
5	4	7	22*
5	5	349	334
6	-6	252	239
6	-5	89	84
6	-4	78	88
6	-3	73	67
6	-2	305	302
6	-1	55	49
6	0	140	129
6	1	85	82
6	2	147	144
6	3	226	224
6	4	116	116
6	5	137	141
7	-6	75	70
7	-5	99	96
7	-4	85	82
7	-3	171	183
7	-2	166	173
7	-1	12	11*
7	0	74	70
7	1	119	117
7	2	213	206
7	3	35	22*
7	4	274	265
7	5	18	16*
8	-5	30	16*
8	-4	61	50
8	-3	24	23*
8	-2	0	4*
8	-1	61	58
8	0	239	229
8	1	101	98
8	2	227	221
8	3	10	19*
8	4	132	127
9	-5	126	129
9	-4	189	184
9	-3	103	97
9	-2	37	37*
9	-1	60	53
9	0	246	236
9	1	97	89
9	2	175	161
9	3	143	144
10	-3	170	167
10	-2	249	246
10	-1	201	202
10	0	52	52
10	1	48	44
10	2	202	197
11	-1	143	186
11	0	44	64
4,K,L			
0	-6	427	426
0	-4	482	489
0	-2	151	149
0	0	598	598
0	2	359	350
0	4	177	177
0	6	264	264
1	-7	252	249
1	-6	61	62
1	-5	282	284
1	-4	339	344
1	-3	309	316
1	-2	423	425
1	-1	474	476
1	0	86	83
1	1	39	37
1	2	242	240
1	3	207	204
1	4	276	266
1	5	49	47
1	6	100	103
2	-7	186	188
2	-6	95	98
2	-5	53	55
2	-4	54	53
2	-3	371	372
2	-2	97	100
2	-1	352	346
2	0	183	180
2	1	115	111
2	2	279	270
2	3	376	363
2	4	154	156
2	5	169	164
2	6	101	105
3	-7	78	74
3	-6	38	52*
3	-5	205	210
3	-4	145	148
3	-3	400	400
3	-2	123	125
3	-1	73	72
3	0	316	315
3	1	542	527
3	2	65	66
3	3	291	285
3	4	177	178
3	5	287	282
4	-7	10	107*
4	-6	94	95
4	-5	85	88
4	-4	76	77
4	-3	176	180
4	-2	28	24*
4	-1	118	117
4	0	112	107
4	1	43	39
4	2	130	131
4	3	94	98
4	4	53	56
4	5	176	178
5	-7	83	81
5	-6	174	171
5	-5	107	111
5	-4	201	200
5	-3	99	101
5	-2	234	229
5	-1	190	186
5	0	345	327
5	1	63	63
5	2	130	132
5	3	35	33*
5	4	336	331
5	5	89	94
6	-6	143	138
6	-5	22	3*
6	-4	134	135
6	-3	40	41*
6	-2	17	27*
6	-1	55	53
6	0	67	62
6	1	42	45
6	2	49	46
6	3	45	31
6	4	86	81
7	-6	44	44
7	-5	160	155
7	-4	156	153
7	-3	64	68
7	-2	90	87
7	-1	142	144
7	0	246	242
7	1	157	158
7	2	23	27*
7	3	91	84
7	4	185	184
8	-5	76	80
8	-4	120	116
8	-3	92	91
8	-2	113	109
8	-1	126	172
8	0	120	119
8	1	57	50
8	2	19	8*
8	3	130	131
9	-4	235	232
9	-3	28	19*
9	-2	206	207
9	-1	82	82
9	0	84	84
9	1	98	96
9	2	136	139
10	-3	203	199
10	-2	88	92
10	-1	108	104
10	0	209	205
10	1	72	75
5,K,L			
0	-7	123	119
0	-5	178	178
0	-3	43	40
0	-1	426	425
0	1	139	138
0	3	495	487
0	5	292	302
1	-7	93	88
1	-6	78	80
1	-5	100	105
1	-4	81	81
1	-3	85	87
1	-2	123	129
1	-1	270	264
1	0	45	39
1	1	207	208
1	2	102	102
1	3	23	26*
1	4	174	174
1	5	166	171
2	-7	57	52
2	-6	64	61
2	-5	367	372
2	-4	178	184
2	-3	303	315
2	-2	138	141
2	-1	307	302
2	0	207	204
2	1	441	436
2	2	301	301
2	3	29	25*
2	4	42	42*
2	5	88	84
3	-7	0	37*
3	-6	58	60
3	-5	118	116
3	-4	141	140
3	-3	153	156
3	-2	188	183
3	-1	113	111
3	0	29	24*
3	1	9	21*
3	2	178	177
3	3	113	114
3	4	176	179
3	5	117	116
4	-7	265	259
4	-6	247	248
4	-5	8	30*
4	-4	39	44*
4	-3	182	183
4	-2	379	375
4	-1	68	70
4	0	193	188
4	1	39	46*
4	2	133	136
4	3	69	70
4	4	86	93
5	-6	74	64
5	-5	186	181
5	-4	51	38
5	-3	254	257
5	-2	8	22*
5	-1	68	48
5	0	59	58
5	1	222	215
5	2	169	166
5	3	125	124
5	4	157	152
6	-6	228	223
6	-5	109	113
6	-4	121	125
6	-3	66	62
6	-2	113	113
6	-1	258	253
6	0	45	41
6	1	142	141
6	2	102	91
6	3	131	129
6	4	72	73
7	-5	93	89
7	-4	95	99
7	-3	75	73
7	-2	227	223
7	-1	36	29*
7	0	298	282
7	1	78	71
7	2	50	45
7	3	66	62
8	-5	52	45
8	-4	271	263
8	-3	72	69
8	-2	316	305
8	-1	57	48
8	0	115	114
8	1	40	41*
8	2	333	325
9	-3	105	103
9	-2	112	113
9	-1	113	110
9	0	46	49
9	1	229	220
6,K,L			
0	-6	164	160
0	-4	148	152
0	-2	44	40
0	0	42	41
0	2	123	124
0	4	0	31*
1	-7	210	213
1	-6	103	103
1	-5	290	301
1	-4	26	23*
1	-3	93	92
1	-2	69	69
1	-1	227	229
1	0	49	54
1	1	97	95
1	2	80	80
1	3	115	114
1	4	48	44
2	-7	173	172
2	-6	35	43*
2	-5	95	96
2	-4	83	81
2	-3	116	119
2	-2	52	40
2	-1	219	219
2	0	45	48
2	1	51	51
2	2	91	90
2	3	191	197
2	4	84	88
3	-7	182	184
3	-6	48	55
3	-5	125	130
3	-4	279	280
3	-3	295	296
3	-2	271	273
3	-1	78	75
3	0	45	41
3	1	362	358
3	2	64	66
3	3	194	194
3	4	47	32
4	-6	219	218
4	-5	57	53
4	-4	426	428
4	-3	87	85
4	-2	131	133
4	-1	56	52
4	0	350	346
4	1	63	56
4	2	377	368
4	3	24	27*
5	-6	221	219
5	-5	58	61
5	-4	113	111
5	-3	136	143
5	-2	353	351
5	-1	54	45
5	0	446	438
5	1	271	262
5	2	97	102
5	3	133	130
6	-5	11	36*
6	-4	118	122
6	-3	317	320
6	-2	59	59
6	-1	338	325
6	0	146	146
6	1	32	14*
6	2	129	126
6	3	181	184
7	-5	287	281
7	-4	203	199
7	-3	190	192
7	-2	57	65
7	-1	91	96
7	0	111	113
7	1	263	256
7	2	31	34*
8	-4	53	37
8	-3	129	130
8	-2	103	104
8	-1	190	181
8	0	41	55*
8	1	69	70
9	-1	120	130
7,K,L			
0	-5	364	358
0	-3	99	100
0	-1	424	413
0	1	289	283
0	3	266	266
1	-6	232	231
1	-5	190	192
1	-4	51	55
1	-3	256	258
1	-2	317	319
1	-1	63	65
1	0	135	135
1	1	118	118
1	2	111	114
1	3	110	110
2	-6	66	64
2	-5	26	4*
2	-4	207	205
2	-3	88	86
2	-2	188	189
2	-1	38	44*
2	0	127	127
2	1	82	82
2	2	295	293
2	3	243	249
3	-6	68	66
3	-5	136	138
3	-4	34	32*
3	-3	47	41
3	-2	50	50
3	-1	238	239
3	0	157	157
3	1	132	133
3	2	48	47
3	3	77	77
4	-6	170	169
4	-5	152	155
4	-4	167	169
4	-3	245	255
4	-2	56	46
4	-1	48	43
4	0	54	53
4	1	89	93
4	2	44	42
5	-5	81	82
5	-4	99	101
5	-3	34	11*
5	-2	115	120
5	-1	89	80
5	0	165	168
5	1	239	234
5	2	36	48*
6	-4	38	41*
6	-3	177	175
6	-2	216	216
6	-1	208	203
6	0	147	144
6	1	76	77
7	-3	93	96
7	-2	262	258
7	-1	166	159
7	0	153	152
8,K,L			
0	-4	162	167
0	-2	189	193
0	0	29	30*
0	2	370	368
1	-5	151	154
1	-4	92	90
1	-3	65	71
1	-2	306	306
1	-1	148	149
1	0	213	222
1	1	51	48
1	2	58	58
2	-5	88	87
2	-4	322	324
2	-3	78	77
2	-2	81	76
2	-1	234	240
2	0	276	278
2	1	152	162
3	-5	189	192
3	-4	46	37
3	-3	297	293
3	-2	44	40
3	-1	38	36*
3	0	133	134
3	1	358	352
4	-4	192	196
4	-3	238	240
4	-2	89	92
4	-1	207	213
4	0	178	179
4	1	79	78
5	-4	95	94
5	-3	54	57
5	-2	101	104
5	-1	38	36*
5	0	182	187
6	-2	42	35
9,K,L			
0	-3	222	228
0	-1	302	305
1	-4	53	54
1	-3	66	65
1	-2	275	278
1	-1	177	184
2	-2	88	87
2	-1	33	43*

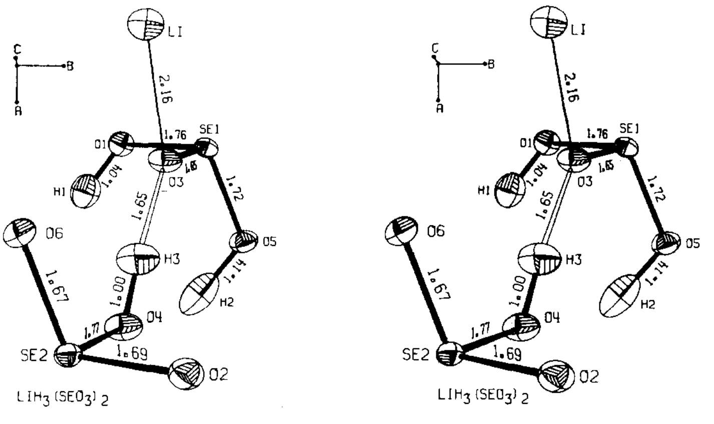

FIG. 1. A stereoscopic illustration of an asymmetric unit in $LiH_3(SeO_3)_2$. The ellipsoids are scaled to include 50% probability. Covalent bonds are filled, O···H bonds are open and ionic bonds are drawn as single lines.

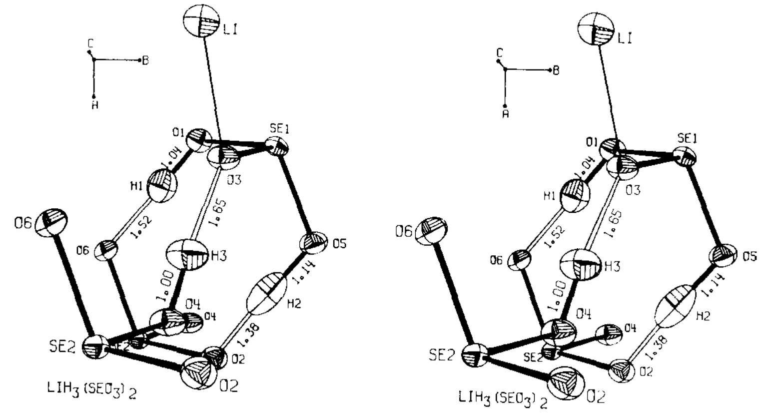

FIG. 2. A stereoscopic pair of drawings showing the hydrogen-bond scheme.

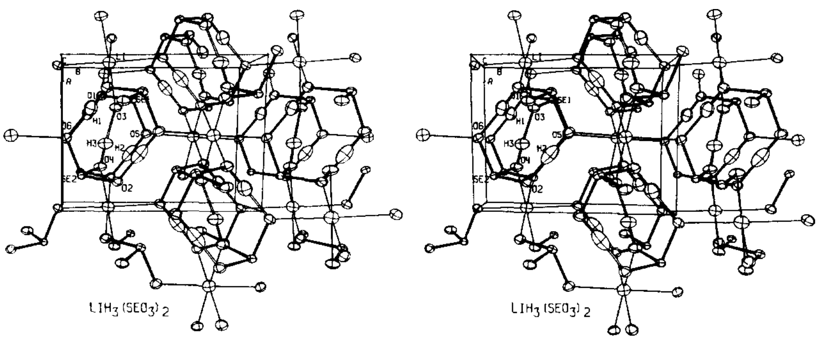

FIG. 3. A stereoscopic view of the structure seen in the direction of the chains.

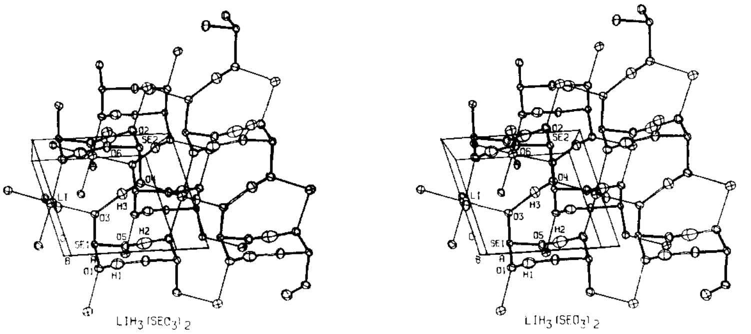

FIG. 4. A stereoscopic view of the structure showing the chains as seen from the side. The ferroelectric axis is nearly perpendicular to the *ab* plane.

The Selenium and Oxygen Atoms

Two independent selenium atoms are present in the structure but with very similar surroundings. Both form covalent bonds with three oxygen atoms so forming a pyramid (Fig. 1). The angles O–Se–O are between 99 and 105° (Table V). The Se–O distances vary from 1.65 to 1.77 Å (Fig. 1 and Table V), which is in good agreement with values reported

TABLE V

INTERATOMIC DISTANCES AND ANGLES IN LiH$_3$(SeO$_3$)$_2$

A. Distances (Å)	
Se(1)–O(1)	1.760(3)
–O(3)	1.653(3)
–O(5)	1.720(3)
–O(2)	2.903(2)
–O(4)	3.184(3)
–O(5)	3.086(3)
–Li	3.097(9)
Se(2)–O(2)	1.691(3)
–O(4)	1.765(3)
–O(6)	1.670(3)
–O(1)	2.913(3)
–O(3)	3.113(3)
–O(6)	2.955(3)
Li–O(1)	2.126(9)
–O(2)	2.127(9)
–O(3)	2.162(9)
–O(4)	2.163(9)
–O(5)	2.216(12)
–O(6)	2.187(12)
B. Angles (degrees)	
O(1)–Se(1)–O(3)	101.52(15)
O(1)–Se(1)–O(5)	100.29(12)
O(3)–Se(1)–O(5)	104.64(12)
Se(1)–O(1)–H(1)	111.97(31)
Se(1)–O(5)–H(2)	116.31(35)
Se(1)–O(3)···H(3)	128.23(21)
O(2)–Se(2)–O(4)	99.43(15)
O(2)–Se(2)–O(6)	103.64(13)
O(4)–Se(2)–O(6)	102.55(13)
Se(2)–O(6)···H(1)	119.21(24)
Se(2)–O(2)···H(2)	117.74(28)
Se(2)–O(4)–H(3)	116.92(30)
O(1)–Li–O(3)	90.22(35)
O(1)–Li–O(4)	88.03(33)
O(1)–Li–O(5)	86.84(37)
O(1)–Li–O(6)	92.36(41)
O(2)–Li–O(3)	92.43(34)
O(2)–Li–O(4)	89.34(35)
O(2)–Li–O(5)	91.90(41)
O(2)–Li–O(6)	88.83(38)
O(3)–Li–O(5)	90.39(41)
O(3)–Li–O(6)	91.36(38)
O(4)–Li–O(5)	90.27(38)
O(4)–Li–O(6)	87.95(40)

in KH$_3$(SeO$_3$)$_2$ (*5*). As is to be expected, the Se–O distances are dependent upon whether or not a hydrogen atom is covalently bonded to the oxygen atom. This will be discussed further in the next section.

TABLE VI

HYDROGEN-BOND DISTANCES (Å) AND ANGLES (DEGREES) IN LiH$_3$(SeO$_3$)$_2$

X H Y	X–H	H···Y	X···Y	∧X–H···Y
O(1)–H(1)···O(6)	1.040(6)	1.517(6)	2.552(3)	173.25(43)
O(5)–H(2)···O(2)	1.141(7)	1.378(7)	2.518(3)	176.56(54)
O(4)–H(3)···O(3)	1.003(4)	1.649(5)	2.646(4)	172.27(40)

Further oxygen atoms and one lithium ion appear in the vicinity of the selenium atoms (2.90–3.20 Å), but these are not arranged in any regular way (Table V).

The Hydrogen-bond Network

The hydrogen-bond network is shown in detail in Fig. 2 and can also be seen in Figs. 3 and 4. Distances and angles are listed in Table VI. There occur three almost linear O–H···O bonds of length 2.553, 2.518, and 2.646 Å, with O–H···O angles of 173.3, 176.6, and 172.3°, respectively.

Two of these hydrogen bonds, namely O(1)–H(1)···O(6) and O(5)–H(2)···O(2) are approximately parallel to the (001) plane and linking two SeO$_3$ groups. These double groups are connected by means of the third hydrogen bond O(4)–H(3)···O(3) to form S-shaped chains running in the *c* direction (Fig. 4).

The O(1)–H(1) distance (1.04 Å) and the O(4)–H(3) distance (1.00 Å) are the expected values for hydrogen bonds of length 2.55 and 2.65 Å. The O(5)–H(2) distance of 1.14 Å is about 0.1 Å longer than that expected for a hydrogen bond of length 2.52 Å (*13*). As can be seen in Fig. 2 and Table III, the hydrogen atom H(2) is also found to have a strongly prolate "thermal" ellipsoid with the longest axis directed along the O–H···O bond. From the present study it is impossible to ascertain whether this should be attributed to a large thermal vibration along the bond or to some disorder effect.

A comparison of the Se–O distances also indicates that this bond is different from the other two. As can be seen in Fig. 1 and Table V, the Se–O distances in the two normal bonds are 1.76 and 1.77 Å when the oxygen atom acts as a donor atom, and 1.65 and 1.67 Å when it acts as an acceptor atom in a hydrogen bond. In the case of the bond O(5)–H(2)···O(2) the Se–O distances are 1.72 and 1.69 Å, respectively. A further discussion of this matter will be made when the result from the neutron diffraction study of the deuterated compound is available.

It is not possible to make a comparison with the crystal structure of the paraelectric phase since, at atmospheric pressure, the compound is ferroelectric from −196°C up to the melting point (*14*, *15*).

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