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Refinement of the Crystal Structure of Ferroelectric Acid Lithium Selenite: Position of the Lithium Ion

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The lithium ion in the ferroelectric acid lithium selenite (not obtained in the original X-ray work of Vedam, Okaya & Pepinsky) has been located at the pseudoinversion centre ($\frac{1}{2}, \frac{3}{4}, 0$) from considerations of symmetry, crystal chemistry and model building. This position is confirmed from three-dimensional Fourier and difference Fourier syntheses, the peak height at the lithium ion site being three times the standard deviation in the electron density. The lithium ion is coordinated octahedrally to six non-equivalent selenite-oxygen atoms. The hydrogen positions have been proposed on the basis of bond-length and bond-angle criteria. They indicate that the selenite groups containing Se(1) and Se(2) have respectively the structures H_2SeO_3 and $HSeO_3^-$.

Introduction

Pepinsky & Vedam (1959) first reported that acid lithium selenite, $LiH_3(SeO_3)_2$, abbreviated hereafter as ALS, is a room-temperature ferroelectric. It melts at 110°C before a Curie point is reached. It is the only soft ferroelectric known so far to exhibit an appreciably high value of spontaneous polarization, P_s , viz. 15 microcoulomb. cm⁻² (Jona & Shirane, 1962). The direction of P_s is in the mirror plane, approximately normal to (001) (Pepinsky & Vedam, 1959; Berlincourt, Cook & Rander, 1963). The mechanism of polarization reversal in ALS single crystals was studied by Fatuzzo (1959 and 1960). Berlincourt and his colleagues, besides dielectric studies, reported investigations on the piezo- and pyro-electric, as well as the elastic, properties of this crystal. Recently, a ferro- to para-electric transition at 72°C was induced in ALS by the application of a hydrostatic pressure of 12.5 kbar, which indicated a hypothetical Curie point of 147°C (Samara & Anderson, 1966; Samara, 1968). ALS was also the first crystal with point group m to show rotatory power along its optic axes and for which a dextro-laevo conversion was obtained by the application of an electric field (Futama & Pepinsky, 1962).

The crystal structure of ALS was first solved by X-ray diffraction by Vedam, Okaya & Pepinsky (1960), using isotropic thermal parameters for all the atoms. They, however, made no attempt to locate the lithium ion in the structure directly, but assigned to it a probable position (0.65, 0.075, 0.23) from packing considerations. Later, a preliminary neutron diffraction study was made by Van den Hende & Boutin (1963) who reported the coordinates of the hydrogen atoms. The lithium ion, however, was not located, probably because of insufficient data and also because of the small neutron scattering cross-section for the most abundant isotope of the lithium ion. From considerations of the angular dependence of ⁷Li (nuclear magnetic resonance study of the crystal), Gavrilova-Podolskaya (1966) concluded that the lithium ion occupies the position ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$).

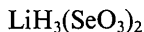
Experimental

In the course of the X-ray analysis of some ferro- and piezo-electric crystals, the authors constructed a three-dimensional model of the structure of ALS and found that the positions assigned to the lithium ion by the earlier workers were not possible. The proposed positions were too close to the heavy selenium atoms and

in addition had highly distorted and irregular lithium coordination polyhedra. A careful examination of the model revealed that the site $(\frac{1}{2}, \frac{3}{4}, 0)$ had six oxygen atoms at distances 2.0 to 2.3 Å occupying the corners of a well-defined octahedron. This and the symmetry related position $(0, \frac{1}{4}, \frac{1}{2})$ seemed to be the most probable sites for the two lithium ions in the unit cell, because these distances were just what one would expect for the Li–O contacts if the lithium ions were octahedrally coordinated. In ferroelectric crystals, octahedral coordination of oxygen atoms for ions of inert-gas configuration is quite common (Matthias, 1967). For example, in lithium niobate (Bailey, 1952; Abrahams, Reddy & Bernstein, 1966; Abrahams, Hamilton & Reddy, 1966) and lithium tantalate (Bailey, 1952; Abrahams & Bernstein, 1967; Abrahams, Hamilton & Sequeira, 1967), the lithium ions are octahedrally coordinated. Also in $\text{NaH}_3(\text{SeO}_3)_2$ (Chou & Tang, 1957, 1958; Vijayan, 1968; Kaplan, Kay & Morosin, 1970) and $\text{NaD}_3(\text{SeO}_3)_2$ (Mohana Rao, 1970), the oxygen-coordination polyhedron for the sodium ion is again an octahedron.

To obtain direct evidence for this position of the lithium ion from electron density maps, a computation of three-dimensional Fourier and difference-Fourier syntheses from the original data of Vedam *et al.* was felt worth while as these syntheses had not been carried out earlier by them. In this structure, the position of the lithium ion is of particular interest not only because of the part it might play in the ferroelectric properties of the crystal, but also because the hydrogen bonding scheme in the structure depends upon a knowledge of the position of the lithium ion. In view of these considerations, the refinement of the crystal structure of ALS was attempted.

Crystal data



Formula weight 263.88

Monoclinic

Space group Pn $Z=2$ $a=6.2534 \pm 0.0004 \text{ \AA}$ $b=7.8830 \pm 0.0002$ $c=5.4335 \pm 0.0011$ $\beta=105^\circ 18.6 \pm 0.6'$ $U=258.35 \text{ \AA}^3$

(after Berlincourt, Cook & Rander, 1963)

Refinement of the structure

The structure-factor data of Vedam *et al.* (document No. 6242 with ADI, Auxiliary Publication Project, Photo Duplication Services) was obtained from the Library of Congress, Washington, D.C. The first three-dimensional structure-factor calculations using the parameters quoted by Vedam *et al.* and after suitably scaling them yielded an R index of 15% where R is defined as

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad (1)$$

After four cycles of least-squares calculations, the problem of locating the lithium ion was attempted.

Location of the lithium ion

Many ferroelectric crystals often possess 'pseudosymmetric structures'. Although ALS belongs to the monoclinic space group Pn , the crystal structure departs only slightly from the space group $P2_1/n$. The two selenite groups in the asymmetric part of the unit cell are related by a pseudo-inversion centre. Since there are only two lithium ions in the unit cell and the general

Table 1. *Electron densities and their errors at the atomic sites*

The coordinates are in fractional units and the electron densities have the dimensions $\text{e.}\text{\AA}^{-3}$.

	x	y	z	ρ_o	ρ_c	$\sigma(\rho)$	ρ_o	ρ_c	$\sigma(\rho)$
				(for all atoms)			(without Li ⁺ ion)		
Se(1)	-0.26723	0.60654	0.58704	131.7	132.0	1.1	131.8	132.0	1.1
Se(2)	0.26636	0.90050	0.41064	137.7	137.4	1.1	137.7	137.4	1.1
O(1)	-0.2931	0.7717	0.3632	23.0	22.8	0.8	22.9	22.8	0.8
O(2)	0.3137	0.7260	0.5958	18.7	19.2	0.7	18.6	19.2	0.8
O(3)	-0.2014	0.7196	0.8519	17.7	17.6	0.8	17.8	17.6	0.8
O(4)	0.1810	0.8081	0.1065	15.1	16.5	0.8	15.1	16.5	0.8
O(5)	-0.0100	0.5293	0.5583	20.6	20.9	0.8	20.8	21.0	0.8
O(6)	0.0232	0.9797	0.4142	17.4	18.0	0.7	17.3	18.0	0.7
Li	0.0000	0.2500	0.5000	4.5	5.1	1.0	3.7	0.2	1.0
*	0.0000	0.2500	0.0000	-0.5	0.6	1.0	-0.5	0.5	1.0
*	0.5000	0.2500	0.0000	-0.2	0.4	1.0	-0.1	0.4	1.0
*	0.5000	0.2500	0.5000	1.5	0.9	1.0	1.4	0.9	1.0
†	0.0000	0.0000	0.0000	-1.1	0.0	0.7	-1.1	0.0	0.7
‡	0.7333	0.6000	0.3333	3.3	-0.6	1.0	3.4	-0.6	1.0
‡	0.2667	0.8750	0.6667	2.9	-0.7	1.0	3.0	-0.6	1.0
§	0.6500	0.0750	0.2300	-0.4	0.9	0.8	-0.4	0.9	0.9
†	0.5000	0.5000	0.5000	-0.6	0.4	0.7	-0.5	0.4	0.7

* Other pseudo-inversion centres in the structure.

† Other special positions in the structure (one of which was concluded to be the position of the lithium ion from NQR studies).

‡ Positions corresponding to the heavy peaks near the Se atoms in the difference map.

§ The position suggested by Vedam *et al.* for the lithium ion.

multiplicity for the space group $P2_1/n$ is four, the lithium ion is likely to occupy a pseudo-inversion centre. There are eight such pseudo-inversion centres in the unit cell, those in the asymmetric part being $(\frac{1}{2}, \frac{3}{4}, \frac{1}{2})$, $(0, \frac{3}{4}, \frac{1}{2})$, $(\frac{1}{2}, \frac{3}{4}, 0)$ and $(0, \frac{3}{4}, 0)$. From a three-dimensional model of the structure, as pointed out previously, the lithium ion was found most likely to occupy $(\frac{1}{2}, \frac{3}{4}, 0)$, with an octahedral coordination of oxygen atoms. A three-dimensional difference-Fourier synthesis computed at the end of the fourth SFLS cycle justified this conclusion by giving a peak of about $3.5 \text{ e.}\text{\AA}^{-3}$ at $(\frac{1}{2}, \frac{3}{4}, 0)$. The final difference-Fourier map computed without the lithium ion is shown in Fig. 1. Besides the peak at $(\frac{1}{2}, \frac{3}{4}, 0)$, there are two other peaks with heights above $3 \text{ e.}\text{\AA}^{-3}$ which are very close to the heavy selenium atoms (indicated by crosses in the figure, the distance from the selenium atom to the peaks being about 1.4\AA) and which are more likely to be diffraction ripples from

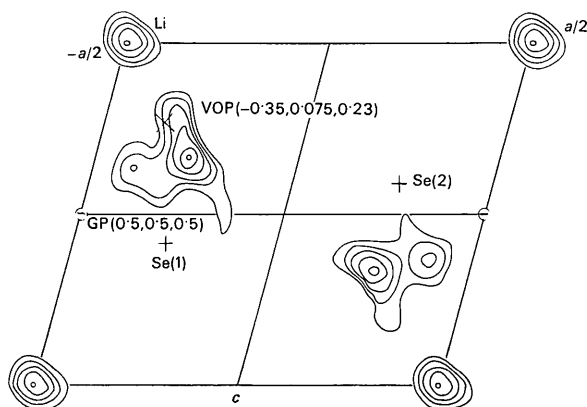


Fig. 1. Composite difference-Fourier map of sections parallel to (010). Peaks having density above $3 \text{ e.}\text{\AA}^{-3}$ only are shown. The contours are drawn at intervals of $0.5 \text{ e.}\text{\AA}^{-3}$ starting at $1.5 \text{ e.}\text{\AA}^{-3}$. + signs indicate the selenium positions. The signs \times , \ominus and Li indicate respectively the positions of the lithium ion as proposed by Vedam *et al.* (VOP), Gavrilova-Podolskaya (GP) and the present study.

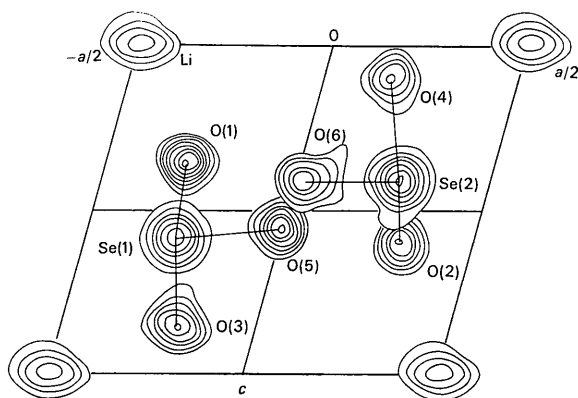


Fig. 2. Composite Fourier map of sections parallel to (010). The contours are drawn at intervals of 1, 2.5 and $20 \text{ e.}\text{\AA}^{-3}$ starting at 1, 5, $10 \text{ e.}\text{\AA}^{-3}$ for Li^+ , O and Se atoms respectively.

the heavy atoms. At the positions proposed by Vedam *et al.* as well as Gavrilova-Podolskaya, and also at the other pseudo-inversion centres in the structure, no peaks are present.

As there exists a possibility of errors occurring at symmetry positions (Lipson & Cochran, 1966), the standard deviation in the peak heights (Cruickshank, 1965) at all the pseudo-inversion centres as well as at the lithium positions chosen by the earlier workers, was calculated by using the formula

$$\sigma^2[\rho(xyz)] = \frac{1}{U^2} \left\{ \sum_{\text{indep}} [\sigma^2(F)] \left(\sum_{\text{form}} \cos\theta \right)^2 \right\} \quad (2)$$

with a Fortran program written by one of the authors (JKMR) for the space group Pn . The symbols have their usual meaning and $\sigma(F)$ was taken as $|F_o - F_c|$. The results of these computations are presented in Table 1. The σ values were calculated both with and without the contribution of the lithium ion to the final structure factors. It can readily be seen from the table that $\rho_o(\frac{1}{2}, \frac{3}{4}, 0) \approx 3\sigma(\rho)$ in both cases. In the final Fourier synthesis (Fig. 2), a peak height of $4.5 \text{ e.}\text{\AA}^{-3}$ was found at the proposed site of the lithium ion, though a few other spurious peaks of the same magnitude were also present, probably because of the presence of the heavy selenium atoms in the structure.

In the final SFLS calculations, the lithium ion was also included and the refinement continued with only isotropic temperature factors and keeping the lithium position fixed. Prior to this, a few anisotropic least-squares refinement cycles were also computed, but it was found that the shifts in the anisotropic thermal parameters were not meaningful. The final R factor for 574 reflections is 0.116 with the lithium ion and 0.117 without it. These R factors reduce to 11.2% and 11.3% if one omits a few strong reflexions (marked *) for which $\Delta F \geq 20.0$ and which seem to suffer from some unknown errors.

The refinement cycles were done on the Elliott 803B computer at Hindustan Aeronautics Limited, Bangalore-17, using a block-diagonal least-squares program written by Dr G. A. Mair. The quantity minimized in the program is $\sum w |KF_o - F_c|^2$. In the final cycles, all positional shifts were less than the corresponding standard deviations, the maximum and the average being 0.72σ and 0.18σ respectively. The weighting scheme of Cruickshank was employed. It was of the form

$$w = 1/[a + b|KF_o| + c|KF_o|^2] \quad (3)$$

where $a = 500$, $b = 0.5$, $c = 0.0002$ and $K = 100$. The atomic scattering factors were those given by Cromer & Waber (1965).

Results

The final positional and thermal parameters of the atoms in the asymmetric part of the unit cell are given in Table 2. Table 3 lists the observed and calculated structure factors. Fig. 2 shows the composite drawing of the three-dimensional Fourier map and Fig. 3 shows

the environment of the lithium ion at $(0, \frac{1}{4}, \frac{1}{2})$. Figs. 4 and 5 give a view of the structure looking down the *b* and *c* axes respectively.

Table 2 (cont.)

Table 2. Fractional coordinates and the isotropic temperature factors for atoms in the asymmetric part of the unit cell

For each atom, below our values, are given the values of Veddam *et al.* The e.s.d.'s are given in parentheses. The asymmetric unit of Veddam *et al.* has been modified to conform to the present scheme.

	x	y	z	B(Å ²)		x	y	z	B(Å ²)
Se(1)	-0.2672 (5)	0.6065 (3)	0.5870 (5)	1.00	Se(2)	0.2664 (5)	0.9005 (3)	0.4106 (5)	0.81
	-0.2670 (10)	0.6060 (0)	0.5880 (10)	1.17	O(1)	0.2660 (10)	0.9010 (0)	0.4130 (10)	1.08
					O(2)	-0.293 (3)	0.772 (2)	0.363 (3)	0.45
					O(3)	-0.290 (5)	0.771 (3)	0.363 (5)	1.19
					O(4)	0.314 (3)	0.726 (2)	0.596 (3)	1.13
					O(5)	0.314 (4)	0.725 (3)	0.599 (4)	1.06
					O(6)	-0.201 (3)	0.720 (2)	0.852 (3)	1.08
					Li	-0.195 (6)	0.732 (4)	0.853 (6)	2.47
						0.181 (4)	0.808 (3)	0.107 (4)	1.81
						0.191 (6)	0.807 (4)	0.130 (6)	2.69
						-0.010 (3)	0.529 (2)	0.558 (4)	0.89
						-0.015 (5)	0.534 (3)	0.561 (5)	1.07
						0.023 (3)	0.980 (2)	0.414 (4)	1.37
						0.021 (6)	0.993 (4)	0.418 (6)	3.10
						0.50 (2)	0.75 (1)	0.00 (2)	3.34

Table 3. Observed and calculated structure factors

For each reflexion, the order of entries is *l*, *h*, *k*, *F_o*, *F_c* and the phase angle (°). Those marked * seem to suffer from large unknown errors.

h	k	l	F _o	F _c	Phase (°)
0	0	1	3.00	4.23	0.00
0	0	2	4.22	6.21	0.00
0	0	3	3.87	3.85	0.00
0	0	4	38.31	40.09	180.00
0	0	5	2.42	0.04	0.00
0	0	6	55.12	56.39	180.00
0	0	7	5.91	6.71	180.00
0	0	8	30.63	28.13	0.00
0	0	9	4.19	4.23	180.00
0	0	10	31.76	40.64	0.00
1	0	1	68.16	65.25	90.76
1	0	2	66.23	74.54	354.36
* 1	0	3	107.20	87.52	87.30
1	0	4	18.51	15.59	29.99
1	0	5	9.56	7.12	73.52
1	0	6	13.15	10.05	161.41
1	0	7	47.53	45.91	275.84
1	0	8	33.14	31.50	192.78
1	0	9	11.50	11.22	242.10
1	0	10	7.88	12.01	331.84
2	0	0	61.68	66.46	356.28
2	0	1	84.95	89.10	266.29
2	0	2	22.11	20.02	350.44
2	0	3	14.30	13.40	90.40
2	0	4	24.09	24.78	202.33
2	0	5	54.61	62.41	89.86
2	0	6	22.27	21.51	152.03
2	0	7	10.44	8.89	112.83
2	0	8	14.10	11.60	10.22
2	0	9	38.95	39.17	267.51
3	0	1	6.91	5.21	257.96
3	0	2	78.37	93.73	356.96
3	0	3	4.55	31.25	3
3	0	4	32.52	33.84	0.39
3	0	5	5.94	3.65	337.41
3	0	6	28.83	26.10	193.01
3	0	7	12.69	9.87	76.41
3	0	8	43.83	45.21	173.98
3	0	9	4.31	9.63	177.47
4	0	0	57.13	56.02	168.85
4	0	1	53.60	57.11	263.10
4	0	2	9.54	10.60	275.22
4	0	3	16.55	12.51	162.96
4	0	4	26.85	22.14	8.87
4	0	5	39.94	39.57	90.36
4	0	6	27.81	25.28	3.28
4	0	7	6.23	7.10	61.75
4	0	8	9.87	12.24	158.25
5	0	1	87.01	37.65	265.01
5	0	2	21.53	19.17	2.74
5	0	3	45.30	45.70	268.82
5	0	4	20.46	19.24	332.48
5	0	5	2.72	2.53	292.23
5	0	6	14.44	12.26	184.41
6	0	0	47.36	52.88	171.99
6	0	1	5.86	5.18	121.30
6	0	2	18.50	17.26	175.99
6	0	3	3.97	4.67	235.11
6	0	4	28.87	32.87	5.23
0	1	1	8.70	7.90	121.15
* 0	1	2	152.64	116.16	359.20
0	1	3	7.90	9.26	333.21
0	1	4	48.85	45.33	5.98
0	1	5	5.18	2.96	205.26
0	1	6	44.78	47.32	178.09
0	1	7	21.71	18.71	286.79
0	1	8	44.10	45.25	180.05
0	1	9	10.08	12.43	206.13
0	1	10	4.13	3.81	8.07
1	1	1	64.12	66.50	178.35
1	1	1	61.57	65.74	269.28
1	1	1	36.63	40.88	182.13
1	1	3	18.87	21.89	99.55
1	1	4	27.43	27.52	345.28
1	1	5	78.36	87.56	86.27
1	1	6	17.42	16.83	41.63
1	1	8	13.89	10.76	151.94
1	1	9	35.43	31.46	275.66
1	1	10	77.85	63.57	353.20
* -1	1	1	108.38	83.58	273.04
-1	1	2	10.62	8.73	216.81
-1	1	3	5.34	6.46	60.51
0	2	1	9.83	7.75	245.16
0	2	2	54.95	60.54	186.75
0	2	3	72.76	71.31	92.46
0	2	4	30.52	33.12	169.43
0	2	5	10.34	9.56	27.89
0	2	6	31.67	27.78	255.52
0	2	7	21.65	26.82	353.50
0	2	8	14.97	16.05	297.83
0	2	9	35.91	49.42	1.90
0	2	10	86.50	99.12	267.56
1	2	1	17.00	12.41	341.27
1	2	2	14.91	13.44	65.43
1	2	3	24.67	25.12	190.18
1	2	4	40.48	38.95	87.35
1	2	5	32.96	30.75	164.01
1	2	6	15.13	13.65	111.35
1	2	7	19.45	24.71	68.96
1	2	8	28.88	32.91	355.73
1	2	9	94.64	97.04	94.70
1	2	10	29.35	32.14	22.49
-1	2	1	19.02	20.45	290.89
-1	2	2	17.54	17.17	158.17
-1	2	3	49.87	57.00	268.54
-1	2	4	9.72	8.08	274.52
-1	2	5	21.32	20.14	263.37
-1	2	6	76.93	93.65	176.76
-1	2	7	10.54	9.32	95.72
-1	2	8	24.40	22.51	182.00
-1	2	9	19.43	16.84	83.35
-1	2	10	50.37	57.58	0.15
-1	2	11	2.89	1.10	269.21
-1	2	12	39.42	38.39	0.49
-1	2	13	13.45	13.41	45.78
-1	2	14	18.93	17.23	171.49
-1	2	15	3.56	3.56	293.67
-1	2	16	59.02	75.75	357.43
-1	2	17	9.81	9.92	326.39
-1	2	18	29.49	33.18	7.25
-1	2	19	8.94	8.94	297.84
-1	2	20	66.15	72.95	181.64
-1	2	21	30.69	29.04	277.23
-1	2	22	35.64	37.16	185.77
-1	2	23	6.80	8.90	171.29
-1	2	24	18.81	16.16	168.81
-1	2	25	3.33	3.44	133.91
-1	2	26	36.76	33.59	272.93
-1	2	27	39.12	36.78	175.35
-1	2	28	47.72	50.86	264.72
-1	2	29	22.32	20.34	191.37
-1	2	30	5.48	3.62	75.78
-1	2	31	15.11	13.10	349.24
-1	2	32	37.48	38.92	89.65
-1	2	33	33.82	34.45	87.25
-1	2	34	49.36	46.92	180.45
-1	2	35	44.80	48.00	100.04
-1	2	36	20.26	17.12	162.75
-1	2	37	3.99	2.79	242.98
-1	2	38	31.14	29.40	10.44
-1	2	39	36.50	32.70	262.44
-1	2	40	26.89	27.69	356.76
-1	2	41	8.95	8.51	218.65
-1	2	42	40.52	43.36	177.06
-1	2	43	11.79	11.20	68.33
-1	2	44	8.35	7.27	179.18
-1	2	45	43.77	42.47	180.17
-1	2	46	20.79	16.36	271.60
-1	2	47	25.14	23.57	192.22
-1	2	48	7.55	11.40	145.53
* -1	2	49	155.52	119.50	178.92
-1	2	50	9.83	7.75	245.16
0	2	1	22.09	18.53	7.86
0	2	2	3.39	4.92	217.21
0	2	3	67.91	70.54	357.21
0	2	4	30.66	30.33	89.28
0	2	5	56.51	59.30	5.11
0	2	6	8.89	10.55	330.61
0	2	7	23.63	20.83	179.56
0	2	8	6.17	6.16	329.12
0	2	9	34.15	42.35	275.78
0	2	10	50.78	55.05	175.92
0	2	11	65.33	76.45	266.50
0	2	12	8.40	10.30	242.61
0	2	13	16.87	13.21	102.53
0	2	14	10.87	11.37	318.28
0	2	15	57.05	63.21	88.83
0	2	16	27.35	24.60	15.35
0	2	17	21.32	20.02	84.72
0	2	18	76.72	69.87	273.27
0	2	19	71.54	76.04	359.64
0	2	20	34.29	38.65	271.34
0	2	21	16.42	15.30	331.23
0	2	22	3.47	3.25	17.44
0	2	23	29.27	26.51	192.68
0	2	24	53.92	53.75	87.29
0	2	25	41.98	40.39	175.79
0	2	26	19.68	17.97	115.02
0	2	27	36.15	41.83	174.19
0	2	28	41.99	44.56	93.55
0	2	29	7.92	7.03	190.47
0	2	30	29.40	28.98	268.42
0	2	31	50.29	51.42	4.31
0	2	32	53.92	56.54	268.59
0	2	33	29.47	27.29	340.47
0	2	34	13.66	12.22	294.67
0	2	35	10.53	8.90	209.10
0	2	36	16.60	13.33	191.93
0	2	37	54.43	58.20	267.16
0	2	38	3.27	3.05	102.38
0	2	39	39.88	40.48	100.21
0	2				

Table 3 (cont.)

5	2	4	15.29	13.98	157.75	-3	3	6	35.49	35.27	4.95	3	4	1	4.60	4.21	168.59
5	2	5	5.37	5.27	231.66	-3	3	7	9.45	8.34	352.34	3	4	2	54.84	53.98	355.98
5	2	1	38.94	42.20	98.18	-3	3	8	17.69	16.06	178.57	3	4	3	29.36	26.86	76.67
5	2	2	7.64	4.68	346.29	-3	3	1	38.38	33.91	92.09	3	4	4	26.43	26.66	5.01
5	2	3	44.21	45.37	84.85	4	3	2	22.73	14.27	358.56	3	4	5	5.46	3.82	293.65
5	2	4	9.72	8.65	46.12	4	3	3	44.56	42.41	83.20	3	4	6	20.96	22.47	181.59
5	2	5	5.49	3.25	302.23	4	3	4	7.95	7.98	42.55	-3	4	1	13.62	11.48	242.66
5	2	6	15.32	11.05	174.18	4	3	5	3.65	1.49	336.26	-3	4	2	64.82	61.47	181.87
6	2	0	28.72	37.10	357.09	4	3	6	11.92	14.19	161.35	-3	4	3	41.41	39.55	277.79
6	2	1	1.37	2.39	302.18	-4	3	1	24.01	23.59	257.86	-3	4	4	34.74	35.08	186.15
-6	2	0	42.89	42.09	1.95	-4	3	2	53.55	58.02	0.89	-3	4	5	7.08	10.35	152.20
-6	2	1	19.33	16.19	87.30	-4	3	3	37.93	35.79	279.56	-3	4	6	27.92	26.68	346.77
-6	2	2	10.37	8.64	326.80	-4	3	4	30.50	28.99	359.28	-3	4	7	26.98	22.47	78.49
-6	2	3	5.95	4.64	292.47	-4	3	5	12.30	8.57	100.68	-3	4	8	23.82	29.12	81.33
-6	2	4	35.61	36.99	179.76	-4	3	6	26.04	23.72	182.29	4	4	0	17.05	12.81	176.74
-6	2	5	15.78	15.41	264.75	-4	3	7	24.87	23.70	87.74	4	4	1	40.15	41.36	267.40
0	3	1	22.17	19.65	293.08	-4	3	8	12.57	24.43	175.48	4	4	2	3.47	3.33	288.80
0	3	2	79.60	82.18	176.43	5	3	0	36.05	36.99	348.30	4	4	3	9.46	7.41	118.62
0	3	3	32.63	30.54	254.97	5	3	1	25.64	22.49	275.94	4	4	4	8.50	5.90	352.16
0	3	4	58.84	36.41	184.52	5	3	2	6.27	4.65	10.57	4	4	0	62.31	62.28	183.53
0	3	5	15.78	9.42	251.95	5	3	3	12.94	13.74	88.05	-4	4	1	38.70	35.40	101.34
0	3	6	42.91	42.05	359.64	5	3	4	10.39	17.44	190.65	-4	4	2	15.31	15.28	181.68
0	3	7	21.46	15.43	371.08	-5	3	0	18.05	13.44	42.96	-4	4	3	16.36	13.38	263.79
0	3	8	44.81	41.61	5.50	-5	3	1	47.96	51.21	273.45	-4	4	4	40.09	39.84	357.08
0	3	9	6.58	9.25	348.33	-5	3	2	4.95	5.78	254.28	-4	4	5	17.80	14.11	251.59
1	3	0	19.49	17.85	177.85	-5	3	3	19.24	16.48	84.12	-4	4	6	29.49	27.91	358.62
1	3	1	62.78	66.85	89.93	-5	3	4	12.48	10.39	32.22	-4	4	7	13.08	12.97	314.29
1	3	2	11.91	11.08	6.41	-5	3	5	43.46	46.86	92.39	-5	4	1	40.66	45.87	230.29
1	3	3	24.50	19.78	280.54	-5	3	6	6.77	5.45	42.72	-5	4	2	6.19	3.42	352.98
1	3	4	35.54	41.17	11.0	-5	3	7	8.74	12.92	87.49	-5	4	3	42.79	43.72	269.91
1	3	5	65.89	69.70	266.07	-6	3	2	44.38	37.83	357.88	-5	4	4	7.10	4.01	245.04
1	3	6	17.30	13.26	223.20	-6	3	3	27.32	23.76	96.05	-5	4	5	6.71	4.35	322.02
1	3	7	6.33	5.76	253.08	*-6	3	4	25.94	26.08	15.27	-5	4	6	4.81	5.19	239.49
1	3	8	21.95	33.23	92.82	0	4	0	70.29	93.46	1.21	-6	4	0	43.47	42.39	191.75
-1	3	0	105.32	113.08	181.70	0	4	1	31.97	26.36	89.01	-6	4	1	20.24	20.84	268.92
-1	3	1	30.79	36.16	88.21	0	4	2	24.45	24.19	3.65	-6	4	2	15.39	15.39	187.51
-1	3	2	10.87	169.83	0	0	4	3	7.92	6.25	5.14	4	4	3	7.89	9.09	101.99
-1	3	3	28.95	26.73	265.09	0	4	4	46.22	41.62	172.29	-6	4	4	19.06	25.72	349.11
-1	3	4	39.32	34.48	355.55	0	4	5	39.65	35.49	266.50	0	5	1	28.07	23.01	104.51
-1	3	5	57.46	54.52	274.26	0	4	6	43.74	37.31	186.09	0	5	2	59.37	55.14	359.87
-1	3	6	36.29	34.68	354.81	0	4	7	13.84	10.01	133.65	0	5	3	29.94	23.13	73.14
-1	3	7	9.39	5.17	300.34	0	4	8	23.04	20.48	358.63	0	5	4	36.55	30.31	6.06
-1	3	8	21.39	18.26	209.95	1	4	1	33.14	31.41	91.94	0	5	5	6.59	4.44	333.28
-1	3	9	20.93	19.64	74.16	1	4	2	13.83	8.74	0.00	0	5	6	30.70	27.30	168.82
2	3	0	23.71	20.43	93.34	1	4	3	74.28	79.07	89.63	0	5	7	29.63	29.93	269.81
2	3	1	53.78	60.34	176.46	1	4	4	9.02	5.31	30.32	1	5	0	8.45	4.98	281.68
2	3	2	48.81	51.73	90.02	1	4	5	7.34	6.23	295.31	1	5	1	53.01	51.31	270.48
2	3	3	23.23	17.36	170.36	1	4	6	5.54	6.10	112.40	1	5	2	22.67	17.91	184.76
2	3	4	17.78	13.88	258.12	1	4	7	39.73	39.09	264.18	1	5	3	24.16	21.37	94.80
2	3	5	22.17	15.28	23.92	1	4	8	10.24	11.37	223.89	1	5	4	4.40	3.96	283.75
2	3	6	41.55	36.11	266.61	-1	1	35.26	46.50	91.97	1	5	5	51.44	49.08	86.86	
2	3	7	30.76	30.54	350.15	-1	4	2	44.82	68.97	178.89	1	5	6	9.90	6.97	123.29
-2	3	1	31.82	39.48	264.53	-1	4	3	35.42	31.36	92.86	1	5	7	7.46	8.75	96.24
-2	3	2	6.52	5.54	62.29	-1	4	4	34.83	31.65	182.21	-1	5	0	60.97	68.35	1.33
-2	3	3	82.25	88.65	272.89	-1	4	5	8.79	7.64	129.74	-1	5	1	32.14	36.13	275.64
-2	3	4	18.76	15.55	209.19	-1	4	6	32.28	26.27	4.92	-1	5	2	5.03	7.50	283.10
-2	3	5	12.34	10.84	124.80	-1	4	7	30.57	25.40	266.53	-1	5	3	8.22	10.22	49.49
-2	3	6	27.35	23.38	359.85	-1	4	8	29.92	29.46	350.65	-1	5	4	49.20	42.83	175.73
-2	3	7	48.86	48.44	87.14	2	4	0	56.34	60.67	353.65	-1	5	5	29.27	19.87	97.82
-2	3	8	5.37	5.73	59.95	2	4	1	37.03	38.81	271.21	-1	5	6	41.25	37.50	183.99
-2	3	9	15.32	16.52	90.64	2	4	2	25.59	22.77	4.12	-1	5	7	5.44	4.38	149.24
3	3	0	63.79	67.85	355.27	2	4	3	14.16	11.86	81.02	2	5	1	22.46	19.83	266.12
3	3	1	26.03	20.69	79.46	2	4	4	37.79	35.77	183.44	2	5	2	47.76	48.27	356.55
3	3	2	10.43	8.39	244.40	2	4	5	39.27	30.34	40.70	2	5	3	34.00	30.66	275.38
3	3	3	4.85	3.66	349.18	2	4	6	25.50	21.06	168.18	2	5	4	18.16	12.97	359.53
3	3	4	46.24	48.23	177.83	2	4	7	7.02	5.59	123.55	2	5	5	17.33	17.43	186.10
3	3	5	7.51	4.52	245.69	-2	4	0	11.82	11.35	48.50	-2	5	1	40.19	46.97	91.30
3	3	6	37.82	36.26	181.24	-2	4	1	74.78	75.78	94.11	-2	5	2	15.10	8.27	176.51
3	3	7	7.12	7.46	215.86	-2	4	2	5.50	2.11	302.30	-2	5	3	50.85	54.67	91.28
-3	3	0	56.93	61.02	173.28	-2	4	3	18.28	17.45	266.88	-2	5	4	19.66	14.81	37.14
-3	3	1	37.11	35.84	271.95	-2	4	4	9.05	8.44	61.25	-2	5	5	5.71	4.36	274.62
-3	3	2	31.67	31.43	192.31	-2	4	5	52.35	55.94	268.08	-2	5	6	3.85	3.86	125.92
-3	3	3	8.64	4.43	265.35	-2	4	6	12.84	10.14	230.72	-2	5	7	40.53	44.46	267.65
-3	3	4	58.52	62.48	1.45	-2	4	7	6.93	7.58	249.66	3	5	0	51.02	56.51	177.91
-3	3	5	28.72	24.40	81.09	-2	4	8	7.34	6.50	324.53	3	5	1	15.96	11.78	264.50

Table 3 (cont.)

3	5	2	10.34	8.57	188.45	0	6	5	45.99	36.06	87.46	-4	6	2	17.39	14.16	359.74
3	5	3	12.24	10.62	106.38	0	6	6	28.44	26.36	8.04	-4	6	3	16.59	12.16	99.74
3	5	4	25.83	24.79	355.29	1	6	1	26.63	24.08	262.71	-4	6	4	40.65	42.26	185.83
3	5	5	10.88	19.11	77.47	1	6	2	8.57	6.12	332.21	-4	6	5	10.51	8.80	94.36
-3	5	0	47.61	42.84	359.64	1	6	3	50.80	48.94	271.75	-5	6	1	29.49	30.81	92.22
-3	5	1	25.71	22.67	80.43	1	6	4	5.41	3.17	254.11	-5	6	2	16.42	11.34	167.08
-3	5	2															

Interatomic distances and geometry of groups

(i) Selenite ions

The dimensions of the two selenite groups are listed in Table 4(a). In each selenite group, the differences between the maximum (~ 1.76 Å) and the minimum

(~ 1.66 Å) Se-O distances are significantly above the standard deviations ($\Delta/\sigma \approx 3$ to 4). The symmetry of both the selenite groups departs from the ideal $3m$ (C_{3v}) symmetry, a result in agreement with the Raman-effect studies by Bazhulin, Myasnikova & Rakov (1964). The deviations of the two selenium atoms, Se(1) and

Table 4. Interatomic distances and group geometry

(a) Dimensions of the selenite ions in the structure. The values of Vedam *et al.* are given below our entries.

Se(1)-O(1)	1.76 ± 0.02 Å	Se(2)-O(2)	1.68 ± 0.02 Å
	1.77 ± 0.05		1.70 ± 0.04
Se(1)-O(3)	1.65 ± 0.02	Se(2)-O(4)	1.76 ± 0.02
	1.71 ± 0.05		1.66 ± 0.05
Se(1)-O(5)	1.77 ± 0.02	Se(2)-O(6)	1.65 ± 0.02
	1.72 ± 0.05		1.71 ± 0.05
O(1)-O(3)	2.60 ± 0.02	O(2)-O(4)	2.65 ± 0.03
	2.59 ± 0.07		2.54 ± 0.06
O(1)-O(5)	2.63 ± 0.02	O(2)-O(6)	2.71 ± 0.03
	2.58 ± 0.07		2.80 ± 0.07
O(3)-O(5)	2.69 ± 0.03	O(4)-O(6)	2.54 ± 0.03
	2.68 ± 0.07		2.57 ± 0.07
O(1)-Se(1)-O(3)	$99.2 \pm 0.8^\circ$	O(2)-Se(2)-O(4)	$100.7 \pm 0.9^\circ$
	97.0 ± 6.0		98.0 ± 6.0
O(1)-Se(1)-O(5)	96.5 ± 0.8	O(2)-Se(2)-O(6)	108.6 ± 1.0
	96.0 ± 6.0		110.0 ± 6.0
O(3)-Se(1)-O(5)	103.9 ± 0.8	O(4)-Se(2)-O(6)	96.7 ± 1.0
	102.0 ± 6.0		99.0 ± 6.0

(b) Non-bonded Se-O contacts less than the van der Waals contact (3.4 Å)

Se(1)-O(2)	$(x-1, y, z)$	2.80 ± 0.02 Å
Se(1)-O(5)	$(\frac{1}{2}+x-1, 1-y, \frac{1}{2}+z-1)$	3.07 ± 0.02
Se(1)-O(4)	$(\frac{1}{2}+x-1, 1-y, \frac{1}{2}+z)$	3.29 ± 0.02
Se(2)-O(6)	$(\frac{1}{2}+x, 2-y, \frac{1}{2}+z)$	2.94 ± 0.02 Å
Se(2)-O(1)	$(x+1, y, z)$	3.01 ± 0.02
Se(2)-O(3)	$(\frac{1}{2}+x, 2-y, \frac{1}{2}+z-1)$	3.02 ± 0.02

(c) Dimensions of the coordination polyhedron around the lithium ion in the structure

Li-O(1)	$(x+1, y, z)$	2.06 ± 0.09 Å	
Li-O(2)	$(x, y, z-1)$	2.21 ± 0.09	
Li-O(3)	$(x+1, y, z-1)$	2.23 ± 0.12	
Li-O(4)		2.27 ± 0.12	
Li-O(5)	$(\frac{1}{2}+x, 1-y, \frac{1}{2}+z-1)$	2.23 ± 0.09	
Li-O(6)	$(\frac{1}{2}+x, 2-y, \frac{1}{2}+z-1)$	2.19 ± 0.09	
O(1)	$(x+1, y, z)$ —O(3)	$(x+1, y, z-1)$	3.01 ± 0.03 Å
O(1)	$(x+1, y, z)$ —O(4)		3.23 ± 0.03
O(1)	$(x+1, y, z)$ —O(5)	$(\frac{1}{2}+x, 1-y, \frac{1}{2}+z-1)$	3.00 ± 0.02
O(1)	$(x+1, y, z)$ —O(6)	$(\frac{1}{2}+x, 2-y, \frac{1}{2}+z-1)$	3.10 ± 0.02
O(2)	$(x, y, z-1)$ —O(3)	$(x+1, y, z-1)$	2.98 ± 0.02
O(2)	$(x, y, z-1)$ —O(4)		3.17 ± 0.03
O(2)	$(x, y, z-1)$ —O(5)	$(\frac{1}{2}+x, 1-y, \frac{1}{2}+z-1)$	3.18 ± 0.02
O(2)	$(x, y, z-1)$ —O(6)	$(\frac{1}{2}+x, 2-y, \frac{1}{2}+z-1)$	2.98 ± 0.02
O(3)	$(x+1, y, z-1)$ —O(5)	$(\frac{1}{2}+x, 1-y, \frac{1}{2}+z-1)$	3.16 ± 0.03
O(3)	$(x+1, y, z-1)$ —O(6)	$(\frac{1}{2}+x, 2-y, \frac{1}{2}+z-1)$	3.00 ± 0.03
O(4)		$(\frac{1}{2}+x, 1-y, \frac{1}{2}+z-1)$	3.34 ± 0.03
O(4)		$(\frac{1}{2}+x, 2-y, \frac{1}{2}+z-1)$	3.11 ± 0.03
O(1)	$(x+1, y, z)$ —Li-O(3)	$(x+1, y, z-1)$	$88.9 \pm 3.8^\circ$
O(1)	$(x+1, y, z)$ —Li-O(4)		96.4 ± 4.3
O(1)	$(x+1, y, z)$ —Li-O(5)	$(\frac{1}{2}+x, 1-y, \frac{1}{2}+z-1)$	88.9 ± 3.3
O(1)	$(x+1, y, z)$ —Li-O(6)	$(\frac{1}{2}+x, 2-y, \frac{1}{2}+z-1)$	93.6 ± 3.5
O(2)	$(x, y, z-1)$ —Li-O(3)	$(x+1, y, z-1)$	84.5 ± 3.8
O(2)	$(x, y, z-1)$ —Li-O(4)		90.1 ± 3.5
O(2)	$(x, y, z-1)$ —Li-O(5)	$(\frac{1}{2}+x, 1-y, \frac{1}{2}+z-1)$	91.7 ± 3.3
O(2)	$(x, y, z-1)$ —Li-O(6)	$(\frac{1}{2}+x, 2-y, \frac{1}{2}+z-1)$	85.3 ± 3.2
O(3)	$(x+1, y, z-1)$ —Li-O(5)	$(\frac{1}{2}+x, 1-y, \frac{1}{2}+z-1)$	90.2 ± 3.6
O(3)	$(x+1, y, z-1)$ —Li-O(6)	$(\frac{1}{2}+x, 2-y, \frac{1}{2}+z-1)$	85.4 ± 3.8
O(4)		$(\frac{1}{2}+x, 1-y, \frac{1}{2}+z-1)$	96.0 ± 4.1
O(4)		$(\frac{1}{2}+x, 2-y, \frac{1}{2}+z-1)$	88.3 ± 3.5

Table 4 (cont.)

(d) The dimensions of the lithium polyhedron from the earlier models. Vedam *et al.* have proposed the lithium ion at (0.65, 0.075, 0.23), indicated by Li(V), whereas Gavrilova-Podolskaya proposed it at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ which is indicated by Li(G).

Li(V)-O(6)	$(\frac{1}{2} + x, 1 - y, \frac{1}{2} + z - 1)$	1.74 Å
Li(V)-Se(2)	$(\frac{1}{2} + x, 1 - y, \frac{1}{2} + z - 1)$	2.06
Li(V)-O(2)	$(\frac{1}{2} + x, 1 - y, \frac{1}{2} + z - 1)$	2.11
Li(V)-O(4)	$(\frac{1}{2} + x, 1 - y, \frac{1}{2} + z)$	2.21
Li(G)-Se(1)	$(x + 1, y, z)$	1.64 Å
Li(G)-O(3)	$(\frac{1}{2} + x, 1 - y, \frac{1}{2} + z - 1)$	2.17
Li(G)-O(2)		2.26
Li(G)-O(5)	$(\frac{1}{2} + x, 1 - y, \frac{1}{2} + z - 1)$	2.40

(e) Hydrogen bond distances and Donohue angles. The values of Vedam *et al.* are quoted below our values.

O(1)-O(6)	2.53 ± 0.03 Å	O(1)-O(6)-Se(2)	116.8 ± 1.0°
	2.57 ± 0.07		109.0
		O(6)-O(1)-Se(1)	118.5 ± 0.8
			119.0
O(2)-O(5)	2.52 ± 0.03	O(2)-O(5)-Se(1)	120.9 ± 0.9°
	2.52 ± 0.07		123.0
		O(5)-O(2)-Se(2)	116.4 ± 0.9
			115.0
O(3)-O(4) (x, y, z + 1)	2.52 ± 0.03 Å	O(4) (x, y, z + 1)-O(3)-Se(1)	127.6 ± 1.0°
	2.56 ± 0.08		104.0
		O(3)-O(4) (x, y, z + 1)-Se(2) (x, y, z + 1)	129.7 ± 1.0
			130.0

Se(2), from the planes of their respective oxygen atoms are 0.80 and 0.74 Å. These oxygen planes themselves are almost parallel ($\theta \approx 1^\circ$).

(ii) *Non-bonded oxygen atoms close to the selenium atoms*

Each selenium atom, in addition to the three covalently-bonded oxygen atoms, has three more oxygen neighbours at 2.8 to 3.3 Å (indicated by full lines in

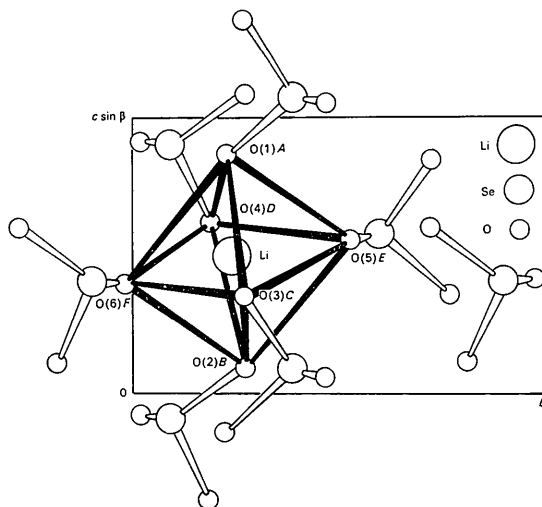


Fig. 3. The environment of the lithium ion at $(0, \frac{1}{2}, \frac{1}{2})$ as viewed down the *a* axis. The nomenclature of atoms is as follows:

- A $\frac{1}{2} + x, -y + 1, \frac{1}{2} + z.$
- B $\frac{1}{2} + x - 1, -y + 1, \frac{1}{2} + z - 1.$
- C $\frac{1}{2} + x, -y + 1, \frac{1}{2} + z - 1.$
- D $\frac{1}{2} + x - 1, -y + 1, \frac{1}{2} + z.$
- E $x, y, z.$
- F $x, y - 1, z.$

Fig. 5), which are shorter [Table 4(b)] than the sum (3.4 Å) of the van der Waals radii for the selenium and oxygen atoms (Pauling, 1960). These six oxygen atoms around each selenium atom are directed towards the corners of a distorted octahedron. Similar octahedral environments for the selenium atom have also been found in the structures of $\text{NaD}_3(\text{SeO}_3)_2$ (Mohana Rao, 1970), $\text{KH}_3(\text{SeO}_3)_2$ (Hansen, Hazell & Rasmussen, 1969), $\text{N}(\text{CH}_3)_4\text{Cl}_2.5\text{SeOCl}_2$ (Hermodsson, 1967), H_2SeO_3 (Wells & Bailey, 1949) and SeO_2 (McCullough, 1937). The non-bonded short contacts are perhaps due to the attraction of the formal positive charge on the selenium atom and the lone-pair electrons of the oxygen atoms.

(iii) *Environment of the lithium ion*

Table 4(c) gives the dimensions of the lithium-oxygen octahedron. The minimum, maximum and mean Li-O distances are 2.06, 2.27, 2.20 Å respectively. The maximum deviation of the Li-O distance (0.14 Å) from the mean value and the maximum standard deviation in the Li-O distance (0.12 Å) are of the same order. The minimum, maximum and mean O-Li-O angles are 85.3, 96.4 and 89.9°. The maximum deviation from the mean is therefore 6.5° and is again of the order of the standard deviation for the O-Li-O angle, *i.e.* 4.3°. On the other hand, the minimum, maximum and average values of the O-O edges in the octahedron are 2.98, 3.34 and 3.11 Å and the maximum deviation of the O-O edge from the mean is 0.23 Å compared to the maximum standard deviation of 0.03 Å. The deviations are therefore significant and the Li-O octahedron is a distorted one, although very nearly regular. The dimensions of the Li-O octahedron compare favourably with those found in LiNbO_3 (Abrahams, Reddy & Bernstein, 1966;

Abrahams, Hamilton & Reddy, 1966) and LiTaO_3 (Abrahams & Bernstein, 1967; Abrahams, Hamilton & Sequeira, 1967). The Li–O and Li–Se distances for the earlier models for the lithium ion are also given in Table 4(d). It can be seen that the lithium ion has no definite coordination polyhedron in these cases.

(iv) *Hydrogen bonding*

The only short O–O distances not involved in the edges of the selenium or the lithium coordination polyhedra are those listed in Table 4(e). Since there are only three such distances per asymmetric unit and three hydrogen atoms to be placed in them, the location of the hydrogen bonds is unambiguously determined. This hydrogen-bonding scheme is the same as the one favoured by Vedam *et al.* purely on consideration of distances alone. From Fig. 4, it can be seen that all the selenite oxygen atoms take part in the bond formation either as donors or acceptors. Two of the bonds, O(1)–O(6) and O(2)–O(5), are almost perpendicular to the direction of P_s and the third crosses the pseudo-inversion centre $(0, \frac{1}{2}, 0)$. There is a closed loop of oxygen atoms [Se(1) O(5) O(2) Se(2) O(6) O(1)] because of hydrogen bonding. A similar loop exists in the crystal structure of H_2SeO_3 (Wells & Bailey, 1949) also, with the difference that two of the oxygen atoms in the loop form additional hydrogen bonds connecting the neighbouring loops. The formation of the closed loop and the direction of P_s being perpendicular to the hydrogen bonds are also somewhat similar to the situation in KH_2PO_4 .

(v) *Location of the hydrogen atoms within the hydrogen bonds*

The difference-Fourier synthesis gave no clue to the position of the hydrogen atoms. They were, however, located from the following considerations:

(a) In each of the hydrogen bonds, O(1)–O(6), O(2)–O(5) and O(3)–O(4) ($x, y, z + 1$) (Fig. 4), we do not know for certain which oxygen atom is the donor and which is the acceptor, resulting therefore in two probable positions for the hydrogen atom. If the structure is fully ordered, only one oxygen atom of each pair can be a donor.

(b) If the choices of the donor oxygen atoms are independent, there are eight possible configurations for the selenite pair in the structure. Two of these give pairs of groups H_3SeO_3^+ and SeO_3^{2-} ; the other six give pairs of groups, H_2SeO_3 and HSeO_3^- . There is infrared evidence to suggest that only the latter pairs are possible (Khanna, Decius & Lippincott, 1965). The six possible configurations are shown schematically in Fig. 6. Of these, (I)–(IV), (II)–(V) and (III)–(VI) are related by the pseudo-inversion operation which interchanges atoms O(1)–O(2), O(3)–O(4), O(5)–O(6) and Se(1)–Se(2).

(c) The possibility of disordered combinations of some or all of these configurations can be ruled out on two grounds:

(i) Disorder allowing both members of a pair would

produce an average structure with an inversion centre which is not found.

(ii) A recent neutron magnetic resonance study of ALS by Soda & Chiba (1969) shows that all protons in the structure occupy ordered sites, the O–H···O bonds being asymmetrical. The only evidence for disorder comes from the neutron diffraction work of Van den Hende & Boutin (1963). They found ‘split hydrogen atoms’ divided between pairs of sites on O(1)–O(6) and O(2)–O(5) bonds and a third, non-bonding hydrogen atom in quite a different position from that suggested

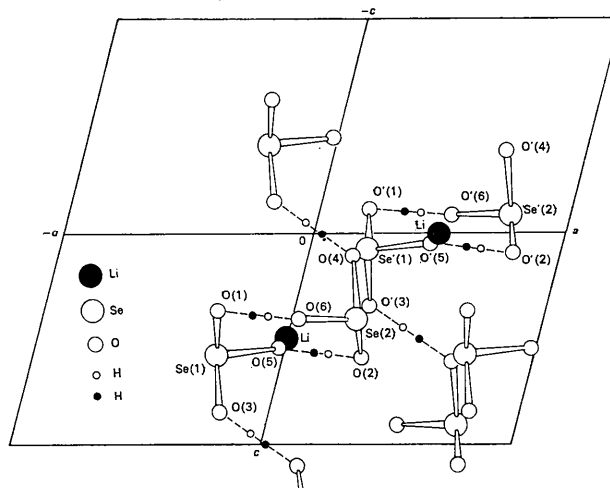


Fig. 4. The contents of the unit cell as viewed down the b axis. The broken lines represent the hydrogen bonds. The dark and open circles on these bonds are the hydrogen atoms proposed by us and Soda & Chiba respectively. The primed atoms have a symmetry $(\frac{1}{2} + x, -y, \frac{1}{2} + z - 1)$.

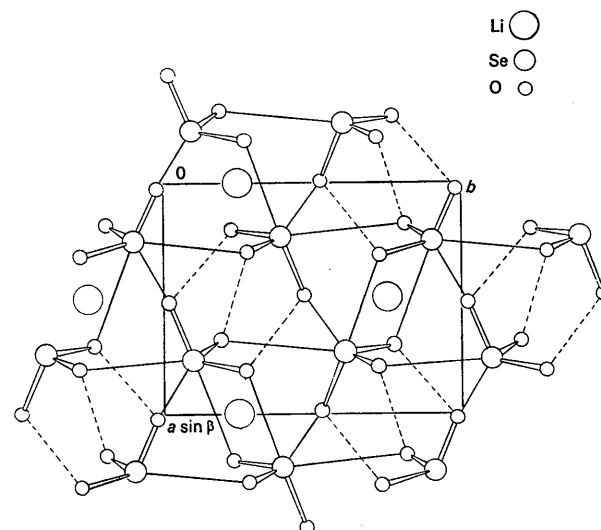


Fig. 5. The structure as viewed down the c axis. The hydrogen bonds in the structure are indicated by broken lines. The full lines from each selenium atom indicate the non-bonded selenium–oxygen contacts.

atom, finds support in other selenite structures in which the hydrogen atoms have been established from diffraction work. For instance, in the structures of both $\text{NaH}_3(\text{SeO}_3)_2$ (Kaplan, Kay & Morosin, 1970) and $\text{KH}_3(\text{SeO}_3)_2$ (Hansen, Hazell & Rasmussen, 1969), the hydrogen atoms are found attached to the oxygen atoms with maximum Se–O length. An additional feature of the selenite groups in these structures is that the O–Se–O angle involving the oxygen atoms with hydrogen atoms attached is much smaller than the O–Se–O angle involving the oxygen atoms with hydrogen atoms not attached. From Table 4(a), it can be seen that this situation also exists in the structure of ALS with the hydrogen positions as proposed above. The criteria of larger bond lengths and smaller bond angles when the hydrogen atoms are attached to the oxygen atoms seem to be valid in many other structures containing inorganic radicals like phosphates (Bacon & Pease, 1955; Kraut, 1961; Sundaralingam, 1966; Sundaralingam & Jensen, 1965; Viswamitra & Reddy, 1970). It is therefore suggested that in structures where the hydrogen atoms are not located, these two criteria can be used with a certain degree of confidence to locate them.

Surroundings of the oxygen atoms

Each oxygen atom of the selenite group, besides being covalently linked to a selenium atom, has three other near neighbours: a lithium ion, a hydrogen-bonded oxygen atom and a distant selenium atom.

The four neighbours are directed towards the corners of a distorted trigonal pyramid, with the distant selenium atom being the apex of the pyramid, and the rest of the atoms including the oxygen atom occupying the base of the pyramid.

Note added in proof: Ferroelectricity and crystal structure: Futama & Pepinsky (1962) found that the optic axial plane is approximately parallel to the (010) plane and the optic axial angle is 68° with the b axis as the acute bisectrix. The optic axes are approximately along the [111] and $[\bar{1}\bar{1}\bar{1}]$ directions. The rotatory powers along the two optic axes were found to be equal in magnitude, but opposite in sign. A dextro-laevo conversion took place with a field of about 1.5 to 2 kV. cm^{-1} applied along the optic axis. The component of this field along the line of intersection of the (010) and (010) planes in the structure is about the same as the component of the coercive field in this direction. This direction, in the structure, coincides closely with the O(3)–O(4) ($x, y, z + 1$) hydrogen bond crossing the pseudo-inversion centre at $(0, \frac{3}{2}, 0)$. If the optical rotation of a particular sign corresponds to a particular state of polarization (Shuvalov & Ivanov, 1964), we can reasonably assume that the structural changes associated with the polarization reversal in ALS are triggered by the movement of the proton along the above hydrogen bond. This movement involves an interchange of H_2SeO_3 group into HSeO_3^- and *vice versa*, thus changing the character of the Se–O bonds. This explanation is in

line with the suggestion of Pepinsky, who ascribed the change in the sign of the optical activity during polarization reversal to the changes in the character of the Se–O bonds of the selenite group.

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The Crystal and Molecular Structure of 3-(2-Diethylammoniumethoxy)-1,2-benzisothiazole Tetrachlorocuprate

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3-(2-Diethylammoniumethoxy)-1,2-benzisothiazole tetrachlorocuprate, $(C_{13}H_{19}N_2OS)_2^+ [CuCl_4]^{2-}$, forms monoclinic crystals ($C2/c$) with cell dimensions $a=25.24$ (1), $b=9.38$ (2), $c=13.58$ (1) Å, $\beta=91.6(3)^\circ$, $Z=4$. The organic ion shows no direct coordinative interactions with copper which forms a tetrachlorocuprate ion having a flattened tetrahedral structure (Cu-Cl=2.259(3), 2.220(2) Å). The organic cation consists of a planar benzisothiazole system with a side chain containing the tetrahedral protonated diethylammonium group. All hydrogen atoms have been located directly from the last ΔF synthesis. Packing is determined mainly by hydrogen-bonding interaction (NH...Cl=3.14 Å) involving the tetrachlorocuprate anion and the organic cation and by a short Cl...S=3.34 Å contact.

Introduction

A series of 1,2-benzisothiazole derivatives has recently been prepared by Vitali, Mossini, Bertaccini & Impicciatore (1968) to study the local anesthetic and antihistaminic properties of the derivatives. Among these products, 3-(2-diethylammoniumethoxy)-1,2-benzisothiazole chloride forms crystalline compounds with $MnCl_2$, $CoCl_2$, $CuCl_2$. This paper reports on the crystal structure of what was originally thought to be a complex between this organic base and copper(II) chloride but which turned out to be the 3-(2-diethylammoniumethoxy)-1,2-benzisothiazole tetrachlorocuprate.

Experimental

3-(2-Diethylammoniumethoxy)-1,2-benzisothiazole tetrachlorocuprate occurs as yellow monoclinic crystals. When the crystals are examined with plane-polarized light looking down the a and b axes, a dichroic effect is observed: the colour ranges from bright yellow to green-yellow when the electric vector vibrates perpendicular to the c axis and when it vibrates parallel to the c axis respectively.

Crystal data, deduced from rotation and Weissenberg photographs (Cu $K\alpha$, $\lambda=1.5418$ Å) are as follows (standard deviations given in parentheses are in units of the last decimal figure):

$$(C_{13}H_{19}N_2OS)_2[CuCl_4], \quad M=708.12, \quad a=25.24(1),$$

$b=9.38$ (2), $c=13.58$ (1) Å, $\beta=91.6$ (3)°, $V=3278$ Å³, $Z=4$, $D_m=1.43$ g.cm⁻³, $D_c=1.41$ g.cm⁻³, $F(000)=1468$, $\mu=53.2$ cm⁻¹ (Cu $K\alpha$). Space group: $C2/c$ (from systematic absences and structure analysis).

Three-dimensional intensity data were determined photometrically on integrated Weissenberg photographs taken up to the eighth and tenth layers along [010] and [001] respectively (multiple-film technique, Cu $K\alpha$). The total number of independent reflexions was 3532 (possible 3914). No absorption correction was used since the samples were small (mean radii: 0.05 and 0.07 mm). After correction for Lorentz and polarization factors, the intensities were placed on the same relative scale (Rollett & Sparks, 1960) and the absolute scale was established by Wilson's (1942) method.

Structure analysis and refinement

The structure was solved with the heavy-atom method starting from the three-dimensional Patterson synthesis, which showed quite clearly that copper was on a twofold axis surrounded by four chlorine atoms that could be arranged planarly as well as tetrahedrally. This last arrangement proved to be the correct one; a three-dimensional Fourier synthesis showed all the other non-hydrogen atoms to be well resolved.

Refinement was then carried out, using all the observed reflexions, by block-diagonal and full-matrix least-squares methods. The minimized function was: