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The Crystal Structure of Sodium Trihydrogen Selenite

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Sodium trihydrogen selenite is ferroelectric below −79 °C. At room temperature this compound crystallizes in the monoclinic space group $P2_1/n$ with two formula units in a unit cell of dimensions $a = 10{\cdot}35$, $b = 4{\cdot}84$, $c = 5{\cdot}84$ Å and $\beta = 89°$. The structure was solved by the interpretation of an unsharpened three-dimensional Patterson synthesis and was refined from photographic X-ray data by the structure-factor least-squares method to an R index of 0·134 for 491 independent observed reflexions. In the structure, the selenite ions have idealized $3m$ (C_{3v}) symmetry. The coordination of oxygen atoms around the sodium ion is a slightly distorted octahedron. The selenite ions are held together by a system of strong hydrogen bonds. These hydrogen bonds form closed loops and may work as switching mechanisms in the ferroelectric phase.

Introduction

Since the discovery of ferroelectricity in sodium trihydrogen selenite, $NaH_3(SeO_3)_2$, below −79 °C by Pepinsky & Vedam (1959), this compound has been subjected to various physical investigations by many workers. Blinc and his co-workers carried out nuclear-magnetic and electron-paramagnetic resonance studies on $NaH_3(SeO_3)_2$ and the deuterated salt $NaD_3(SeO_3)_2$ (Blinc & Pintar, 1961; Blinc, Poberaj, Sehara & Stepinsnik, 1966). The dielectric behaviour of the two compounds as a function of temperature has been reported (Blinc, Jovanovic, Levstik & Prelesnik, 1965; Gavrilova-Podol'skaya, Yudin & Lundin, 1965). The Raman and infrared spectra of sodium trihydrogen selenite have also been analysed (Bazhulin, Mysasnikova & Rakov, 1964; Khanna, Decius & Lippincott, 1965). However, no detailed structural information on it is so far available. Hence it was thought worth while to analyse its structure to understand the structural characteristics that are responsible for the occurrence of ferroelectricity in this crystal. The determination of the structure at room temperature is reported here. Preliminary crystallographic data on this compound have already been published (Vijayan, 1967).

The corresponding lithium salt, $LiH_3(SeO_3)_2$, is a room-temperature ferroelectric and its structure has been solved (Vedam, Okaya & Pepinsky, 1960). However, it is not isomorphous with sodium trihydrogen selenite.

Experimental

Transparent plate-shaped crystals of sodium trihydrogen selenite, elongated along the b axis, were grown by slow evaporation at room temperature of a saturated aqueous solution of selenium dioxide and sodium carbonate in stoichiometric molar ratio. The space group and unit-cell dimensions were determined from oscillation and Weissenberg photographs taken about crystallographic axes with Cu $K\alpha$ radiation. The density of the crystal was measured by flotation in a liquid mixture of methylene iodide and bromoform.

Crystal data

$NaH_3(SeO_3)_2$ F.W. 279·93
Monoclinic $P2_1/n$
$a = 10{\cdot}35 \pm 0{\cdot}02$, $b = 4{\cdot}84 \pm 0{\cdot}02$, $c = 5{\cdot}84 \pm 0{\cdot}02$ Å, $\beta = 89 \pm 1°$. $D_m = 3{\cdot}20 \pm 0{\cdot}01$ g.cm^{-3}, $U = 292{\cdot}37$ Å^3, $Z = 2$, $D_x = 3{\cdot}18$ g.cm^{-3}.
Absorption coefficient for X-rays, ($\lambda = 1{\cdot}5418$) $\mu = 185{\cdot}5$ cm^{-1}.

Intensity data were collected for reciprocal levels hkl, $k = 0$–4, from a nearly cylindrical specimen of mean radius 0·016 cm using nickel-filtered copper radiation. $hk0$ zonal data were also recorded with a specimen of mean radius 0·015 cm. The well known multiple-film equi-inclination Weissenberg method was used for data

Table 1. *Fractional positional coordinates and isotropic temperature factors*

The standard deviations (× 10^5) of the positional coordinates are given in parentheses.

	x	y	z	B
Se	0·16907 (29)	0·11496 (70)	−0·00682 (53)	1·023 Å^2
Na	0·50000 (0)	0·00000 (0)	0·00000 (0)	2·595
O(1)	0·31108 (208)	0·30205 (475)	0·06351 (361)	1·534
O(2)	0·05123 (224)	0·30523 (518)	0·12641 (405)	2·028
O(3)	0·14103 (231)	0·20148 (532)	−0·29748 (417)	2·139

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collection and the intensities were estimated visually. Out of the 715 independent reflexions in the copper sphere, 638 were recorded, of which 491 were in the measurable range. The data were corrected for Lorentz and polarization factors. Absorption corrections were applied assuming the specimens to be perfect cylinders (*International Tables for X-ray Crystallography*, 1959). However, it may be mentioned that the specimens were

Table 2. *Observed and calculated structure factors*

• l	k	
h	Fo	Fc
• 0	0	
2	-2560	-2550
4	-2432	-2236
6	4402	5595
8	-2315	-2336
10	-1351	-1087
12	2794	2140
• 1	0	
1	2218	2763
3	-3840	-4611
7	933	555
9	-2892	-3174
11	942	359
13	787	642
• 2	0	
0	4980	6179
2	-2585	-2675
4	-2440	-2384
6	4215	4573
8	-2485	-2347
10	-580	-822
12	2932	2685
• 3	0	
3	-4580	-5770
5	1301	1133
7	1595	1391
9	-2715	-2727
11	975	940
• 4	0	
0	3162	3986
2	-870	-554
4	-2620	-2642
6	3304	3683
8	-623	-548
10	-930	-925
• 5	0	
1	1017	1177
3	-2409	-2986
5	1223	1339
7	1043	1023
9	-1820	-1902
• 6	0	
0	2269	2662
2	-423	-349
4	-1242	-1371
6	2552	2720
• 7	0	
1	1798	1763
3	-2059	-2207
• -1	0	
1	1978	1855
3	-4675	-4612
5	2930	2688
7	1655	1342
9	-3975	-3951
11	1559	1230
13	609	579
• -2	0	
2	-1941	-2079
4	1282	754
6	4763	4361
8	-2607	-1992
12	2344	1839
• -3	0	
1	2108	2093
3	-4230	-5023
5	2201	1681
7	2335	1681
9	-3404	-2709
11	1686	1381
• -5	0	
3	-3207	-3617
5	1855	1718
9	-2648	-2187
• -6	0	
2	-1658	-1588
4	-580	-491
6	1992	1662
• -7	0	
1	838	576
3	-2731	-2446
• 0	1	
1	1074	1308
2	-3240	-4349
3	-4910	-5755
4	1575	1536
5	1519	1522
6	354	165
7	1031	912
8	-2029	-2392
9	-2716	-2572
10	1665	1412
11	1093	1094
12	363	246
• 0	2	
0	-1429	-1029
1	-3584	-4097
2	905	501
3	332	218
4	911	712
5	3281	4005
6	671	531
7	-2305	-2589
8	706	427
10	333	275
11	1529	1537
12	570	553
• 0	3	
1	-2057	-1575
2	-2687	-2582
3	2750	2059
4	3045	3211
5	-1860	-1804
6	-615	-433
7	-1394	-1287
8	-1388	-1542
9	1115	1113
10	2032	1922
11	-1184	-1036
• 0	4	
0	-2718	-2602
1	-1243	-968
2	2265	1969
4	1757	1536
6	-2137	-2328
7	-1042	-1035
8	1621	1488
9	425	402
• 0	5	
1	-1538	-1337
2	1193	1006
3	1536	1463
4	-1089	-933
5	-1330	-1149
6	-785	-687
• 0	6	
0	-464	-421
1	1674	1750
2	634	510
• -1	1	
0	3120	4511
-1	3210	4219
-2	-906	-774
-3	1786	1653
-4	-1066	-862
-5	-2009	-2170
-6	2860	3453
-7	2363	2354
-8	-732	-758
-9	-733	-688
-10	-462	-529
-11	-1302	-1270
-12	1845	1710
1	-3170	-4569
2	-2052	-1876
3	2148	1848
4	-1389	-1028
5	2007	1815
6	3147	3538
7	-3154	-3590
8	-1355	-1219
9	745	570
10	-442	-486
11	1168	1099
12	2149	1886
• -2	1	
0	2070	1951
-1	1647	1560
-2	1730	1909
-3	-3507	-4163
-4	-1880	-1955
-5	1634	1474
-7	1054	969
-8	1284	1184
-9	-2413	-2582
-10	-1508	-1751
-11	951	946
1	764	580
2	-1397	-1331
3	-3983	-4285
4	2210	1871
5	1619	1370
8	-2170	-1825
9	-2437	-2295
10	1497	1434
11	706	1144
• -3	1	
0	3180	4225
-1	2723	3371
-2	-860	-793
-4	-1050	-917
-5	-3166	-3536
-6	2904	3047
-7	2194	1963
-8	-790	-799
-9	-370	-70
-10	-701	-798
-11	-1654	-1571
1	-2477	-2770
2	-1411	-1141
3	1521	1153
4	-1227	-931
5	2657	2053
6	2977	2827
7	-2127	-1711
8	-1519	-1249
9	404	310
10	-436	-404
11	591	532
• -4	1	
0	-346	-378
-1	1542	1326
-2	1743	1895
-3	-2554	-3053
-4	-1991	-1944
-5	459	520
-6	-684	-476
-7	949	398
-8	1055	1055
-9	-2071	-2070
-10	-714	-676
-11	[illegible]	558
1	606	490
2	-2066	-2019
3	-3046	-2957
4	3104	2965
5	1855	1497
8	-2011	-1512
9	-2290	-1894
10	1969	1625
• -5	1	
0	2149	2679
-1	701	710
-2	-472	-559
-3	410	262
-4	-948	-987
-5	-1632	-1837
-6	1859	1995
-7	1221	1301
-8	-524	-684
1	-1767	-1909
2	-1172	-1155
3	1251	940
5	1070	691
6	2763	2129
7	-1464	-1184
8	-1516	-1194
9	948	732
• -6	1	
-1	973	1106
-2	1151	1455
-3	-1867	-2107
-4	-1485	-1632
-6	247	116
-7	696	866
1	342	285
2	-1816	-1714
3	-2048	-1795
4	1587	1491
5	1347	1103
• -7	1	
0	1681	1707
-1	931	746
-2	-359	-368
-3	685	644
1	-1766	-1507
2	-1120	-1109
3	290	281
• -1	2	
0	-1683	-1392
-1	-998	-577
-2	3284	4069
-3	-2217	-2198
-4	-3364	-4182
-5	1195	886
-8	1921	2534
-9	-985	-816
-10	-1966	-2278
-11	301	272
-12	575	570
1	-445	-369
2	-3693	-3986
3	-2246	-2120
4	4249	4832
5	-745	-490
6	-817	-734
7	-658	-441
8	-1964	-2165
9	-315	-246
10	2606	2684
12	-555	-542
• -2	2	
0	1590	1284
-1	2428	2961
-2	1368	915
-3	-715	-561
-4	675	548
-5	-2869	-2777
-6	1128	770
-7	2733	2893
-8	936	667
-11	-1679	-1665
1	-2998	-3695
2	415	103
4	-1139	-751
5	3096	2778
6	1269	649
7	-2717	-2705
8	863	699
10	-400	-286
11	1967	1694
• -3	2	
0	-1092	-923
-1	1042	708
-2	3152	4053
-3	-757	-429
-4	-2938	-3208
-8	2436	2966
-9	-653	-585
-10	-1849	-2037
1	-1190	-912
2	-3221	-3503
3	-1175	-781
4	3236	3143
5	350	213
6	-920	-802
7	-1238	-852
8	-1821	-1725
9	-814	-566
10	2543	2055
• -4	2	
0	920	1021
-1	2216	2517
-3	602	604
-4	952	-64
-5	-2226	-2330
-6	443	453
-7	2001	2092
1	-2603	-3432
2	1165	556
3	445	412
5	2531	2230
6	597	479
7	-3287	-2832
8	639	554
• -5	2	
0	-663	-681
-1	527	411
-2	2160	2803
-3	-1064	-847
-4	-1625	-1804
-5	-344	-426
-8	1691	1915
2	-1722	-1651
3	-581	-359
4	2786	2364
6	-1295	-990
8	-1544	-1265
• -6	2	
0	719	580
-1	2011	2115
-5	-1691	-2016
1	-2091	-2189
4	309	203
5	1616	1483
• -1	3	
0	-1089	-780
-1	2370	2658
-2	1303	999
-3	-767	-499
-4	1369	1100
-5	-2267	-2559
-6	-1325	-1207
-7	1984	2196
-8	620	520
-10	625	531
1	-3380	-2666
2	2334	2165
3	-550	-221
4	1645	1562
5	2232	2475
6	-1476	-1414
7	-1762	-1827
8	1117	1118
11	1213	1288
• -2	3	
0	-1144	-950
-1	-1899	-1839
-2	2748	3150
-3	1554	1514
-4	-2565	-2650
-5	-2122	-1947
-7	-1075	-1132
-8	2107	2038
-9	1397	1400
-10	-1468	-1539
1	-1160	-967
2	-2035	-2690
3	1995	1723
4	2945	2982
5	-1637	-1377
8	-690	-520
9	980	967
10	1901	1787
• -3	3	
0	-1723	-1955
-1	1735	1953
-2	1278	1173
-3	355	146
-4	918	855
-5	-1572	-1713
-6	-1363	-1395
-7	1631	1780
-8	957	785
-10	676	852
1	-1940	-2605
2	1223	1004
3	421	254
4	1835	1585
5	1863	1761
6	-1107	-1174
7	-2141	-2184
8	1185	1061
9	555	533
10	601	567
• -4	3	
0	[illegible]	-444
-1	-1845	-2125
-2	1957	2420
-3	1250	1295
-4	-1598	-1536
-5	-664	-523
-6	-1012	-1010
-7	1533	[illegible]
-8	920	1132
1	[illegible]	-701
2	-1734	-1746
3	[illegible]	1223
4	2071	1574
5	-1725	-1463
6	-683	-704
7	-415	-255
8	-1157	-1034
• -5	3	
0	-1225	-1270
-1	[illegible]	1553
-2	[illegible]	515
-3	604	363
-4	870	763
-5	-1527	-1704
-6	-519	-745
-7	1163	1350
1	-2007	-2087
2	993	970
4	391	358
5	1600	1445
6	-1227	-1172
• -6	3	
0	-755	-550
-1	-921	-892
-2	1761	1741
-3	1170	1152
-4	-909	-1045
1	-611	-438
2	-991	-957
3	576	650
• -1	4	
0	877	753
-1	-1847	-1985
-2	879	741
-3	2394	2925
-4	-405	-349
-5	-1745	-1305
-7	-1345	-1343
-8	610	521
-9	1761	1980
1	-1911	-1827
2	-804	-636
3	2499	2844
5	-1930	-1857
8	-872	-670
9	1733	1801
• -2	4	
0	-2017	-2759
-1	1180	1206
-2	1519	1548
-3	659	590
-4	1615	1583
-5	-1069	-1042
-6	-2081	-2258
-7	524	492
-8	1192	1157
1	-1055	-1044
2	1947	2076
3	711	633
4	1589	1432
5	778	624
6	-2352	-2273
7	-985	-869
8	1585	1531
• -3	4	
-1	-1623	-2022
-3	1830	2329
-5	-1342	-1290
-6	-327	-77
-7	-1243	-1250
1	-991	-1134
3	2277	2334
4	992	808
5	-2177	-1865
7	-680	-606
8	-584	-563
• -4	4	
0	-1835	-2241
-1	367	366
-2	1174	1169
-4	1235	1383
-5	-890	-897
-6	-1577	-1682
-7	507	511
1	-394	-429
2	1547	1615
3	483	401
4	1082	861
5	303	267
6	-1631	-1788
• -5	4	
-1	-1515	-1625
-2	377	404
-3	1721	1525
-4	-731	-684
1	-844	-765
2	-837	-782
3	1563	1765
4	549	692

not perfectly cylindrical and this is a limiting factor for the accuracy of thermal parameters derived from this analysis.

Structure analysis

The multiplicity of general positions in the space group is fourfold, and as there are only two formula units in the elementary cell, the sodium ion and one of the hydrogen atoms should occupy twofold special positions at the inversion centres. The rest of the atoms are at general positions.

The structure was solved by the direct interpretation of a three-dimensional unsharpened Patterson function. The atomic coordinates thus derived were confirmed by a selenium and sodium phased three-dimensional Fourier synthesis and projection minimum maps. The positional and individual isotropic temperature parameters were refined in several cycles of structure-factor least-squares calculations to an R index, defined as

$$\Sigma\, \| F_o| - |F_c\| / \Sigma\, |F_o|\,,$$

of 0·134 for all the observed reflexions. These refinement cycles were done on the Elliott 803-B Computer at the Hindustan Aeronautics Ltd., Bangalore, using a block-diagonal SFLS program devised by Dr G.A. Mair of the Royal Institution, London. The quantity minimized in the program is $\Sigma\, w|kF_o - F_c|^2$. In the final cycle, all the indicated shifts were less than half the corresponding standard deviations, the maximum and the average shifts being 0·38σ and 0·13σ respectively. The weighting scheme employed in these calculations was of the form

$$\sqrt{w} = 1 \Big/ \left\{ 1 + \left(\frac{kF_o - b}{a} \right)^2 \right\}^{1/2}$$

with $a = 32$, $b = 20$ for $k = \frac{1}{2}$. The atomic scattering factors used were those given by Cromer & Waber (1965).

The final positional and isotropic thermal parameters of the atoms in the asymmetric part of the unit cell are given in Table 1. Table 2 lists the observed and calculated structure factors (unobservables excluded). Superposed sections through atomic centres of the final electron density distribution are shown in Fig. 1. A final $F_o - F_c$ synthesis was computed, but the positions of the hydrogen atoms could not be located.

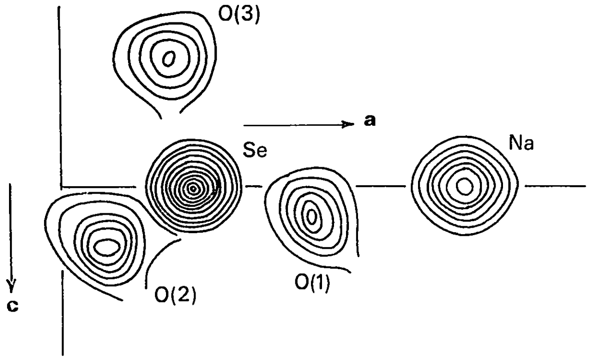

Fig. 1. Superposed sections of the final electron density distribution through atomic centres parallel to (010). The contours start at 2 e.Å^{-3} and are at intervals 2 e.Å^{-3} for oxygen, 3 e.Å^{-3} for sodium and 10 e.Å^{-3} for selenium atoms.

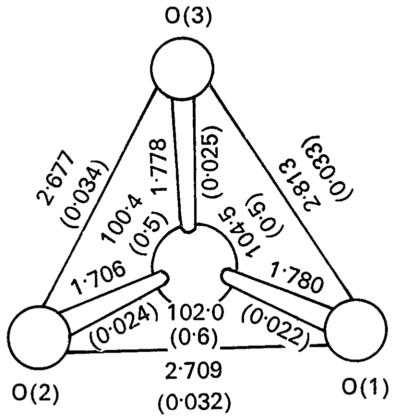

Fig. 2. Dimensions of the selenite ion. Standard deviations are given in parentheses.

Discussion

Dimensions of the SeO_3^{2-} *ion*

The dimensions of the selenite ion in the structure are shown in Fig. 2.

The pyramidal selenite ion has an idealized $3m$ (C_{3v}) symmetry. However, the departure from this symmetry is statistically significant. The Raman spectrum of this compound also shows that, in the crystalline state, the symmetry of SeO_3^{2-} ion is decreased from $3m$ (Bazhulin *et al.*, 1964). Two Se–O bonds in the ion are almost equal in length whereas the length of the third is significantly different ($\Delta > 2\sigma$) from the other two. The O–Se–O angles are unequal though comparable in magnitude. The selenium atom is 0·77 Å away from the plane of the three oxygen atoms. The normal to this plane makes an angle of 12° with the crystallographic b axis.

It may be mentioned that Vedam *et al.* (1960) have quoted the dimensions of the selenite ion in sodium trihydrogen selenite from a private communication. But neither the details nor the other results of this work have been published so far. However, the values quoted compare well with those obtained from the present analysis.

Coordination around the Na^+ *ion*

The sodium ion in the structure occupies a centre of symmetry at $\frac{1}{2},0,0$. The coordination polyhedron of selenite oxygen atoms around this ion is a slightly distorted octahedron. The dimensions of this octahedron are listed in Table 3 and the environment of the sodium ion, as seen down the b axis, is shown in Fig. 3.

Table 3. *Dimensions of the coordination octahedron around the* Na^+ *ion*

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

Na——O(1)*A*	2·464 Å	(×2)
Na——O(2)*B*	2·427	(×2)
Na——O(3)*C*	2·383	(×2)
O(1)*A*–O(3)*C*	3·524	(×2)
O(3)*C*–O(2)*E*	3·542	(×2)
O(2)*E*–O(1)*A*	3·570	(×2)
O(1)*A*–O(2)*B*	3·344	(×2)
O(2)*B*–O(3)*C*	3·254	(×2)
O(3)*C*–O(1)*D*	3·329	(×2)
O(1)*A*–Na–O(2)*B*	86·3°	(×2)
O(2)*B*–Na–O(3)*C*	85·2	(×2)
O(3)*C*–Na–O(1)*D*	86·7	(×2)
O(2)*B*–Na–O(1)*D*	93·8	(×2)
O(1)*D*–Na–O(3)*F*	93·3	(×2)
O(3)*F*–Na–O(2)*B*	94·9	(×2)

Crystal structure and hydrogen bonding

The contents of the unit cell as viewed in the [010] direction are shown in Fig. 4. Fig. 5 shows a view of the structure projected on the (001) plane.

The selenite ions in the structure are held together by a three-dimensional network of strong hydrogen bonds which are indicated by broken lines in Fig. 5. All the oxygen atoms in the structure take part in hydrogen bond formation either as donors or as acceptors. The two crystallographically non-equivalent hydrogen-bonded O···O distances and the relevant angles are given in Table 4. These bonds may be considered strong judging by the short O···O distances. It may be mentioned that hydrogen bonds of comparable lengths are found in other hydrogen-bonded ferroelectrics like potassium dihydrogen phosphate and lithium trihydrogen selenite (Frazer & Pepinsky, 1953; Bacon & Pease, 1953, 1955; Vedam *et al.*, 1960). The hydrogen bonds involving O(1)*A*, O(3)*B* and O(2)*A*, O(2)*C* are inclined to the crystallographic *b* axis at 40° and 42° respectively. The oxygen atoms O(2)*A* and O(2)*C* are related by a centre of inversion and hence the bond connecting them should be symmetrical. The length of this bond is, however, greater than that normally found for symmetric hydrogen bonds.

Table 4. *Hydrogen bond distances and relevant angles*

$A\ \ x, y, z$
$B\ \ \frac{1}{2}-x, \frac{1}{2}+y, (\frac{1}{2}-z)-1$
$C\ \ -x, -y+1, -z$

O(1)*A*···O(3)*B*	2·524 Å
O(2)*A*···O(2)*C*	2·629
Se*A*–O(1)*A*···O(3)*B*	113·7°
Se*B*–O(3)*B*···O(1)*A*	112·0
Se*A*–O(2)*A*···O(2)*C* Se*C*–O(2)*C*···O(2)*A*	115·0

Khanna *et al.* (1965) have explained the infrared spectrum of sodium trihydrogen selenite in the paraelectric phase assuming an even proton-density distribution along the hydrogen bond length. This might be due, as observed in potassium dihydrogen phosphate (Bacon & Pease, 1953, 1955), to a symmetric double minimum potential or a broad single minimum potential for the proton. The former situation may be described physically as resulting from a statistical disorder of the proton in the structure whereas the latter as a result of a high thermal-vibration amplitude for the proton. This probably explains the comparatively large length of the symmetrical hydrogen bond between O(2)*A* and O(2)*C*.

Dielectric studies show that the ferroelectric transition point is altered from −79 °C for $NaH_3(SeO_3)_2$ to −29 °C for $NaD_3(SeO_3)_2$ (Blinc *et al.*, 1965; Gavrilova-Podol'skaya *et al.*, 1965). This result indicates that hydrogen bonds play a finite role in the ferroelectric

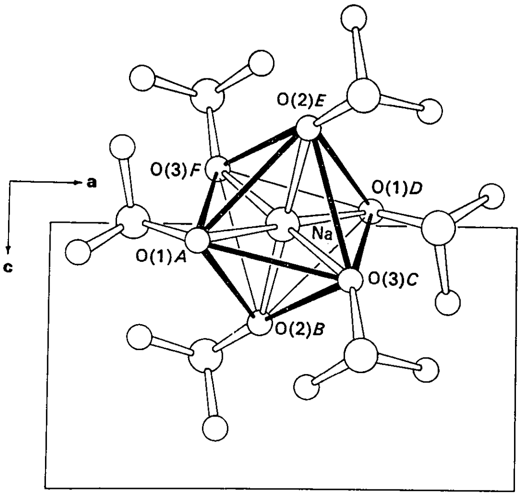

Fig. 3. Environment of the sodium ion as seen down the *b* axis.

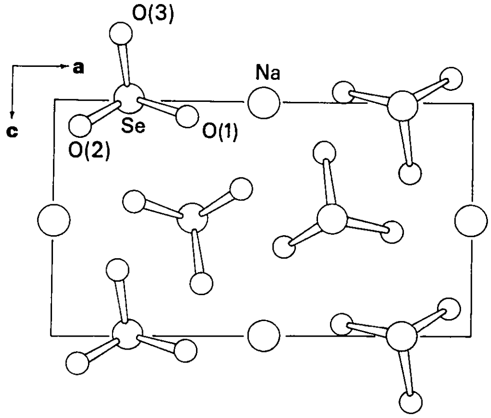

Fig. 4. The contents of the unit cell as viewed in the [010] direction.

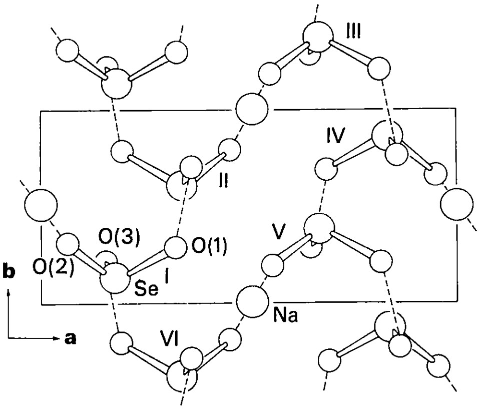

Fig. 5. A view of the structure projected onto the (001) plane. Hydrogen bonds are indicated by broken lines. The code of symmetry-related positions is as follows:

I x, y, z
II $\frac{1}{2}-x, \frac{1}{2}+y, (\frac{1}{2}-z)-1$
III $\frac{1}{2}+x, (\frac{1}{2}-y)+1, (\frac{1}{2}+z)-1$
IV $-x+1, -y+1, -z-1$
V $\frac{1}{2}+x, \frac{1}{2}-y, (\frac{1}{2}+z)-1$
VI $\frac{1}{2}-x, (\frac{1}{2}-y)-1, (\frac{1}{2}-z)-1$.

transition in this compound. In the ferroelectric phase the centre of symmetry vanishes and consequently, the selenite ions related by it become non-equivalent. The infrared studies quoted above show that the transition to the ferroelectric phase is accompanied by an ordering of the protons in the structure. The disposition of hydrogen bonds in the structure is such that they form closed loops (Fig. 5). All these results suggest that the system of hydrogen bonds works, as in the case of potassium dihydrogen phosphate, as a switching mechanism in the ferroelectric phase, *i.e.* the roles of the donor and acceptor oxygen atoms are reversed when the polarity of the applied electric field is reversed.

All the oxygen atoms in the structure are coordinated to one or another of the sodium ions. The coordination octahedron possesses a centre of symmetry with the sodium ion at the centre. In the ferroelectric phase, the centre of symmetry vanishes and the sodium ion may occupy an asymmetric site giving rise to a net dipole moment. Alternatively, in the ferroelectric phase the oxygen octahedron may undergo reversible distortions in an applied electric field. It is probable that these distortions contribute substantially to the ferroelectric behaviour of the crystal. However, definite conclusions can be drawn only after the crystal structure is analysed in the ferroelectric phase also.

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