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On the Crystal Structure of Potassium Trihydrogen Selenite, $KH_3(SeO_3)_2$, and its Relation to the Dielectric Properties

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An X-ray investigation of potassium trihydrogen selenite has been carried out at room temperature. The orthorhombic cell (space group *Pbcn*) with dimensions $a=16.152$ Å, $b=6.249$ Å, $c=6.307$ Å contains four formula units. The structure was solved by Patterson and Fourier methods from 653 significant reflexions collected on an automatic diffractometer and corrected for absorption. Refinement of coordinates of all atoms and of anisotropic temperature factors for K, Se, and O was carried out by the method of least squares to a final R-value of 3.9 %.

The SeO_3 system has three different Se–O distances: 1.669 Å, 1.707 Å, and 1.730 Å. One hydrogen atom is probably statistically distributed with one half on each of two symmetry related sites. Dielectric anomalies at lower temperature are probably due to an ordering of these hydrogen atoms.

$KH_3(SeO_3)_2$ and other alkali selenites have been known since 1875.[1] Pepinsky and Vedam [2] found in 1959 that $LiH_3(SeO_3)_2$ showed ferroelectric activity and the structure of this compound as well as that of the sodium compound, also shown to be ferroelectric, was determined.[2,3] The properties of the cesium compound have also been investigated.[4] No investigations of $KH_3(SeO_3)_2$ had been reported till recently when an account of its dielectric anomalies and twin structure was published.[5] It appears from this that a phase-transformation takes place at −61.6°C, so the structure reported in this paper is that of the high-temperature form of $KH_3(SeO_3)_2$.

EXPERIMENTAL

The crystals were prepared according to Ref. 1 from aqueous solutions of 0.02 mol K_2CO_3 and 0.08 mol SeO_2 mixed at room temperature and left to evaporate. Well shaped crystals developed, some of them very big. The selenium content was determined by chemical analysis:[6] Found 53.90; calc. for $KH_3(SeO_3)_2$: 53.35.

The unit cell and space group were determined from Weissenberg and precession photographs using Cu*Kα* and Mo*Kα* radiations. Intensities were obtained from a crystal of dimensions 0.1 × 0.1 × 0.3 mm^3 on a linear diffractometer of the Arndt-Phillips type[7] with Mo-radiation. Balanced filters and pulse height discrimination were used. All reflexions in a hemisphere with $\sin\theta/\lambda < 0.7$ were recorded giving four symmetry related measurements of each of the 940 independent structure factors. All reflexions for which $F^2 < 2\sigma(F^2)$ were left out, leaving 653 significant reflexions. The data were corrected for absorption effects according to Wells.[8] No correction for extinction was applied.

STRUCTURE DETERMINATION

The position of the selenium atom was found from the three dimensional Patterson function and a Fourier synthesis calculated with the signs from the selenium coordinates gave the positions of the oxygen and potassium atoms. The structure was refined by means of a full matrix least squares program, ORFLS.[9] At a value of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.10$ anisotropic temperature factor parameters were introduced, and the R-value dropped to 0.048. At this point a difference Fourier synthesis was calculated; this showed a small peak at a position 1 Å from an oxygen atom in the direction of another oxygen atom located only 2.6 Å from the first one. This was taken to be a hydrogen atom. Another hydrogen atom was expected between two oxygen atoms which are 2.57 Å apart and related by a twofold axis. A hydrogen bond of this length is not expected to be symmetrical, so one hydrogen atom is probably statistically distributed on two symmetry related positions approximately 1 Å from oxygen. Conclusive evidence for this could not be found in the difference map, but inclusion of both hydrogen atoms in the structure factor calculation brought the R-value down to 0.046 with improvement particularly of the reflexions with low $\sin\theta$ values. The coordinates of the hydrogen atoms changed little when allowed to refine indicating that the positions of these atoms are probably correct. The final R-value was 0.039.

The function minimised in the least squares refinement is $\sum w(|F_o| - |F_c|)^2 = \sum w\Delta^2$ where w is the weight given to each reflexion; this should be $w = 1/(\sigma(F))^2$. The standard deviation $\sigma(F^2)_{\text{count}}$ was found not to account for all errors but a term proportional to the intensity had to be added: $\sigma(F^2) = \sigma(F^2)_{\text{count}} + A \cdot F^2$; the constant A $(= 0.045)$ was varied so that $\sigma(F) = \sqrt{\sigma(F^2) + F^2} - F$ gave weights for which the average of $w \cdot \Delta^2$ was nearly independent of the size of F.

CRYSTAL DATA

Crystal system: orthorhombic.
Unit cell: $a = 16.152 \pm 0.005$ Å, $b = 6.249 \pm 0.002$ Å, $c = 6.307 \pm 0.002$ Å. $U = 636.6$ Å^3.

These lattice constants were obtained by least squares analysis of Guinier powder data. The errors are estimated standard deviations as given by this method. No measurement of the density was made, but a calculated density of 3.05 g/cm^3 assuming $Z = 4$ is in accordance with densities of most alkali selenites and selenates.

Systematic absences: $hk0$ for $h + k \neq 2n$
$0kl$ for $k \neq 2n$
$h0l$ for $l \neq 2n$

Space group: *Pbcn* (No. 60).

Final atomic parameters are given in Table 1, bond lengths and angles in Table 2, and Table 3 is a list of observed and calculated structure factors. The scattering factors used were taken from *International Tables*, Vol. III, Table A for H, O, and K^+, Table B for Se.

DISCUSSION

The structure contains only one sort of selenite ion, selenium occupying a general, 8-fold position. The formula of the anion can be written as $H_{1\frac{1}{2}}SeO_3^{-\frac{1}{2}}$, one hydrogen atom being statistically distributed on two sym-

Table 1. Final atomic parameters. Coordinates with standard deviations $\times 10^5$ in parentheses.

	x	σx	y	σy	z	σz
Se	0.15153	(4)	0.18806	(9)	0.21329	(9)
K	0.50000	(0)	0.18848	(32)	0.25000	(0)
O_1	0.11114	(26)	0.38798	(67)	0.07151	(66)
O_2	0.06727	(26)	0.11189	(70)	0.35833	(68)
O_3	0.20691	(29)	0.32281	(75)	0.40645	(75)
H_1	0.1830	(500)	0.4415	(1350)	0.4735	(1225)
H_2	0.0135	(1000)	0.1164	(2600)	0.2700	(2700)

Temperature factor parameters, u_{ij}, in $Å^2 \times 10^{-4}$.

	u_{11}	σu_{11}	u_{22}	σu_{22}	u_{33}	σu_{33}	u_{12}	σu_{12}	u_{13}	σu_{13}	u_{23}	σu_{23}
Se	161	(3)	243	(3)	239	(3)	23	(2)	10	(2)	8	(2)
K	256	(10)	284	(10)	246	(9)	0	(0)	48	(7)	0	(0)
O_1	245	(24)	299	(23)	268	(21)	24	(19)	−77	(18)	65	(17)
O_2	225	(22)	390	(25)	235	(20)	−43	(19)	19	(17)	34	(18)
O_3	243	(23)	429	(27)	366	(25)	16	(21)	−130	(20)	−118	(22)

Table 2. Interatomic distances and angles. Standard deviations in parentheses.

	Å	$Å \times 10^{-3}$		Å		Å
Se—O_1	1.669	(4)	Se—O_3'	2.996	K—O_2	2.973
Se—O_2	1.707	(4)	Se—O_2	3.221	K—O_1	2.831
Se—O_3	1.730	(5)	Se—O_3''	3.453	K—O_1	2.750
O_2—H_2	1.032	(165)	O_1—O_3	2.597	K—O_2	2.941
O_3—H_1	0.937	(83)	O_2—O_2	2.567		

Angles	Degrees	
O_1—Se—O_2	100.61	(.21)
O_1—Se—O_3	102.41	(.21)
O_2—Se—O_3	99.82	(.22)
Se—O_2—H	111.96	
Se—O_3—H	119.34	

Table 3. List of observed and calculated structure factors, 10 × absolute scale.

h	k	l	Fobs	Fcal
4	0	0	1534	-1544
6	0	0	1727	1795
8	0	0	554	588
10	0	0	940	-932
12	0	0	630	655
14	0	0	1202	1236
16	0	0	622	-641
20	0	0	604	855
1	1	0	283	300
3	1	0	523	-530
5	1	0	241	-247
7	1	0	321	344
9	1	0	1042	-1009
11	1	0	448	-436
13	1	0	635	630
17	1	0	349	-356
0	2	0	1828	-2050
2	2	0	384	380
4	2	0	539	565
6	2	0	1448	-1487
8	2	0	442	-448
10	2	0	705	717
12	2	0	480	-480
14	2	0	778	-776
16	2	0	518	531
20	2	0	542	-508
1	3	0	480	-511
3	3	0	1483	1579
5	3	0	454	456
7	3	0	1045	-1075
9	3	0	1362	1380
11	3	0	795	799
13	3	0	930	-922
15	3	0	262	261
17	3	0	694	709
19	3	0	247	-239
0	4	0	479	-473
2	4	0	141	-147
4	4	0	162	187
6	4	0	261	266
1	5	0	364	366
3	5	0	1280	-1311
5	5	0	309	-311
7	5	0	893	904
9	5	0	635	-642
11	5	0	530	-521
13	5	0	466	461
15	5	0	333	-351
17	5	0	489	-517
0	6	0	771	755
2	6	0	191	-178
4	6	0	288	-278
6	6	0	653	657
8	6	0	245	226
10	6	0	368	-369
12	6	0	211	199
14	6	0	418	420
16	6	0	298	-268
3	7	0	363	345
7	7	0	144	-179
9	7	0	179	198
11	7	0	137	115
0	8	0	594	-585
4	8	0	220	235
6	8	0	533	-550
10	8	0	285	319
1	1	1	1095	-1118
2	1	1	389	-390
3	1	1	2432	2654
4	1	1	58	58
5	1	1	408	393
6	1	1	869	815
7	1	1	851	-821
8	1	1	483	-449
9	1	1	1312	1250
11	1	1	982	938
13	1	1	890	-879
14	1	1	244	-224
15	1	1	272	245
17	1	1	868	880
18	1	1	226	153
19	1	1	410	-427
0	2	1	1667	-1774
1	2	1	195	-205
2	2	1	291	-277
3	2	1	686	644
4	2	1	655	656
5	2	1	347	339
6	2	1	1195	-1188
7	2	1	420	-402
8	2	1	296	-310
9	2	1	165	-157
10	2	1	1009	993
11	2	1	126	111
12	2	1	684	-665
13	2	1	126	100
14	2	1	818	-797
15	2	1	257	-291
16	2	1	337	348
19	2	1	221	193
20	2	1	443	-474
1	3	1	86	-76
3	3	1	803	-810
5	3	1	107	105
6	3	1	121	137
7	3	1	508	502
8	3	1	214	222
9	3	1	453	-440
10	3	1	201	-205
11	3	1	306	-310
12	3	1	251	-247
13	3	1	300	300
15	3	1	184	-191
17	3	1	373	-367
0	4	1	1582	1606
1	4	1	483	475
2	4	1	81	-79
3	4	1	85	80
4	4	1	815	-826
5	4	1	273	-263
6	4	1	1358	1363
7	4	1	96	95
8	4	1	631	613
9	4	1	109	110
10	4	1	864	-865
12	4	1	617	607
14	4	1	689	680
15	4	1	223	204
16	4	1	485	-489
19	4	1	177	-86
20	4	1	564	590
1	5	1	210	225
2	5	1	103	95
3	5	1	492	-497
6	5	1	171	-170
7	5	1	218	205
8	5	1	120	98
9	5	1	240	-241
11	5	1	252	-252
13	5	1	181	199
17	5	1	222	-235
0	6	1	758	-740
1	6	1	234	-232
2	6	1	115	103
3	6	1	159	-141
4	6	1	383	383
5	6	1	109	119
6	6	1	666	-648
8	6	1	317	-298
10	6	1	353	354
12	6	1	311	-291
14	6	1	292	-288
16	6	1	236	277
1	7	1	169	-166
3	7	1	735	724
7	7	1	399	-407
8	7	1	182	-176
9	7	1	400	409
11	7	1	347	346
12	7	1	215	165
13	7	1	274	-312
3	0	2	468	-439
4	0	2	756	708
5	0	2	1424	1345
6	0	2	1851	-1834
7	0	2	118	100
8	0	2	634	-620
9	0	2	913	-859
10	0	2	1232	1208
11	0	2	362	345
12	0	2	902	-881
13	0	2	193	-186
14	0	2	1017	-1014
15	0	2	321	-313
16	0	2	602	586
17	0	2	266	274
19	0	2	205	243
20	0	2	665	-677
1	1	2	479	-484
2	1	2	91	71
3	1	2	989	988
4	1	2	756	724
5	1	2	264	246
7	1	2	352	-338
8	1	2	348	-326
9	1	2	393	364
11	1	2	342	321
12	1	2	155	169
13	1	2	247	-234
14	1	2	156	-144
15	1	2	97	96
16	1	2	133	-138
17	1	2	302	288
18	1	2	220	228
19	1	2	178	-150
0	2	2	1406	1473
1	2	2	276	292
3	2	2	309	298
4	2	2	633	-635
5	2	2	512	-515
6	2	2	1157	1153
7	2	2	184	192
8	2	2	510	498
9	2	2	408	395
10	2	2	696	-682
11	2	2	481	-474
12	2	2	529	525
14	2	2	587	564
15	2	2	283	287
16	2	2	394	-387
19	2	2	123	-125
20	2	2	390	450
1	3	2	553	551
2	3	2	525	531
3	3	2	1620	-1653
4	3	2	739	-732
5	3	2	252	-256
6	3	2	147	-143
7	3	2	720	722
8	3	2	438	447
9	3	2	843	-829
11	3	2	680	-665
12	3	2	388	-387
13	3	2	561	565
14	3	2	227	226
15	3	2	208	-216
16	3	2	251	236
17	3	2	664	-663
18	3	2	360	-366
19	3	2	253	292
0	4	2	124	-110
4	4	2	91	107
5	4	2	190	-185
7	4	2	165	-162
9	4	2	101	97
10	4	2	96	-59
11	4	2	146	162
1	5	2	244	-235
2	5	2	651	-648
3	5	2	1057	1062
4	5	2	202	191
6	5	2	180	178
7	5	2	535	-527
8	5	2	225	-235
9	5	2	685	684
11	5	2	470	466
12	5	2	300	292
13	5	2	463	-472
14	5	2	159	-126
15	5	2	173	182
17	5	2	491	532
0	6	2	641	-639
1	6	2	148	-142
3	6	2	110	-130
4	6	2	322	320
5	6	2	249	223
6	6	2	509	-504
8	6	2	267	-263
9	6	2	204	-192
10	6	2	332	324
11	6	2	258	262
12	6	2	203	-215
14	6	2	313	-299
15	6	2	186	-164
16	6	2	218	181
2	7	2	121	117
3	7	2	290	-285
7	7	2	140	132
9	7	2	210	-204
0	8	2	544	540
1	8	2	181	142
4	8	2	239	-260
6	8	2	411	415
2	1	3	724	764
3	1	3	1237	-1277
4	1	3	757	-769
5	1	3	302	-300
6	1	3	608	-596
7	1	3	913	917
8	1	3	893	880
9	1	3	1098	-1080
11	1	3	638	-644
12	1	3	556	-538
13	1	3	636	642
14	1	3	411	416
15	1	3	343	-337
16	1	3	216	205
17	1	3	582	-605
18	1	3	437	-464
19	1	3	172	155
0	2	3	1409	1508
1	2	3	551	573
2	2	3	222	-220
4	2	3	506	-529
5	2	3	823	-848
6	2	3	853	866
7	2	3	140	136
8	2	3	506	510
9	2	3	534	544
10	2	3	221	-211
11	2	3	248	-239
12	2	3	209	205
14	2	3	409	405
15	2	3	394	392
16	2	3	274	-315
17	2	3	179	-200
19	2	3	226	-229
20	2	3	370	429
1	3	3	312	-326
2	3	3	460	-481
3	3	3	560	579
5	3	3	295	309
6	3	3	97	111
7	3	3	222	-229
8	3	3	234	-234
9	3	3	243	273
10	3	3	92	106
11	3	3	174	191
12	3	3	281	279
13	3	3	167	-158
14	3	3	109	-104
17	3	3	172	146
19	3	3	143	-118
0	4	3	1236	-1278
1	4	3	646	-672
2	4	3	163	159
3	4	3	240	-242
4	4	3	334	345
5	4	3	637	659
6	4	3	921	-943
7	4	3	248	-253
8	4	3	281	-278
9	4	3	430	-443
10	4	3	450	463
11	4	3	475	484
12	4	3	370	-379
14	4	3	591	-619
15	4	3	432	-458
16	4	3	338	332
17	4	3	143	149
2	5	3	173	-163
3	5	3	263	266
4	5	3	162	147
6	5	3	151	161
7	5	3	207	-230
8	5	3	221	-218
9	5	3	220	230
11	5	3	187	169
12	5	3	174	149
13	5	3	130	-149
0	6	3	546	538
1	6	3	287	285
3	6	3	120	137
4	6	3	122	-134
5	6	3	257	-266
6	6	3	469	463
7	6	3	152	151
9	6	3	183	192
10	6	3	289	-283
11	6	3	311	-289
12	6	3	221	239
14	6	3	313	322
15	6	3	211	220
1	7	3	207	182
2	7	3	376	370
3	7	3	492	-490
4	7	3	158	-155
5	7	3	191	-201
6	7	3	152	-177
7	7	3	291	270
8	7	3	295	280
9	7	3	269	-298
11	7	3	249	-232
12	7	3	249	-257
4	0	4	391	-355
5	0	4	1141	-1086
6	0	4	1250	1193
7	0	4	623	611
8	0	4	633	608
9	0	4	685	669
10	0	4	510	-489
11	0	4	715	-690
12	0	4	527	505
13	0	4	163	-191
14	0	4	414	412
15	0	4	760	757
16	0	4	303	-283
17	0	4	177	-195
19	0	4	393	-411
2	1	4	470	487
3	1	4	523	-527
4	1	4	215	-219
6	1	4	449	-444
7	1	4	231	233
8	1	4	312	314
9	1	4	116	-106
11	1	4	193	-195
12	1	4	193	-187
14	1	4	165	172
15	1	4	143	-146
17	1	4	237	-236
18	1	4	201	-195
0	2	4	736	-774
1	2	4	691	-735
2	2	4	101	-106
3	2	4	190	-200
4	2	4	288	289
5	2	4	671	688
6	2	4	614	-609
7	2	4	270	-265
8	2	4	268	-284
9	2	4	423	-413
10	2	4	336	323
11	2	4	405	406
12	2	4	368	-355
13	2	4	116	118
14	2	4	316	-326
15	2	4	447	-434
16	2	4	145	154
17	2	4	141	151
1	3	4	109	-109
2	3	4	812	-837
3	3	4	923	952
4	3	4	426	439
5	3	4	74	65
6	3	4	605	616
7	3	4	517	-511
8	3	4	721	-723
9	3	4	433	424
11	3	4	405	403
12	3	4	538	530
13	3	4	240	-243
14	3	4	362	-376
15	3	4	159	194
17	3	4	450	445
18	3	4	346	377
0	4	4	201	193
1	4	4	101	98
3	4	4	159	143
6	4	4	90	-71
1	5	4	168	166
2	5	4	409	492
3	5	4	613	-607
4	5	4	331	-324
5	5	4	105	-110
6	5	4	261	-268
7	5	4	148	150
8	5	4	588	580
9	5	4	444	-444
10	5	4	178	-138
11	5	4	284	-306
12	5	4	493	-486
13	5	4	240	253
14	5	4	283	295
0	6	4	370	371
1	6	4	349	364
3	6	4	143	135
4	6	4	123	-158
5	6	4	335	-346
6	6	4	262	264
7	6	4	197	102
8	6	4	122	150
9	6	4	242	223
10	6	4	172	-160
11	6	4	236	-192
12	6	4	155	175
3	7	4	195	165
4	7	4	162	102
8	7	4	162	-153
0	8	4	339	-330
1	8	4	308	-295
2	1	5	890	-954
3	1	5	732	756
4	1	5	682	698
5	1	5	187	180
6	1	5	344	338
7	1	5	214	-239
8	1	5	760	-747
9	1	5	323	309
10	1	5	97	84
11	1	5	298	279
12	1	5	726	690
14	1	5	367	-359
15	1	5	226	214
16	1	5	309	-308
17	1	5	313	299
0	2	5	200	-201
1	2	5	536	-557
3	2	5	360	-389
5	2	5	664	673
6	2	5	507	-519
7	2	5	164	-136
8	2	5	235	-250
9	2	5	480	-475
10	2	5	146	134
11	2	5	476	466
12	2	5	223	-222
14	2	5	229	-216
15	2	5	354	-354
16	2	5	155	154
17	2	5	144	143
2	3	5	385	388
3	3	5	186	-183
4	3	5	229	-229
6	3	5	214	-213
7	3	5	83	-65
8	3	5	254	240
9	3	5	289	-277
11	3	5	120	-114
12	3	5	187	-165
13	3	5	143	139
0	4	5	563	559
1	4	5	527	533
2	4	5	80	101
3	4	5	240	247
4	4	5	128	-109
5	4	5	723	-728
6	4	5	406	394
7	4	5	266	268
8	4	5	234	218
9	4	5	542	543
10	4	5	160	-148
11	4	5	555	-555
12	4	5	238	249
14	4	5	270	264
15	4	5	463	446
2	5	5	255	251
3	5	5	168	-158
4	5	5	171	-169
8	5	5	160	168
11	5	5	125	-61
12	5	5	193	-192
0	6	5	345	-356
1	6	5	265	-261
2	6	5	103	-83
4	6	5	105	96
5	6	5	371	351
6	6	5	187	-162
7	6	5	169	-161
8	6	5	150	-106
9	6	5	294	-250
11	6	5	235	260
2	7	5	386	-391
3	7	5	211	219
4	7	5	231	240
3	0	6	305	-373
5	0	6	827	788
6	0	6	343	-340
7	0	6	294	-281
8	0	6	286	-269
9	0	6	565	-548
10	0	6	218	-179
11	0	6	626	508
12	0	6	130	-106
13	0	6	195	176
3	1	6	67	85
4	1	6	108	130
6	1	6	117	131
8	1	6	313	-294
9	1	6	168	141
10	1	6	146	116
11	1	6	183	[illegible]
12	1	6	204	279
14	1	6	159	-140
0	2	6	280	310
1	2	6	462	506
2	2	6	75	52
3	2	6	142	147
4	2	6	82	80
5	2	6	570	-563
6	2	6	229	224
7	2	6	214	211
9	2	6	409	386
11	2	6	395	-368
12	2	6	122	117
14	2	6	174	166
1	3	6	157	-156
2	3	6	658	651
3	3	6	218	-216
4	3	6	376	-369
5	3	6	156	-151
6	3	6	361	-348
8	3	6	632	610
9	3	6	256	-248
10	3	6	146	-126
11	3	6	171	-157
12	3	6	533	-502
1	4	6	76	63
3	4	6	95	75
2	5	6	492	-468
3	5	6	201	201
4	5	6	346	351
5	5	6	201	202
6	5	6	307	305
8	5	6	455	-436
0	6	6	152	-138
1	6	6	284	-263
5	6	6	318	291
4	1	7	262	-293
5	1	7	65	-91
6	1	7	381	-379
7	1	7	207	-211
8	1	7	332	313
9	1	7	90	-86
11	1	7	105	-91
12	1	7	468	-461
2	2	7	127	147
3	2	7	130	135
4	2	7	94	97
5	2	7	332	-347
7	2	7	251	254
9	2	7	230	245
11	2	7	396	-388
12	2	7	148	101
1	3	7	70	60
2	3	7	113	-105
3	3	7	68	56
4	3	7	194	212
6	3	7	108	113
8	3	7	247	-253
1	4	7	448	-460
2	4	7	157	-160
3	4	7	145	-130
4	4	7	83	-109
5	4	7	515	511
6	4	7	116	-88
7	4	7	177	-183
8	4	7	141	-102
9	4	7	359	-332
2	5	7	179	-177

metrical sites. Selenium is apex in a trigonal pyramid with Se—O bonds around 1.70 Å; this is significantly shorter than a pure Se—O σ bond which is 1.83 Å.[10]

Thus some degree of π-bonding involving the *d*-orbitals of Se is likely, as is also indicated by the fact that the angles at Se are significantly smaller (101°) than the tetrahedral angle. The three Se—O bonds differ in the following way: the oxygen atom which has no hydrogen attached to it forms the shortest Se-O bond, the oxygen atom with a hydrogen atom has the longest distance to selenium, and the third oxygen which has on average half a hydrogen atom has a Se—O distance which is nearly the mean of the two others. This again is easily explained by varying degrees of π-bonding depending on the ability of oxygen to supply electrons. The bond lengths found are within the range of Se—O bonds reported earlier, but most of these have big standard deviations.

Selenium has two more oxygen neighbours closer than the expected van der Waals distance of 3.40 Å, namely at 2.996 and 3.221 Å. The angles are such that the coordination round selenium could be described as a distorted octahedron of which one corner is unoccupied and two ligands are only weakly bound. In H_2SeO_3[11] and $SnCl_4,2SeOCl_2$[10] all six positions of the octahedron are occupied, and also in the present compound a sixth ligand at a distance of 3.45 Å can be found in nearly the right direction as can be seen from Fig. 1; packing probably determines the lengths of these weak bonds.

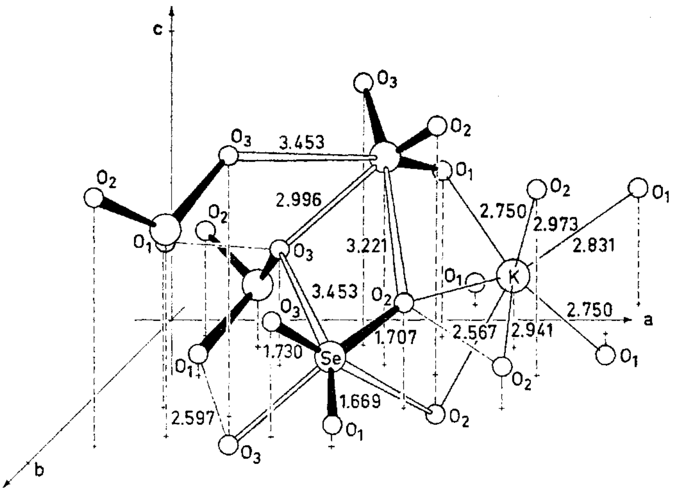

Fig. 1. Clinographic projection of part of the structure.

The ions are joined in two directions by fairly strong hydrogen bonds ($O_1—O_3$=2.597 Å, $O_2—O_2$=2.567 Å) forming double sheets of selenite ions. Potassium is found on a twofold axis in the middle of such a double layer surrounded by eight oxygen atoms at distances from 2.75 to 2.97 Å. The coordination polyhedron around potassium is not simple.

The hydrogen bond $O_2 \cdots H \cdots O_2$ is the most interesting point of the structure, since this is probably responsible for any electrical anomalies of the crystals. At room temperature the hydrogen atoms are almost certainly statistically distributed on two symmetrical sites. Shuvalov, Ivanov and Sitnik[5] report a change in dielectric properties at −61.6°C and they find indications that below this temperature the structure belongs to the space group $P1$. Apparently a twin-formation occurs at the phase transition. They are not able to detect any ferro- or antiferroelectric effect as found in all other alkali trihydrogen selenites. The transformation probably consists of an ordering of the hydrogen atoms within certain domains, neighbouring domains having hydrogens displaced in opposite directions giving rise to twinning; possible mechanical strains connected with this might prevent the reorientation of domains and thereby a ferroelectric effect. It may also be worth noticing that the length of the hydrogen bond is 2.567 Å whereas it is only 2.52 Å in the ferroelectric $LiH_3(SeO_3)_2$. Reid[12] has given some potential energy curves for hydrogen atoms in hydrogen bonds of different lengths, and it appears that a high electrical energy is required to shift the hydrogen atom from one oxygen atom to the other if the bond is as long as this one, thus making the compound only pyroelectric. However, the low temperature phase may have a shorter $O_2\cdots H\cdots O_2$ bond than the one found at room temperature.

An ordering of the hydrogen atoms will probably give rise to a change of position of the selenium atoms in such a way that the $Se-O_1$ and $Se-O_3$ distances are retained. This means a shift mainly in the x-direction in agreement with the dielectric anomalies reported in Ref. 5.

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REFERENCES

1. Nilson, L. F. *Nova Acta Soc. Sci. Upsaliensis* [3] 9 II, No. 7 (1875) 1/120, 35.
2. Pepinsky, R. and Vedam, K. *Phys. Rev.* **114** (1959) 1217.
3. Vijayan, M. *Current Sci.* **36** (1967) 230.
4. Makita, Y. *J. Phys. Soc. Japan* **20** (1965) 1567.
5. Shuvalov, L. A., Ivanov, N. R. and Sitnik, T. K. *Kristallografiya* **12** (1967) 366 (transl. 315).
6. Charlot, G. and Bezier, D. *Quantitative Inorganic Analysis*, Methuen, London 1957, p. 557.
7. Arndt, U. W. and Phillips, D. C. *Acta Cryst.* **14** (1961) 807.
8. Wells, M. *Acta Cryst.* **13** (1960) 722.
9. Busing, W. R., Martin, K. O. and Levy, H. A. *IUCr World List of Crystallographic Computer Programs*, No. 363.
10. Hermodsson, Y. *Acta Cryst.* **13** (1960) 656.
11. Wells, A. F. and Bailey, M. *J. Chem. Soc.* **1949** 1282.
12. Reid, C. *J. Chem. Phys.* **30** (1959) 182.

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