

On the Crystal Structure of Potassium Trihydrogen Selenite, $\text{KH}_3(\text{SeO}_3)_2$, 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 $a=16.152 \text{ \AA}$, $b=6.249 \text{ \AA}$, $c=6.307 \text{ \AA}$ 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.

$\text{KH}_3(\text{SeO}_3)_2$ and other alkali selenites have been known since 1875.¹ Pepinsky and Vedam² found in 1959 that $\text{LiH}_3(\text{SeO}_3)_2$ 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 $\text{KH}_3(\text{SeO}_3)_2$ 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 $\text{KH}_3(\text{SeO}_3)_2$.

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 $\text{KH}_3(\text{SeO}_3)_2$: 53.35.

The unit cell and space group were determined from Weissenberg and precession photographs using $\text{CuK}\alpha$ and $\text{MoK}\alpha$ radiations. Intensities were obtained from a crystal

of dimensions $0.1 \times 0.1 \times 0.3$ mm³ on a linear diffractometer of the Arndt-Phillips type⁷ 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.
 $U = 636.6$ Å³.

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/cm³ 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 H₁₄SeO₃⁻⁴, one hydrogen atom being statistically distributed on two sym-

Table 1. Final atomic parameters. Coordinates with standard deviations × 10⁵ in parentheses.

	<i>x</i>	<i>σx</i>	<i>y</i>	<i>σy</i>	<i>z</i>	<i>σz</i>
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 Å² × 10⁻⁴.

	<i>u</i> ₁₁	<i>σu</i> ₁₁	<i>u</i> ₂₂	<i>σu</i> ₂₂	<i>u</i> ₃₃	<i>σu</i> ₃₃	<i>u</i> ₁₂	<i>σu</i> ₁₂	<i>u</i> ₁₃	<i>σu</i> ₁₃	<i>u</i> ₂₃	<i>σu</i> 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 × 10 ⁻³	Å	Å
Se—O ₁	1.669	(4)	Se—O ₃ '	2.996
Se—O ₂	1.707	(4)	Se—O ₃	3.221
Se—O ₃	1.730	(5)	Se—O ₃ ''	3.453
O ₂ —H ₂	1.032	(165)	O ₁ —O ₃	2.597
O ₃ —H ₁	0.937	(83)	O ₂ —O ₃	2.567
			K—O ₂	2.973
			K—O ₁	2.831
			K—O ₃	2.750
			K—O ₂	2.941

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, $10 \times$ absolute scale.

h	k	l	F _{obs}	F _{calc}	h	k	l	F _{obs}	F _{calc}	h	k	l	F _{obs}	F _{calc}	h	k	l	F _{obs}	F _{calc}
4	0	0	1534	-1544															
6	0	0	1727	1795															
6	0	0	594	508															
10	0	0	940	-952															
12	0	0	630	655															
14	0	0	1202	1256															
16	0	0	622	-641															
20	0	0	804	855															
1	1	0	205	300															
1	1	0	523	-530															
5	1	0	241	-247															
7	1	0	321	344															
9	1	0	1042	-1059															
11	1	0	440	-456															
13	1	0	635	650															
17	1	0	349	-356															
0	2	0	1820	-2050															
2	2	0	534	500															
4	2	0	1599	1585															
6	2	0	440	-448															
10	2	0	705	717															
12	2	0	400	-423															
14	2	0	770	-776															
16	2	0	518	531															
20	2	0	542	-568															
1	3	0	400	-511															
3	3	0	1403	1579															
5	3	0	454	-454															
7	3	0	1045	-1070															
9	3	0	1362	1380															
11	3	0	795	799															
13	3	0	950	-940															
15	3	0	262	261															
17	3	0	694	709															
19	3	0	247	-235															
0	4	0	479	-475															
2	4	0	141	-147															
4	4	0	162	170															
6	4	0	201	-246															
1	5	0	364	366															
3	5	0	1280	-1311															
5	5	0	309	-311															
7	5	0	093	904															
9	5	0	695	-642															
11	5	0	530	-521															
13	5	0	466	461															
15	5	0	353	-351															
17	5	0	449	-517															
20	5	0	419	719															
2	6	0	192	-170															
4	6	0	200	-270															
6	6	0	653	649															
8	6	0	245	226															
10	6	0	368	-369															
12	6	0	211	159															
14	6	0	410	-420															
16	6	0	298	-284															
18	6	0	363	385															
2	7	0	144	-179															
4	7	0	179	198															
6	7	0	137	113															
8	7	0	594	-595															
10	7	0	220	235															
12	7	0	533	-550															
14	7	0	205	319															
1	1	1	1095	-1110															
2	1	1	309	-390															
3	1	1	2432	2656															
4	1	1	82	50															
5	1	1	408	593															
6	1	1	869	781															
7	1	1	891	-821															
8	1	1	403	-449															
9	1	1	1312	1390															
11	1	1	982	930															
13	1	1	890	-879															
15	1	1	244	-224															
17	1	1	272	285															
19	1	1	068	890															
21	1	1	226	153															
23	1	1	410	-427															
25	1	1	1667	-1774															
27	1	1	159	-205															
29	1	1	291	-277															
31	1	1	686	644															
33	1	1	655	650															
35	1	1	347	339															
37	1	1	1195	-1188															
39	1	1	420	-402															
41	1	1	296	-310															
43	1	1	165	-137															
45	1	1	1009	993															
47	1	1	126	111															
49	1	1	604	-665															
51	1	1	126	100															
53	1	1	818	-797															
55	1	1	257	-291															
57	1	1	337	348															
59	1	1	221	193															
61	1	1	443	-474															
63	1	1	86	-176															
65	1	1	803	-810															
67	1	1	107	105															
69	1	1	121	137															
19	2	1	123	-125															
20	2	1	390	456															
21	2	1	353	385															
22	2	1	525	551															
23	2	1	1620	-1652															
24	2	1	739	-732															
25	2	1	492	-496															
26	2	1	147	-143															
27	2	1	720	722															
28	2	1	430	447															
29	2	1	680	-665															
30	2	1	993	-907															
31	2	1	561	565															
32	2	1	227	226															
33	2	1	294	-216															
34	2	1	204	-236															
35	2	1	604	-603															
36	2	1	360	-366															
37	2	1	233	292															
38	2	1	124	-117															
39	2	1	91	107															
40	2	1	106	119															
41	2	1	165	-162															
42	2	1	101	97															
43	2	1	196	-199															
44	2	1	244	-235															
45	2	1	651	-640															
46	2	1	170	180															
47	2	1	272	291															
48	2	1	180	179															
49	2	1	240	-227															
50	2	1	225	-235															
51	2	1	695	694															
52	2	1	249	233															
53	2	1	300	292															
54	2	1	463	-472															
55	2	1	139	-124															
56	2	1	159	-164															
57	2	1	493	532															
58	2	1	661	-659															
59	2	1	110	-110															
60	2	1	322	320															
61	2	1	249	233															
62	2	1	599	-592															
63	2	1	277	-263															
64	2	1	204	-192															
65	2	1	339	334															
66	2	1	250	262															
67	2	1	205	-215															
68	2	1	315	-294															
69	2	1	136	-104															
70	2	1	218	114															
71	2	1	121	117															
72	2	1	290	-205															
73	2	1	140	132															
74	2	1	343	-337															
75	2	1	544	540															
76	2	1	101	142															
77	2	1	239	-220															
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83	2	1	693	-696															
84	2	1	321	-313															
85	2	1	093	930															
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87	2	1	650	-644															
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143	2	1	544	540															
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150	2	1	302	-300															
151	2	1	693	-696															
152	2	1	321	-313															
153	2	1	093	930															
154	2	1	1090	-1080															
155	2	1	650	-644															
156	2	1	556	-530															
157	2	1	636	642															
158	2	1	411	416															
159	2	1	343	-337															
160	2	1	544	540															
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165	2	1	1237	-1277															
166	2	1	787	769															
167	2	1	302	-300															
168	2	1	693	-696															
169	2	1	321	-313															
170	2	1	093	930															
171	2	1	1090	-1080															
172	2	1	650	-644															
173	2	1	556	-530															
174	2	1	636	642															
175	2	1	411	416															
176	2	1	343	-337															
177	2	1	544	540															
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181	2	1	724	764															
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184	2	1	302	-300															
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200	2	1	787	769															
201	2	1	302	-300															
202	2	1	693	-696															
203	2	1	321	-313															
204	2	1	093	930															
205	2	1	1090	-1080															
206	2	1	650	-644															
207	2	1	556	-530															
208	2	1	636	642															
209	2	1	411	416															
210	2	1	343	-337															
211	2	1	544	540															
212	2	1	101																

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 $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ 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.

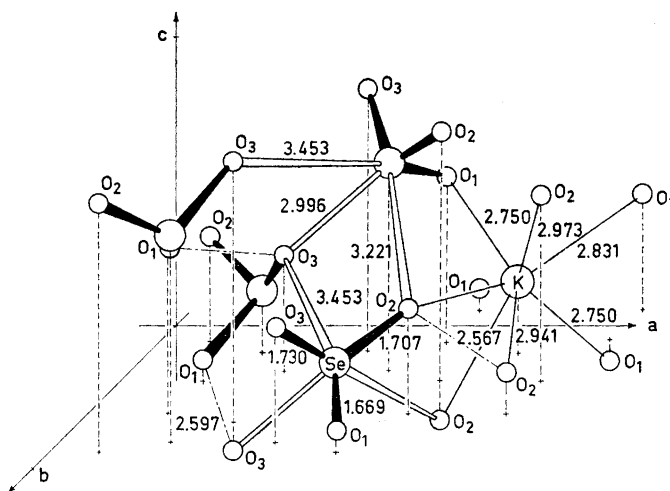


Fig. 1. Clinographic projection of part of the structure.

The ions are joined in two directions by fairly strong hydrogen bonds ($\text{O}_1-\text{O}_3=2.597$ Å, $\text{O}_2-\text{O}_2=2.567$ 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 $\text{O}_2 \cdots \text{H} \cdots \text{O}_2$ 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 Sitnik⁵ 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 \AA whereas it is only 2.52 \AA in the ferroelectric $\text{LiH}_3(\text{SeO}_3)_2$. Reid¹² 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 $\text{O}_2 \cdots \text{H} \cdots \text{O}_2$ 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 $\text{Se}-\text{O}_1$ and $\text{Se}-\text{O}_3$ 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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