

The Hydrogen Bond System in Potassium Trihydrogen Bis-selenite, $\text{KH}_3(\text{SeO}_3)_2$, and in Potassium Trideuterio Bis-selenite $\text{KD}_3(\text{SeO}_3)_2$, as Determined by Neutron Diffraction

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Neutron diffraction studies have been carried out on potassium trihydrogen bis-selenite, $\text{KH}_3(\text{SeO}_3)_2$, and on potassium trideuterio bis-selenite, $\text{KD}_3(\text{SeO}_3)_2$. The cell is in both cases orthorhombic, space group *Pbcn* (No. 60), with 8 units of $\text{K}_4\text{H}_{14}\text{SeO}_3$ per unit cell.

Three dimensional sets of data were collected. Positional and anisotropic temperature factors for all atoms were refined by the method of least squares, leading to final *R*-values of 0.037 and 0.033 for $\text{KH}_3(\text{SeO}_3)_2$ and $\text{KD}_3(\text{SeO}_3)_2$, respectively.

The scattering length of selenium in $\text{KH}_3(\text{SeO}_3)_2$ was determined to be $8.01f$ ($\sigma = 0.04f$).

The hydrogen positions proposed by Hansen *et al.*¹ from X-ray analysis are confirmed, and there is good agreement between the temperature factors obtained from the three analyses.

A correlation is found between the selenium-oxygen distances and the corresponding oxygen-hydrogen distances for three different selenites containing hydrogen.

The hydrogen bond systems in $\text{KH}_3(\text{SeO}_3)_2$ and $\text{KD}_3(\text{SeO}_3)_2$ are compared. The change in distances by the deuterium substitution is of the same magnitude for the two independent hydrogen bonds.

The X-ray structure of the high temperature form of potassium trihydrogen bis-selenite, $\text{KH}_3(\text{SeO}_3)_2$, has previously been determined by Hansen *et al.*¹ At -61.6°C the structure undergoes a phase transformation,² and the probable changes in the hydrogen bonding system at this transformation were discussed.¹

The neutron diffraction study was undertaken to confirm the hydrogen positions obtained from the X-ray analysis, and to compare the hydrogen bonding system with that previously determined for selenious acid,³ H_2SeO_3 .

As both ordered and statistically distributed hydrogen atoms occur in the structure a similar analysis was carried out on the deuterated substance, $\text{KD}_3(\text{SeO}_3)_2$, to investigate to which extent the bond lengths are changed by the substitution for the two types of hydrogen bonds.

EXPERIMENTAL

In Table 1 are summarized some of the experimental conditions for the two compounds.

Table 1. Experimental quantities for $\text{KH}_3(\text{SeO}_3)_2$ and $\text{KD}_3(\text{SeO}_3)_2$.

	$\text{KH}_3(\text{SeO}_3)_2$	$\text{KD}_3(\text{SeO}_3)_2$
Crystal shape and dimensions in mm	Cylinder diameter: 2.6 Length: 6.1	Sphere diameter: 4.3
Maximum $\sin\theta/\lambda$	0.74	0.70
Number of reflections	1993	1803
Number of symmetry independent reflections	1041	916
Number of reflections with $F^2 > 2\sigma(F^2)_{\text{count}}$	848	830
Standard reflection	3,3,2	3,3,2
Interval between measurement of standard	15	10
Central scan range: Δ_1, δ_1 , in degrees	3.04, 0.04	3.20, 0.04
Outer scan range: Δ_2, δ_2 in degrees	0.80, 0.16	0.80, 0.08
μ (calculated) in cm^{-1}	0.86	0.14
μ (measured) in cm^{-1}	0.91	

Crystals were prepared by slow evaporation of an aqueous solution of K_2CO_3 (2 mol) and SeO_3 (8 mol). For $\text{KD}_3(\text{SeO}_3)_2$ the solvent was heavy water, D_2O , and the experiment was carried out in a dry atmosphere in a glovebox.

The cylinder axis of the $\text{KH}_3(\text{SeO}_3)_2$ crystal was parallel to the c -axis and the crystal was mounted in a thinwalled aluminium container. The spherical $\text{KD}_3(\text{SeO}_3)_2$ crystal was packed in thin aluminium foil.

Three-dimensional sets of neutron data were collected on an automatic Hilger-Ferranti four-circle diffractometer, located at the DR 3 reactor at the Danish Atomic Energy Commission Research Establishment, Risø.

The wavelength of the neutron beam was 1.025 \AA , with standard deviation 0.002 \AA , and the flux at the specimen was $0.9 \times 10^6 \text{ n/cm}^2/\text{sec}$. The beam was uniform within $\pm 5\%$ for the neutrons impinging on the crystal.

The crystals were mounted with the c -axis parallel to the ϕ -axis of the instrument. For measuring the reflections the crystal was rotated an angle ψ about the diffraction vector from the A -setting position, ψ being different for symmetry related reflections. The possible values for ψ were $\pm 1.33^\circ$, $\pm 2.67^\circ$, and $\pm 4.00^\circ$. The reflections with $k \geq 0$ and $l \geq 0$ were recorded in increasing order of $\sin\theta/\lambda$.

The reflections were measured by the $\omega-2\theta$ scan technique, and counts for each step were recorded. The scan range was divided into three parts, a central range, Δ_1 , with short step lengths, δ_1 , and two outer ranges, Δ_2 , with longer step lengths, δ_2 . The

profile measurements were reduced to structure factors by use of a method which places the points of division between the peak and the background in such a way that $\sigma I/I$ is minimized. I is the integrated intensity and σI is the standard deviation based on counting statistics.⁴

The structure factors were corrected for drift in the experimental conditions, which is reflected in the variation of the intensities of the standard reflection. This variation was 2 % within the measuring period. The data for $\text{KH}_3(\text{SeO}_3)_2$ was corrected for absorption, using the observed value for μ . It was assumed that the reflections had been measured in the A-setting position. A program written by Wells⁵ was used. The crystal cylinder was described by 18 planes, 16 of these forming a column around the cylinder axis with the remaining 2 planes intersecting at right angles, the lines of intersection forming two regular 16-gons.

The reflections included in the refinement had $F^2 > 2\sigma(F^2)_{\text{count}}$ where $\sigma(F^2)_{\text{count}}$ is the standard deviation based on counting statistics.

STRUCTURE REFINEMENTS

Two least squares programs were used in the refinements, namely a block-diagonal program G 403,⁶ and the full-matrix program ORFLS⁷ as found in the X-ray 63⁸ system. A correction for isotropic extinction following the formula of Zachariasen,⁹ as modified by Larson¹⁰

$$F_c^* = K \times F_c (1 + g\beta(2\theta)F_c^2)^{-\frac{1}{2}}$$

can be included in G 403. K is the scale factor, F_c is the calculated structure factor, and $\beta(2\theta)$ is given by $A(dA^*/d\mu)/\sin(2\theta)$, where $A(dA^*/d\mu)$ is obtained from the absorption correction calculations. ($A^* = A^{-1}$ is the absorption factor.) For $\text{KD}_3(\text{SeO}_3)_2$ $A(dA^*/d\mu)$ was set to 1, as no absorption correction was carried out. The weights used in the refinements were of the form $1/(\mu F^2)$ with

$$\mu F = \sqrt{\sigma(F^2)_{\text{count}} + pF_o^2} - |F_o|$$

where F_o is the observed structure factor, and p is an adjustable constant, the weight constant.

$\text{KH}_3(\text{SeO}_3)_2$. The starting position for the refinement was the coordinates and temperature factors given by Hansen *et al.*¹ The program G 403 was used, extinction correction was included and the refinement gave a final R -factor of 0.037. The extinction factor was $g = 3.74 \times 10^{-4}$, and the weight constant was $p = 1.025$.

The scattering lengths used were $b_{\text{H}} = -3.72f$, $b_{\text{K}} = 3.70f$ (The Neutron Diffraction Commission¹¹), $b_{\text{O}} = 5.88f$,¹² and $b_{\text{Se}} = 8.10f$.³

The scattering length for selenium was redetermined by least squares refinement using ORFLS. The extinction correction was applied to the structure factors, and a refinement on all parameters plus the site occupation factor of the selenium atom was carried out. The R factor after the refinement was still 0.037. The scattering length obtained was $b_{\text{Se}} = 8.01f$ ($\sigma = 0.04f$). As this is in good agreement with the one previously determined for selenium in selenious acid, H_2SeO_3 ,³ which was $8.10f$ ($\sigma = 0.05f$), it seems that a weighted mean of these two values, $b_{\text{Se}} = 8.05f$, should be preferred for future use.

One of the hydrogen atoms, H(2), was assumed to be statistically distributed on two positions which were symmetry related by a two-fold axis. As these atoms were quite near the axes, a refinement was carried out using the program

G 403 with the hydrogen atom in special position on the two-fold axis. This led to a final R -value of 0.039 and a weighted R -value of 0.045. As the weighted R -value for the refinement with the hydrogen atom statistically distributed is 0.042, the Hamilton¹³ test on the weighted R factor ratio gives that this description is significantly better than one with a single hydrogen atom H(2) in a special position.

$KD_3(SeO_3)_2$. Refinements were carried out on $KD_3(SeO_3)_2$ using as starting values the coordinates and temperature factors obtained for $KH_3(SeO_3)_2$. The program G 403 was used and the extinction correction was included. The scattering lengths for potassium and oxygen were unaltered, whereas $b_D = 6.21f$ (The Neutron Diffraction Commission) and $b_{Se} = 8.05f$. A final R -value of 0.046 was obtained but as this value seemed to be too high compared to the final R factor for $KH_3(SeO_3)_2$, an investigation was carried out to see whether $KD_3(SeO_3)_2$ was fully deuterated.

All the coordinates, the temperature factors, the scale factor and the site occupation factors for the two independent deuterium atoms were refined using ORFLS, but no extinction correction was carried out. This led to an R value of 0.044 with scattering length 4.66 f for the deuterium atom being distributed in two symmetrical sites (D(2)) and 4.97 f for the singly positioned deuterium (D(1)). The corresponding percentages of hydrogen were 15.6 % and 12.5 % with standard deviations obtained from the least squares refinement of 0.8 % and 0.5 %.

The preference of the hydrogen atoms for the two symmetrical positions (D(2)) which corresponds to the longest O—D distance, is in agreement with the isotope distribution found in α -oxalic acid dihydrate.^{14,15} However, as the difference between the two percentages is small and as extinction was not included in the refinement, it was assumed in the subsequent refinement that the scattering lengths for the two independent deuterium atoms were identical.

A series of refinements were now carried out for different scattering lengths for the deuterium atoms. The extinction correction was included, and the weight constant used was $p = 1.030$. The results are given in Fig. 1 where the

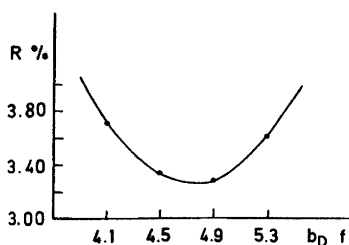


Fig. 1. The R factor for four different values of b_D . The curve drawn is the least squares parabola put through the points.

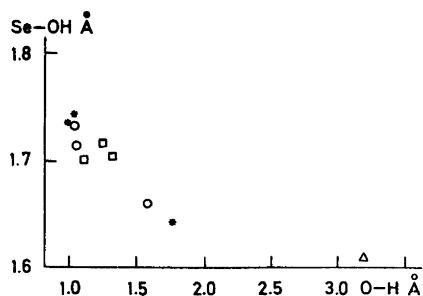


Fig. 2. Se—O distances as a function of the corresponding O—H distances where the hydrogen atom is the one nearest to the oxygen atom. $NaH_3(SeO_3)_2$, \square ; H_2SeO_3 , $*$; $KH_3(SeO_3)_2$, \circ ; and SeO_2 , \triangle . For $NaH_3(SeO_3)_2$ atom H(1) is assumed to be disordered.

R -value is plotted against b_D . A least squares parabola was put through the obtained points and the minimum was found for $b_D = 4.74f$. The corresponding extinction factor was found by linear interpolation to be $g = 3.11 \times 10^{-5}$. This extinction factor was applied to the structure factors, and a final refinement was carried out using ORFLS. The site occupation factors for the deuterium atoms were included in the refinement, and as in the earlier refinement there was a small difference between the site occupancies for the two different deuterium atoms. The final R value was 0.033 and the scattering lengths were $b_{D(1)} = 4.93f$ and $b_{D(2)} = 4.68f$, corresponding to hydrogen contents of 12.9 % for D(1) and 15.4 % for D(2) with standard deviations 0.4 % and 0.6 %. The hydrogen probably originates from water absorbed in the SeO_2 and K_2CO_3 which were not dried before they were dissolved in heavy water.

CRYSTAL DATA

Crystal system: orthorhombic

Unit cell:

$\text{KH}_3(\text{SeO}_3)_2$	$\text{KD}_3(\text{SeO}_3)_2$
$a = 16.152 (5) \text{ \AA}$	$a = 16.176 (11) \text{ \AA}$
$b = 6.249 (2) \text{ \AA}$	$b = 6.259 (3) \text{ \AA}$
$c = 6.307 (2) \text{ \AA}$	$c = 6.309 (5) \text{ \AA}$

Space group: $Pbcn$ (No. 60)

The cell dimensions for $\text{KH}_3(\text{SeO}_3)_2$ are the ones given by Hansen *et al.*¹ The cell dimensions for $\text{KD}_3(\text{SeO}_3)_2$ were determined from measurements performed on the neutron diffractometer. 13 axial reflections were used for this calculation. The final coordinates and temperature factors for $\text{KH}_3(\text{SeO}_3)_2$ and $\text{KD}_3(\text{SeO}_3)_2$ are given in Tables 2 and 3.

Table 2a. Positional coordinates for $\text{KH}_3(\text{SeO}_3)_2$.

	x	y	z
Se	0.15144(4)	0.18797(11)	0.21251(11)
K	0.50000	0.18765(37)	0.25000
O(1)	0.11137(6)	0.38720(17)	0.07141(17)
O(2)	0.06710(6)	0.11161(19)	0.35883(17)
O(3)	0.20684(7)	0.32159(20)	0.40655(18)
H(1)	0.17140(14)	0.44243(40)	0.47011(37)
H(2)	0.01335(30)	0.12669(61)	0.26801(149)

Table 2b. Anisotropic temperature factors in \AA^2 for $\text{KH}_3(\text{SeO}_3)_2$.

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Se	0.0158(3)	0.0182(3)	0.0197(3)	0.0027(2)	0.0013(2)	0.0005(2)
K	0.0242(10)	0.0233(9)	0.0216(9)	0.0000	0.0045(7)	0.0000
O(1)	0.0217(5)	0.0238(4)	0.0261(4)	0.0002(3)	-0.0045(3)	0.0069(4)
O(2)	0.0192(5)	0.0335(5)	0.0235(4)	-0.0036(4)	0.0031(3)	0.0049(4)
O(3)	0.0216(5)	0.0339(6)	0.0331(5)	0.0019(4)	-0.0114(4)	-0.0058(4)
H(1)	0.0388(11)	0.0443(11)	0.0413(10)	-0.0071(8)	-0.0123(8)	0.0002(10)
H(2)	0.0240(41)	0.0336(14)	0.0399(33)	0.0014(12)	0.0059(30)	0.0019(19)

Table 3a. Positional coordinates for $\text{KD}_3(\text{SeO}_3)_2$.

	<i>x</i>	<i>y</i>	<i>z</i>
Se	0.15135(4)	0.18744(11)	0.21156(11)
K	0.50000	0.18832(38)	0.25000
O(1)	0.11121(6)	0.38686(16)	0.07165(17)
O(2)	0.06741(7)	0.11010(19)	0.35921(18)
O(3)	0.20723(7)	0.31991(20)	0.40555(21)
D(1)	0.17243(10)	0.43678(27)	0.46787(27)
D(2)	0.01463(19)	0.12677(49)	0.27042(79)

Table 3b. Anisotropic temperature factors in \AA^2 for $\text{KD}_3(\text{SeO}_3)_2$.

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Se	0.0167(3)	0.0198(3)	0.0202(4)	0.0023(3)	0.0011(2)	0.0005(2)
K	0.0272(10)	0.0242(10)	0.0220(9)	0.0000	0.0056(8)	0.0000
O(1)	0.0235(5)	0.0239(5)	0.0258(5)	-0.0006(3)	-0.0037(4)	0.0066(4)
O(2)	0.0204(5)	0.0348(6)	0.0246(5)	-0.0035(4)	0.0034(4)	0.0050(4)
O(3)	0.0219(5)	0.0340(6)	0.0345(6)	0.0039(4)	-0.0105(4)	-0.0075(5)
D(1)	0.0370(9)	0.0407(9)	0.0371(8)	-0.0054(6)	-0.0104(6)	-0.0008(7)
D(2)	0.0268(32)	0.0341(13)	0.0292(23)	0.0013(10)	0.0016(22)	0.0019(12)

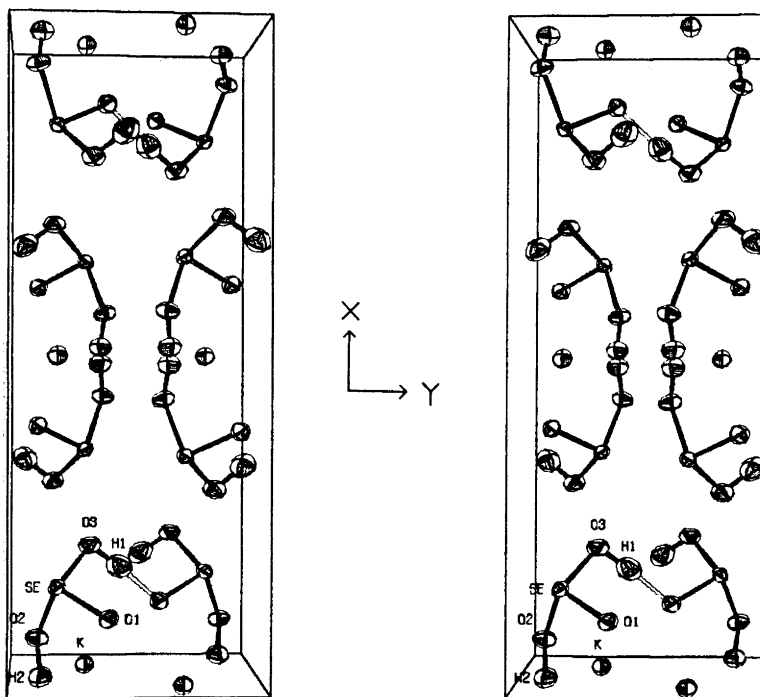


Fig. 3. Unit cell content for $\text{KH}_3(\text{SeO}_3)_2$ viewed along the *z*-axis. Thermal ellipsoids are with 50% probability. Bonds within the unit cell are given, heavy bonds are intramolecular bonds, open bonds are hydrogen bonds.

Various interatomic distances and angles for $\text{KH}_3(\text{SeO}_3)_2$, $\text{KD}_3(\text{SeO}_3)_2$ and related compounds are given in Tables 4 to 8. Numbers in parenthesis in the tables and in the text are standard deviations in unit of the last digit. Tables 9 and 10 give observed and calculated structure factors for $\text{KH}_3(\text{SeO}_3)_2$ and $\text{KD}_3(\text{SeO}_3)_2$.

Fig 3 gives the content of the unit cell for $\text{KH}_3(\text{SeO}_3)_2$ viewed along the z direction of the crystal. The programme ORTEP¹⁶ was used to make this drawing.

DISCUSSION

The following discussion is divided into two parts, one concerning $\text{KH}_3(\text{SeO}_3)_2$, and one being a comparison between $\text{KH}_3(\text{SeO}_3)_2$ and $\text{KD}_3(\text{SeO}_3)_2$.

$\text{KH}_3(\text{SeO}_3)_2$. The hydrogen positions proposed by Hansen *et al.*¹ are confirmed by this analysis and the differences between the corresponding positions for the two analysis are only 0.19 Å for H(1) and 0.07 Å for H(2). The coordinates of the other atoms agree within two standard deviations except for the x and z coordinates of selenium. The shift in position in going from the neutron position for selenium to the X-ray position is in a direction near the bisector to the angle $\angle \text{O}(2) - \text{Se} - \text{O}(3)$, and its size is 0.005 Å. There does not seem to be any simple explanation for this shift. There is, however, good accordance between the distances found in the two cases, as seen from Table 4.

Table 4. Distances in Å and angles in degrees for $\text{KH}_3(\text{SeO}_3)_2$ (X-ray data), $\text{KH}_3(\text{SeO}_3)_2$ and $\text{KD}_3(\text{SeO}_3)_2$ (neutron data).

	$\text{KH}_3(\text{SeO}_3)_2$ (X-ray)	$\text{KH}_3(\text{SeO}_3)_2$	$\text{KD}_3(\text{SeO}_3)_2$
Se—O(1)	1.669(4)	1.662(1)	1.661(1)
Se—O(2)	1.707(4)	1.713(1)	1.716(1)
Se—O(3)	1.730(5)	1.731(1)	1.733(1)
O(2)—H(2)	1.032(165)	1.044(7)	1.026(4)
O(3)—H(1)	0.937(83)	1.029(3)	1.003(2)
K—O(1)	2.831	2.834(2)	2.839(2)
K—O(1)	2.750	2.750(1)	2.752(1)
K—O(2)	2.973	2.972(1)	2.976(2)
K—O(2)	2.941	2.944(2)	2.938(2)
$\angle \text{O}(1) - \text{Se} - \text{O}(2)$	100.61(21)	100.81(6)	101.02(6)
$\angle \text{O}(1) - \text{Se} - \text{O}(3)$	102.41(21)	102.63(6)	102.69(7)
$\angle \text{O}(2) - \text{Se} - \text{O}(3)$	99.82(22)	99.47(6)	99.46(7)

The individual anisotropic temperature factors u_{ij} of the selenium and oxygen atoms for the two analysis are in agreement and the signs for the u_{ij} with $i \neq j$ are the same for all the atoms. On the average, the u_{ij}^{X} for the X-ray analysis are somewhat bigger than the u_{ij}^{N} for the neutron analysis. The scale factor ($K_u = \sum |u_{ij}^{\text{X}}| / \sum |u_{ij}^{\text{N}}|$) is $K_u = 1.16$. This is in correspondence with the expected deviation of the electron density from spherical distribution, whereby electrons are spread out more than assumed, and the sizes of the temperature factors are increased.

The agreement factor between the two sets of u_{ij} ($\sum |K_{ij}u_{ij}^N - u_{ij}^X| / \sum |u_{ij}^X|$) is 0.10, and this is of the same size as the mean relative error ($\sum \sigma(u_{ij}^X) / \sum |u_{ij}^X|$) which is 0.09.

At the present time, neutron studies have been carried out on three selenites containing hydrogen, namely $\text{NaH}_3(\text{SeO}_3)_2$,¹⁷ H_2SeO_3 ,³ and $\text{KH}_3(\text{SeO}_3)_2$. The selenium-oxygen distances in the pyramidal selenite group, SeO_3 , for these studies are in the range 1.64 Å to 1.73 Å. If these Se—O distances are plotted against the corresponding O—H (or O···H) distances, where H is the nearest (intra or intermolecular) hydrogen atom to the oxygen, it is seen from the plot (Fig. 2) that the length of the Se—O bond is correlated to the nearness of the hydrogen atom. As the O···H distance becomes longer, the Se—O distance gets shorter, and we would therefore expect the minimal Se—O distance in hydrogen bonded selenite groups to be 1.61 (3) Å which is the value obtained from the electron diffraction of SeO_2 in the gas phase.¹⁸ The corresponding O···H distance could be 3.2 Å, namely the sum of the van der Waals radii of the selenium and the hydrogen atoms. This point is therefore put on the plot too.

In Table 5 are given the intramolecular angles $\angle \text{Se—O—H}$ for the four compounds, two for $\text{KH}_3(\text{SeO}_3)_2$, $\text{KD}_3(\text{SeO}_3)_2$, and H_2SeO_3 each and three for $\text{NaH}_3(\text{SeO}_3)_2$. The weighted mean (not including $\text{KD}_3(\text{SeO}_3)_2$) is 112.2° and the sample standard deviation is 2.3°.

Table 5. The angles $\angle \text{Se—O—H}$ for $\text{KH}_3(\text{SeO}_3)_2$, $\text{KD}_3(\text{SeO}_3)_2$, H_2SeO_3 , and $\text{NaH}_3(\text{SeO}_3)_2$ in degrees. In case of $\text{NaH}_3(\text{SeO}_3)_2$ H (1) is assumed to be disordered.

	$\text{KH}_3(\text{SeO}_3)_2$	$\text{KD}_3(\text{SeO}_3)_2$
$\angle \text{Se—O(2)—H(2)}$	109.9(4)	109.5(3)
$\angle \text{Se—O(3)—H(1)}$	110.0(2)	109.5(1)
	H_2SeO_3	
$\angle \text{Se—O(2)—H(1)}$	113.6(2)	
$\angle \text{Se—O(3)—H(2)}$	113.3(2)	
	$\text{NaH}_3(\text{SeO}_3)_2$	
$\angle \text{Se—O(1)—H(1)}$	113(3)	
$\angle \text{Se—O(2)—H(2)}$	108.8(5)	
$\angle \text{Se—O(3)—H(2)}$	114.9(4)	

There are two types of hydrogen bonds in the structure (Fig. 3). One type, in which the atoms O(1), H(1), and O(3) take part, is a zigzag bond along the *c*-axis. In this bond H(1) is in a single position. The other type of hydrogen bond in which O(2) and H(2) take part with H(2) statistically distributed in two symmetrically related positions consists of bonds in the *x*-direction. The zigzag chains are linked together two by two by this hydrogen bond to form tubes with the tube axis parallel to the *c*-axis. A zigzag chain is found, too, in selenious acid, involving one of the hydrogen atoms but in that case, the other hydrogen atom interlinks the chains in such a way that a two-dimensional double layer is formed. In $\text{NaH}_3(\text{SeO}_3)_2$ the hydrogen bonds form a three-dimensional network.

The selenium atoms are on the surface of the tube and the potassium atoms are situated in special positions inside the tube.

In Table 6 are given distances and angles in the hydrogen bond for $\text{KH}_3(\text{SeO}_3)_2$ and $\text{KD}_3(\text{SeO}_3)_2$. Both the $\text{O}\cdots\text{O}$ distances are shorter than the

Table 6. Distances in Å and angles in degrees in the hydrogen bonds for $\text{KH}_3(\text{SeO}_3)_2$ and $\text{KD}_3(\text{SeO}_3)_2$. Different marking of the atoms indicates atoms from different molecules.

	$\text{KH}_3(\text{SeO}_3)_2$	$\text{KD}_3(\text{SeO}_3)_2$
$\text{O}(2)\cdots\text{O}'(2)$	2.566(1)	2.580(2)
$\text{O}(2)\cdots\text{H}'(2)$	1.529(6)	1.562(4)
$\angle\text{O}(2)-\text{H}(2)\cdots\text{O}'(2)$	171.1(4)	170.2(3)
$\text{O}(3)\cdots\text{O}'(1)$	2.602(2)	2.623(2)
$\text{O}(1)\cdots\text{H}'(1)$	1.575(3)	1.621(2)
$\angle\text{O}(3)-\text{H}(1)\cdots\text{O}'(1)$	175.2(2)	176.0(2)

distances found for H_2SeO_3 , but there is good agreement with the distances and angles found for $\text{NaH}_3(\text{SeO}_3)_2$, where $\text{O}(1)\cdots\text{O}'(1)$ is 2.602 Å, $\angle\text{O}(1)-\text{H}(1)\cdots\text{O}'(1)$ (disordered hydrogen) is 170° , $\text{O}(2)\cdots\text{O}(3)$ is 2.556 Å and $\angle\text{O}(2)-\text{H}(2)-\text{O}(3)$ is 176.1° . However, for $\text{NaH}_3(\text{SeO}_3)_2$ the distance involving the disordered hydrogen (H(1)) is the longest, and the shortest $\text{O}\cdots\text{O}$ distance has the hydrogen atom H(2) very near the centre of the bond which is not the case for any of the hydrogen atoms in $\text{KH}_3(\text{SeO}_3)_2$.

Table 7. Intramolecular distances, in Å, corrected for thermal motion,²⁰ the light atom riding on the heavy atom.

	$\text{KH}_3(\text{SeO}_3)_2$	$\text{KD}_3(\text{SeO}_3)_2$
Se—O(1)	1.668(1)	1.666(1)
Se—O(2)	1.721(1)	1.724(1)
Se—O(3)	1.742(1)	1.743(1)
O(2)—H(2)	1.050(5)	1.030(3)
O(3)—H(1)	1.035(3)	1.005(2)

The correlation between the O—H distances and the $\text{O}\cdots\text{O}$ distances is in agreement with that found for other $\text{O}-\text{H}\cdots\text{O}$ bonds, as for example given by Hamilton and Ibers.¹⁹

Table 8. Changes in atomic coordinates (Tables 2 and 3) by the substitution of hydrogen by deuterium. Δ_i is the difference in Å between the *i*-coordinate for the deuterated compound and the *i*-coordinate for the non-deuterated compound. Δ is the total shift in Å. The origin of the unit cell for this calculation is at the selenium atom and all atoms belong to the same molecule.

	Δ_x	Δ_y	Δ_z	Δ
O(1)	-0.002(1)	0.003(1)	0.007(2)	0.008
O(2)	0.005(1)	-0.007(2)	0.009(2)	0.012
O(3)	0.009(2)	-0.006(2)	-0.006(2)	0.012
D,H(1)	0.019(3)	-0.030(3)	-0.008(3)	0.036
D,H(2)	0.019(6)	0.002(5)	0.022(11)	0.029

Table 10. Observed and calculated structure amplitudes for $KD_3(SeO_3)_2$.

h k l	F_o	$ F_c $	1 2	22.6	21.8	10 2 1	95.3	56.0	11 3 0	22.5	21.5	2 3 8	35.0	34.9	7 3 0	71.6	71.2	7 6 2	14.3	14.9	
2 0 0	10.3	10.7	10 1 2	6.1 2	23.0	25.5	11 2 1	5.9	6.0	13 3 0	46.1	67.8	4 3 8	27.4	28.6	9 5 0	35.4	44.1	8 6 2	16.6	16.6
4 0 0	48.9	49.5	13 1 2	6.1 2	17.3	18.3	12 2 1	9.2	9.0	15 3 0	16.2	16.9	5 8 0	12.0	17.8	13 5 0	16.3	16.8	6 6 2	12.7	12.7
6 0 0	16.2	16.3	14 1 2	10.3	9.4	19 2 1	38.9	32.0	17 3 0	14.4	14.5	0 4 0	76.6	76.7	13 5 0	9.1	4.0	10 6 2	19.6	19.5	
8 0 0	10.3	10.7	15 1 2	12.9	13.0	17 2 1	9.3	9.5	19 3 0	13.1	11.8	2 4 0	35.0	34.9	15 5 0	96.0	96.4	11 6 2	44.3	44.6	
10 0 0	5.3	7.3	19 1 2	14.9	14.8	18 2 1	7.8	7.9	21 3 0	11.1	15.4	4 4 0	20.2	20.9	17 5 0	10.4	10.2	12 6 2	20.1	21.8	
12 0 0	22.0	20.9	16 1 2	32.7	33.2	20 2 1	31.7	31.2	3 3 1	38.4	39.4	6 4 0	33.1	32.3	1 5 1	26.3	26.3	13 6 2	8.5	5.7	
14 0 0	55.5	56.1	18 1 2	14.9	14.8	20 2 1	11.0	12.7	4 3 1	10.8	10.4	12 4 0	10.8	10.4	2 5 1	20.8	22.0	15 6 2	8.1	7.4	
16 0 0	9.1	9.1	19 1 2	15.4	15.3	21 2 1	11.3	12.2	5 3 1	15.9	15.8	14 4 0	24.2	24.1	3 5 1	15.6	15.6	16 6 2	20.1	19.4	
18 0 0	41.4	41.0	20 1 2	39.8	20.1	0 2 2	52.4	52.9	6 3 1	32.0	32.9	16 4 0	25.2	24.1	4 5 1	22.3	27.5	3 6 3	16.8	16.2	
20 0 0	34.9	33.8	1 1 3	25.4	22.3	1 2 2	3.2	0.6	7 3 1	23.5	23.5	18 4 0	24.4	23.9	7 5 1	4.7	4.1	4 6 3	5.5	4.8	
22 0 0	67.9	67.1	2 1 3	14.1	14.7	2 2 2	7.6	6.2	8 3 1	37.4	39.1	20 4 0	7.6	8.5	8 5 1	19.0	20.3	5 6 3	7.3	7.0	
0 2 0	17.0	16.8	3 1 3	45.5	11.3	3 2 2	21.8	22.4	9 3 1	12.2	12.6	0 1 1	45.1	44.9	10 5 1	10.8	20.6	6 6 3	27.4	27.3	
1 0 2	23.1	24.0	4 1 3	48.3	47.9	4 2 2	33.0	32.8	10 3 1	53.5	54.3	1 1 1	24.7	23.3	11 5 1	15.7	16.0	7 6 3	9.5	7.0	
2 0 2	43.7	42.6	5 1 3	8.2	8.2	5 2 2	21.9	22.2	11 3 1	22.5	22.6	2 1 1	4.2	3.0	12 5 1	14.4	14.1	8 6 3	31.5	30.9	
3 0 2	25.2	25.4	6 1 3	32.1	32.4	6 2 2	52.4	52.8	12 3 1	32.0	32.9	3 1 1	26.5	21.8	13 5 1	13.5	23.8	9 6 3	10.5	8.6	
4 0 2	18.8	17.4	7 1 3	63.5	62.5	7 2 2	13.9	13.7	13 3 1	6.2	5.5	4 1 1	40.6	41.2	14 5 1	13.1	12.5	10 6 3	28.8	26.3	
5 0 2	67.4	66.4	8 1 3	45.5	46.8	8 2 2	15.2	14.7	14 3 1	19.0	20.2	5 1 1	14.2	15.4	15 5 1	9.6	8.5	11 6 3	26.1	25.7	
6 0 2	41.7	41.6	9 1 3	53.7	53.5	9 2 2	20.9	21.1	15 3 1	16.6	16.5	6 1 1	36.1	39.1	16 5 1	17.2	25.9	12 6 3	17.8	18.2	
7 0 2	50.3	50.3	10 1 3	7.4	6.7	10 2 2	34.6	33.9	16 3 1	10.8	9.4	7 1 1	17.7	18.1	17 5 1	17.2	16.7	13 6 3	15.4	16.1	
8 0 2	36.9	36.9	11 1 3	26.2	26.2	11 2 2	44.8	45.4	17 3 1	37.6	38.2	8 1 1	38.8	39.1	18 5 1	8.0	6.3	14 6 3	36.9	36.1	
9 0 2	84.8	84.8	12 1 3	24.1	11.0	12 2 2	38.4	39.3	18 3 1	21.8	22.1	9 1 1	7.9	5.8	19 5 1	15.8	16.0	15 6 3	16.2	15.5	
10 0 2	23.3	24.3	13 1 3	46.6	46.4	13 2 2	15.4	15.3	19 3 1	10.2	9.5	10 1 1	42.1	42.2	2 5 2	65.7	65.5	16 6 3	30.1	30.4	
11 0 2	12.2	12.4	14 1 3	25.9	27.0	14 2 2	10.2	8.4	20 3 1	3.7	4.7	11 1 1	26.0	26.9	3 5 2	45.6	44.6	17 6 3	22.9	23.4	
12 0 2	39.5	39.5	15 1 3	27.3	27.8	15 2 2	5.1	5.5	21 3 1	17.4	18.4	12 1 1	37.3	37.9	4 5 2	7.7	7.3	18 6 3	14.7	15.2	
13 0 2	43.3	44.0	16 1 3	27.0	28.0	16 2 2	2.2	2.0	1 3 2	35.7	36.6	13 1 1	30.9	30.9	5 5 2	9.5	9.2	19 6 3	17.6	17.7	
14 0 2	68.8	69.2	17 1 3	32.5	33.1	17 2 2	14.4	14.2	2 3 2	6.3	6.6	14 1 1	12.6	11.4	6 5 2	13.5	12.8	20 6 3	33.5	33.0	
15 0 2	17.2	18.3	18 1 3	22.3	22.4	18 2 2	22.3	22.3	3 3 2	37.7	35.4	15 1 1	16.1	16.1	7 5 2	10.7	10.8	21 6 3	15.2	15.5	
16 0 2	21.0	22.7	19 1 3	17.3	17.8	0 2 3	84.6	86.9	4 3 2	57.3	58.0	16 1 1	24.1	24.8	8 5 2	36.8	36.8	22 6 3	45.4	45.2	
17 0 2	39.0	39.8	20 1 3	24.1	25.0	1 2 3	7.2	4.0	5 3 2	7.3	6.8	18 1 1	6.3	5.3	9 5 2	32.9	33.1	9 6 4	8.4	8.2	
18 0 2	17.2	18.3	21 1 3	11.4	11.4	2 2 3	24.5	24.5	6 3 2	17.4	17.4	19 1 1	15.5	15.5	10 5 2	10.5	10.5	10 6 4	17.3	15.5	
19 0 2	25.7	27.3	22 1 3	13.3	13.2	3 2 3	21.5	22.0	7 3 2	22.1	23.1	0 1 2	6.0	6.0	11 5 2	22.7	22.8	11 6 4	11.9	11.9	
20 0 2	36.0	35.5	23 1 3	10.5	7.8	4 2 3	24.0	24.2	8 3 2	3.9	3.0	2 1 2	13.9	14.0	12 5 2	9.9	9.1	12 6 4	15.8	17.3	
21 0 2	5.6	5.5	4 1 4	11.3	11.5	5 1 3	10.7	11.6	9 3 2	19.0	18.6	3 2 2	28.9	29.7	13 5 2	50.5	49.9	13 6 4	27.4	28.5	
2 0 4	45.5	46.1	6 1 4	19.4	22.5	6 2 3	22.5	23.3	11 3 2	20.5	20.9	4 2 2	36.2	35.2	1 3 3	3.0	1.7	2 6 5	16.7	16.8	
2 0 4	3.3	3.7	7 1 4	19.8	20.5	6 3 3	41.5	41.7	12 3 2	17.9	18.4	4 2 2	12.8	12.9	2 3 3	12.7	14.3	4 6 5	21.7	22.7	
3 0 4	50.9	50.9	8 1 4	24.5	24.5	7 2 3	35.4	35.3	13 3 2	13.8	13.8	5 2 2	10.2	10.2	3 3 3	3.0	3.0	5 6 5	10.5	10.5	
4 0 4	10.6	9.6	9 1 4	40.1	39.9	10 2 3	32.9	40.1	14 3 2	5.7	5.1	9 2 2	18.3	18.5	4 3 3	5.5	1.3	6 6 5	19.0	17.9	
4 0 4	92.9	93.4	10 1 4	30.3	31.2	11 1 3	24.2	25.9	15 3 2	33.8	33.9	10 4 2	12.6	12.9	5 3 3	10.5	9.9	7 6 5	20.8	21.8	
5 0 4	87.7	87.2	11 1 4	13.7	14.2	12 2 3	15.7	15.5	16 3 2	38.1	38.1	11 4 2	36.3	38.8	6 3 3	11.5	15.3	8 6 5	27.6	28.6	
6 0 4	63.5	63.5	13 1 4	16.1	15.9	13 2 3	6.1	6.5	18 3 2	49.1	48.0	12 4 2	14.7	13.8	7 3 3	31.6	31.2	9 6 5	27.6	28.3	
7 0 4	49.3	49.0	14 1 4	11.3	10.9	14 2 3	4.3	4.3	19 3 2	24.5	24.8	13 4 2	26.8	26.2	8 3 3	6.2	6.6	10 6 5	5.9	5.9	
8 0 4	8.4	8.4	15 1 4	23.3	23.3	15 2 3	20.6	20.6	20 3 2	34.7	34.7	14 4 2	26.8	26.2	9 3 3	27.6	28.0	11 6 5	31.7	31.7	
10 0 4	27.1	27.0	17 1 4	30.1	30.2	16 2 3	22.8	23.6	2 3 3	23.8	22.5	15 4 2	27.7	22.2	10 3 3	8.1	6.5	1 6 6	27.0	27.4	
11 0 4	39.4	39.7	18 1 4	20.4	20.9	17 2 3	29.0	28.7	3 3 3	43.3	43.8	16 4 2	26.3	25.3	11 3 3	13.2	11.1	3 6 6	4.7	5.1	
12 0 4	48.2	48.2	19 1 4	28.5	28.5	18 2 3	19.5	19.5	4 3 3	37.0	38.5	17 4 2	17.0	16.8	12 3 3	13.6	13.6	4 6 6	13.8	13.8	
13 0 4	14.2	14.2	20 1 4	6.9	6.5	19 2 3	34.7	34.1	5 3 3	42.8	43.6	18 4 2	10.8	11.1	13 3 3	4.0	2.6	5 6 6	27.4	26.9	
14 0 4	16.3	17.0	21 1 4	39.1	39.3	20 2 3	35.3	34.8	7 3 3	4.9	3.5	0 1 3	54.2	54.6	14 3 3	13.9	13.6	7 6 6	4.6	5.0	
15 0 4	50.1	50.1	22 1 4	45.7	45.7	21 2 3	18.1	18.1	8 3 3	8.8	7.7	1 1 3	1.4	1.4	15 3 3	16.6	16.6	8 6 6	21.6	22.8	
16 0 4	22.9	22.7	23 1 4	12.5	12.3	22 2 3	31.7	31.9	9 3 3	15.9	15.6	2 1 3	18.0	17.5	1 1 4	16.6	16.1	9 6 6	5.0	5.0	
17 0 4	8.6	8.6	6 1 5	42.4	43.7	2 2 4	23.4	24.9	10 3 3	5.7	1.7	3 1 3	13.6	14.2	2 2 4	9.3	9.3	7 7 6	7.0	6.8	
19 0 4	46.1	46.1	7 1 5	19.5	19.5	3 2 4	7.7	6.1	11 3 3	29.2	29.8	4 1 3	17.9	17.8	3 2 4	37.9	38.0	8 7 6	10.7	10.7	
20 0 4	19.7	20.4	8 1 5	16.1	15.4	4 2 4	12.9	13.5	13 3 3	5.0	4.6	5 1 3	32.9	34.1	4 1 4	9.6	8.0	13 7 6	6.7	6.1	
0 0 6	46.1	47.3	9 1 5	9.6	9.4	5 2 4	17.1	16.2	14 3 3	8.2	8.2	6 1 3	31.4	31.6	7 5 4	23.5	22.8	1 7 1	10.9	10.9	
1 0 6	46.5	47.6	10 1 5	22.1	22.1	6 2 4	8.5	7.9	15 3 3	19.2	19.2	7 2 4	16.7	16.7	8 5 4	7.2	7.2	2 7 7	17.3	17.3	
2 0 6	9.4	7.3	13 1 5	22.1	23.0	7 2 4	6.0	1.4	16 3 3	23.4	22.3	8 1 3	10.5	10.1	9 5 4	39.7	40.2	3 7 1	51.1	50.9	
3 0 6	38.8	38.2	14 1 5	5.7	5.7	8 2 4	21.0	21.2	17 3 3	19.3	19.2	10 1 3	7.7	8.3	10 4 4	26.3	29.3	4 7 1	17.9	17.9	
4 0 6	8.7	8.7	15 1 5	11.4	11.4	9 2 4	12.0	11.6	18 3 3	7.6	7.2	11 1 3	10.2	10.2	11 4 4	17.3	17.3	5 7 1	17.0	16.2	
5 0 6	13.0	12.8	16 1 5	41.8	40.8	10 2 4	17.2	17.5	19 3 3	9.5	9.0	12 1 3	6.2	3.8	12 5 4	48.2	46.8	6 7 1	4.0	4.5	
6 0 6	13.4	15.4	17 1 5	13.5	15.5	11 2 4	3.8	3.1	1 3 4	10.6	8.9	14 1 3	61.0	60.0	13 5 4	25.8	25.5	7 7 1	23.1	23.0	
7 0 6	13.7</																				

$KH_3(SeO_3)_2$ and $KD_3(SeO_3)_2$. When hydrogen is substituted by deuterium the oxygen-hydrogen bonds are expected to become shorter (see, for example, Ref. 19). This will alter the hydrogen bond system, the selenite group, SeO_3 , may move a little and the thermal movements of the atoms may be influenced. However, the configuration of the selenite group should be nearly unaltered and this is seen to be the case (Tables 4 and 7). According to the correlation mentioned previously between the Se—O distance and the corresponding O—H distance (Fig. 2), Se—O(1) should decrease as O(1)···D(3) increases whereas Se—O(2) and Se—O(3) should increase, as O(2)—D(2) and O(3)—D(1) decreases. This is observed, but the shifts are very small. The potassium-oxygen distances are unaltered, too, and the reorientation seems therefore to be done under the condition of fixed configuration for the selenite group and fixed K—O distances.

The shifts along the crystal axis for going from the hydrogen containing compound to the deuterium containing compound are given in Table 8 for the oxygen and the hydrogen atoms together with the total shifts. The origin of the unit cell for this calculation is at the selenium atom. In all cases, the direction of the shift is near the direction of the hydrogen bond and the orientation of the shift is so that O···H distances are increased and O—H distances are decreased (Tables 4 and 6).

The changes in the distances between the hydrogen bonded oxygen atoms are 0.014 (2) Å for O(2)···O(2) and 0.021 (3) Å for O(3)···O(1), and changes in the corresponding molecular oxygen-hydrogen distances are 0.018 (8) Å for O(2)—H(2) and 0.026 (4) Å for O(3)—H(1), so the main distances in the two hydrogen bonds agree within two standard deviations. The O(2)···O(2) hydrogen bond has a component in the x and z direction, and the O(3)···O(1) bond has a component in the x and the y direction, so we would expect the unit cell changes to be biggest for the a -axis, as found. Because of the small reorientation of the selenite group, it is, however, not possible in a simple way to calculate the net effect for the change in unit cell dimensions.

The agreement between the temperature factors is good. We define as before a scale factor between the two sets of selenium, potassium and oxygen temperature factor as $K_u = \sum |u_{ij}^D| / \sum |u_{ij}^H|$ and an R factor as $R_u = \sum |K_u| |u_{ij}^H| - |u_{ij}^D| / \sum |u_{ij}^D|$. K_u is found to be 1.04 and $R_u = 0.044$ which compares well with the mean relative error ($\sum \sigma(u_{ij}^D) / \sum |u_{ij}^D|$) of 0.032. The thermal movements for the deuterium atoms are somewhat smaller than for the corresponding hydrogen atoms. The only drastic change is for the u_{33} for D(2).

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