

variations in length of the hydrogen bridges involving the ordered H atoms (*AC*, Table 4). On the basis of well known O—H *vs* O...O correlations, H(1),...,H(6) are, therefore, expected to move slightly along the corresponding *W*—H direction; in fact, this secondary type of disorder is witnessed by the thermal motion which is systematically larger for H(1),...,H(6) than for the other H atoms.

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Neutron Diffraction Refinement of Paraelectric CsH₃(SeO₃)₂

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The crystal structure of the paraelectric phase of caesium trihydrogenselenite has been refined with a three-dimensional set of single-crystal neutron diffraction data. The crystals are triclinic, space group *P*1, with two formula units in a cell of dimensions: $a = 9.3474$ (5), $b = 6.5398$ (4), $c = 5.8498$ (3) Å, $\alpha = 91.443$ (6), $\beta = 105.336$ (6), and $\gamma = 91.629$ (6)°. A full-matrix least-squares refinement based on *F* gave a final *R* value of 0.032. The structure consists of H₂SeO₃ molecules and HSeO₃⁻ ions hydrogen-bonded together to form chains by means of four different hydrogen bonds all crossing centres of symmetry. This situation results in disordered half-occupied H positions. A fifth disordered hydrogen bond without symmetry restrictions interlinks the two types of chains to form a three-dimensional network. The refinement indicates that the occupancies of the two possible H sites in this bond are 0.68 and 0.32.

Introduction

Caesium trihydrogenselenite undergoes a transition to an antiferroelectric phase at -128°C, as reported by Makita (1965). It is quite common, in the paraelectric phase of hydrogen-bonded ferro- or antiferroelectric crystals, for the H atoms to be disordered. A well-known example is the KDP family of ferroelectrics. In the paraelectric phase the H bonds often cross some

symmetry element such as an inversion centre, necessitating that the H atom be either located at the centre of symmetry or disordered in half-occupied positions. The latter assumption is normally the more reasonable, especially for hydrogen bonds longer than 2.5 Å. It was shown in a previous X-ray diffraction study of CsH₃(SeO₃)₂ (Tellgren & Liminga, 1974a) that four of the five hydrogen bonds cross centres of symmetry, with the H atoms disordered over the two sites of a double-minimum well. The remaining hydrogen bond has no symmetry restrictions imposed, however. The X-ray study indicated that this bond is

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also disordered, and furthermore that the H atoms are unequally distributed over the two possible sites. This observation was in conflict with the result of a preliminary two-dimensional neutron diffraction study by Sato (1972), who reported that this bond was ordered. In order to resolve this ambiguity it was decided to refine the structure of CsH₃(SeO₃)₂ with a three-dimensional set of neutron diffraction data.

Experimental

Crystals were grown from a saturated aqueous solution of Cs₂CO₃ and SeO₂ by slow evaporation at room temperature. The crystal used for the data collection had a volume of 31.3 mm³. The crystal had six boundary planes, ±(100), ±(110) and ±(001), with interplanar spacings of 1.80, 4.13 and 4.12 mm respectively. The unit-cell dimensions used were those reported earlier (Tellgren & Liminga, 1974a) and given in Table 1 together with other crystallographic data.

The intensity data were collected at the Swedish Atomic Energy R2 reactor at Studsvik, on a Hilger & Watts four-circle diffractometer controlled by a PDP-8 computer. The neutron flux at the specimen was 1.26 × 10⁶ n cm⁻² s⁻¹ at a wavelength of 1.210 Å.

Table 1. *Crystal data at 25 °C for CsH₃(SeO₃)₂*

Numbers in parentheses here and throughout the paper give the estimated standard deviations of the least significant digits.

Formula	CsH ₃ (SeO ₃) ₂
FW	289.846
Crystal system	Triclinic
Space group	P1
<i>a</i>	9.3474 (5) Å
<i>b</i>	6.5398 (4)
<i>c</i>	5.8498 (3)
α	91.443 (6) ^o
β	105.336 (6)
γ	91.629 (6)
<i>V</i>	344.53 Å ³
<i>D</i>	3.76 g cm ⁻³
μ_{obs}	0.82 cm ⁻¹

Table 2. *Final unweighted and weighted R values*

$$R(F) = \frac{\sum (|F_o| - |F_c|) / \sum |F_o|}{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2}^{1/2}$$

$$R_w(F) = \frac{\sum w(|F_o| - |F_c|) / \sum |F_o|}{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2}^{1/2}$$

$$S = \left[\frac{\sum w(|F_o| - |F_c|)^2}{(\text{NO} - \text{NV})} \right]^{1/2}$$

where NO is the number of observations, NV the number of parameters varied. *n* is the number of parameters refined; *m* is the number of reflexions with non-zero weight.

Refined model	<i>n</i>	<i>m</i>	<i>S</i>	<i>R(F)</i>	<i>R_w(F)</i>
1	137	1809	1.96	3.20	4.08
2	137	1809	1.61	3.16	3.65
3	128	1808	2.23	3.67	4.68

2079 independent reflexions with $\sin \theta / \lambda < 0.693$ were collected at room temperature with an ω step-scan technique. Of these, 270 had intensities less than $3\sigma_{\text{count}}$ and were given zero weight in the refinements. Three standard reflexions were measured at regular intervals to provide a check on the stability of the experiment. Only small random fluctuations were observed. The intensities were corrected for background according to the method of Lehmann & Larsen (1974). The intensities were then reduced to observed structure factors after correction for Lorentz and absorption effects. The experimentally determined linear absorption coefficient $\mu = 0.82 \text{ cm}^{-1}$ corresponds to an incoherent scattering cross-section for H of 36.3 barns. The transmission factors varied between 0.71 and 0.94.

Refinement

The structure was refined with the full-matrix least-squares program UPALS (Lundgren, 1976),* minimizing $\sum w(|F_o| - |F_c|)^2$. The refinement started with the X-ray-determined positional parameters given by Tellgren & Liminga (1974a), and with assumed isotropic temperature factors, which after a few cycles of refinement were converted to anisotropic for further refinement. An isotropic model (Coppens & Hamilton, 1970) was used to correct for the moderately strong secondary extinction effects. About 13% of the reflexions were corrected by more than 20% and two reflexions by more than a factor of two. Each reflexion was assigned a weight $w = 1/\sigma^2(F)$, where $\sigma^2(F) = \sigma^2(F^2)_{\text{count}}/4F^2 + K^2$, and *K* was empirically chosen as 0.015*F* for $F \geq 1.5$ on an absolute scale, and 0.015(3.0 - *F*) for all other *F* values.

* All computer programs used are described in this report.

Table 3. *Atomic coordinates (× 10⁵; for H × 10⁴) for model 2 in CsH₃(SeO₃)₂*

	<i>x</i>	<i>y</i>	<i>z</i>
Cs	83884 (12)	23298 (16)	89073 (20)
Se(1)	21390 (7)	25648 (10)	59247 (12)
Se(2)	52845 (7)	24999 (10)	18862 (12)
O(1)	15393 (11)	26063 (16)	28549 (18)
O(2)	13300 (15)	2888 (18)	63388 (25)
O(3)	9928 (14)	42605 (19)	66614 (21)
O(4)	48467 (15)	1545 (15)	27668 (26)
O(5)	59459 (12)	38031 (16)	45347 (18)
O(6)	36030 (12)	34863 (17)	8263 (18)
H(1)	2386 (4)	2904 (6)	2152 (7)
H(2)	286 (5)	95 (11)	5266 (12)
H(3)	252 (5)	4826 (10)	5284 (11)
H(4)	4991 (9)	130 (13)	4541 (10)
H(5)	5138 (14)	4728 (13)	3890 (20)
H(6)	2851 (10)	3040 (14)	1735 (18)

As reported in the X-ray study (Tellgren & Liminga, 1974*a*), there exist five different hydrogen bonds in the structure. Four of these link the H_2SeO_3 molecules and $HSeO_3^-$ ions to form chains across centres of symmetry, whereas no symmetry restrictions are imposed on the fifth bond which serves to interlink the two types of chains. A difference Fourier synthesis based on the non-hydrogen atoms resulted in elongated negative regions along the $O\cdots O$ bonds, indicating either fully occupied H positions with large thermal motion along the bond or, more likely, disordered half-occupied H sites. The proton density along the $O(1)\cdots O(6)$ bond (without symmetry restriction) was asymmetric and displaced from the centre of the bond towards O(1). In the first series of refinements (model 1) it was assumed that all H atoms were located in half-occupied positions. This resulted in expected O—H distances of 1.00–1.04 Å for the four hydrogen bonds crossing centres of symmetry. These distances are in agreement

with predicted values for 2.55–2.58 Å $O\cdots O$ bonds, as indicated in correlation curves of O—H vs $O\cdots O$ distances (Lundgren, 1974). The $O(1)$ —H(1) and $O(6)$ —H(6) distances in the fifth hydrogen bond were 0.96 and 1.17 Å, respectively; *i.e.* outside the expected values for an $O\cdots O$ bond of 2.58 Å. This observation, together with the observed asymmetry in the difference Fourier density along this bond, indicated that the disorder in this H position is not of the 50–50% type. This situation was already predicted in the X-ray study (Tellgren & Liminga, 1974*a*). Considerable correlation difficulties prevented the refinement of the occupation numbers (α) of H(1) and H(6). A series of refinements (model 2) were made, with variation of the same parameters as earlier, with $\alpha[H(1)] = 0.60, 0.65, 0.68, 0.70, 0.80$ and the constraint that $\alpha[H(1)] + \alpha[H(6)] = 1.00$. The lowest R value was obtained for $\alpha[H(1)] = 0.68$, and $\alpha[H(6)] = 0.32$, which also resulted in the expected O—H distances of about 1.00 Å. The R values and related information for both models are presented in Table 2. The hypothesis that model 1 describes the situation better than model 2 can be rejected at the 0.5% significance level by comparison of experimental and calculated R -value ratios (Hamilton, 1965). A third model was tried, where the H atoms in the bonds across inversion centres were treated as previously, but the H atom in $O(1)\cdots O(6)$ was assumed to fully occupy a single-minimum potential well. This resulted in an O—H distance of 1.09 Å and a thermal ellipsoid with a very large component along the $O\cdots O$ bond. This model could be rejected in favour of model 2 by use of a significance test as described above.

The final agreement between F_o and F_c was checked by computing the δR normal probability plot (Abrahams & Keve, 1971). The plot was close to linear, except for a few data points at the ends, with the slope of the least-squares line 1.33 and an intercept of 0.05.

The coherent scattering amplitudes used were those compiled by Bacon (1972). The final parameters corresponding to model 2 are given in Table 3 and bond distances and angles in Table 4.*

Table 4. *Interatomic distances (Å) and angles (°) in $CsH_3(SeO_3)_2$*

A prime indicates an atom outside the asymmetric unit.

Ionic bonds

Cs—O(1)	3.223 (1)	Cs—O(4)	3.308 (2)
Cs—O(2)	3.281 (2)	Cs—O(5)	3.123 (2)
Cs—O(3)	3.270 (2)	Cs—O(6)	3.342 (2)
Cs—O(3)	3.278 (2)	Cs—H(1)	3.217 (4)
		Cs—H(6)	3.229 (9)

Covalent bonds

O—Se—O	O—Se	Se—O	$\angle O$ —Se—O
O(1)—Se(1)—O(2)	1.735 (1)	1.702 (1)	99.06 (7)
O(1)—Se(1)—O(3)	1.735 (1)	1.689 (1)	100.22 (6)
O(2)—Se(1)—O(3)	1.702 (1)	1.689 (1)	101.92 (7)
O(4)—Se(2)—O(5)	1.703 (1)	1.705 (1)	101.79 (7)
O(4)—Se(2)—O(6)	1.703 (1)	1.683 (1)	102.33 (7)
O(5)—Se(2)—O(6)	1.705 (1)	1.683 (1)	102.52 (6)

Hydrogen bonds

O—H \cdots O	O—H	H \cdots O	$O\cdots O$
O(1)—H(1) \cdots O(6)	1.000 (4)	1.581 (4)	2.577 (1)
O(6)—H(6) \cdots O(1)	1.028 (9)	1.558 (9)	2.577 (1)
O(2)—H(2) \cdots O(2)'	1.013 (5)	1.563 (5)	2.576 (3)
O(3)—H(3) \cdots O(3)'	1.000 (6)	1.543 (5)	2.539 (2)
O(4)—H(4) \cdots O(4)'	1.011 (6)	1.558 (6)	2.566 (3)
O(5)—H(5) \cdots O(5)'	1.040 (11)	1.511 (11)	2.529 (2)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33052 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4 (cont.)

Se—O—H \cdots O—Se	\angle Se—O—H	\angle O—H \cdots O	\angle H \cdots O—Se
Se(1)—O(1)—H(1) \cdots O(6)—Se(2)	111.2 (2)	174.0 (4)	116.4 (2)
Se(1)—O(2)—H(2) \cdots O(2)′—Se(1)′	112.0 (4)	177.7 (7)	114.3 (3)
Se(1)—O(3)—H(3) \cdots O(3)′—Se(1)′	114.7 (3)	174.0 (5)	120.2 (2)
Se(2)—O(4)—H(4) \cdots O(4)′—Se(2)′	112.0 (5)	173.8 (8)	118.1 (3)
Se(2)—O(5)—H(5) \cdots O(5)′—Se(2)′	110.7 (6)	175.7 (10)	113.7 (5)
Se(2)—O(6)—H(6) \cdots O(1)—Se(1)	113.1 (5)	170.8 (9)	111.7 (4)

Discussion

Neutron diffraction studies of all alkali trihydrogen-selenites have now been reported. It has been confirmed that all these structures contain hydrogen-bonded chains of HSeO_3^- ions and H_2SeO_3 molecules cross-linked by means of further hydrogen bonds from the selenite molecules. The $\text{O}-\text{H}\cdots\text{O}$ bonds are moderately strong, $2.52\text{--}2.65$ Å, with $\text{O}-\text{H}$ distances in the range of $1.00\text{--}1.05$ Å. These values are found to follow the general correlation of $\text{O}-\text{H}$ vs $\text{O}\cdots\text{O}$ distances reported in a large number of compounds (Lundgren, 1974).

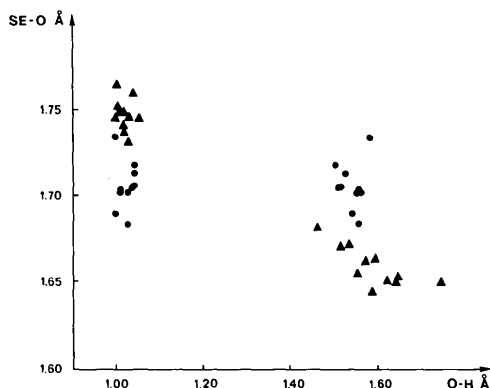


Fig. 1. The Se—O distance vs O—H or $\text{H}\cdots\text{O}$ distance in $\text{O}-\text{H}\cdots\text{O}$ bonds, where O is bonded to Se. Triangles indicate bonds with ordered H positions; circles denote disordered cases. The structures included are: H_2SeO_3 (Larsen, Lehmann & Sætofte, 1971); $\text{LiH}_3(\text{SeO}_3)_2$ (Tellgren & Liminga, 1972; two H bonds omitted, see text); $\text{NaH}_3(\text{SeO}_3)_2$ (Chomnilpan *et al.*, 1977); $\text{KH}_3(\text{SeO}_3)_2$ (Lehmann & Larsen, 1971); $\text{RbH}_3(\text{SeO}_3)_2$ (Tellgren & Liminga, 1977); $\text{CsH}_3(\text{SeO}_3)_2$ (present study); $\text{NH}_4\text{H}_3(\text{SeO}_3)_2$ (Tellgren & Liminga, 1974b).

Disorder has been reported for the H atoms in the RT phases of $\text{NaH}_3(\text{SeO}_3)_2$ (Chomnilpan, Tellgren & Liminga, 1977), $\text{KH}_3(\text{SeO}_3)_2$ and $\text{KD}_3(\text{SeO}_3)_2$ (Lehmann & Larsen, 1971) and $\text{CsH}_3(\text{SeO}_3)_2$ (present study). One of the H atoms in the ferroelectric RT phase of $\text{LiH}_3(\text{SeO}_3)_2$ (Tellgren & Liminga, 1972) also appeared as disordered, but this could be attributed to the use of a multidomain crystal. The O atoms are also involved in the disorder of the H atoms. A pure Se—O bond is about 1.65 Å, whereas an Se—OH bond is about 1.75 Å. For the disorder cases, a superposition of the two types occurs, resulting in apparent Se—O bonds of about 1.70 Å. A plot of Se—O distances as a function of O—H distances clearly demonstrates the existence of the three groups of Se—O bonds (Fig. 1).

In the present study the Se—OH bonds for those O atoms involved in hydrogen bonds across inversion centres are $1.689\text{--}1.705$ Å, as would be expected for a 50–50% superposition of Se—O and Se—OH bonds. As described above, the refinement indicates that the occupancies of the H(1) and H(6) sites are 0.68 and 0.32, respectively, in the $\text{O}(1)-\text{H}(1)\cdots\text{O}(6)/\text{O}(1)\cdots\text{H}(6)-\text{O}(6)$ bond, free from symmetry restrictions. This would result in Se—O bonds closer to the values for the pure Se—O and Se—OH bonds, in agreement with the observed distances of 1.735 and 1.683 Å (Table 4). The results of the present study are in excellent agreement with the previous X-ray study (Tellgren & Liminga, 1974a). It was somewhat surprising in the X-ray case that, in the presence of atoms as heavy as Cs and Se, it was possible to locate and refine half-hydrogen atoms. The 68–32% disorder in the $\text{O}(1)\cdots\text{O}(6)$ hydrogen bond was inferred in the X-ray study and is confirmed here. This observation is in disagreement with the result of Sato (1972), who, on the basis of two-dimensional neutron diffraction data, reported an ordered $\text{O}(1)\cdots\text{O}(6)$ hydrogen bond. It

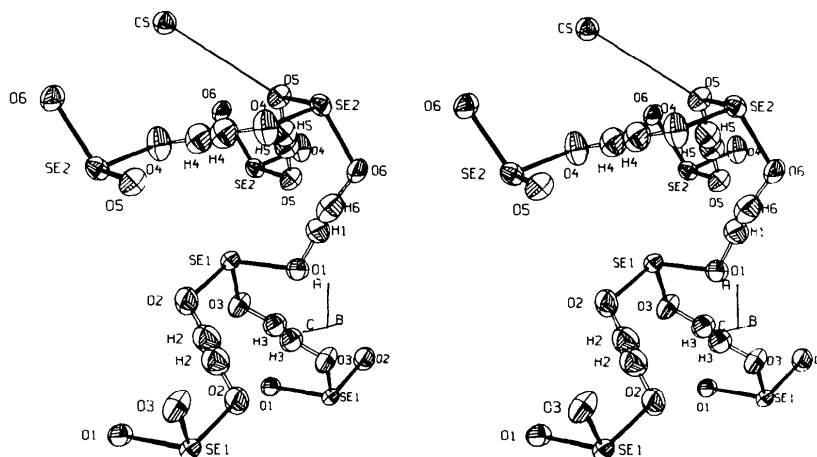


Fig. 2. A stereoscopic illustration of the disordered hydrogen-bond scheme. The ellipsoids are scaled to include 50% probability.

should be pointed out, however, that the disorder may vary from crystal to crystal, although this has not been the case in our studies. Disorder of a similar nature with unequal distribution of H and D atoms over two possible sites has been reported earlier in KHCO_3 and KDClO_3 (Thomas, Tellgren & Olovsson, 1974).

It can thus be concluded that the structure of $\text{CsH}_3(\text{SeO}_3)_2$ can be described as being composed of hydrogen-bonded chains of H_2SeO_3 molecules and HSeO_3^- ions, statistically distributed in opposite directions, resulting in a disordered structure (Fig. 2). There seems, however, to be a preference for the H atom in the $\text{O}(1)\cdots\text{O}(6)$ hydrogen bond to be closer to $\text{O}(1)$ than to $\text{O}(6)$, resulting formally in unequal occupancies of the two possible sites. A reason for this preference may be that H(6) has the two possible H(5) atoms at 2.623 and 2.660 Å, whereas the corresponding distances from H(1) are about 0.2 Å longer. With a van der Waals radius of about 1.2 Å for H, the H(1) position may be energetically more favourable than H(6), resulting in a higher occupancy for H(1). As mentioned above, the structure consists of chains of HSeO_3^- ions and H_2SeO_3 molecules. As a result of the higher occupancy of the H(1) site in the $\text{O}(1)\cdots\text{O}(6)$ bond, the chain containing Se(1) occurs more frequently as the 'molecular' chain. A reasonable assumption might be that, as the paraelectric structure orders to produce the antiferroelectric phase, the Se(1) chain transforms into the H_2SeO_3 chain.

The average angle between the line joining the two disordered H sites and the $\text{O}\cdots\text{O}$ lines is 9° , in agreement with the similar situation in $\text{NaH}_3(\text{SeO}_3)_2$ (Chomnilpan *et al.*, 1977) and KH_2PO_4 (Nelmes & Rouse, 1974).

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