

ing will be larger for the hydrogen-bonded H atoms in view of the larger motion of these atoms in the direction of the N—H bonds.

The X-ray data were collected with the assistance of the Crystallography Group of the University of Göteborg in Sweden. The neutron data were collected with the assistance of Dr F. H. Moore of the Australian Institute of Nuclear Science and Engineering at Lucas Heights in Sydney.

While most of the calculations were carried out on the University of Western Australia's PDP-6 and Cyber 72 computers with programs written by the authors, access to the XRAY system (1972) and the ORTEP plotting program of Johnson (1965) is gratefully acknowledged.

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Neutron Diffraction Refinement of Paraelectric $\text{NaH}_3(\text{SeO}_3)_2$

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A three-dimensional single-crystal neutron diffraction refinement of paraelectric sodium trihydrogen selenite has been made. The crystals are monoclinic, space group $P2_1/n$, with two formula units in a cell of dimensions $a = 10.3428$ (8), $b = 4.8372$ (3), $c = 5.7876$ (3) Å, $\beta = 91.162$ (5)°. A full-matrix least-squares refinement based on F gave a final R value of 0.040. The structure consists of hydrogen-bonded chains of H_2SeO_3 molecules and HSeO_3^- ions. The H atoms are disordered as a result of a statistical superposition of chains running in opposite directions.

Introduction

Sodium trihydrogen selenite has been the subject of a number of NMR and diffraction studies. One previous neutron diffraction study has been reported (Kaplan, Kay & Morosin, 1970; this paper should be consulted for further references). There has been some uncer-

tainty as to whether the H atoms are disordered in double-minimum potential wells or are located in a single-minimum potential. Both types of interpretation of NMR results have been presented (Gavrilova-Podol'skaya, Gabuda & Lundin, 1967; Soda & Chiba, 1969; Blinc & Pirš, 1971; Silvidi & Workman, 1971). Kaplan *et al.* (1970), in their neutron diffraction study, came to the conclusion that one of the H atoms was probably disordered, whereas the other was situated in a shallow skew potential well. In this situation, the

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O—H distances were reported to be 1.24 and 1.31 Å, respectively. This result is in conflict with previous observations. Correlation curves, O—H vs O...O distances, indicate that an O...O hydrogen bond of 2.55 Å should have an O—H length of about 1.03 Å (Lundgren, 1974). It was felt that a refinement based on a good set of neutron diffraction data should resolve this ambiguity.

Experimental

Crystals were grown from an aqueous solution of SeO₂ and Na₂CO₃. The unit-cell dimensions were determined with a Guinier-Hägg XDC powder camera calibrated with silicon. 31 observed θ values were used in the least-squares refinement. Crystallographic data are given in Table 1.

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 experimental set-up at Studsvik is described elsewhere (Tellgren, Ramanujam & Liminga, 1974). The neutron flux at the specimen was 1.26×10^6 n cm⁻² s⁻¹ at a wavelength of 1.210 Å.

The crystal used for the data collection had a volume of 28.1 mm³. 852 independent reflexions with $\sin \theta/\lambda$ up to 0.693 Å⁻¹ were collected with the ω step-scan technique. Of these, 95 had intensities less than $2\sigma_{\text{count}}$ and were given zero weight in the refinements. Three standard reflexions, measured at regular intervals during the experiment, showed only the variations expected from counting statistics. The intensities were corrected for Lorentz and absorption effects. The experimentally determined linear absorption coefficient $\mu = 1.25$ cm⁻¹ corresponds to an incoherent scattering cross-section for H of 54.4 b. The transmission factors varied between 0.673 and 0.797.

Refinement

The structure was refined, starting with the parameters given by Kaplan *et al.* (1970), by minimizing $\sum w(|F_o| - |F_c|)^2$ with the full-matrix least-squares program *UPALS*.^{*} Each reflexion was assigned a weight $w =$

^{*} All computer programs used are described in the report UUIIC-B13-4-01, which may be obtained on request.

Table 1. *Crystal data for sodium trihydrogen selenite*

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

NaH ₃ (SeO ₃) ₂ , FW 279.94	$\beta = 91.162(5)^\circ$
Space group $P2_1/n$, $Z = 2$	$V = 289.496 \text{ \AA}^3$
$a = 10.3428(8) \text{ \AA}$	$D_x = 3.211 \text{ g cm}^{-3}$
$b = 4.8372(3)$	$\mu_{\text{obs}} = 1.25 \text{ cm}^{-1}$
$c = 5.7876(5)$	

Table 2. *Final unweighted and weighted R values*

$R(F) = (\sum ||F_o| - |F_c||) / \sum |F_o|$ and $R_w(F) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. P is the number of parameters refined. N is the number of reflexions with non-zero weight. Values within parentheses include reflexions with zero weight.

Refinement model	P	N	$R(F)$	$R_w(F)$
(i)	76	757 (852)	0.040 (0.046)	0.0464
(ii)	67	757 (852)	0.041 (0.047)	0.0484
(iii)	64	757 (852)	0.042 (0.048)	0.0492

$1/\sigma^2(F)$, where $\sigma^2(F) = \sigma_{\text{count}}^2(F^2)/4F^2 + K^2$, where K was empirically chosen as $0.04 \times F$ for $F \geq 1.0$ on an absolute scale, and $0.04 \times (2.0 - F)$ for all others. The data were heavily affected by extinction. An anisotropic type I mosaic-spread-dominated model (Coppens & Hamilton, 1970) was used to correct for secondary extinction.

Two different hydrogen bonds exist in the structure. The first crosses a centre of symmetry with H(1) located either at the centre of symmetry, or disordered in half-occupied positions. No symmetry restrictions are imposed on the other hydrogen bond. A difference Fourier synthesis based on the non-hydrogen atoms resulted in elongated negative regions along the O...O bonds indicating either fully occupied H sites with large thermal motion along the bond or disordered half-occupied H sites. Three different models were refined: (i) both H atoms disordered, resulting in two centrosymmetrically related half-H atom positions H(1), and two independent half-occupied positions H(21) and H(22), (ii) atom H(1) disordered as above, whereas the other atom H(2) is in an ordered site close to the centre of the bond, (iii) atom H(1) fixed at the centre of symmetry, and H(2) as in the previous case. The R values and related information are presented in Table 2. The hypothesis that either model (ii) or (iii) describes the situation better than model (i) can be rejected at the 0.5% significance level by comparison of experimental and calculated R -value ratios (Hamilton, 1965).

The final agreement between F_o and F_c was examined by computing the δR normal probability plot (Abrahams & Keve, 1971). The plot was slightly S-shaped indicating some deviation from a random normal distribution. The least-squares line passing through the origin had a slope of 1.04. Part of the indicated systematic error is probably due to the inappropriate model used for the secondary-extinction correction (see above). About 11% of the reflexions had extinction correction factors in the range 1.8–2.9. Exclusion of these 94 reflexions in the refinement did not change any parameter significantly. The final anisotropic extinction tensor components corresponding to model (i) are: 48 (11), 62 (6), 59 (8), -37 (13), -6 (10), -56 (8).

As mentioned above, a significance test indicated that model (i) is preferable. Although systematic errors

in the data and high correlations between some hydrogen parameters (up to 0.8) tend to reduce the reliability of such a test, model (i) is still considered the most reasonable, as will be further discussed below.

The refinement of model (ii) resulted in an H(2) position displaced from the centre of the $\text{O} \cdots \text{O}$ bond with O—H distances of 1.251 (5) and 1.291 (4) Å. The elongated region along this bond, as observed in the difference Fourier synthesis, was slightly asymmetric. These observations may well indicate that a difference in the occupancies of the H(21) and H(22) sites should be built into model (i). However, various least-squares and structure factor calculations were made to test this possibility, but no significant differences could be found.

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

Discussion

A feature common to all the alkali trihydrogen selenite structures is hydrogen-bonded chains of HSeO_3^- ions and H_2SeO_3 molecules cross-linked by means of further hydrogen bonds from the H_2SeO_3 molecules. The O—H \cdots O hydrogen bonds are in the range of 2.52–2.65 Å, with corresponding O—H distances in the range 1.00–1.05 Å. These values have been found in neutron diffraction studies of $\text{LiH}_3(\text{SeO}_3)_2$, $\text{NH}_4\text{H}_3(\text{SeO}_3)_2$, $\text{RbH}_3(\text{SeO}_3)_2$ (Tellgren & Liminga, 1972, 1974*a*, 1977), $\text{KH}_3(\text{SeO}_3)_2$, $\text{KD}_3(\text{SeO}_3)_2$ (Lehmann & Larsen, 1971) and are seen to follow the general correlations of O—H vs O \cdots O distances

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32416 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Atomic coordinates of model (i)*

Hydrogen coordinates are $\times 10^4$, others $\times 10^5$.

	x	y	z
Na	0	0	0
Se	16891 (6)	38551 (14)	50628 (11)
O(1)	5206 (10)	18962 (26)	37533 (18)
O(2)	14478 (9)	29265 (20)	78863 (16)
O(3)	30715 (10)	20737 (23)	45239 (18)
H(1)	147 (7)	398 (14)	4810 (15)
H(21)	1649 (7)	4651 (20)	8914 (11)
H(22)	1802 (7)	5335 (20)	9450 (14)

Table 4. *Interatomic distances (Å) and angles (°) in $\text{NaH}_3(\text{SeO}_3)_2$*

A prime indicates atoms outside the asymmetric unit.

Ionic bonds

Na—O(1)	2.409 (1)
Na—O(2)	2.412 (1)
Na—O(3)	2.457 (1)

Covalent bonds

O—Se—O	O—Se	Se—O	\angle O—Se—O
O(1)—Se—O(2)	1.702 (1)	1.718 (1)	99.36 (6)
O(1)—Se—O(3)	1.702 (1)	1.704 (1)	103.17 (6)
O(3)—Se—O(2)	1.704 (1)	1.717 (1)	100.40 (6)

Hydrogen bonds

O—H \cdots O	O—H	H \cdots O	O \cdots O
O(1)—H(1) \cdots O(1)'	1.029 (5)	1.557 (5)	2.583 (2)
O(2)—H(21) \cdots O(3)'	1.043 (8)	1.505 (9)	2.547 (2)
O(2)—H(22) \cdots O(3)'	1.037 (8)	1.515 (9)	2.547 (2)

Z—O—H \cdots O—W	\angle Z—O—H	\angle O—H \cdots O	\angle H \cdots O—W
Se—O(1)—H(1) \cdots O(1)'—Se'	113.5 (5)	174.8 (8)	118.5 (3)
Se—O(2)—H(21) \cdots O(3)'—Se'	107.6 (4)	177.8 (7)	115.9 (3)
Se—O(2)—H(22) \cdots O(3)'—Se'	109.2 (3)	172.9 (8)	113.7 (4)

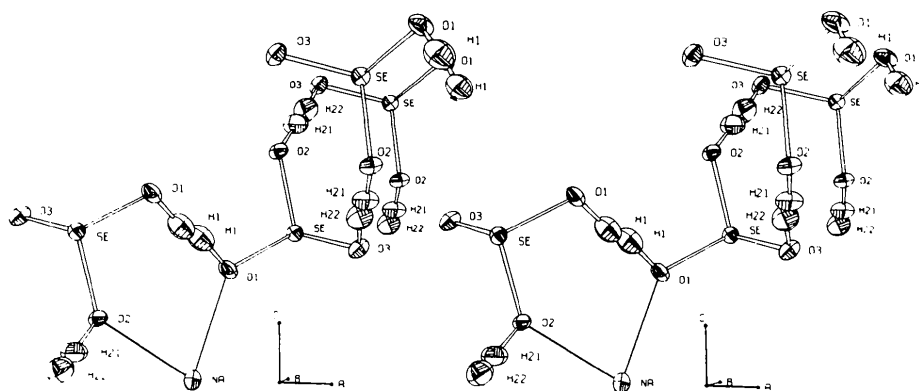


Fig. 1. A stereoscopic illustration of the disordered hydrogen-bond scheme.

found in a large number of compounds (Lundgren, 1974).

The Se—O bond lengths also give information about the positions of the H atoms. Previous studies have shown that an Se—O bond is about 1.65 Å, whereas an Se—OH bond is about 1.75 Å. Inspection of Se—O distances alone can thus reveal information about the H positions. In cases where the H atoms are disordered in half-occupied positions, Se—O distances of about 1.70 Å have been observed, as in the case of the K compound mentioned above and for CsH₃(SeO₃)₂ (Tellgren & Liminga, 1974b).

In the present study, the Se—O bonds are 1.702–1.718 Å (Table 4), for the model with disordered, half-occupied H positions. These values indicate neither a pure Se—O nor a pure Se—OH bond, but a superposition of the two. The O atoms must also be disordered in a similar way, but the distance between the disordered positions will be less than 0.1 Å and hence unresolvable. The O—H distances (1.029, 1.037, 1.043 Å) are in good agreement with values expected for O···O bonds of lengths 2.583 and 2.547 Å. This combined evidence strongly indicates that the structure can be described formally as having half an H attached to each of the three O atoms of the independent SeO₃ group (Fig. 1). Even for an O—H—O bond as short as 2.45 Å, as found in N₂H₅HC₂O₄ (Thomas & Liminga, 1977), an O—H···O/O···H—O superposition of the type suggested here would seem to be the more correct description of the structure.

The thermal ellipsoids, as obtained from the standard least-squares refinement, give some information as to the reasonability of the model. The r.m.s. components associate the largest anisotropy with the O atoms. This may be due to the fact that these atoms occupy disordered sites (about 0.1 Å apart) and that this disorder was not allowed for in the models refined. The H atoms are reasonably described in this disordered model, which was not true of the models in which one or both atoms were placed at the centre of the appropriate O···O bond. In these cases, the ellipsoids became very elongated, with the largest component (0.35–0.40 Å) roughly along the direction of the bond. The largest amplitude of thermal motion is expected approximately perpendicular to the O—H···O bond (Dickens, Prince, Schroeder & Brown, 1973).

It is thus concluded that the structure of NaH₃(SeO₃)₂ can be described as being composed of normal hydrogen-bonded chains of H₂SeO₃ molecules and HSeO₃⁻ ions, statistically distributed in opposite directions, resulting in a disordered structure. The H atoms are thus formally located in half-occupied positions, about 1.04 Å from the O atoms.

The angle between the line joining the two disordered H sites and the corresponding O—O line is 12 (2)° for H(1)—H(1) and 10 (2)° for H(21)—H(22). This observation is in agreement with a similar situation in

KH₂PO₄, where the corresponding angle is 9 (3)° (Nelmes & Rouse, 1974).

Comparison with the previous neutron diffraction study

The interpretation made by Kaplan *et al.* (1970) of their neutron diffraction result was that H(1) was disordered, whereas H(2) was situated in a shallow, skew potential well near the centre of the O(2)···H(2)···O(3) bond. This gives O—H bond distances of 1.24 and 1.31 Å, which are too long for an O···O bond of 2.56 Å. Furthermore, the thermal ellipsoid of H(2) was very elongated, with an r.m.s. component of 0.30 Å roughly along the direction of the bond. These observations indicate that it is most probable that H(2) is also disordered.

The parameters from the study of Kaplan *et al.* (1970) and from the present study are based on refinements of different models, and are thus not directly comparable. Although the non-hydrogen atom parameters are rather insensitive to the different models refined, we observe differences of up to three estimated standard deviations in their refined values. As different models have been used, a comparison of the two sets of parameters with the normal probability method (Abrahams & Keve, 1971) is thus not justifiable.

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The Reaction between Potassium Permanganate and Formic Acid. Structural Characterization of the Polymeric Compound $(\text{K}_2\{\text{Mn}(\text{H}_2\text{O})_2[\text{Mn}_3\text{O}(\text{HCOO})_9]_2\})_n$

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When potassium permanganate and concentrated formic acid solutions are mixed, a red–brown solution is formed. From this solution various crystalline compounds precipitated, depending on the HCOOH concentrations and temperatures used. One of these compounds is a red–brown, paramagnetic complex with the formula $\text{K}_2\{\text{Mn}(\text{H}_2\text{O})_2[\text{Mn}_3\text{O}(\text{HCOO})_9]_2\}$, as established by a single-crystal X-ray diffraction study. This complex crystallizes in the triclinic space group $P\bar{1}$, with $a = 6.884$ (4), $b = 12.440$ (6), $c = 15.414$ (8) Å, $\alpha = 97.59$ (6), $\beta = 108.72$ (6), $\gamma = 120.88$ (6)°. Data to $2\theta \sim 114^\circ$ (Cu $K\alpha$ radiation) for 2498 reflexions were measured on a Syntex $P2_1$ four-circle diffractometer. The structure was solved by the heavy-atom technique and refined by the full-matrix least-squares method. The final R and R_w were 0.054 and 0.056 for 1815 non-zero reflexions. The structure consists of the $\{\text{Mn}(\text{H}_2\text{O})_2[\text{Mn}_3\text{O}(\text{HCOO})_9]_2\}^{2-}$ polymeric anion and potassium cations. In the complex anion, the Mn^{2+} ions (which lie on the symmetry points of the crystal) coordinate two water molecules and are bonded with the Mn_3O groups through the four formate groups. The equilateral triangle of the Mn^{3+} ions is bridged by the six formate groups and the central O atom, which lies essentially in the Mn_3 plane. All Mn atoms have distorted octahedral coordination; the Mn–O distances vary between 1.87 and 2.21 Å.

Introduction

The overall reaction between permanganate and formic acid is expressed by the equation



This reaction has not, until recently, been systematically investigated. The well known interaction between KMnO_4 and oxalic or malonic acid suggested that this process would also be complicated.

Solutions of freshly prepared MnO_2 in formic acid are known to form a red Mn^{III} formate complex with the formula $\text{Mn}_3(\text{form})_6(\text{form})_3 \cdot 2\text{H}_2\text{O}$ (Weinland & Stark, 1926). It was observed by us that this compound can also be obtained from the reaction of 100% HCOOH with solid KMnO_4 at room temperature. However, if a diluted solution of HCOOH was used, the brown MnO_2 precipitated and the reaction stopped. When the concentration of HCOOH varies in the range

70–95% and reaction proceeds at 0°C , a few different products may be obtained.

In this work a compound was isolated which was shown by X-ray diffraction to contain the novel $\{\text{Mn}(\text{H}_2\text{O})_2[\text{Mn}_3\text{O}(\text{HCOO})_9]_2\}^{2-}$ anion. In order to obtain more information and a better understanding of this and related anions, an extensive study involving the methods of synthesis, the properties, and the molecular and crystal structures was undertaken.

Experimental

Materials

KMnO_4 (POCh or Analar), 98–100% HCOOH (Merck) or 99.5% HCOOH (Fluka AG) without further purification and distilled water were used.