

X-ray Diffraction Study of $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{D}_2\text{O}$

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Abstract

The crystal structures of $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ and its deuterated homologue $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{D}_2\text{O}$ have been reinvestigated by single-crystal X-ray diffractometry. Conventional refinements of both data sets with the assumption of neutral S and O atoms yielded agreement factors of $R_{\text{unobs. omitted}} = 0.0198$ and 0.0229 respectively. The geometric results of both compounds investigated on different diffractometers show a high degree of agreement, indicating the absence of bias due to systematic experimental errors.

Introduction

First X-ray structure analysis results on $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ were reported by Martínez, García-Blanco & Rivoir (1956). An improved structure analysis by the conventional Weissenberg film technique was undertaken by Berthold & Weiss (1967). The authors were able to locate the H atoms and finally reached an R of 0.103. The aim of their investigation was to obtain more accurate positional parameters in order to determine the electric-field gradient at the Na position and hence to obtain information about the magnitude and orientation of the nuclear quadrupole moment of ^{23}Na . This structure determination was also used as a basis for a subsequent ^2H NMR study of $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{D}_2\text{O}$ (Ketudat, Berthold & Weiss, 1967).

Further investigations on the structures of both $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{D}_2\text{O}$ by neutron diffraction were performed by Zwoll (1974). The data, however, turned out to yield atomic parameters of relatively large uncertainty except for the H and D atoms, which cannot be located with comparable precision by X-ray diffraction.

The present redetermination of the structures of the title compounds served for the improvement of the atomic positions and the evaluation of meaningful

vibrational parameters. In the course of this work different refinement models were tested and the charge distribution in the $[\text{S}_2\text{O}_6]^{2-}$ anion was investigated in detail. These results will be described separately. This first part is confined to the presentation of the conventional structure analysis results. In the following, $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ and its deuterated homologue will be referred to as NAH and NAD respectively.

Experimental

Large single crystals, 10–20 mm in each dimension, of both NAH and NAD were grown by the slow cooling of saturated solutions of $\text{Na}_2\text{S}_2\text{O}_6$ in H_2O and D_2O , respectively, from 308 to 293 K. The cooling rate was about 0.5 K h^{-1} .

The specimens selected for the X-ray diffraction experiments were ground to almost perfect spheres of 0.2 mm radius. Room-temperature measurements were carried out on two automatic four-circle diffractometers [Hilger & Watts (University of York, England) for NAH and Syntex P2, (Bonn) for NAD]. The $\text{Mo K}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) was filtered by Zr in one case and monochromatized by a graphite crystal in the other. The lattice constants were refined from the adjusted angular settings of 14 (NAH) and 25 (NAD) independent reflections and are given with other crystallographic data in Table 1. Both intensity measurements were in the θ - 2θ mode with a 2° scan range. Up to a maximum $\theta = 30^\circ$, for NAH 2448 and for NAD 2548 reflections were recorded excluding the repeated measurements of two standard reflections after every 32 records. In both cases the time spent for the peak count equalled the total background counting time. The data-reduction procedure included adjustment of the intensities for the fluctuations of the sums of the check-reflection intensities, averaging of symmetry-related reflections, and a spherical absorption correction ($\mu = 0.367 \text{ mm}^{-1}$). The internal

agreement factors of the data sets based on the deviations of individual $|F|$'s from the average of the equivalent reflections were 0.021 for NAH and 0.023 for NAD. The final lists of structure amplitudes contained for NAH 1112 unique reflections with 306 regarded as unobserved ($I < 3\sigma$) and for NAD 1129 unique, 140 unobserved.

Structure refinement and results

The structure refinements with both data sets were by full-matrix least squares with the positional parameters given by Berthold & Weiss (1967) as starting values. With the assumption that the bonding in the [S₂O₆]²⁻ anion is predominantly covalent and that the twofold negative charge is distributed rather uniformly over the group, the S and O atoms were treated as neutral. Hence, the scattering factors were taken from *International Tables for X-ray Crystallography* (1974) for

Na⁺, S, O, and H. All atoms except H were refined anisotropically. The allocation of weights [$w = 1/\sigma^2(F)$] affected neither the refinement results nor the R values. Secondary extinction was taken into account (Zachariasen, 1963) $\{F_c = kF_o[1 + \beta(2\theta)gI_o]\}$ by including g in the list of variables (final values 7×10^{-5} for NAH and 1×10^{-5} for NAD). The refinements were stopped when the shifts of the parameters were below one third of the corresponding e.s.d. The final $R_{\text{overall}} = 0.0255$ ($R_{\text{unobs. omitted}} = 0.0198$) for NAH and $R = 0.0278$ ($R_{\text{u.o.}} = 0.0229$) for NAD. A control refinement for NAH with $f(\text{O}^-)$ and $f(\text{S}^{2+}) = f(\text{S}) - [f(\text{O}^{2-}) - f(\text{O})]$ as used by Berthold & Weiss (1967) yielded agreement factors above 0.05 and hence the ionic model of the dithionate anion is discarded as being inappropriate to the real electron distribution.

The results of the conventional refinements are listed in Tables 2 and 3.* The agreement of the positional parameters of corresponding atoms of both substances is very good and only two differences exceed the sum of the associated e.s.d.'s. Since the H and D positions determined by Zwoll (1974) by neutron diffraction are more reliable than those from the X-ray measurements these coordinates are included in Table 2 for comparison.

Significant differences are found for the vibrational parameters. Though the relative distribution of the U_{ij} values is very similar for NAH and NAD the atomic vibrations of the latter are about 18% smaller on average than those of NAH. To some extent this may be accounted for by the 1.6% higher density of NAD, but it is also possible that different crystal qualities are responsible.

* Lists of structure factors for both compounds and Table 3 (anisotropic thermal parameters for both) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34775 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystallographic data and data collection*

	NAH	NAD
a (Å)	6.407 (1)	6.413 (1)
b (Å)	10.751 (4)	10.756 (1)
c (Å)	10.665 (3)	10.671 (1)
Space group	<i>Pnma</i>	<i>Pnma</i>
Z	4	4
V (Å ³)	734.6	736.0
M_r	242.16	246.16
D_x (Mg m ⁻³)	2.186	2.221
Diffractometer	Hilger & Watts (York)	Syntex P2 ₁ (Bonn)
Wavelength (Å)	0.71069 (Zr filter)	0.71069 (C monochromatized)
θ_{max} (°)	30	30
Reflections recorded	2448	2548
Unique	1112	1129
Unobserved ($I < 3\sigma$)	306	140
Internal R	0.021	0.023

Table 2. *Fractional coordinates ($\times 10^4$) and B_{eq} values (B for H/D) (Å²) with e.s.d.'s in parentheses*

$$B_{\text{eq.}} = \frac{2}{3}\pi^2 \text{trace } \tilde{U}.$$

	NAH				NAD			
	x	y	z	$B_{\text{eq.}}/B$	x	y	z	$B_{\text{eq.}}/B$
S(1)	2495 (1)	2500	4586 (1)	1.32 (2)	2495 (1)	2500	4586 (1)	1.13 (2)
S(2)	-18 (1)	2500	5908 (1)	1.38 (2)	-19 (1)	2500	5908 (1)	1.18 (2)
O(1)	3647 (2)	1366 (1)	4832 (1)	2.14 (5)	3648 (2)	1366 (1)	4831 (1)	1.95 (5)
O(2)	1432 (3)	2500	3380 (2)	1.93 (5)	1431 (3)	2500	3381 (1)	1.73 (5)
O(3)	-1146 (2)	1365 (1)	5630 (1)	2.41 (5)	-1141 (2)	1362 (1)	5632 (1)	2.17 (5)
O(4)	955 (3)	2500	7138 (2)	2.14 (7)	951 (3)	2500	7136 (2)	1.89 (7)
O(5)	2516 (2)	442 (1)	1891 (1)	2.15 (5)	2514 (2)	444 (1)	1892 (1)	1.96 (5)
Na	687 (1)	621 (1)	8471 (1)	2.21 (3)	684 (1)	621 (1)	8471 (1)	2.04 (3)
H/D(1)	8120 (40)	4430 (30)	3700 (30)	1.8 (6)	8000 (50)	4390 (30)	3700 (30)	2.7 (8)
H/D(2)	7310 (40)	3930 (20)	2780 (20)	1.5 (6)	7250 (40)	3880 (20)	2750 (20)	1.0 (5)
Neutron diffraction data (Zwoll, 1974)								
H/D(1)	8171 (14)	4353 (7)	3878 (11)		8179 (14)	4379 (7)	3884 (8)	
H/D(2)	7160 (12)	3761 (8)	2793 (9)		7174 (14)	3777 (7)	2734 (7)	

Discussion

Interatomic distances and angles in both compounds are compiled in Table 4. Almost all corresponding values of NAH and NAD agree within the limits of

tolerance. Very small differences are only observable for the results involving O(3). This overall agreement achieved with different samples investigated on different diffractometers implies a lack of severe systematic errors in the reflection data sets. A thorough descrip-

Table 4. Distances (Å) and angles (°) in NAH and NAD with *e.s.d.*'s in parentheses

S ₂ O ₆ octahedron		NAH	NAD		NAH	NAD	
S(1)—O(1)	1.449 (1)	1.450 (1)	O(1)—O(2)	2.428 (2)	2.429 (2)		
S(1)—O(2)	1.455 (2)	1.455 (2)	O(1)—O(3)	3.187 (2)	3.188 (2)		
S(1)—S(2)	2.140 (1)	2.142 (1)	O(1)—O(4)	3.242 (2)	3.245 (2)		
S(2)—O(3)	1.449 (1)	1.450 (1)	O(2)—O(3)	3.158 (2)	3.160 (2)		
S(2)—O(4)	1.452 (2)	1.451 (2)	O(3)—O(3 ^{vi})	2.441 (2)	2.448 (2)		
O(1)—O(1 ^{vi})	2.438 (2)	2.439 (2)	O(3)—O(4)	2.426 (2)	2.423 (2)		
O(1)—S(1)—O(1 ^{vi})	114.56 (8)	114.52 (8)	O(3)—O(1)—O(4)	44.33 (4)	44.25 (4)		
O(1)—S(1)—O(2)	113.49 (6)	113.49 (6)	O(1)—O(2)—O(1 ^{vi})	60.27 (6)	60.28 (6)		
O(1)—S(1)—S(2)	105.30 (5)	105.37 (5)	O(1)—O(2)—O(3)	68.13 (5)	68.12 (5)		
O(2)—S(1)—S(2)	103.29 (8)	103.18 (8)	O(3)—O(2)—O(3 ^{vi})	45.47 (4)	45.57 (4)		
O(3)—S(2)—O(3 ^{vi})	114.73 (8)	115.17 (8)	O(1)—O(3)—O(3 ^{vi})	89.88 (5)	89.92 (5)		
O(3)—S(2)—O(4)	113.51 (6)	113.29 (6)	O(2)—O(3)—O(3 ^{vi})	67.27 (4)	67.21 (4)		
O(3)—S(2)—S(1)	103.92 (6)	103.93 (6)	O(4)—O(3)—O(3 ^{vi})	59.80 (5)	59.66 (5)		
O(4)—S(2)—S(1)	105.81 (9)	105.79 (8)	O(1)—O(3)—O(2)	45.00 (4)	44.99 (4)		
O(1 ^{vi})—O(1)—O(3)	90.02 (5)	90.08 (5)	O(1)—O(3)—O(4)	69.03 (6)	69.11 (6)		
O(1 ^{vi})—O(1)—O(2)	59.86 (4)	59.86 (5)	O(1)—O(4)—O(1 ^{vi})	44.18 (4)	44.16 (4)		
O(1 ^{vi})—O(1)—O(4)	67.91 (4)	67.92 (4)	O(1)—O(4)—O(3)	66.64 (5)	66.64 (5)		
O(3)—O(1)—O(2)	66.87 (6)	66.89 (5)	O(3 ^{vi})—O(4)—O(3)	60.41 (6)	60.67 (3)		
NaO ₆ octahedron		NAH	NAD	NAH	NAD		
Na—O(1 ^{vii})	2.617 (1)	2.618 (1)	Na—O(5 ^{vii})	2.339 (1)	2.343 (1)		
Na—O(1 ^{viii})	2.372 (1)	2.373 (1)	Na—O(3 ^{viii})	2.383 (1)	2.386 (1)		
Na—O(5 ⁱⁱ)	2.380 (2)	2.381 (2)	Na—O(4)	2.477 (1)	2.479 (1)		
O(1)—O(5)	3.369 (2)	3.369 (2)	O(3)—O(5 ⁱⁱ)	3.396 (2)	3.396 (2)		
O(1)—O(5 ^{viii})	3.241 (2)	3.242 (2)	O(5)—O(5 ^{viii})	3.457 (2)	3.459 (2)		
O(1)—O(1 ⁱⁱ)	3.429 (2)	3.431 (2)	O(4)—O(3 ^{viii})	3.257 (3)	3.264 (2)		
O(1)—O(3 ⁱⁱ)	3.381 (2)	3.382 (2)	O(4)—O(1 ^{vi})	3.242 (2)	3.245 (2)		
O(1)—O(5 ^{vii})	3.026 (2)	3.031 (2)	O(4)—O(5 ^{iv})	3.321 (2)	3.327 (1)		
O(1)—O(3)	3.443 (2)	3.449 (2)	O(4)—O(5 ^v)	4.002 (2)	4.006 (2)		
O(1 ^{vii})—Na—O(4)	166.61 (4)	166.61 (4)	O(3 ⁱⁱ)—O(5)—O(5 ^{viii})	89.95 (5)	87.04 (4)		
O(3)—O(1)—O(5 ^{vii})	93.37 (5)	93.31 (5)	O(1 ^{vii})—O(5)—O(5 ^{viii})	92.56 (5)	92.53 (5)		
O(1)—O(3)—O(5 ⁱⁱ)	86.70 (5)	86.70 (4)					
Water molecule		NAH		NAD		SC	BLT
	X-ray	Neutron	X-ray	Neutron			
O(5)—H(1 ⁱⁱⁱ)	0.75 (3)	0.95 (1)	0.73 (3)	0.95 (1)			
O(5)—H(2 ⁱⁱⁱ)	0.78 (3)	0.95 (1)	0.83 (3)	0.95 (1)			
O(5)—O(2)	2.811 (2)		2.810 (2)				
O(5)—O(3 ^{viii})	2.991 (2)		2.995 (2)				
O(2)—H(2 ⁱⁱⁱ)	2.05 (3)	1.90 (1)	1.99 (3)	1.88 (1)	1.98	2.00	
O(3)—H(1 ^{vi})	2.28 (3)	2.07 (1)	2.28 (3)	2.07 (1)	2.06	2.07	
H(1)—H(2)	1.24 (4)	1.47 (1)	1.24 (4)	1.53 (1)			
H(1 ⁱⁱⁱ)—O(5)—H(2 ⁱⁱⁱ)	108 (3)	101.7 (7)	106 (3)	107.0 (7)			
O(2)—O(5)—O(3 ^{viii})	108.51 (6)		108.69 (6)				
O(2 ⁱⁱⁱ)—H(2)—O(5 ⁱⁱⁱ)	167 (3)	159.4 (8)	168 (3)	165.0 (7)			
O(3 ^{vi})—H(1)—O(5 ⁱⁱⁱ)	158 (3)	164.3 (8)	167 (3)	162.6 (7)			
H(2 ⁱⁱⁱ)—O(5)—O(2)	9 (2)	13.8 (6)	8 (2)	10.0 (5)			
H(1 ⁱⁱⁱ)—O(5)—O(3 ^{viii})	16 (2)	10.8 (5)	10 (3)	12.0 (5)			
Symmetry code							
(ii)	$-x, -y, -z$	(iv)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$	(vi)	$x, \frac{1}{2} - y, z$	(viii)	$\frac{1}{2} + x, y, \frac{1}{2} - z$
(iii)	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$	(v)	$-x, \frac{1}{2} + y, -z$	(vii)	$\frac{1}{2} - x, -y, \frac{1}{2} + z$		

tion of the structure (Fig. 1) has already been given by Berthold & Weiss (1967). Therefore only some additional structural considerations are given below.

The structure can be understood as being built up of S_2O_6 and NaO_6 octahedra sharing common corners at O(1) and O(4).

(a) The $[\text{S}_2\text{O}_6]^{2-}$ anion: The configuration of the atoms corresponds to a dumb-bell lying on a mirror plane with a non-crystallographic inversion centre X on the S—S bond, which is identical with the geometric point of gravity within the limits of tolerance. The S—S distance is 2.140 (1) Å in NAH and 2.142 (1) Å in NAD, and the bond angles around the S atoms vary

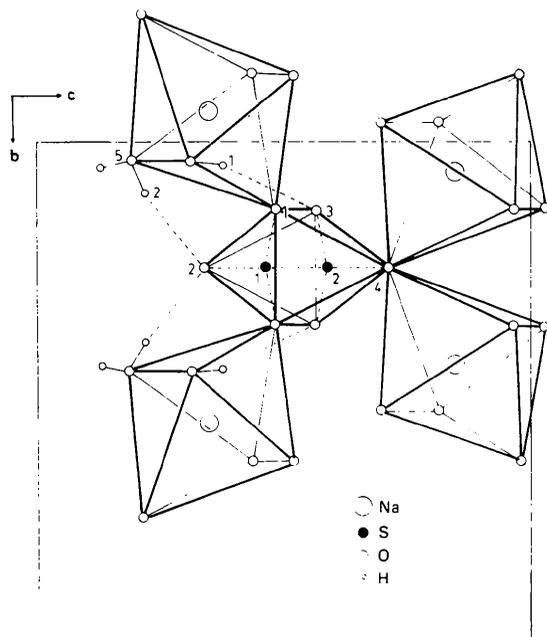


Fig. 1. The structure of $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ viewed in projection on (100).

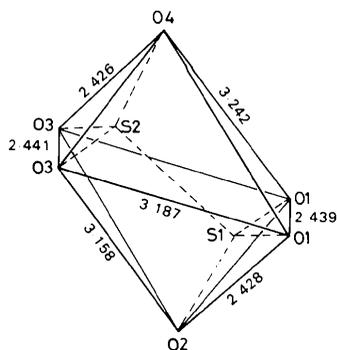


Fig. 2. Atomic arrangement of the $[\text{S}_2\text{O}_6]^{2-}$ anion.

from 103.18 to 115.17° with mean values of 109.33 (NAH) and 109.34° (NAD). Thus the bond angles around S clearly reflect the tetrahedral bond character due to sp^3 hybridization of the valence electrons. Simultaneously the $[\text{S}_2\text{O}_6]^{2-}$ anion can be regarded as a distorted octahedron (Fig. 2) with O(2) and O(4) in the top and bottom positions and with a rectangular base with 3.187 and 2.440 Å edge lengths.

(b) The Na^+O_6 polyhedron: Each Na^+ is sixfold coordinated by O atoms (Fig. 3) forming an octahedron with little distortion. The centring Na^+ is not exactly at the mid-point of the distance O(1)—O(4) (point Y in Fig. 5) but is shifted somewhat, leading to the distances O(4)—Na 2.477 (1) (NAH), 2.479 (1) Å (NAD) and O(1)—Na 2.617 (1) (NAH), 2.618 (1) Å (NAD), which include an angle of 166.61 (4)° (NAH, NAD).

(c) The two water molecules in each Na^+O_6 polyhedron provide further connections to the $[\text{S}_2\text{O}_6]^{2-}$ anions via O—H...O hydrogen bonds (Fig. 1). These bonds are of different strength, reflected in the distances O(5)—H(1)...O(3) 2.991 (2) (NAH), 2.995 (2) Å (NAD) and O(5)—H(2)...O(2) 2.811 (2) (NAH), 2.810 (2) Å (NAD). Due to the unfavourable ratio of the scattering factors of O and H for X-rays and the influence of their covalent bonding we obtain the usual shortening of O—H bonds (Almlöf & Ottersen, 1979), which range from 0.75 to 0.83 Å. Since this shortcoming is avoided in neutron diffraction the positional parameters of H and D obtained by Zwoll (1974) are certainly more meaningful, and lead to O—H distances of 0.95 (1) Å. Therefore, the geometrical results concerning the water molecule obtained by use of the neutron parameters of the H atoms have been added in Table 4.

From the empirical relation proposed by Soda & Chiba (1969), which connects the nuclear quadrupole

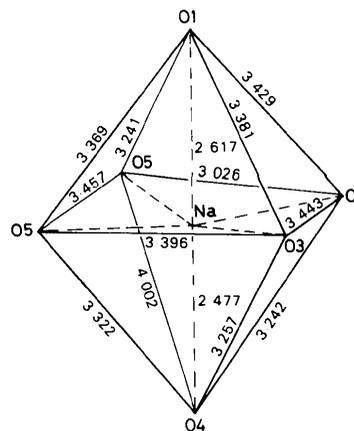


Fig. 3. Atomic arrangement of the Na^+O_6 coordination polyhedron.

moment coupling constant $e^2 q Q h^{-1}$ of ^2H with the distance $R(\text{D}\cdots\text{O})$ together with the experimental data of $e^2 q Q h^{-1}$ for $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{D}_2\text{O}$ (Ketudat, Berthold & Weiss, 1967), the distances $\text{O}(2)\text{--H}(2^{\text{III}})$ and $\text{O}(3)\text{--H}(1^{\text{VI}})$ are calculated to be 1.98 and 2.06 Å respectively (SC, Table 4). Additional calculations based on the formula given by Berglund, Lindgren & Tegenfeldt (1978) yield 2.00 and 2.07 Å respectively (BLT, Table 4). Both calculations are in better agreement with the H atom positions from the neutron diffraction data.

The arrangement of the water molecule and the connected $\text{O}(2)$ and $\text{O}(3)$ is almost planar (Table 5). From NMR spectroscopy and theoretical arguments Berthold & Weiss (1967) predicted non-linear hydrogen bonds for NAH with calculated angles $\text{H}(1)\text{--O}(5)\text{--O}(3)$ 10.8 and $\text{H}(2)\text{--O}(5)\text{--O}(2)$ 13.2°. The quality of these calculations can be estimated from the experimental corroboration with the corresponding angles of 10.8 (5) and 13.8 (6)° respectively.

The bonding conditions for the $\text{O}\text{--D}\cdots\text{O}$ bonds are similar; however, a clear difference between the H_2O and the D_2O molecules is found for the intramolecular angles of 101.7 (7) for H_2O and 107.0 (7)° for D_2O , which for NAD lead to somewhat different deviations from linear hydrogen bonds.

(d) If one considers the geometric point of gravity X of the $[\text{S}_2\text{O}_6]^{2-}$ anion along with the Na position,

Table 5. Deviations (Å) of atoms from least-squares planes

Atoms marked with asterisks are not used for plane definitions.

	Plane A		Plane B	
	NAH	NAD	NAH	
O(5)	-0.040	-0.048	O(2)	-0.009
H/D(1 ^{III})	0.100	0.099	O(4)	-0.033
H/D(2 ^{III})	-0.059	-0.046	Na	-0.012
O(2)	0.028	0.021	Na ^{VI}	-0.012
O(3 ^{III})	-0.026	-0.026	O(1)*	0.541
			O(1 ^{VI})*	0.541

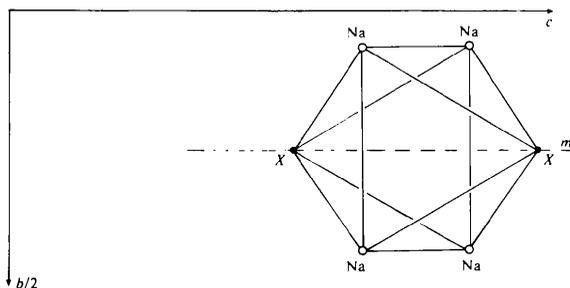


Fig. 4. The octahedron $X_2\text{Na}_4$ composed of Na^+ cations and $[\text{S}_2\text{O}_6]^{2-}$ anion points of gravity X viewed in projection on (100).

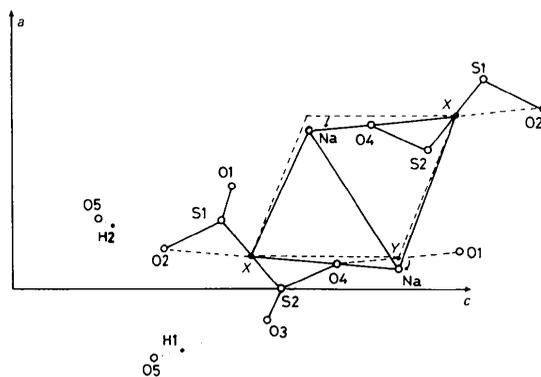


Fig. 5. The $X_2\text{Na}_4$ octahedron and the influence of the hydrogen bonds on the $[\text{S}_2\text{O}_6]^{2-}$ anion viewed in projection on (010).

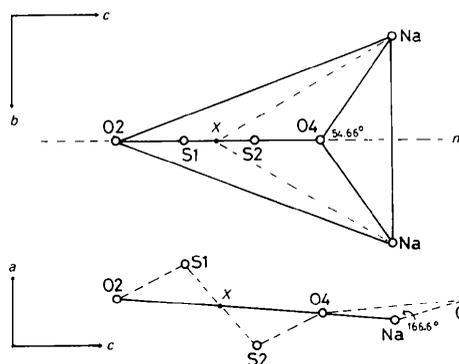


Fig. 6. Planar arrangement of anion $\text{O}(2)$, $\text{O}(4)$ and cations Na^+ viewed in projections on (100) and (010).

these points again constitute a slightly distorted $X_2\text{Na}_4$ octahedron (Fig. 4) and the structure is then built up of layers of such octahedra parallel to (010). The distortion of the $X_2\text{Na}_4$ octahedron results from the shift of Na from the Y position, which represents the mid-point of $\text{O}(1)\text{--O}(4)$ of the Na^+O_6 coordination polyhedron (Fig. 3). Since the S_2O_6 dumb-bell is twisted around an axis through X parallel to $[010]$ due to the hydrogen bonds (Fig. 5), Na^+ can be thought to follow into the most favourable energetical position with respect to the $[\text{S}_2\text{O}_6]^{2-}$ anions, and this leads to a planar arrangement of X , $\text{O}(2)$, $\text{O}(4)$ and adjacent Na^+ cations (Table 5), in which X and the cations form an almost equilateral triangle (Fig. 6).

After the accurate establishment of the structure of NAH and NAD the ensuing stage of investigation will deal with refinement studies using different models for describing the electron distribution in the dithionate anion. Related results and residual electron density distributions will be reported in a subsequent paper.

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Note added in proof: Recently we became aware of a similar structure refinement on NAH by Kiers, Piepenbroek & Vos (1978).

Our positional parameters are generally in good agreement with their results. Differences are at most twice the sum of the associated e.s.d.'s [O(3) atom]. The same applies for the bond lengths and angles, except for $\text{Na}''\text{—O}''(1) = 2.342 \text{ \AA}$ of Kiers, Piepenbroek & Vos, which seems to be a misprint. The corresponding distance determined in our study is 2.617 \AA .

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A Structural Investigation of $\alpha\text{-Al}_2\text{O}_3$ at 2170 K

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Abstract

The crystal structures of $\alpha\text{-Al}_2\text{O}_3$ at 300 and 2170 K were studied by three-dimensional X-ray data which were measured in the ranges $\sin \theta/\lambda < 1.08 \text{ \AA}^{-1}$ at 300 K and $\sin \theta/\lambda < 0.70 \text{ \AA}^{-1}$ at 2170 K on a four-circle diffractometer equipped with a gas-heating furnace. The structures were refined to conventional R values of 0.027 at 300 K and 0.038 at 2170 K. Significant changes in the positional parameters of the Al atoms and slight changes in those of the O atoms were observed. The distorted hexagonal-close-packed plane of O atoms becomes more regular at 2170 K and the Al atom moves towards the vacant octahedral interstice between the oxygen layers. The two independent Al—O bond lengths are 1.971 (2) and 1.852 (1) \AA at 300 K, while they are 2.024 (2) and 1.880 (1) \AA at 2170 K. Of the Al—Al distances, the largest expansion was observed in that across the shared face of the AlO_6 octahedra along the c axis (hexagonal setting).

Introduction

In corundum-type structures, the O atom is located at $(x, 0, \frac{1}{2})$ and the Al atom at $(0, 0, z)$ in the hexagonal

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setting of $R\bar{3}c$. The O atoms arrange approximately in hexagonal close packing with metal atoms occupying two thirds of the octahedral interstices. The metal–metal distance along the threefold axis across the face shared by two MO_6 coordination octahedra is the shortest of the various metal–metal contacts in a corundum-type structure. Several studies have referred to changes in these structural parameters. Moss & Newnham (1964) reported that the Cr position in ruby ($\alpha\text{-Al}_2\text{O}_3$ with 4% Cr_2O_3) is shifted by 0.06 \AA from the normal Al position in the $\alpha\text{-Al}_2\text{O}_3$ structure. Rice & Robinson (1976, 1977) investigated the structural changes in Ti_2O_3 accompanying the semiconductor–metal transition when warmed through the temperature range 400–600 K and reported a large elongation of Ti–Ti distance across the threefold axis. d'Amour, Schiferl, Denner, Schulz & Hazapfel (1978) found that the positional parameters in ruby were constant up to $8.6 \times 10^3 \text{ MPa}$ in their study by high-pressure single-crystal X-ray diffractometry. Nukui, Tagai, Morikawa & Iwai (1976) investigated the structural conformation of molten alumina at 2370 K. Structural information on $\alpha\text{-Al}_2\text{O}_3$ at high temperatures has never been reported. The object of this study is to clarify structural changes of $\alpha\text{-Al}_2\text{O}_3$ at high