The Crystal Structure of Anhydrous Sodium Thiosulphate

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Strongly deliquescent crystals of anhydrous $Na_2S_2O_3$ were grown from aqueous solution in a thermostat set at 93 °C. The crystals are monoclinic, space group $P2_1/a$ with four formula units in the unit cell. The unit-cell parameters are

$$a = 6\cdot50 \pm 0\cdot05, \quad b = 8\cdot12 \pm 0\cdot01, \quad c = 8\cdot52 \pm 0\cdot02 \text{ Å}; \quad \beta = 95^\circ \ 4' \pm 16'.$$

The structure has been determined from three Fourier projections, and signs of the respective structure factors were determined by direct methods from three-dimensional data. Of a total of 353 recorded reflexions the signs of 219 were determined. The approximate structure was refined by computing successive $(F_o - F_c)$ syntheses first in two then in three dimensions. The final R factor was 15·0%. In the S_2O_3 thiosulphate group one S and the three O atoms are arranged tetrahedrally around the other S atom with S–S distance of $2\cdot01 \pm 0\cdot02$ Å and with an average S–O distance of $1\cdot47 \pm 0\cdot05$ Å. The mean S–S–O and O–S–O bond angles are $108\cdot5 \pm 1\cdot5^\circ$ and $110\cdot5 \pm 1\cdot5^\circ$ respectively.

Introduction

Although the crystal structure of several thiosulphates have been studied (Cabrera & Gamboa, 1945; Brunt, 1946; Taylor & Beevers, 1952; Cavalca, Nardelli & Braibanti, 1956; Keglevich, 1958a, b; Zsoldos, 1958), only two investigations have been carried as far as the determination of the atomic arrangement of the S_2O_3 group. The two results are rather conflicting. Brunt (1946) concludes that the S_2O_3 group in $(NH_4)_2S_2O_3$, $Mg_2O_3.6 H_2O$ and $NiS_2O_3.6 H_2O$ is essentially planar, but Taylor & Beevers (1952) derive a distorted tetrahedral configuration in $Na_2S_2O_3.5H_2O$.

In view of this discrepancy it was thought worthwhile to study the configuration of the S_2O_3 group in yet another thiosulphate. It was also expected that this investigation might decide whether the differences found by Taylor & Beevers in the lengths of the S–O bonds are genuine, or whether they are due to the limited accuracy of the atomic parameters, as the authors themselves suggested.

Experimental procedure and crystal data

Single crystals of anhydrous sodium thiosulphate were grown by the slow evaporation of the aqueous solution in a thermostat set at 93 °C. The starting material was crystalline $Na_2S_2O_3.5 H_2O$ purified by repeated crystallization and dissolved in its water of crystallization at the temperature of the thermostat. This temperature was considerably higher than the limit (70 °C.) above which sodium thiosulphate crystallizes without water from aqueous solution (Young & Burke, 1906).

The crystals grown in the thermostat were irregularly shaped transparent blocks without flat reflecting faces and with traces of the mother liquor on their surfaces. Under the polarizing microscope they appeared to be good-quality single crystals. In particular they did not show any twinning. According to the chemical analysis, they contained only insignificant impurities. They were very hygroscopic and deliquesced rapidly when exposed to air. In water-free amyl alcohol they could be preserved indefinitely, and a thin film of collodion was sufficient to prevent them from decomposition in air during the X-ray work.

The density of the crystals was determined by flotation in a mixture of bromoform and ethylene bromide, the temperature of which was controlled by an ultra-thermostat. The measured density $d^{20°} = 2\cdot345 \pm 0\cdot001$ g.cm.$^{-3}$ was in good agreement with the density calculated from the X-ray data $d^X = 2\cdot342$ g.cm.$^{-3}$. It differed, however, considerably from the data of previous authors: 2·119 g.cm.$^{-3}$ (Pape, 1864) and 1·667 g.cm.$^{-3}$ (Gerlach, 1886). Pape's value is probably that of an intermediate hydrate, perhaps $Na_2S_2O_3.2 H_2O$. This view is supported by the fact that Pape obtained his material by desiccating $Na_2S_2O_3.5H_2O$, the first step in the transition being the transformation of $Na_2S_2O_3.5 H_2O$ into $Na_2S_2O_3.2H_2O$ (Picon, 1924).

At the beginning of the X-ray work nothing was known about the morphology of anhydrous sodium thiosulphate, and in the absence of suitable reflecting faces the morphological data could not be obtained by standard optical methods. Thus both the determination of the crystal symmetry and the orientation of the crystallographic axes was carried out by X-rays

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using the method described by one of the authors (Sándor, 1956). This method requires one single Laue photograph taken in a cylindrical camera and has the additional advantage that photographs around all three crystallographic axes can be taken without removing the crystal from the goniometer head. The Laue photograph revealed that the diffraction symmetry of the crystal corresponds to the monoclinic (2/m) Laue-group and indicated also the orientation of the crystallographic axes.

The parameter of the unit cell were derived by the least squares method (Cohen, 1935, 1936) from high-angle reflexions recorded on oscillation photographs around the three crystallographic axes. The photographs were taken with Cu K radiation on a Unicam Weissenberg goniometer with the film in the asymmetric setting (Straumanis & Ievinš, 1936). The lattice parameters obtained were:

$$a = 6 \cdot 50 \pm 0 \cdot 05, \quad b = 8 \cdot 12 \pm 0 \cdot 01, \quad c = 8 \cdot 52 \pm 0 \cdot 02 \text{ Å};$$
$$\beta = 95° \, 4' \pm 16'.$$

These values agree well with the lattice parameters derived by Zsoldos (1958) for polycrystalline $Na_2S_2O_3$, obtained by desiccating $Na_2S_2O_3 . 5 \, H_2O$. They also agree with the powder data published in the X-ray Powder Data File for $Na_2S_2O_3$ (Card No. 3-0258). From the above lattice parameters the volume of the unit cell is $V = 447 \cdot 9$ Å^3 and the number of formula units in the unit cell is $Z = 4$. The number of electrons in the unit cell $F(000)$ is 312 and the linear absorption coefficient for Cu $K\alpha$ is $\mu = 116 \cdot 87$ cm.$^{-1}$.

Equi-inclination Weissenberg photographs were taken with the same equipment using the multiple-film method (Robertson, 1943). Altogether six layers were recorded, three around the a-axis (0–2), two around the b-axis (0–1) and one around the c-axis (0). All photographs were taken from the same specimen, a small block with fairly uniform cross section. The zero layer Weissenberg photograph taken around the c-axis was of much worse quality than the rest. The shadow of the specimen holder screened off a substantial part of the film so that only 29 reflexions of the $F(hk0)$ type could be properly assessed. Of the 1024 independent reflexions possible within the Cu $K\alpha$ limiting sphere, 353 appeared on the photographs. Reflexions $h0l$ with h odd, and reflexions $0k0$ with k odd were absent, specifying uniquely the centrosymmetric space group $P2_1/a$.

The integrated intensities of the reflexions were measured with an AMG microdensitometer. The measurements were extended to all spots whose densities were within the linear section of the density-exposure curve of the X-ray film (Laue Feinstruktur film), and reflexions due to both Cu $K\alpha$ and Cu $K\beta$ were measured. The various intensity values obtained for the same reflexion on any particular layer were correlated and averaged by using the film transmission factor and the intensity ratio of the $K\alpha/K\beta$ radiations. The

various layers were placed on the same relative scale by correlation through common reflexions.

The set of relative intensities obtained this way was first corrected for Lorentz and polarization factor by means of the charts given by Cochran (1948), and then converted to absolute values by the statistical method of Wilson (1942). As no absorption correction was applied, the graph of $\ln \langle f^2 \rangle / \langle I \rangle$ against $\sin^2 \theta$ departed considerably from the straight line, particularly at low angles where the absorption was greatest. Nevertheless, the high-angle section of the curve was straight enough to allow the derivation of an effective overall temperature factor. The slope of the high-angle section gave $B = 0 \cdot 5$, and this value was used in all structure factor calculations.

Structure analysis

An attempt was first made to find the approximate atomic arrangement from the Patterson function, calculating its value in the two Harker sections $(\frac{1}{2}, v, 0)$ and $(u, \frac{1}{2}, w)$ (Harker, 1936). The one dimensional Harker-section $(\frac{1}{2}, v, 0)$ showed only three distinct peaks (see Fig. 1), which were attributed to the four heavier atoms in the asymmetric unit (two S and two Na atoms) assuming that two of them have approximately the same y coordinate mod $\frac{1}{2}$. This assumption has later proved to be correct (see the arrows in Fig. 1 indicating the positions of the Harker peaks calculated from the final atomic coordinates). Owing to the smaller atomic number of the oxygen
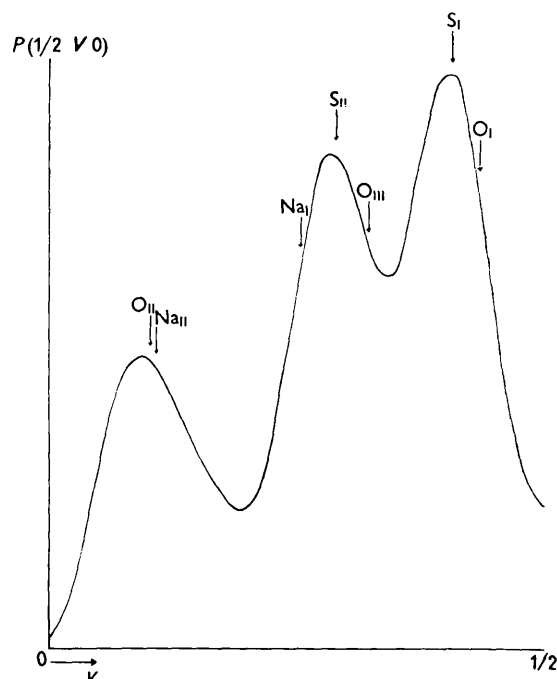

Fig. 1. The one dimensional Harker section $(\frac{1}{2}, v, 0)$ for $Na_2S_2O_3$. The arrows indicate peak positions calculated from the final atomic coordinates.

atoms no importance was attached to the apparent absence of individual O–O peaks but it was by no means expected that all three O–O peaks would almost coincide with one or other of the three observed peaks, as in fact turned out.
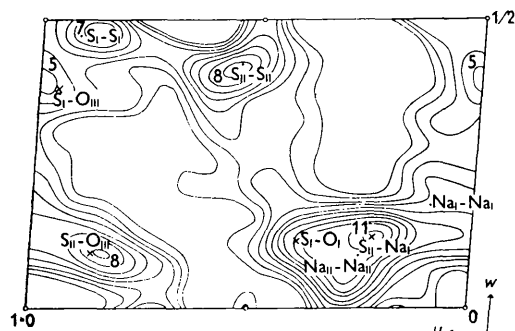

Fig. 2. The two dimensional Harker section $(u, \frac{1}{2}, w)$ for $Na_2S_2O_3$. The positions of the two Harker peaks calculated from the final atomic coordinates are marked by •, and the calculated positions of other Patterson peaks near to the Harker section are marked by ×. Contours at equal arbitrary intervals.

In the two-dimensional Harker section $(u, \frac{1}{2}, w)$ five distinct peaks could be discerned (see Fig. 2), the highest being a fairly extensive and apparently composite peak and the lowest being far lower than the rest. The four higher peaks were attributed to the two S and the two Na atoms, assuming that the highest peak was a S–S peak. This turned out to be wrong, and the trial structure based on this assumption had to be abandoned. It can be seen from Fig. 2 that only two of the five peaks appearing in the $(u, \frac{1}{2}, w)$ section are genuine Harker peaks (S_I–S_I and S_{II}–S_{II}) the three other being due to multiple coincidences of the y coordinates that makes the correct interpretation of this section a very difficult task.

After two unsuccessful attempts, the deciphering of the $(u, \frac{1}{2}, w)$ Harker section was abandoned and it was decided to use Fourier projections instead, the signs of the $F(h0l)$ and $F(0kl)$ structure factors being calculated by direct methods. The procedure of the sign determination was as follows.

In the space group $P2_1/a$ three signs can be specified arbitrarily, provided that the three vectors (hkl) and those related to them by space-group symmetry are linearly independent with mod 2 (Hauptman & Karle, 1954; Bertaut, 1955). Correspondingly, three large structure factors (014), (112) and (205) were assigned positive signs. Next the signs of four structure factors of the $(2h, 0, 2l)$ type were derived, using the formula given by Hauptmann & Karle (1953) for the space group $P2_1/a$. Only a small number of the signs were determined in this way because somewhat arbitrarily, only those signs were accepted for which the probability calculated from the formula of Cochran & Woolfson (1955) turned out to be > 0.9. Considerably more signs could be determined by the inequalities of

Harker & Kasper (1948), which provided 26 signs, so that the total number of known signs increased to 33. At this stage the equation of Sayre (1952) was applied in its statistical form as suggested by Zachariasen (1952). From those signs for which the probability calculated from the formula of Cochran & Woolfson (1955) exceeded 0.9, 186 more signs could be derived. Thus the total number of known signs rose finally to 219, more than half of all reflexions observed.

The distribution of the determined signs among the three projections and the general hkl reflexions is listed in Table 1.

Table 1. *Distribution of the determined signs*

Type of reflexion	No. of F_o's	No. of determined signs
$0kl$	64	51
$h0l$	52	46
$hk0$	29	26
hkl	223	107
Total	353	219

The missing signs in the three projections belong to reflexions for which the above-mentioned methods of sign determination failed to furnish a sign with the required high probability. As opposed to this, the determination of signs among the general reflexions was not followed up to its practical limit, because these signs had only indirect importance for the calculation of the three Fourier projections, and owing to the lack of suitable calculating aids, no three-dimensional Fourier synthesis was considered at this stage. This accounts for the rather low ratio of the determined signs among general hkl reflexions in Table 1.

It may be thought that the requirement of a 0.9 probability as an acceptance level is far too cautious, and that by lowering it one could obtain more correct
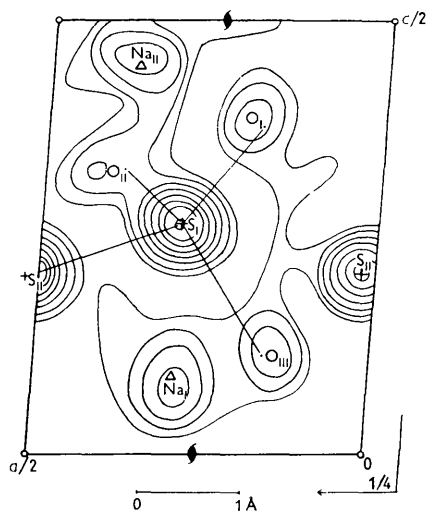

Fig. 3. Final electron density projection along the [010]. Contours at every 2 e.Å^{-2}, zero contours omitted. The position of the final atomic peaks marked, the inner bonds of the S_2O_3 tetrahedron indicated by straight lines.

signs and thus a better resolution in the Fourier maps. On the other hand it is worth mentioning that all the 219 signs determined with such high probability turned out to be correct although some of them belonged to reflexions with fairly small unitary structure factors (among the 219 determined signs 66, i.e. nearly one third belonged to reflexions with $|U_{hkl}| < 0.2$). It may also be noted that the number of signs determined with such a high acceptance level was large enough to provide an unambiguous solution for the atomic arrangement, even if only two-dimensional projections of the electron density were used.

The first [010] electron-density projection calculated with the 46 structure factors of known sign was very similar to the final map in Fig. 3. Peaks corresponding to all seven atoms of the asymmetric unit could be clearly recognized, and their relative heights indicated unambiguously the type of atom responsible for their occurrence. Only one oxygen atom (O_{II}) was not very well resolved, but even so there was no doubt about its approximate position.

The first electron-density projection down the [100] axis calculated from 51 structure factors of known sign showed all the six peaks appearing in the final map (see Fig. 4), and in addition to it there was also a rather blurred and broad seventh peak, just below the S_{II} peak. As the z coordinate of this seventh peak agreed well with the z-coordinate of the Na_I atom in the [010] projection, it was wrongly assigned to the Na_I atom. Thus at this stage it was not realized that this seventh peak was in fact a spurious peak due to series termination, and that the true Na_I peak merged in one single unit with the O_{III} peak, as can be seen in the final map in Fig. 4.

The atomic coordinates derived this way from the first two electron-density maps clearly indicated that the S_2O_3 group has an approximately tetrahedral arrangement, in agreement with the results of Taylor & Beevers (1952). The structure-factor calculations based on the first set of atomic coordinates gave the following R factors: $R_{h0l} = 46.8\%$ and $R_{0kl} = 32.6\%$. The initial atomic coordinates were refined by computing successive $(F_o - F_c)$ syntheses (Cochran, 1951) in both the [010] and the [100] projections. After seven cycles the R factors dropped to $R_{h0l} = 17.3\%$ and $R_{0kl} = 21.2\%$ respectively. This was rather promising, except for the fact that the z-coordinates of the Na_I atom in the two projections diverged more and more as the refinement proceeded. A three-dimensional structure factor calculation undertaken at this stage gave a reliability factor $R > 50\%$ which made it obvious that in spite of the reasonable arrangement of the S_2O_3 group and the small R factors in the two projections something was basically wrong with the structure.
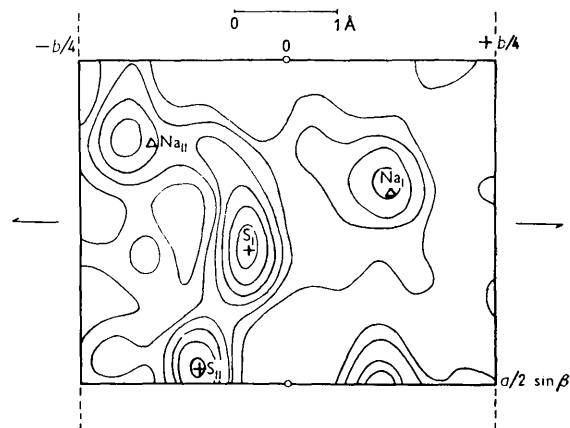
Fig. 5. Final electron density projection down [001]. Contours at every 2 e.Å^{-2}, zero contour omitted. The position of the final atomic peaks marked.

To find the error a third projection of the electron density down the [001] axis was calculated and though its resolution was distinctly poorer than that of the other two projections, the two S and the two Na peaks could be clearly recognized (see Fig. 5). Only the O peaks were absent and there were some small spurious peaks instead due to series termination. From the position of the Na peaks the error in locating the Na_I atom could be easily recognized. On removing this the three-dimensional R factor dropped immediately to 22.1%.

The further refinement was carried out by computing successive three-dimensional $(F_o - F_c)$ syntheses on EDSAC II, using a programme devised by Mr M. Wells. The programme refined the atomic coordinates and scaled the observed structure factors to the calculated ones after each cycle. The temperature factor was not refined, the same isotropic temperature factor $B = 0.5$
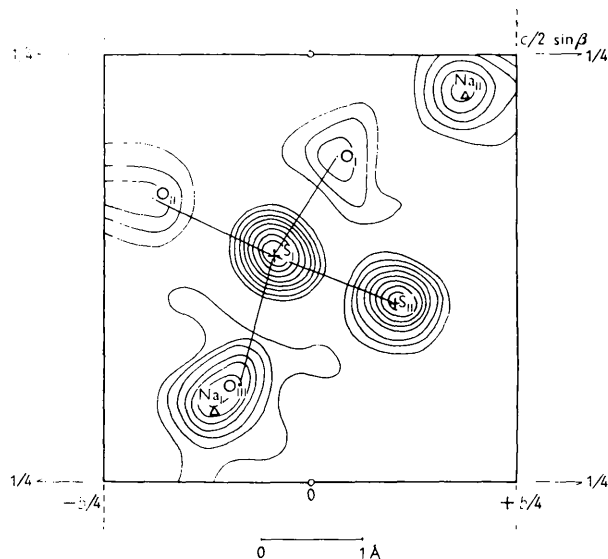

Fig. 4. Final electron density projection down [100]. Contours at every 2 e.Å^{-2}, zero contour omitted. The inner bonds of the S_2O_3 tetrahedron are indicated by straight lines, the position of the final atomic peaks marked.

Table 2. *Observed and calculated structure factors*

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
0 0 2	41	−56	0 10 2	6	+9	1 5 $\bar{3}$	46	−41	2 0 8	29	−38
3	18	−16	3	17	−22	$\bar{2}$	7	−9	9	52	+37
4	6	+3				0	28	+28			
5	14	−23	1 1 $\bar{10}$	23	−18	1	33	−33	2 1 $\bar{8}$	23	−21
6	41	−51	$\bar{9}$	18	+19	2	9	−11	$\bar{5}$	23	+23
7	19	−24	$\bar{8}$	40	+37	3	29	−28	$\bar{3}$	41	−47
8	8	+5	$\bar{7}$	26	−13	5	45	+46	$\bar{2}$	79	+81
9	20	+26	$\bar{5}$	19	−27	6	24	−27	$\bar{1}$	43	+25
10	13	+6	$\bar{4}$	30	−28	9	27	+24	1	64	−65
			$\bar{3}$	20	−24				3	32	−33
0 1 1	15	+17	$\bar{2}$	21	+24	1 6 $\bar{8}$	17	−25	5	15	−16
2	18	+23	$\bar{1}$	44	+57	$\bar{7}$	16	+14	7	27	+32
3	13	+12	0	19	−21	$\bar{6}$	18	−21	9	15	+17
4	78	+84	1	71	−67	$\bar{5}$	20	−21			
5	20	−30	2	96	+95	$\bar{1}$	54	+51	2 2 $\bar{10}$	31	+18
6	10	−15	3	50	+38	0	62	+55	$\bar{9}$	21	+19
7	27	−29	4	67	−48	1	48	−44	$\bar{8}$	44	−44
8	16	+11	5	17	−23	4	44	+37	$\bar{6}$	19	+13
10	6	−6	7	45	+44	5	51	−54	$\bar{4}$	17	−18
			8	26	−23	6	32	−32	$\bar{3}$	19	+25
0 2 0	40	+42	9	31	−33	8	26	+20	$\bar{1}$	31	+35
1	32	+28							0	48	−40
2	52	−54	1 2 $\bar{10}$	33	−31	1 7 $\bar{7}$	12	+11	2	53	+45
6	33	−34	$\bar{9}$	25	+27	$\bar{4}$	23	−26	3	59	−62
7	12	+1	$\bar{8}$	41	+33	$\bar{3}$	21	+15	5	11	+22
8	36	+36	$\bar{7}$	39	+37	$\bar{2}$	26	−29	6	17	+22
9	23	−28	$\bar{6}$	27	−25	$\bar{1}$	21	−17	7	36	−34
			$\bar{4}$	41	+47	1	28	+29	9	15	+17
0 3 2	30	+33	$\bar{3}$	12	+8	4	23	+24			
3	35	+38	$\bar{2}$	76	−92	7	19	−23	2 3 $\bar{8}$	18	−19
4	29	+35	$\bar{1}$	70	−61				$\bar{7}$	16	−14
5	27	+34	0	32	+34	1 8 $\bar{7}$	11	0	$\bar{6}$	29	+27
6	67	−68	2	34	+28	$\bar{5}$	17	−2	$\bar{5}$	26	+23
7	27	−29	3	32	−26	$\bar{4}$	12	+13	$\bar{4}$	27	−25
8	22	+16	6	31	+39	$\bar{3}$	13	−11	$\bar{3}$	20	−18
9	18	+17	9	16	−15	$\bar{1}$	31	+30	$\bar{2}$	50	+39
10	29	−27				1	19	−20	$\bar{1}$	81	+83
			1 3 $\bar{9}$	14	+12	2	33	−32	0	38	−32
0 4 0	42	−34	$\bar{7}$	42	−40	3	24	+21	1	61	−49
1	63	−60	$\bar{5}$	61	+58	4	41	+37	2	40	−38
3	46	+38	$\bar{3}$	27	+34	5	18	−14	3	34	+35
7	30	+36	$\bar{2}$	39	−35	6	27	−28	4	22	−24
8	14	+15	$\bar{1}$	46	+47				5	32	−39
9	26	−29	1	46	−37	1 9 $\bar{5}$	39	−42	6	15	+18
10	27	−28	2	33	−28	$\bar{4}$	11	−16	7	20	+20
			5	18	−17	$\bar{3}$	23	+21	9	14	+17
0 5 1	24	+24	6	30	+28	$\bar{2}$	13	+13			
3	52	−51	9	15	−2	$\bar{1}$	30	−26	2 4 $\bar{10}$	8	−13
5	37	+28	10	41	+35	0	11	−13	$\bar{5}$	52	−46
6	23	−20				1	24	+24	$\bar{4}$	20	−21
8	16	+16	1 4 $\bar{10}$	18	−15	2	13	+19	$\bar{3}$	29	+28
9	15	+16	$\bar{9}$	14	−10				$\bar{2}$	39	+47
			$\bar{8}$	50	+51	1 10 $\bar{2}$	15	−16	0	19	−20
0 6 0	20	−21	$\bar{6}$	23	−21	$\bar{1}$	8	−10	1	27	+33
1	23	−29	$\bar{5}$	21	−23	0	11	−16	2	38	+42
2	25	+27	$\bar{4}$	67	+44				4	40	−44
			$\bar{3}$	11	−14	2 0 $\bar{10}$	38	+28	5	26	−34
0 7 1	36	+33	$\bar{2}$	60	−43	$\bar{9}$	30	+26			
3	63	−76	$\bar{1}$	16	+14	$\bar{8}$	24	−20	2 5 $\bar{9}$	31	+31
5	17	+16	1	82	+63	$\bar{7}$	57	−50	$\bar{8}$	13	+10
6	12	+19	2	56	−41	$\bar{6}$	72	+82	$\bar{7}$	24	−18
			3	7	+9	$\bar{5}$	13	+16	$\bar{6}$	18	−15
0 8 0	15	−12	5	8	−10	$\bar{3}$	35	−33	$\bar{3}$	47	−47
1	28	+34	6	29	−28	$\bar{2}$	12	+16	$\bar{1}$	34	+32
3	13	−12	7	37	+35	$\bar{1}$	27	−34	0	17	−13
4	11	−16	9	25	−21	0	43	−50	2	27	+25
5	12	+13				1	18	+19	3	24	+25
7	22	−28	1 5 $\bar{8}$	14	−14	2	42	−49	4	23	−20
			$\bar{7}$	26	−27	3	23	−29	5	22	−23
0 9 3	4	−9	$\bar{5}$	28	+29	4	18	+36	6	30	+25
5	25	+34	$\bar{4}$	61	+58	5	78	+95	8	30	−31

Table 2 (cont.)

| h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
2 6 8̄	18	+21	2 8 1	22	−23	4 1 6̄	8	+13	6 0 5	19	+23
7̄	13	+12	4	24	+34	5̄	37	−44	6	29	−33
5̄	27	−25				2̄	19	+18			
2	17	+18	2 9 5̄	13	+16	1̄	15	+23	6 1 7̄	18	+12
3	17	+19	0	16	−25	1	5	−11	6̄	34	+38
4	18	−15	4	10	−12	3	30	+36	4̄	25	−25
5	20	−20							1̄	6	+9
7	16	+22	2 10 2̄	13	−15	5 1 9̄	13	+10	0	37	−40
			1̄	17	+6	6̄	8	−5	3	31	+34
2 7 8̄	9	+14	0	27	+33	4̄	48	−50			
7̄	13	−13	1	23	−9	2̄	35	+32	7 1 6̄	26	−25
6̄	28	−31				0	25	−19	5̄	13	−18
5̄	17	+15	4 0 7̄	31	−36	1	29	+27	4̄	20	+22
4̄	29	+25	6̄	24	−28	2	49	+55	3̄	19	+18
3̄	41	−39	5̄	64	+71	4	48	−57	2̄	25	−25
1̄	8	−17	4̄	39	+37	5	18	−20	1	4	−7
1	17	+17	3̄	46	−43	6	22	+25			
2	39	+42	2̄	18	−22	7	15	−15	8 0 3̄	27	−29
4	14	−12	1̄	55	+76				2̄	20	+18
6	26	+30	2	64	−76	6 0 8̄	18	−21	1̄	32	+30
			3	24	+25	7̄	16	+24	2	32	−9
2 8 6̄	14	−13	4	17	+16	4̄	43	−48			
5̄	24	+26	5	20	−21	2̄	35	−36	8 1 3̄	9	+14
4̄	14	+13	6	17	−17	0	37	+39	2̄	11	+15
2̄	51	−50				1	20	+11	1̄	13	+12
0	21	+16	4 1 10̄	9	+17	3	26	−24	1	13	−8
			9̄	21	−25	4	35	+37			
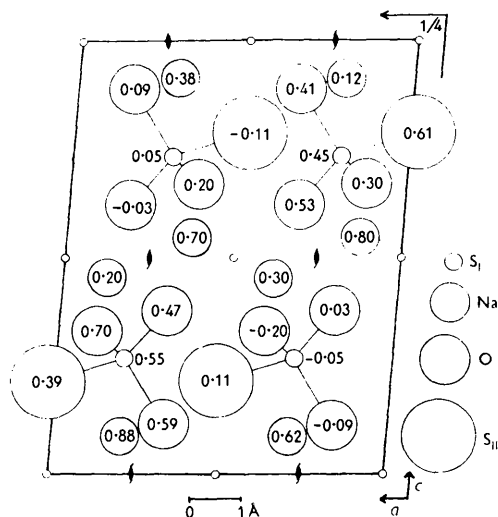
Fig. 6. The arrangement of atoms in the unit cell viewed along [010]. The fractional y co-ordinates are indicated. The full lines show the inner bonds of the S_2O_3 tetrahedra.

being used for all atoms during the whole refinement process. Altogether twelve cycles were performed after which the refinement process came virtually to a standstill. The final R factor was $R_{hkl} = 15.0\%$. The final calculated structure factors and the observed structure factors scaled to them are listed in Table 2. The final values of the fractional atomic coordinates are listed in Table 3, and the bond lengths and bond angles of the S_2O_3 thiosulphate group in Table 4.

Discussion

It can be seen from Table 4 that the S_2O_3 group has tetrahedral configuration in agreement with the results obtained by Taylor & Beevers (1952) for $Na_2S_2O_3 . 5 H_2O$. The deviations from the regular tetrahedron both in bond lengths and bond angles are about half as much as those found by the above mentioned authors. This is probably due to the somewhat higher accuracy of our data, reflected also in the smaller value of the R factor. The remaining deviations do not seem to be significant, and with increasing accuracy they would probably diminish still further.

Table 3. Final atomic coordinates and their standard deviations

The standard deviations were calculated from the ΔF's by Cruickshank's method (Cruickshank, 1949, 1954).

Atom	x	y	z	σ
S_I	1·91 Å	−0·38 Å	2·26 Å	0·01 Å
S_{II}	3·39	0·86	1·80	
O_I	1·20	0·27	3·24	
O_{II}	2·50	−1·62	2·82	0·03
O_{III}	1·06	−0·72	0·97	
Na_I	1·94	5·06	0·75	0·02
Na_{II}	2·43	2·47	3·87	

The length of the S–S bond (2·01 Å) is an intermediate value between the length given by Pauling (1948) for the S–S single bond (2·08 Å) and the length derived for the double bond spectroscopically from S_2 in the ground state (1·89 Å) by Ikenoue (1953). The S_I–O bonds seem to be largely double in character as

their mean value (1·47 Å) is very near to the bond length given by Moffitt (1950) for double S–O bonds (1·425 Å).

Table 4. *Bond lengths and bond angles in the* S_2O_3 *group with standard deviations*

		σ			σ
S_I–S_{II}	2·01 Å	0·02 Å	S_{II}–S_I–O_I	107·6°	
S_I–O_I	1·42		S_{II}–S_I–O_{II}	109·3	2·4°
S_I–O_{II}	1·46	0·03	S_{II}–S_I–O_{III}	108·3	
S_I–O_{III}	1·52				
S_{II}–O_I	2·79		O_I–S_I–O_{II}	109·4	
S_{II}–O_{II}	2·85	0·03	O_I–S_I–O_{III}	114·4	3·6°
S_{II}–O_{III}	2·88		O_{II}–S_I–O_{III}	107·9	
O_I–O_{II}	2·35				
O_I–O_{III}	2·47	0·04			
O_{II}–O_{III}	2·41				

The Na_I atom has four, and the Na_{II} atom five, oxygen atoms as nearest neighbours at distances varying between 2·37 and 2·64 Å. The next nearest neighbours are, for both Na atoms, one S_I and two S_{II} atoms with distances ranging from 2·87 to 3·10 Å. The nearest and next nearest neighbours do not form any regular arrangement around the Na atoms. The arrangement of the atoms in the unit cell is shown in Fig. 6.

The X-ray work and most of the structure analysis was carried out in the Physics Department of the Eötvös University in Budapest, and the refinement of the structure was done in the Cavendish Laboratory in Cambridge. It is a pleasure for the authors to make the following acknowledgements: Dr W. H. Taylor for the use of the facilities of the Crystallographic Laboratory, Cambridge, Mr G. Merczel for the preparation of the specimens, Mr P. Gadó for the density measurement, the Computational Department of the Hungarian Bureau of Statistics (SGAGI) for computing the Fourier projections on Hollerith machines, Mr G. Striker for the X-ray equipment and the microdensitometer, Dr K. Sasvári for the Weissenberg camera, Mr M. Wells for structure factor and refinement programmes for EDSAC II, Dr M. V. Wilkes

for permission to use EDSAC II, Mrs A. O'Brien and Mrs A. Newton for computational aid.

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