

The Crystal Structure of Sodium Tetrathionate Dihydrate

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Sodium tetrathionate dihydrate, $\text{Na}_2\text{S}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$, crystallizes in the space group C_2^3-C2 with two formula units per unit cell, of dimensions $a = 14.50 \text{ \AA}$, $b = 6.37 \text{ \AA}$, $c = 5.47 \text{ \AA}$, $\beta = 105.6^\circ$. The structure has been determined by X-ray methods, through projections along the b and c axes.

The tetrathionate ion lies on a twofold axis of symmetry in the crystals. The derived atomic coordinates give a length of $2.02 \pm 0.01 \text{ \AA}$ for the middle S-S bond across the twofold axis, and $2.12 \pm 0.01 \text{ \AA}$ for the terminal S-S bonds. The S-S-S bond angles are $103.8^\circ \pm 0.5^\circ$ and the dihedral angle SSS/SSS is $90.4^\circ \pm 1^\circ$. This confirms the results of an earlier structure analysis of barium tetrathionate dihydrate.

The sodium ion is surrounded by six nearest oxygen atoms at distances from 2.35 to 2.47 \AA , in a distorted octahedral arrangement. Columns of such sodium-oxygen octahedra, joined through shared opposite faces, run through the crystal in the direction of the b axis.

The reaction between sodium thiosulphate and iodine to produce tetrathionate was discovered in 1842 by Fordos and Gélis.¹ They isolated and analyzed barium tetrathionate dihydrate, and from the barium salt by metathesis with the sulphates prepared other salts, among them the sodium salt, without giving details. Sodium tetrathionate dihydrate was described in 1888 by Villiers,²⁻⁴ who obtained it from sulphurous acid and sodium thiosulphate. He first^{2,3} thought the salt had the composition $\text{Na}_2\text{S}_4\text{O}_8$ and was derived from a new sulphur-oxy acid, but later⁴ realized that it contained hydrogen and was the dihydrate of sodium tetrathionate. The salt was described crystallographically by Villiers³ and listed as 'sodium disulphopersulphate' by Groth.⁵

Following a survey of unit cells and space groups,⁶ the first crystal structure analysis of a salt of tetrathionic acid, the dihydrate of the barium salt, was published in 1954.⁷ The structure of the sodium salt has been briefly reported in a preliminary note⁸ and in a review article.⁹

CRYSTAL DATA

Sodium tetrathionate dihydrate, $\text{Na}_2\text{S}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$, was prepared from sodium thiosulphate and an excess of iodine essentially as described by Sander.¹⁰

It was recrystallized from 1 % acetic acid, by dissolving 20 g in 15 ml at about 40° , adding 30 ml of ethanol and cooling in ice and later in ice-salt. The crystallization is very slow.

The salt is monoclinic, space group C_2^3-C2 with two formula units per unit cell, and ^{6,8} $a = 14.50 \text{ \AA}$, $b = 6.37 \text{ \AA}$, $c = 5.47 \text{ \AA}$, $\beta = 105.6^\circ$. The crystals were invariably twinned on (100) and had an orthorhombic appearance: Short bipyramidal prisms {110} with {010} and often also {100} developed, and terminated by {201} and {001}.

Villiers ^{3,5} described the crystals as orthorhombic prisms {110}, sometimes with large {010}, and terminated by {011}. The measured angles gave the axial ratios $a:b:c = 0.4628:1:1.0692$. The monoclinic X-ray cell transforms to Villiers' orthorhombic cell by interchange of the a and b axes, taking d_{100} instead of a , and using a repeat distance along the c axis equal to $2c + a \cos \beta$. The axial ratios then become $a':b':c' = 6.37:13.97:14.84 = 0.4560:1:1.0623$, which agrees satisfactorily with Villiers' data.

Because of the twinning, hkl and $hkl\bar{}$ reflections occur superimposed on the X-ray photographs, with $hk0$ reflections from the twin parts coinciding exactly.

The intensities of 81 observed $h0l$ reflections and 56 observed $hk0$ reflections, out of 94 and 61, respectively, accessible with $\text{CuK}\alpha$ radiation, were estimated visually from zero-layer Weissenberg photographs of an approximately spherical crystal with a diameter of 0.12 mm. No correction for absorption was applied (μ for $\text{CuK}\alpha = 100 \text{ cm}^{-1}$). On the b -axis photographs, the intensities of both superimposed sets of $h0l$ and $h0\bar{l}$ reflections were estimated. The ratio between the intensities of equivalent reflections in the two sets was found to increase approximately linearly with $\sin \theta$, from a value of 1.32 at $\sin \theta = 0$ to 1.87 at $\sin \theta = 1$. These ratios at the appropriate $\sin \theta$ were used to separate the intensities of the exactly coinciding $h00$ reflections of the sets, and the strongest set of intensities was then used in the subsequent work.

The calculated structure factors were based on the atomic scattering curve of Viervoll and Ögrim ¹¹ for sulphur and of Berghuis *et al.* ¹² for oxygen. The sodium curve was based on the neon curve of Berghuis *et al.* ¹² at low scattering angles and on the electroneutral sodium curve at intermediate and larger scattering angles. The hydrogen contributions were ignored. Summations were made by means of Beevers-Lipson strips, at 6° intervals along the a axis and at 12° intervals along the b and c axes.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The tetrathionate ion lies across a crystallographic twofold axis of symmetry, and the asymmetric unit consists of one thiosulphate group, *i.e.*, of two sulphur and three oxygen atoms, and of one sodium ion and one water oxygen atom. Only the projection along the b axis is centrosymmetric.

The approximate x and z coordinates of the two sulphur atoms were found from the $h0l$ Patterson map, and the other atoms showed up in the first Fourier map based on 43 strong $h0l$ reflections with signs from the sulphur contributions. The approximate y coordinates of all atoms except the water

oxygen atom were derived from the $hk0$ Patterson map, by reference to the x and z coordinates and assumed molecular dimensions. The projections were refined through Fourier syntheses and repeated difference syntheses.

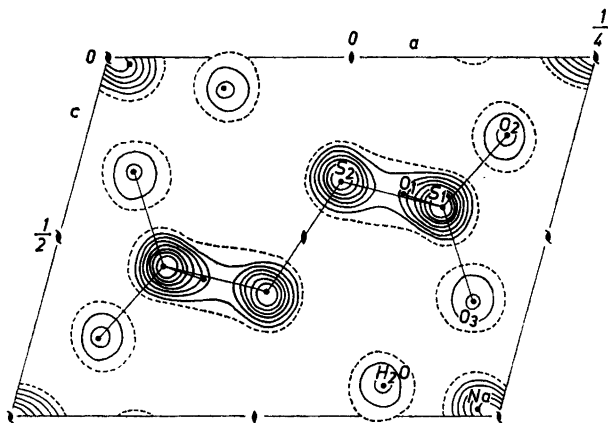


Fig. 1. Electron density projection of sodium tetrathionate dihydrate along the b axis, with lines drawn to show the outline of the tetrathionate ion. Contour intervals: $3 \text{ e} \cdot \text{\AA}^{-3}$. The 4-electron line is dashed.

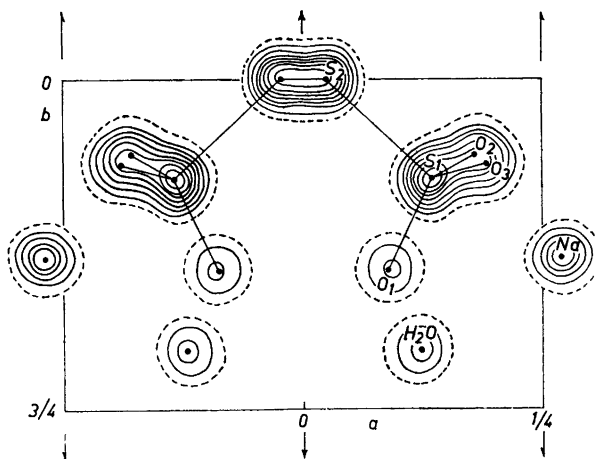


Fig. 2. Electron density projection of sodium tetrathionate dihydrate along the c axis. Contours etc. as in Fig. 1.

The final Fourier maps are reproduced in Figs. 1 and 2, and the final atomic coordinates are listed in Table I. The refined x coordinates from the $h0l$ zone, except for the O_1 atom and the sodium ion where overlappings occurred, were used in the subsequent refinement of the $hk0$ zone, and showed no indication

Table 1. Atomic coordinates for sodium tetrathionate dihydrate, in fractions of monoclinic cell edges. Origin on a twofold axis.

	x	y	z
S_2	0.0234	0	0.342
S_1	0.1340	0.227	0.420
O_1	0.090	0.435	0.379
O_2	0.180	0.169	0.223
O_3	0.192	0.193	0.678
Na	0.2710	0.406	0.020
H_2O	0.123	0.619	-0.088

of change. The x coordinates of O_1 and Na, listed in Table 1, are those from the $hk0$ zone, and differ from the $h0l$ coordinates only on the case of Na where it was $x = 0.2717$. The value, 0.0232, for the x coordinate of S_2 was used in the last structure-factor calculations for both zones, and was changed to 0.0234 on the basis of gradients in the subsequent last difference maps.

In the temperature factor $\exp[-B(\sin^2\theta/\lambda^2)]$ applied to the calculated structure factors, the values of B (\AA^2 units) finally chosen were: In the $h0l$ zone, $B = 2.3$ for S_1 , $2.7 + 1.2 \cos^2\varphi$ for S_2 , 3.5 for Na, O_1 , and the water oxygen atom, $2.3 + 3.0 \cos^2\varphi$ for O_2 , and $3.0 + 0.4 \cos^2\varphi$ for O_3 , where φ is the angle between the normal of the reflecting plane and the direction of maximum vibration of the atom. For S_2 this direction made an angle of 40° with the c axis in the obtuse angle, for O_2 60° with the c axis in the obtuse angle, and for O_3 40° with the c axis in the acute angle. In the $hk0$ zone, $B = 3.0$ for all atoms.

The observed and calculated $h0l$ and $hk0$ structure factors are listed in Table 2. The reliability index R , with non-observed reflections included when $|F_c|$ exceeds the observable limit, is 0.076 for both zones.

The standard deviations of the atomic coordinates were estimated from the root-mean-square gradients of the difference maps and the curvatures of the peaks in the electron density maps. Where overlapping occurred, the s.d. were increased, and in the non-centrosymmetric $hk0$ zone, they were doubled. The s.d. thus arrived at, and used for the calculation of the s.d. of bond lengths and angles, were: $\sigma(x) = 0.01 \text{ \AA}$ for S_1 , 0.007 \AA for S_2 , 0.012 \AA for Na and 0.02 \AA for the oxygen atoms; $\sigma(y) = 0.01 \text{ \AA}$ for S_1 , 0.016 \AA for Na, 0.03 \AA for O_1 and the water oxygen atom, 0.04 \AA for O_2 and O_3 ; $\sigma(z) = 0.006 \text{ \AA}$ for S_1 , 0.004 \AA for S_2 , 0.01 \AA for Na, 0.03 \AA for O_1 , and 0.015 \AA for the other oxygen atoms.

THE TETRATHIONATE ION

The bond lengths and angles, as calculated from the atomic coordinates of Table 1, are listed in Table 3 together with estimated standard deviations.

The earlier structure analysis⁷ of barium tetrathionate dihydrate gave the following values for bond lengths and angles in the sulphur chain of the tetrathionate ion (there, twofold symmetry is not crystallographically required):

Table 2. Observed and calculated $h0l$ and $hk0$ structure factors for sodium tetrathionate dihydrate.

			$h0l$ zone					
$h l$	$ F_o $	F_c	$h l$	$ F_o $	F_c	$h l$	$ F_o $	F_c
2 0	12	-16	2 2	37	+37	2 4	6	+ 6
4 0	22	-21	4 2	21	+21	4 4	9	- 6
6 0	21	+23	6 2	46	-47	6 4	22	-23
8 0	30	+33	8 2	39	+40	8 4	13	-11
10 0	5	+ 8	10 2	21	+21	10 4	3	+ 4
12 0	19	-19	12 2	7	- 9	2 $\bar{4}$	65	-66
14 0	< 4	+ 2	14 2	13	+12	4 $\bar{4}$	48	+47
16 0	< 3	+ 2	2 $\bar{2}$	82	-89	6 $\bar{4}$	15	+15
0 1	40	-44	4 $\bar{2}$	61	-61	8 $\bar{4}$	< 4	- 5
0 2	14	+13	6 $\bar{2}$	13	-10	10 $\bar{4}$	5	- 7
0 3	61	+57	8 $\bar{2}$	26	+26	12 $\bar{4}$	27	+24
0 4	17	-18	10 $\bar{2}$	67	-68	14 $\bar{4}$	19	+18
0 5	18	+16	12 $\bar{2}$	13	-13	16 $\bar{4}$	< 3	+ 1
0 6	< 3	- 3	14 $\bar{2}$	9	+ 8	2 5	13	-12
2 1	81	-91	16 $\bar{2}$	13	-13	4 5	< 4	+ 2
4 1	5	+ 7	18 $\bar{2}$	5	- 6	6 5	7	+ 8
6 1	31	-31	2 3	15	-15	8 5	8	+ 6
8 1	28	-28	4 3	19	+21	2 5 $\bar{5}$	5	- 4
10 1	15	-13	6 3	18	+17	4 5 $\bar{5}$	27	-26
12 1	< 4	0	8 3	< 4	- 7	6 5 $\bar{5}$	22	-22
14 1	13	-13	10 3	< 4	- 3	8 5 $\bar{5}$	7	+ 8
16 1	9	-10	12 3	< 3	+ 4	10 5 $\bar{5}$	22	-20
2 $\bar{1}$	16	-14	2 $\bar{3}$	26	+22	12 5 $\bar{5}$	11	-10
4 $\bar{1}$	55	+62	4 $\bar{3}$	59	+56	14 5 $\bar{5}$	11	-10
6 $\bar{1}$	25	-27	6 $\bar{3}$	28	-25	2 6	< 3	0
8 $\bar{1}$	30	+28	8 $\bar{3}$	20	+18	4 6	15	+16
10 $\bar{1}$	17	+14	10 $\bar{3}$	23	+22	2 6 $\bar{6}$	9	+ 6
12 $\bar{1}$	21	+18	12 $\bar{3}$	12	-10	4 6 $\bar{6}$	28	+29
14 $\bar{1}$	8	+ 8	14 $\bar{3}$	10	- 9	6 6 $\bar{6}$	< 4	+ 2
16 $\bar{1}$	8	+ 7	16 $\bar{3}$	4	+ 5	8 6 $\bar{6}$	< 4	- 6
18 $\bar{1}$	18	+20	18 $\bar{3}$	6	- 6	10 6 $\bar{6}$	< 3	+ 2
						12 6	17	+16

			$hk0$ zone				
$h k$	$ F_o $	$ F_c $	α	$h k$	$ F_o $	$ F_c $	α
2 0	12	16	180°	9 1	14	17	295.7
4 0	20	21	180	11 1	12	14	153.0
6 0	21	22	0	13 1	7	9	273.6
8 0	35	32	0	15 1	17	16	123.3
10 0	5	6	0	17 1	< 2	4	243.6
12 0	18	16	180	2 2	59	59	357.1
14 0	< 4	1	180	4 2	81	77	325.0
16 0	< 3	2	0	6 2	46	49	114.5
0 2	27	24	85.5°	8 2	3	7	311.5
0 4	69	61	286.0	10 2	10	10	18.3
0 6	12	10	93.9	12 2	15	16	316.2
0 8	6	7	342.3	14 2	11	10	202.8
1 1	58	61	55.3	16 2	19	20	145.0
3 1	69	67	289.2	1 3	29	27	301.8
5 1	86	84	5.1	3 3	81	76	36.5
7 1	20	19	82.0				

h	k	$ F_o $	$ F_c $	α	h	k	$ F_o $	$ F_c $	α
5	3	8	11	269.1°	5	5	22	21	276.6
7	3	20	23	320.0	7	5	27	26	27.0
9	3	19	21	297.8	9	5	6	7	93.2
11	3	29	29	99.5	11	5	6	8	290.0
13	3	< 4	2	184.0	13	5	11	11	177.7
15	3	11	11	225.0	2	6	20	19	329.5
2	4	46	44	33.8	4	6	16	16	358.9
4	4	6	7	81.9	6	6	18	19	19.3
6	4	25	25	0.6	8	6	10	10	167.0
8	4	13	11	5.8	10	6	6	7	327.6
10	4	6	6	221.0	1	7	4	6	21.3
12	4	10	7	175.4	3	7	15	19	345.4
14	4	< 3	2	339.2	5	7	9	9	45.6
1	5	44	41	21.3	7	7	8	8	254.9
3	5	7	8	248.0	2	8	8	9	336.3

$S_1-S_2 = 2.10 \text{ \AA}$, $S_2-S_3 = 2.02 \text{ \AA}$, $S_3-S_4 = 2.13 \text{ \AA}$ ($\pm 0.03 \text{ \AA}$); $\angle S_1-S_2-S_3 = 104^\circ$, $\angle S_2-S_3-S_4 = 102^\circ$ ($\pm 2^\circ$); dihedral angle $S_1S_2S_3/S_2S_3S_4 = 90^\circ$. These are in good agreement with the present, more accurate results.

The two types of sulphur-sulphur bonds in the tetrathionate ion are of significantly different lengths: The middle one, between two divalent sulphur atoms, is $2.02 \pm 0.01 \text{ \AA}$ while the terminal ones, between a divalent and a sulphonate sulphur atom, are $2.12 \pm 0.01 \text{ \AA}$. The latter ones have the same length as the analogous, terminal bonds in the pentathionate and hexathionate ions, and the selenopentathionate and telluropentathionate ions. As noted earlier,⁹ the weighted average of the observed lengths of the terminal bonds in these ions, including the tetrathionate ion, is $2.11 \pm 0.01 \text{ \AA}$. The value for the middle bond, $2.02 \pm 0.01 \text{ \AA}$, and the latest value,¹³ $2.059 \pm 0.002 \text{ \AA}$ for the divalent S-S bonds in orthorhombic S_8 , encompass the reported values of $2.04 \pm 0.02 \text{ \AA}$ for the two middle bonds in the pentathionate ion^{9,14} and the three middle bonds in the hexathionate ion,^{9,15} and the average of 0.04 \AA in six non-cyclic organic disulphides: N,N'-diglycyl-L-cystine dihydrate¹⁶ ($2.04 \pm 0.005 \text{ \AA}$), hexagonal L-cystine¹⁷ ($2.032 \pm 0.004 \text{ \AA}$), L-cystine dihydrochloride¹⁸ ($2.044 \pm 0.01 \text{ \AA}$), L-cystine dihydrobromide¹⁹ ($2.024 \pm 0.014 \text{ \AA}$), formamidinium disulphide dibromide monohydrate²⁰ ($2.044 \pm 0.01 \text{ \AA}$) and the diode monohydrate²⁰ ($2.044 \pm 0.02 \text{ \AA}$).¹

Table 3. Dimensions of the tetrathionate ion.

$S_2-S_2' = 2.019 \pm 0.010 \text{ \AA}$	$S_1-O_1 = 1.46 \pm 0.03 \text{ \AA}$
$S_1-S_2 = 2.116 \pm 0.011$	$S_1-O_2 = 1.46 \pm 0.02$
$\angle S_1-S_2-S_2' = 103.8 \pm 0.5^\circ$	$S_1-O_3 = 1.45 \pm 0.02$
$\angle S_2-S_1-O_1 = 108.1 \pm 1.2^\circ$	$\angle O_1-S_1-O_2 = 112.6 \pm 1.4^\circ$
$\angle S_2-S_1-O_2 = 98.6 \pm 0.9$	$\angle O_1-S_1-O_3 = 113.5 \pm 1.4$
$\angle S_2-S_1-O_3 = 107.6 \pm 0.9$	$\angle O_2-S_1-O_3 = 114.8 \pm 1.1$

Dihedral angle $S_1S_2S_2'/S_2S_2'S_1' = 90.4 \pm 1^\circ$

The difference in lengths of the two types of bonds in the polythionate ions is in line with the statement by Truter²¹ that "The experimental evidence strongly suggests that the σ -bond radius does vary with the oxidation state of sulphur." From a discussion of the observed lengths of S—S, S—C, and S—Cl bonds, Truter²¹ concludes that "It is evident that many factors contribute to the observed bond lengths; they include the oxidation state of sulphur, its hybridisation, the electronegativities of all the atoms, and the existence of π -bonding, and they are not independent."

The S—O bond length, 1.45–1.46 Å, is as in organic sulphonates, *e.g.*, potassium methylenedisulphonate, $K_2CH_2(SO_3)_2$, for which 1.461 ± 0.005 Å has been reported.²² As remarked by Cruickshank,²³ this is intermediate between the 1.49 Å of the sulphate ion and the 1.43 Å of the sulphones.

The sulphonate groups have trigonal symmetry, the S—O bond lengths and the O—S—O angles (average: 113.6°) being equal within the experimental accuracy. From the S—S—O angles it appears that the trigonal axis of the SO_3 pyramid does not coincide with the direction of the terminal S—S bond; this may be due to packing forces in the crystal.

It is of interest to compare the dimensions of the thiosulphate groups in the tetrathionate ion with the thiosulphate ion. The S—S bond lengths reported from crystal structure determinations of sodium thiosulphate pentahydrate,²⁴ anhydrous sodium thiosulphate,²⁵ magnesium thiosulphate hexahydrate,²⁶ and barium thiosulphate monohydrate,²⁷ vary from 1.96 to 2.02 Å, the weighted mean is 1.99 Å. The bond there probably has some double-bond character.^{28,29} The average of the reported S—O bond lengths is 1.485 Å, of the O—S—O angles, 110°, and of the S—S—O angles, 109°; although the individual values differ considerably the averages may be fairly accurate. The oxidation of thiosulphate to tetrathionate thus brings about a pronounced lengthening of the S—S bond, a widening of the O—S—O angles, and perhaps a slight shortening of the S—O bonds.

THE IONIC ENVIRONMENT

The sodium ion lies 0.35 Å from the twofold screw axis at $\frac{1}{4}, y, 0$, and is thus repeated every $b/2 = 3.19$ Å in an only slightly zigzagging line. The ion is surrounded by six oxygen atoms in a distorted octahedral arrangement. Columns of such sodium-oxygen octahedra, symmetry related through the screw axis and joined through common faces, run through the crystal in the direction of the b axis. The corners of the common face of two adjacent octahedra are made up of one O_2 and one O_3 atom, belonging to tetrathionate ions in adjacent unit cells along the c axis, and of one water oxygen atom. Each of these oxygen atoms coordinates to two sodium ions, at O—Na distances of 2.46, 2.35, and 2.35 Å, respectively, to one side of the face and at 2.36, 2.43, and 2.47 Å to the other side, and at Na—O—Na angles of 85°, 86°, and 85°, respectively. The O—O edges of the shared face are 3.04, 3.04, and 3.15 Å, and the six edges between the two, screw axis-related, shared faces of an octahedron range from 3.27 to 4.09 Å.

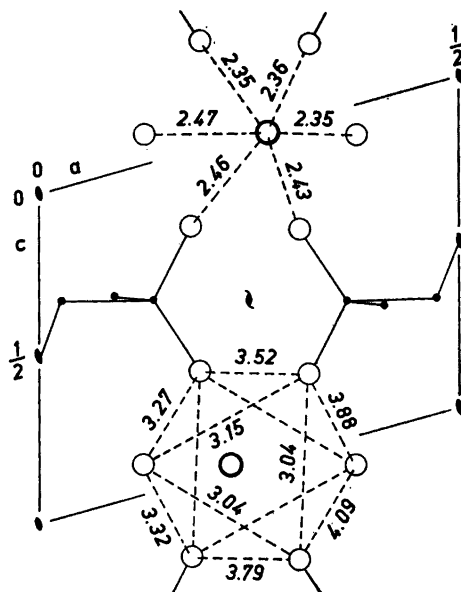


Fig. 3. The sodium-oxygen octahedra as seen along the b axis, with Na—O distances and O—O octahedral edges (Å). Heavy circles: sodium; light circles: oxygen. The screw axes at $\frac{1}{2}, y, 0$ and $\frac{1}{2}, y, 1$ (cf. Fig. 1) and the sodium ions on the other side of these screw axes, are not drawn.

In the c -axis direction, parallel chains of octahedra $c = 5.47$ Å apart, and symmetry related through a twofold screw axis at $\frac{1}{2}, y, \frac{1}{2}$, are held together through sulphonate groups of tetrathionate ions. Two $\text{O}_2\text{—S}_1\text{—O}_3$ bridges per octahedron occur on each side of a chain.

Similar layers of sulphonate-bridged chains of sodium-oxygen octahedra occur in sodium methanethiosulphonate monohydrate,²⁹ which crystallizes in the space group $D_{2h}^{16}\text{—}Pnma$ with $a = 6.49$ Å, $b = 5.55$ Å, $c = 16.23$ Å. There, the sodium ion lies in a mirror plane, 0.21 Å from the glide plane a which intersects the mirror plane, and the octahedra are thus more symmetrical than in the present structure, but the arrangements are otherwise the same. In the methanethiosulphonate, the chains of octahedra run in the direction of the a axis and the layers of octahedra are parallel to the c plane. Corresponding axes in the two structures are of nearly equal lengths: 6.37 and 6.49 Å, and 5.47 and 5.55 Å.

The oxygen atom O_1 of the sulphonate group does not coordinate to any sodium ion. Each sulphonate group, through the O_2 and O_3 atoms, thus coordinates to four different sodium ions, in two different chains of octahedra, and each tetrathionate ion coordinates to eight sodium ions, in two different layers of parallel chains of octahedra.

The water oxygen atom lies 2.96 and 3.06 Å from O_1 atoms, and 3.28 Å from the nearest S_2 atom; this might indicate a $\text{O—H}\cdots\text{S}$ hydrogen bond but the probable direction of the O—H bond, judging from the two sodium contacts of the water molecule, is not favourable.

There is in the structure an approximate glide plane of symmetry, parallel to the a plane at $x = \frac{1}{4}$ and $\frac{3}{4}$, and with translation $b/2$; this may explain the observed twinning on the a plane.

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