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Crystal Structure of Sodium Dithionate Dihydrate

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The crystal structure of sodium dithionate dihydrate has been determined, using single-crystal X-ray diffraction techniques. The unit cell is orthorhombic with $a = 6{\cdot}42 \pm 0{\cdot}01$, $b = 10{\cdot}75 \pm 0{\cdot}01$, $c = 10{\cdot}62 \pm 0{\cdot}01$ Å. There are four molecules per unit cell. The space group is *Pnma*.

A detailed crystal-structure analysis by means of Fourier and difference syntheses of the electron density projected perpendicular to the a and b axes is given. The size and shape of the dithionate ion have been determined; the interatomic distances are: S–S = 2·16 Å; S–O = 1·45 Å; O · · · O = 2·44 Å; and ∠ S–S–O = 103°. The sodium ion lies inside a somewhat distorted octahedron at the vertices of which six oxygen atoms are located.

1. Introduction

The size and the shape of the dithionate ion has been the subject of a number of crystal-structure investigations. The crystal structures of potassium dithionate (Huggins & Frank, 1931; Huggins, 1933; Helwig, 1932), cesium dithionate (Hägg, 1932) and rubidium dithionate (Barnes & Wendling, 1938) have been determined by the trial-and-error method only. Later, a crystal-structure analysis of barium dithionate dihydrate was made by means of Fourier syntheses (García-Blanco, Gomis & Abbad, 1953), but, owing to the presence of a heavy atom (barium) in the structure, the positions of the lighter atoms could not be accurately determined, making the arrangement of the dithionate ion only approximate.

In order to achieve better results, we began by working on another dithionate compound without any heavy atom, namely, $Na_2S_2O_6.2H_2O$. While we were engaged in this work Stanley (1953) published a paper on the structure of $Na_2K_5Cl_2(S_2O_6)_2$ and $Na_2K_2Cl(S_2O_6)$, which had also been determined with the help of Fourier projections.

2. Experimental

Crystals of $Na_2S_2O_6.2H_2O$ were obtained from a solution of warm barium dithionate dihydrate to which the equivalent amount of sodium carbonate was added, and the filtered solution was then evaporated spontaneously. The crystals obtained were recrystallized twice in order to purify the product.

These crystals are stable in air. According to Groth (1906–19) these crystals belong to the orthorhombic system, holohedral symmetry, and their axial ratio is:

$$a:b:c = 0{\cdot}9922:1:0{\cdot}5981\ .$$

The axial ratios from the lattice constants, obtained from rotation photographs around each of the three principal axes, are

$$a:b:c: = 0{\cdot}60:1:0{\cdot}99$$

in good agreement with Groth's values, allowing for the fact that the notation has been changed (the a axis has been substituted for c, and vice versa) in order to suit the space group *Pnma* to the *International Tables* (1935).

The lattice constants are:

$$a = 6{\cdot}42 \pm 0{\cdot}01,\quad b = 10{\cdot}75 \pm 0{\cdot}01,\quad c = 10{\cdot}62 \pm 0{\cdot}01\ \text{Å}\ .$$

The number of molecules, taking as density the value 2·189 g.cm.$^{-3}$ given by Groth (1906–19), is $N = 4{\cdot}01$. For $N = 4$ the calculated density is 2·181 g.cm.$^{-3}$.

Weissenberg photographs were obtained with Cu $K\alpha$ radiation (zero and n-levels corresponding to the [100], [010] and [001] axes). From the reflexions found by indexing these diagrams by the Huerta (1952) method, the following extinctions are deduced: $(0kl)$ with $k+l = 2n+1$, and $(hk0)$ with $h = 2n+1$.

Consequently the probable space groups are D_{2h}^{16}–*Pnma* or the hemimorphic group $C_{2v}^{9(b)}$–$Pn2_1a$. A rather close agreement between the F_o and F_c was obtained, as may be seen later, with the space group D_{2h}^{16}–*Pnma*, which is considered as final.

3. Determination of the structure

(*a*) *The* [100] *projection*

The data for this projection were obtained from the measurements of the intensities of the reflexions from Weissenberg photographs obtained with a six-film pack. The intensities were visually estimated by comparing to standard scales previously rated by photometry.

The values thus obtained were used, after correction for polarization and Lorentz factors, to make the corresponding Patterson projections (Fig. 1), employing the Beevers & Lipson strips. No correction for absorption was made because small crystals were employed, all being less than the optimum size ($\mu_{\text{Cu}} = 79{\cdot}5$ cm.$^{-1}$).

A preliminary examination of the Patterson projections showed that atoms are arranged in rows parallel to the *c* axis with marked peaks at 0 and $\frac{1}{2}y$.

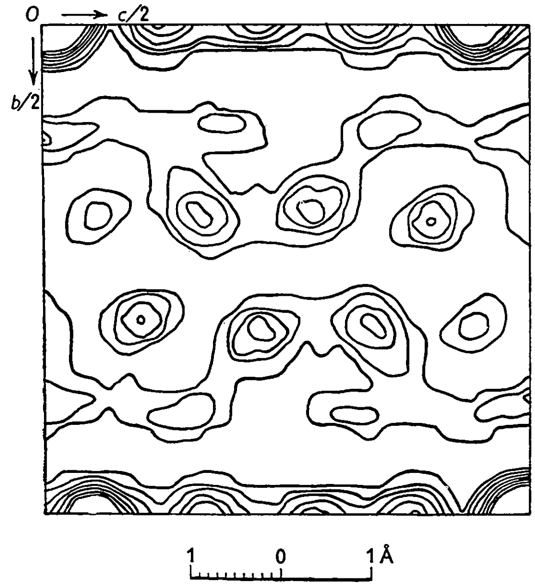

Fig. 1. Patterson projection on (100). Contours at equal arbitrary intervals.

To interpret this projection Buerger's (1951) method of minimum function was followed. This consists in converting the Patterson projection into an approximate electron-density map. Together with this method, the trial-and-error approach was also used, since the rotation peaks and satellites would seem, at first sight, to merge together with other peaks, which accounted for this great concentration of peaks on $y = 0$.

All minimum functions corresponding to the peaks found along $y = 0$ were made; in all of them was found a structure arranged in rows parallel to the *c* axis and it was also observed that the dithionate ions were located on reflexion planes. At first, the inclination of the ion was not known since there appeared a row packed with atoms and the oxygen atoms corresponding to the dithionate ion were not clearly defined.

A first M_4 function was tried, with which the fundamental assumption of the structure was made, but the results were unsatisfactory as the value of $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$ did not go lower than 0·36 through the successive Fourier projections. Then a [010] Patterson projection was made; there appeared a peak at a distance from the origin of 2·09 Å, which was attributed to the S–S distance of the ion, and it was deduced that, on the *c* axis, the S–S distance should be less than 2·09 Å.

Another M_4 function (Fig. 2) was tried in which the sulphur atoms of the ions appeared at a distance of less than 2·09 Å, and a Fourier projection was made using only the coordinates of the ions, as there was some uncertainty as to the coordinates corresponding to the water and the sodium. This Fourier projection appeared satisfactory: in places where sodium and the oxygen atoms of water were thought to have been located there appeared peaks. With their coordinates, and employing a temperature factor with $B = 1{\cdot}21$ Å^2 (deduced from the plot of F_c/F_o against $\sin^2\theta/\lambda^2$) a *R* value of 0·33 was obtained. A second Fourier synthesis was made, and the *R* value found was 0·29, which indicated an improvement although several signs still changed. In the following Fourier synthesis, *R*, through the introduction of *F*(000), fell to 0·24, and no changes of signs were observed. At this point a second temperature factor with $B = 0{\cdot}25$ Å^2 was calculated, and *R* became 0·23 for all the planes of the [100] projection (the non-observed *F*'s were given values equal to half of the lowest observed *F*'s).

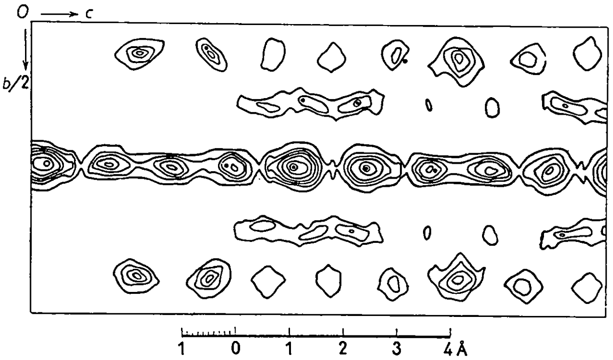

Fig. 2. Map of the minimum function $M_4(y, z)$. Dots: final positions of Fourier projection.

Fig. 3(*a*) shows the final Fourier synthesis. In comparing it with Fig. 2 it may be seen that the positions of the atoms do not differ greatly from those found by the minimum-function method. Fig. 3(*b*) shows a projection of the structure.

(*b*) *The* [010] *projection*

For this projection a series of Weissenberg photographs were used; the diagrams were obtained by the multiple-film technique using Cu $K\alpha$ radiation. The intensities were estimated with the same scales previously used, and then corrected for polarization and Lorentz factors.

To convert the F_o^2 into an absolute scale, the method of (Wilson, 1942) was used, and with these data the corresponding Patterson projection was made.

Several minimum-function diagrams were drawn, but nothing final was achieved since the peaks were not sufficiently resolved; to establish the arrangement of the structures we had to follow a method of successive approximations.

The (*h*00) reflexions of this projection are, as a whole, rather suitable for a first deduction of the x coordinate of the different atoms since (200) and (400) are almost zero, and (800) is one of the strongest reflexions in the projection.

With the first trial structure, obtained by successive approximations, a Fourier synthesis was made, applying a temperature factor with $B = 1{\cdot}23$ Å^2; the agreement factor was found to be $R = 0{\cdot}38$. In this projection the oxygen atoms were not sufficiently resolved. A second synthesis was made with signs corresponding to those in the previous synthesis; in the second synthesis all the atoms were already well resolved, and the agreement factor dropped to 0·33. Changes of signs were still observed. The next synthesis made this value fall to 0·26. With the coordinates of the fourth Fourier (Fig. 3(*c*)) there were no further changes of signs, and consequently this projection was considered as final. Then a second temperature factor was calculated, and the value of B obtained was 0·25 Å^2, which was exactly the same as that of the [100] projection; the agreement factor for all the reflections was found to be 0·23. Fig. 3(*d*) shows the projection of the structure.

4. Refinement and accuracy of coordinates

Refinement of coordinates was carried out by application of the $(F_o - F_c)$ technique (Cochran, 1951) to both projections.

Starting with the [100] projection, and after making seven difference syntheses, the R factor was successfully brought down from 0·231 to 0·153, all reflexions included. No attempt was made to introduce individual temperature factors; the temperature factor finally employed for all the atoms in the structure was $\exp\,[-0{\cdot}10 \sin^2 \theta/\lambda^2]$. The values for f_0 were taken from the *International Tables* (1935). Fig. 4 shows the difference syntheses corresponding to the initial and final stages of this [100] projection. There may be seen several peaks which should be ascribed to experimental errors, as well as to the omission of individual temperature factors. The fact that Hartree's values for the f_0' have been taken instead of those actually corresponding to the structure also accounts for these peaks.

Proceeding with the [010] projection, and following a similar procedure, after ten successive difference

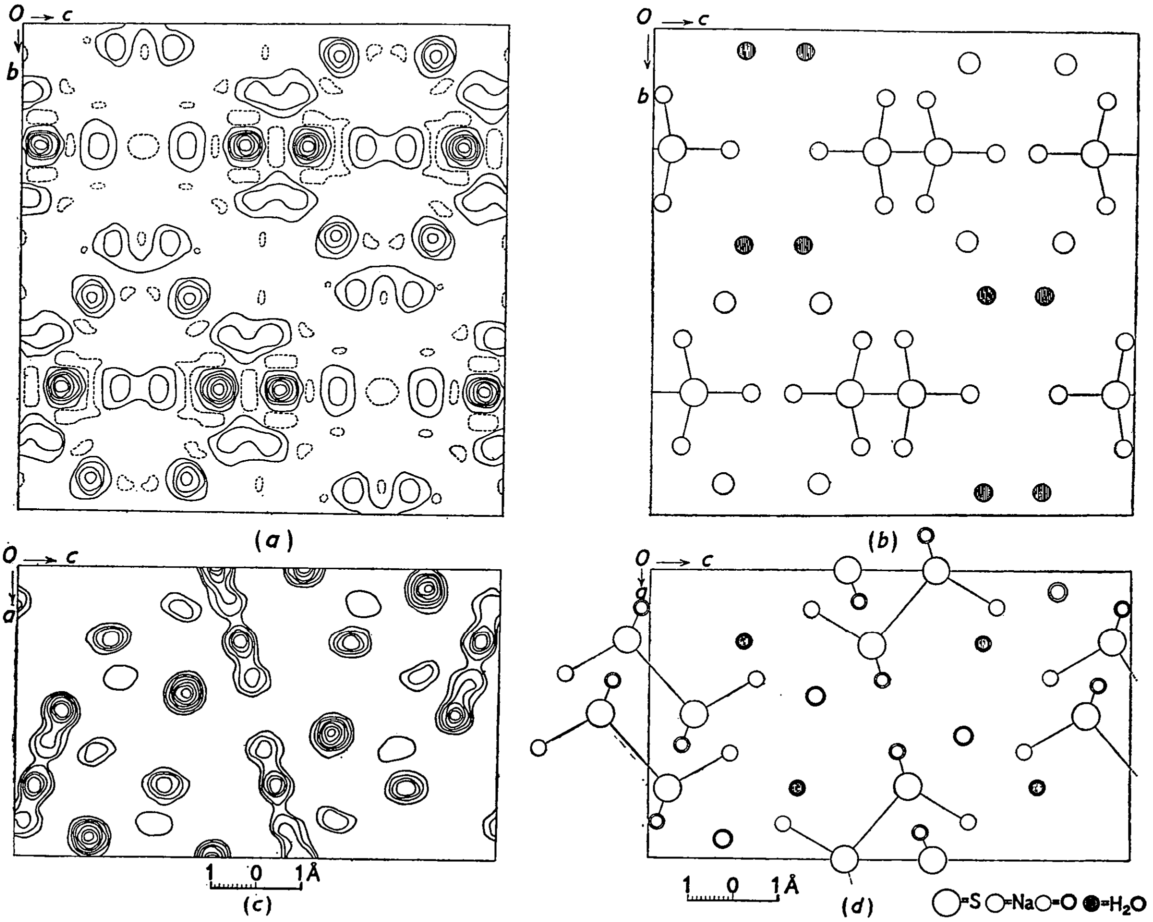

Fig. 3. (*a*) Electron density projected on (100). Contours are drawn at intervals of 5 e.Å^{-2}, the zero contour being broken. (*b*) Arrangement of the ions in the *a*-axis projection. (*c*) Electron density projected on (010). Contours are drawn at intervals of 5 e.Å^{-2}, starting at 10 e.Å^{-2}. (*d*) Arrangement of the ions in the *b*-axis projection.

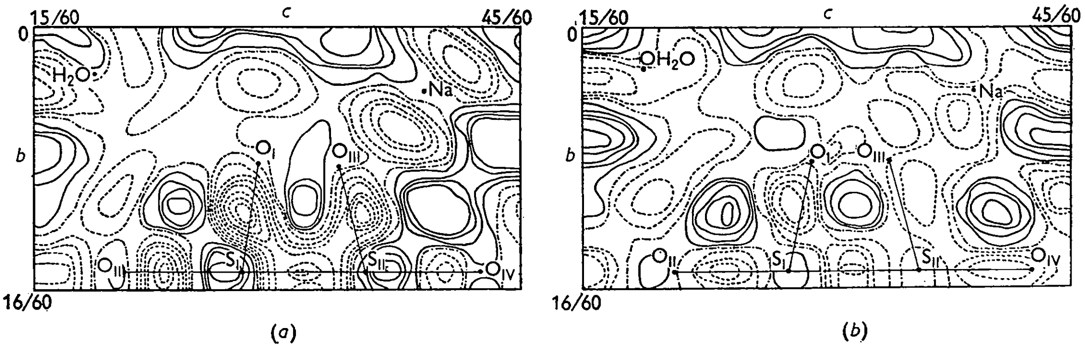

Fig. 4. (a) First projection of $(\varrho_o - \varrho_c)$ on (100). Contours drawn at intervals of ½ e.Å^{-2}. Zero contour chain, negative contours broken. (b) Final projection of $(\varrho_o - \varrho_c)$ on (100). Contour scale as in (a).

syntheses the agreement factor was reduced from 0·230 to 0·185. Here, also, non-observed reflexions were given a value equal to one-half of the smallest observed value, as was the standard procedure throughout the work. Table 1 gives the final coordinates obtained—for both projections—by this method. Table 2 shows a comparison between observed and calculated structure factors for the zones (0*kl*) and (*h*0*l*).

Table 1. *Final atomic parameters*

		(100) projection		(010) projection	
		y	*z*	*x*	*z*
4 S_I	(*c*)	0·250	0·458	0·253	0·458
4 S_{II}	(*c*)	0·250	0·591	−0·001	0·591
8 O_I	(*d*)	0·139	0·484	0·376	0·484
4 O_{II}	(*c*)	0·250	0·341	0·137	0·341
8 O_{III}	(*d*)	0·139	0·563	−0·122	0·563
4 O_{IV}	(*c*)	0·250	0·707	0·119	0·707
8 O_{H_2O}	(*d*)	0·044	0·191	0·250	0·189
8 Na	(*d*)	0·065	0·850	0·063	0·848

To determine the standard deviations of the coordinates Booth's (1947) formula for two-dimensional projections was employed:

$$\sigma(x_i) = \frac{3{\cdot}56}{N\sqrt{A}}\left(\frac{\pi}{\lambda p}\right)^2 \sigma(F_o)\,.$$

The average values of *p*, for both projections, which were found in this structure for resolved atoms were 6·4, 5·4 and 5·3 for sulphur, sodium and oxygen, respectively.

For $\sigma(F_o)$ two values were obtained for each projection, one of them starting from $(F_o - F_c)$ and the other from two independent intensity measurements. The mean value resulting from averaging both methods was taken as a measure of $\sigma(F_o)$, and the values finally found were $\sigma F_{0kl} = 5{\cdot}3$ and $\sigma F_{h0l} = 4{\cdot}8$.

From these data, the results were

$\sigma(x_i) = 0{\cdot}013$ Å for the sulphur atom;
$\sigma(x_i) = 0{\cdot}026$ Å for the sodium atom;
$\sigma(x_i) = 0{\cdot}038$ Å for the oxygen atom;

for the [100] projection, and

$\sigma(x_i) = 0{\cdot}011$ Å for the sulphur atom;
$\sigma(x_i) = 0{\cdot}023$ Å for the sodium atom;
$\sigma(x_i) = 0{\cdot}032$ Å for the oxygen atom;

for the [010] projection.

The standard deviations of interatomic distances determined by Cochran's (1953) formula were as follows:

$\sigma(b) = 0{\cdot}02$ Å for S–S ,
$\sigma(b) = 0{\cdot}05$ Å for S–O ,
$\sigma(b) = 0{\cdot}06$ Å for O–O ,
$\sigma(b) = 0{\cdot}06$ Å for Na–O .

These standard-deviation values were obtained from the mean values of the two projections.

5. Description and discussion of the structure

The structure of sodium dithionate dihydrate is typically ionic. Each sulphur atom of the dithionate

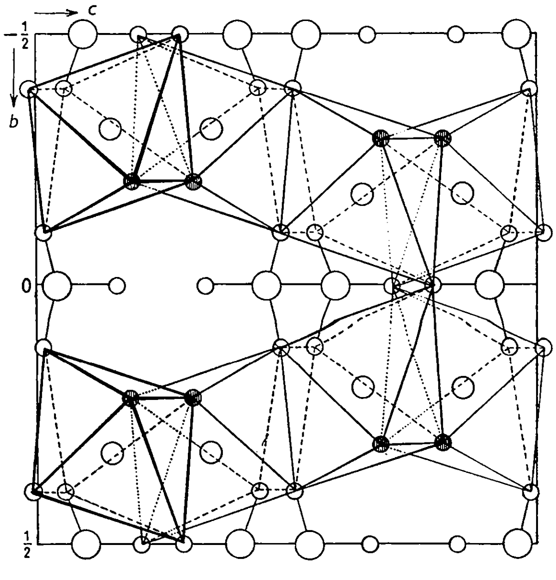

Fig. 5. Structure of $Na_2S_2O_6.2H_2O$, showing octahedral coordination.

Table 2. *Comparison of calculated and observed structure factors*

(1) 0*kl*

The calculation of F_c is based on the final atomic coordinates of the (100) projection

0*kl*	F_c	F_o	0*kl*	F_c	F_o	0*kl*	F_c	F_o
000	496	—	035	−35·0	37·3	0,7,11	−16·6	12·4
020	−58·7	52·2	037	+54·2	56·5	082	+77·1	71·4
040	+51·8	55·3	039	+88·2	87·6	084	+38·9	55·9
060	−116·4	98·8	0,3,11	−51·9	47·8	086	−51·8	62·8
080	+61·4	75·2	042	−59·7	49·7	088	−25·4	28·6
0,10,0	−137·6	107·4	044	−32·1	44·1	0,8,10	+15·9	13·7
0,12,0	+43·3	40·4	046	−16·9	18·0	091	−11·8	6·2
002	+41·8	39·1	048	−30·3	30·4	093	+11·3	17·4
004	−16·6	13·7	0,4,10	+10·4	6·2	095	+18·6	16·8
006	+48·6	50·3	051	+11·5	13·0	097	−64·0	81·4
008	−44·3	49·7	053	+ 6·1	6·2	099	−64·0	59·0
0,0,10	−22·8	19·3	055	−54·6	52·8	0,10,2	−28·7	34·8
011	+28·9	26·7	057	−57·3	69·6	0,10,4	+ 7·1	13·7
013	+29·3	25·5	059	+ 7·2	6·2	0,10,6	− 6·5	11·2
015	+12·1	6·2	0,5,11	− 1·7	6·2	0,10,8	+32·1	27·9
017	−69·2	52·8	062	+16·7	21·7	0,11,1	−34·5	32·9
019	−59·1	57·2	064	+57·7	55·3	0,11,3	−10·7	6·2
0,1,11	−25·4	26·7	066	− 6·4	6·2	0,11,5	+34·5	33·5
022	−79·7	78·8	068	+15·0	23·6	0,11,7	+30·3	31·1
024	−32·6	28·0	0,6,10	+18·6	19·3	0,12,2	+18·8	23·6
026	+60·4	52·8	071	−24·8	19·3	0,12,4	−15·9	13·0
028	+18·7	18·0	073	+13·0	16·2	0,12,6	−20·3	19·9
0,2,10	−12·7	6·2	075	+ 1·5	6·2	0,13,1	− 7·5	6·2
031	+12·8	6·2	077	+41·7	62·8	0,13,3	−15·1	11·2
033	+55·2	55·9	079	+74·7	87·6			

(2) *h*0*l*

The calculation of F_c is based on the final atomic coordinates of the (010) projection

*h*0*l*	F_c	F_o	*h*0*l*	F_c	F_o	*h*0*l*	F_c	F_o
200	− 4·2	5·2	4,0,10	+12·0	17·6	2,0,13	+13·1	5·2
400	+10·7	10·9	4,0,12	− 9·1	5·2	302	+84·9	81·2
600	−43·8	46·0	501	−28·7	25·8	304	−55·8	56·4
800	+74·6	91·0	503	+ 3·2	16·0	306	−25·9	31·0
101	− 6·4	16·5	505	+18·4	26·9	308	+26·9	24·8
103	− 5·4	5·2	507	−20·4	22·7	3,0,10	−31·7	39·3
105	+55·1	57·4	509	−17·6	12·9	3,0,12	− 9·7	9·3
107	+97·1	95·6	602	+ 6·2	12·4	401	+46·0	36·2
109	−14·0	19·6	604	−17·6	16·5	403	+ 8·2	5·2
1,0,11	−29·2	28·9	606	−48·1	40·8	405	−48·8	63·6
1,0,13	+ 8·4	5·2	608	+19·9	20·7	407	+14·8	17·1
202	+ 4·2	9·3	701	−43·3	31·0	409	+22·3	18·6
204	−73·4	74·1	703	+41·8	39·3	4,0,11	−22·0	16·5
206	−23·0	32·1	705	+27·1	32·6	502	+18·8	15·5
208	+37·1	31·5	707	+ 7·8	5·2	504	+ 8·5	23·2
2,0,10	+12·7	21·7	102	+53·0	35·7	506	− 9·5	8·8
2,0,12	+52·8	49·1	104	+103·9	89·4	508	+31·2	34·6
301	− 9·7	16·0	106	+14·2	18·1	5,0,10	+20·3	10·9
303	−50·7	59·9	108	+70·5	73·9	601	+20·1	20·2
305	+20·6	23·3	1,0,10	+19·8	20·2	603	+15·9	13·4
307	+10·5	19·1	1,0,12	−28·2	19·1	605	−27·1	21·7
309	−39·5	45·0	201	+28·7	19·6	607	+ 5·9	9·3
3,0,11	−34·6	34·6	203	−32·3	29·5	609	+ 9·0	5·2
402	− 6·3	5·2	205	−33·5	25·8	702	− 0·8	9·8
404	−23·7	21·2	207	+17·1	15·0	704	−60·6	49·6
406	−28·0	41·9	209	+31·6	33·1	706	−23·9	18·1
408	−23·9	32·6	2,0,11	+25·3	21·2			

ion is surrounded by the other sulphur atom and three oxygen atoms of the ion, forming an irregular tetrahedron. The interatomic distances in the ion are:

$$\mathrm{S{-}S} = 2{\cdot}16\ \text{Å}\,,$$
$$\mathrm{S_I{-}O_I} = 1{\cdot}46\ \text{Å},\ \mathrm{S_I{-}O_{II}} = 1{\cdot}45\ \text{Å}\,,$$
$$\mathrm{S_{II}{-}O_{III}} = 1{\cdot}45\ \text{Å},\ \mathrm{S_{II}{-}O_{IV}} = 1{\cdot}45\ \text{Å}\,,$$

with a mean S–O distance of 1·45 Å, and an average angle S–S–O of 103°.

The distance S–S found in this structure is 2·16 Å, slightly above the values given by Abrahams & Grison (1953) for the cesium hexasulphide (2·11 Å), by Stanley (1953) for the two potassium sodium chloride dithionates, and by Barnes & Wendling

(1938) for the potassium dithionate (2·08 Å). Notwithstanding, this value shows good agreement with the distance found by Zachariasen (1932, 1934) for the structures of potassium pyrosulphite (2·18 Å) and potassium trithionate (2·15 Å).

It is to be noted that, after finishing the Fourier analyses of the two projections under study, the value of the S–S distance was 2·14 Å, but its refinement by difference syntheses led to the 2·16 Å value and the agreement factor improved markedly.

The sodium ion lies inside a somewhat distorted octahedron at the vertices of which six oxygen atoms are located, namely two oxygen atoms of the water of crystallization, and four others of the different dithionate ions. The distances from the sodium ion are 2·38 and 2·36 Å for the oxygen atoms of the water, and 2·64, 2·53, 2·36 and 2·28 Å for the oxygen atoms of the dithionate ions. These values agree with those found in other structures (Jeffrey, 1954).

Table 3 gives the details of distances and ionic coordination.

Table 3. *Ionic coordination of* $Na_2S_2O_6.2H_2O$

Atom	Point position	Neighbour	Point position	Coordination number	Bond length (Å)
Na	(*d*)	O_{H_2O}	(*d*)	1	2·38
		O_{H_2O}	(*d*)	1	2·36
		O_I	(*d*)	1	2·64
		O_{IV}	(*c*)	1	2·53
		O_{III}	(*d*)	1	2·36
		O_I	(*d*)	1	2·28
O_{H_2O}	(*d*)	O_{II}	(*c*)	2	2·82
		Na	(*d*)	1	2·38
		Na	(*d*)	1	2·36
O_I	(*d*)	O_I	(*d*)	1	2·39
		O_{II}	(*c*)	1	2·47
		Na	(*d*)	1	2·64
		Na	(*d*)	1	2·28
O_{II}	(*c*)	O_I	(*d*)	2	2·47
		O_{H_2O}	(*d*)	2	2·82
O_{III}	(*d*)	O_{III}	(*d*)	1	2·39
		O_{IV}	(*c*)	2	2·49
		Na	(*d*)	1	2·36
O_{IV}	(*c*)	O_{III}	(*d*)	2	2·49
		Na	(*d*)	2	2·53

The distances were calculated with *z* coordinates of the (100) projection.

The octahedra of coordination have one vertex in common in which O_{IV} is located. They also share another vertex through one of the oxygen atoms of the water of crystallization; at the same time, they are linked through a common edge, O_I–O_I. Between these octahedra there are empty spaces where the sulphur atoms and the O_{IV} of the corresponding dithionic ions are located. This ionic coordination is illustrated in Fig. 5.

It is to be noted that the coordination of the sodium with the O_{III} connects dithionate ions having equal *y* values, while the coordination of the sodium with the O_I connects dithionate ions having different *y* values. The oxygen atoms of the water molecules act as the final connecting links for the different dithionate ions, thus forming the coordination octahedra which finally result in the coordinated ionic structure.

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