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The Crystal Structure of $NaHSO_4H_2O$

SIV GRIMVALL

Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg, P.O. Box, S-402 20 Göteborg 5, Sweden

The crystal structure of $NaHSO_4H_2O$, previously determined by Pringle and Broadbent,[1] has been refined and some of the original coordinates have been corrected. Crystals of $NaHSO_4H_2O$ crystallise in space group *Cc* (No. 9) with the unit cell dimensions: $a = 7.799 \pm 0.005$ Å, $b = 7.790 \pm 0.004$ Å, $c = 8.230 \pm 0.004$ Å, $\beta = 119.95 \pm 0.03°$, and $V = 433.22$ Å^3. There are four formula units in the unit cell.

The structure has been refined isotropically to a final R value of 0.074.

The distances within the HSO_4^- group are $S-O = 1.45_1$ Å (average) and $S-OH = 1.59_9$ Å. These groups are linked by hydrogen bonds to form zig-zag chains running along [101], the $O-H\cdots O$ distance being 2.65_8 Å. The sodium atoms are octahedrally surrounded by oxygen atoms at a mean distance of 2.41_6 Å.

As part of a series of investigations on titanium(IV) sulphate performed at this Department during the years 1963–66, attempts were made to prepare single crystals of $TiOSO_4(H_2O)_2$ according to the method of Pamfilov and Khudyakova.[2] It proved to be very difficult to reproduce their results but, after one of the attempts, a few single crystals appeared. Two or three of them were mounted in Weissenberg cameras and X-ray diffraction photographs were taken with Cu$K\alpha$-radiation. A structure determination was commenced assuming that the crystals had the formula $TiOSO_4(H_2O)_2$. After a while, however, it became evident that the substance was, in fact, $NaHSO_4H_2O$, and that the crystals must have been formed from impurities in the chemicals used in the synthesis. Since at that time the structure of $NaHSO_4H_2O$ was not known, the investigation was continued with a view to determining the bond distances in the HSO_4^- group. When the investigation was almost complete a paper on the structure of sodium hydrogen sulphate monohydrate was published by Pringle and Broadbent.[1] It was not at that time considered worthwhile to continue the work, but, later on, when there were indications that the experimental data obtained independently at this Department were of such a quality that it ought to be possible to reach a better R value than that published by Pringle and Broadbent,[1] it was decided to complete the investigation to see whether or not there would be any significant deviations between the results of the two structure determinations.

EXPERIMENTAL

Since the original aim was to prepare titanium sulphate, the method of Pamfilov and Khudyakova [2] was used. In order to obtain freshly prepared titanium(IV) oxide, which is soluble in sulphuric acid, a solution of sodium hydroxide was poured into titanium tetrachloride, and the resulting solution was heated to remove chloride as gaseous hydrogen chloride. The solution was then stored in an oven at 120°C for three weeks after which the sodium ions present gave rise to the by-product $NaHSO_4H_2O$. Stored in the acid, the crystals proved to be stable for several months, but they were very hygroscopic in air. Prior to the X-ray investigation they therefore had to be mounted in glass capillaries.

The investigation was based on X-ray single crystal methods. Rotation photographs (around [001] and [110]) and Weissenberg equiinclination protographs taken with Cu$K\alpha$-radiation showed the crystals to be monoclinic with $a=8.0$ Å, $b=7.9$ Å, $c=8.2$ Å, and $\beta=121.5°$. More accurate values of the cell parameters were calculated from photographs taken in a Guinier focusing camera with Cu$K\alpha_1$-radiation, using lead sulphate as an internal standard. The lead sulphate lines were then calibrated by means of a Guinier powder photograph of lead sulphate with lead nitrate ($a=7.840$ Å^3) as an internal standard. The resulting cell parameters of $NaHSO_4H_2O$, which were calculated with the ALGOL programme XALG POWDER,[4] were:

$a=7.799\pm0.005$ Å; $b=7.790\pm0.004$ Å; $c=8.230\pm0.004$ Å; $\beta=119.95\pm0.03°$; $V=433.22$ Å^3.

Observed and calculated $\sin^2\theta$ values are listed in Table 1. Assuming the cell content to be 4 formula units, the calculated density is 2.11 g/cm^3, which seems reasonable.

Table 1. Powder photograph of $NaHSO_4H_2O$. Cu$K\alpha_1$ radiation. $\lambda=1.5405$ Å.

h k l	$10^4\times\sin^2\theta$	$10^5\times\sin^2\theta$	*F* calc	*I* obs
−1 1 1	2221	2214	24	w
1 1 0	2288	2277	34	m
−2 0 2	4952	4947	108	vst
2 0 0	5213	5197	52	st
−1 1 3	9116	9089	41	m
1 1 2	9424	9403	38	m
−1 3 1	10055	10036	30	m
1 3 0	10123	10098	40	m
−2 2 3	12211	12232	66	st
−1 3 2	12309	12306	2	vvw
1 3 1	12475	12494	60	st
−2 0 4	14045	14030	48	m
−3 1 4	16581	16586	48	m
3 1 1	17532	17527	51	m
−2 2 4	17948	17940	81	st
2 2 2	18698	18693	51	m
2 4 0	20845	20840	58	st
−4 4 4	35451	35429	40	m

The single crystal reflections (391 independent reflections in all) were recorded using the multiple film technique. The relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with different exposure times.

The systematically absent reflections were:

hkl with $h+k=2n+1$
$h0l$ with $l=2n+1$

which is characteristic for the space groups $C2/c$ (No. 15) and Cc (No. 9).[5]

STRUCTURE DETERMINATION

The estimated intensity values were corrected for Lorentz and polarisation effects using the programme General Data Reduction.[6] A Patterson projection $P(uvp)$ and a generalized Patterson projection $P_1(uv)$ were then calculated using a Fourier programme.[7] $P(uvp)$ is shown in Fig. 1.

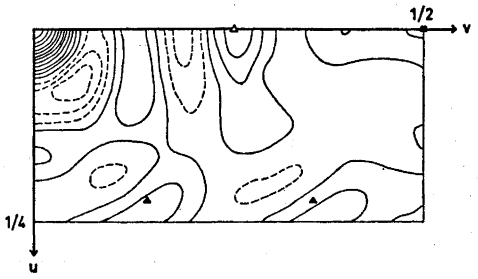

Fig. 1. Patterson projection $P(uvp)$. The final S–S (△), S–Na (▲) and Na–Na (■) vectors are indicated.

According to space group $C2/c$ the sulphur and sodium atoms should occupy fourfold positions. In order to explain the large maximum at $u=0$, $v=0.26$ in $P(uvp)$ the sulphur atoms must be assumed to be situated in 4(e). The S–S vectors are then $(0,0;\frac{1}{2},\frac{1}{2})\pm(0,2y_S)$, giving $y_S=0.13$. An electron density projection $\varrho(xyp)$ was then calculated using the signs of F_{hk0} obtained from the sulphur positions. This projection indicated that the sodium atoms ought to occupy one of the fourfold positions 4(c) or 4(d). At this stage of the structure determination it was possible to arbitrarily assign the sodium atoms to the position 4(c). Good agreement was obtained between the Na–Na vectors ($u=\frac{1}{2}$, $v=0$; $u=\frac{1}{2}$, $v=\frac{1}{2}$; $u=\frac{1}{2}$, $v=0$) and the corresponding peaks in the Patterson projection $P(uvp)$. The S–Na vectors are then $u=\pm 1/4$, $v=1/4-y_S=0.12$ and $u=\pm 1/4$, $v=1/4+y_S=0.38$. The corresponding peaks were, however, elongated away from the line $u=1/4$, which suggests that the correct space group is Cc (No. 9). The electron density projection $\varrho(xyp)$ also showed some indication of a symmetry lower than $C2/c$, especially for the oxygen arrangement. The space group was therefore subsequently assumed to be No. 9 – Cc. The sulphur parameters were identical with those determined for the space group $C2/c$, but the x-parameter of the sodium atom had to be shifted to a somewhat lower value. A close examination of $P(uvp)$ and $P_1(uv)$ yielded the following positions for sulphur and sodium:

4 S	in 4(a)	(Cc)	$x=0$	$y\approx 0.13$	$z=0.25$
4 Na	in 4(a)	(Cc)	$x\approx 0.22$	$y\approx 0.25$	$z\approx 0.00$

To determine the positions of the oxygen atoms, $\varrho(xyz)$ was calculated, using the $hk0-hk4$ reflections and the signs obtained by considering the contributions to the structure factors from sulphur and sodium. The first

electron density calculation revealed the positions of three of the oxygen atoms, namely:

O_1	$x \approx 0.04$	$y \approx 0.26$	$z \approx 0.14$
O_2	$x \approx 0.81$	$y \approx 0.10$	$z \approx 0.13$
O_4	$x \approx 0.13$	$y \approx 0.00$	$z \approx 0.33$

These parameters were checked against $P(uvp)$ by calculating the Na – O and S – O vectors, all of which could be found in the Patterson projection. After a few cycles of refinement of these parameters another $\varrho(xyz)$ was calculated using structure factors with signs determined from the Na, S, O_1, O_2, and O_4 contributions. The two remaining oxygen atoms could then be located in the positions:

O_3	$x \approx 0.00$	$y \approx 0.22$	$z \approx 0.38$
O_W	$x \approx 0.45$	$y \approx 0.11$	$z \approx 0.25$

The distances from the sulphur atom to the oxygen atoms $O_1 - O_4$, which lie in the range 1.4 – 1.6 Å, indicate that these atoms belong to the sulphate group. Since the $S - O_3$ distance is a little longer than the others, O_3 ought to correspond to the OH group of the HSO_4^- ion. O_W must then be the oxygen atom of the water molecule present in the structure.

In order to refine the structural parameters, least square full matrix calculations were performed, using the programme LALS.[8] Isotropic temperature factors were refined for all atoms and throughout the refinement Hughes' weighting scheme ($w^{-\frac{1}{2}} = F_o$ if $F_o > 4F_{o,min}$ and $w^{-\frac{1}{2}} = 4F_{o,min}$ if $F_o < 4F_{o,min}$) was employed. Isotropic refinement based on the [001] data yielded an R value of 0.103.

The O – O distances were used to identify the hydrogen bonds. The bond involving the acid hydrogen atom is $O_2 - O_3'$ the $O_2 - O_3'$ distance being 2.66 Å. The other two hydrogen bond distances, $O_W - O_4$ and $O_W - O_1$, are 2.84 Å and 2.90 Å, respectively. This is in good agreement with the results of Pringle and Broadbent.[1] Apart from the O – O distances in the sulphate group, there are no other O – O distances shorter than 3.10 Å. The hydrogen atoms were then assigned reasonable positions using the O – H distances cited in Ref. 9.

The refinement was then continued taking the scattering power of all atoms present in the unit cell into acount. The atomic scattering factors used for S, Na^+, O, and H were taken from the *International Tables*[3] and the independent reflections from [110] were added. The hydrogen parameters were not, however, refined. A final R value of 0.074 was obtained.

A list of all observed and calculated structure factors is given in Table 2. The resulting parameters, together with their standard deviations, are given in Table 3. Selected interatomic distances and angles, calculated with the programme DISTAN,[8] are given in Table 4.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of $NaHSO_4H_2O$ is not centrosymmetric. The sodium atom is octahedrally coordinated by six oxygen atoms, four of which belong to

Table 2. Observed and calculated structure factors for $NaHSO_4H_2O$. Unobserved reflexions are indicated by a dash.

0 K 0			
2	34	30	
4	18	16	
6	33	31	
8	41	37	
10	-	2	
1 K 0			
1	40	34	
3	40	40	
5	6	4	
7	49	47	
9	15	18	
2 K 0			
0	51	52	
2	26	24	
4	62	58	
6	12	14	
8	38	39	
3 K 0			
1	41	40	
3	60	60	
5	6	6	
7	29	26	
9	17	22	
4 K 0			
0	74	81	
2	46	47	
4	28	26	
6	21	22	
8	20	23	
5 K 0			
1	33	36	
3	30	29	
5	36	39	
7	15	16	
6 K 0			
0	34	33	
2	38	38	
4	37	38	
6	14	15	
7 K 0			
1	29	30	
3	29	29	
5	4	4	
8 K 0			
0	31	32	
2	16	16	
4	-	18	
-9 K 1			
1	14	15	
-8 K 1			
0	21	20	
2	15	13	
4	-	13	
-7 K 1			
1	37	35	
3	19	21	
5	27	28	
-6 K 1			
2	47	49	
4	15	14	
6	16	16	
-5 K 1			
1	25	25	
3	53	54	
5	39	38	
7	-	14	
-4 K 1			
2	49	44	
4	32	29	
6	44	40	
8	23	24	
-3 K 1			
1	55	55	
3	34	32	
5	26	24	
7	21	22	
9	33	35	
-2 K 1			
2	70	68	
4	34	30	
6	33	32	
8	-	4	
-1 K 1			
1	30	24	
3	56	50	
5	36	34	
7	22	20	
9	27	26	
0 K 1			
2	78	83	
4	54	50	
6	45	45	
8	25	23	
10	-	25	
1 K 1			
1	71	83	
3	59	60	
5	17	15	
7	30	28	
9	39	38	
2 K 1			
2	42	43	
4	8	6	
6	49	42	
8	12	13	
3 K 1			
1	49	51	
3	23	20	
5	39	38	
7	16	17	
9	38	36	
4 K 1			
2	37	38	
4	20	19	
6	30	30	
8	-	8	
5 K 1			
1	53	57	
3	-	8	
5	-	10	
7	19	24	
6 K 1			
2	30	29	
4	8	11	
6	34	36	
7 K 1			
1	30	30	
3	21	24	
5	-	36	
-9 K 2			
1	25	27	
3	20	23	
-8 K 2			
0	13	12	
2	16	18	
4	29	32	
-7 K 2			
1	37	36	
3	13	12	
5	33	34	
7	-	32	
-6 K 2			
0	62	61	
2	6	7	
4	41	43	
6	5	5	
8	-	19	
-5 K 2			
1	28	25	
3	43	42	
5	33	30	
7	25	24	
-4 K 2			
0	39	40	
2	22	22	
4	75	81	
6	20	19	
8	23	25	
-3 K 2			
1	15	13	
3	48	45	
5	34	31	
7	-	56	
9	11	13	
-2 K 2			
0	89	108	
2	18	16	
4	42	38	
6	21	20	
8	42	39	
-1 K 2			
1	53	55	
3	-	2	
5	15	13	
7	45	38	
9	13	14	
0 K 2			
0	45	49	
2	59	62	
4	63	61	
6	33	28	
8	35	35	
1 K 2			
1	36	38	
3	34	31	
5	48	43	
7	55	49	
9	27	29	
2 K 2			
0	69	63	
2	51	51	
4	31	30	
6	25	21	
8	35	37	
3 K 2			
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3	30	26	
5	51	46	
7	27	30	
4 K 2			
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2	40	40	
4	52	48	
6	6	7	
8	-	25	
5 K 2			
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3	32	28	
5	14	16	
7	-	31	
6 K 2			
0	42	42	
2	14	13	
4	12	13	
7 K 2			
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3	16	15	
-9 K 3			
1	25	26	
3	20	21	
-8 K 3			
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4	19	21	
6	-	28	
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4	18	17	
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5	35	33	
7	12	13	
-4 K 3			
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4	34	31	
6	42	38	
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-3 K 3			
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3	75	70	
5	58	61	
7	11	12	
9	23	26	
-2 K 3			
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4	35	29	
6	48	50	
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3	19	16	
5	36	35	
7	21	20	
9	22	25	
0 K 3			
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4	11	8	
6	57	53	
8	13	14	
1 K 3			
1	35	32	
3	30	37	
5	57	55	
7	8	8	
9	32	42	
2 K 3			
2	47	46	
4	20	18	
6	49	45	
8	16	16	
3 K 3			
1	48	48	
3	30	28	
5	7	8	
7	18	23	
4 K 3			
2	42	39	
4	17	15	
6	39	44	
5 K 3			
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3	24	22	
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6 K 3			
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4	11	11	
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7	31	34	
-4 K 4			
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4	42	40	
6	32	30	
8	27	29	
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3	27	26	
5	32	32	
7	28	26	
9	27	32	
-2 K 4			
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7	36	40	
9	19	23	
0 K 4			
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4	39	37	
6	18	17	
8	28	32	
1 K 4			
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3	43	44	
5	34	32	
7	30	32	
2 K 4			
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6	6	6	
8	14	18	
3 K 4			
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7	19	21	
4 K 4			
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5 K 4			
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6 K 4			
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1 K 5			
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5 K 5			
1	-	35	
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1	-	39	
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-8 K 6			
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6	-	2	
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-1 K 6			
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7	-	31	
0 K 6			
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2	-	12	
4	-	61	
6	-	9	
1 K 6			
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3	-	40	
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7	-	20	
2 K 6			
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6	-	9	
3 K 6			
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3	21	22	
4 K 6			
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-8 K 7			
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-6 K 8			
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-5 K 8			
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-4 K 8			
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0 K 8			
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-7 K 10			
1	19	20	
-6 K 10			
0	42	43	
2	-	5	
-5 K 10			
1	34	34	
3	21	19	
-4 K 10			
0	34	27	
2	23	19	
-3 K 10			
1	12	11	
-2 K 10			
0	47	47	

Table 3. Atomic coordinates and isotropic temperature factors with their standard deviations.

Atom	x	y	z	β	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(\beta)$
S	0.0000	0.1290	0.2500	0.25	0.0000	0.0003	0.0000	0.05
Na	0.2318	0.2777	0.0006	0.47	0.0009	0.0007	0.0009	0.10
O_1	0.0537	0.2596	0.1581	0.63	0.0014	0.0014	0.0014	0.17
O_2	0.7957	0.0730	0.1305	0.20	0.0013	0.0012	0.0013	0.15
O_3	0.9986	0.2136	0.4263	0.64	0.0015	0.0014	0.0016	0.17
O_4	0.1435	0.9917	0.3204	0.66	0.0015	0.0014	0.0014	0.16
O_W	0.4521	0.0889	0.2511	0.83	0.0014	0.0013	0.0015	0.18
H_1	0.345	0.057	0.274	2.00				
H_2	0.950	0.509	0.154	2.00				
H_3	0.113	0.293	0.508	2.00				

Table 4. Selected distances and angles. O–O distances within a sulphate group are denoted by an asterisk.

$Na-O_1$	2.329 ± 0.012 Å	O_1-O_4*	2.386 ± 0.015 Å
$Na-O_W$	2.363 ± 0.012 Å	O_1-O_2*	2.399 ± 0.014 Å
$Na-O_W'$	2.414 ± 0.012 Å	O_1-O_3*	2.477 ± 0.015 Å
$Na-O_3'$	2.445 ± 0.012 Å	O_2-O_3*	2.405 ± 0.014 Å
$Na-O_4'$	2.462 ± 0.012 Å	O_2-O_4*	2.443 ± 0.014 Å
$Na-O_2'$	2.480 ± 0.011 Å	O_3-O_4*	2.451 ± 0.015 Å
$S-O_4$	1.444 ± 0.011 Å	$O_W-H\cdots O_4$	2.839 ± 0.014 Å
$S-O_1$	1.448 ± 0.010 Å	$O_W-H\cdots O_1$	2.898 ± 0.015 Å
$S-O_2$	1.460 ± 0.009 Å	$O_3\cdots H-O_3'$	2.658 ± 0.014 Å
$S-OH\ (O_3)$	1.599 ± 0.011 Å		
O_1-S-O_2	$111.2 \pm 0.5°$		
O_1-S-O_3	$108.6 \pm 0.6°$		
O_1-S-O_4	$111.2 \pm 0.6°$		
O_2-S-O_3	$103.6 \pm 0.5°$		
O_2-S-O_4	$114.5 \pm 0.6°$		
O_3-S-O_4	$107.2 \pm 0.6°$		

the sulphate groups (*cf.* Fig. 2). The octahedron is somewhat distorted and the water oxygen atoms are in *trans* positions. The octahedra are linked together in the [101] direction to form zig-zag chains by the sharing of corners

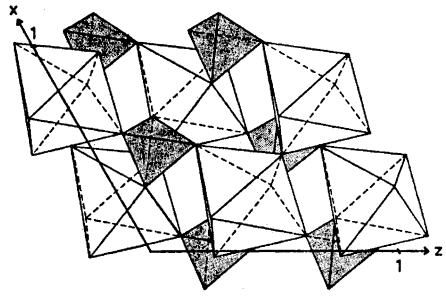

Fig. 2. Projection on the xz-plane. The positions of the chains of octahedra in relation to the sulphate groups are indicated.

occupied by water oxygen atoms, the chains being held together by sulphate groups. The Na – O distances vary from 2.33 Å to 2.48 Å (*cf.* Table 4) with a mean value of 2.42 Å. This is in good agreement with the values 2.25 – 2.78 Å given in the *International Tables*.[3] In Fig. 2 the chains of octahedra and the positions of the sulphate groups in relation to the octahedra are shown.

The configuration of the HSO_4^- group is distorted tetrahedral, the distortion being caused by the fact that the oxygen atoms participate in hydrogen bonding. The acid hydrogen atom of the HSO_4^- ion links the sulphate groups together forming a zig-zag chain running parallel to [101]. The water molecule is hydrogen-bonded to an HSO_4^- chain as well as to a chain of octahedra, which results in a more stable structure. The S – OH distance, 1.599 Å (Table 4), in this crystal approaches the single bond value of 1.70 Å given by Pauling.[10] The mean value of the S – O distances (Table 4) is 1.451 Å, which is somewhat shorter than the observed mean value of 1.49 Å in a regular sulphate group (Pauling [10]). The value 1.49 is, however, in good agreement with the mean distance 1.488 Å between all sulphur and oxygen atoms in the $NaHSO_4H_2O$ crystal. In a regular sulphate group, the O – S – O angle is 109.5°, but the distortion due to the acid hydrogen bond here causes three of the O – S – O angles to be smaller and the remaining three to be larger (*cf.* Table 4).

All interatomic distances and angles found in this work are in good agreement with those determined by Pringle and Broadbent.[1] There are, however, discrepancies between the x- and z-parameters of O_1 and the y-parameter of O_2 in the two investigations. Since structure factors calculated for the parameter values given by Pringle and Broadbent [1] are not in complete agreement with the calculated values published in their paper, the discrepancies would appear to be attributable to typographical errors in the x- and z- parameters of O_1 and the y-parameter of O_2, the two structure investigations thus, in fact, yielding similar results.

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