Acta Cryst. (1958). **11**, 349

The Crystal Structure of $KHSO_4$ (Mercallite)

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(*Received* 19 *November* 1957)

The structure of $KHSO_4$ has been determined and refined in two projections. The two HSO_4^- groups in the asymmetric unit are differently linked by hydrogen bridges: one set forms 'dimers' across a symmetry centre; the other is linked into infinite chains along a glide plane. All hydrogen bridges are approximately along the shortest unit cell edge (a axis); their lengths are 2·68 Å and 2·67 Å respectively.

1. Introduction

Very short hydrogen bridges having been reported for some acid salts (KH_2PO_4 (West, 1930; Frazer & Pepinsky, 1953) and $NaHCO_3$ (Zachariasen, 1933)), it was deemed of interest to investigate the bridge length in another acid salt. $KHSO_4$ was chosen. A paper by Oda (1939) reports cell dimensions and some information about symmetry. Some preliminary work was done in this laboratory about ten years ago (P. Bruyn & C. Berntsen, unpublished), and in Osaka University (T. Watanabe, private communication).

2. Experimental part

Crystals were prepared according to Stortenbeker's (1902) method: a solution of 20 ml. sulphuric acid of density 1·85 g.cm.$^{-3}$ and of 12·5 g. K_2SO_4 in 75 ml. water is left for a few days in a cool place. Crystals used for intensity measurements were ground on a small lathe to cylindrical shape, about 0·4 mm. in diameter. The following Weissenberg diagrams were made by Bruyn, Berntsen, and ourselves:

Reciprocal-lattice plane	Radiation
$0kl$	Cu K and Mo K
$1kl$	Cu K
$h0l$	Cu K and Mo K
hhl	Cu K
$h, -h+1, l$	Cu K

Intensities of $0kl$ and $h0l$ were estimated visually by the multiple-film method, and by using single films with different exposure time. The other films were used only for confirmation of the space group, and general information about intensity characteristics (see below).

3. Structure determination

The crystal symmetry is orthorhombic. Systematic absences indicate the space group D_{2h}^{15}–$Pbca$. Cell dimensions were found in close agreement with Oda's data:

$$a = 8{\cdot}40,\ b = 9{\cdot}79,\ c = 18{\cdot}93\ \text{Å}\quad (\text{accuracy about } \tfrac{1}{2}\%);$$

$$\text{Oda: } a = 8{\cdot}48,\ b = 9{\cdot}80,\ c = 18{\cdot}90\ \text{Å}\,.$$

$$a:b:c = 0{\cdot}859:1:1{\cdot}928\ (\text{our cell constants});$$
$$0{\cdot}8609:1:1{\cdot}9344\ (\text{Groth})\,.$$

Density (Groth) = 2·322 g.cm.$^{-3}$; this leads to 16 molecules $KHSO_4$ per unit cell, that is, two in the asymmetric unit.

On all films there is a marked tendency for $h+l$ = even to have a larger intensity than for $h+l$ = odd; it is therefore probable that K and S occupy positions which are nearly centred in the a–c plane. A plausible interpretation would be that between K_1 and K_2 there would be a shift $\frac{1}{2}\mathbf{a}+\frac{1}{2}\mathbf{c}$; likewise for S_1 and S_2. However, our trials with such configurations met with no success.

The [010] *projection*

Bruyn & Berntsen also made some diagrams of the isomorphous substance $KHSeO_4$. The intensity data were not good enough to use the straight-forward isomorphous method. However, the $h0l$ data of this compound were used in conjunction with those of $KHSO_4$ to find the K and S positions in the following way. Both sets of $h0l$ data were scaled by Wilson's method, and a subtraction Patterson function was computed (Buerger, 1942):

$$\Delta P(u,w) = \sum_h \sum_l \{|F_{h0l}|^2_{KHSeO_4} - |F_{h0l}|^2_{KHSO_4}\} \cos(hu+lw)\,.$$

Such a map should show S–S peaks with a relative weight of roughly $\frac{1}{2}(f_{Se}+f_S)$, and S–K and S–O peaks

Table 1. *Atom parameters of the structure of* $KHSO_4$

	x	y	z		x	y	z
K_1	0·383	0·180	0·125	K_2	0·877	0·322	0·119
S_1	0·250	0·423	0·004	S_2	0·980	0·018	0·207
O_{11}	0·283	0·576	0·005	O_{21}	0·060	0·983	0·277
O_{12}	0·410	0·352	0·998	O_{22}	0·840	0·112	0·224
O_{13}	0·156	0·396	0·937	O_{23}	0·914	0·890	0·172
O_{14}	0·160	0·392	0·071	O_{24}	0·086	0·096	0·156

Table 2. KHSO$_4$: *calculated and observed structure factors for* 0*kl and h*0*l*

hkl	$F_c.T$	$F_o.N^*$
002	7·3	5·7
4	2·9	6·0
6	15·7	16·2
8	28·6	25·9
10	20·7	21·6
12	7·1	10·3
14	21·1	20·1
16	19·1	19·3
18	19·9	19·4
20	4·7	1·9
22	2·7	3·7
24	14·9	13·5
26	6·4	8·1
28	0·3	2·4
30	1·8	2·7
020	17·7	17·8
2	9·5	9·5
4	36·2	33·4
6	7·3	8·2
8	15·3	17·7
10	7·9	9·7
12	8·3	10·5
14	13·1	15·0
16	9·2	8·3
18	3·0	2·3
20	10·4	12·0
22	1·1	1·2
24	0·1	(1·6)
26	2·4	(1·6)
28	6·0	4·7
30	3·6	4·3
040	25·2	23·3
2	18·4	20·3
4	3·3	3·0
6	7·7	9·8
8	7·1	8·0
10	5·7	3·4
12	14·3	12·7
14	1·9	1·7
16	10·3	9·8
18	7·9	8·4
20	3·4	2·1
22	2·9	4·3
24	0·1	(1·5)
26	4·8	4·0
28	0·5	(1·6)
30	0·5	(1·7)
060	6·1	6·3
2	15·3	17·2
4	17·3	19·4
6	10·9	11·0
8	9·1	9·3
10	4·8	4·8
12	26·8	25·5
14	6·4	8·3
16	2·5	(1·3)
18	2·7	4·7
20	9·4	9·6
22	6·5	7·2
24	7·9	4·1
26	1·2	(1·6)
28	5·9	7·2
30	4·4	3·8
080	5·5	9·0
2	12·6	13·0
4	11·2	12·3
6	6·0	5·6
8	22·4	20·6
10	4·9	4·2
12	4·0	2·5
14	3·4	2·6
16	14·2	13·1
18	3·1	4·5
20	2·7	3·5
22	1·2	(1·5)
24	6·9	6·5
26	5·4	5·6
28	3·8	2·2
30	2·0	(1·8)
0,10,0	13·3	13·4
2	4·2	3·5
4	3·2	2·4
6	1·9	1·8
8	2·5	(1·1)
10	1·3	(1·0)
12	3·1	3·5
14	3·1	3·2
16	0·2	(1·4)
18	2·7	2·2
20	3·7	2·4
22	3·4	2·6
24	0·5	(1·7)
26	0·2	(1·8)
28	1·0	(1·8)
0,12,0	11·8	11·4
2	4·9	5·5
4	1·1	2·0
6	5·0	5·4
8	10·3	9·7
10	5·8	6·9
12	1·7	2·7
14	3·3	4·3
16	6·8	6·0
18	4·2	5·3
20	0·9	(1·7)
22	0·1	(1·8)
24	5·2	4·5
26	3·3	3·7
0,14,0	8·3	4·1
2	4·9	4·8
4	12·2	12·5
6	6·2	6·2
8	1·2	(1·6)
10	4·4	4·1
12	8·9	9·0
14	3·8	5·3
16	2·8	2·4
18	0·7	(1·8)
20	9·3	7·5
22	5·1	4·1
24	0·9	(1·8)
0,16,0	2·3	2·5
2	0·3	(1·7)
4	3·9	4·2
6	0·9	(1·7)
8	4·7	4·0
10	1·1	(1·8)
12	3·7	3·7
14	1·9	(1·8)
16	3·6	3·1
021	7·1	8·1
3	6·0	7·8
5	2·3	(1·3)
7	0·2	(1·4)
9	6·9	5·4
11	1·0	3·5
13	9·6	9·8
15	4·5	5·0
17	1·3	3·1
19	3·4	3·3
21	0·4	2·8
23	1·5	1·3
25	1·3	(1·5)
27	0·4	1·5
29	4·8	4·7
041	4·6	7·1
3	0·8	3·1
5	0·8	(1·3)
7	0·5	(1·3)
9	3·8	4·8
11	2·9	5·0
13	2·0	(1·5)
15	0·9	(1·5)
17	5·8	7·4
19	1·1	(1·2)
21	6·1	5·8
23	4·3	4·4
25	3·7	4·0
27	0·2	(1·6)
29	1·6	(1·6)
061	2·6	3·1
3	0·2	3·2
5	4·6	2·7
7	4·2	5·3
9	5·5	5·0
11	2·4	3·6
13	2·0	3·3
15	0·6	(1·2)
17	3·7	4·5
19	3·3	3·7
21	—	(1·4)
23	5·5	2·4
25	4·9	3·3
27	3·1	2·4
29	1·3	(1·7)
081	0·8	3·4
3	2·0	3·1
5	0·1	(1·5)
7	4·0	3·6
9	4·0	4·8
11	4·5	4·8
13	0·9	3·3
15	2·1	1·7
17	5·3	2·0
19	2·0	1·8
21	1·1	(1·5)
23	2·4	(1·6)
25	5·6	4·3
27	2·0	(1·7)
29	0·6	(1·7)
0,10,1	2·9	4·0
3	2·6	2·3
5	2·8	3·6
7	—	(1·2)
9	3·4	3·9
11	4·1	7·1
13	1·4	1·7
15	1·3	3·1
17	1·5	(1·4)
19	—	(1·5)
21	6·1	6·2
23	2·2	2·6
25	0·1	(1·7)
27	0·7	(1·8)
0,12,1	4·1	3·7
3	2·4	3·7
5	0·1	(1·4)
7	1·5	(1·5)
9	0·2	(1·5)
11	2·8	3·4
13	5·9	4·9
15	2·7	4·6
17	1·0	(1·7)
19	2·5	(1·7)
21	2·0	(1·8)
23	0·9	(1·8)
25	3·0	4·3
0,14,1	2·3	(1·6)
3	1·0	(1·6)
5	0·8	(1·6)
7	2·8	2·3
9	2·7	3·6
002	7·3	5·4
4	2·9	5·7
6	15·7	15·3
8	28·6	25·0
10	20·7	20·5
12	7·1	9·7
14	21·1	19·1
16	19·1	18·1
18	19·9	18·4
20	4·7	1·8
22	2·7	3·4
24	14·9	12·7
26	6·4	7·6
28	0·3	2·3
30	1·8	2·5
200	1·2	2·0
2	34·1	29·8
4	12·3	11·9
6	4·8	4·2
8	12·6	13·7
10	2·6	2·8
12	15·9	17·0
14	4·2	6·0
16	11·2	11·0
18	5·1	7·3
20	2·6	2·5
22	7·5	8·9
24	1·5	(1·4)
26	5·5	4·8
28	2·5	3·2
30	3·4	2·5
400	20·0	17·8
2	2·5	(1·3)
4	36·0	31·8
6	12·6	12·6
8	9·2	12·7
10	13·7	13·3
12	12·6	13·8
14	10·9	13·0
16	8·7	8·3
18	2·6	2·4
20	17·6	17·7
22	3·3	4·8
24	0·1	(1·7)

Table 2 (*cont.*)

hkl	$F_c.T$	$F_o.N^*$
26	3·2	(1·7)
28	7·4	7·1
30	3·7	4·7
600	9·5	9·5
2	10·2	11·4
4	2·0	2·5
6	19·5	18·4
8	17·3	17·5
10	4·4	5·0
12	11·8	12·9
14	0·2	(1·0)
16	6·2	6·8
18	7·0	6·5
20	2·7	(1·3)
22	7·4	7·4
24	5·3	4·1
26	4·9	5·4
28	0·3	(1·7)
30	0·8	(1·7)
800	16·6	16·1
2	5·8	5·5
4	7·1	6·2
6	3·5	4·7
8	14·7	15·3
10	9·5	10·6
12	8·7	9·5
14	1·8	1·6
16	12·5	11·4
18	3·5	4·5
20	1·7	(1·6)
22	2·5	(1·6)
24	9·1	9·1
26	2·9	(1·7)
28	2·1	(1·7)
30	0·7	(1·7)
10,0,0	1·0	(0·9)
2	4·0	4·2
4	7·5	7·3
6	2·2	(1·4)
8	1·1	(1·4)
10	0·9	(1·5)

hkl	$F_c.T$	$F_o.N^*$
12	4·4	4·5
14	4·5	3·2
16	0·3	(1·6)
18	2·6	3·7
20	0·6	(1·7)
22	2·4	3·2
24	3·5	2·4
12,0,0	0·7	2·5
2	2·2	2·7
4	10·0	10·4
6	2·4	4·8
8	5·8	4·3
10	—	(1·6)
12	10·4	9·1
14	5·8	5·2
16	3·0	(1·7)
18	2·0	2·3
20	5·1	5·6
22	2·5	2·5
14,0,0	3·4	4·4
2	1·7	2·8
4	0·9	2·3
6	1·6	(1·7)
8	4·1	3·2
10	2·2	2·8
12	1·5	(1·7)
14	0·7	2·8
16	3·1	3·2
16,0,0	1·7	3·5
2	1·2	2·5
4	2·7	2·1
6	0·1	2·1
8	5·5	4·8
102	2·3	2·8
4	7·5	7·5
6	7·9	9·2
8	12·2	13·1
10	1·7	3·1
12	2·6	(1·8)
14	2·9	2·6

hkl	$F_o.T$	$F_o.N^*$
16	9·6	9·2
18	3·3	3·5
20	—	(1·3)
22	2·9	1·1
24	2·4	3·4
26	5·0	3·5
28	0·9	(1·5)
30	2·0	(1·6)
302	3·6	2·1
4	4·1	5·6
6	14·3	14·0
8	7·3	10·3
10	4·7	3·9
12	6·8	6·9
14	4·0	(1·6)
16	0·5	1·8
18	3·2	1·8
20	7·9	5·7
22	2·0	1·4
24	3·5	(1·5)
26	0·8	(1·5)
28	3·4	2·7
30	5·6	3·7
502	0·5	(1·3)
4	6·5	6·8
6	4·6	6·5
8	5·2	5·6
10	2·4	(1·4)
12	2·3	2·4
14	3·1	4·1
16	3·3	4·1
18	4·0	2·8
20	3·5	3·5
22	5·5	3·6
24	0·8	(1·5)
26	0·5	(1·5)
28	5·2	4·4
702	4·6	5·7
4	6·4	7·1
6	6·1	7·0
8	2·5	3·2

hkl	$F_c.T$	$F_c.N^*$
10	7·9	7·3
12	3·2	2·5
14	0·8	(1·1)
16	6·5	5·7
18	1·2	(1·4)
20	2·2	2·3
22	0·1	(1·5)
24	4·4	3·4
26	3·9	3·7
902	4·2	4·8
4	3·4	4·6
6	1·6	3·0
8	5·1	4·7
10	2·8	2·7
12	1·6	(1·4)
14	4·2	2·4
16	0·8	2·1
18	5·3	5·4
20	2·9	3·9
22	0·9	(1·7)
24	4·5	3·0
11,0,2	0·6	2·0
4	1·0	2·0
6	2·5	3·2
8	1·7	2·1
10	1·1	(1·5)
12	4·0	2·8
14	0·5	(1·6)
16	3·7	3·4
18	3·4	3·5
20	3·6	3·9
22	1·6	2·0
13,0,2	0·8	(1·7)
4	2·9	4·0
6	3·8	3·7
8	1·3	2·7
10	1·1	(1·7)
12	3·1	(1·7)
14	1·1	(1·7)
16	1·8	2·6
18	2·5	2·8

* Values in brackets are maximum values of $F_o.N$.

with relative weights of f_K and f_O respectively. All other peaks should be approximately cancelled if the scaling is correct and the temperature factor is the same in both cases. From the Wilson statistics the latter assumption seems to be sufficiently accurate.

From this map, and also by comparison with the Pattersons for $KHSeO_4$ and $KHSO_4$, the x and z coordinates of Se(S) and K could be derived. All atoms are in general position, S_1 at $x \approx \frac{1}{4}$, $z \approx 0$; S_2 at $x \approx 0$, $z \approx 0{\cdot}2$. From the coordinates of equipoints in the space group *Pbca*:

$$\pm(x, y, z);\ (\tfrac{1}{2}-x, \tfrac{1}{2}+y, z);\ (x, \tfrac{1}{2}-y, \tfrac{1}{2}+z);\ (\tfrac{1}{2}+x, y, \tfrac{1}{2}-z)$$

it is seen that atoms in general position are pseudo-centred in the a–c plane if either $z = 0$ or both x and y are near zero. It is thus clear that both the set S_1 and the set S_2 are pseudo-centred in b projection. Moreover, it is easily seen that in the point set of S_1, because $x = \frac{1}{4}$, the b axis is halved, whereas the set S_2 is pseudo-centred in all coordinate planes if y_2 is indeed approximately zero.

On the other hand, the following parameters for the potassium atoms were found:

$$K_1 \text{ at } x = 0{\cdot}38,\ z = \tfrac{1}{8};$$
$$K_2 \text{ at } x = 0{\cdot}88,\ z = \tfrac{5}{8}.$$

That is, K_1 is centred by K_2 and vice versa. Since the pseudo-centring in the a–c plane holds for all reflexions, the y coordinates of both sets of K atoms must be about the same.

A sufficient number of signs could be ascertained from these positions to carry out a Fourier synthesis $h0l$. This confirmed the chosen positions, but gave too little information about the O atoms. In order to find their positions, a variant of the F^2 series, suggested by Rogers (1951), was carried out. The series

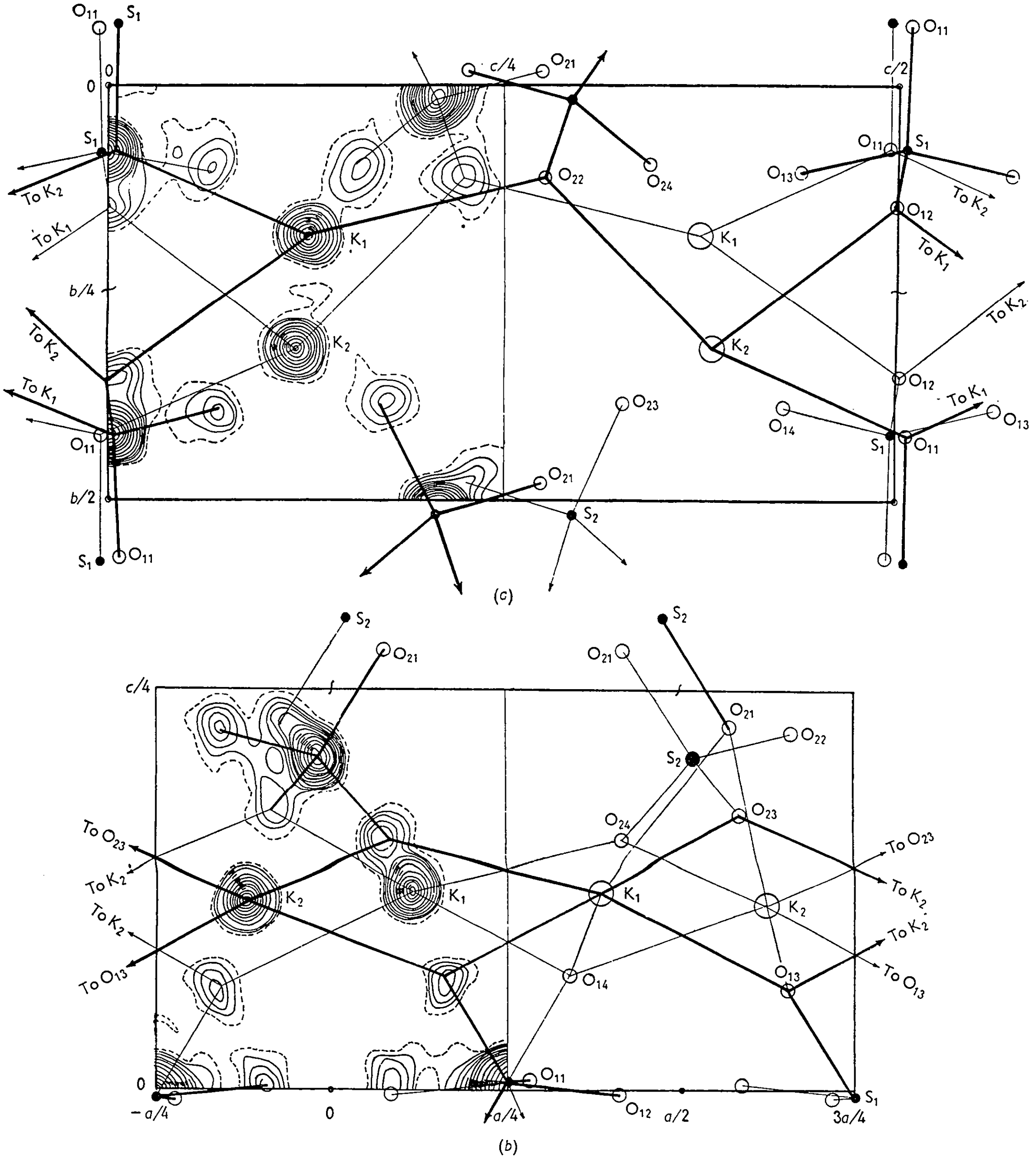

Fig. 1. (*a*) Fourier synthesis of $KHSO_4$, projection along the *a* axis. Contour levels on arbitrary scale. Left and right halves of the figure are connected by the glide plane *a*. The linkage of K polyhedra in the direction of the *z* axis is indicated. For linkage in the direction of the other axes see (*b*). (*b*) Fourier synthesis of $KHSO_4$, projection along the *b* axis. S_1 atoms overlap completely two by two. K polyhedra are linked in the *x* direction through $O_{13}O_{23}$ and $O_{14}O_{24}$. Upper and lower levels of potassium atoms are connected in the *y* direction through the common triangle O_{14}–O_{13}–O_{21}. Other K–O 'bonds' are not drawn.

$$\sum_h \sum_l \frac{F_o^2}{(F_K+F_S)_c} \cos(hu+lw)$$
$$\approx \sum_h \sum_l \left[F_K+F_S+2F_O+\frac{F_O^2}{(F_K+F_S)_c}\right] \cos(hu+lw)$$

is seen to show up the Fourier peaks of the K and S atoms and those of O with double weight, whereas the last term in brackets on the right-hand side will give a blurred picture, neither corresponding to the Patterson nor to the Fourier map, but with relatively low weight. Many terms with low calculated contribution of S and K had to be left out of the summation since (*a*) the sign would be uncertain, (*b*) the small denominator would enhance these terms greatly so that the consequences of a wrong sign would be large.

From the map so obtained, the position of six of the eight O atoms in the asymmetric unit could be assigned. By subsequent Fourier syntheses $h0l$ the last two O atoms were found.

The [100] *projection*

Some information on the y parameters of S and K has already been gleaned from the pseudo B-centring, in connection with the x and z parameters. From the Patterson projection $0kl$ and from the subsequent Fourier maps, the y values could be found with the help of the known z coordinates. The structure was then refined by several cycles of difference maps in both projections. The final structure parameters are given in Table 1.

In calculating the structure factors, the scattering factors of K and O computed by Berghuis *et al.* (1955) were used. For sulphur, James & Brindley's values were taken. An isotropic temperature factor $\exp(-B\sin^2\theta/\lambda^2)$ with $B = 0{\cdot}86$ Å^2 was introduced. Calculated and observed structure factors for $0kl$ and $h0l$ are given in Table 2.

$R = 0{\cdot}156$ for $0kl$ and $0{\cdot}146$ for $h0l$. There is a fairly large difference in discrepancy index for reflexions with odd $h+l$ and those with even $h+l$:

$$0kl \text{ with } l = \text{odd},\ R = 0{\cdot}292;\quad \text{with } l = \text{even},\ R = 0{\cdot}120.$$

$$h0l \text{ with } h+l = \text{odd},\ R = 0{\cdot}214;\quad \text{with } h+l = \text{even},\ R = 0{\cdot}121.$$

This is rather to be expected: small deviations from the pseudo B-centring affect the structure factors with odd $h+l$ relatively more than those with even $h+l$; also, the former are largely due to the contributions of the oxygen atoms, and their position is somewhat less certain than those of the heavier atoms.

Although the intensity data of the other diagrams mentioned above were not used in the refinement, it was checked that they fit the model qualitatively. Fig. 1 shows the final density maps.

4. Discussion of the structure

A survey of interatomic distances is given in Table 3 and in Fig. 2. It is seen that the HSO_4 groups are fairly regular tetrahedra with average S–O bond length of 1·52 Å and tetrahedron edges varying from 2·43 to 2·55 Å. In particular, there is no indication of the S–OH bond being longer than the S–O bond.

Table 3. *Some interatomic distances and angles in* $KHSO_4$

SO_4, group 1	SO_4, group 2
S_1–O_{11} = 1·52 Å	S_2–O_{21} = 1·53 Å
S_1–O_{12} = 1·51	S_2–O_{22} = 1·53
S_1–O_{13} = 1·52	S_2–O_{23} = 1·52
S_1–O_{14} = 1·51	S_2–O_{24} = 1·52
O_{11}–O_{12} = 2·44	O_{21}–O_{22} = 2·45
O_{11}–O_{13} = 2·43	O_{21}–O_{23} = 2·51
O_{11}–O_{14} = 2·43	O_{21}–O_{24} = 2·55
O_{12}–O_{13} = 2·47	O_{22}–O_{23} = 2·47
O_{12}–O_{14} = 2·54	O_{22}–O_{24} = 2·44
O_{13}–O_{14} = 2·54	O_{23}–O_{24} = 2·50
O_{11}–S_1–O_{12} = 109°	O_{21}–S_2–O_{22} = 109°
O_{11}–S_1–O_{13} = 108	O_{21}–S_2–O_{23} = 113
O_{11}–S_1–O_{14} = 109	O_{21}–S_2–O_{24} = 117
O_{12}–S_1–O_{13} = 111	O_{22}–S_2–O_{23} = 110
O_{12}–S_1–O_{14} = 117	O_{22}–S_2–O_{24} = 108
O_{13}–S_1–O_{14} = 116	O_{23}–S_2–O_{24} = 113
$O_{11}\cdots H\cdots O'_{12}$ = 2·68 Å	$O_{21}\cdots H\cdots O'_{22}$ = 2·67 Å

K–O distances, sharing edge with tetrahedron

K_1–O_{11} = 2·86 Å	K_2–O_{11} = 2·88 Å
K_1–O_{12} = 2·95	K_2–O_{12} = 2·81
K_1–O_{14} = 2·98	K_2–O_{13} = 2·97
K_1–O'_{14} = 3·02	K_2–O'_{13} = 3·02
K_1–O_{21} = 3·06	K_2–O_{22} = 2·88
K_1–O_{22} = 2·96	K_2–O_{24} = 2·91

K–O distances, sharing corner with tetrahedron

K_1–O_{13} = 2·68 Å	K_2–O_{14} = 2·64 Å
K_1–O_{23} = 2·82	K_2–O_{21} = 2·58
K_1–O_{24} = 2·69	K_2–O_{23} = 2·73

The system of hydrogen bonds is interesting (Fig. 2). They link up the tetrahedra in the direction of the

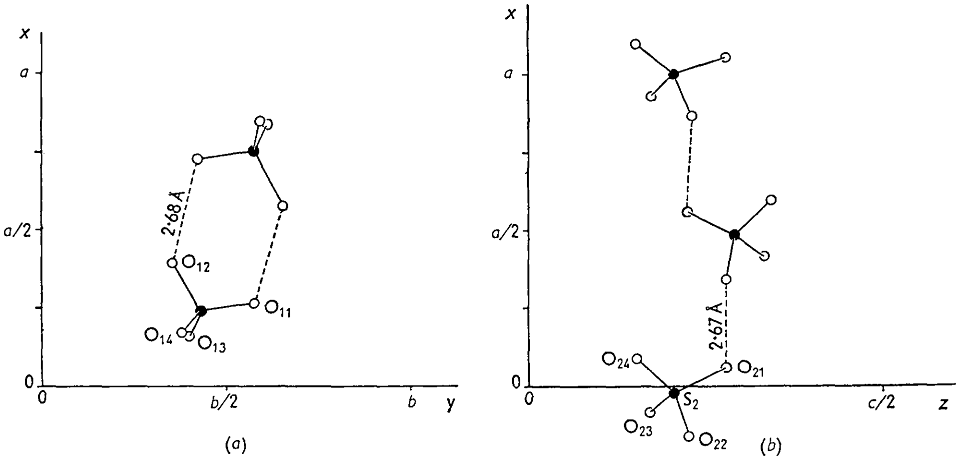

Fig. 2. Hydrogen bond systems, (a) of S_1 tetrahedra, (b) of S_2 tetrahedra.

a axis, and this may be related to the fact that light vibrating in this direction has the largest refractive index (Groth). Two S_1 tetrahedra are linked by a double hydrogen bridge on both sides of a symmetry centre, forming a sort of double molecule as frequently found with organic molecules containing carboxyl groups.

S_2 tetrahedra, however, are linked by bridges repeating through the glide plane *a*, thus forming infinite chains along the *a* axis. This is in principle the same system as found in other acid salts, KH_2PO_4 and $NaHCO_3$. One might have expected, by analogy with the latter, that this bridge would be shorter than the bridges linking S_1 tetrahedra, but practically the same length is found in both cases: 2·68 Å for O_{11}–O_{12}, and 2·67 Å for O_{21}–O_{22}.

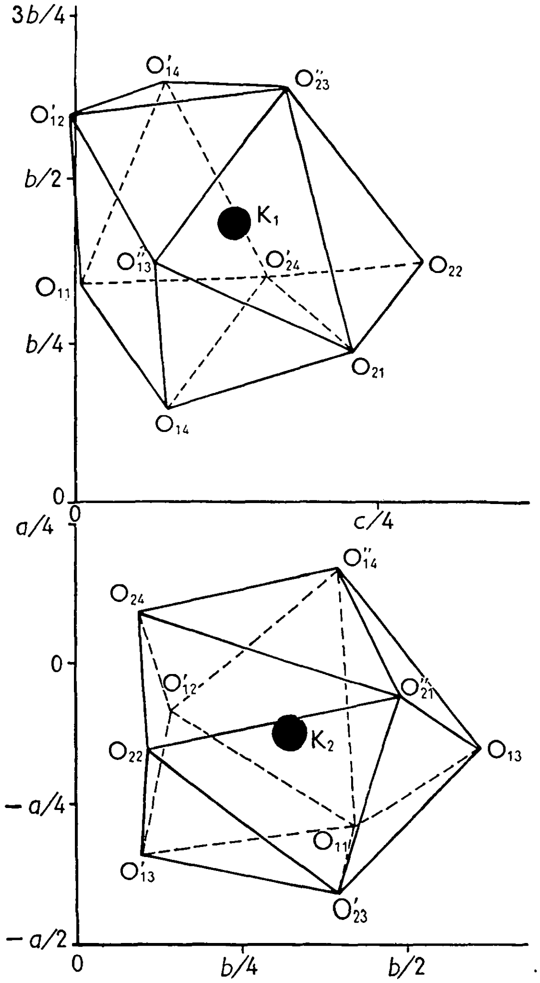

Fig. 3. Surroundings of potassium ions: around K_1 in projection along the *a* axis (see also Fig. 1(*a*)); around K_2 in projection along the *c* axis.

Both potassium atoms are surrounded in about the same way by nine oxygen atoms; eight of these form a strongly deformed antiprism, with the ninth oxygen on top of one of the 'squares' (Fig. 3). These polyhedra around potassium atoms are linked in the direction of all three axes: along *a* alternately by edges O_{13}–O_{23} and O_{14}–O_{24}; along *b* by the face O_{13}–O'_{14}–O_{21} (where the prime indicates that this atom does not belong to the same tetrahedron as O_{13}); along *c* alternately by the edge O_{11}–O'_{12} and by the corner O_{22}. The K polyhedra are, of course, also frequently connected through SO_4 groups. In agreement with this three-dimensional linking there is no pronounced cleavage in the crystal, according to Groth.

SO_4 tetrahedra share both edges and corners with the polyhedra around K. One SO_4 group shares two edges, namely $O_{11}O_{14}$ and $O_{12}O_{14}$, with two different K_1 ions, and two edges, $O_{11}O_{13}$ and $O_{12}O_{13}$, with K_2 ions; the other SO_4 shares the edge $O_{21}O_{22}$ with K_1 and the edge $O_{22}O_{24}$ with K_2. As expected, the average distance from K to an 'edge' oxygen atom is significantly larger than from K to a 'corner' oxygen. From the values in Table 3 one finds 2·97 and 2·91 Å for the former K–O distance, for K_1 and K_2 respectively, and 2·73 and 2·65 Å for the latter K–O bond.

In view of these differences in K–O distances, it is not possible to test Pauling's coordination rules. It may, however, be significant that the oxygens O_{11}, O_{12}, O_{21}, O_{22}, which are involved in hydrogen bonding, are predominantly edge-shared between S and K (see Table 3).

Part of this investigation was carried out with X-ray apparatus, put at the disposal of the senior author (C. H. MacG.) by the Netherlands Organisation for Pure Scientific Research. We thank Mr A. Kreuger, of this same Organisation, for his skilful cooperation in handling the crystals.

References

Berghuis, J., Haanappel, Y. M., Potters, M. L., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Buerger, M. J. (1942). *Proc. nat. Acad. Sci., Wash.* **28**, 281.

Frazer, B. C. & Pepinsky, R. (1953). *Acta Cryst.* **6**, 273.

Oda, S. (1939). *J. Chem. Soc. Japan*, **60**, 162.

Rogers, D. (1951). *Research*, **4**, 295.

Stortenbeker, W. (1902). *Rec. Trav. Chim. Pays-Bas*, **21**, 405.

West, J. (1930). *Z. Kristallogr.* **74**, 306.

Zachariasen, W. H. (1933). *J. Chem. Phys.* **1**, 634.