The small shifts in the oxygen atomic coordinates found in this refinement do not affect the description of the Rb^+ anion coordination polyhedron given by Corbridge. No Rb–O distance changes by more than 0·02 Å. Each Rb^+ is coordinated to seven oxygen atoms, six of them (three O(2) and three O(3)) in a distorted octahedral arrangement with a mean Rb–O length of 2·95 Å, while the seventh (O(1)) is slightly further away at 3·19 Å.

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Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N. VIII. $KHSO_4$ (Mercallite)

By D. W. J. Cruickshank*

School of Chemistry, The University, Leeds 2, England

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The crystallographic data given by Loopstra & MacGillavry (1958) have been used in a structure refinement. The oxygen atoms to which hydrogen atoms are attached have been identified. The average dimensions are $S-O(H) = 1·56$ and $S-O = 1·47$ Å, both $\pm 0·015$ Å.

The crystal structure of $KHSO_4$ (mercallite) was determined by Loopstra & MacGillavry (1958) from the 0*kl* and *h*0*l* projections. There are two distinct HSO_4^- groups in the asymmetric unit and these are differently linked by hydrogen bonds: one group forms dimers across a symmetry centre, the other is linked into infinite chains along a glide plane. The reported lengths (1·51–1·53 Å) of the eight independent S–O bonds in two groups were practically all equal, so that there was no indication of a difference between S–O(H) and S–O bonds. This is a little surprising as in the $H_2PO_4^-$ ion in the ordered low-temperature form (Bacon & Pease, 1955) of KH_2PO_4, the P–O(H) bond at 1·58 Å is 0·07 Å longer than the P–O bond, while in phosphoric acid (Furberg, 1955) the three P–O(H) bonds at 1·57 Å are 0·05 Å longer than the P–O bond. Further in $KC_2H_5SO_4$ (Truter, 1958) the S–O(R) bond at 1·60 Å is distinctly larger than the three S–O bonds at 1·46 Å. Accordingly it seemed worthwhile refining $KHSO_4$ to see if it conformed to the general pattern.

The space group is *Pbca*, with cell dimensions $a = 8·40$, $b = 9·79$, $c = 18·93$ Å. Both K atoms and both HSO_4 groups are in general positions, but S(1) is virtually at $x = \frac{1}{4}$ and its *x* coordinate cannot be located with precision from the available 0*kl* and *h*0*l* data.

The data used in the refinement were the 325 non-zero $|F_o|$ given by Loopstra & MacGillavry (the 14,0,4 and 063 reflexions were omitted as their phases were persistently uncertain). Seven cycles of least-squares refinement were carried out. These produced shifts of less than 0·005 Å for K, 0·02 Å for S and 0·11 Å for O. The residual *R* dropped from an initial 15% to a final 8·8%. In particular for the weak 0*kl* reflexions with *l* odd *R* dropped from the 29·2% of Loopstra & MacGillavry to 11·7%, and for the weak *h*0*l* reflexions with $h+l$ odd from 21·4% to 10·7%. The final coordinates and e.s.d.'s are given in Table 1 and the vibration parameters in Table 2. Anisotropic vibrations were allowed for K and S but not for O. The vibration e.s.d.'s are about 0·001 Å^2 for K and S, and 0·003 Å^2 for O. If the $|F_o|$ listed by Loopstra & MacGillavry are for $\frac{1}{8}$th of the cell contents, the $|F_o|$ scale determined by the least-squares process was $0·986 \pm 0·012$. The weighting scheme used was

$$w = 1/(30 + |F_o| + |F_o|^2/178)\,,$$

with $|F_o|$ appropriate to whole cell, but without the factor 0·986.

With the available reflexions the *x* coordinate of S(1) cannot be precisely determined, because its contributions to the structure factors are very insensi-

Table 1. *Atomic coordinates and e.s.d.'s*

Atom	*x*	*y*	*z*
K(1)	3·212 ± 0·005 Å	1·760 ± 0·005 Å	2·369 ± 0·003 Å
K(2)	− 1·031 ± 0·005	3·144 ± 0·004	2·245 ± 0·003
S(1)	2·100 ± 0·02(?)	4·139 ± 0·005	0·059 ± 0·003
S(2)	− 0·171 ± 0·005	0·180 ± 0·005	3·901 ± 0·004
O(11)	2·408 ± 0·018	5·669 ± 0·016	0·041 ± 0·012
O(12)	3·457 ± 0·018	3·478 ± 0·016	0·054 ± 0·012
O(13)	1·375 ± 0·020	3·888 ± 0·019	− 1·163 ± 0·013
O(14)	1·367 ± 0·018	3·908 ± 0·018	1·272 ± 0·013
O(21)	0·502 ± 0·019	− 0·059 ± 0·017	5·199 ± 0·013
O(22)	− 1·357 ± 0·018	1·111 ± 0·017	4·247 ± 0·012
O(23)	− 0·673 ± 0·025	− 1·089 ± 0·023	3·354 ± 0·016
O(24)	0·679 ± 0·016	0·912 ± 0·015	2·981 ± 0·011

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* Present address: Chemistry Department, The University, Glasgow, W.2, Scotland.

tive to its position (its $z/c=0{\cdot}003$ is also small). Correspondingly the least-squares process registered a falsely large e.s.d. At the end of the refinement an attempt was made to alter x(S(1)) by 0·03 Å in the direction which would have given slightly more reasonable bond lengths, but the residual increased very slightly and a shift back towards $x=\frac{1}{4}$ was indicated. A subjective estimate is that S(1) has the coordinate $x=\frac{1}{4}$ with an e.s.d. of about 0·02 Å.

Table 2. *Mean square vibration amplitudes* (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
K(1)	0·015	0·014	0·013	—	0·002	0·001
K(2)	0·016	0·011	0·011	—	0·001	0·002
S(1)	0·008	0·008	0·014	—	0·001	0·000
S(2)	0·008	0·010	0·012	—	0·003	−0·002

Atom	U	Atom	U
O(11)	0·018	O(21)	0·019
O(12)	0·016	O(22)	0·018
O(13)	0·023	O(23)	0·034
O(14)	0·020	O(24)	0·013

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

SO_4, group 1		SO_4, group 2	
S(1)–O(11)	= 1·56 Å	S(2)–O(22)	= 1·55 Å
S(1)–O(12)	= 1·51	S(2)–O(21)	= 1·48
S(1)–O(13)	= 1·44	S(2)–O(23)	= 1·47
S(1)–O(14)	= 1·44	S(2)–O(24)	= 1·45
O(11)–O(12)	= 2·42	O(22)–O(21)	= 2·39
O(11)–O(13)	= 2·38	O(22)–O(23)	= 2·47
O(11)–O(14)	= 2·38	O(22)–O(24)	= 2·41
O(12)–O(13)	= 2·45	O(21)–O(23)	= 2·42
O(13)–O(14)	= 2·44	O(23)–O(24)	= 2·44
O(12)–O(14)	= 2·46	O(21)–O(24)	= 2·43
O(11)–S(1)–O(12)	= $104\frac{1}{2}$°	O(22)–S(2)–O(21)	= $104\frac{1}{2}$°
O(11)–S(1)–O(13)	= 105	O(22)–S(2)–O(23)	= 110
O(11)–S(1)–O(14)	= $105\frac{1}{2}$	O(22)–S(2)–O(24)	= $106\frac{1}{2}$
O(12)–S(1)–O(13)	= 112	O(21)–S(2)–O(23)	= 110
O(12)–S(1)–O(14)	= 113	O(21)–S(2)–O(24)	= 112
O(13)–S(1)–O(14)	= $115\frac{1}{2}$	O(23)–S(2)–O(24)	= $113\frac{1}{2}$
O(11)···H···O(12′)	= 2·62 Å	O(21)···H···O(22′)	= 2·62 Å

The revised interatomic distances and angles are shown in Table 3. Both hydrogen bonds, O(11) · · · O(12′) which connects the group 1 sulphates in dimers, and O(21) · · · O(22′) which connects the group 2 sulphates in chains along the a axis, are 2·62 Å in length. In the group 2 sulphate the S–O bonds, with S–O(22) = 1·55 and the others = 1·48, 1·47 and 1·45 Å, indicate that O(22′) rather than O(21) is the atom to which the hydrogen is attached. The angles, which average O(22)–S–O = 107° and O–S–O = 112°, also support this identification. In the group 1 sulphate the situation is complicated by the uncertainty of the x coordinate of S(1). However, S(1)–O(11) = 1·56 Å is the largest S–O bond and is hardly affected by the uncertainty in x(S(1)). The other three bonds, S(1)–O(12) = 1·51, S(1)–O(13) = 1·44, S(1)–O(14) = 1·44 Å, would be more nearly equal if $x(S_1)$ was increased by, say, 0·03 Å, but as mentioned above, such a shift increased the residual very slightly. The attachment of the hydrogen to O(11) rather than to O(12) is also supported by the O(11)–S–O angles, which are all less than tetrahedral, and by the other O–S–O angles which are all greater than tetrahedral.

A conceivable method of circumventing the x(S(1)) difficulty would be to detect the odd oxygen atom in a tetrahedron from a study of the non-bonded O–O distances. However, in both tetrahedra the variations among these are less than among the S–O distances and they suggest no definite pattern. An attempt was also made to verify the positions of the hydrogen atoms directly, but the results were inconclusive, as might be expected from the low scattering power of hydrogen. In the O(11) · · · O(12′) bond a hydrogen atom attached to either oxygen atom slightly worsened the residual, while in the O(21) · · · O(22′) bond either hydrogen position slightly improved the residual.

The values of the vibration parameters, which average $U=0{\cdot}010$ Å^2 for S and 0·020 Å^2 for O, suggest that the HSO_4 groups are making small angular oscillations (4–5° r.m.s.). The S–O distances listed in Table 3 will consequently (Cruickshank, 1956) be about 0·008 Å too short. With this correction, and if the suggested assignments of the hydrogen atoms are correct, the average results from the two HSO_4 groups give S–O(H) = 1·56 and S–O = 1·47 Å with e.s.d.'s which may be put somewhat subjectively at 0·015 Å. This difference of 0·09 Å is a little greater than the corresponding differences of 0·07 Å in $K_2H_2PO_4$ and 0·05 Å in H_3PO_4. It is probably not significant, though it is in the sense suggested by the fact that the hydrogen bonds in the two phosphate structures are all rather stronger (O · · · O = 2·50 − 2·59 Å).

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