

The Structure of Potassium Hydrogen Sulfate

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Abstract. KHSO_4 , orthorhombic, space group $Pbca$, $a=8.412$ (2), $b=9.800$ (3), $c=18.957$ (5) Å. There are two HSO_4^- ions in the asymmetric unit. One type of ion is linked into a polymeric chain by hydrogen bonding along a glide plane; the other forms a dimer across a center of symmetry. The hydrogen atoms were located, thus allowing a more complete description of the hydrogen bonding.

Introduction. The crystal structure of KHSO_4 was determined from two-dimensional data by Loopstra & MacGillavry (1958) and further refined by Cruickshank (1964). When crystals of KHSO_4 were isolated as a side product in an attempt to prepare $\text{Mn}_2(\text{SO}_4)_2$, it was decided to redetermine the structure for several reasons: (1) it was previously determined only as a two-dimensional structure; (2) S(1) was located at the special position with $x=\frac{1}{4}$, since the x coordinate could not be determined precisely from the $0kl$ and $h0l$ data that were collected; (3) the hydrogen atoms were not located directly; (4) more recent papers on structures containing the HSO_4^- ion (Nelmes, 1971; Jönsson & Olovsson, 1968; and references therein) cite the KHSO_4 structure as refined by Cruickshank (1964) as the major source for the geometry of the SO_4^{2-} tetrahedron and hydrogen bonding in the HSO_4^- ion.

Since KHSO_4 is intrinsically a good standard, and has been so used, for the structural characteristics of the hydrogen sulfate ion, it seemed worth while to employ contemporary techniques of data collection and refinement to provide an accurate determination.

Crystals were obtained accidentally from a reaction of MnSO_4 and KMnO_4 in 50% H_2SO_4 after allowing it to stand at 0°C for several weeks. Preliminary examination of the compound using precession techniques indicated bca symmetry in the orthorhombic system. The space group $Pbca$ was fully confirmed during refinement of the structure. The data crystal having approximate dimensions of $0.1 \times 0.2 \times 0.4$ mm was mounted on a glass fiber. There was no evidence of deterioration or movement of the crystal during the data collection.

Least-squares refinement of 15 reflections, chosen to give a good sampling of reciprocal space and instrument settings ($30^\circ < 2\theta < 40^\circ$) and recorded at a temperature of 20° , gave lattice constants: $a=8.421$ (2), $b=9.800$ (2), and $c=18.957$ (5) Å. They compare with the previously reported values of $a=8.40$, $b=9.79$, $c=18.93$ Å (Loopstra & MacGillavry, 1958). For $V=1562.8$ (6) Å³, $M=136.17$, and assuming $Z=16$ (2 molecules per asymmetric unit) the calculated density was 2.322 g cm⁻³ while the experimental density was 2.329 g cm⁻³. Several strong reflections showed peaks with a width at half-height of 0.2° on ω scans. Data were collected at $21 \pm 1^\circ$ with Mo $K\alpha$ radiation on a diffractometer equipped with a graphite-crystal incident-beam monochromator. The θ - 2θ scan technique with a variable scan rate from 1.0 - 24.0° min⁻¹ and an asymmetric scan range from $2\theta(\text{Mo } K\alpha_1) - 0.6$ to $2\theta(\text{Mo } K\alpha_2) + 0.7^\circ$ was used to collect 2100 independent reflections up to a maximum 2θ value of 55° .

The intensities of 3 reflections were measured every 100 reflections as a check on crystal stability and

Table 2. Positional and thermal parameters

The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K(1)	0.3824 (1)	0.1806 (1)	0.12496 (5)	0.0060 (1)	0.0064 (1)	0.00130 (3)	-0.0003 (1)	0.00001 (5)	0.00020 (4)
K(2)	-0.1227 (1)	0.3197 (1)	0.11841 (5)	0.0059 (2)	0.0053 (1)	0.00121 (3)	-0.0001 (1)	-0.00000 (5)	-0.00009 (4)
S(1)	0.2543 (1)	0.4227 (1)	0.00266 (5)	0.0034 (1)	0.0043 (1)	0.00110 (3)	-0.0003 (1)	-0.00000 (5)	-0.00006 (5)
S(2)	-0.0192 (1)	0.0167 (1)	0.20600 (6)	0.0037 (1)	0.0056 (1)	0.00109 (3)	0.0004 (1)	-0.00012 (5)	0.00006 (5)
O(11)	0.2901 (4)	0.5793 (3)	0.0016 (2)	0.0041 (5)	0.0045 (4)	0.0019 (1)	-0.0001 (3)	-0.0003 (2)	0.0001 (1)
O(12)	0.4079 (4)	0.3521 (3)	0.0032 (2)	0.0042 (4)	0.0044 (3)	0.0019 (1)	0.0009 (3)	0.00004 (2)	0.0002 (1)
O(13)	0.1669 (4)	0.3967 (3)	-0.0613 (2)	0.0083 (5)	0.0069 (4)	0.0016 (1)	-0.0003 (4)	-0.0014 (2)	-0.0007 (2)
O(14)	0.1657 (4)	0.3987 (4)	0.0665 (2)	0.0077 (5)	0.0075 (4)	0.0018 (1)	-0.0003 (4)	0.0017 (2)	0.0001 (2)
O(21)	0.0607 (4)	-0.0012 (4)	0.2741 (2)	0.0070 (5)	0.0105 (5)	0.0015 (1)	-0.0012 (4)	-0.0009 (2)	0.0016 (2)
O(22)	-0.1625 (4)	0.1128 (4)	0.2223 (2)	0.0047 (5)	0.0060 (4)	0.0019 (1)	0.0002 (4)	0.0005 (2)	-0.0002 (2)
O(23)	-0.0812 (5)	-0.1797 (4)	0.1784 (2)	0.0079 (5)	0.0071 (4)	0.0031 (1)	0.0003 (4)	-0.0007 (2)	-0.0016 (2)
O(24)	0.0767 (4)	0.0946 (4)	0.1579 (2)	0.0060 (5)	0.0109 (5)	0.0015 (1)	-0.0005 (4)	0.0007 (2)	0.0010 (2)
	x	y	z	$B(\text{Å}^2)$	x	y	z	$B(\text{Å}^2)$	
H(1)	0.373 (7)	0.601 (6)	0.504 (2)	1.6 (12)	H(2)	-0.272 (8)	0.065 (7)	0.272 (3)	4.0 (18)

movement. A correction for Lorentz and polarization factors was applied to the data. The linear absorption coefficient for the compound is 17.2 cm^{-1} ; no absorption correction was applied. In structural refinement only the 1151 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used. The parameter p used in the calculation of standard deviations was set equal to 0.07 (Cotton, Deganello, Frenz & Shaver, 1973).

The following computer programs written for the IBM 360 were used: *DATARED*, a data reduction program by Frenz; *FOURIER*, a Fourier summation program (based on Zalkin's *FORDAP*) by Dellaca & Robinson; *NUCLS*, a least-squares program by Ibers & Doedens which closely resembles Busing & Levy's *ORFLS* program; the quantity minimized is $\sum w(|F_o| - |F_c|)^2$; *SADIAN*, a program for calculating atomic distances and angles by Baur; *PERFACT*, a program for analysis of structure factors by Frenz; *ORTEP*, a plotting program by Johnson; *ORFFE*, a function and error program by Busing, Martin & Levy and modified by Brown, Johnson & Thiessen; and *LIST* a data listing program by Snyder.

The reported values of Cruickshank (1964) for the coordinates of all the non-hydrogen atoms were used as input to least-squares refinement. Two cycles of isotropic refinement yielded agreement indices, $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.068$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0.090$. The function minimized in least-squares procedures is $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and w is $4F_o^2/\sigma^2(F_o^2)$. The scattering factors used were taken from Cromer & Waber (1974). Anomalous dispersion effects were included for all non-hydrogen atoms and values for $\Delta f'$ and $\Delta f''$ were those of Cromer & Liberman (1970).

Anisotropic refinement reduced the R values to 0.043 and 0.060, for R_1 and R_2 , respectively. A difference Fourier map then revealed the positions of the two hydrogen atoms. Two subsequent least-squares cycles in which the hydrogen atoms were refined isotropically (117 variables) using the scattering factor of Stewart, Davidson & Simpson (1965) produced the final R values of 0.040 and 0.057. In the last cycle of refinement the largest parameter shift was less than 0.1 times its standard deviation. The error in an observation of unit weight is 1.17. A final difference Fourier synthesis revealed two peaks that were approximately the same as the hydrogen atoms ($0.58 \text{ e } \text{Å}^{-3}$). These two maxima, as well as the remaining peaks which were less than $0.50 \text{ e } \text{Å}^{-3}$, did not correspond to any chemically significant feature.

The observed and final values of the calculated structure factors are given in Table 1.* The final positional and thermal parameters are given in Table 2.

* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30723 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The root-mean-square thermal amplitudes of vibration are given in Table 3.

Table 3. *Root-mean-square amplitudes of vibration*

	Min.	Intermed.	Max.
K(1)	0.146 (2) Å	0.153 (2) Å	0.178 (2) Å
K(2)	0.145 (2)	0.148 (2)	0.161 (2)
S(1)	0.110 (2)	0.141 (2)	0.146 (2)
S(2)	0.113 (2)	0.141 (2)	0.166 (2)
O(11)	0.120 (7)	0.147 (6)	0.188 (5)
O(12)	0.115 (7)	0.151 (6)	0.185 (5)
O(13)	0.128 (7)	0.184 (6)	0.208 (5)
O(14)	0.127 (7)	0.191 (5)	0.210 (5)
O(21)	0.130 (7)	0.162 (6)	0.244 (5)
O(22)	0.127 (7)	0.170 (6)	0.191 (5)
O(23)	0.159 (6)	0.169 (6)	0.256 (5)
O(24)	0.128 (7)	0.168 (6)	0.237 (5)

Discussion. Loopstra & MacGillavry (1958) and Cruickshank (1964) have discussed the general features of the structure; that type of description need not be reiterated. A listing of some interatomic distances and angles is given in Tables 4 and 5. Fig. 1 is a stereoscopic drawing of the unit cell.

Table 4. *Interatomic distances (Å)*

	Present paper	Cruickshank (1964)	Loopstra (1958)
S(1)—O(11)	1.564 (4)	1.56	1.52
S(1)—O(12)	1.465 (3)	1.51	1.51
S(1)—O(13)	1.441 (3)	1.44	1.52
S(1)—O(14)	1.440 (3)	1.44	1.51
O(11)—H(1)	0.73 (6)	—	—
O(12)—H(1)	1.91 (6)	—	—
O(11)—H...O'(12)	2.630 (5)	2.62	2.68
O(21)—H(2)	1.89 (7)	—	—
O(22)—H(2)	0.73 (6)	—	—
O(21)—H...O'(22)	2.583 (5)	2.62	2.67
S(2)—O(21)	1.467 (3)	1.48	1.53
S(2)—O(22)	1.561 (3)	1.55	1.53
S(2)—O(23)	1.428 (4)	1.47	1.52
S(2)—O(24)	1.437 (4)	1.45	1.52
O(11)—O(12)	2.437 (5)	O(22)—O(21)	2.396 (5)
O(11)—O(13)	2.387 (5)	O(22)—O(23)	2.417 (5)
O(11)—O(14)	2.395 (5)	O(22)—O(24)	2.361 (5)
O(12)—O(13)	2.407 (5)	O(21)—O(23)	2.412 (5)
O(12)—O(14)	2.407 (5)	O(21)—O(24)	2.399 (5)
O(13)—O(14)	2.422 (5)	O(23)—O(24)	2.420 (5)

Table 5. *Bond angles*

O(11)—S(1)—O(12)	107.1 (2)°	O(22)—S(2)—O(21)	104.6 (2)°
O(11)—S(1)—O(13)	105.1 (2)	O(22)—S(2)—O(23)	107.9 (2)
O(11)—S(1)—O(14)	105.7 (2)	O(22)—S(2)—O(24)	103.8 (2)
O(12)—S(1)—O(13)	111.8 (1)	O(21)—S(2)—O(23)	112.8 (2)
O(12)—S(1)—O(14)	111.9 (2)	O(21)—S(2)—O(24)	111.4 (2)
O(13)—S(1)—O(14)	114.4 (2)	O(23)—S(2)—O(24)	115.3 (2)
O(11)—H(1)—O(12)	173 (5)	O(22)—H(2)—O(21)	158 (7)
S(1)—O(11)—H(1)	118 (5)	S(2)—O(22)—H(2)	103 (5)
S(1)—O(12)—H(1)	138 (2)	S(2)—O(21)—H(2)	112 (2)

The two different formula units in the asymmetric unit can be readily discerned in Fig. 1. One forms a polymer and the other a dimer. The polymeric unit

Table 6. Comparison of NH_4HSO_4 and KHSO_4 structures

	SO	SO(\cdots H)	SO(H)	OH	O \cdots H	O \cdots O	\angle OHO
NH_4HSO_4	1.442 (2) Å	1.455 (2) Å	1.557 (2) Å	0.690 (30) Å	1.920 (30) Å	2.598 (5) Å	172 (6)°
	1.430 (2)	1.441 (3)	1.546 (3)	0.760 (40)	1.790 (40)	2.514 (6)	160 (4)
KHSO_4	1.448 (3)	1.465 (3)	1.564 (4)	0.727 (59)	1.907 (61)	2.630 (5)	173 (5)
	1.444 (4)	1.467 (3)	1.561 (3)	0.728 (65)	1.894 (66)	2.583 (5)	158 (7)

containing the S(2) atoms is hydrogen bonded along an a -glide plane. The dimer containing the S(1) atoms resembles a carboxylic acid dimer, with the hydrogen bonds lying nearly parallel to the a axis.

Table 4 also compares some of the present data with those of Cruickshank. With the three-dimensional structure, there are some significant changes in interatomic distances. One of the more noticeable changes is that not only can the oxygen to which the hydrogen is bonded be detected on the basis of S–O bond lengths, but also the oxygen to which the hydrogen is bonded can be determined. The S–O(H) bond is the longest as the double-bond character of the SO_4^{2-} tetrahedron is decreased when a hydrogen atom is bonded to an oxygen (Cruickshank, 1961). In the case of the proton-receptor oxygen, the electrostatic interaction also yields a slight increase in the S–O bond length, so that while the average S–O bond length is 1.438 (4) Å, the average length of the S–O \cdots H bonds is 1.466 (3) Å.

Jönsson & Olovsson (1968) compare some bond lengths for several HSO_4^- containing structures in which the hydrogen atoms were not located directly. The distances in the present work are in good agreement with those found earlier. The hydrogen atoms in NH_4HSO_4 were located directly (Nelmes, 1971) and Table 6 gives a comparison of several interatomic distances and angles.

In Cruickshank's (1964) refinement, the exact position could not be determined for the x coordinate of S(1) and was left at $x = \frac{1}{4}$. With the three-dimensional structure, the result was $x = 0.2543$ (1).

Fig. 2 shows one other important feature, namely the geometry of the O–H \cdots O systems. It can be seen that in O(22)–H(2) \cdots O'(21) the OH \cdots O group deviates further from linearity than does the O(11)–H(1) \cdots O'(12) group. A similar situation is also observed for the two different HSO_4^- units in NH_4HSO_4 , but there each of the ions is in a chain system. In KHSO_4 , the more linear hydrogen bonding is in the dimeric unit.

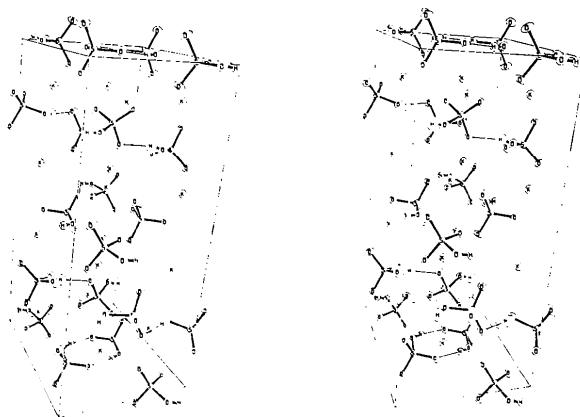


Fig. 1. A stereoscopic pair showing the three-dimensional structure of the unit cell. The a axis occupies a vertical position in the drawing.

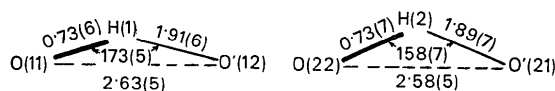


Fig. 2. The geometry of the hydrogen bond.

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