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On the Hydrogen Bonding in Potassium Hydrogen Sulphate. Comparison with a Previous Crystal Structure Determination

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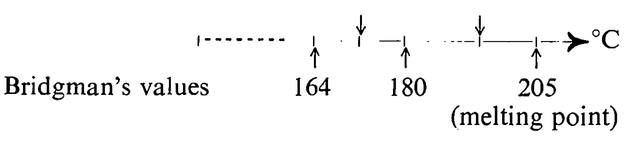
The room-temperature structure of potassium hydrogen sulphate [$a=8{\cdot}429$ (3); $b=9{\cdot}807$ (3); $c=18{\cdot}976$ (6) Å; *Pbca*; $Z=16$] has been refined with data collected on a single-crystal diffractometer to a conventional R value of 0·035 for 1323 reflexions. The results are compared by means of statistical tests with those of another recent accurate determination of $KHSO_4$. Although neglect of absorption corrections may partly explain the discrepancies between the two analyses, it seems likely that the different crystal growth conditions have led to slightly different phases of the same material. The changes are mainly observed in the hydrogen-bonding features of the polymeric HSO_4^- chain which is considered to play an essential role in the conduction process and in the polymorphic behaviour of $KHSO_4$. It is suggested that these differences might be related to some degree of substitution of $(HSO_4)^-$ ions by (SO_4^{2-},H^+) groups within the polymeric chain.

Introduction

Some materials containing the hydrogen sulphate ion, such as NH_4HSO_4 and $PbHSO_4$, are well-known ferroelectric compounds. Knowledge of the accurate sulphate tetrahedron geometry and of the hydrogen-bonding pattern between the HSO_4^- ions is essential for the understanding of the properties of these compounds (Nelmes, 1971). The corresponding potassium salt is, however, not ferroelectric. Its structure was first described by Loopstra & MacGillavry (1958) and further refined by Cruickshank (1964) on the basis of two-dimensional data. These results are often cited in comparative studies of related substances. It appeared therefore that greater accuracy would be desirable. This material indeed shows some interesting physical properties, *e.g.* its conduction process (Glasser, 1975) and thermoelasticity (Gerlich & Siegert, 1975), the understanding of which depends greatly on accurate structural information.

The compound is also known to exist in three different forms at atmospheric pressure in the temperature range 15–200 °C (Bridgman, 1916/1917). However, we have only found one transition point at 175 ± 1 °C by heating the crystalline powder (21 °C/h) in a high-temperature X-ray Guinier–Lenné camera. The transition is also seen very clearly by optical observation.



We were in the final stages of the structure determination of phase I when an independent analysis was reported by Cotton, Frenz & Hunter (1975). Nevertheless, in view of some significant differences we feel that a comparison of our results (hereinafter referred to as PH) with those of Cotton *et al.* (hereinafter CFH) will be of interest and also suggest further work.

Experimental

Potassium hydrogen sulphate was obtained during the investigation of the system ($H_2SO_4.H_3Fe(CN)_6.K_3Fe(CN)_6.H_2O$). Crystals were grown at room temperature by concentration of an aqueous solution of sulphuric acid (1·8N) containing ferricyanic acid (1N) and varying amounts of potassium ferricyanide. Crystal data are listed and compared in Table 1. In Table 2 we give the methods used to collect diffraction data and to refine the structure and also other relevant details. The listing of our final positional and vibrational parameters is shown in Tables 3 and 4; in Table 5 we compare some interatomic distances and angles. (For clarity the atom numbering scheme is the same as in CFH's paper.) The larger number of reflexions used in refinement and fewer absorption effects (Tables 1 and 2) may explain

Table 1. *Comparison of crystal data*

		PH	CFH
Space group		*Pbca*	*Pbca*
Unit-cell constants (Å)	a	8·429 (3)	8·412 (2)
(from diffractometer	b	9·807 (3)	9·800 (3)
measurements)	c	18·976 (6)	18·957 (5)
Volume (Å³)		1568·6	1562·8
Density (g cm^{-3})		2·30 (1) (flotation in $CHBr_3$–$CHCl_3$)	2·322
Absorption coefficient (cm^{-1})		17·2	17·2
Crystal size (mm)		Sphere radius 0·20	0·1 × 0·2 × 0·4

Table 2. *Methods of data collection, treatment of data, and refinement for the two investigations*

Data collection	PH	CFH
Radiation used	Mo $K\alpha$	Mo $K\alpha$
Monochromator	Graphite	Graphite
Diffractometer	Nonius CAD-4	Syntex $P\bar{1}$
Scan mode	θ–2θ	θ–2θ
2θ max (°)	60	55
Number of independent reflexions measured	1599	2100
Number of reflexions included in refinement N_o with $I>3\sigma(I)$	1323	1151
Data collected at T (°C)	20 (1)	21 (1)
Treatment of data and refinement		
Extinction correction	None	None
Absorption correction	None	None
Function minimized in full-matrix least-squares refinement	$\sum w\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert^2$	$\sum w\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert^2$
Program used	*SFLS* 5 (Prewitt, 1966)	*NUCLS*
Weighting scheme w	$[a(1+0{\cdot}05F_o+0{\cdot}005F_o^2]^{-1}$ $(a=0{\cdot}667)$	$4F_o^2/\sigma^2(F_o^2)$
Scattering factors	Moore (1963)	Cromer & Waber (1974)
Anomalous dispersion	Cromer (1965)	Cromer & Liberman (1970)
Thermal parameters	All atoms, except H, anisotropic	
Number of variables N_v	113	117
R_w*	0·046	0·057
R* (with N_o reflexions)	0·035	0·040
Final R (all measured reflexions)	0·041	Not given
Goodness-of-fit S†	0·98	1·17

* $R=(\sum\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\sum\lvert F_o\rvert)$; $R_w=\{[\sum w(F_o-F_c)^2/\sum wF_o^2]^{1/2}\}$.

† $S=\{[\sum w(F_o-F_c)^2/(N_o-N_v)]^{1/2}\}$.

Table 4. *Root mean square vibrational amplitudes of atoms along the principal axes of the thermal ellipsoids*

	$R1$	$R2$	$R3$
K(1)	0·135 (2) Å	0·146 (3) Å	0·136 (3) Å
K(2)	0·137 (2)	0·127 (3)	0·130 (3)
S(1)	0·099 (3)	0·108 (4)	0·124 (3)
S(2)	0·102 (3)	0·136 (3)	0·125 (3)
O(11)	0·117 (9)	0·110 (9)	0·165 (9)
O(12)	0·112 (9)	0·110 (9)	0·171 (9)
O(13)	0·165 (9)	0·164 (9)	0·160 (9)
O(14)	0·160 (9)	0·167 (9)	0·160 (9)
O(21)	0·139 (8)	0·194 (9)	0·148 (9)
O(22)	0·115 (9)	0·141 (7)	0·176 (9)
O(23)	0·156 (9)	0·151 (9)	0·230 (8)
O(24)	0·139 (8)	0·204 (9)	0·142 (9)

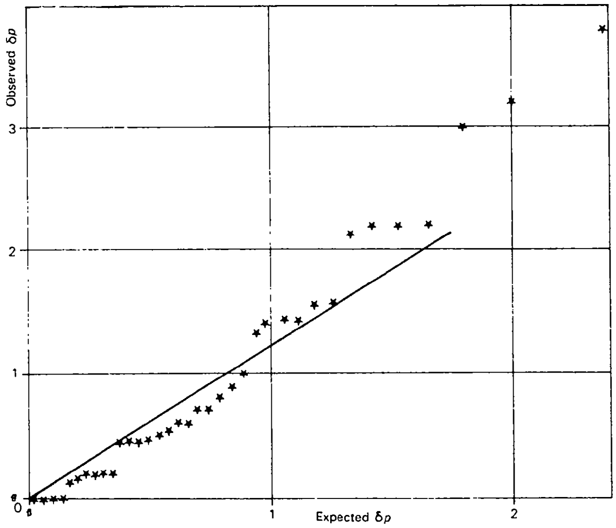


Fig. 1. Half-normal probability plots of 36 δp_i from positional coordinates. The weighted differences between corresponding pairs are defined as: $\delta p_i=\lvert\lvert p(\mathrm{PH})_i\rvert-\lvert p(\mathrm{CFH})_i\rvert\rvert/\{\sigma^2p(\mathrm{PH})_i+\sigma^2p(\mathrm{CFH})_i\}^{1/2}$, where $p(\ )_i$ is the parameter value, $\sigma(\ )_i$ is its associated standard deviation, and the 'expected δp_i' as in Abrahams & Keve (1971).

Table 3. *Positional and thermal parameters* ($\times 10^4$, *except* $B_{\rm iso}$) *with e.s.d.'s in parentheses*

The anisotropic temperature factor is defined as: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}, $B_{\rm iso}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K(1)	3827·2 (8)	1806·3 (8)	1250·6 (4)	51 (1)	45 (1)	10·1 (2)	−3 (1)	−0·1 (3)	2·0 (3)
K(2)	−1227·2 (8)	3196·6 (7)	1183·1 (4)	52 (1)	33 (1)	9·3 (2)	0 (1)	0·0 (3)	−1·0 (3)
S(1)	2544·7 (8)	4228·1 (7)	26·7 (4)	27 (1)	24 (1)	8·4 (2)	−1 (1)	−0·1 (3)	0·2 (3)
S(2)	−193·1 (8)	169·3 (8)	2059·9 (4)	29 (1)	38 (1)	8·5 (2)	0 (1)	−1·3 (3)	0·0 (4)
O(11)	2916 (3)	5801 (2)	17 (1)	38 (3)	25 (2)	15 (1)	0 (2)	−3 (1)	1 (1)
O(12)	4080 (3)	3523 (2)	33 (1)	35 (3)	25 (2)	16 (1)	4 (2)	1 (1)	1 (1)
O(13)	1664 (3)	3965 (3)	−610 (1)	76 (4)	55 (3)	14 (1)	−7 (3)	−17 (1)	−3 (1)
O(14)	1658 (3)	3986 (3)	665 (1)	71 (4)	57 (3)	14 (1)	−10 (3)	17 (1)	2 (1)
O(21)	604 (3)	−9 (3)	2746 (1)	54 (3)	77 (4)	12 (1)	−12 (3)	−10 (1)	14 (1)
O(22)	−1641 (3)	1117 (3)	2224 (1)	37 (3)	41 (2)	17 (1)	1 (2)	5 (1)	−4 (1)
O(23)	−815 (3)	−1098 (3)	1788 (2)	68 (4)	47 (3)	29 (1)	2 (3)	−7 (2)	−17 (1)
O(24)	767 (3)	942 (3)	1577 (1)	54 (3)	85 (4)	11 (1)	−5 (3)	7 (1)	7 (1)
H(1)	3790 (7)	5920 (5)	10 (2)	3					
H(21)	2480	800	2750	3					
H(22)	1510	1700	2820	3					

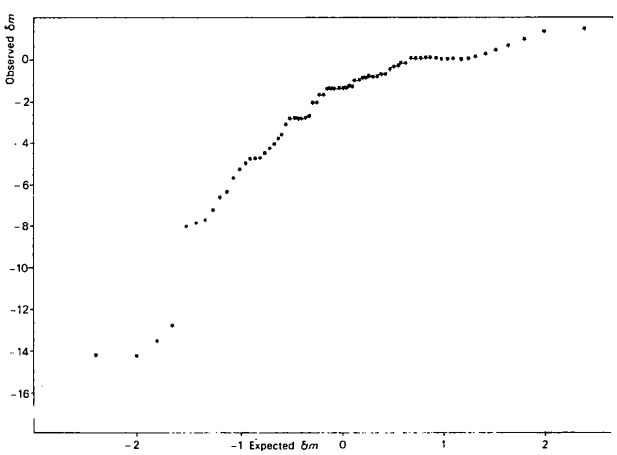


Fig. 2. Normal probability plots of δm_i from 72 vibrational parameters: $\delta m_i=[p(\mathrm{PH})_i-p(\mathrm{CFH})_i]/[\sigma^2p(\mathrm{PH})_i+\sigma^2p(\mathrm{CFH})_i]^{1/2}$, $p(\;)_i$ and $\sigma(\;)_i$ are defined as in Fig. 1.

Table 5. *Interatomic distances and bond angles*

	PH	CFH
S(1)—O(11)	1·574 (3) Å	1·564 (4) Å
S(1)—O(12)	1·467 (2)	1·465 (3)
S(1)—O(13)	1·441 (2)	1·441 (3)
S(1)—O(14)	1·443 (2)	1·440 (3)
O′(12)–H(1)	1·88 (6)	1·91 (6)
O(11)–H(1)	0·75 (6)	0·73 (6)
O(11)–H(1)···O′(12)	2·619 (3)	2·630 (5)
O(21)–H(21)	1·77	1·89 (7)
O′(22)–H(21)	0·80	0·73 (6)
O(21)–H(22)	1·85	
O′(22)–H(22)	1·66	
O′(22)–H·····O(21)	2·573 (3)	2·583 (5)
S(2)—O(21)	1·475 (2)	1·467 (3)
S(2)—O(22)	1·566 (2)	1·561 (3)
S(2)—O(23)	1·444 (3)	1·428 (4)
S(2)—O(24)	1·438 (3)	1·437 (4)
O(11)—O(12)	2·440 (3)	2·437 (5)
O(11)—O(13)	2·402 (3)	2·387 (5)
O(11)—O(14)	2·409 (3)	2·395 (5)
O(12)—O(13)	2·414 (3)	2·407 (5)
O(12)—O(14)	2·411 (3)	2·407 (5)
O(13)—O(14)	2·420 (3)	2·422 (5)
O(22)—O(21)	2·404 (3)	2·396 (5)
O(22)—O(23)	2·427 (4)	2·417 (5)
O(22)—O(24)	2·379 (3)	2·361 (5)
O(21)—O(23)	2·423 (4)	2·412 (5)
O(21)—O(24)	2·409 (3)	2·399 (5)
O(23)—O(24)	2·438 (3)	2·420 (5)

the slightly lower values of the standard deviations in PH's analysis.

Comparison with CFH's structure

Prior to any statistical treatment it was necessary to take into account several misprints and inconsistencies in CFH's publication: the lattice constant *a* is given as 8·412 and later as 8·421; the *y* coordinate of O(23) must be 0·1079 instead of 0·1797; and the positions given for the H atoms do not agree with the interatomic distances.

Comparison of our coordinates and thermal parameters with those of CFH shows some significant discrepancies especially for the β_{ij} values, as checked by means of normal probability plots (Abrahams & Keve, 1971). The half-normal probability plot (Fig. 1) for the 36 coordinates is essentially linear, with zero intercept, indicating that the errors are normally distributed; the slope of the line ($\sim$1·20) suggests that the standard deviations have been slightly underestimated in both structures. The χ^2 test (Table 6) does show small but significant differences at the 0·05 probability level (Hamilton, 1969). Similar calculations were performed to compare the interatomic distances. The normal probability plot (for 24 parameters) is again linear but the non-zero intercept usually indicates that some systematic error is present. The distances in PH's structure show a tendency to be greater than those in CFH's analysis; this fact might be partly related to the slight discrepancy between the unit-cell dimensions.

Table 6. χ^2 *tests*

	Atomic coordinates		
	N parameters	χ^2 obs	$\chi^2_{N,0\cdot05}$
χ^2_x	12	28·13	21·03
χ^2_y	12	28·32	21·03
χ^2_z	12	15·12	21·03
χ^2_{xyz}	36	71·57	55·76

Considering the anisotropic thermal parameters, the plot (Fig. 2) shows obviously that the two sets of parameters differ significantly; this observation is confirmed by the χ^2 tests, especially for the r.m.s. displacements of the O atoms along the *b* axis.

Table 5 (*cont.*)

	PH	CFH		PH	CFH
O(11)–S(1)—O(12)	106·6 (1)°	107·1 (2)°	O(22)–S(2)—O(24)	104·6 (1)°	103·8 (2)°
O(11)–S(1)—O(13)	105·5 (1)	105·1 (2)	O(21)–S(2)—O(23)	112·2 (1)	112·8 (2)
O(11)–S(1)—O(14)	105·9 (1)	105·7 (2)	O(21)–S(2)—O(24)	111·6 (1)	111·4 (2)
O(12)–S(1)—O(13)	112·1 (1)	111·8 (1)	O(23)–S(2)—O(24)	115·5 (1)	115·3 (2)
O(12)–S(1)—O(14)	111·9 (1)	111·9 (2)	O′(22)–H(2)—O(21)		158 (7)
O(13)–S(1)—O(14)	114·1 (1)	114·4 (2)	O′(22)–H(21)–O(21)	175 (8)	
O(11)–H(1)—O′(12)	172 (4)	173 (5)	O′(22)–H(22)–O(21)	94 (8)	
S(1)—O(11)–H(1)	110 (2)	118 (5)	S(2)—O(21)–H(2)		112 (2)
O(22)–S(2)—O(21)	104·5 (1)	104·6 (2)	S(2)—O(21)–H(21)	111 (5)	
O(22)–S(2)—O(23)	107·4 (1)	107·9 (2)	S(2)—O(21)–H(22)	99 (5)	

Discussion

Hydrogen bonding

A general view of the three-dimensional arrangement is given in CFH's paper. However, the additional information obtained from the present study again implies some extra detail of description; the two independent HSO_4^- ions in the asymmetric unit are involved in different hydrogen-bonding schemes: one type forms closed dimers across the symmetry centres (Fig. 3), the second generates infinite chains with the components related by a glide plane (Fig. 4). The H atoms were located on difference Fourier maps as well-resolved peaks (0·52 e Å^{-3}) for the dimer, H(1), but clearly they are distributed over two sites of equal height (0·25 e Å^{-3}) in the polymeric chain, H(21) and H(22). With the introduction of these H positions ($B_{\text{iso}}=3$ Å^2) the R value decreased from 0·0365 to 0·0355.

This distribution of hydrogen sites appears to be consistent with the observed differences between corresponding S–O distances in the systems S–O··· H–O–S of the dimer $[(HSO_4)^-]_2$ and of the polymer $[(HSO_4)^-]_n$. The following scheme illustrates this situation, the O–H distance given for the polymeric unit being the mean value of O(22)–H(21) and O(21)–H(22):

Dimer	1·574	0·75	1·88	1·467
	S —— O	—— H	----- O	—— S
Chain	1·566	1·23	1·81	1·475

This internal comparison provides some evidence that the interactions of the H atoms with neighbouring O atoms have to be different within the chain and the dimer, and further, should affect the S–O distances: in fact the longer mean distance O–H in the chain is consistent with the shortening of the closest S–O bond and with the elongation of the other.

At this stage it is worthwhile to add two remarks. (1) The presence of some disorder affecting the intrachain components in PH's structure can be ruled out by the normal thermal behaviour of all the O atoms. (2) In CFH's structure both H atoms were clearly defined, forming O–H links of approximately 0·80 Å length; moreover the internal comparison of homologous S–O distances shows that these are equal within experimental error.

Finally what can be concluded from this comparison? The differences between the two sets of refined parameters, especially thermal parameters, may be attributed to some systematic errors in the data: of course no account for absorption effects has been made for the irregular-shaped CFH's crystal (these effects are negligible with PH's spherical specimen) and neglect of absorption correction is known to affect mainly vibrational parameters (Murray-Rust & Murray-Rust, 1975; Kratky & Dunitz, 1975; Coppens, 1969).

Obviously secondary extinction has seriously attenuated a few intense low-angle reflexions in PH's data set; these have been omitted from refinement and Fourier calculations but not from the final R calculation.* This phenomenon was not observed with CFH's crystal.

Ultimately one could raise the question of being concerned with two slightly different phases, owing to different crystal growth conditions: CFH and PH materials were grown after several weeks at 0°C in 50% H_2SO_4 and after two days at 25°C in 10% H_2SO_4 respectively.

A plausible explanation for the different bonding situation in PH's type of crystals is as follows: the polymeric unit has not the ideal formula $[(HSO_4)^-]_n$ but corresponds to a mixed composition $[(HSO_4)^-_{n-n'}(SO_4)^{2-}_{n'}(H)^+_{n'}]$. This suggestion arises from the observation that for low H_2SO_4 concentration the second stage of dissociation of the acid, *i.e.* $HSO_4^- \rightleftarrows SO_4^{2-}+H^+$, becomes important (Cox, 1974; and refer-

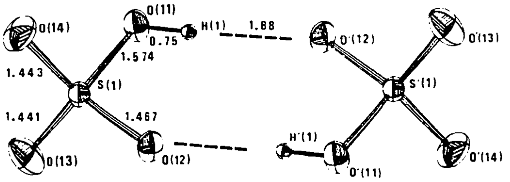


Fig. 3. *ORTEP* drawing (Johnson, 1965) of the dimer.

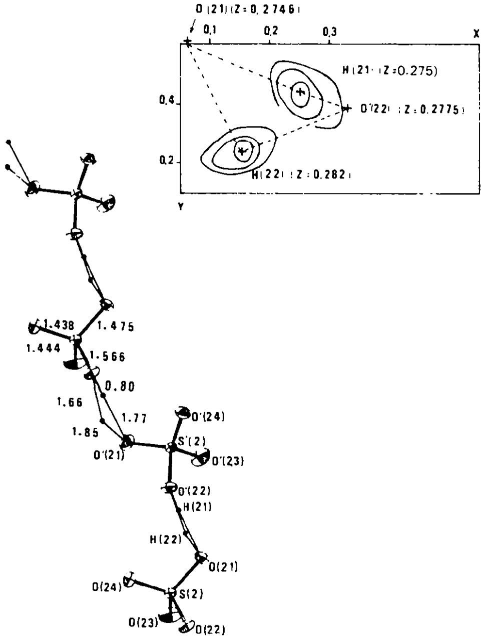


Fig. 4. The polymeric chain and difference Fourier map in the O(21)···O′(22) region: contours are drawn at intervals of 0·05 e Å^{-3}, starting at 0·10.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31532 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

ences therein); therefore during the growth of $KHSO_4$ crystals, it seems that the possibility of substitution of some HSO_4^- by (SO_4^{2-}, H^+) groups cannot be excluded. If one considers that the H atom positions are mainly dictated by the crystalline field, it is likely that these equilibrium positions are not necessarily coincident with those expected between two equivalent HSO_4^- ions linked through normal hydrogen bonds. For that reason, the H(22) atom positions are regarded as interstitial sites and assumed to play a similar electrostatic role as the potassium cations.

Furthermore, it is worthwhile to point out that the growth parameters used for CFH's material do not favour the interchange mechanism we have proposed, the SO_4^{2-} species concentration probably being very small in view of the above-mentioned conditions. On the other hand, the possibility of some degree of replacement of HSO_4^- ions by (SO_4^{2-}, H^+) groups appears to be in agreement with the conduction behaviour of $KHSO_4$ (Rogers & Ubbelohde, 1950). These authors have reported conductivity measurements on the solid frozen from the melt and find an exceptionally low activation energy, well below the melting point. In the absence of the structure at that time, they suggested that the proton could enter both substitutional and interstitial positions and therefore could participate in the conduction process. With the structure in hand, it becomes clear that the continuous hydrogen-bond chain allows a favourable path for proton transfer.

In order to clarify the mechanism of the structural modifications of $KHSO_4$ in relation to its physical properties some further extensions of our analysis could be valuable, such as information on the anisotropy of conductivity in single crystals, the determination of the structure of the next high-temperature modification and a low-temperature diffraction analysis of PH's type of crystals.

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