Table 1. *Analysis of the uranium diffraction pattern*

hkl	Estimated diameters in mm.	Measured diameters in mm.	Intensity
311	19·75	19·75	*vf*
330	22·60	22·50	*f*
212	24·50	24·25	*f*
312	26·40	26·50	*vs*
620	33·00	33·00	*s*
611	34·20	34·50	*vf*
114	41·10	41·50	*vs*
424	47·00	47·00	*s*
434	48·50	48·30	*s*
115	51·00	51·00	*vf*
860	53·60	53·50	*vf*
084	58·80	58·50	*f*

v = very; *f* = faint; *s* = strong.

rings. Also in the electron micrograph (Fig. 1(*a*)) some tetragonal crystals can be identified.

In the thin film state uranium thus assumes the β-phase structure which according to X-ray studies should occur at a high temperature. It may be pointed out that the heating of the specimen during the examination in the electron microscope might be responsible for the phase transformation. In this respect special care was taken to keep the intensity of the electron beam at a minimum. The experiment was repeated with different films prepared under the same condition but the result was always the same. Similar structural anomalies in the thin film state have been observed by other authors in several cases. Quarrel (1937) reported that many metals which normally crystallize as face-centred cubes were found to develop the hexagonal close-packed structure in the thin film. Aggarwal & Goswami (1957) observed very recently a new phase (face-centred cube) of molybdenum in thin film. The mechanism of such phase transformations in the thin film state is not yet clearly understood and hence deserves special attention.

The author is indebted to Prof. N. N. Das Gupta for his kind interest in the present work.

References

AGGARWAL, P. S. & GOSWAMI, A. (1957). *Proc. Phys. Soc.* B, **70**, 708.

JACOB, C. W. & WARREN, B. E. (1937). *J. Am. Chem. Soc.* **59**, 2588.

QUARREL, A. G. (1937). *Proc. Phys. Soc.* **49**, 279.

TUCKER, C. W. (1951). *Acta Cryst.* **4**, 425.

WILSON, A. S. & RUNDLE, R. E. (1949). *Acta Cryst.* **2**, 126.

Acta Cryst. (1958). **11**, 680

A Detailed Refinement of the Crystal Structure of Potassium Ethyl Sulphate

BY MARY R. TRUTER

Department of Inorganic and Structural Chemistry, The University, Leeds, 2, England

(*Received* 11 *February* 1958)

Refinement of the crystal structure of potassium ethyl sulphate using Jarvis's three-dimensional data has been carried out until $R = 0{\cdot}098$. Anisotropic thermal parameters have been determined, and an estimate has been made of the error arising from rotational oscillation. The bond lengths are S–O$_1$ = 1·466 Å, S–O$_2$ = 1·466 Å, S–O$_3$ = 1·451 Å (mean S–O = 1·46 ± 0·01 Å), S–O$_4$ = 1·60 ± 0·01 Å, C–O = 1·45 ± 0·02 Å and C–C = 1·51 ± 0·02 Å.

Introduction

In most compounds in which oxygen is bonded only to sulphur the S–O bond lengths are close to 1·43 Å (see Abrahams, 1956 for a summary); it is probable, therefore, that 1·43 Å is the double-bond length. The S–O bond may be longer, about 1·6 Å, when the oxygen is bonded to another atom as in $K_2S_2O_7$ (Lynton, 1955) and the ion $HS_2O_7^-$ (Steeman & MacGillavry, 1954) but these interatomic distances have not been determined accurately. Jarvis (1953) studied the structure of potassium ethyl sulphate, $KO_3SOC_2H_5$, by three-dimensional X-ray crystal structure analysis and found that the three chemically equivalent S=O bonds were 1·44, 1·45 and 1·49 Å while the S–O bond to the esterified oxygen was 1·60 Å. Jarvis's results were obtained after one cycle of correction for series

Table 1. *Electron densities and curvatures*

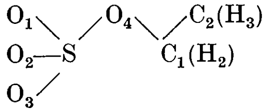
Ratios between observed and calculated values

	ϱ	$\partial^2\varrho/\partial x^2$	$\partial^2\varrho/\partial y^2$	$\partial^2\varrho/\partial z^2$
K^+	0·976	1·005	0·952	0·911
S	0·998	1·027	0·987	0·943
O_1	0·975	0·950	1·020	0·990
O_2	1·023	1·013	1·026	1·011
O_3	0·972	1·035	0·906	0·883
O_4	1·000	1·008	1·016	1·018
C_1	0·900	0·874	0·779	0·868
C_2	0·871	0·862	0·720	0·890

Table 2. *Parameters used for structure factor calculation*

	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
K^+	$\overline{0{\cdot}12826}$	$\overline{0{\cdot}08572}$	0·10956	1554×10^{-5}	$\overline{171}\times10^{-5}$	671×10^{-5}	958×10^{-5}	$\overline{239}\times10^{-5}$	880×10^{-5}
S	0·42102	0·06691	0·15973	1562	$\overline{129}$	578	760	$\overline{171}$	822
O_1	0·46478	0·19654	0·06999	2725	$\overline{98}$	909	1087	$\overline{299}$	985
O_2	0·25223	$\overline{0{\cdot}03742}$	0·12314	2431	469	550	1035	$\overline{414}$	895
O_3	0·56424	$\overline{0{\cdot}06230}$	0·20973	1747	102	423	1940	$\overline{220}$	1108
O_4	0·39596	0·21356	0·26168	1983	$\overline{353}$	474	1264	$\overline{149}$	788
C_1	0·33246	0·13007	0·36026	2250	30	734	2067	$\overline{248}$	894
C_2	0·33767	0·28710	0·44943	2468	253	821	2784	$\overline{454}$	940

termination errors which affected one S=O bond by as much as 0·05 Å. This, and the disparity in the S=O bonds suggested that more accurate values for the interatomic distances could be obtained by further refinement, which is described in this paper. Reference should be made to Jarvis's paper for the general description of the structure. The axes have been interchanged to make the space group $P2_1/a$ with a = 7·51, b = 6·99, c = 11·62 Å and β = 100·3°. Jarvis's designations for the atoms of the anion, also used here, are



Three-dimensional anisotropic refinement

Differential syntheses using the 908 $F(hkl)$ measured by Jarvis were used to refine co-ordinates and a back-shift correction was applied to compensate for finite series errors.

For the first cycle the structure factors were calculated from Jarvis's final co-ordinates, using the scattering factors for C and O given by McWeeny (1951), for S in *Internationale Tabellen* (1935), and for K^+ by Berghuis *et al.* (1955), with a common isotropic temperature factor $\exp-(B\sin^2\theta/\lambda^2)$ where B = 4·0 $Å^2$. The first set of differential syntheses was then computed, and the results showed that changes in the co-ordinates and in the thermal vibration parameters were required. Comparison of the values for the peak electron density, ϱ, and of the six curvatures $\delta^2\varrho/\delta x_i\delta x_j$ corresponding to ϱ_o and ϱ_c confirmed Jarvis's finding that the thermal motion parallel to the b-axis was less than in the other directions. It was also evident that considerable changes in the isotropic temperature factors were required. Accordingly the values of B were decreased to 3·5 $Å^2$ for S and K^+ and increased to 4·5 $Å^2$ for O_1, O_2, O_3 and C_2 (i.e. for the light atoms not bonded to two atoms other than hydrogen). A second set of structure factors was calculated from the new co-ordinates using the new temperature factors together with Jarvis's empirical anisotropic temperature factor $\exp(0{\cdot}46k^2/b^2)$. The agreement index

$$(R = \Sigma||F_o|-|F_c||/\Sigma|F_o|)$$

fell from 0·178 to 0·124.

From the co-ordinates obtained from a second set of differential syntheses the values for the three S=O bonds were 1·444, 1·472 and 1·458 Å all having estimated standard deviations of 0·009 Å. Table 1 shows the ratios between the observed and calculated values for the peak electron densities and curvatures. It can be seen that, despite the use of an overall anisotropic temperature factor, the curvature differences are too large to give trustworthy back-shift corrections. Individual anisotropic thermal parameters for each atom were required and these were determined by the refinement procedure described by Cruickshank (1956*a*), (the equations are given in § 3 of his paper). This method leads to values of b_{ij} such as to make $\partial^2\varrho_o/\partial x_i\partial x_j$ equal to $\partial^2\varrho_c/\partial x_i\partial x_j$, where the b_{ij} are the coefficients in the temperature factor expression for each atom,

$$\exp-\{h^2b_{11}+hkb_{12}+hlb_{13}+k^2b_{22}+klb_{23}+l^2b_{33}\}\,.$$

Two cycles of refinement with anisotropic thermal vibration parameters reduced R to 0·098. The structure factors are shown in Table 4 and were calculated from the parameters in Table 2 which are the actual values used by the electronic computer, not rounded off to the number of truly significant figures. In the final set of differential syntheses the largest co-ordinate shift (0·008 Å) and the largest change in b_{ij} were the same as the corresponding standard deviations indicating that further refinement was unlikely to produce significant changes. Final co-ordinates derived from these differential syntheses are given in Table 3 together with standard deviations obtained from the formula of Cruickshank & Robertson (1953). The final thermal parameters, also derived from these differential syntheses, are given in Table 5 where they are expressed as the mean square amplitudes (U_{ij}) of the atomic vibrations. The U_{ij} are related to the

Table 3. *Final co-ordinates and standard deviations*

	x/a	y/b	z/c	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)
K^+	$\overline{0{\cdot}1283}$	$\overline{0{\cdot}0859}$	0·1095	0·002	0·002	0·002
S	0·4211	0·0668	0·1597	0·002	0·002	0·002
O_1	0·4659	0·1962	0·0704	0·007	0·006	0·007
O_2	0·2516	$\overline{0{\cdot}0374}$	0·1232	0·007	0·006	0·007
O_3	0·5645	$\overline{0{\cdot}0624}$	0·2101	0·006	0·008	0·007
O_4	0·3956	0·2131	0·2610	0·007	0·005	0·006
C_1	0·3335	0·1297	0·3606	0·011	0·011	0·009
C_2	0·3381	0·2874	0·4501	0·012	0·013	0·012

b_{ij} by $U_{ii} = a_i^2 b_{ii}/2\pi^2$ and $U_{ij} = a_i a_j b_{ij}/4\pi^2$ $(i \neq j)$ where a_i and a_j may be $a \sin\beta$, b or $c \sin\beta$. As the estimated standard deviations $\sigma(U_{ij})$ for any atom were approximately equal whatever i and j were, only the average $\sigma(U)$ is shown in Table 5.

Corrections for rotational oscillation

It has been shown (Cox, Cruickshank & Smith, 1955) that systematic errors in atomic positions may arise from rotational oscillations, the atoms in a molecule

Table 4. *Observed and calculated structure factors*

hkl	F_o	F_c
000		336
001	101	106
002	26	-33
003	89	-91
004	69	-73
005	37	-39
006	14	-16
007	10	11
008	19	17
009	7	7
0,0,10	7	-6
0,0,11	9	8
200	28	28
201	124	121
$\bar{2}01$	68	-66
202	38	36
$\bar{2}02$	87	-85
203	42	43
$\bar{2}03$	80	-79
204	22	26
$\bar{2}04$	10	8
205	6	-3
$\bar{2}05$	37	37
206	30	-34
$\bar{2}06$	44	49
207	23	-22
$\bar{2}07$	13	12
208	9	-9
$\bar{2}08$	19	-20
$\bar{2}09$	31	-31
2,0,10	9	-8
2,0,11	4	-3
$\bar{2}$,0,11	8	5
2,0,12	9	12
2,0,13	7	8
400	53	-48
$\bar{4}01$	28	-21
402	45	37
$\bar{4}02$	23	-18
403	23	19
$\bar{4}03$	17	15
404	12	13
$\bar{4}04$	19	14
$\bar{4}05$	35	29
$\bar{4}06$	20	17
$\bar{4}07$	20	19
408	7	8
$\bar{4}08$	43	-40
$\bar{4}09$	13	-12
4,0,10	9	-7
$\bar{4}$,0,10	9	9
4,0,11	15	-12
4,0,11	6	6
4,0,12	4	-4
$\bar{4}$,0,12	5	6
600	25	-21
601	36	-30
602	7	3
$\bar{6}02$	39	34
603	15	13
$\bar{6}03$	36	31
$\bar{6}04$	8	8
605	4	-4
$\bar{6}05$	7	-7
$\bar{6}06$	27	-27
607	3	3
$\bar{6}07$	33	-32
608	5	5
$\bar{6}08$	11	-13
609	5	5
$\bar{6}09$	10	12
$\bar{6}$,0,10	12	13
$\bar{6}$,0,11	15	14
$\bar{8}01$	10	11
$\bar{8}02$	11	12
$\bar{8}04$	13	-14
$\bar{8}05$	21	-23
$\bar{8}06$	16	-15
$\bar{8}08$	20	19
$\bar{8}09$	14	14
$\bar{8}$,0,10	6	6
110	47	-48
111	24	-21
$\bar{1}11$	11	10
112	47	46
$\bar{1}12$	38	42
113	30	27
$\bar{1}13$	19	22
114	2	-3
$\bar{1}14$	19	-22
115	15	-16
$\bar{1}15$	63	-64
116	28	-27
$\bar{1}16$	23	-26
117	13	-12
$\bar{1}17$	15	14
118	4	-4
$\bar{1}18$	33	33
119	10	10
$\bar{1}19$	33	33
1,1,10	20	19
$\bar{1}$,1,10	8	8
1,1,11	10	10
$\bar{1}$,1,11	9	-9
$\bar{1}$,1,12	12	-13
1,1,13	7	-5
$\bar{1}$,1,13	11	-10
1,1,14	4	-5
310	37	-35
311	20	-19
$\bar{3}11$	47	-43
312	10	10
312	25	-24
313	35	36
$\bar{3}13$	8	7
314	30	27
315	21	22
$\bar{3}15$	9	10
$\bar{3}16$	22	23
317	20	-23
$\bar{3}17$	25	29
318	21	-24
$\bar{3}18$	26	27
319	11	11
$\bar{3}19$	5	-6
3,1,10	6	6
$\bar{3}$,1,10	25	-27
3,1,11	12	13
$\bar{3}$,1,11	20	-22
3,1,12	6	6
$\bar{3}$,1,12	7	-7
$\bar{3}$,1,13	4	6
$\bar{3}$,1,14	9	10
510	5	5
511	22	-20
$\bar{5}11$	19	17
512	47	-44
$\bar{5}12$	25	23
513	34	-33
$\bar{5}13$	20	17
514	3	4
$\bar{5}14$	9	11
515	23	24
$\bar{5}15$	5	2
516	26	27
$\bar{5}16$	8	-9
517	8	10
$\bar{5}17$	4	-1
518	6	-7
$\bar{5}18$	7	-6
519	9	-10
$\bar{5}19$	8	-12
$\bar{5}$,1,10	8	-8
$\bar{5}$,1,12	8	9
$\bar{5}$,1,13	9	10
710	22	25
711	16	15
$\bar{7}11$	9	15
$\bar{7}12$	6	-6
713	17	-20
$\bar{7}13$	12	-13
714	12	-15
715	3	-3
020	48	41
021	59	55
022	26	-22
023	60	-62
024	64	-59
025	4	1
026	27	27
027	14	13
028	9	11
029	4	7
0,2,10	6	7
0,2,11	5	-5
220	10	-9
221	20	-20
$\bar{2}21$	23	-21
222	24	23
$\bar{2}22$	56	-56
223	17	15
$\bar{2}23$	48	-44
224	8	5
$\bar{2}24$	15	14
225	15	-15
$\bar{2}25$	68	70
$\bar{2}26$	34	33
$\bar{2}27$	4	4
$\bar{2}28$	14	-13
$\bar{2}29$	4	-4
$\bar{2}$,2,10	5	-6
$\bar{2}$,2,14	4	-3
420	5	-6
421	13	-17
$\bar{4}21$	14	-16
422	6	-5
$\bar{4}22$	9	-10
423	12	13
$\bar{4}24$	34	35
425	10	-11
$\bar{4}25$	23	23
426	8	-9
$\bar{4}26$	9	7
427	9	11
$\bar{4}27$	8	-8
428	8	9
$\bar{4}28$	9	-8
429	3	2
$\bar{4}29$	5	-6
4,2,10	4	-5
4,2,11	3	-3
$\bar{4}$,2,11	7	6
$\bar{4}$,2,14	4	-4
620	16	-16
621	10	-10
622	6	-7
$\bar{6}22$	13	13
623	4	5
$\bar{6}23$	30	29
624	4	4
$\bar{6}24$	17	16
$\bar{6}25$	3	-5
626	4	-6
$\bar{6}26$	8	-12
$\bar{6}27$	6	-11
628	3	-4
$\bar{6}$,2,10	6	8
$\bar{6}$,2,11	6	5
$\bar{8}21$	3	4
$\bar{8}22$	8	9
$\bar{8}23$	4	5
$\bar{8}24$	7	-9
$\bar{8}25$	11	-12
$\bar{8}26$	4	-6
$\bar{8}27$	4	5
$\bar{8}28$	5	7
$\bar{8}29$	7	7
130	4	8
131	5	5
$\bar{1}31$	7	6
132	13	-14
$\bar{1}32$	24	26
133	5	6
$\bar{1}33$	41	40
134	14	14
$\bar{1}34$	5	-5
135	3	-4
$\bar{1}35$	21	-21
$\bar{1}36$	27	-29
137	7	-7
$\bar{1}37$	7	-7
$\bar{1}38$	4	4
330	2	3
331	21	19
$\bar{3}31$	4	-5
332	19	18
$\bar{3}32$	6	8
333	3	-3
$\bar{3}33$	3	-4
334	9	8
$\bar{3}34$	12	-10
335	4	4
$\bar{3}35$	19	-18
336	8	-7
$\bar{3}36$	7	-6
337	9	-7
$\bar{3}37$	10	10
338	9	-8
$\bar{3}$,3,12	5	-0
$\bar{3}$,3,13	7	-4
530	7	5
$\bar{5}31$	9	9
$\bar{5}32$	3	4
533	4	-4
$\bar{5}33$	4	-4
534	3	-4
$\bar{5}34$	11	-11
535	8	10
$\bar{5}35$	9	-11
536	6	6
$\bar{5}37$	5	-5
538	3	-4
539	4	-4
$\bar{5}39$	4	4
730	3	4
731	4	5
$\bar{7}32$	5	-8
$\bar{7}33$	6	-9
$\bar{7}34$	3	-5
$\bar{7}35$	4	6
$\bar{7}36$	3	3
040	7	-7
041	9	-8
042	5	-4
044	20	23
045	7	5
049	4	-5
0,4,10	4	-5
240	4	-3
241	14	-13
$\bar{2}41$	4	-5
242	16	-17
$\bar{2}42$	15	15
243	9	-11
$\bar{2}43$	32	31
244	3	-1
$\bar{2}44$	11	11
245	17	17
$\bar{2}45$	12	-13
$\bar{2}46$	7	-6
$\bar{2}47$	13	-14
$\bar{2}48$	8	-10
$\bar{2}$,4,11	7	7
$\bar{2}$,4,12	4	5
440	15	16
441	18	17
$\bar{4}41$	12	13
$\bar{4}42$	10	10
443	7	-7
$\bar{4}43$	7	-7
444	14	-12
$\bar{4}44$	30	-27
445	10	-8
$\bar{4}45$	13	-13
$\bar{4}46$	8	-8
$\bar{4}47$	3	2
$\bar{4}48$	10	8
449	7	5
$\bar{4}49$	8	7
$\bar{4}$,4,10	8	7
$\bar{4}$,4,12	4	-4
640	5	-3
$\bar{6}41$	6	-5
642	9	10
$\bar{6}42$	7	-8
643	4	6
$\bar{6}43$	12	-13
644	4	4
$\bar{6}45$	3	5
$\bar{6}46$	5	7
$\bar{6}47$	8	8
$\bar{8}41$	4	-3
842	3	-1
$\bar{8}42$	5	-3
$\bar{8}44$	7	5
$\bar{8}45$	6	4
$\bar{8}46$	6	4
150	14	-17
151	27	-31
152	25	-29
$\bar{1}52$	12	13
153	15	-17
$\bar{1}54$	8	-11
$\bar{1}54$	17	20
155	17	18
$\bar{1}55$	24	28
156	29	31
$\bar{1}56$	9	12
157	19	22
$\bar{1}57$	11	-12
$\bar{1}58$	12	-15
$\bar{1}59$	8	-10
1,5,10	13	-11
1,5,11	11	-9
$\bar{1}$,5,11	5	4
$\bar{1}$,5,12	6	6
350	12	10
351	6	5
$\bar{3}51$	20	20
352	8	-8
$\bar{3}52$	4	-1
353	11	-12
$\bar{3}53$	5	-5
354	19	-21
$\bar{3}54$	8	7
355	19	-21
$\bar{3}55$	4	3
356	3	-2
$\bar{3}56$	8	-8
357	12	15
$\bar{3}57$	10	-11
358	12	15
359	7	7
3,5,10	3	3
$\bar{3}$,5,10	9	10
$\bar{3}$,5,11	6	6
550	7	6
551	7	7
$\bar{5}51$	3	-6
552	12	12
$\bar{5}52$	13	-13
553	7	7
555	16	-13
556	16	-14
557	4	-5
$\bar{5}57$	8	6
558	6	4
$\bar{5}58$	9	8
$\bar{5}59$	9	8
750	12	-11
751	4	-4
$\bar{7}51$	15	-14
752	3	3
753	8	9
$\bar{7}53$	7	5
$\bar{7}54$	8	7
$\bar{7}55$	6	5
$\bar{7}56$	8	6
$\bar{7}57$	4	5
060	40	-43
061	21	-25
062	8	9
063	26	30
064	19	24
065	7	9
066	4	-5
067	9	-11
068	8	-8
069	3	-3
260	8	-9
261	23	-27
$\bar{2}61$	15	20
262	19	-23
$\bar{2}62$	36	39

appearing closer to its mass centre than they really are. A rigorous analysis of the thermal motion (Cruickshank, 1956*b*) is possible only for rigid molecules, but the ethyl sulphate anion is probably not rigid so that only an approximate correction for rotational oscillation can be given.

Cruickshank (1956*c*) has shown that the approximate correction, ε, to the length OP from the mass centre O to an atom P is $\varepsilon = (U_a+U_b)/2(OP)$ where U_a and U_b are the mean square amplitudes of oscillation about two axes through O orthogonal to OP. Except for the potassium ion which must be undergoing translatory motions only, the values of U_{ij} in Table 5 include both rotational and translational

Table 4 (*cont.*)

hkl	F_o	F_c
263	6	- 9
$\bar{2}$63	25	29
265	9	10
$\bar{2}$65	17	- 21
266	8	9
$\bar{2}$66	23	- 26
$\bar{2}$67	12	- 13
$\bar{2}$69	6	6
460	24	25
461	10	10
$\bar{4}$61	24	25
462	7	- 6
$\bar{4}$62	8	9
463	13	- 13
$\bar{4}$63	12	- 13
464	8	- 8
$\bar{4}$64	25	- 26
$\bar{4}$65	24	- 27
$\bar{4}$66	8	- 9
$\bar{4}$67	8	10
$\bar{4}$68	16	18
469	10	11
660	10	8
661	12	12
$\bar{6}$61	4	- 5
662	6	6
$\bar{6}$62	23	- 17
$\bar{6}$63	23	- 18
$\bar{6}$64	11	- 9
$\bar{6}$65	6	6
$\bar{6}$66	19	16
$\bar{6}$67	16	15
170	12	13
171	4	6
$\bar{1}$71	4	5
172	13	- 13
$\bar{1}$72	11	- 12
173	20	- 20
$\bar{1}$74	9	11
175	9	9
$\bar{1}$75	10	13
176	12	13
$\bar{1}$76	6	7
177	11	12
$\bar{1}$77	4	- 5
178	4	- 5
$\bar{1}$78	16	- 18
179	13	- 16
370	16	16
371	19	17
372	10	8
373	10	- 10
374	19	- 17
375	12	- 11
$\bar{3}$76	14	- 4
$\bar{3}$77	14	- 12
570	9	- 7
571	10	11
$\bar{5}$71	11	- 10
572	18	19
$\bar{5}$72	4	- 5
573	13	14
$\bar{5}$73	7	- 6
080	27	- 27
081	16	- 17
082	5	6
083	18	20
084	10	12
086	5	- 6
280	10	- 11
281	15	- 17
$\bar{2}$81	7	7
282	11	- 13
$\bar{2}$82	18	20
$\bar{2}$83	11	12
284	7	7
285	4	6
$\bar{2}$85	9	- 12
$\bar{2}$86	10	- 12
480	7	7
481	3	- 4
$\bar{4}$81	10	13
$\bar{4}$82	3	6
$\bar{4}$83	3	- 4
011	41	- 41
012	33	32
013	2	2
014	2	- 2
015	22	- 25
016	7	- 7
017	15	- 17
018	13	- 15
019	9	- 9
0,1,10	15	16
0,1,11	20	17
210	46	49
211	41	- 36
$\bar{2}$11	13	- 10
212	54	- 53
$\bar{2}$12	15	11
213	14	- 11
$\bar{2}$13	15	16
214	11	9
$\bar{2}$14	46	45
215	14	14
$\bar{2}$15	23	22
216	9	7
$\bar{2}$16	3	- 0
217	4	4
218	11	- 11
219	11	- 11
$\bar{2}$19	15	- 16
2,1,10	9	- 10
$\bar{2}$,1,10	24	- 22
2,1,11	4	6
2,1,12	4	5
$\bar{2}$,1,13	7	6
$\bar{2}$,1,14	4	3
410	22	22
411	28	27
$\bar{4}$11	19	18
412	30	- 30
$\bar{4}$12	10	10
413	32	- 29
$\bar{4}$13	14	14
414	11	- 10
$\bar{4}$14	16	17
$\bar{4}$15	5	- 5
$\bar{4}$16	4	- 4
417	8	7
$\bar{4}$17	7	- 7
418	7	6
$\bar{4}$18	12	- 14
419	5	0
$\bar{4}$19	15	- 18
4,1,10	8	- 4
$\bar{4}$,1,11	5	6
$\bar{4}$,1,12	4	6
$\bar{4}$,1,13	3	3
610	11	12
611	14	17
$\bar{6}$11	7	9
612	11	12
613	9	- 9
614	6	- 10
$\bar{6}$14	10	- 12
615	6	- 8
616	6	- 4
$\bar{6}$18	9	- 8
$\bar{6}$,1,10	6	8
812	9	10
813	8	9
120	62	- 64
121	19	21
$\bar{1}$21	78	- 79
122	68	66
$\bar{1}$22	35	- 39
123	52	52
$\bar{1}$23	33	- 33
124	43	42
$\bar{1}$24	10	9
125	8	- 10
$\bar{1}$25	36	34
126	18	- 18
$\bar{1}$26	21	25
127	7	- 6
$\bar{1}$27	14	15
128	4	- 3
$\bar{1}$28	17	- 15
$\bar{1}$29	8	- 8
1,2,10	8	- 7
$\bar{1}$,2,10	5	3
1,2,11	9	- 8
1,2,13	5	5
320	74	- 78
321	62	- 65
$\bar{3}$21	20	- 21
322	4	4
$\bar{3}$22	31	31
323	27	25
$\bar{3}$23	54	53
324	20	18
$\bar{3}$24	37	38
325	17	20
$\bar{3}$25	5	- 2
326	4	4
$\bar{3}$26	8	- 9
327	4	6
$\bar{3}$27	29	- 29
$\bar{3}$28	19	- 19
$\bar{3}$29	3	3
$\bar{3}$,2,10	7	6
3,2,11	7	- 6
$\bar{3}$,2,11	8	7
3,2,12	7	- 6
$\bar{3}$,2,12	4	5
520	3	4
521	14	- 13
$\bar{5}$21	24	24
522	12	- 14
$\bar{5}$22	34	31
523	4	- 3
$\bar{5}$23	17	16
524	7	- 8
$\bar{5}$24	22	- 22
525	4	- 5
$\bar{5}$25	33	- 31
$\bar{5}$26	27	- 28
$\bar{5}$27	5	- 7
$\bar{5}$28	19	21
$\bar{5}$29	15	17
$\bar{5}$,2,10	9	9
$\bar{7}$25	8	11
$\bar{7}$27	16	20
$\bar{7}$28	14	17
$\bar{7}$,2,11	8	- 8
031	39	41
032	44	39
033	24	27
034	29	29
035	36	35
036	22	- 22
037	45	- 39
038	34	- 31
039	7	- 6
0,3,10	14	14
0,3,11	17	18
0,3,12	11	10
230	23	- 20
231	20	- 20
$\bar{2}$31	12	- 9
232	39	- 39
$\bar{2}$32	3	- 5
233	20	- 21
$\bar{2}$33	4	4
234	18	18
$\bar{2}$34	5	- 8
235	64	58
$\bar{2}$35	25	24
236	55	50
$\bar{2}$36	23	23
$\bar{2}$37	5	5
238	24	- 22
$\bar{2}$38	4	- 5
239	25	- 23
$\bar{2}$39	15	- 17
2,3,10	10	- 11
$\bar{2}$,3,10	14	- 14
$\bar{2}$,3,11	8	- 8
2,3,12	7	6
$\bar{2}$,3,13	11	12
$\bar{2}$,1,14	8	9
430	29	25
$\bar{4}$31	24	22
432	19	- 20
433	37	- 36
$\bar{4}$33	21	- 22
434	18	- 19
$\bar{4}$35	21	21
436	22	23
437	20	22
$\bar{4}$37	10	- 12
438	6	6
$\bar{4}$38	17	- 20
$\bar{4}$39	4	- 6
4,3,10	6	- 6
4,3,11	6	- 6
$\bar{4}$,3,11	11	11
$\bar{4}$,3,12	15	13
$\bar{4}$,3,13	9	8
630	24	23
631	18	18
$\bar{6}$31	7	7
632	7	8
$\bar{6}$32	16	- 17
633	4	- 4
$\bar{6}$33	21	- 20
634	14	- 16
635	13	- 16
636	8	- 8
637	6	7
$\bar{6}$37	8	- 6
638	9	10
$\bar{6}$39	8	9
$\bar{6}$,3,10	9	11
$\bar{6}$,3,11	8	9
140	25	- 25
$\bar{1}$41	25	- 24
142	25	27
$\bar{1}$42	30	- 31
143	45	46
$\bar{1}$44	34	37
145	31	- 34
$\bar{1}$45	33	38
146	25	- 27
$\bar{1}$46	18	19
$\bar{1}$47	6	- 7
148	10	10
$\bar{1}$48	9	- 9
$\bar{1}$49	10	- 11
340	45	- 45
341	41	- 41
$\bar{3}$41	15	- 15
342	10	- 9
$\bar{3}$42	34	33
343	19	18
$\bar{3}$43	67	70
344	24	24
$\bar{3}$44	42	43
345	3	- 3
346	9	- 8
$\bar{3}$46	27	- 29
$\bar{3}$47	22	- 24
348	5	5
$\bar{3}$48	17	- 17
$\bar{3}$49	8	- 7
$\bar{3}$,4,10	3	5
$\bar{3}$,4,11	8	7
$\bar{3}$,4,12	6	3
540	5	6
541	4	- 5
$\bar{5}$41	20	21
542	6	- 8
$\bar{5}$42	42	40
543	10	- 10
$\bar{5}$43	22	22
544	5	- 5
$\bar{5}$44	14	- 15
$\bar{5}$45	43	- 40
546	5	- 5
$\bar{5}$46	27	- 27
$\bar{5}$48	11	11
549	6	6
$\bar{5}$49	15	14
$\bar{5}$,4,10	7	6
$\bar{5}$,4,12	7	- 6
740	6	6
741	6	6
$\bar{7}$41	9	8
$\bar{7}$42	4	3
$\bar{7}$43	9	- 9
$\bar{7}$44	19	- 17
$\bar{7}$45	14	- 13
$\bar{7}$46	4	4
$\bar{7}$47	12	12
$\bar{7}$48	13	13
$\bar{7}$49	3	4
053	12	14
054	14	16
057	17	- 19
058	19	- 19
059	3	- 3
0,5,10	11	11
0,5,11	14	12
0,5,12	4	5
250	11	12
251	9	- 11
$\bar{2}$51	12	16
252	23	- 28
$\bar{2}$53	22	- 23
$\bar{2}$53	9	- 7
254	9	10
255	23	27
256	15	18
257	4	5
$\bar{2}$57	6	8
258	11	- 13
259	11	- 14
$\bar{2}$59	6	- 7
2,5,10	3	- 5
$\bar{2}$,5,10	8	- 9
$\bar{2}$,5,11	4	- 3
$\bar{2}$,5,12	4	5
450	23	23
451	13	13
$\bar{4}$51	4	5
452	8	- 8
$\bar{4}$52	18	- 15
453	15	- 17
$\bar{4}$53	12	- 11
454	13	- 13
$\bar{4}$54	3	- 3
455	4	4
$\bar{4}$55	8	9
456	7	8
$\bar{4}$56	12	12
457	7	7
458	4	4
$\bar{4}$58	8	- 8
$\bar{4}$59	9	- 9
$\bar{4}$,5,11	6	6
650	8	8
651	12	13
652	3	5
$\bar{6}$52	8	- 7
$\bar{6}$53	8	- 8
654	8	- 8
655	9	- 8
$\bar{6}$55	8	7
$\bar{6}$57	5	- 3
$\bar{6}$58	7	- 5
161	7	9
$\bar{1}$61	14	- 14
162	18	21
164	8	- 8
$\bar{1}$64	8	- 9
165	7	- 7
166	4	- 5

Table 4 (*cont.*)

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
$\bar{1}67$	4	-4	$\bar{5}64$	3	-4	$\bar{4}71$	4	-5
168	12	12	$\bar{5}65$	9	-8	472	8	8
$\bar{1}68$	7	-6	$\bar{5}66$	5	-5	$\bar{4}72$	13	-12
169	8	8	$\bar{5}67$	7	6	473	3	5
$\bar{1}69$	4	5	$\bar{5}68$	12	11	$\bar{4}73$	11	-11
1,6,10	3	-3	$\bar{5}69$	8	8	$\bar{4}74$	3	-4
$\bar{1}$,6,10	8	7				$\bar{4}75$	5	-5
1,6,11	6	7	071	7	-6	$\bar{4}76$	11	10
			072	12	-12	$\bar{4}77$	5	6
360	25	-25	073	10	-9			
361	8	-8	074	4	-5	180	14	17
$\bar{3}61$	15	-14	076	4	3	$\bar{1}81$	22	24
362	11	11				182	11	-13
$\bar{3}62$	10	10	270	14	15	$\bar{1}82$	10	13
363	20	20	271	4	5	183	12	-14
364	6	6	$\bar{2}71$	16	18	184	13	-14
$\bar{3}66$	5	-6	272	6	-6	$\bar{1}84$	6	-7
$\bar{3}67$	7	-8	$\bar{2}72$	7	9	185	8	-7
$\bar{3}69$	8	7	273	11	-13	$\bar{1}85$	10	-13
$\bar{3}$,6,10	9	8	274	8	-9	$\bar{1}86$	11	-12
			$\bar{2}74$	6	-7			
560	8	-9	275	4	-4	380	12	11
561	7	-8	$\bar{2}75$	9	-10	381	14	12
$\bar{5}61$	7	6	$\bar{2}76$	6	-7	382	8	7
$\bar{5}62$	3	2				$\bar{3}82$	12	-10
563	4	5	470	7	6	$\bar{3}83$	9	-9
564	4	4	471	9	9	$\bar{3}84$	8	-8
						$\bar{3}85$	4	-3

Table 5. *Mean square amplitudes of vibration*

(Values in 10^{-3} Å^2)

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}	$\sigma(U)$
K^+	42	-2	13	26	4	59	2
S	42	-2	11	23	-3	54	2
O_1	76	-2	22	30	-3	63	6
O_2	64	4	10	31	-6	59	6
O_3	46	1	7	46	-7	72	6
O_4	54	-3	10	32	-5	49	5
C_1	63	0	15	49	-6	59	10
C_2	74	3	23	65	-10	65	12

vibrations. It was assumed that the sulphur atom did not undergo rotation, partly because it is close to the mass centre (0·7 Å) and partly because the values of U_{ij} are the same as those for the potassium ion of similar mass indicating that possibly these U_{ij} refer to the translatory motion of the ion as a whole. Accordingly the U_{ij} values for sulphur were subtracted from those for the light atoms to give a set of mean square amplitudes due to rotational oscillation; these were transposed to orthogonal axes perpendicular and parallel to the crystallographic b and c axes, and are quoted as U'_{ij} in Table 6.

Table 6. *Mean square amplitudes of rotational oscillation referred to orthogonal axes parallel to a^*, b and c*

(Values in 10^{-3} Å^2)

	U'_{11}	U'_{12}	U'_{13}	U'_{22}	U'_{23}	U'_{33}
O_1	34	0	9	7	0	6
O_2	22	7	-3	8	-4	6
O_3	4	4	-5	23	-4	20
O_4	12	-1	-2	9	-2	-4
C_1	21	3	2	26	-3	3
C_2	32	6	9	42	-8	8

For each atom U_a was taken to be $U'_{\text{max.}}$, the maximum mean square amplitude of oscillation. The largest value for U_b was found in one of two ways; if the direction of maximum oscillation was nearly perpendicular to OP, U_b was the mean square amplitude of oscillation in the third orthogonal direction; if, however, the direction of $U'_{\text{max.}}$ was not perpendicular to OP, then U_b was taken as the value of U' in the direction perpendicular to those of $U'_{\text{max.}}$ and $U'_{\text{min.}}$. Table 7 shows the values of $U'_{\text{max.}}(U_a)$, the angles between the direction of $U'_{\text{max.}}$ and OP, U_b, and ε. A new set of atomic co-ordinates was obtained by moving each atom by a distance ε along the line joining it to the mass centre. For the oxygen atoms the values of ε are maximum and may be too large; for the carbon atoms, however, there is the possibility that the centre of rotation is nearer than the mass centre so that the use of OP will give too small a value of ε while the use of $U'_{\text{max.}}$ tends to give too large a value.

Table 7. *Corrections for rotational oscillation*

	$U'_{\text{max.}} = U_a$ (10^{-3} Å^2)	$\sphericalangle U'_{\text{max.}}$ and OP	U_b (10^{-3} Å^2)	ε (Å)
O_1	37	91·6°	7	0·011
O_2	26	133·0	7	0·010
O_3	27	85	10	0·011
O_4	12	74	2	0·008
C_1	28	77·6	20	0·013
C_2	45	77	34	0·013

Interatomic distances and bond angles

Bond lengths and their estimated standard deviations, σ, calculated from the uncorrected co-ordinates (Table 3) are shown in Table 8; values corrected for rotational oscillation appear in the fourth column followed by ψ, the uncertainty in the bond lengths arising from calculable uncertainties in the rotational corrections, i.e. ψ is obtained from $\sigma(\varepsilon)$ which is derived by assuming that the values of U_a and U_b are correct and each has the standard deviation $\sigma(U)$. The uncorrected and corrected bond angles and their

Table 8. *Bond lengths and angles*

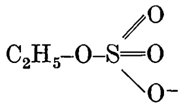
Bonds	Uncorr. Å	σ Å	Corr. Å	ψ Å	Final Å	
S–O_1	1·461	0·007	1·472	0·002	1·466	1·46 ± 0·01 Å
S–O_2	1·461	0·007	1·471	0·003	1·466	
S–O_3	1·446	0·007	1·456	0·003	1·451	
S–O_4	1·597	0·006	1·604	0·004		1·60 ± 0·01
O_4–C_1	1·444	0·011	1·455	0·005		1·45 ± 0·02
C_1–C_2	1·512	0·016	1·514	0·005		1·51 ± 0·02

Angles	Uncorr.	Corr.	σ	Final	
O_1–S–O_2	113·7°	113·4°	0·4°	113·5°	± 0·4°
O_1–S–O_3	115·1	115·0	0·4	115·0	
O_1–S–O_4	101·4	101·7	0·4	101·5	
O_2–S–O_3	110·7	110·4	0·4	110·5	
O_2–S–O_4	108·4	108·8	0·4	108·5	
O_3–S–O_4	106·0	106·3	0·4	106·0	
C_1–O_4–S	115·2	115·4	0·6	115·3 ± 0·6°	
C_2–C_1–O_4	106·6	106·4	0·9	106·5 ± 0·9	

estimated standard deviations also appear in Table 8. To obtain final values a mean of the minimum (uncorrected) and maximum (corrected) bond lengths was taken. The limits of error quoted allow for the estimated standard deviations in the co-ordinates and the uncertainties in the corrections for rotational vibrations.

Discussion

The independent values for the lengths of the three chemically equivalent sulphur–oxygen bonds are identical, 1·46±0·01 Å. In a similar anion, aminedisulphonate $(NH(SO_3)_2)^{2-}$, Jeffrey & Jones (1956) obtained a mean S–O bond length of 1·447 Å, which, being derived from three-dimensional isotropic refinement, is comparable with the mean uncorrected value, 1·456 Å in the ethyl sulphate anion. This very good agreement indicates that for an anion of the type R–SO_3^- the minimum sulphur–oxygen bond length is 1·45 Å. There is a significant difference ($\Delta/\sigma = 12$) between the S–O_4 bond length and the mean of the other three sulphur–oxygen bond lengths. For the carbon–carbon and carbon–oxygen bonds the lengths do not differ significantly from the accepted single bond lengths. However, there appears to be a significant difference between the measured S–O_4 length of 1·60 Å and the single bond length calculated by the Schomaker–Stevenson (1941) rule, 1·69 Å. Pauling (1952) pointed out that for elements like sulphur, which can form π-bonds using $3d$ orbitals, the Schomaker–Stevenson rule might not allow for the double-bond character in a formally single bond between elements of different electronegativities. Pauling (1952) gave an empirical relation connecting the bond number with interatomic distance in oxides and oxy-anions. Approximate application of his method to the S–O_4 bond gives a predicted distance 1·61 Å, the reduction by 0·08 Å from the ideal single bond length arising from π-bonding the extent of which depends solely upon the electronegativity difference between sulphur and oxygen. For the other three sulphur–oxygen bonds the π-bonding depends not only upon the electronegativity difference but also on the average bond order i.e. 1·66 of the bonds in the three equivalent forms



From Pauling's empirical relation the expected bond length is 1·48 Å in satisfactory agreement with the observed value, 1·46 Å.

The S–O bonds are not arranged in a regular tetrahedron; the angles including O_4 are all less than the tetrahedral, and the other angles (between the charged atoms) are all greater. This divergence is reasonable and is similar to that found in the aminedisulphonate, but the highly significant variation in the angles between equivalent S–O bonds requires explanation. The identity of the equivalent S–O bond lengths suggests that the explanation of the angular distortion does not lie in the type of bond orbitals but in the environment of the oxygen atoms in the solid. Atom O_1 is included in both the largest and the smallest angles; apart from atoms in the same anion, this oxygen atom has as nearest neighbours two potassium ions, at 2·97 Å and at 3·01 Å, and three oxygen atoms, O_1 at 3·27 Å, O_2 at 3·14 Å and O_3 at 3·36 Å. The co-ordinates of a position O_1' were found to satisfy the conditions that S–O_1' = S–O_1 and O_1'–S–O_4 = 107° (i.e. equal to the mean value for O_2–S–O_4 and O_3–S–O_4, and incidentally satisfying the condition that the angles O_1'–$\hat{S}$–O_2, O_1'–$\hat{S}$–O_3 and O_2–$\hat{S}$–O_3 do not differ significantly); in this new position the oxygen would be further from one of the potassium ions, the K–O_1' distances being 3·04 Å and 3·01 Å, and nearer to another oxygen identically charged, O_1' at 2·88 Å, the other distances are O_1'–O_2 = 3·17 Å and O_1'–O_3 = 3·20 Å. Hence, there is a strong probability that the variations in the bond angles arise from electrostatic interactions in the solid.

It is a pleasure to thank Dr J. A. J. Jarvis for allowing his data to be used for this refinement, Prof. E. G. Cox, F. R. S. for valuable advice, Dr D. W. J. Cruickshank and Miss D. E. Pilling for carrying out the calculations on the Manchester University electronic computer, the use of which has been made possible by a grant from the Department of Scientific and Industrial Research.

References

Abrahams, S. C. (1956). *Quart. Reviews*, **10**, 407.

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

Cox, E. G., Cruickshank, D. W. J. & Smith, J. A. S. (1955). *Nature, Lond.* **175**, 766.

Cruickshank, D. W. J. (1956*a*). *Acta Cryst.* **9**, 747.

Cruickshank, D. W. J. (1956*b*). *Acta Cryst.* **9**, 752.

Cruickshank, D. W. J. (1956*c*). *Acta Cryst.* **9**, 757.

Cruickshank, D. W. J. & Robertson, A. P. (1953). *Acta Cryst.* **6**, 698.

Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Borntraeger.

Jarvis, J. A. J. (1953). *Acta Cryst.* **6**, 327.

Jeffrey, G. A. & Jones, D. W. (1956). *Acta Cryst.* **9**, 283.

Lynton, H. (1955). PhD. Thesis, University of Leeds.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.

Pauling, L. (1952). *J. Phys. Chem.* **56**, 361.

Schomaker, V. & Stevenson, D. P. (1941). *J. Amer. Chem. Soc.* **63**, 37.

Steeman, J. W. M. & MacGillavry, C. H. (1954). *Acta Cryst.* **7**, 402.