

Crystal Structure of Potassium Ethyl Sulphate

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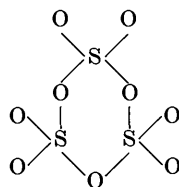
The crystal structure of potassium ethyl sulphate has been determined in order to establish whether a bond from sulphur to an oxygen atom which is also bonded to another atom is longer than that to an oxygen atom not so bonded.

Crystals of $K(C_2H_5)SO_4$ are monoclinic, space-group $P2_1/c$. The dimensions of the unit cell, which contains 4 molecules, are: $a = 11.62$, $b = 6.99$, $c = 7.51$ Å, $\beta = 100.3^\circ$.

Atomic coordinates were determined by three-dimensional Fourier methods, and corrections for termination-of-series errors were applied for the oxygen and sulphur atoms. Bond lengths in the ethyl sulphate radical are: $S-O_1 = 1.49$, $S-O_2 = 1.44$, $S-O_3 = 1.45$, $S-O_4 = 1.60$, $O_4-C_1 = 1.44$, $C_1-C_2 = 1.51$ Å. The bond between S and O_4 is significantly longer than that to the other O's, which are bonded to S only. Each K ion is surrounded by eight O atoms at distances ranging from 2.80 to 3.02 Å.

Introduction

The length of the S-O bond in many molecules and ions has been found to have a value close to 1.44 Å, which is rather shorter than the value to be expected for a double bond. An exception is the S-O bond in the ring of the cyclic S_3O_9 molecule, the length of which has been determined (MacGillavry & Westrick, 1941) as approximately 1.6 Å compared with 1.4 Å for the S-O bonds outside the ring. The crystal structure of potassium ethyl sulphate has been determined in order to confirm this difference between the lengths of bonds from S to (a) an O atom attached only to the S atom or (b) an O atom which is also bonded to a second atom.



The only previous X-ray work on ethyl sulphates of which we are aware is an incomplete study of some hydrated rare-earth ethyl sulphates (Ketelaar, 1937). The object of this study was to determine the symmetry of the atomic arrangement about the rare-earth ion, and S-O distances were assumed to be 1.50 Å, no attempt being made to refine this value.

Experimental

Large crystals, several millimetres across, tabular on (100) with {011} as the principal boundaries, were grown by slow evaporation of a solution in a water-ethanol mixture. Crystals suitable for X-ray photography about a , b , c and [011] axes were obtained by

carefully dissolving away parts of large crystals to form cylinders, about 0.05 mm. in diameter, about these axes.

The dimensions of the unit cell are:

$$a = 11.62, b = 6.99, c = 7.51 \text{ \AA}, \beta = 100.3^\circ.$$

With the measured density of 1.843 g.cm.⁻³, and molecular weight of 164, these dimensions show that there are four molecules of $K(C_2H_5)SO_4$ per unit cell. The only systematic absences are $0k0$ for k odd, and $h0l$ for l odd, from which the space group may be uniquely determined as $P2_1/c$.

The intensities of all reflexions observable with Cu $K\alpha$ radiation were recorded on equi-inclination Weissenberg photographs, which were taken by the method described by Stadler (1950). Layers 0, 1, 2 and 3 about the a , b and c axes, and 0, 1, 2, 3 and 4 about [011] were photographed; two exposures, of 20 hr. and 1 hr., were made of each layer, with three films superposed in the camera for each exposure.

Intensities (I) were estimated visually; after corrections for the rotation factor D had been applied, the values of $I \times D$ for the various layers about a given axis were put on the same scale by comparison of the zero-layer reflexions (Stadler, 1950) and finally all four sets of layers were correlated by comparison of common reflexions.

No correction was made for absorption, but the assumption, that the approximately cylindrical shape of the crystals used would render this unnecessary, seemed justified by the agreement obtained when a given reflexion was measured on photographs about two or more axes.

The values of $I \times D$ were corrected for the Lorentz polarisation factor (Goldstein & Pitt, 1948) to give values of $F^2(hkl)$ on an arbitrary scale. The method of Wilson (1942) was used to obtain the absolute scale and temperature factor ($B = 4 \times 10^{-16}$ cm.²). A total

Table 3. *Observed and calculated structure factors*

<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c
100	99	107	406	< 4	4	540	7	5
200	26	-32	506	4	1	640	< 3	-6
300	87	-88	606	< 4	1	740	< 3	-5
400	68	-71	706	3	2	840	< 3	-5
500	36	-36	806	5	4	940	4	-3
600	14	-15	906	5	4	10,4,0	4	-4
700	10	12	10 $\bar{0}$	< 4	-2	11,4,0	< 3	-1
800	19	18	20 $\bar{6}$	38	28	150	< 3	3
900	7	9	30 $\bar{6}$	35	26	250	< 3	4
10,0,0	7	-6	40 $\bar{6}$	8	5	350	12	-13
11,0,0	9	6	50 $\bar{6}$	7	-6	450	14	-17
12,0,0	< 4	1	60 $\bar{6}$	27	-21	550	< 3	-3
13,0,0	< 4	-3	70 $\bar{6}$	32	-28	650	< 3	-1
14,0,0	< 4	-3	80 $\bar{6}$	11	-14	750	17	18
002	28	28	90 $\bar{6}$	10	10	850	19	20
102	122	116	10,0, $\bar{6}$	12	11	950	3	4
202	37	42	11,0, $\bar{6}$	15	13	10,5,0	11	-8
302	41	46	008	< 4	3	11,5,0	14	-13
402	22	26	10 $\bar{8}$	10	10	12,5,0	4	-5
502	6	-5	20 $\bar{8}$	11	10	060	39	-41
602	29	-34	30 $\bar{8}$	< 4	-5	160	21	-24
702	23	-24	40 $\bar{8}$	13	-13	260	8	8
802	9	-9	50 $\bar{8}$	21	-20	360	26	29
902	< 4	3	60 $\bar{8}$	16	-13	460	19	24
10,0,2	9	-9	70 $\bar{8}$	< 3	3	560	7	9
11,0,2	4	-5	80 $\bar{8}$	20	16	660	4	-3
12,0,2	9	12	90 $\bar{8}$	14	11	760	9	-10
13,0,2	7	8	10,0, $\bar{8}$	6	6	860	8	-5
10 $\bar{2}$	67	-69	11,0, $\bar{8}$	41	40	960	3	-4
20 $\bar{2}$	85	-90	210	32	-30	170	7	4
30 $\bar{2}$	79	-76	310	2	-3	270	12	10
40 $\bar{2}$	10	7	410	2	1	370	10	7
50 $\bar{2}$	36	41	510	22	23	470	4	5
60 $\bar{2}$	43	50	610	7	9	570	< 4	1
70 $\bar{2}$	13	11	710	15	20	670	4	-4
80 $\bar{2}$	19	-21	810	13	16	080	27	-24
90 $\bar{2}$	30	-32	910	9	9	180	16	-16
10,0, $\bar{2}$	< 3	-2	10,1,0	15	-15	280	5	3
11,0, $\bar{2}$	8	4	11,1,0	20	-17	380	18	17
12,0, $\bar{2}$	< 3	-2	12,1,0	< 3	-3	480	10	11
13,0, $\bar{2}$	< 3	1	13,1,0	< 3	-3	580	< 3	3
14,0, $\bar{2}$	< 3	1	020	47	45	680	5	-4
004	52	-47	120	58	55	011	46	-45
104	< 3	0	220	26	-22	012	45	-45
204	44	36	320	59	-61	013	36	-29
304	23	19	420	63	-58	014	22	-22
404	12	19	520	4	-5	015	5	4
504	< 4	3	620	27	24	016	11	-12
604	< 4	-2	720	14	13	017	22	21
704	< 4	-1	820	9	14	018	< 5	0
804	7	8	920	4	12	021	61	62
904	< 4	-2	10,2,0	6	12	022	10	-6
10,0,4	9	-10	11,2,0	5	-5	023	73	76
11,0,4	15	-14	12,2,0	< 3	-3	024	5	-5
12,0,4	4	-5	130	38	-37	025	4	-3
10 $\bar{4}$	28	-23	230	43	-36	026	16	-16
20 $\bar{4}$	23	-15	330	24	-27	027	< 4	-2
30 $\bar{4}$	17	14	430	29	-26	028	< 4	1
40 $\bar{4}$	19	14	530	35	-38	031	4	7
50 $\bar{4}$	34	25	630	22	20	032	23	21
60 $\bar{4}$	20	13	730	44	37	033	2	3
70 $\bar{4}$	20	-19	830	33	34	034	29	-24
80 $\bar{4}$	42	-38	930	7	8	035	7	1
90 $\bar{4}$	13	-13	10,3,0	14	-17	036	24	-19
10,0, $\bar{4}$	9	12	11,3,0	17	-21	037	3	3
11,0, $\bar{4}$	6	7	12,3,0	11	-12	041	25	27
12,0, $\bar{4}$	5	6	040	7	-6	042	4	-4
006	25	-21	140	9	-9	043	44	42
106	35	-33	240	5	-4	044	15	14
206	7	5	340	< 3	3	045	5	-8
306	15	18	440	20	22	046	5	-3

Table 3 (cont.)

<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c
047	6	-7	057	12	-9	072	14	-11
048	< 2	-2	061	< 3	2	073	16	15
051	14	-11	062	8	-11	074	7	-6
052	11	-10	063	25	22	075	9	-5
053	12	8	064	24	23	081	14	-11
054	23	-20	065	8	7	082	10	-10
055	7	6	066	10	7	083	12	-11
056	8	-6	071	12	8	084	7	8

projections enabled the signs of about 500 $F(hkl)$ structure factors to be determined, and these were included in syntheses of electron density along lines parallel to the b axis and sections parallel to (010) through the positions indicated by the projections. Recalculation of structure factors from the new coordinates made possible the determination of 664 signs, and a second set of syntheses was calculated.

The third and final set of lines and sections, including 875 out of the 908 observable reflexions, gave the coordinates listed in Table 1. Structure factors calculated from these gave a disagreement factor ($R = \sum |F_o - F_c| / \sum |F_o|$) of 0.177; on multiplying the F_c by $\exp(Bk^2/b^2)$, corresponding to the introduction of an asymmetric temperature factor, the value of R was reduced to 0.138.

The coordinates of Table 1 give the following bond lengths within the ethyl sulphate radical:

$$S-O_1 = 1.48 \text{ \AA}, S-O_2 = 1.39 \text{ \AA}, S-O_3 = 1.44 \text{ \AA}, \\ S-O_4 = 1.60 \text{ \AA}, O_4-C_1 = 1.44 \text{ \AA}, C_1-C_2 = 1.51 \text{ \AA}.$$

Although the $S-O_4$ bond is longer than the other $S-O$ bonds the comparison is made less convincing by the divergence these show among themselves, since one would expect them to be equivalent. However, in a structure containing two comparatively heavy atoms, K and S, there may well be diffraction effects which would displace the O and C electron-density peaks. A correction for termination of series was applied, as suggested by Booth (1945), to the coordinates of the oxygen and sulphur atoms. The corrections were mostly of the order of 0.01 \AA , except for the x coordinate of O_1 (0.03 \AA) and the z coordinate of O_2 (0.04 \AA).

The corrected coordinates are given in Table 2. The bond lengths calculated from these are:

$$S-O_1 = 1.49 \text{ \AA}, S-O_2 = 1.44 \text{ \AA}, S-O_3 = 1.45 \text{ \AA}, \\ S-O_4 = 1.60 \text{ \AA}.$$

Since the corrected coordinates differ by so little from the previous ones it was not considered profitable to recalculate the structure factors. The values for the three principal zones listed in Table 3 were calculated from the coordinates of Table 1.

Description of structure

The structure consists of layers parallel to (100). In each layer the ethyl sulphate ions have their polar

(sulphate) ends directed inwards, being held by electrostatic interaction with the potassium ions, while adjacent layers make contact only through the van der Waals approaches of the methyl groups terminating the outwardly directed non-polar ends of the ions. A similar double-layer structure is found in the salts of long-chain fatty acids. Each potassium ion has eight oxygen atoms, as nearest neighbours at distances between 2.80 and 3.02 \AA , belonging to the six surrounding ethyl sulphate ions. At the other ends of these ions the methyl group has two neighbours at 3.80 \AA in the same layer, and four in the next layer, at 3.90, 3.97 (2) and 4.40 \AA .

The bond lengths within the ethyl sulphate ion are:

$$S-O_1 = 1.49 \text{ \AA}, S-O_4 = 1.60 \text{ \AA}, \\ S-O_2 = 1.44 \text{ \AA}, O_4-C_1 = 1.44 \text{ \AA}, \\ S-O_3 = 1.45 \text{ \AA}, C_1-C_2 = 1.51 \text{ \AA}.$$

The mean of the bond lengths $S-O_1$, $S-O_2$ and $S-O_3$ is 1.46 \AA with a maximum divergence of 0.03 \AA from the mean, which agrees well with the results of other investigations (Wells, 1950). The bond lengths C_1-O_4 and C_1-C_2 are also within 0.03 \AA of accepted values, so that the value of 1.60 \AA for $S-O_4$ appears to be significantly longer than the other $S-O$ bonds.

Other interatomic distances are:

$$O_1-O_2 = 2.43 \text{ \AA}, O_1-O_4 = 2.41 \text{ \AA}, \\ O_2-O_3 = 2.36 \text{ \AA}, O_2-O_4 = 2.46 \text{ \AA}, \\ O_3-O_1 = 2.50 \text{ \AA}, O_3-O_4 = 2.44 \text{ \AA}.$$

Bond angles at the sulphur atom are:

$$O_1-S-O_2 = 112^\circ, O_1-S-O_4 = 101^\circ, \\ O_2-S-O_3 = 110^\circ, O_2-S-O_4 = 109^\circ, \\ O_3-S-O_1 = 116^\circ, O_3-S-O_4 = 106^\circ.$$

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