The Crystal and Molecular Structure of Potassium Hydroxymethanesulphonate

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Abstract

The title compound $K^+[CH_3O_4S]^-$ crystallizes in space group $P2_1/c$, $a = 8.347$ (5), $b = 7.527$ (3), $c = 14.173$ (6) Å, $\beta = 148.44$ (2)°. The structure has been determined by three-dimensional X-ray methods from 657 reflections and refined by a full-matrix least-squares procedure; $R = 0.04$. The crystal is constructed only from hydrogen-bonded dimeric hydroxymethanesulphonate $[(HO-CH_2-SO_3)^-]_2$ and K ions. The compound is anhydrous and the K^+ ion is surrounded by seven O atoms. These are arranged in a pentagonal bipyramid with $K^+\cdots O$ contact distances in the range 2.76–2.92 Å.

Introduction

As the result of a discussion with a first-year undergraduate class it was found that there was no X-ray crystallographic evidence to support the assumption that a C–S, rather than an O–S, bond is formed in the reaction between a bisulphite ion and an aliphatic aldehyde or ketone. The X-ray structure of benzaldehyde potassium bisulphite, however, is known (Kuroda, Ashida, Sasada & Kakudo, 1967) and this has a C–S bond. The presence of a C–S bond in the aliphatic ketone and aldehyde bisulphites has been inferred from chemical evidence (Raschig & Prahl, 1926; Sheppard & Bourns, 1954) and deduced from the Raman spectra (Caughlan & Tartar, 1941), though Phillips & Williams (1965) do raise some queries about the structure of the bisulphite ion itself and thus about the derivatives it will form. In order to resolve any remaining uncertainty the structure of potassium hydroxymethanesulphonate has been determined. This compound is frequently classified under the trivial name of potassium formaldehyde bisulphite.

Experimental

Massive needle crystals, prepared by the method of Lauer & Langkammerer (1935), were deposited from an aqueous solution by methanol diffusion.

Crystal data

$K^+[CH_3O_4S]^-$, $M_r = 150.2$, $F(000) = 304$, monoclinic, $P2_1/c$, $a = 8.347$ (5), $b = 7.527$ (3), $c = 14.173$ (6) Å, $\beta = 148.44$ (2)°, $Z = 4$, $D_c = 2.14$ Mg m^{-3}, Cu $K\alpha_1$ (graphite-monochromated), $\lambda = 1.54051$ Å, $\mu = 13.13$ mm^{-1}.

The crystal was mounted along the needle axis which corresponds to a $(10\bar{2})$ axis in a unit cell of space group $P2_1/c$. The unit cell defined by the $(10\bar{2})$, b and c axes of the conventional cell quoted above has dimensions $a' = 8.739$ (5), $b = 7.526$ (3), $c = 14.174$ (6) Å, $\beta = 90.34$ (1)°. 657 independent reflections with $I > 3\sigma(I)$ were measured on a Picker FACS-I four-circle diffractometer, using the circle settings calculated from an orientation matrix based on the non-conventional cell given above. The data were corrected for reflection geometry and polarization effects and the reflection indices were then transformed to correspond to the conventional cell: $h_{conv} = (h_{meas} - l_{meas})/2$.

Solution and refinement of structure

The phases of 120 reflections with E values greater than 1.2 were determined by a multisolution (Sheldrick, 1976) application of the tangent formula (Karle & Hauptman, 1958). The E map, calculated in space group $P2_1/c$ from the solution with the lowest Karle R factor clearly showed the positions of the seven non-hydrogen atoms. The structure was refined by a full-matrix least-squares method minimizing $\sum w(\Delta F)^2$. The large obtuse angle of the conventional monoclinic cell causes significant correlations in the least squares between the x and z parameters and, to avoid these, the structure was refined in the original non-conventional cell which has equivalent positions $\pm(x,y,z; \frac{1}{2} + x, y, \frac{1}{2} + z; \frac{1}{2} - x, \frac{1}{2} + y, -z; -x, \frac{1}{2} + y, \frac{1}{2} - z)$. The refinement converged at $R = 0.04$, with weights calculated from $w = [\sigma^2(F_o) + 0.0006F_o^2]^{-1}$ where σ is the individual e.s.d. for each reflection and was calculated from the diffractometer counting statistics. The final atomic coordinates are given in Table 1.* The atomic

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scattering factors used were those recorded in *International Tables for X-ray Crystallography* (1974) and were corrected for the real part of the anomalous-dispersion effect. The interatomic distances and bond angles are given in Table 2. Fig. 1 shows the packing of the ions in the unit cell, and Fig. 2 indicates the immediate O environment of the K ions. All calculations were computed with the Sheldrick (1976) system.

Results and discussion

The crystal is constructed from K^+ and hydrogen-bonded dimeric hydroxymethanesulphonate ions

Table 1. *Atomic parameters* ($\times 10^4$, *hydrogen atoms* $\times 10^3$)

	x	y	z
K(1)	3537 (2)	3585 (1)	1212 (1)
S(1)	8846 (2)	1405 (1)	662 (1)
O(1)	8620 (6)	1298 (3)	2430 (4)
O(2)	8417 (6)	2819 (3)	−245 (3)
O(3)	11945 (5)	748 (3)	2250 (3)
O(4)	6576 (6)	−5 (3)	−585 (3)
C(1)	8053 (9)	2439 (4)	1375 (5)
H(1)	584 (4)	281 (5)	28 (4)
H(2)	929 (6)	356 (3)	203 (4)
H(3)	697 (10)	42 (8)	174 (5)

Table 2. *Interatomic distances* (Å) *and interbond angles* (°)

S(1)–O(2)	1·458 (2)	O(1)···O(4)	2·695
S(1)–O(3)	1·442 (2)	K···O(1)^{ii}	2·845
S(1)–O(4)	1·461 (2)	K···O(2)^{iv}	2·841
S(1)–C(1)	1·790 (3)	K···O(2)^{v}	2·838
C(1)–O(1)	1·412 (4)	K···O(2)^{vi}	2·797
O(1)–H(3)	0·994 (18)	K···O(3)^{vii}	2·759
C(1)–H(1)	1·006 (17)	K···O(4)^{iii}	2·814
C(1)–H(2)	1·002 (16)	K···O(4)^{iv}	2·927
		[K···O(1)	3·385]
		[K···O(3)^{vi}	3·439]

O(2)–S(1)–O(3)	113·1 (1)	O(1)^{ii}···K···O(2)^{v}	75·4
O(2)–S(1)–O(4)	111·9 (1)	O(2)^{v}···K···O(4)^{iv}	77·5
O(2)–S(1)–C(1)	104·4 (1)	O(4)^{iv}···K···O(2)^{iv}	49·6
O(3)–S(1)–O(4)	113·0 (1)	O(2)^{iv}···K···O(4)^{iii}	79·3
O(3)–S(1)–C(1)	107·6 (2)	O(4)^{iii}···K···O(1)^{ii}	80·1
O(4)–S(1)–C(1)	106·0 (1)	O(2)^{vi}···K···O(1)^{ii}	76·8
O(1)–C(1)–S(1)	112·5 (2)	O(2)^{vi}···K···O(2)^{v}	87·3
C(1)–O(1)–H(3)	115 (2)	O(2)^{vi}···K···O(4)^{iv}	88·8
O(1)–H(3)···O(4)^{iii}	146·0	O(2)^{vi}···K···O(2)^{iv}	102·4
		O(2)^{vi}···K···O(4)^{iii}	87·2
Symmetry code		O(3)^{vii}···K···O(1)^{ii}	106·1
(i) x,y,z		O(3)^{vii}···K···O(2)^{v}	69·8
(ii) $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$		O(3)^{vii}···K···O(4)^{iv}	76·4
(iii) $1 - x, -y, -z$		O(3)^{vii}···K···O(2)^{iv}	83·5
(iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$		O(3)^{vii}···K···O(4)^{iii}	118·0
(v) $1 - x, 1 - y, -z$			
(vi) $x - 1, y, z$			
(vii) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$			
(viii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$			
(ix) $2 - x, 1 - y, 1 - z$			

$[(HO–CH_2–SO_3)^-]_2$ with the ion containing therefore a S–C bond. The K^+ ions are close to the twofold screw axis and are completely surrounded by O atoms from several sulphonate ions. There are seven K···O contact distances in the range 2·76–2·92 Å; one from O(1) and O(3), two from O(4) and three contacts from O(2); these form a reasonably regular pentagonal bipyramid. In addition there are two much longer contacts from O(1) and O(3) at 3·39 and 3·44 Å which appear to be outside the immediate coordination sphere of the K ion. Around the twofold screw axes, adjacent pentagonal bipyramids share an equatorial edge, thus forming a continuous chain and the chains link together to form a continuous layer parallel to (001). The link is formed with a common O atom, the axial atom in one bipyramid becoming the equatorial of the other. An idealized picture of a fragment of the layer is given in Fig. 3.
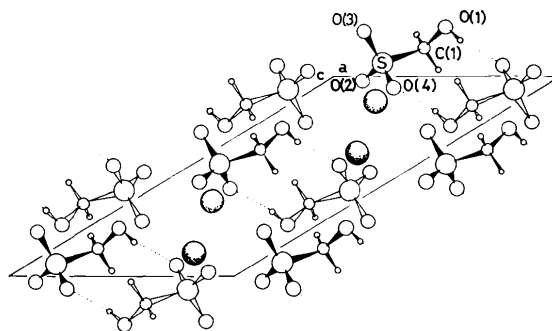

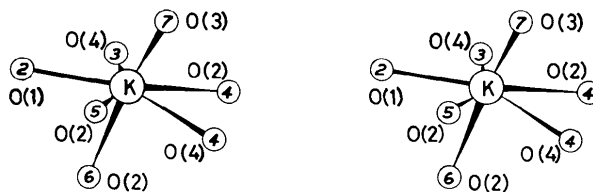Fig. 1. The unit cell viewed along *b*.

Fig. 2. The immediate environment of the K ion. The equivalent positions are given in Table 2.
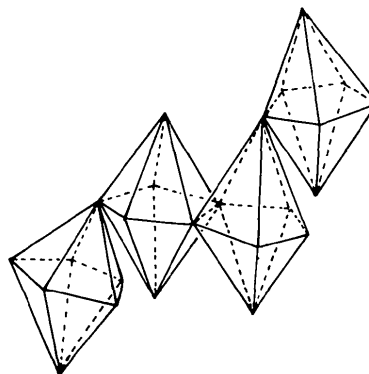

Fig. 3. Idealized picture of the K coordination spheres.

Table 3. *Bond-valence calculations for* $K^+[CH_3O_4S]^-$ *including all intermolecular distances less than* 3·5 Å

K—O, S—O valences calculated according to Brown & Wu (1976), H—O from Brown (1976), C—O calculated from $S = (R/1·378)^{-4·065}$, C—S calculated from $S = (R/1·869)^{-4·29}$. Valences in parentheses were determined by requiring the sums at H to be 1·00.

	K	S	H(1)	H(2)	H(3)	C	Σ anion
O(1)	0·03 0·13		0·05		0·05 (0·75)	0·91	2·04
O(2)	0·15 0·14 0·13	1·58					2·08
O(3)	0·17	1·66	0·05 0·06 0·10	0·07 0·09			2·20
O(4)	0·15 0·10	1·57	0·06	0·05	0·20		2·13
C		1·20	(0·68)	(0·79)			3·58
Σ cation	1·00	6·01	(1·00)	(1·00)	(1·00)		

The anion forms a dimer about the centre of symmetry with hydrogen bonds between O(1) of the hydroxyl group and O(4) in the centrosymmetrically related molecule. The O(1)···O(4) distance is 2·695 Å which is not unusually short and the C(1)–O(1)···O(4′), O(1)–H(3)···O(4′) and S(1′)–O(4′)···O(1) angles are 112·5, 166·4 and 142·4°; H(3) refines to a position close to O(1) and at a distance of 0·99 (1) Å is clearly strongly bonded to that atom. This is consistent with the hydrogen-bond length (Olovsson & Jönsson, 1976). The three S—O distances of 1·458 (2), 1·442 (2) and 1·461 (2) Å for O(2), O(3) and O(4) respectively compare with a range of 1·429–1·460 Å in the benzaldehyde bisulphite (Kuroda *et al.*, 1967). Of the three S—O bond lengths S–O(2) and S–O(4) are equivalent and S–O(3) is significantly shorter. A calculation of bond valences by the method of Brown & Wu (1976) indicates that the methylene H atoms are slightly acidic and form a weak association with some of the sulphonate O atoms. The full results

for the bond valences between atoms less than 3·5 Å apart are given in Table 3 where it can be seen that the chemical environment at O(3) is different from that at O(2) and O(4). This factor probably contributes to the observed differences in the S—O bond lengths. The S—C and C—O bond lengths of 1·790 (3) and 1·412 (4) Å are in good agreement for single-bond lengths (Brown, Brown & Hawthorne, 1976).

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