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## The Crystal Structure of Acid Potassium Hydrogen Fumarate: A Re-determination

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The crystal structure of acid potassium hydrogen fumarate (empirical formula  $2\text{KC}_4\text{H}_3\text{O}_4 + \text{C}_4\text{H}_4\text{O}_4$  or  $2\text{C}_4\text{H}_4\text{O}_4 + \text{K}_2\text{C}_4\text{H}_2\text{O}_4$ ) has been redetermined with final  $R$  values:  $R(hk0) = 0.084$ ,  $R(0kl) = 0.083$ ,  $R(h0l) = 0.081$ . It has been shown that the X-ray analysis favours the formula  $2\text{KC}_4\text{H}_3\text{O}_4 + \text{C}_4\text{H}_4\text{O}_4$  rather than  $2\text{C}_4\text{H}_4\text{O}_4 + \text{K}_2\text{C}_4\text{H}_2\text{O}_4$ . Values of inter- and intramolecular distances are given. The fumarate groups are non-planar with one of the COOH groups twisted by about  $8^\circ$  from the plane of the rest of the atoms in the molecule. Hydrogen bonds of  $2.58 \text{ \AA}$  link the fumarate groups to form extensive chains along the  $[010]$  axis, these chains being cross-linked by hydrogen bonds of  $2.57 \text{ \AA}$  from the molecule of fumaric acid occupying a special position ( $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ ).  $\text{K}^+ - \text{O}$  distances range from  $2.71$  to  $3.01 \text{ \AA}$  giving a sevenfold coordination.

Several potassium salts of fumaric acid ( $\text{KC}_4\text{H}_3\text{O}_4$ ,  $\text{K}_2\text{C}_4\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ,  $2\text{KC}_4\text{H}_3\text{O}_4 + \text{C}_4\text{H}_4\text{O}_4$ ) have been investigated in the past and their structures reported (Gupta, 1956; Roy, 1967) the earliest one being what Gupta & Barnes (1956) called acid potassium hydrogen fumarate and whose empirical chemical formula could be given either as  $2\text{KC}_4\text{H}_3\text{O}_4 + \text{C}_4\text{H}_4\text{O}_4$  or

$\text{K}_2\text{C}_4\text{H}_2\text{O}_4 + 2\text{C}_4\text{H}_4\text{O}_4$ , both giving the same value of 423.8 atomic mass units for the total unit-cell content in a triclinic unit cell. Gupta (1956) published a description of the gross features of this structure but neither the positions of the atoms nor the inter- or intramolecular distances were given by him. The unusual point of interest remained unsettled, however,

*viz.* whether the correct chemical formula was  $2\text{KC}_4\text{H}_3\text{O}_4 + \text{C}_4\text{H}_4\text{O}_4$  or  $\text{K}_2\text{C}_4\text{H}_2\text{O}_4 + 2\text{C}_4\text{H}_4\text{O}_4$  for the compound.

Gupta (1956) pointed out that 'considerable interest lies in the determination of the exact differences between the molecules in the special and general positions, especially in respect of the hydrogen bond configuration'. In one case the monopotassium fumarate 'molecule' of the acid (two such formula units per cell) was present in the crystal structure with an extra acid molecule occupying a special position at the centre of symmetry and in the other case the dipotassium fumarate 'molecule' of the acid occupied a centre of symmetry with two formula units of the acid itself in general positions. In either case, there was the unique feature of the molecule of the acid crystallizing together with its own salt in the same compound, this acid molecule of crystallization being somewhat similar to water molecules of crystallization.

We present below the results of a redetermination of this crystal structure with new data and we believe that the evidence from the X-ray diffraction data favours the formula  $2\text{KC}_4\text{H}_3\text{O}_4 + \text{C}_4\text{H}_4\text{O}_4$  for this compound rather than the formula  $\text{K}_2\text{C}_4\text{H}_2\text{O}_4 + 2\text{C}_4\text{H}_4\text{O}_4$ .

### Crystal data

The unit-cell dimensions were redetermined from high  $\sin \theta$  reflexions on Weissenberg films, with silver lines as an internal calibration standard; the values obtained are:

$$\begin{aligned} a &= 8.63_1 \text{ \AA} & \alpha &= 78^\circ 20' \\ b &= 7.48_3 & \beta &= 112^\circ 30' \\ c &= 6.94_7 & \gamma &= 107^\circ 55' \end{aligned}$$

The unit cell chosen has the same orientation as that given by Gupta (1956) and is the most convenient one from the point of view of the crystal structure determination.

$$\rho_{\text{obs}} = 1.785 \text{ g.cm}^{-3} \quad \rho_{\text{calc}} = 1.787 \text{ g.cm}^{-3}.$$

Linear absorption coefficient for X-rays (Cu  $K\alpha$  radiation) =  $60.8 \text{ cm}^{-1}$ . Space group,  $P\bar{1}$ .

Number of molecules in the unit cell,  $Z=2$  (with

the extra molecule always in the special position of the centre of symmetry ( $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ ). For the purpose of refinement, two-dimensional data were collected from small single crystals ( $0.02 \times 0.02 \times 0.03 \text{ cm}$ ) around the  $a$ ,  $b$  and  $c$  crystallographic axes with unfiltered copper radiation and normal-beam Weissenberg photography. About 90% of the theoretically possible reflexions were collected, the balance being too weak to be recorded.

### Refinement of the structure

The rough positions of the atoms in the structure as given by Gupta (unpublished) were used as the trial coordinates, the  $R$  values being  $R(hk0)=0.212$ ,  $R(0kl)=0.228$ ,  $R(h0l)=0.241$  at this stage. At first an overall isotropic temperature factor was used in the least-squares refinement but in the later stages anisotropic temperature factors were included for individual atoms and the calculations were done by means of an *SFLS* program written by Milledge & Milledge (1961) for the Pegasus computer at University College, London. Four cycles of least-squares refinement with extinction corrections for the 200,  $\bar{1}20$ , 012 and  $10\bar{2}$  reflexions finally brought  $R$  to the following values:

$$R(hk0)=0.084, \quad R(0kl)=0.083, \quad R(h0l)=0.081.$$

No attempt has been made to include the contributions of the hydrogen atoms although the  $(F_o - F_c)$  syntheses (contributions of carbon and oxygen subtracted) indicated possible sites.

### Results

The atomic coordinates together with their standard deviations, from the expression given by Ibers & Cromer (1958), are given in Table 1.

The bond lengths and angles with their estimated standard deviations are given in Table 2(a) and (b); the e.s.d.'s were calculated with the expressions given by Ahmed & Cruickshank (1953). The dashed symbols represent the atoms of the molecule derived from the operation of a centre of symmetry, while a symbol such as  ${}_b\text{O}(2)$  represents the oxygen atom O(2) obtained after a  $\mathbf{b}$  translation of O(2), and so on.

Table 1. Atomic coordinates

	$x$ ( $\text{\AA}$ )	$\sigma(x)$ ( $\text{\AA}$ )	$y$ ( $\text{\AA}$ )	$\sigma(y)$ ( $\text{\AA}$ )	$z$ ( $\text{\AA}$ )	$\sigma(z)$ ( $\text{\AA}$ )
C(1)	0.5368	0.0162	0.2282	0.0152	1.9229	0.0162
C(2)	0.2969	0.0158	1.7263	0.0150	1.7284	0.0167
C(3)	-1.0944	0.0161	1.8603	0.0154	1.2025	0.0174
C(4)	-1.2921	0.0145	3.3120	0.0158	1.3588	0.0150
C(5)	4.1153	0.0146	3.2072	0.0133	3.9494	0.0143
C(6)	4.7358	0.0142	1.9314	0.0144	4.3988	0.0161
O(1)	1.8539	0.0101	0.2222	0.0102	2.2557	0.0112
O(2)	-0.5619	0.0115	-0.7910	0.0103	1.5957	0.0119
O(3)	-2.5341	0.0104	3.5088	0.0101	0.7718	0.0114
O(4)	-0.0811	0.0110	4.2638	0.0102	1.7541	0.0129
O(5)	4.5520	0.0107	1.1082	0.0108	5.4326	0.0106
O(6)	5.4660	0.0103	1.8056	0.0106	3.6208	0.0106
K <sup>+</sup>	3.4688	0.0034	1.5078	0.0033	0.5009	0.0035

Table 2(a). *Intramolecular distances*

	Bond lengths $l$	Deviation $\sigma(l)$		
C(1)–C(2)	1.54 Å	0.022	} Molecule in the general position	
C(1)–O(1)	1.23	0.019		
C(1)–O(2)	1.25	0.019		
C(2)–C(3)	1.32	0.023		
C(3)–C(4)	1.56	0.022		
C(4)–O(3)	1.22	0.018		
C(4)–O(4)	1.28	0.019		
C(6)–C(5)	1.50	0.020		} Molecule in the special position
C(6)–O(5)	1.22	0.019		
C(6)–O(6)	1.30	0.018		
C(5)–C(5')	1.35	0.051		

Table 2(b). *Bond angles*

O(1)–C(1)–O(2)	126.4°	1.3	} Molecule in the general position	
O(1)–C(1)–C(2)	113.3	1.0		
O(2)–C(1)–C(2)	119.5	1.2		
C(1)–C(2)–C(3)	118.1	1.3		
C(2)–C(3)–C(4)	116.0	1.2		
C(3)–C(4)–O(3)	116.7	1.0		
C(3)–C(4)–O(4)	114.7	1.0		
O(3)–C(4)–O(4)	125.5	1.2		} Molecule in the special position
O(5)–C(6)–O(6)	124.7	1.1		
O(5)–C(6)–C(5)	120.5	1.1		
O(6)–C(6)–C(5)	114.5	1.1		
C(6)–C(5)–C(5')	123.5	1.2		

Significant intermolecular contacts up to 4.0 Å are listed in Table 3(a), the hydrogen bonds being clearly indicated. Table 3(b) gives the  $K^+ - O$  distances up to a distance of 3.0 Å there being seven such oxygen atoms around each  $K^+$  ion.

Table 3(a). *Intermolecular distances less than 4.0 Å*

Oxygen	Oxygen	Distance	
O(4)	<sub>b</sub> O(2)	2.58 Å	Hydrogen bonds
O(6)	<sub>b</sub> O(1')	2.57	
O(4)	O(6')	2.91	
O(3)	<sub>b</sub> O(2)	3.28	
<sub>a</sub> O(3)	O(6)	3.19	
O(4)	<sub>a</sub> O(4')	3.34	
O(4)	<sub>b</sub> O(1)	3.44	
O(5)	<sub>b</sub> O(1')	3.27	
<sub>a</sub> O(3)	<sub>a</sub> , <sub>c</sub> O(3')	3.97	
<sub>b</sub> O(2)	<sub>a</sub> , <sub>c</sub> O(2')	3.69	
O(4)	<sub>a</sub> , <sub>c</sub> O(4')	3.92	

Table 3(a) (cont.)

Carbon	Carbon	
C(1)	<sub>a</sub> , <sub>b</sub> , <sub>c</sub> C(1')	3.66
C(1)	<sub>a</sub> , <sub>b</sub> C(1')	3.56
C(1)	<sub>a</sub> , <sub>b</sub> C(2')	3.66
C(2)	<sub>a</sub> , <sub>c</sub> C(4')	3.79
Carbon	Oxygen	
C(1)	<sub>a</sub> , <sub>b</sub> , <sub>c</sub> O(2')	3.46
C(2)	<sub>a</sub> , <sub>c</sub> O(4')	3.45
C(3)	<sub>a</sub> , <sub>c</sub> O(4')	3.48
C(3)	<sub>a</sub> O(6)	3.73
C(4)	<sub>a</sub> O(6)	3.33
C(4)	<sub>a</sub> O(4')	3.58
C(4)	<sub>a</sub> , <sub>c</sub> O(4')	3.87

Table 3(b). *Metal–oxygen contact distances less than 3.0 Å*

Atoms		Distance
$K^+$	O(1)	2.71 Å
	<sub>a</sub> O(3)	2.74
	O(6)	3.01
	<sub>c</sub> O(5)	2.77
	<sub>a</sub> , <sub>b</sub> , <sub>c</sub> O(2')	2.84
	<sub>a</sub> , <sub>c</sub> O(3')	2.79
	<sub>b</sub> O(5')	2.77
Average value		2.80

The thermal parameters obtained after the last cycle of least-squares refinement are given in Table 4.

The equations to the best planes passing through the atoms of the molecules in the general position are as follows:

$$X_i - 0.0328 Y_i - 2.0247 Z_i + 5.4269 = 0$$

A. For atoms O(3), C(4), O(4) of the molecule in the general position.

$$X_i + 0.0809 Y_i - 3.0228 Z_i + 5.4326 = 0$$

B. For rest of the atoms of the molecule in the general position.

The planes *A* and *B* make an angle of  $8^\circ 18'$  with each other indicating that one of the COOH groups is twisted by  $8^\circ 18'$  from the plane passing through the atoms of the rest of the molecule.

Table 4. *Thermal parameters*

$$T = \exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{31}hl + b_{12}hk)]$$

	$b_{11}$	$b_{22}$	$b_{33}$	$b_{23}$	$b_{31}$	$b_{12}$
C(1)	0.01041	0.00958	0.01267	0.01093	0.00289	0.00618
C(2)	0.00858	0.00979	0.01473	-0.00598	0.00610	0.00562
C(3)	0.00865	0.00926	0.01622	0.00285	0.00347	0.00011
C(4)	0.00755	0.01304	0.01141	0.00278	0.01070	-0.00703
C(5)	0.00773	0.00809	0.00880	-0.00097	0.00401	0.00789
C(6)	0.00624	0.00949	0.01476	-0.00118	0.00456	0.00640
O(1)	0.00763	0.00994	0.01631	0.00730	0.00978	0.00545
O(2)	0.01003	0.00917	0.01734	-0.00001	0.00297	0.00507
O(3)	0.00768	0.00938	0.01639	0.00101	0.00638	0.00548
O(4)	0.00991	0.01033	0.02294	0.00684	0.00598	0.00580
O(5)	0.01086	0.01188	0.01344	0.00565	0.01308	0.00554
O(6)	0.00807	0.01186	0.01284	0.00725	0.00879	0.00685
$K^+$	0.00732	0.00896	0.01243	0.00339	0.00720	0.00396



Table 6 gives the list of observed and calculated structure factors.

### Discussion of the structure

Fig. 1 gives a three-dimensional view of the structure while Fig. 2 gives the structure as seen down the [001] axis. Distinct chains of fumarate groups are aligned approximately parallel to the [010] axis at heights of nearly  $\frac{1}{4}c$  and  $\frac{3}{4}c$ , each fumarate group being linked with the adjacent one at the same height through hydrogen bonds of length 2.58 Å between two oxygen atoms [O(4) and  ${}_b$ O(2)]. The two distinct chains at  $\frac{1}{4}c$  and  $\frac{3}{4}c$  are cross-linked by the extra molecule of fumaric acid at the special position ( $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ ), again through a hydrogen bond of length 2.57 Å, between oxygen atoms [O(6) and  $-{}_b$ O(1')]. The distances 2.58 and 2.57 Å correspond to real hydrogen bonds as they satisfy the coplanarity criterion as well as the tetrahedral-angle criterion [angles C(6')...O(6')... ${}_b$ O(1')] and C(4)...O(4)... ${}_b$ O(2) are all 112°] for the formation of a hydrogen bond.

### The correct chemical composition of the compounds

The authors believe that the present analysis of this structure gives clear evidence that the correct composition of the salt is in fact  $2\text{KC}_4\text{H}_3\text{O}_4 + \text{C}_4\text{H}_4\text{O}_4$ , for the following reasons:

(1) Gupta & Barnes (1956) have pointed out in their paper on the preparation of the potassium salts of

fumaric acid [(i)  $2\text{KC}_4\text{H}_3\text{O}_4 + \text{C}_4\text{H}_4\text{O}_4$ , (ii)  $\text{KC}_4\text{H}_3\text{O}_4$  and (iii)  $\text{K}_2\text{C}_4\text{H}_2\text{O}_4$ ] that an increasing amount of alkali, KOH or  $\text{K}_2\text{CO}_3$ , (far in excess of that which simple chemical calculations of stoichiometric proportions would indicate) is required to produce the three salts in stages, the pH values of the solution being 3.3 for  $2\text{KC}_4\text{H}_3\text{O}_4 + \text{C}_4\text{H}_4\text{O}_4$ , 4 for  $\text{KC}_4\text{H}_3\text{O}_4$  and 8 for  $\text{K}_2\text{C}_4\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . This is a clear indication that the first stage in the salt formation and crystallization is in fact  $\text{KC}_4\text{H}_3\text{O}_4$  with molecules of  $\text{C}_4\text{H}_4\text{O}_4$  being included as 'acid molecules of crystallization'. As Gupta & Barnes (1961) point out, there is a great difference in the solubilities of  $2\text{KC}_4\text{H}_3\text{O}_4 + \text{C}_4\text{H}_4\text{O}_4$  and  $\text{K}_2\text{C}_4\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  which further indicates that in the initial stages  $\text{K}_2\text{C}_4\text{H}_2\text{O}_4$  could not have been formed.

(2) Table 7 gives the dimensions of the 'molecules' in the special and general positions and also the dimensions of the fumaric acid molecule (determined by means of three-dimensional data) as reported by Brown (1966) and Post & Bednowitz (1966) with *R* values of 5.9% and 6.2% respectively. The accuracy of bond lengths in this structure is  $\pm 0.02$  Å and of bond angles  $\pm 1^\circ$ . Bearing this in mind, if one compares the dimensions of the molecules in the special and general positions in this structure with those reported by Brown (1966) and Post & Bednowitz (1966) the evidence for the molecule in the special position in this structure being a molecule of fumaric acid is overwhelming, thus leading to the formula  $2\text{KC}_4\text{H}_3\text{O}_4 + \text{C}_4\text{H}_4\text{O}_4$ . The dimensions, particularly the bond angles, of the molecule in the general position in this structure are significantly

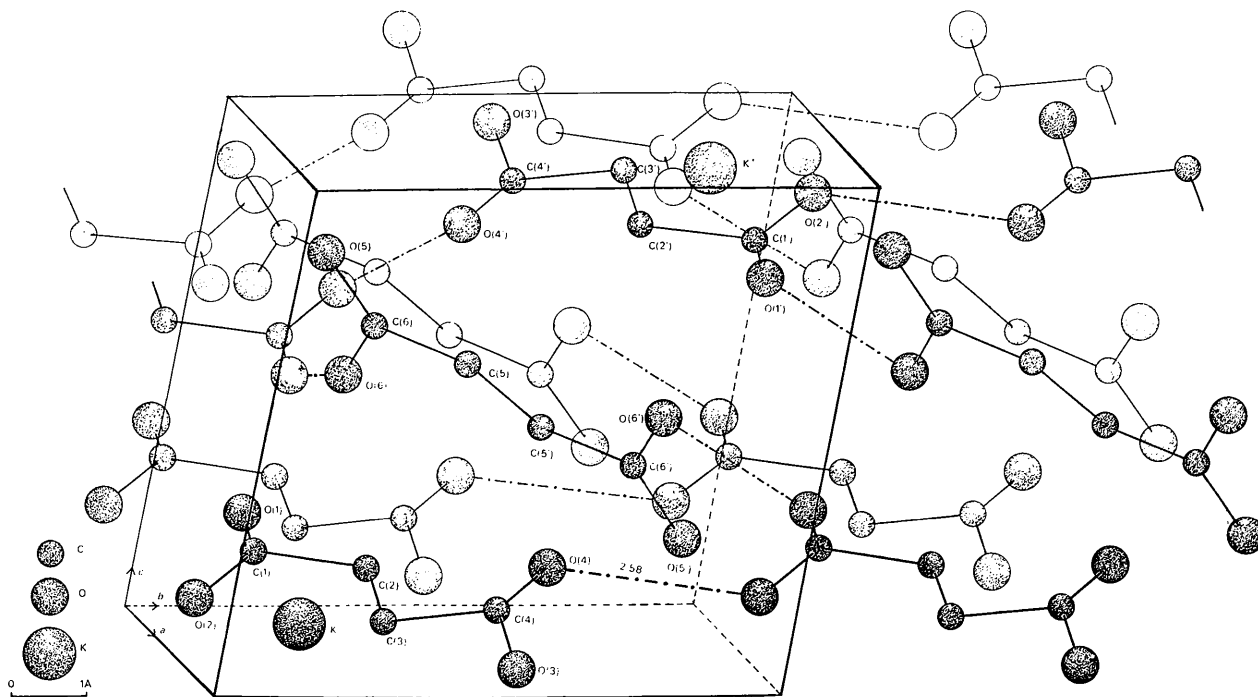


Fig. 1. A three-dimensional view of the structure.

Table 7. 'Molecular' dimensions

Bond	Fumaric acid molecule				2K <sub>2</sub> C <sub>4</sub> H <sub>3</sub> O <sub>4</sub> + C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> molecule	
	I Special position (Brown, 1966)	I General position	II (Post & Bednowitz, 1966)	II Average of I and II	Special position (This work)	General position
C-C	1.46 Å	1.46 Å 1.47	1.49 Å	1.47 Å	1.50 Å	1.54 Å 1.56
C=C	1.36	1.33	1.32	1.34	1.35	1.32
C-O...H	1.29	1.30 1.29	1.29	1.29	1.30	1.28 1.25
C=O	1.23	1.21 1.22	1.23	1.22	1.22	1.23 1.22
C...H-O	2.68	2.68	2.67	2.68	2.57	2.58
O-C-O	124.3°	124.3°	124.4°	124.3°	124.7°	126.4° 125.5
O-C-C	116.7	114.2	116.0	115.6	114.5	119.5 114.7
O=C-C	119.0	121.5	119.5	120.0	120.5	113.3 116.7
C-C=C	122.8	125.4	122.5	123.6	123.5	118.1 116.1

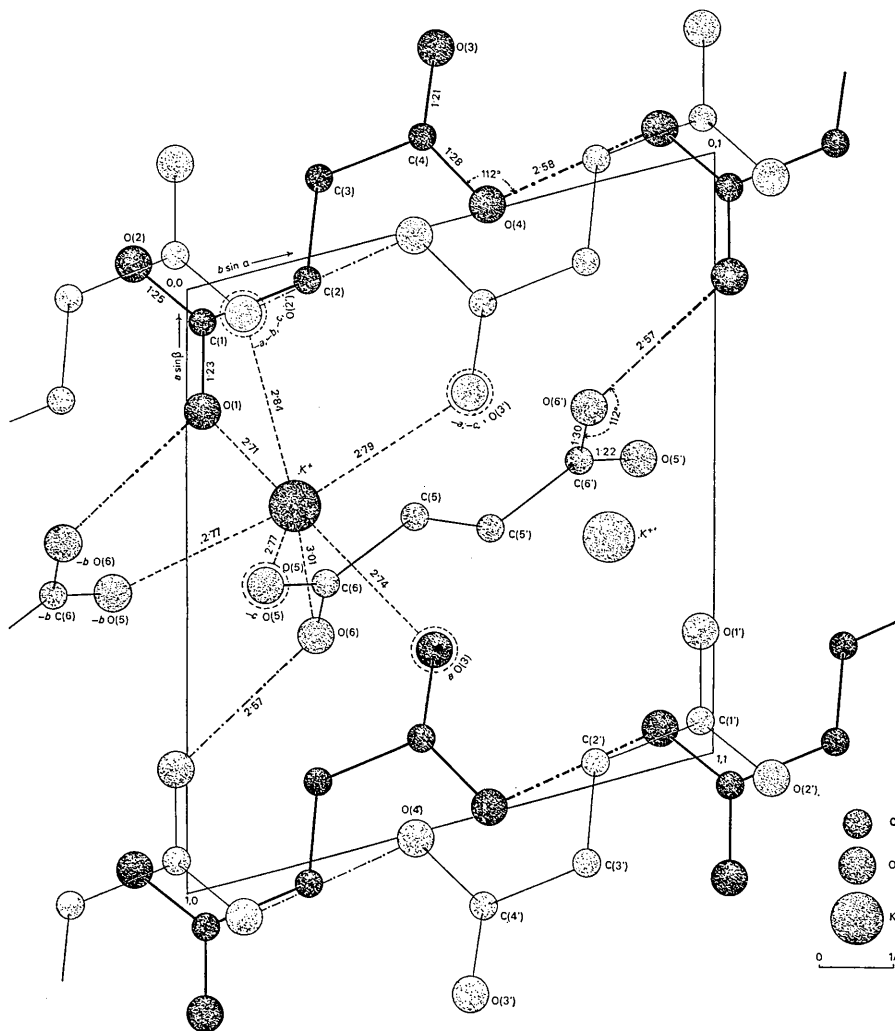


Fig. 2. The structure viewed down [001].

different from the values reported for the acid molecule  $C_4H_4O_4$  by the above workers.

(3) Brown (1966) and Post & Bednowitz (1966) have shown the fumaric acid to be planar (the greatest deviations being 0.002 and 0.01 Å in the two structures). As Table 5(b) shows, the molecule in the special position is far more planar than the one in the general position. This is additional evidence for the molecule in the special position being the fumaric acid molecule. The slight lack of planarity is probably the result of packing of the molecules in the structure, including the balancing of charges locally around the metal ions ( $K^+$ ).

(4) Fig. 2 gives the scheme of hydrogen bonds of 2.57 and 2.58 Å in the crystal structure as seen down the [001] axis, together with the carbon-oxygen bond lengths in the COOH groups which are involved in the hydrogen bonding and the  $K^+$ -O contacts. The fumaric acid molecule must be regarded as centrosymmetric as revealed by the work of Brown and Post & Bednowitz. If this assumption is correct, the following reasoning leads to the conclusion that the molecule in the special position cannot be the dipotassium fumarate  $K_2C_4H_2O_4$  'molecule' but that it must be the acid molecule itself, *i.e.*  $C_4H_4O_4$ . For the sake of argument, let us assume that the molecule in the special position is the dipotassium fumarate 'molecule',  $K_2C_4H_2O_4$ , *i.e.* it has no hydrogen atoms in its two COOH groups, both having been replaced by the  $K^+$  ions. However, this molecule is involved in the hydrogen bond formation with a hydrogen bond of 2.57 Å and must be, therefore, at the receiving end of the hydrogen bond, *i.e.* an acceptor and not a donor. Apart from the difficulty that at the 'receiving' end this C-O bond is the longer of the two C-O bonds in a COOH group and hence of the type C-O(H), contradicting the earlier assumption that both the hydrogen atoms in this molecule are replaced by  $K^+$  ions, there is another serious difficulty. The hydrogen atom attached to the oxygen atom O(1) of the molecule in the general position must therefore, in that case, be considered to be involved in the hydrogen bond formation, the 'donor' being the molecule in the general position and the C(1)-O(1) bond being regarded as C(1)-O(1)(H). As the molecules must be assumed to be centrosymmetric, the C(4)-O(3) bond in the same molecule must be regarded as C(4)-O(3)(H) and as a logical corollary C(4)-O(4) and C(1)-O(2) must be regarded as C(4)=O(4) and C(1)=O(2) respectively. However, oxygen atoms O(4) and O(2) are definitely hydrogen bonded (2.58 Å) and we cannot regard these bonds as C=O bonds. The bond lengths themselves [1.28 Å for C(4)-O(4) and 1.25 Å for C(1)-O(2)] indicate that these bonds are the longer of the two C-O bonds in a COOH group, *i.e.* of the type C-O(H). Thus we cannot regard the molecule in the special position as a molecule of  $K_2C_4H_2O_4$ : it must be regarded as a molecule of  $C_4H_4O_4$ .

Precisely similar arguments to those presented above apply, however, and also successfully explain the

scheme of hydrogen bond formation and the C-O bonds, if one assumes the molecule in the special position to be an acid molecule. Thus C(6')-O(6') (1.30 Å) is of the type C-O(H) and at the donor's end, C(1)-O(1) (1.23 Å) being of the type C=O and at the receiving end. As a consequence, the C(1)-O(2) (1.25 Å) and C(4)-O(4) (1.28 Å) bonds of the molecule in the general position are both of the type C-O(H) and hydrogen bonded (2.58 Å), presumably with the hydrogen atom 'attached' to the oxygen atom O(2) replaced by a  $K^+$  ion [ $K^+$ -O(2) distance 2.84 Å]. This bond C(1)-O(2) (1.25 Å) is shorter than the C(4)-O(4) (1.28 Å) bond and the carboxyl group C(1)O(1)O(2)(H) is ionized as indicated by the near equality of its C-O bonds (1.23, 1.25 Å).

It is worth while here to mention that in several structures (Roy, 1967; Bacon & Curry, 1957) it has been observed that there is hydrogen bonding between the oxygen atoms of COOH groups, *both* of which are of the type O(H)···O(H) (*i.e.* the longer of the two C-O bonds in a COOH group), one of the hydrogen atoms of the group being replaced in that case by a metal ion. Thus the above feature observed in this structure is not new but already reported for a number of other structures.

(5) The angles C(6')···O(6')···<sub>b</sub>O(1) and C(4)···O(4)···<sub>b</sub>O(2) are all 112° *i.e.* near to the tetrahedral value expected for hydrogen bond formation. On this basis also, the molecule in the special position should be regarded as the acid molecule and not the dipotassium fumarate 'molecule'.

(6) There is no evidence from the X-ray photographs or structure factor calculations that there is a statistical distribution, *i.e.* random distribution of  $K_2C_4H_2O_4$ ,  $C_4H_4O_4$  and  $K_2C_4H_2O_4$  molecules, in the structure. Had this been so, it would have become apparent in some of the reflexions in which the hydrogen atom contributions were likely to be large.

(7) Finally, neutron diffraction work on the crystal (Gupta & Prasad, unpublished) has shown the positions of the hydrogen atoms quite clearly in the [001] projection and the molecule at  $\frac{1}{2} \frac{1}{2} \frac{1}{2}$  is definitely shown to be the fumaric acid molecule. The constitution of the salt is, therefore, firmly established as being  $2K_2C_4H_2O_4 + C_4H_4O_4$ .

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## Electrostatic Charge Distributions in the Structure of Low Albite, NaAlSi<sub>3</sub>O<sub>8</sub>

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Computer programs are described which calculate the positive charges contributed by the metallic cations to the surrounding oxygen anions in the low albite, NaAlSi<sub>3</sub>O<sub>8</sub>, structure. The unknown variables are taken to be the assumed pure Si-O and Al-O distances, and the coordination number of the sodium ion. The charges are distributed in amounts that are inversely proportional to the cation-anion distances. The most satisfactory charge distribution occurs when Si-O = 1.602 (± 0.002), Al-O = 1.777 (± 0.003) Å and C.N. = 6 for Na (single atom); the total charges on the four tetrahedral groups of oxygen ions are then: 8.007, 7.999, 8.001 and 7.995 e.s.u. (σ = 0.01<sub>2</sub> e.s.u.) giving a total 'charge unbalance' of 0.014 e.s.u. (σ = 0.02<sub>4</sub> e.s.u.) and a total Al content of 1.000 atoms (σ = 0.005). It is concluded that the crystal is ideally ionic and that the structure is 'largely ordered' with 82% Al in one site. It is thought that the small integral C.N. for the Na ion may have important implications for the nature of ionic bonding. An Appendix gives the derivation of relationships for determining the proportion of an oxygen atom shielded by closer atoms from a Na ion.

### I. THEORETICAL CONSIDERATIONS AND METHOD

#### Introduction

The feldspar minerals which are mainly KAlSi<sub>3</sub>O<sub>8</sub>-NaAlSi<sub>3</sub>O<sub>8</sub>-CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> are characterized by polymorphism which is now known to be due to silicon-aluminum (Si-Al) 'order-disorder'. High-temperature forms such as high albite (NaAlSi<sub>3</sub>O<sub>8</sub>) and sanidine (KAlSi<sub>3</sub>O<sub>8</sub>), analysed by three-dimensional methods in the 'quenched' state at room temperature, have disordered structures with the Si-Al atoms distributed randomly among the tetrahedral sites. In contrast, feldspars that are generally accepted from geological evidence to be low-temperature forms (cooled slowly to ordinary temperatures) such as low albite (NaAlSi<sub>3</sub>O<sub>8</sub>) and microcline (KAlSi<sub>3</sub>O<sub>8</sub>), also analysed by three-dimensional methods, are known to have structures in which the Si and Al atoms are segregated into structurally different tetrahedral sites.

The generally accepted view is that in low-temperature feldspars such as low albite and (maximum) micro-

cline, the Si and Al atoms are completely segregated, that is, the structures are fully ordered with respect to Si-Al. A dissenting view was put forth by Ferguson, Traill & Taylor (1958), who proposed that in such low-temperature feldspars the Si and Al atoms may not be completely segregated; in this case these structures would be only largely and not fully ordered with respect to Si-Al. The basis for this view was an interpretation of the structures as ionic, that is, that the atoms behave as ions and that therefore the most likely low-temperature feldspar would be, in general, the one with the most satisfactory electrostatic charge distribution. It can be shown that such a structure cannot have the Si and Al atoms fully ordered; in the case of low albite, for example, Ferguson *et al.* showed in 1958 that the ideal ionic structure has the Al atoms segregated to only about 75% into one site.

This ionic interpretation appeared to the authors (Ferguson, Traill & Taylor, 1958) to explain a number of the structural features of the feldspars, and in a later paper Ferguson (1960) extended these ideas particularly with reference to the alkali feldspar phase relationships implied by the ionic interpretation of the structures. However, exception to these views was taken by a number of authors, for example, MacKenzie & Smith

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