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The Crystal Structures of Potassium and Rubidium Hydrogen Fumarates

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Potassium and rubidium hydrogen fumarates are triclinic but not isomorphous. Both contain *fumaric acid of crystallization.* Each has two metal ions and either ($C_4H_2O_4+2C_4H_4O_4$) or ($2C_4H_3O_4+C_4H_4O_4$) in the unit cell. These alternatives differ only in the positions of two hydrogen atoms and it may not be possible to distinguish between them. The fumaric acid molecules and the fumarate radicals are both planar and generally similar, both having the *trans* configuration, but with unrelated orientations in the unit cell. In both structures the metal ion is coordinated by seven oxygen atoms at somewhat different distances, and the centrosymmetrical molecule at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ cross-links chains of fumaric acid groupings in successive (100) planes. These chains, whose configurations differ markedly in the two (K and Rb) compounds, in each case lie at approximately $z = \frac{1}{4}$ and $z = \frac{3}{4}$ along the [010] directions, with short hydrogen bonds along the chains, but with only van der Waals forces, in the [001] direction, between the chains.

Crystallographic data are given by Groth (1910) for potassium hydrogen fumarate, but these were found to be different from those determined by X-rays for the compound synthesized. The substance was prepared by the addition of fumaric acid to KOH, in calculated amounts, with subsequent boiling and filtering. Rubidium hydrogen fumarate was similarly prepared, and recrystallized with some difficulty from a hot aqueous solution. In each case only one face (taken as (100)) was well developed. The unit cells chosen are not the reduced cells (see *International Tables* (1952)) but are structurally the most convenient:

	K compound	Rb compound
a (Å)	8·64	7·55
b (Å)	7·48	8·15
c (Å)	6·96	7·41
α (°)	78·1	75·0
β (°)	112·9	106·8
γ (°)	107·9	101·5
d_{100} (Å)	7·75	7·16
d_{010} (Å)	7·13	7·82
d_{001} (Å)	6·38	6·97
V (Å^3)	392·5	417·9
ϱ (g.cm.$^{-3}$)	1·785	2·059
W*	421·9	518·2

* W = total mass of material in the unit cell, in atomic units.

The molecular weight of $KC_4H_3O_4$ is 154·2 and of $K_2C_4H_2O_4$ is 192·3. The possibility that the unit cell might contain $2KC_4H_3O_4+6H_2O$ (total mass 416·4) is excluded by a chemical analysis and by the subsequent X-ray analysis. The chemical analysis gave 33·03% C, 2·03% H, which would correspond to calculated values 33·95% C, 2·35% H for either ($2KC_4H_3O_4+C_4H_4O_4$) or ($K_2C_4H_2O_4+2C_4H_4O_4$), both giving $W = 424·4$. Similarly, $Rb_2C_{12}H_{10}O_{12}$ would have $W = 517·0$.

Application of Wilson's statistical test to the intensities of reflexion in the $\{hk0\}$ and $\{h0l\}$ zones of the potassium salt gave good agreement with a centric distribution.

The rubidium atom was too heavy for such a test to be applied successfully to the rubidium compound. No positive results could be obtained from tests for piezo- and pyro-electricity on either compound. This indicated that the space group was $P\bar{1}$ and that the odd molecule in the unit cell, whether $C_4H_4O_4$ or $M_2C_4H_2O_4$ must be centrosymmetrical, as would be expected from a *trans* configuration of the chemical molecule. In either case the structure shows the unusual feature of including *acid of crystallization*, which takes part both in the coordination of the metal atom and in the hydrogen bond system, as will be seen later (Figs. 1 and 2).

Patterson syntheses and sign determination by inequality methods were tried on the potassium compound without success, so the rubidium compound was first analysed by the direct heavy-atom and difference Fourier techniques. Refinement gave the final atomic positions shown in Fig. 1. The projection along [010] served in particular to demonstrate the planarity of the molecules in general positions. The molecule at the centre of symmetry does not give a clear projection along any of these three axes. The assignment of coordinates to the light atoms is not precise enough to distinguish C=O from C–OH.

The reliability factors at the final stage were $R(hk0) = 0·181$ (136 out of a possible 146 reflexions), $R(h0l) = 0·185$ (132 out of a possible 134 reflexions). No systematic ($0kl$) data were collected.

An attempt to determine the root-mean-square thermal-vibration amplitude by plotting $\log(\Sigma|F_c| \div \Sigma|F_o|)$ for groups of $\sin^2\theta$ values against

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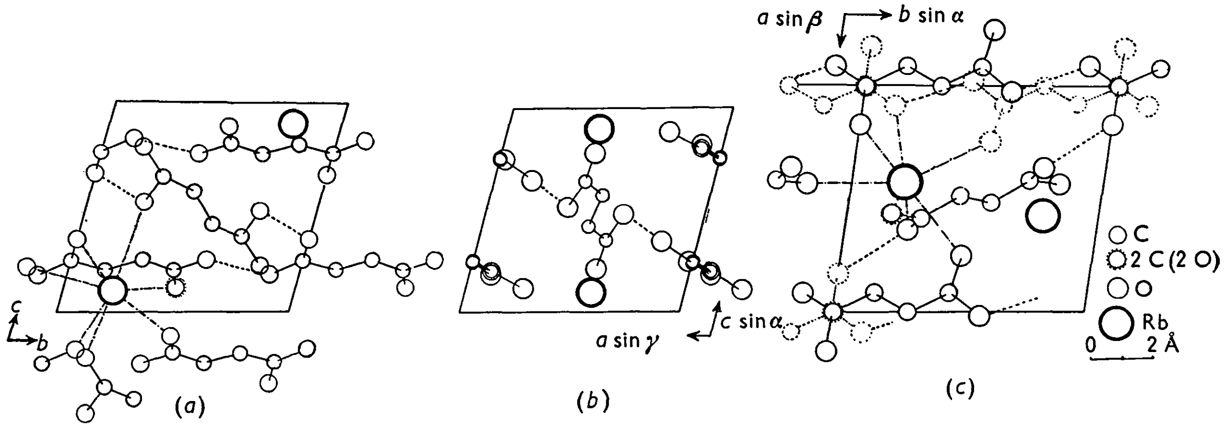

Fig. 1. Rubidium compound; (*a*) projection on (100), (*b*) projection along [010], (*c*) projection along [001]. Chain lines: Rb–O bonds; broken lines: hydrogen bonds.

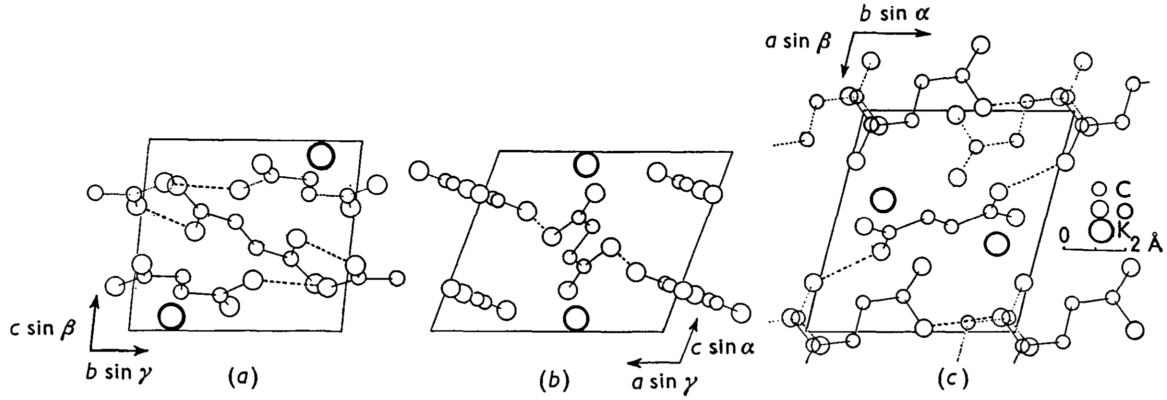

Fig. 2. Potassium compound; projections along (*a*) [100], (*b*) [010], (*c*) [001]. Broken lines: hydrogen bonds.

$\sin^2\theta$ gave $\sqrt{(\overline{u^2})} = 0{\cdot}22$ Å ($B = \frac{8}{3}\pi^2\overline{u^2}$), and this value did not change for high-order terms to which the Rb^+ ions alone might be expected to contribute. This value may be compared with that of $\sqrt{(\overline{u^2})} = 0{\cdot}26$ Å found by Wasastjerna (1945) for Rb^+ in RbCl.

The Rb^+ ion (at 0·424, 0·212, 0·105) is coordinated to seven nearest oxygen neighbours at distances of 2·88–3·09 Å. There is no clear indication that the Rb^+ ion is more firmly attached either to the molecule in the special position or to one in a general position, and a decision between

$$(2RbC_4H_3O_4+C_4H_4O_4) \quad \text{and} \quad (Rb_2C_4H_2O_4+2C_4H_4O_4)$$

therefore rests essentially upon the positions of the hydrogens along the cross-linking hydrogen bonds, which have not been determined in this analysis. It may even be that there is no real distinction between these formulae.

The potassium compound, although not isomorphous, was eventually analysed by assuming that the metal ions probably occupy similar positions in the two compounds, and by assuming that similar reflexions have similar signs in the two structures. This was justified because of a general similarity of intensity sequences in the main zones. The further application of statistical sign relationships led to a structure which would refine, giving the projections shown in Fig. 2. The atomic coordinates are not given because, although undoubtedly generally correct, they are not believed to be sufficiently accurate to be included in this preliminary note.

It will be seen that the two compounds, although not iso-structural, differ only in the configuration of the chains lying along the [010] direction. The centrosymmetrical group of $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ serves to cross-link the chains at $0, 1, \frac{1}{4}$ and $1, 0, \frac{3}{4}$ by means of hydrogen bonds. Apart from this cross-linking, there are only van der Waals forces operating along the [001] direction between the chains.

The K^+ ion is coordinated by seven oxygen atoms from seven different molecules at distances of 2·65–2·89 Å. The maximum deviation of atoms from a plane is 0·03 Å for either molecule.

Considerable interest lies in a determination of the exact differences between the molecules in the special and general positions, especially in respect of the hydrogen bond configuration. It may be possible to determine this for the potassium compound by a three-dimensional analysis. The reliability factors for the present structure are $R(hk0) = 0{\cdot}212$, $R(h0l) = 0{\cdot}228$, $R(0kl) = 0{\cdot}241$.

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Densities of Trigons and Ultra-Violet Absorption of Diamonds

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Two opposite faces of each of 37 small transparent octahedral diamonds were examined microscopically by phase-contrast illumination for the density of trigons on them. Ultra-violet absorption edges were also determined for the same diamonds.

The two faces of the same diamond were found usually to have about the same density of trigons.

On all the diamonds the faces examined could be classified into two groups with regard to the density of trigons. These results support a conclusion reached previously that critical conditions of growth exist for the initiation of trigon formation.

Analysis of the results, including the ultra-violet absorption edges of the diamonds examined, indicates that the ultra-violet absorption might be correlated with the surface texture shown by the trigons.

Introduction

It is well known (Miers, 1902; Smith, 1930; Williams, 1932; Tolansky, 1953; Tolansky & Wilcock, 1946; Halperin, 1954) that diamonds often have their octahedral faces covered with small equilateral triangular pits, or 'trigons' as named by Sutton (1928). It is now certain that the trigons were formed during the growth of the crystals (Williams, 1932; Tolansky & Wilcock, 1946), and that they are not due to etching, as assumed by earlier investigators (Miers, 1902; Smith, 1930).

The formation of trigons was discussed in a previous communication (Halperin, 1954). The main assumption in the theory proposed to explain the formation of the trigons was that imperfect steps, only a fraction of the lattice unit in height, were formed on the growing surfaces as a result of accumulation of faults in the lattice. It was further claimed that these imperfect steps should grow into observable trigons at certain conditions of growth. Trigons should be formed, on these ideas, only when growth is continued below a certain critical temperature, while at higher temperatures growth does not stop at the imperfect steps when the whole face is covered, and no observable trigons are formed.

Such a process of growth on imperfect steps should affect the texture of the diamond, giving it a 'domain' structure. This involves stacking-fault surfaces, dislocations and other imperfections in the bulk of the crystal, imperfections which might affect the structure-sensitive properties of the diamond. It was therefore suggested (Halperin, 1954) that the well known (Robertson, Fox & Martin, 1934) peculiarities of diamond with regard to its structure-sensitive properties might be connected with the imperfections mentioned.

Now the trigons describe the surface texture of the diamond, and from the above consideration it follows that this is built on the texture in the bulk of the crystal. If this is true, a correlation should exist between the trigons on the surface and the structure-sensitive properties of a diamond. To look for such a correlation, the absorption edge in the ultra-violet was chosen as one of the structure-sensitive properties. Thirty-seven small colourless octahedral diamonds (about 1 mm. thick) were examined for the density of trigons on their faces, and for their absorption edges in the ultra-violet. One pair of octahedral faces was examined on each crystal, and ultra-violet absorption edges were determined for light passing through the crystal at normal incidence to the same faces.