

X-RAY CRYSTALLOGRAPHIC DATA ON RUBIDIUM FUMARATE, MONOHYDRATE ($\text{Rb}_2 \text{C}_4 \text{H}_2 \text{O}_4, \text{H}_2 \text{O}$)

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Plate III

ABSTRACT. Single crystal photographs show rubidium fumarate, monohydrate ($\text{Rb}_2 \text{C}_4 \text{H}_2 \text{O}_4, \text{H}_2 \text{O}$) to be triclinic with,

$$a = 9.23 \text{ \AA}, \quad b = 7.51 \text{ \AA}, \quad c = 6.66 \text{ \AA}$$

$$\alpha = 81^\circ 5', \quad \beta = 96^\circ 42', \quad \gamma = 91^\circ 48'$$

There are two formula units in the cell. The space group is suggested to be $P\bar{1}$. Attention is drawn towards the pseudo-monoclinic symmetry. Indexed powder diffraction data for the compound is given at the end in tabular form.

Several potassium and rubidium salts of fumaric acid have been reported in Beilstein's Organische Chemie (Band II, Syst. No. 179, p. 637) and their X-ray crystallographic examination was completed by Gupta (1953) and Gupta and Barnes (1958). While the work on the determination of the crystal structure of potassium fumarate, dihydrate ($\text{K}_2 \text{C}_4 \text{H}_2 \text{O}_4, 2\text{H}_2 \text{O}$) was in progress, the desirability of preparing an isomorphous rubidium salt, rubidium fumarate, dihydrate ($\text{Rb}_2 \text{C}_4 \text{H}_2 \text{O}_4, 2\text{H}_2 \text{O}$) was felt. This compound is not reported anywhere in the chemical literature but it was anticipated that by mixing stoichiometric proportions of fumaric acid and rubidium carbonate, such a compound could be prepared. In the event that the compound so prepared did not turn out to be isomorphous with the corresponding potassium fumarate, this result is being published.

Preparation. One gram of rubidium carbonate (Fischer, reagent) was mixed with the stoichiometric amounts of fumaric acid in water solution and the resulting solution was warmed, filtered off and left for crystallization (by the method of slow evaporation) in crystallizing dishes. After a fortnight, several platy crystals were obtained with the (100) as the platy face. These were considered suitable for X-ray work after the usual examination in the polarizing microscope.

Unit cell: The unit cell which was found to be triclinic was determined by mounting a single crystal (1 mm \times 1 mm \times 0.25 mm) on the Buerger precession camera. The reciprocal cell angles γ^* and β^* were measured directly on the zero level precession photographs showing the reciprocal nets a^*-b^* and a^*-c^* respectively while the interaxial direct cell angle $\alpha(b \wedge c)$ was measured directly

from the precession camera dial readings. These lead, using the formula for a triclinic cell, to the following values of the interaxial angles

$$\alpha = 81^{\circ}5', \quad \beta = 96^{\circ}42', \quad \gamma = 91^{\circ}48'$$

The values of a^* , b^* , c^* measured from zero level precession photographs showing the a^*-b^* net and a^*-c^* net and the above values of α , β and γ lead to the following values of the unit cell lengths : -

$$a = 9.23 \text{ \AA}, \quad b = 7.51 \text{ \AA}, \quad c = 6.66 \text{ \AA}$$

$$d_{100} = 9.17 \text{ \AA}, \quad d_{010} = 7.42 \text{ \AA}, \quad d_{001} = 6.54 \text{ \AA}.$$

Radiation used throughout was Mo K_{α} , $\lambda = 0.7107 \text{ \AA}$. The reciprocal net a^*-b^* shows a marked amount of monoclinic pseudo-symmetry (Plate III).

The density, measured by floatation method using a mixture of methyl iodide (density 2.279 gm/cc) and toluene (density 0.867 gm/cc) was found to be 2.23 gm/cc. Using the above values of the cell constants, the volume of the unit cell = 452.99 \AA^3 and the weight of the unit cell contents = 608.54 (atomic units). Theoretical molecular weight for $\text{Rb}_2 \text{C}_4 \text{H}_2 \text{O}_4$ is 284.88 (atomic units). If there are two such formula units per unit cell, the balance of 38.78 (atomic unit) can be ascribed only to the presence of two water molecules in the unit cell ($2 \times 18 = 36$ atomic units). Thus the chemical formula of the compound was uniquely fixed as $\text{Rb}_2 \text{C}_4 \text{H}_2 \text{O}_4 \cdot \text{H}_2 \text{O}$, no other possibility being consistent with the above data.

Space group : The diffraction symmetry observed is, of course, $P\bar{1}$. With the presence of two molecules per unit cell and in view of the pseudo-monoclinic symmetry that the crystal shows (figure. 1) the space group is suggested to be $P\bar{1}$.

The corresponding potassium salt of fumaric acid ($\text{K}_2 \text{C}_4 \text{H}_2 \text{O}_4$) crystallizes with two molecules of water of crystallization and is monoclinic, space group $P2_{1/c}$. Since the rubidium salt ($\text{Rb}_2 \text{C}_4 \text{H}_2 \text{O}_4$) crystallizes with only one molecule of water, this would explain that the potassium and rubidium salts are not isomorphous, the rubidium salt crystallizing with lower triclinic symmetry, although pseudo-monoclinic symmetry persists. It may be noted in passing that a similar lack of isomorphism exists in other corresponding rubidium and potassium salts of fumaric acid (Gupta, 1956).

In order to check whether a higher hydrated form of $\text{Rb}_2 \text{C}_4 \text{H}_2 \text{O}_4$ exists or not a powder photograph of $\text{Rb}_2 \text{C}_4 \text{H}_2 \text{O}_4 \cdot \text{H}_2 \text{O}$, sealed in a Lindemann glass capillary tube was taken. One end of the capillary tube was then broken and this was made to touch a trace of water. By capillary action, the whole tube was then saturated with water. The resulting powder pattern of this water saturated sample did not show any changes from the corresponding powder photograph of $\text{Rb}_2 \text{C}_4 \text{H}_2 \text{O}_4 \cdot \text{H}_2 \text{O}$. Thus the possibility of a higher hydrated form of $\text{Rb}_2 \text{C}_4 \text{H}_2 \text{O}_4$ had to be ruled out.

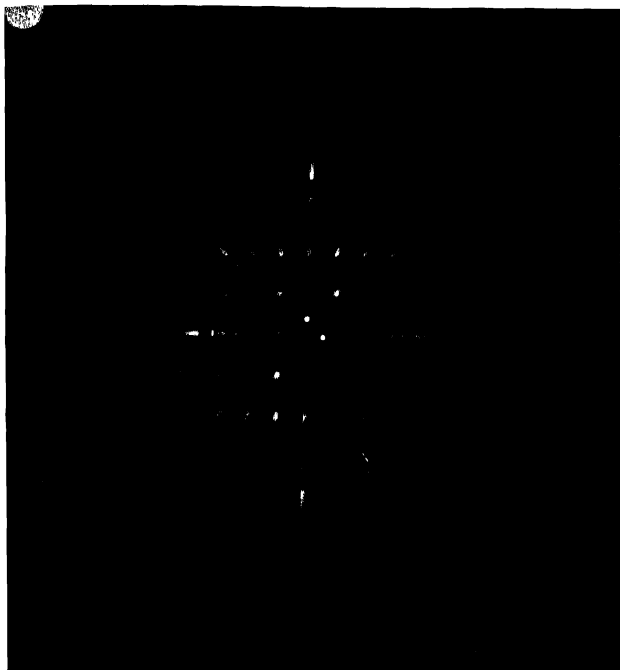


Fig. 1. Zero level precession photograph of rubidium fumarate, monohydrate. Triclinic, a^*-b^* net with a^* along the horizontal axis. $\mu=30^\circ$, $F=6.00$ cms. Mo $K\alpha$ radiation, $\lambda=0.7107$ Å. The pseudo-orthogonality of the net may be noticed. The four spots in the centre making a square array are due to accidental leakage of light in the camera.



Fig. 2. X-ray diffraction powder photograph of rubidium fumarate, monohydrate. Camera diameter = 114.6 mm; radiation, Cu $K\alpha$.

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The powder photograph of $\text{Rb}_2\text{C}_4\text{H}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is reproduced in figure 2, while the indexed powder data are given in Table I. The powder data (film method) were also checked by obtaining a diffraction curve from the Norelco Geiger counter

TABLE I
X-ray diffraction powder data (Indexed upto $d \approx 2A$)

| I/I_1 | $d(A)$ | | hkl | I/I_1 | $d(A)$ | | hkl |
|---------|----------|------------|--------------|---------|----------|------------|-------|
| | Observed | Calculated | | | Observed | Calculated | |
| 20 | 9.22 | 9.17 | 100 | 35 | 2.65 | 2.65 | 301 |
| 9 | 6.52 | 6.54 | 001 | | | 2.64 | 112 |
| | | | | | | 2.66 | 022 |
| | | | | | | 2.67 | 221 |
| 29 | 5.66 | 5.63 | 101 | 20 | 2.56 | 2.57 | 221 |
| 10 | 5.30 | 5.33 | 011 | | | | |
| 10 | 5.04 | 5.05 | 101 | 12 | 2.53 | 2.54 | 311 |
| | | | | | | 2.53 | 202 |
| 9 | 4.62 | 4.58 | 200 | | | 2.52 | 212 |
| 30 | 4.39 | 4.39 | 111 | 8 | 2.49 | 2.47 | 030 |
| | | | | | | 2.48 | 221 |
| 50 | 3.98 | 3.97 | 20 $\bar{1}$ | | | 2.49 | 122 |
| | | | | | | 2.48 | 212 |
| 25 | 3.69 | 3.71 | 020 | | | | |
| 25 | 3.58 | 3.56 | 201 | 25 | 2.40 | 2.40 | 130 |
| | | | | | | 2.41 | 222 |
| 30 | 3.45 | 3.45 | 120 | | | | |
| | | 3.45 | 021 | 13 | 2.34 | 2.34 | 320 |
| | | 3.42 | 120 | | | 2.34 | 312 |
| 75 | 3.32 | 3.31 | 211 | 35 | 2.31 | 2.32 | 131 |
| | | 3.31 | 121 | | | 2.31 | 212 |
| 15 | 3.24 | 3.27 | 002 | 5 | 2.27 | 2.25 | 122 |
| 50 | 3.16 | 3.18 | 012 | 12 | 2.20 | 2.18 | 230 |
| | | 3.18 | 102 | | | 2.21 | 410 |
| | | 3.16 | 121 | | | 2.20 | 013 |
| | | | | | | 2.19 | 031 |
| 100 | 3.09 | 3.13 | 211 | | | 2.21 | 113 |
| 50 | 3.02 | 3.03 | 02 $\bar{1}$ | 8 | 2.16 | 2.16 | 230 |
| | | | | | | 2.17 | 103 |
| 35 | 2.89 | 2.90 | 220 | | | | |
| | | 2.90 | 112 | 16 | 2.12 | 2.11 | 302 |
| | | 2.90 | 301 | | | 2.13 | 032 |
| | | 2.86 | 221 | | | 2.12 | 131 |
| | | | | | | 2.12 | 132 |
| 35 | 2.81 | 2.83 | 012 | | | 2.11 | 411 |
| | | 2.84 | 121 | | | 2.13 | 322 |
| | | 2.81 | 310 | | | | |
| | | 2.81 | 202 | | | | |
| | | 2.84 | 310 | | | | |
| 25 | 2.76 | 2.77 | 311 | | | | |
| | | 2.76 | 212 | | | | |

TABLE I (contd.)

| I/I_1 | $d(A)$ | | hkl | I/I | $d(A)$ | | hkl |
|---------|----------|------------|---------------|-------|----------|------------|-------|
| | Observed | Calculated | | | Observed | Calculated | |
| 10 | 2.08 | 2.08 | 312 | 5 | 1.69 | | |
| 9 | 2.05 | 2.06 | 20 $\bar{3}$ | 7 | 1.68 | | |
| 20 | 1.99 | 1.99 | 411 | 9 | 1.65 | | |
| | | 1.99 | 3 $\bar{1}$ 2 | 4 | 1.63 | | |
| | | 1.98 | 421 | | | | |
| | | 1.99 | 222 | | | | |
| 4 | 1.95 | | | 3 | 1.58 | | |
| 4 | 1.90 | | | 3 | 1.55 | | |
| 10 | 1.87 | | | 3 | 1.52 | | |
| 10 | 1.85 | | | 3 | 1.50 | | |
| 5 | 1.81 | | | | | | |
| 3 | 1.78 | | | 4 | 1.46 | | |
| 4 | 1.74 | | | 4 | 1.43 | | |
| 4 | 1.71 | | | | | | |

diffractometer capable of greater resolution. There were good agreements regarding the diffraction angles but not regarding the intensities for which the agreement with film method was only qualitative. This may be due to preferred orientation of grains in the sample prepared for the Norelco diffractometer and absorption

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