

The pattern of bond lengths and angles in the un-ionized carboxyl group is as expected with the C–O distance involving the O bonded to the proton 0.12(1) Å longer than the other. The differences in C–O lengths of un-ionized carboxyl groups in light-atom structures is 0.11 Å as in the structure of D-tartaric acid (Okaya, Kay & Stemple, 1966). The difference in C–O distances is around 0.07 Å where the carboxyl group is ‘half ionized’ (Ferguson, Sime, Speakman & Young, 1968) and the difference is expected to be zero for fully ionized carboxyl groups and, indeed, the two C–O distances on the ionized carboxyl group are not significantly different in this case. The presence of water of crystallization in sodium acid phthalate hemihydrate renders it unsuitable for general use as a monochromator crystal in X-ray fluorescence analysis because of its tendency to effloresce in air or *in vacuo*.

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The Crystal Structures of a Series of Salts of Phthalic Acid. III. The Crystal Structure of Rubidium Acid Phthalate

BY R. A. SMITH

Department of Geology, University of Alberta, Edmonton, Alberta, Canada

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Abstract. $\text{Rb}(\text{HOOC}\cdot\text{C}_6\text{H}_4\cdot\text{COO})$ is orthorhombic, $a=6.561(1)$, $b=10.064(2)$, $c=13.068(2)$ Å, $P2_1ab$, $\rho_{\text{obs}}=1.94$, $\rho_{\text{calc}}=1.93$ g cm⁻³, $Z=4$. The structure was solved by assuming isomorphism with the K salt (Okaya. *Acta Cryst.* (1965). **19**, 879–882). The final R for 333 counter reflexions was 4.6% and the structure shows no unusual features.

Introduction. The structure analysis of rubidium acid phthalate was undertaken as part of an investigation of a series of salts of phthalic acid. Anomalous properties had been observed in these compounds by Mattson & Ehlert (1966). Details are given in part I of this series (Smith, 1975).

Rubidium carbonate and phthalic acid in stoichiometric amounts for the formation of the acid salt were dissolved in water. Large rhombic bipyramidal crystals possessing perfect cleavage in the plane of the largest face formed and were the sole product upon complete evaporation of the water. Preliminary photographs indicated that rubidium acid phthalate crystallized in space group $P2_1ab$ and was isomorphous with the K salt (Okaya, 1965). General positions for this space group, a non-standard setting of $Pca2_1$ (No. 29), are x, y, z ; $\frac{1}{2}+x, \bar{y}, \bar{z}$; $x, \frac{1}{2}+y, \bar{z}$; $\frac{1}{2}+x, \frac{1}{2}-y, z$.

A fresh well formed crystal, $0.15 \times 0.15 \times 0.05$ mm, was taken and mounted about a on a manual Picker four-circle diffractometer. 12 high-angle intense reflexions were carefully centred in 2θ with Cu $K\alpha_1$ radiation (no monochromator) and from these values cell dimensions were derived as $a=6.561(1)$, $b=10.064(2)$, $c=13.068(2)$ Å at 22°C. Intensities were collected for one octant by the coupled θ – 2θ scan method. Of the 446 unique reflexions available within the limit $3^\circ \leq 2\theta \leq 90^\circ$, 56 were systematically absent and the intensities of the remaining 390 reflexions were measured and reduced to $|F|$ and σF by the method of Doedens & Ibers (1967). The criterion for observation was $I \geq 3\sigma I$; 333 reflexions satisfied this condition and were used in subsequent calculations. In view of the tabular nature of the crystal and the high absorption coefficient ($\mu=84$ cm⁻¹ with Cu $K\alpha$ radiation) corrections were applied with a local version of the program originally written by Coppens, Leiserowitz & Rabinovich (1965). Transmission factors ranged from 0.555 to 0.813.

The structure was solved by assuming that the Rb was isomorphous with the K salt (Okaya, 1965). With anisotropic temperature factors for Rb⁺ the structure was refined to $R=4.8\%$. Scattering factors were from

Cromer (1968). Anomalous dispersion corrections were applied to the Rb^+ ion. Ueki, Zalkin & Templeton (1966) reported the particularly severe effects of ignoring these corrections in polar space groups. The x coordinates of all atoms were therefore reversed and the structure refined thereafter to $R=4.6\%$. The choice of the latter enantiomorph for the study crystal can be justified with Hamilton's (1965) test. The final atomic coordinates and thermal parameters are reported in Table 1. Comparison between the 390 measured and calculated structure factors for which $R=5.6\%$ is available.*

Table 1. Heavy atom parameters and standard deviations

Anisotropic in the form
 $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$.

	x	y	z	U_{11}	U_{22}
Rb	-0.2500*	0.1014 (2)	0.0459 (1)	0.033 (1)	0.045 (1)
	U_{33}	U_{12}	U_{13}	U_{23}	
	0.062 (1)	0.005 (2)	-0.001 (2)	-0.009 (1)	

Isotropic in the form $\exp[-2\pi^2U(1/d_{hkl}^2)]$.

	x	y	z	U
O(1)	0.184 (2)	0.133 (1)	0.100 (1)	0.048 (5)
O(2)	0.397 (3)	-0.014 (1)	0.157 (1)	0.046 (4)
O(3)	-0.013 (2)	-0.163 (2)	0.134 (1)	0.043 (5)
O(4)	-0.039 (2)	-0.287 (1)	0.275 (1)	0.047 (4)
C(1)	0.127 (3)	0.051 (2)	0.267 (1)	0.027 (6)
C(2)	0.009 (3)	-0.054 (2)	0.296 (2)	0.035 (6)
C(3)	-0.088 (4)	-0.055 (2)	0.392 (1)	0.041 (6)
C(4)	-0.070 (4)	0.053 (2)	0.453 (2)	0.048 (7)
C(5)	0.048 (4)	0.164 (2)	0.425 (1)	0.042 (6)
C(6)	0.136 (4)	0.161 (2)	0.332 (2)	0.041 (6)
C(7)	0.239 (5)	0.060 (2)	0.168 (1)	0.035 (5)
C(8)	-0.011 (3)	-0.176 (2)	0.226 (2)	0.030 (6)

Unrefined parameters for the hydrogen atoms ($U=0.051 \text{ \AA}^2$)

	x	y	z
H(3)	-0.174	-0.136	0.413
H(4)	-0.150	0.055	0.524
H(5)	0.051	0.246	0.477
H(6)	0.214	0.244	0.313
H(O)	0.001	-0.370	0.245

* Not varied.

Discussion. The structure consists of Rb^+ and phthalate ions. All bond angles and distances in the latter are as expected and are deposited as Table 2 ($\sigma \sim 0.03 \text{ \AA}, 2^\circ$).* The planes of the ionized and un-ionized carboxyl groups make angles of 71° and 32° respectively with that of the aromatic ring. Fig. 1 shows the packing diagram down a and was plotted with ORTEP (Johnson, 1965). The Rb^+ ion is surrounded by O atoms, the six nearest at 2.80, 2.95, 2.96, 2.97, 2.98 and 3.06 \AA , all $\pm 0.01 \text{ \AA}$. The average value of these distances is 0.14 \AA greater than that for the six equivalent $\text{K} \cdots \text{O}$

* A list of structure factors and Table 2 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31076 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

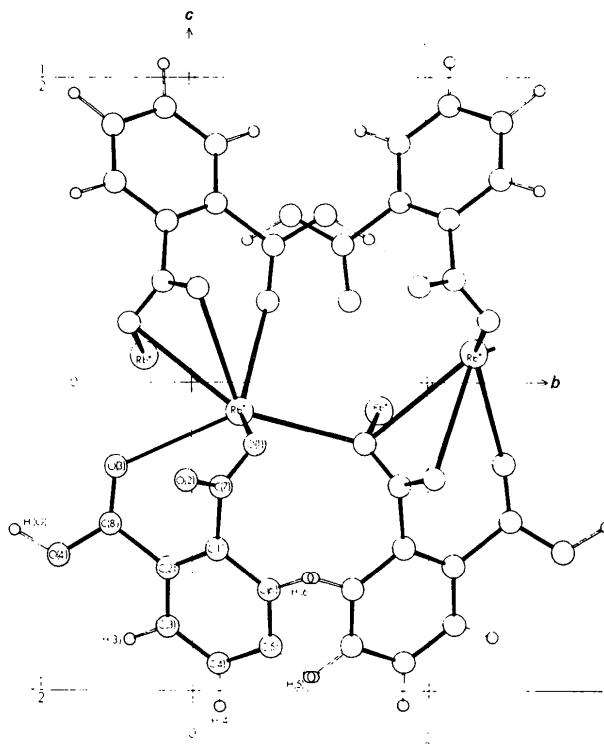


Fig. 1. Packing diagram for rubidium acid phthalate seen down a .

distances and reflects the increase in ionic radius of the cation. Truter (1971) commented on the difficulties in assigning coordination numbers to similar salts and in this case a seventh O atom is located only 3.28 \AA from the Rb^+ ion. In the next and last projected paper in this series the redetermined crystal structure of ammonium acid phthalate will be reported. Discussion of attempts to correlate the heights of the spurious reflectivity spikes reported by Mattson & Ehlert (1966) will be deferred until then.

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