Potassium Hydrogen Malonate—a New Type of Crystal Structure Involving Short "Symmetrical" Hydrogen Bonds

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SOME of the crystalline acid salts formed by monobasic acids (HX) include "very short" hydrogen bonds.[1] The two anion residues of such a formula as KHX_2 prove to be crystallographically equivalent; and the O··H··O bond connecting them lies across a symmetry element of the crystal. We have now discovered an analogous situation in acid salts of some dibasic acids.

Potassium hydrogen malonate would traditionally be represented by the formula

$$K^+{}^-O_2C{\cdot}CH_2{\cdot}CO_2H.$$

In fact this salt has the carboxyl groups crystallographically equivalent. The anion which is better represented as in the sequence, $\cdots H\cdots{}^{\frac{1}{2}-}O_2C{\cdot}CH_2{\cdot}CO_2{}^{\frac{1}{2}-}\cdots H\cdots$, is linked into infinite chains by hydrogen bonds lying across the centres of inversion.

Crystal data: $KHC_3H_2O_4$, $M = 142{\cdot}2$, monoclinic, $a = 9{\cdot}473$ (6), $b = 11{\cdot}559$ (7), $c = 4{\cdot}726$ (5) Å, $\beta = 91{\cdot}6$ (0·1)°, $U = 517{\cdot}3$ Å^3, $D_m \approx 1{\cdot}7_5$, $Z = 4$ $D_c = 1{\cdot}825$; space group $C2/m$ (No. 12): the malonate residue has a two-fold axis of symmetry, the K^+-ion lies on a plane of symmetry, and the acidic H-atom (effectively) at a centre.

The structure was easily solved in the c-axial projection and z-co-ordinates were allocated by trial. Full three-dimensional intensity data were then collected, using Mo-K_α radiation, with a Hilger–Watts four-circle, computer-controlled diffractometer fitted with balanced filters. Initial refinement has been based on 484 independent reflexions with $\theta < 25°$. Six cycles of full-matrix, least-squares analysis,† using anisotropic vibrational parameters in the later cycles, and including the methylenic H-atom isotropically, converged at $R = 5{\cdot}8\%$ ($R' = 0{\cdot}5\%$), there being an 11-fold excess of data over parameters.

The structure (Figure), is of inorganic elegance. Most of the bond lengths shown have standard deviations ~0·005 Å. The short hydrogen bond has O(2)···O(2′) = 2·459 (7) Å. The infrared spectrum of the salt resembles those of type A acid salts.[2]

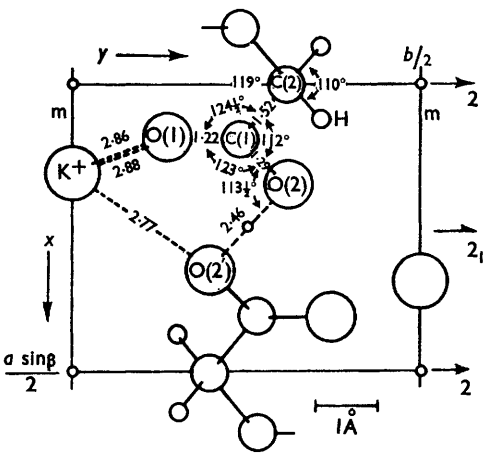

FIGURE. *The crystal structure of potassium hydrogen malonate as seen in its c-axial projection.* (Bond lengths are given in Å, and certain bond-angles are also shown. The smallest circles represent centres of inversion.)

Further refinement is to be done with data out to $\theta = 34°$. Neutron-diffraction data are also being collected. We have found several other acid salts of dibasic acids homologous to malonic with similarly symmetrised structures which will also be studied.

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† Program developed by D. W. J. Cruickshank, J. G. F. Smith, and J. G. Sime for KDF 9.

[1] J. C. Speakman, *Chem. Comm.*, 1967, 32.
[2] *E.g.*, H. N. Shrivastava and J. C. Speakman, *J. Chem. Soc.*, 1961, 1151.