Crystal Structure of Potassium Tri-hydrogen Di-malonate: a Neutron Diffraction Study

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Summary Potassium tri-hydrogen di-malonate is an acid salt of Type B_2, and has three very short, but unsymmetrical hydrogen bonds; two of these, with O · · · O = 2·543(8) and 2·554(7) Å respectively, are intermolecular, whilst the third, with O · · · O = 2·513(9) Å, is intramolecular, and completes a planar six-membered ring.

DURING the preparation of the acid salt potassium hydrogen malonate (KHM), which has been studied by both *X*-ray[1] and neutron[2] diffraction, crystals of a second salt, potassium tri-hydrogen di-malonate (KH_3M_2) were produced. The crystal structure of this salt, which has a Type B_2 i.r. spectrum free from the anomalies shown in the Type A_2 spectrum of KHM itself,[1] has now been determined.

Crystal data: $KH_3(C_3H_2O_4)_2$, $M = 244{\cdot}2$, Monoclinic, $a = 8{\cdot}489(6)$, $b = 12{\cdot}201(11)$, $c = 9{\cdot}658(7)$ Å, $\beta = 108°10'$ ($\pm 4'$), $U = 950{\cdot}22$ Å^3, $Z = 4$, $D_c = 1{\cdot}706$. Space group $P2_1/c$ (C_{2h}^5); no molecular symmetry required.

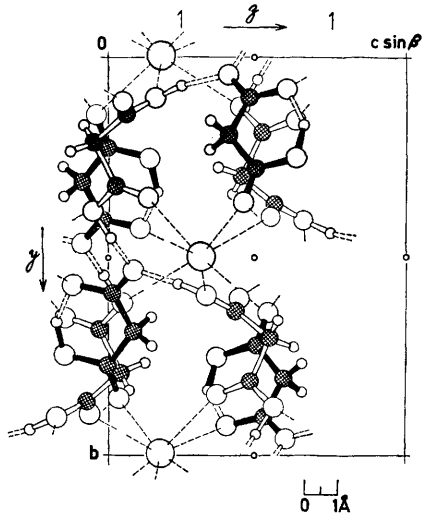

FIGURE. *The crystal structure as seen in the* a*-axial projection. In order of decreasing size the open circles represent* K$^+$, O, *and* H; *the hatched,* C.

The structure was solved by direct methods using *X*-ray data. Neutron-diffraction data were collected on a four-circle diffractometer in the DIDO reactor at A.E.R.E., Harwell, and after least-squares refinement with anisotropic vibrational parameters *R* was 0·079 for the 1051 reflexions with $|F_0| > 3\sigma(F_0)$.

The structure is shown in the Figure. Two different H_2M molecules are linked through intermolecular O–H · · · O hydrogen bonds to one atom of the HM^- residue, which itself has an intramolecular hydrogen bond. Some dimensions in the malonate residues are as follows:

The hydrogen bonds are all very short and unsymmetrical. In the intermolecular bonds O · · · O = 2·543(8) and 2·554(7) Å, O–H = 1·050(12) and 1·018(10) Å, and O–H · · · O = 172° and 163°, respectively. Of particular interest, however, is the much less common intramolecular bond, which has O · · · O = 2·513(9) Å, O–H = 1·033(14) Å and O–H · · · O = 155°, the O–H bond and H · · · O contact

TABLE

	C=O[a]	C–O(H)[a]	C–C=O[b]	C–C–O(H)[b]
HM^-	1·243(6)		120·0	
	1·260(6)		116·8	
	1·219(7)	1·318(7)	121·2	117·8
H_2M	1·205(8)	1·318(8)	124·3	111·7
	1·219(5)	1·320(7)	123·8	112·0

[a] Distances in Å. [b] Angles in degrees.

each forming one side of an almost planar six-membered ring (a similar situation is found in salicylic acid).[3] This may be contrasted with the symmetrical hydrogen bond in potassium hydrogen chloromaleate,[4] which has O · · · O = 2·403(3) Å and O–H · · · O = 175·4°; in this case the O · · · O contact forms one side of a six-membered ring, thus accounting for the shortness and almost complete linearity of the bond.

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