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Racemic Potassium Hydrogen 1-Malate Monohydrate, $KH[C_4H_4O_5].H_2O$

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Abstract. $M_r = 190{\cdot}2$, monoclinic, Cc, $a = 8{\cdot}592$ (2), $b = 13{\cdot}009$ (6), $c = 7{\cdot}234$ (1) Å, $\beta = 118{\cdot}63$ (2)°, $V = 595{\cdot}7$ Å^3, $Z = 4$, $D_x = 2{\cdot}12$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1{\cdot}284$ mm^{-1}, room temperature. $R_w = 0{\cdot}029$ for 758 observed reflections. The OOC–CH$_2$–CHOH–COO chain has the *trans* conformation.

Introduction. In the course of our research on malic acid and its derivatives we investigated the structure of potassium hydrogen (±)-1-malate monohydrate. The conformation of the singly ionized hydrogen malates (Van Havere & Lenstra, 1980) was shown to be unstable towards incorporation of various counter ions into the crystal lattice. So far, such information can only be obtained from experiment, since a model is still lacking to predict the conformation (*gauche* or *trans*) of the OOC–CH$_2$–CHOH–COO chain as a function of the chemical and crystal environment.

Experimental. Crystals grown at room temperature by slow evaporation of an aqueous solution, 3 × 0·1 × 0·15 mm, Enraf–Nonius CAD-4 diffractometer, Zr-filtered Mo radiation, 774 total intensities measured using a pure ω-scan up to a glancing angle θ of 25°, 758 observed with $I > 2\sigma(I)$; structure solved through Patterson function and heavy-atom Fourier analysis, all H atoms determined from difference electron density functions; structure refined by a least-squares procedure with a Gauss–Seidel algorithm (Sparks, 1974), $w = 1/\sigma^2(F)$ where $\sigma(F)$ is based on counting statistics, $R_w = 0{\cdot}029$; in view of crystal size and μ absorption correction not applied, no extinction parameter, maximum noise level in the final difference Fourier map 0·15e Å^{-3}, largest shift/error 0·23; atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974), $F(000) = 392$.

Discussion. Refined parameters* are listed in Table 1; the atomic numbering and the packing are depicted in Fig. 1.

Table 1. *Positional parameters as fractions of the cell edges, with e.s.d.'s in parentheses, and isotropic thermal parameters*

Isotropic temperature parameters (Å^2) of non-H atoms are calculated from anisotropic thermal parameters according to Lipson & Cochran (1968) [$B_{\rm iso} = 8\pi^2(U^\circ_{11}U^\circ_{22}U^\circ_{33})^{1/3}$], assuming equal volume of the 50% probability region. All anisotropic thermal parameters are physically acceptable. H(j,x)(j = 1,2,3) is attached to atom x. Isotropic temperature factors of H atoms were fixed at 3·0 Å^2. E.s.d.'s are about 0·2 Å^2.

	x	y	z	$B_{\rm iso}$
K	0·0000	0·05531 (8)	0·0000	2·46
O(1)	0·6702 (4)	0·3938 (3)	0·2937 (5)	2·69
O(2)	0·8544 (5)	0·2607 (3)	0·4072 (5)	2·28
O(3)	0·8471 (4)	0·2666 (3)	−0·2541 (5)	2·60
O(4)	1·0198 (5)	0·4037 (3)	−0·1766 (5)	2·95
O(5)	0·6007 (4)	0·3636 (3)	−0·1080 (4)	2·08
C(1)	0·7550 (5)	0·3257 (4)	0·2673 (6)	1·94
C(2)	0·7493 (5)	0·3124 (3)	0·0532 (6)	1·76
C(3)	0·9154 (5)	0·3584 (4)	0·0623 (6)	2·09
C(4)	0·9305 (5)	0·3443 (4)	−0·1358 (7)	1·98
O(*W*1)	1·2357 (5)	0·5424 (3)	0·1289 (6)	3·01
H(O3)	0·892 (7)	0·267 (4)	0·605 (8)	
H(O5)	0·513 (7)	0·330 (4)	−0·112 (8)	
H(1,C1)	0·736 (7)	0·235 (5)	0·015 (8)	
H(1,C3)	0·919 (7)	0·438 (4)	0·079 (9)	
H(2,C3)	1·026 (7)	0·330 (5)	0·173 (8)	
H(1,O*W*)	1·158 (8)	0·584 (5)	0·187 (9)	
H(2,O*W*)	1·143 (7)	0·497 (5)	0·022 (8)	

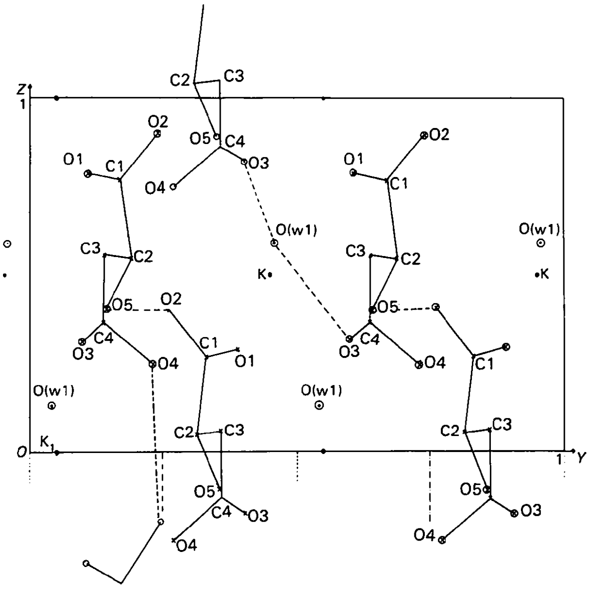

Fig. 1. The crystal packing and numbering of atoms in the title compound.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38191 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Bond lengths (Å) and valence angles (°) with e.s.d.'s in parentheses*

C(1)—O(1)	1·219 (2)	C(4)—O(4)	1·220 (2)
C(1)—O(2)	1·280 (2)	C(4)—O(3)	1·297 (2)
C(1)—C(2)	1·536 (2)	⟨C—H⟩	1·02 (2)
C(2)—O(5)	1·417 (2)	O(5)—H	0·85 (2)
C(2)—C(3)	1·519 (2)	⟨O(*W*)—H⟩	1·04 (2)
C(3)—C(4)	1·511 (2)		
O(1)—C(1)—O(2)	125·3 (1)	C(3)—C(4)—O(4)	120·1 (1)
O(1)—C(1)—C(2)	120·5 (1)	C(3)—C(4)—O(3)	116·7 (1)
O(2)—C(1)—C(2)	114·2 (1)	O(3)—C(4)—O(4)	123·2 (1)
C(1)—C(2)—O(5)	110·9 (1)	⟨H—C—O⟩	105 (1)
C(1)—C(2)—C(3)	109·7 (1)	⟨H—C—C⟩	109 (1)
C(3)—C(2)—O(5)	107·9 (1)	H—O(*W*)—H	100 (2)
C(2)—C(3)—C(4)	114·6 (1)		

Table 3. *Distances (Å) and angles (°) in the potassium coordination with e.s.d.'s in parentheses*

K—O(1^{i})	2·844 (1)	K—O($W1^{iv}$)	2·843 (1)
K—O(1^{ii})	2·626 (1)	K—O($W1^{v}$)	2·852 (1)
K—O(5^{i})	2·868 (1)	K—O(3^{vi})	3·216 (1)
K—O(5^{iii})	2·748 (1)		
O(1^{i})—K—O(1^{ii})	112·6 (1)	O(1^{ii})—K—O($W1^{iv}$)	162·0 (1)
O(1^{i})—K—O(5^{i})	56·4 (1)	O(1^{ii})—K—O($W1^{v}$)	89·2 (1)
O(1^{i})—K—O(5^{iii})	73·6 (1)	O(1^{i})—K—O(5^{iii})	128·9 (1)
O(1^{i})—K—O($W1^{iv}$)	85·2 (1)	O(5^{i})—K—O($W1^{iv}$)	115·5 (1)
O(1^{i})—K—O($W1^{v}$)	105·5 (1)	O(5^{i})—K—O($W1^{v}$)	64·2 (1)
O(1^{i})—K—O(5^{i})	75·0 (1)	O($W1^{iv}$)—K—O($W1^{v}$)	83·2 (1)
O(1^{ii})—K—O(5^{iii})	120·3 (1)		

Symmetry code: (i) $-\frac{1}{2}+x,-\frac{1}{2}+y,z$; (ii) $-\frac{1}{2}+x,\frac{1}{2}-y,-\frac{1}{2}+z$; (iii) $-\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; (iv) $-\frac{3}{2}+x,-\frac{1}{2}+y,z$; (v) $-\frac{3}{2}+x,\frac{1}{2}-y,-\frac{1}{2}+z$; (vi) $-1+x,y,z$.

Table 4. *Hydrogen-bonding scheme in the title compound*

D: donor, *A*: acceptor.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
O(3)—H(O3)···O(2^{i})	1·25 (2)	1·31 (2)	2·482 (2)	152 (2)
O(*W*1)—H(1,O*W*1)···O(3^{ii})	1·00 (2)	1·79 (2)	2·765 (2)	166 (2)
O(*W*1)—H(2,O*W*1)···O(3^{iii})	1·09 (2)	1·88 (2)	2·901 (2)	155 (2)
O(5)—H(O5)···O(2^{iv})	0·85 (2)	1·86 (2)	2·707 (2)	170 (2)

Symmetry code: (i) $x,y,-1+z$; (ii) x,y,z; (iii) $x,1-y,\frac{1}{2}+z$; (iv) $\frac{1}{2}+x,\frac{1}{2}-y,-\frac{1}{2}+z$.

The conformation in the OOC—CH$_2$—CHOH—COO chain is *trans* with torsion angles C(1)C(2)C(3)C(4) and O(5)C(2)C(3)C(4) of 176·3 and −62·5° respectively.

Bond lengths and valence angles are listed in Table 2. Comparing these values with those found in the corresponding ammonium hydrogen (±)-1-malate monohydrate (Van Loock, Van Hooste & Lenstra, 1981) one finds a similarity. All ammonium H atoms participate in the hydrogen-bonding scheme of the latter compound. Obviously, such hydrogen bridges are not present in the title compound.

Nevertheless the internal geometry of the hydrogen malate moiety has not changed. Moreover the two compounds can be regarded as isomorphous structures, in spite of the difference of 0·1 Å between the ionic radii of NH$_4^+$ and K$^+$.

The K$^+$ ion is coordinated by six O atoms. A seventh, long-range Coulomb interaction links the K$^+$ ion to O(3) of a neighbouring hydrogen malate moiety. Relevant data are listed in Table 3. The packing of the structure is based on Coulomb interactions and hydrogen bonding, the latter being summarized in Table 4. In particular O(3)—H···O(2) is very short (2·48 Å) and stabilizes the structure.

Within this bridge it is hardly possible to discriminate between the donor and acceptor atom. This is also reflected in the similarity between the C—O carboxyl distances at the two ends of the molecule. The data do not determine which COOH group is ionized, although the C(1)OO group, activated by the α-hydroxyl at C(2), would be the most likely acceptor and ionized group. Arguments that this is the case can be found in the geometry of the isomorphous ammonium hydrogen (±)-malate (Van Loock *et al.*, 1981).

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