

A second C-centred monoclinic modification of racemic potassium hydrogen malate monohydrate

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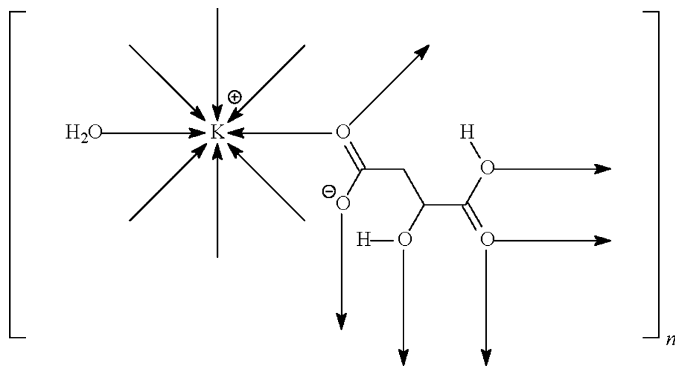
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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.034; wR factor = 0.124; data-to-parameter ratio = 8.8.

The K^+ cation in the racemic title compound, poly[aqua- μ_6 -malato-potassium(I)], $[\text{K}(\text{C}_4\text{H}_5\text{O}_5)(\text{H}_2\text{O})]_n$, exists in an irregular eight-coordinate environment. The anions are linked through hydrogen bonds into a three-dimensional network. The coordination environment differs from the six-coordinate environment reported in another C-centred monoclinic modification [Geise, van Loock & Lenstra (1983). *Acta Cryst. C* **39**, 69–70].

Related literature

For the first C-centred monoclinic modification, see: Geise *et al.* (1983).



Experimental

Crystal data

$[\text{K}(\text{C}_4\text{H}_5\text{O}_5)(\text{H}_2\text{O})]$
 $M_r = 190.20$
 Monoclinic, C_c
 $a = 10.534$ (1) Å
 $b = 10.494$ (1) Å
 $c = 7.5640$ (8) Å
 $\beta = 120.801$ (1)°

$V = 718.19$ (13) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.72$ mm⁻¹
 $T = 291$ (2) K
 $0.42 \times 0.21 \times 0.15$ mm

Data collection

Bruker APEX area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.717$, $T_{\max} = 0.900$

1561 measured reflections
 876 independent reflections
 839 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.014$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.124$
 $S = 1.19$
 876 reflections
 100 parameters
 2 restraints

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.41$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³
 Absolute structure: Flack (1983), with 82 Friedel pairs
 Flack parameter: -0.1 (1)

Table 1

Selected bond lengths (Å).

K1—O1	2.972 (4)	K1—O4 ^{iv}	2.671 (4)
K1—O2 ⁱ	2.858 (4)	K1—O4 ⁱⁱⁱ	2.740 (4)
K1—O2 ⁱⁱ	2.689 (4)	K1—O5 ^v	2.876 (4)
K1—O3 ⁱⁱⁱ	3.094 (4)	K1—O6	3.038 (5)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3—H3 ⁱ ···O6 ^{vi}	0.82	2.13	2.607 (5)	117
O5—H5 ⁱ ···O1 ^{vii}	0.82	1.70	2.491 (5)	160
O6—H61 ⁱ ···O1 ^{viii}	0.82	2.34	2.831 (6)	119
O6—H62 ⁱ ···O3	0.82	2.27	2.815 (6)	124

Symmetry codes: (vi) $x, -y + 1, z - \frac{1}{2}$; (vii) $x, y, z - 1$; (viii) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.

Data collection: SMART (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: publCIF (Westrip, 2007).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2280).

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supplementary materials

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Comment

In the previous C-centered monoclinic modification of racemic potassium hydrogen malate hydrate (Geize *et al.*, 1983), the potassium atom is in an octahedron of oxygen atoms, and for the carboxylate anion the ionized and un-ionized groups cannot be distinguished. In the present C-centered monoclinic modification, the potassium atom exists in an irregular, eight-coordinate environment (Table 1). The anion features unambiguous ionized and un-ionized groups; interestingly, the double-bond oxygen atom of the ionized group is the oxygen atom that is closest to potassium despite being involved in another bridging interaction.

Experimental

DL-Malic acid (27 mg, 0.2 mmol) was mixed with potassium hydroxide (12 mg, 0.2 mmol) in water (10 ml) to give a blue solution. Slow evaporation of the solution gave colorless prismatic crystals.

Refinement

Carbon- and oxygen-bound H atoms were positioned geometrically (C–H 0.97 – 0.97, O–H 0.82 Å), and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H})$ set to 1.2 or $1.5U_{\text{eq}}(\text{C}, \text{O})$.

The Flack parameter was refined from 82 Friedel pairs.

Figures

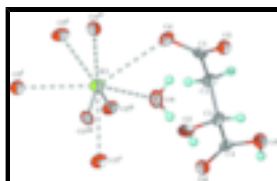


Fig. 1. **Figure 1.** Thermal ellipsoid plot of potassium hydrogen malate hydrate; displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms as spheres of arbitrary radius. [Symmetry codes are given in Table 1.]

poly[aqua- μ_6 -malato-potassium(I)]

Crystal data

[K(C₄H₅O₅)(H₂O)]

$M_r = 190.20$

Monoclinic, *Cc*

Hall symbol: C -2yc

$a = 10.534(1)$ Å

$F_{000} = 392$

$D_x = 1.759$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1338 reflections

$\theta = 3.0\text{--}27.0^\circ$

supplementary materials

$b = 10.494 (1) \text{ \AA}$
 $c = 7.5640 (8) \text{ \AA}$
 $\beta = 120.801 (1)^\circ$
 $V = 718.19 (13) \text{ \AA}^3$
 $Z = 4$

$\mu = 0.72 \text{ mm}^{-1}$
 $T = 291 (2) \text{ K}$
Prism, colorless
 $0.42 \times 0.21 \times 0.15 \text{ mm}$

Data collection

Bruker APEX area-detector diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
 $T = 291(2) \text{ K}$
 φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.717, T_{\max} = 0.900$
1561 measured reflections

876 independent reflections
839 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.014$
 $\theta_{\text{max}} = 27.0^\circ$
 $\theta_{\text{min}} = 2.9^\circ$
 $h = -13 \rightarrow 10$
 $k = -13 \rightarrow 11$
 $l = -3 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.124$
 $S = 1.19$
876 reflections
100 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0732P)^2 + 2.0212P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
Extinction correction: none
Absolute structure: Flack (1983), 82 Friedel pairs
Flack parameter: $-0.1 (1)$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	0.50000 (12)	0.56252 (10)	0.50000 (14)	0.0192 (3)
O1	0.6110 (4)	0.8267 (4)	0.5299 (6)	0.0203 (8)
O2	0.8346 (4)	0.8883 (4)	0.5947 (6)	0.0203 (8)
O3	0.7334 (4)	0.6285 (3)	0.3048 (6)	0.0202 (8)
H3	0.8143	0.5933	0.3621	0.030*
O4	0.6024 (4)	0.6425 (4)	-0.1149 (6)	0.0214 (8)
O5	0.7244 (4)	0.8251 (3)	-0.0892 (6)	0.0212 (8)
H5	0.6844	0.8079	-0.2120	0.032*
O6	0.8351 (5)	0.5749 (4)	0.7211 (7)	0.0273 (9)
H61	0.8632	0.6450	0.7751	0.041*

H62	0.8621	0.5636	0.6381	0.041*
C1	0.7049 (6)	0.8543 (5)	0.4753 (8)	0.0158 (10)
C2	0.6503 (6)	0.8418 (5)	0.2466 (8)	0.0163 (10)
H2A	0.6570	0.9236	0.1921	0.020*
H2B	0.5477	0.8151	0.1729	0.020*
C3	0.7450 (6)	0.7435 (5)	0.2164 (7)	0.0163 (11)
H3A	0.8482	0.7717	0.2860	0.020*
C4	0.6835 (6)	0.7304 (5)	-0.0148 (8)	0.0153 (10)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0231 (5)	0.0221 (5)	0.0108 (5)	0.0012 (5)	0.0076 (4)	-0.0016 (5)
O1	0.0222 (18)	0.0286 (19)	0.0117 (18)	0.0017 (16)	0.0098 (16)	0.0009 (15)
O2	0.0234 (19)	0.0249 (18)	0.0124 (18)	-0.0062 (16)	0.0092 (16)	-0.0031 (16)
O3	0.027 (2)	0.0168 (16)	0.017 (2)	0.0058 (15)	0.0117 (17)	0.0033 (14)
O4	0.0211 (19)	0.0282 (19)	0.0129 (18)	-0.0082 (16)	0.0072 (16)	-0.0055 (15)
O5	0.026 (2)	0.0260 (19)	0.0121 (17)	-0.0078 (16)	0.0097 (16)	-0.0032 (15)
O6	0.030 (2)	0.032 (2)	0.022 (2)	-0.0099 (19)	0.0149 (18)	-0.0025 (18)
C1	0.024 (3)	0.009 (2)	0.014 (3)	0.0053 (18)	0.009 (2)	0.0013 (17)
C2	0.017 (2)	0.020 (2)	0.010 (2)	0.003 (2)	0.006 (2)	0.0007 (19)
C3	0.015 (2)	0.025 (2)	0.009 (3)	-0.0009 (19)	0.007 (2)	0.000 (2)
C4	0.019 (2)	0.017 (2)	0.014 (2)	0.0032 (19)	0.011 (2)	0.0000 (18)

Geometric parameters (\AA , $^\circ$)

K1—O1	2.972 (4)	O4—C4	1.222 (6)
K1—O2 ⁱ	2.858 (4)	O4—K1 ^{ix}	2.671 (4)
K1—O2 ⁱⁱ	2.689 (4)	O4—K1 ^{viii}	2.740 (4)
K1—O3 ⁱⁱⁱ	3.094 (4)	O5—C4	1.318 (6)
K1—O4 ^{iv}	2.671 (4)	O5—K1 ^x	2.876 (4)
K1—O4 ⁱⁱⁱ	2.740 (4)	O5—H5	0.8200
K1—O5 ^v	2.876 (4)	O6—H61	0.8200
K1—O6	3.038 (5)	O6—H62	0.8200
O1—C1	1.285 (7)	C1—C2	1.524 (7)
O2—C1	1.243 (6)	C2—C3	1.531 (7)
O2—K1 ^{vi}	2.689 (4)	C2—H2A	0.9700
O2—K1 ^{vii}	2.858 (4)	C2—H2B	0.9700
O3—C3	1.415 (7)	C3—C4	1.529 (6)
O3—K1 ^{viii}	3.094 (4)	C3—H3A	0.9800
O3—H3	0.8200		
O4 ^{iv} —K1—O2 ⁱⁱ	147.89 (13)	K1 ^{vi} —O2—K1 ^{vii}	92.34 (12)
O4 ^{iv} —K1—O4 ⁱⁱⁱ	126.01 (15)	C3—O3—K1 ^{viii}	115.4 (3)
O2 ⁱⁱ —K1—O4 ⁱⁱⁱ	85.38 (12)	C3—O3—H3	108.4
O4 ^{iv} —K1—O2 ⁱ	83.42 (12)	K1 ^{viii} —O3—H3	108.4
O2 ⁱⁱ —K1—O2 ⁱ	106.65 (14)	C4—O4—K1 ^{ix}	132.6 (3)

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O4 ⁱⁱⁱ —K1—O2 ⁱ	88.08 (13)	C4—O4—K1 ^{viii}	131.3 (4)
O4 ^{iv} —K1—O5 ^v	85.55 (12)	K1 ^{ix} —O4—K1 ^{viii}	95.41 (12)
O2 ⁱⁱ —K1—O5 ^v	70.55 (11)	C4—O5—K1 ^x	136.1 (3)
O4 ⁱⁱⁱ —K1—O5 ^v	139.62 (12)	C4—O5—H5	103.1
O2 ⁱ —K1—O5 ^v	69.48 (12)	K1 ^x —O5—H5	103.1
O4 ^{iv} —K1—O1	72.57 (11)	K1—O6—H61	109.5
O2 ⁱⁱ —K1—O1	84.69 (12)	K1—O6—H62	109.5
O4 ⁱⁱⁱ —K1—O1	123.58 (12)	H61—O6—H62	109.5
O2 ⁱ —K1—O1	147.59 (12)	O2—C1—O1	124.9 (5)
O5 ^v —K1—O1	86.90 (11)	O2—C1—C2	119.0 (5)
O4 ^{iv} —K1—O6	71.32 (12)	O1—C1—C2	116.1 (5)
O2 ⁱⁱ —K1—O6	120.74 (12)	C1—C2—C3	109.3 (4)
O4 ⁱⁱⁱ —K1—O6	70.91 (12)	C1—C2—H2A	109.8
O2 ⁱ —K1—O6	125.09 (12)	C3—C2—H2A	109.8
O5 ^v —K1—O6	149.39 (12)	C1—C2—H2B	109.8
O1—K1—O6	67.50 (11)	C3—C2—H2B	109.8
O4 ^{iv} —K1—O3 ⁱⁱⁱ	70.60 (11)	H2A—C2—H2B	108.3
O2 ⁱⁱ —K1—O3 ⁱⁱⁱ	141.05 (12)	O3—C3—C4	112.1 (4)
O4 ⁱⁱⁱ —K1—O3 ⁱⁱⁱ	55.67 (11)	O3—C3—C2	106.5 (4)
O2 ⁱ —K1—O3 ⁱⁱⁱ	75.66 (11)	C4—C3—C2	107.7 (4)
O5 ^v —K1—O3 ⁱⁱⁱ	139.64 (12)	O3—C3—H3A	110.1
O1—K1—O3 ⁱⁱⁱ	114.59 (11)	C4—C3—H3A	110.1
O6—K1—O3 ⁱⁱⁱ	50.32 (11)	C2—C3—H3A	110.1
C1—O1—K1	121.6 (3)	O4—C4—O5	125.6 (5)
C1—O2—K1 ^{vi}	135.4 (3)	O4—C4—C3	121.9 (5)
C1—O2—K1 ^{vii}	125.8 (3)	O5—C4—C3	112.4 (4)
O4 ^{iv} —K1—O1—C1	127.0 (4)	O1—C1—C2—C3	-119.5 (5)
O2 ⁱⁱ —K1—O1—C1	-76.0 (4)	K1 ^{viii} —O3—C3—C4	-21.2 (5)
O4 ⁱⁱⁱ —K1—O1—C1	4.9 (4)	K1 ^{viii} —O3—C3—C2	96.4 (4)
O2 ⁱ —K1—O1—C1	171.0 (3)	C1—C2—C3—O3	57.7 (5)
O5 ^v —K1—O1—C1	-146.7 (4)	C1—C2—C3—C4	178.1 (4)
O6—K1—O1—C1	50.5 (4)	K1 ^{ix} —O4—C4—O5	12.0 (8)
O3 ⁱⁱⁱ —K1—O1—C1	68.7 (4)	K1 ^{viii} —O4—C4—O5	-179.5 (3)
K1 ^{viii} —K1—O1—C1	-33.2 (4)	K1 ^{ix} —O4—C4—C3	-170.3 (3)
K1 ^{vi} —O2—C1—O1	-3.5 (8)	K1 ^{viii} —O4—C4—C3	-1.8 (7)
K1 ^{vii} —O2—C1—O1	-147.1 (4)	K1 ^x —O5—C4—O4	-126.8 (5)
K1 ^{vi} —O2—C1—C2	177.4 (3)	K1 ^x —O5—C4—C3	55.3 (6)
K1 ^{vii} —O2—C1—C2	33.8 (6)	O3—C3—C4—O4	17.0 (7)
K1—O1—C1—O2	-112.4 (5)	C2—C3—C4—O4	-99.9 (6)
K1—O1—C1—C2	66.7 (5)	O3—C3—C4—O5	-165.0 (4)
O2—C1—C2—C3	59.7 (6)	C2—C3—C4—O5	78.1 (5)

Symmetry codes: (i) $x-1/2, y-1/2, z$; (ii) $x-1/2, -y+3/2, z-1/2$; (iii) $x, -y+1, z+1/2$; (iv) $x, y, z+1$; (v) $x-1/2, -y+3/2, z+1/2$; (vi) $x+1/2, -y+3/2, z+1/2$; (vii) $x+1/2, y+1/2, z$; (viii) $x, -y+1, z-1/2$; (ix) $x, y, z-1$; (x) $x+1/2, -y+3/2, z-1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3 \cdots O6 ^{viii}	0.82	2.13	2.607 (5)	117
O5—H5 \cdots O1 ^{ix}	0.82	1.70	2.491 (5)	160
O6—H61 \cdots O1 ^{vi}	0.82	2.34	2.831 (6)	119
O6—H62 \cdots O3	0.82	2.27	2.815 (6)	124

Symmetry codes: (viii) $x, -y+1, z-1/2$; (ix) $x, y, z-1$; (vi) $x+1/2, -y+3/2, z+1/2$.

Fig. 1

