

Potassium hydrogen *trans*-glutaconate monohydrate at 295, 245 and 40 K, and its rubidium analogue at 298 K

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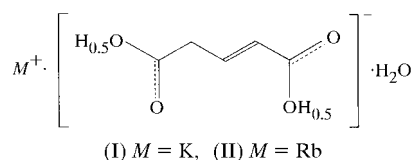
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A centrosymmetric and short O—H...O hydrogen bond was found in isomorphous crystals of potassium hydrogen *trans*-glutaconate monohydrate (potassium hydrogen *trans*-pent-2-ene-1,5-dioate, $K^+ \cdot C_5H_5O_4 \cdot H_2O$), (I), and rubidium hydrogen *trans*-glutaconate monohydrate (rubidium hydrogen *trans*-pent-2-ene-1,5-dioate, $Rb^+ \cdot C_5H_5O_4 \cdot H_2O$), (II). The O...O distance at room temperature is 2.444 (3) Å in (I), and 2.417 (4) Å in (II). The O...O distance for (I) showed no significant decrease at low temperatures.

Comment

In the crystals of sodium and ammonium hydrogen *trans*-glutaconate, an asymmetric O—H...O hydrogen bond is formed between the carboxyl and carboxylate groups of neighbouring anions (Taka & Kashino, 1999). We report here on a symmetric and short O—H...O hydrogen bond formed in potassium hydrogen *trans*-glutaconate monohydrate, (I). The effect of temperature on the O...O distance has been examined for (I) by crystal structure determination at room and low temperatures. The structure of rubidium hydrogen monohydrate, (II), has been determined at room temperature to investigate the effect of chemical substitution.



In (I), the carboxyl groups at both ends of the acid moiety are ionized with an equal probability of 0.5 (Fig. 1). A chain of the anions is formed along $[1\bar{1}1]$ by two O—H...O hydrogen bonds lying on inversion centres at $(\frac{1}{2}, 0, 1)$ and $(0, \frac{1}{2}, 0)$ in a manner similar to that found in ammonium hydrogen succinate (Hirano *et al.*, 1996; Kashino *et al.*, 1998) (Fig. 3 and

Table 2). The chains related by a translation along the c axis are linked by hydrogen bonds through a water molecule. A K^+ cation is coordinated by five anion O atoms and two water molecule O atoms. The K^+ cations related by the c translation are bridged by three O atoms (Table 1).

The structure of (II) (Fig. 2) is isomorphous with (I). The $Rb^+ \cdots O$ distances averaged for the first coordination sphere are longer by 0.12 Å compared with the $K^+ \cdots O$ distances in (I) (Tables 1 and 7). The O...O distances of the hydrogen bonds involving the water molecule in (II) are significantly shorter than those in (I) (Tables 2 and 8). The distances of $O1 \cdots O1^x$ [symmetry code: (x) $1 - x, -y, 2 - z$], 2.455 (5) Å, and $O4 \cdots O4^{xi}$ [symmetry code: (xi) $-x, 1 - y, -z$], 2.417 (4) Å, in (II) are also shorter than the corresponding distances in (I) at room temperature (Table 2).

Difference scanning calorimetry (DSC) measurements for (I) showed a weak and broad endothermic peak [$\Delta H = 90$ (10) $J mol^{-1}$] over 260 to 270 K in the heating step. An anomaly in the temperature dependence of the lattice constants was observed from 230 to 270 K corresponding to the result of the DSC measurement. However, the reflection data were not collected in this temperature range to avoid the crystal deterioration accompanied by the phase transition, and the nature of the phase transition was not elucidated. The structures at low temperatures could only be refined based on the same space group as that at room temperature. No structural anomaly was detected at low temperatures. Neither

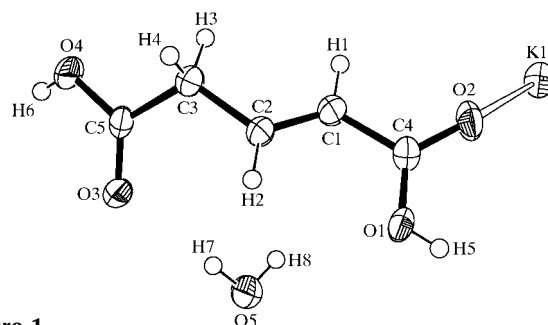


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of the asymmetric unit of (I) at 295 K with the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The occupancy factor for the H5 and H6 atoms is 0.5.

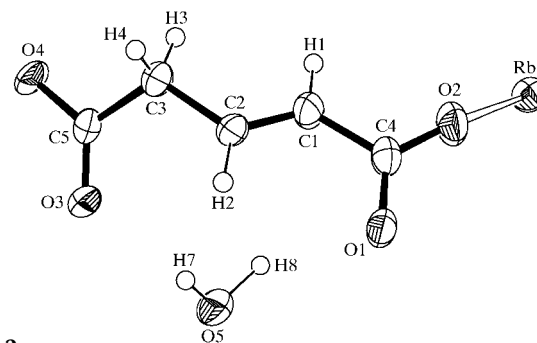
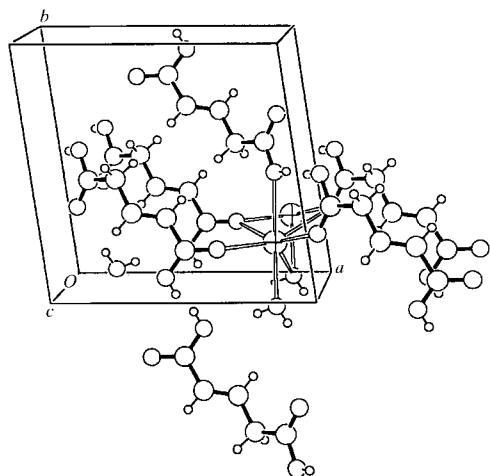


Figure 2
ORTEP-3 (Farrugia, 1997) drawing of the asymmetric unit of (II) with the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The H atom attached to the carboxyl group is not shown because it was not found in a difference Fourier map.

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Figure 3

The arrangement of the anions and the coordination around the cation based on the atomic parameters of (I) at 295 K.

the systematic absences which might occur for a monoclinic centred lattice, nor the superstructure reflections which might occur after a second-order phase transition were observed at 40 K.

In (I), the $K^+ \cdots O$ distances and hydrogen-bond $O \cdots O$ distances involving the water molecule decrease with a decrease in temperature (Tables 1–6). On the other hand, the temperature dependence of the $O1 \cdots O1^{ii}$ and $O4 \cdots O4^{iii}$ distances is small, showing that any librational effects on these distances are small. The latter distance is one of the shortest observed for hydrogen bonds in the acid salts of carboxylic acids (Misaki *et al.*, 1986; Kalsbeek & Larsen, 1991).

Difference Fourier maps calculated at 295 and 40 K by including all refined atoms show peaks with residual electron densities of 0.29 and 0.20 $e \text{ \AA}^{-3}$, respectively, on the inversion centre at $(0, \frac{1}{2}, 0)$ near O4. Least-squares refinements constrained the H-atom position to the inversion centre giving almost the same values for R , wR and S as the unconstrained refinements, and resulted in $U_{iso} = 0.110$ (10) and 0.15 (2) \AA^2 for the H atom at 295 and 40 K, respectively, although the U_{iso} values are higher than those determined by the unconstrained refinements [0.016 (8) and 0.10 (2) \AA^2 at 295 and 40 K, respectively]. This evidence suggests that the H atom involved in the hydrogen bond lies in a single-minimum potential well as confirmed for a symmetric hydrogen bond [$O \cdots O$ 2.4321 (8) \AA at 136 K] in dimethylammonium hydrobis(squarate) (Lin *et al.*, 1994). There is a possibility that the H-atom position obtained by the unconstrained refinement is shifted from the inversion centre by the influence of polarized electrons from O4.

Experimental

Crystals of (I) and (II) were grown by evaporation at room temperature from aqueous solutions of *trans*-glutaconic acid and the respective metal carbonates in a 2:1 molar ratio. A preliminary examination showed that the lattice constants of (I) could be converted to a centred triclinic lattice with $a = 13.021$ (4), $b = 15.018$ (4), $c = 4.068$ (2) \AA , $\alpha = 89.66$ (3), $\beta = 110.54$ (4), $\gamma = 90.34$ (3) $^\circ$ and $V = 744.9$ (3) \AA^3 . The intensity distribution for the converted cell

showed neither the Laue symmetry $2/m$ nor the systematic absences for a centred monoclinic lattice. Thus, the reflection data were collected based on the primitive triclinic lattice. A crystal of (I) was sealed in a glass capillary for X-ray diffraction measurement at low temperatures. A thermocouple was fixed on the capillary adjacent to the crystal. The temperature was regulated within ± 0.3 K using a closed-cycle He refrigerator (APD Cryogenics Inc., HC-2) equipped with a temperature controller (Chino, KP-1000). The cell constants were determined from 294 to 40 K from 24 reflections in $11.5 > \theta > 10^\circ$. The X-ray diffraction data at low temperatures were collected at 45 and 245 K. DSC measurements were carried out for (I) with cooling and heating rates of 10 K min^{-1} using a Perkin-Elmer DSC-7. The DSC curves were recorded in the range 173–323 K.

Compound (I) at 295 K

Crystal data

$K^+ \cdot C_5H_5O_4^- \cdot H_2O$
 $M_r = 186.21$
 Triclinic, $P\bar{1}$
 $a = 9.968$ (3) \AA
 $b = 9.909$ (4) \AA
 $c = 4.068$ (2) \AA
 $\alpha = 103.06$ (4) $^\circ$
 $\beta = 103.51$ (4) $^\circ$
 $\gamma = 98.15$ (3) $^\circ$
 $V = 372.5$ (3) \AA^3

$Z = 2$
 $D_x = 1.660 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 10.5\text{--}11.0^\circ$
 $\mu = 0.69 \text{ mm}^{-1}$
 $T = 295 \text{ K}$
 Prismatic, colourless
 $0.36 \times 0.15 \times 0.10 \text{ mm}$

Data collection

Rigaku AFC-5R diffractometer
 ω - 2θ scans
 Absorption correction: ψ scans
 (North *et al.*, 1968)
 $T_{min} = 0.901$, $T_{max} = 0.934$
 1807 measured reflections
 1707 independent reflections
 1658 reflections with $I > 0.1\sigma(I)$

$R_{int} = 0.018$
 $\theta_{max} = 27.5^\circ$
 $h = -12 \rightarrow 12$
 $k = -5 \rightarrow 12$
 $l = -5 \rightarrow 5$
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.051$
 $S = 1.74$
 1658 reflections
 132 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o) + 0.00002|F_o|^2]$
 $(\Delta/\sigma)_{max} = 0.01$
 $\Delta\rho_{max} = 0.29 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.32 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I) at 295 K.

K1–O2	2.7437 (17)	O2–C4	1.2343 (19)
K1–O5 ⁱ	2.804 (2)	O3–C5	1.225 (2)
K1–O4 ⁱⁱ	2.814 (2)	O4–C5	1.290 (2)
K1–O2 ⁱⁱⁱ	2.844 (2)	C1–C2	1.311 (2)
K1–O5 ^{iv}	2.869 (2)	C1–C4	1.482 (2)
K1–O3 ^v	2.924 (2)	C2–C3	1.488 (2)
K1–O3 ^{vi}	3.0250 (17)	C3–C5	1.508 (3)
O1–C4	1.284 (2)		
O2–K1–O2 ⁱⁱⁱ	93.42 (5)	C2–C1–C4	126.70 (18)
O2–K1–O3 ^{vi}	156.99 (4)	C1–C2–C3	123.15 (18)
O2–K1–O3 ^v	87.47 (5)	C2–C3–C5	117.17 (16)
O2–K1–O4 ⁱⁱ	85.10 (5)	O1–C4–O2	123.89 (17)
O2–K1–O5 ⁱ	130.94 (6)	O1–C4–C1	116.94 (16)
O2–K1–O5 ^{iv}	67.97 (5)	O2–C4–C1	119.16 (17)
K1–O2–K1 ^{viii}	93.42 (5)	O3–C5–O4	125.17 (16)
K1 ^{viii} –O3–K1 ^{ix}	86.27 (5)	O3–C5–C3	123.07 (16)
K1 ⁱ –O5–K1 ^{iv}	91.63 (6)	O4–C5–C3	111.76 (16)

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

Table 2
Hydrogen-bonding geometry (Å, °) for (I) at 295 K.

D—H...A	D—H	H...A	D...A	D—H...A
O5—H7...O3	0.82 (2)	2.13 (2)	2.939 (2)	171 (2)
O5—H8...O1 ⁱ	0.78 (2)	2.25 (2)	2.973 (2)	153 (2)
O1—H5...O1 ⁱⁱ	0.75 (3)	1.74 (3)	2.471 (3)	167 (4)
O4—H6...O4 ⁱⁱⁱ	0.72 (3)	1.73 (3)	2.444 (3)	172 (5)

Symmetry codes: (i) $x, y, z - 1$; (ii) $1 - x, -y, 2 - z$; (iii) $-x, 1 - y, -z$.

Compound (I) at 245 K

Crystal data

$K^+ \cdot C_5H_5O_4^- \cdot H_2O$
 $M_r = 186.21$
 Triclinic, $P\bar{1}$
 $a = 9.944 (2) \text{ \AA}$
 $b = 9.885 (2) \text{ \AA}$
 $c = 4.0314 (8) \text{ \AA}$
 $\alpha = 103.22 (2)^\circ$
 $\beta = 103.08 (2)^\circ$
 $\gamma = 98.44 (2)^\circ$
 $V = 367.4 (3) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.683 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 24 reflections
 $\theta = 10.5\text{--}11.5^\circ$
 $\mu = 0.69 \text{ mm}^{-1}$
 $T = 245 \text{ K}$
 Prismatic, colourless
 $0.49 \times 0.18 \times 0.13 \text{ mm}$

Data collection

Huber off-centre four-circle diffractometer
 ω -2 θ scans
 3039 measured reflections
 2709 independent reflections
 2455 reflections with $I > 0.1\sigma(I)$
 $R_{int} = 0.041$

$\theta_{max} = 33.0^\circ$
 $h = -16 \rightarrow 16$
 $k = -15 \rightarrow 15$
 $l = 0 \rightarrow 6$
 3 standard reflections every 97 reflections intensity decay: none

Table 3
Selected geometric parameters (Å, °) for (I) at 245 K.

K1—O2	2.726 (2)	O2—C4	1.236 (3)
K1—O5 ⁱ	2.787 (2)	O3—C5	1.236 (3)
K1—O4 ⁱⁱ	2.808 (2)	O4—C5	1.289 (3)
K1—O2 ⁱⁱⁱ	2.836 (2)	C1—C2	1.313 (3)
K1—O5 ^{iv}	2.845 (2)	C1—C4	1.486 (3)
K1—O3 ^v	2.913 (2)	C2—C3	1.491 (3)
K1—O3 ^{vi}	2.986 (2)	C3—C5	1.510 (4)
O1—C4	1.282 (3)		
O2—K1—O2 ⁱⁱⁱ	92.88 (6)	C2—C1—C4	126.4 (2)
O2—K1—O3 ^{vi}	156.41 (6)	C1—C2—C3	123.0 (2)
O2—K1—O3 ^v	87.40 (6)	C2—C3—C5	117.2 (2)
O2—K1—O4 ⁱⁱ	84.89 (6)	O1—C4—O2	123.9 (2)
O2—K1—O5 ⁱ	131.07 (6)	O1—C4—C1	117.1 (2)
O2—K1—O5 ^{iv}	68.61 (6)	O2—C4—C1	119.0 (2)
K1—O2—K1 ⁱⁱ	92.88 (6)	O3—C5—O4	124.8 (2)
K1 ^{viii} —O3—K1 ^{ix}	86.21 (5)	O3—C5—C3	123.1 (2)
K1 ⁱ —O5—K1 ^{iv}	91.41 (6)	O4—C5—C3	112.1 (2)

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

Table 4
Hydrogen-bonding geometry (Å, °) for (I) at 245 K.

D—H...A	D—H	H...A	D...A	D—H...A
O5—H7...O3	0.75 (3)	2.18 (3)	2.929 (3)	178 (3)
O5—H8...O1 ⁱ	0.94 (3)	2.08 (3)	2.948 (3)	153 (3)
O1—H5...O1 ⁱⁱ	0.80 (4)	1.68 (4)	2.465 (4)	169 (5)
O4—H6...O4 ⁱⁱⁱ	0.76 (7)	1.69 (6)	2.443 (4)	172 (9)

Symmetry codes: (i) $x, y, z - 1$; (ii) $1 - x, -y, 2 - z$; (iii) $-x, 1 - y, -z$.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.094$
 $wR(F^2) = 0.107$
 $S = 2.14$
 2455 reflections
 132 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o)]$
 $(\Delta/\sigma)_{max} = 0.03$
 $\Delta\rho_{max} = 0.95 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.90 \text{ e \AA}^{-3}$

Compound (I) at 40 K

Crystal data

$K^+ \cdot C_5H_5O_4^- \cdot H_2O$
 $M_r = 186.21$
 Triclinic, $P\bar{1}$
 $a = 9.927 (2) \text{ \AA}$
 $b = 9.866 (2) \text{ \AA}$
 $c = 4.0015 (8) \text{ \AA}$
 $\alpha = 103.40 (1)^\circ$
 $\beta = 102.77 (2)^\circ$
 $\gamma = 98.73 (2)^\circ$
 $V = 363.2 (3) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.703 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 24 reflections
 $\theta = 10.5\text{--}11.5^\circ$
 $\mu = 0.70 \text{ mm}^{-1}$
 $T = 40 \text{ K}$
 Prismatic, colourless
 $0.49 \times 0.18 \times 0.13 \text{ mm}$

Data collection

Huber off-centre four-circle diffractometer
 ω -2 θ scans
 3476 measured reflections
 3093 independent reflections
 2927 reflections with $I > 0.1\sigma(I)$
 $R_{int} = 0.044$

$\theta_{max} = 35.0^\circ$
 $h = -16 \rightarrow 16$
 $k = -15 \rightarrow 15$
 $l = 0 \rightarrow 6$
 3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.069$
 $wR(F^2) = 0.085$
 $S = 2.01$
 2927 reflections
 132 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o)]$
 $(\Delta/\sigma)_{max} = 0.01$
 $\Delta\rho_{max} = 0.58 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.72 \text{ e \AA}^{-3}$

Table 5
Selected geometric parameters (Å, °) for (I) at 40 K.

K1—O2	2.7142 (13)	O2—C4	1.2419 (18)
K1—O5 ⁱ	2.7814 (14)	O3—C5	1.2440 (19)
K1—O4 ⁱⁱ	2.7962 (13)	O4—C5	1.2917 (18)
K1—O2 ⁱⁱⁱ	2.8242 (14)	C1—C2	1.328 (2)
K1—O5 ^{iv}	2.8295 (13)	C1—C4	1.489 (2)
K1—O3 ^v	2.9043 (15)	C2—C3	1.494 (2)
K1—O3 ^{vi}	2.9498 (13)	C3—C5	1.519 (2)
O1—C4	1.2925 (19)		
O2—K1—O2 ⁱⁱⁱ	92.50 (4)	C2—C1—C4	125.86 (14)
O2—K1—O3 ^{vi}	155.65 (4)	C1—C2—C3	121.97 (14)
O2—K1—O3 ^v	87.04 (4)	C2—C3—C5	116.91 (13)
O2—K1—O4 ⁱⁱ	84.58 (4)	O1—C4—O2	123.86 (14)
O2—K1—O5 ⁱ	131.57 (4)	O1—C4—C1	117.33 (13)
O2—K1—O5 ^{iv}	69.48 (4)	O2—C4—C1	118.80 (14)
K1—O2—K1 ⁱⁱ	92.50 (4)	O3—C5—O4	124.73 (14)
K1 ^{viii} —O3—K1 ^{ix}	86.24 (4)	O3—C5—C3	122.96 (13)
K1 ⁱ —O5—K1 ^{iv}	90.98 (4)	O4—C5—C3	112.30 (13)

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

Table 6
Hydrogen-bonding geometry (Å, °) for (I) at 40 K.

D—H...A	D—H	H...A	D...A	D—H...A
O5—H7...O3	0.83 (3)	2.09 (3)	2.9121 (17)	171 (2)
O5—H8...O1 ⁱ	0.85 (3)	2.11 (3)	2.929 (2)	157 (2)
O1—H5...O1 ⁱⁱ	0.80 (4)	1.70 (4)	2.460 (2)	167 (5)
O4—H6...O4 ⁱⁱⁱ	0.84 (10)	1.66 (9)	2.438 (2)	154 (10)

Symmetry codes: (i) $x, y, z - 1$; (ii) $1 - x, -y, 2 - z$; (iii) $-x, 1 - y, -z$.

Compound (II)

Crystal data

Rb ⁺ ·C ₅ H ₅ O ₄ ⁻ ·H ₂ O	Z = 2
M _r = 232.58	D _x = 1.951 Mg m ⁻³
Triclinic, P $\bar{1}$	Mo K α radiation
a = 10.015 (5) Å	Cell parameters from 25 reflections
b = 9.988 (4) Å	θ = 10.9–11.4°
c = 4.2432 (15) Å	μ = 6.22 mm ⁻¹
α = 101.50 (3)°	T = 298 K
β = 104.41 (3)°	Prismatic, colourless
γ = 97.29 (3)°	0.50 × 0.30 × 0.25 mm
V = 395.8 (3) Å ³	

Data collection

Rigaku AFC-5R diffractometer	R _{int} = 0.030
ω -2 θ scans	θ_{\max} = 27.5°
Absorption correction: ψ scans (North <i>et al.</i> , 1968)	h = -5 → 12
T _{min} = 0.115, T _{max} = 0.211	k = -12 → 12
1927 measured reflections	l = -5 → 5
1821 independent reflections	3 standard reflections
1710 reflections with I > 0.1 σ (I)	every 97 reflections
	intensity decay: none

Refinement

Refinement on F ²	H atoms treated by a mixture of independent and constrained refinement
R[F ² > 2 σ (F ²)] = 0.054	w = 1/[$\sigma^2(F_o) + 0.00002 F_o ^2$]
wR(F ²) = 0.052	(Δ/σ) _{max} = 0.03
S = 1.59	$\Delta\rho_{\max}$ = 0.62 e Å ⁻³
1710 reflections	$\Delta\rho_{\min}$ = -0.91 e Å ⁻³
108 parameters	

Table 7

Selected geometric parameters (Å, °) for (II).

Rb1—O2	2.871 (3)	O2—C4	1.230 (4)
Rb1—O5 ⁱ	2.927 (3)	O3—C5	1.226 (4)
Rb1—O4 ⁱⁱ	2.941 (3)	O4—C5	1.297 (4)
Rb1—O2 ⁱⁱⁱ	2.965 (3)	C1—C2	1.308 (4)
Rb1—O5 ^{iv}	2.990 (3)	C1—C4	1.479 (5)
Rb1—O3 ^v	3.049 (3)	C2—C3	1.493 (4)
Rb1—O3 ^{vi}	3.103 (3)	C3—C5	1.509 (4)
O1—C4	1.277 (4)		
O2—Rb1—O2 ⁱⁱⁱ	93.26 (8)	C2—C1—C4	126.8 (3)
O2—Rb1—O3 ^{vi}	153.86 (7)	C1—C2—C3	124.6 (3)
O2—Rb1—O3 ^v	85.22 (8)	C2—C3—C5	116.7 (3)
O2—Rb1—O4 ⁱⁱ	83.04 (7)	O1—C4—O2	123.6 (3)
O2—Rb1—O5 ⁱ	129.51 (8)	O1—C4—C1	118.2 (3)
O2—Rb1—O5 ^{iv}	66.80 (8)	O2—C4—C1	118.2 (3)
Rb1—O2—Rb1 ^{vii}	93.26 (8)	O3—C5—O4	124.2 (3)
Rb1 ^{viii} —O3—Rb1 ^{ix}	87.20 (7)	O3—C5—C3	122.8 (3)
Rb1 ⁱ —O5—Rb1 ^{iv}	91.64 (9)	O4—C5—C3	113.0 (3)

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

Table 8

Hydrogen-bonding geometry (Å, °) for (II).

D—H...A	D—H	H...A	D...A	D—H...A
O5—H7...O3	0.71 (3)	2.18 (3)	2.886 (4)	175 (4)
O5—H8...O1 ⁱ	1.08 (4)	1.92 (4)	2.929 (4)	154 (3)

Symmetry code: (i) x, y, z - 1.

H atoms were located from difference Fourier maps and were refined by assuming the isotropic displacement. The presence of superstructure reflections was examined at 40 K by doubling the periods along the a, b and c axes, but no significant intensities were

detected. The diffraction data at 40 K were collected based on the same lattice as that at 295 K. The structure was refined by assuming the space group P $\bar{1}$. The refinement converged to essentially the same structure as obtained at 295 K. An attempt to refine the structure in space group P1 was made, but the refinement did not converge because of large parameter correlations. The structure at 245 K was refined in the same manner as at 40 K. The H atom attached to the carboxyl group of (II) was not found in a difference Fourier map, and was not included in the refinement. The H atoms of the water molecules were refined isotropically. The other H atoms in (II) were fixed at calculated positions and their isotropic displacements were assumed to be 1.2 times the equivalent displacements of their parent atoms.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–1999) for compound (I) at 295 K and compound (II), and *TEXSAN* (Molecular Structure Corporation, 1985) for compound (I) at 245 and 40 K; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993) for compound (I) and *PATY* in *DIRDIF92* (Beurskens *et al.*, 1992) for compound (II); program(s) used to refine structure: *TEXSAN for Windows* for compound (I) at 295 K and compound (II), and *TEXSAN* for compound (I) at 245 and 40 K; software used to prepare material for publication: *TEXSAN for Windows* for compound (I) at 295 K and compound (II), and *TEXSAN* for compound (I) at 245 and 40 K.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1024). Additional figures and a table showing the temperature dependence of cell parameters of (I) are also available. Services for accessing these data are described at the back of the journal.

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