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A Crystallographic Study of the Phase Transition in Rubidium Dihydrogen Citrate

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Abstract

$Rb^+ \cdot C_6H_7O_7^-$, $M_r = 275 \cdot 58$, monoclinic, $P2_1/a$, $a = 14 \cdot 903$ (2), $b = 9 \cdot 731$ (2), $c = 19 \cdot 220$ (3) Å, $\beta = 108 \cdot 62$ (2)°, $V = 2641 \cdot 6$ (6) Å³, $Z = 12$, $D_x = 2 \cdot 079$ g cm^{-3}, λ (Mo $K\alpha$) = $0 \cdot 71069$ Å, $\mu = 54 \cdot 8$ cm^{-1}, $F(000) = 1620$, $T = 295$ (2)K. Bragg reflections with $l = 3n$ are stronger than those with $l \neq 3n$. In a phase transition at approximately 308 K the $l \neq 3n$ reflections vanish, giving a high-temperature cell with $a = 14 \cdot 917$ (3), $b = 9 \cdot 763$ (3), $c = 6 \cdot 423$ (2) Å, $\beta = 108 \cdot 54$ (2)°, $V = 886 \cdot 8$ (3) Å³, $Z = 4$, $D_x = 2 \cdot 064$ g cm^{-3}, $F(000) = 540$, $T = 323$ (3) K, corresponding to a reduced cell in $P2_1/n$, with $a = 14 \cdot 242$ (3), $b = 9 \cdot 763$ (3), $c = 6 \cdot 423$ (2) Å, $\beta = 96 \cdot 77$ (2)°. The nature of the phase transition is revealed by the results of structure determinations of the low-temperature phase at 225 (3) K based on 4387 measured reflections with $|F_o| > 0$, and giving $R = 0 \cdot 0636$, and of the high-temperature phase at 323 (3) K, with 1710 measured reflections with $|F_o| > 0$ and $R = 0 \cdot 0398$. All O-bound H atoms in both structures participate in intermolecular hydrogen bonds, forming three-dimensional networks. In the low-temperature phase, the $c/3$ translational pseudosymmetry is broken by a 15° rotation of one of the three independent molecules. This is accompanied by a switch in the position of a hydrogen-bonding H from one O atom to the other in a terminal carboxyl group of the rotated citrate ion. The instability of the high-temperature phase at lower temperature can be qualitatively understood in terms of a close (C–)H···O contact, with H···O = 2·33 (3) Å. One of every three such contacts is removed by the rotation of one citrate ion; the other two contacts are relieved, to a lesser degree, by accompanying small shifts in the positions of the other citrate ions and the Rb^+ ions. A disorder exists in the position of one CH_2CO_2H group of the high-temperature structure, with the minor component approximating the rotated citrate ion in the low-temperature phase. Short hydrogen bonds, approximately in the x direction, with O···O distances 2·492 (6), 2·524 (6) and 2·502 (6) Å, link glide-plane-related molecules in the low-temperature phase. Upon deuteration, the length of the a axis of the low-temperature phase increases by 0·019 (3) Å.

Introduction

A crystallographic study of the substrates of the enzyme aconitase was undertaken in the 1950's by Patterson and co-workers. The crystal structures of citric acid and several citrates were determined as part of this program; the results of these and related structure determinations have been reviewed by Glusker (1980).

In the course of these studies, it was found that rubidium dihydrogen citrate crystallizes with three formula units per asymmetric unit of space group $P2_1/a$, and that the diffracted intensities with $l \neq 3n$ were very weak compared to those with $l = 3n$ (Nordman, Weldon & Patterson, 1960). Ignoring these $l \neq 3n$ superstructure reflections the approximate structure of the subcell was determined, using photographic $h0l$ and $hk0$ data only. It was also reported that the $l \neq 3n$ superstructure reflections disappear at approximately 308 K.

We decided to carry out accurate structure determinations of rubidium dihydrogen citrate well below, and above, the apparently reversible phase transition, in the hope of gaining insight into the nature of this transformation. The reported presence of a short, approximately 2·48 Å hydrogen bond in the substructure provided additional incentive for the study reported here.

Experimental

Crystals were prepared by slow evaporation of 50:50 ethanol:water solutions containing stoichiometric amounts of rubidium carbonate and citric acid. The crystals were ground to nearly spherical shape in a simple air tumbling device as described by Bond (1951). A sphere of diameter 0·22 (1) mm was used for the X-ray data collection. For this specimen $\mu R = 0·20$, and the correction factor for X-ray absorption, max. = 1·35, min. = 1·33, by which the intensities were corrected, varies only slightly with 2θ (*International Tables for X-ray Crystallography*, 1959).

The deuterated material was prepared by recrystallization from 99·8% D_2O. For the X-ray work, a crystal of nearly equal dimensions of $0·20 \pm 0·03$ mm was used, sealed in a glass capillary.

Cell-parameter and intensity data were collected on a Syntex $P2_1$ diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. The cell-parameter determinations were based on 15 reflections with $33 < 2\theta < 45°$.

The cell parameters were measured at 225 (3), 295 (2) and 323 (3) K before, during and after the data collection. In addition, a second crystal, and a deuterated crystal were used for cell-parameter determination at 225 (3) and 295 (2) K. Table 1 summarizes the results of the cell-parameter determinations. The data listed, and used in all calculations of bond

Table 1. *Cell parameters of rubidium dihydrogen (H) and dideuterium (D) citrate*

$T(K)$	H, D	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$\beta(°)$	$V(\text{Å}^3)$
225 (3)	H	14·897 (4)	9·697 (2)	19·182 (3)	108·77 (2)	2623·5 (6)
225 (3)	D	14·917 (3)	9·699 (2)	19·189 (3)	108·78 (2)	2628·5 (6)
295 (2)	H	14·903 (2)	9·731 (2)	19·220 (3)	108·62 (2)	2641·6 (6)
295 (2)	D	14·922 (2)	9·734 (2)	19·229 (3)	108·63 (2)	2646·7 (6)
323 (3)	H	14·917 (3)	9·763 (3)	6·423 (2)	108·54 (2)	886·8 (3)

lengths and angles, refer to fresh crystals, *i.e.* specimens not subjected to prolonged irradiation. The crystal used in data collection showed a 0·015 (3) Å increase in the length of the b axis, at 225 and 295 K, following 370 h of exposure to the X-ray beam. The other cell parameters were unchanged. This effect was not studied at 323 K. There was no evidence of hysteresis in the lattice-parameter values following the transition to and from the high-temperature form.

Diffracted intensities were measured with θ-2θ scans over 1·7-2·1° ranges using 2·55-11·72° min^{-1} scan speeds. Data at 225 (3) K were collected for $+h$, $\pm k$, $\pm l$ in the range $2\theta = 0$-30°, and for $+h$, $+k$, $\pm l$ in the range $2\theta = 30$-60°. A total of 4387 unique, non-negative data were obtained from 5677 measurements following merging, with $R_{int}(F) = 0·0326$, and removal of negatively measured intensities. Data at 323 (3) K were collected for $2\theta \leq 55°$ and hkl ranges $0 \leq h \leq 18$, $0 \leq k \leq 12$, $-8 \leq l \leq 8$. The 2133 measurements of space-group-allowed reflections yielded 1710 unique, non-negative intensities, with $R_{int}(F) = 0·0257$.

The low-temperature structure was solved with incomplete $(h < 7)$ data, using the program *SHELX*76 (Sheldrick, 1976). In order to achieve an automatic solution, it was necessary to renormalize the $|E|^2$ values, boosting the $E^2(h, k, l)$ with $l \neq 3n$ by a factor of 8·7 relative to the $E^2(h, k, 3n)$. Following some refinement, all H atoms were located. In the subsequent refinement the 12 methylene H atoms were restrained to tetrahedral positions with C–H = 1·02 Å, and their isotropic thermal parameters were kept at 1·3 times the isotropic equivalents of the thermal parameters of their adjacent C atoms. All O-bonded H atoms were unrestrained and isotropic, while the non-H atoms were refined anisotropically. An empirical extinction correction of the form $1 - xF_c^2/\sin\theta$ was applied to the F_c values; refinement of the parameter x gave the value $0·73 (4) \times 10^{-7}$. The least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F_o)$ from counting statistics; the parameter k of the term kF_o^2 in the w^{-1} expression refined to zero and was set to that value. The full-matrix refinement was based on all 4387 data with $|F_o| > 0$ and gave $R = 0·0636$, $wR = 0·0470$, and $S = 1·56$. The maximum value of $|\Delta/\sigma|$ in the last cycle was 0·05 [for $x_{H(26)}$], mean $|\Delta/\sigma| < 0·01$; maximum and minimum $\Delta\rho$ in the final ΔF synthesis +0·91 and $-0·83$ e Å^{-3}, both in the vicinity of Rb$^+$ ions. The final parameters are given in Table 2.

Table 2. *Fractional atomic coordinates and equivalent isotropic (isotropic for H) thermal parameters ($\mathring{A}^2$) for the low-temperature (225 K) structure*

$$U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	U_{eq}/U
Rb(1)	0·12358(4)	0·12491(6)	0·02482(3)	0·0212(1)
O(11)	0·5230(2)	0·2547(4)	0·1936(1)	0·0263(11)
O(12)	0·4706(2)	0·3872(4)	0·0945(1)	0·0260(10)
O(13)	0·3121(2)	0·1404(4)	0·3406(1)	0·0271(9)
O(14)	0·3510(2)	−0·0665(4)	0·3129(1)	0·0314(11)
O(15)	0·2288(2)	0·4111(4)	0·2516(1)	0·0262(9)
O(16)	0·1829(2)	0·2273(4)	0·1791(1)	0·0259(10)
O(17)	0·4123(2)	0·3493(4)	0·2842(1)	0·0171(8)
C(11)	0·4572(4)	0·3263(5)	0·1452(2)	0·0178(13)
C(12)	0·3609(4)	0·3309(5)	0·1552(2)	0·0152(12)
C(13)	0·3488(4)	0·2739(5)	0·2254(2)	0·0150(11)
C(14)	0·3666(4)	0·1180(5)	0·2367(2)	0·0186(12)
C(15)	0·3404(4)	0·0674(5)	0·3011(2)	0·0196(13)
C(16)	0·2451(4)	0·3072(5)	0·2200(2)	0·0155(12)
H(15)	0·600(5)	0·259(6)	0·183(4)	0·075(24)
H(16)	0·325(4)	−0·092(5)	0·354(3)	0·027(15)
H(17)	0·408(4)	0·314(6)	0·320(3)	0·044(22)
Rb(2)	0·11672(4)	0·11042(5)	0·34932(3)	0·0218(1)
O(21)	0·5353(2)	0·2644(4)	0·5270(1)	0·0236(10)
O(22)	0·4739(2)	0·4014(4)	0·4300(1)	0·0221(9)
O(23)	0·3286(4)	0·0504(5)	0·6551(2)	0·0579(15)
O(24)	0·4181(4)	−0·1093(4)	0·6300(1)	0·0531(14)
O(25)	0·2483(2)	0·3418(4)	0·6068(1)	0·0312(10)
O(26)	0·1950(2)	0·2023(4)	0·5101(1)	0·0275(10)
O(27)	0·4268(2)	0·3002(4)	0·6220(1)	0·0244(10)
C(21)	0·4651(4)	0·3325(5)	0·4803(2)	0·0174(12)
C(22)	0·3694(2)	0·3225(5)	0·4922(2)	0·0166(13)
C(23)	0·3601(4)	0·2418(5)	0·5571(2)	0·0167(12)
C(24)	0·3818(4)	0·0873(5)	0·5527(2)	0·0224(13)
C(25)	0·3772(4)	0·0010(5)	0·6154(2)	0·0276(14)
C(26)	0·2584(4)	0·2636(5)	0·5595(2)	0·0169(12)
H(25)	0·594(4)	0·267(7)	0·515(4)	0·072(26)
H(26)	0·325(4)	−0·041(7)	0·684(4)	0·071(23)
H(27)	0·408(4)	0·293(7)	0·654(3)	0·044(23)
Rb(3)	0·12370(4)	0·13059(5)	0·68671(3)	0·0209(1)
O(31)	0·5336(2)	0·2462(4)	0·8599(1)	0·0298(11)
O(32)	0·4772(2)	0·3890(4)	0·7653(1)	0·0246(9)
O(33)	0·3171(2)	0·1428(4)	1·0097(1)	0·0328(11)
O(34)	0·3622(2)	−0·0676(4)	0·9949(1)	0·0365(12)
O(35)	0·2361(2)	0·3939(4)	0·9163(1)	0·0271(9)
O(36)	0·1924(2)	0·2069(4)	0·8464(1)	0·0254(10)
O(37)	0·4196(2)	0·3384(4)	0·9476(1)	0·0194(9)
C(31)	0·4654(4)	0·3160(5)	0·8132(2)	0·0185(14)
C(32)	0·3676(4)	0·3000(5)	0·8195(2)	0·0252(15)
C(33)	0·3566(4)	0·2560(5)	0·8920(2)	0·0148(12)
C(34)	0·3772(4)	0·1019(5)	0·9100(2)	0·0199(12)
C(35)	0·3501(4)	0·0617(5)	0·9767(2)	0·0176(12)
C(36)	0·2539(4)	0·2892(5)	0·8865(2)	0·0181(13)
H(35)	0·633(5)	0·271(7)	0·848(3)	0·071(26)
H(36)	0·327(5)	−0·085(7)	1·029(4)	0·069(24)
H(37)	0·417(4)	0·324(7)	0·993(3)	0·058(23)

Table 3. *Atomic coordinates and equivalent isotropic [isotropic for H, C(4B), C(5B)] thermal parameters ($\mathring{A}^2$) for the high-temperature (323 K) structure, referred to the cell $a = 14\cdot917$ (3), $b = 9\cdot763$ (3), $c = 6\cdot423$ (2) $\mathring{A}$, $\beta = 108\cdot54$ (2)°*

Atoms marked with an asterisk have occupancy 0·715 (6). Atoms designated '*B*' represent alternative sites with occupancy 0·285 (6).

	x	y	z	U_{eq}/U
Rb	0·12203(2)	0·12173(4)	0·06272(6)	0·0328(1)
O(1)	0·5308(1)	0·2557(2)	0·5824(4)	0·0422(7)
O(2)	0·4749(1)	0·3903(2)	0·2923(4)	0·0369(6)
O(3)*	0·3172(2)	0·1378(5)	1·0262(6)	0·0468(11)
O(4)*	0·3576(4)	−0·0689(5)	0·9606(8)	0·0556(12)
O(5)*	0·2394(6)	0·3747(9)	0·7940(13)	0·0810(26)
O(6)	0·1908(1)	0·2117(2)	0·5386(4)	0·0429(7)
O(7)	0·4195(1)	0·3318(2)	0·8539(4)	0·0365(6)
C(1)	0·4629(1)	0·3245(4)	0·4409(5)	0·0257(7)
C(2)	0·3663(1)	0·3179(4)	0·4693(5)	0·0297(8)
C(3)	0·3557(1)	0·2573(4)	0·6779(5)	0·0242(7)
C(4)*	0·3751(4)	0·1077(5)	0·7201(10)	0·0262(11)
C(5)*	0·3482(5)	0·0626(9)	0·9217(12)	0·0319(14)
C(6)	0·2526(1)	0·2855(4)	0·6672(5)	0·0333(9)
H(5)	0·6090(26)	0·2578(45)	0·5471(54)	0·0566
H(6)*	0·3192(47)	−0·0686(64)	1·0816(84)	0·0804
H(7)	0·4155(31)	0·3035(47)	0·9541(60)	0·0475
O(3B)	1·3243(12)	0·0499(20)	0·9655(31)	0·065(3)
O(4B)	1·4105(10)	−0·1076(10)	0·8812(20)	0·066(3)
O(5B)	0·2335(12)	0·3989(13)	0·7361(23)	0·017(2)
C(4B)	0·3761(13)	0·0929(19)	0·6545(27)	0·029(4)
C(5B)	0·3718(9)	0·0064(15)	0·8471(21)	0·028(3)

A cycle of full-matrix refinement using only those 3400 reflections with $F_o > 4\sigma(F_o)$ gave $R = 0\cdot0453$ and $wR = 0\cdot0391$. The e.s.d.'s of this refinement tended to be higher, and no shifts approaching the value of σ were found. Thus the $F_o > 0$ parameters were adopted.

The refinement of the high-temperature structure began with a model based on the $0\cdot0 \le z < \tfrac{1}{3}$ subcell of the low-temperature structure. The four methylene H atoms were tetrahedrally restrained, with C–H = $1\cdot02$ Å. The isotropic thermal parameters of all H atoms were kept at $1\cdot3$ times those of the adjacent C or O atoms. Difference ΔF syntheses revealed a disorder in one terminal carboxyl group, C(5)O(3)O(4), and its adjacent methylene, C(4), with a clearly recognizable alternative site for this group. This terminal carboxyl group is hydrogen-bonded to

O(5) of the central carboxyl of a neighbor molecule; a close-lying alternative site for O(5) was also found. It must be assumed that the positions of C(3), bonded to C(4), and of the rest of the central carboxyl group, are somewhat affected by this disorder, but in the absence of unambiguous indication in ΔF syntheses, alternative sites for other atoms were not introduced. The atom occupancies of the alternative sites, including the C(4) methylene H atoms, were kept equal. The refined value was $0\cdot285$ (6); the sum of this occupany factor and that of the major site was found to equal approximately unity, and was then restrained to unity. The major-site non-H atoms and the two minor-site O atoms were refined anisotropically, the minor-site C atoms isotropically. The minor-site carboxyl H was not detected above background in the ΔF syntheses. The refined value of the extinction parameter was $x = 4\cdot3$ (4) $\times 10^{-7}$. The full-matrix refinement, on F, with $w^{-1} = \sigma^2(F_o)$ gave $R = 0\cdot0398$, $wR = 0\cdot0351$ and $S = 1\cdot53$ for 1710 reflections with $|F_o| > 0$. The maximum Δ/σ in the last cycle was $0\cdot08$ (minor-site O U_{13}), mean $<0\cdot01$. The final ΔF synthesis had extremes of $\Delta\rho = +0\cdot58$ and $-0\cdot49$ e Å^{-3}, both in the vicinity of the Rb$^+$ ion. The final parameters are listed in Table 3.* All structure-factor calculations used atomic scattering factors for C and O from Cromer & Liberman (1970) and for H from Stewart, Davidson & Simpson (1965).

Table 4. *Bond distances* (Å) *and angles* (°), *torsion angles* (°) *and selected hydrogen-bond distances* (Å) *and angles* (°) *in rubidium dihydrogen citrate*

	Low-temp. form			High-temp.
	Molecule (1)	Molecule (2)	Molecule (3)	form
C(1)–C(2)	1·509 (7)	1·518 (7)	1·509 (7)	1·511 (4)
C(2)–C(3)	1·518 (6)	1·514 (7)	1·513 (7)	1·518 (4)
C(3)–C(4)	1·538 (6)	1·542 (7)	1·541 (7)	1·496 (7)
C(4)–C(5)	1·493 (7)	1·485 (7)	1·511 (7)	1·537 (9)
C(3)–C(6)	1·549 (7)	1·545 (7)	1·534 (7)	1·543 (4)
C(1)–O(1)	1·311 (6)	1·315 (6)	1·306 (6)	1·310 (4)
C(1)–O (2)	1·209 (6)	1·215 (6)	1·217 (6)	1·210 (4)
C(5)–O (3)	1·208 (6)	1·299 (7)	1·209 (6)	1·183 (9)
C(5)–O (4)	1·319 (6)	1·218 (6)	1·300 (6)	1·307 (10)
C(6)–O(5)	1·239 (6)	1·229 (6)	1·235 (6)	1·250 (10)
C(6)–O(6)	1·267 (6)	1·252 (6)	1·271 (6)	1·252 (4)
C(3)–O(7)	1·420 (6)	1·435 (6)	1·418 (6)	1·425 (4)
C(1)–C(2)–C(3)	119·4 (4)	119·7 (4)	119·7 (5)	119·6 (3)
C(2)–C(3)–C(4)	114·8 (4)	112·4 (4)	114·0 (4)	118·2 (4)
C(3)–C(4)–C(5)	111·2 (4)	115·9 (5)	110·6 (4)	110·1 (5)
C(2)–C(3)–C(6)	105·4 (4)	107·7 (4)	106·1 (4)	105·9 (3)
C(4)–C(3)–C(6)	109·7 (4)	111·1 (4)	109·9 (4)	108·4 (3)
C(2)–C(1)–O(1)	116·8 (5)	116·3 (5)	116·7 (5)	116·8 (3)
C(2)–C(1)–O(2)	119·8 (5)	120·1 (5)	119·9 (5)	120·2 (3)
C(4)–C(5)–O(3)	124·2 (5)	116·6 (5)	122·7 (5)	123·7(7)
C(4)–C(5)–O(4)	114·6 (5)	122·0 (6)	115·2 (5)	113·6 (7)
C(3)–C(6)–O(5)	119·0 (4)	117·4 (5)	120·0 (5)	117·2 (6)
C(3)–C(6)–O(6)	115·3 (5)	114·9 (4)	114·8 (5)	116·2 (3)
C(2)–C(3)–O(7)	106·1 (4)	106·8 (4)	106·9 (4)	105·7 (3)
C(4)–C(3)–O(7)	110·7 (4)	109·4 (4)	110·0 (4)	108·2 (4)
C(6)–C(3)–O(7)	109·9 (4)	109·5 (4)	109·7 (4)	110·4 (3)
O(1)–C(1)–O(2)	123·4 (5)	123·6 (5)	123·3 (5)	123·0 (3)
O(3)–C(5)–O(4)	121·1 (5)	121·5 (6)	122·1 (5)	122·6 (7)
O(5)–C(6)–O(6)	125·5 (5)	127·6 (5)	125·1 (5)	126·6 (5)
C(1)C(2)C(3)C(4)	−64·2 (6)	−63·5 (6)	−74·6 (6)	−66·3 (5)
C(2)C(3)C(4)C(5)	−172·2 (6)	178·2 (6)	−171·2 (6)	−172·6 (6)
C(1)C(2)C(3)C(6)	175·0 (6)	173·9 (6)	164·3 (6)	172·1 (5)
C(5)C(4)C(3)C(6)	−53·8 (6)	−61·1 (6)	−52·2 (6)	−52·3 (6)
O(1)C(1)C(2)C(3)	9·6 (6)	2·4 (6)	23·9 (7)	11·4 (5)
O(2)C(1)C(2)C(3)	−170·3 (6)	−177·2 (6)	−157·5 (7)	−168·9 (5)
O(3)C(5)C(4)C(3)	−2·4 (6)	20·6 (7)	−0·1 (6)	−0·5 (9)
O(4)C(5)C(4)C(3)	178·0 (6)	−158·2 (8)	178·1 (6)	175·9 (9)
O(5)C(6)C(3)C(2)	−97·3 (6)	−104·8 (7)	−100·9 (6)	−107·7 (7)
O(5)C(6)C(3)C(4)	138·7 (6)	131·8 (6)	135·4 (6)	124·6 (7)
O(6)C(6)C(3)C(2)	78·8 (6)	72·6 (6)	75·1 (6)	75·5 (5)
O(6)C(6)C(3)C(4)	−45·3 (6)	−50·9 (6)	−48·6 (6)	−52·2 (5)
O(7)C(3)C(6)O(5)	16·7 (6)	10·9 (6)	14·3 (6)	6·2 (7)
O(7)C(3)C(6)O(6)	−167·2 (6)	−171·8 (6)	−169·8 (6)	−170·6 (5)
O(7)C(3)C(2)C(1)	58·4 (6)	56·4 (6)	47·3 (6)	54·9 (5)
O(7)C(3)C(4)C(5)	67·7 (6)	59·9 (6)	68·7 (6)	67·4 (6)
O(7)···O(2)'	2·695 (6)	2·745 (6)	2·713 (6)	2·731 (4)
O(7)–H(7)	0·78 (6)	0·76 (6)	0·89 (6)	0·72 (4)
O(7)–H(7)···O(2)'	122 (6)	124 (6)	142 (7)	127 (4)
H(7)···O(2)'	2·19 (7)	2·25 (7)	1·95 (7)	2·24 (4)
H(7)···O(3)	2·33 (7)	2·64 (7)	2·39 (7)	2·33 (4)
H(7)···O(5)	2·74 (7)	2·31 (7)	2·71 (7)	2·59 (4)
O(1)···O(6)'	2·492 (6)	2·524 (6)	2·502 (6)	2·511 (5)
O(1)–H(5)	1·23 (7)	0·97 (7)	1·58 (7)	1·26 (4)
O(1)–H(5)···O(6)'	173 (5)	167 (4)	172 (4)	165 (3)
H(5)···O(6)'	1·26 (7)	1·56 (7)	0·93 (7)	1·27 (4)

Discussion

Bond distances, bond angles, torsion angles, and selected hydrogen-bond parameters are given in Table 4. The atom numbering (Figs. 1 and 2) employs one digit for the high-temperature form, two for the low-temperature form, with the tens digit identifying one of the three independent molecules. The atom numbering follows the conventions adopted by Glusker (1980) in her review of citrate conformation. This permits direct comparison of the values listed in Table 4 with average values of bond lengths and angles derived from other citrate structures. Generally, for each bond length and angle, the three values from

the low-temperature structure, and the fourth from the high-temperature one, agree well among each other, and also with the values reported by Glusker (1980). In each of the four independent dihydrogen citrate ions the central carboxyl group is the one which is ionized, as can be seen from the location of the H atoms, and from the carboxyl C–O bond lengths and C–C–O angles. The C–O(H) bonds, C(1)–O(1)
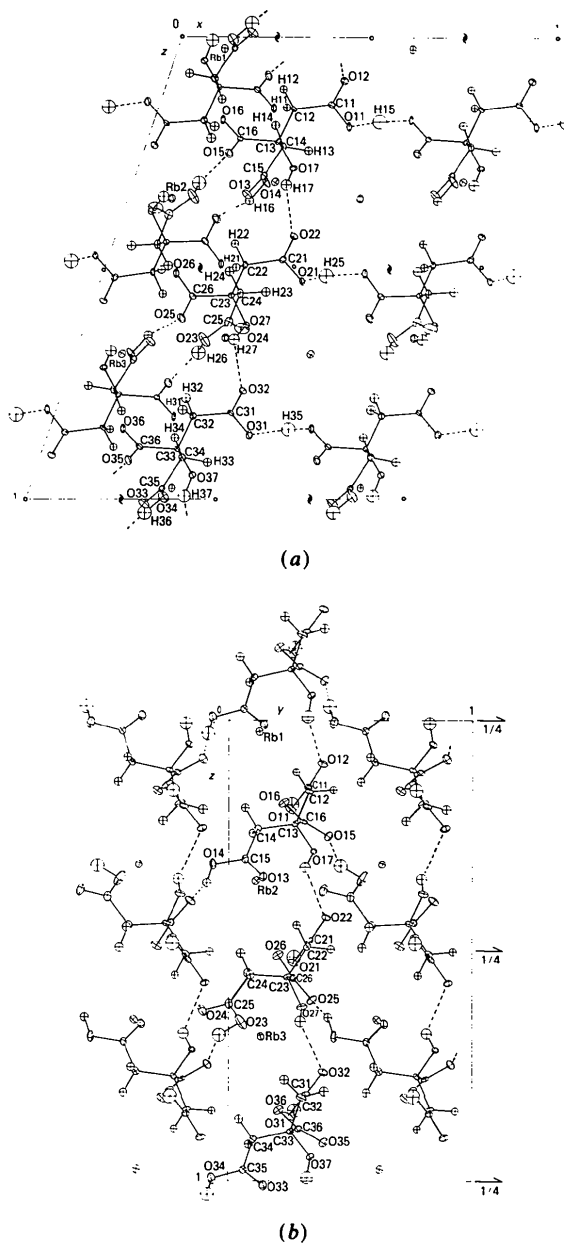

(a)

(b)

Fig. 1. *ORTEP* (Johnson, 1976) 20% probability thermal-ellipsoid drawings of the structure of rubidium dihydrogen citrate at 225 (3) K, showing the atom labeling, the c/3 translational pseudosymmetry, and the hydrogen-bonding patterns. (a) View along y, with the positive direction out of the page. (b) View along x, with the positive direction into the page. H-atom labels omitted for clarity.

and C(5)–O(4), are longer than the C=O bonds, C(1)–O(2) and C(5)–O(3), while the C–C–O(H) angles, C(2)–C(1)–O(1) and C(4)–C(5)–O(4), are smaller than the C–C=O angles, C(2)–C(1)–O(2) and C(4)–C(5)–O(3). A reversal of this pattern occurs in molecule (2) of the low-temperature structure as will be discussed below. Ionization of the central carboxyl of the dihydrogen citrate ion is expected, as it has been found in the previously studied lithium and sodium salts (Glusker, van der Helm, Love, Dornberg, Minkin, Johnson & Patterson, 1965).

The conformation of the four molecules, as expressed in the values of the 16 torsion angles, fits very well the pattern (Glusker, 1980) found to be obeyed by citric acid and all citrate structures studied so far. A notable general feature is the near coplanarity of the central carboxyl group and the hydroxyl O, expressed in a small value of the torsion angle O(7)C(3)C(6)O(5). Less common is the near coplanarity of the terminal carboxyls and C(3) found in the present structures.

Each Rb$^+$ ion is surrounded by seven O atoms at distances ranging from 2·82–2·94 to 3·02–3·15 Å, and one to three additional O atoms at distances up to 3·26 Å. All C=O O atoms of the carboxyl groups are strongly coordinated to Rb, as are the hydroxyl O atoms, O(7), and the ionized carboxyl O atoms, O(6). The carboxyl OH O atoms tend to be slightly farther from the Rb$^+$ ions, at distances of 3·02 to 3·39 Å, with the exception of O(14), at 2·961 Å. All O atoms in the two structures participate in Rb coordination. Each Rb$^+$ ion is coordinated to two of its neighboring citrates by bidentate chelation involving, respectively, O(1) and O(7), with O(1)–Rb–O(7) = 55 to 57°, and O(5) and O(7), with O(5)–Rb–O(7) = 48 to 54°. All

Fig. 2. *ORTEP* drawing of the structure of rubidium dihydrogen citrate at 323 (3) K. Open ellipsoids, or spheres, represent an alternative site of occupancy 0·285 (6). The thermal ellipsoids are for 20% probability.

O(7) hydroxyl O atoms are coordinated to two Rb$^+$ ions. The carboxyl O(2) also participates in two coordination spheres, although only weakly in one of them.

The coordination spheres of the three Rb$^+$ ions related by c/3 in the low-temperature structure are similar to each other, and to the coordination sphere in the high-temperature form. This similarity is closest between the high-temperature structure (major site) and Rb(1) of the low-temperature form. The reason for this is that the Rb(1) coordination only involves O atoms from molecules (1) and (3), and their symmetry-related mates, not from molecule (2). The position of molecule (2) differs the most from the (major site) high-temperature structure; this affects the coordination spheres of Rb(2) and Rb(3), in which O atoms of molecule (2) participate.

All O-bound H atoms form intermolecular hydrogen bonds. Every citrate ion is linked to its a-glide-related neighbor through an O(1)···O(6) hydrogen bond. The infinite chains so formed are linked into infinite sheets by O(7)–H···O(2) hydrogen bonds joining neighbors related by c in the high-temperature form, or ≈c/3 in the low-temperature form. The sheets are linked into a three-dimensional network by a helical arrangement of hydrogen bonds joining molecules related by screw axes or pseudo-screw axes. The citrate ions in the high-temperature form are helically joined through O(4)–H(6)···O(5)' hydrogen bonds, with O···O distance 2·517 (5) Å about the screw axes at $x = \frac{1}{4}, \frac{3}{4}, z = 0$. Analogously, in the low-temperature structure, O(34)–H(36)···O(35)' hydrogen bonds of 2·606 (6) Å form helices of molecules (3) about the $x = \frac{1}{4}, \frac{3}{4}, z = 0$ screw axes. Between these screw axes, spaced at c/3, there are pseudo-screw axes, with hydrogen-bonded helical chains. The hydrogen bonds at $x \simeq 0·25$, $z \simeq 0·33$ are O(14)–H(16)···O(25)' and O(23)'–H(26)'···O(15)" of 2·611 (6) and 2·596 (6) Å. The interactions at $x \simeq 0·25$, $z \simeq 0·67$ are equivalent to these, by symmetry.

Data for the hydrogen bonds which join pairs of citrate ions related by the c/3, or c translations, or by the a-glide operation, are given in Table 4. A notable feature of the former is the O(7)–H(7)···O(2)' angle, and the disposition of the hydroxyl H(7) toward O(3) of a terminal carboxyl and O(5) of the central carboxyl, in each of the four cases. The tendency of H(7) to approach O(5), while participating in an intermolecular hydrogen bond, has also been observed in crystalline citric acid (Glusker, Minkin & Patterson, 1969). In the present structure the intramolecular H(7)···O(5) distances are somewhat longer than in the citric acid structure, but the intermolecular O(7)···O(2) distances are shorter. The approach of H(7) to the terminal carboxyl O(3) is generally closer than to O(5). This is reversed in molecule (2), where O(3) itself is hydrogen-bonded (Fig. 1).
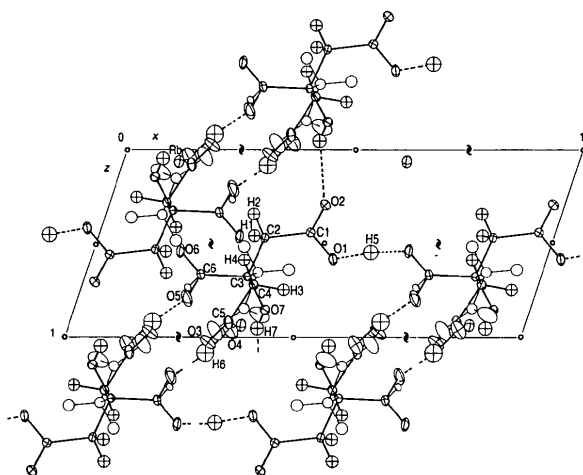
The hydrogen bonds of type $O(1)\cdots O(6)'$, which join a-glide-related citrate ions, are remarkably short. The position of the H atom in short hydrogen bonds is of particular interest. The $O(1)-H(5)$ and $H(5)\cdots O(6)'$ distances in Table 4 indicate that the H may reside near the center of the bond, but the accuracy is too low to permit a firm assessment. Clearly, a neutron diffraction study would be in order. It is perhaps noteworthy that unlike these four $O(1)\cdots O(6)'$ hydrogen bonds, the other eight independent hydrogen bonds in the two structures all have their H atoms placed near the expected OH O atoms.

It is well known that short O–H–O hydrogen bonds tend to show a slight increase in the $O\cdots O$ distance upon replacement of H with D (Hamilton & Ibers, 1968). Since the short hydrogen bonds in rubidium dihydrogen citrate are directed along x, an expansion of the a axis would be expected. The cell-parameter determinations, made for the low-temperature form at two temperatures (Table 1), show expansions of 0·020 (5) and 0·019 (3) Å in a, with no significant change in b, c, or β.

Nature of the phase transition

The main features which distinguish the structure of the low-temperature cell from a tripled high-temperature cell can be described as follows:

1. Molecule (2) is rotated approximately 15° about the x direction, and the H atom of its $O(3)-C(5)-O(4)$ carboxyl group is switched from $O(4)$ to $O(3)$. While molecules (1) and (3) have an $O(4)-H(6)\cdots O(5)'$ hydrogen bond, where $O(4)$ is *trans* to C(3), molecule (2) is correspondingly hydrogen-bonded $O(3)-H(6)\cdots O(5)'$, where $O(3)$ is *cis* to C(3).

2. The centers of molecules (1) and (2), taken as atoms C(13) and C(23), are shifted in opposite sense in the x and y directions, molecule (1) by $-0·10$, $+0·16$ Å, molecule (2) by $+0·07$, $-0·15$ Å, while molecule (3) is unchanged.

3. There are shifts in the Rb positions, the largest being $\Delta z = +0·087$ Å for Rb(1), $\Delta y = -0·113$, $\Delta z = -0·083$ Å for Rb(2), and $\Delta y = +0·083$ Å for Rb(3).

4. The torsion angles (Table 4) show relatively little change, the largest being in the torsion angles defining the plane of the $C(4)-C(5)O(3)O(4)$ carboxyl group of molecule (2).

By comparing the intermolecular contacts in these two structures we find qualitative support for the conclusion that the low-temperature structure represents an energetically more favorable packing.

In the high-temperature structure there is a very short (Taylor & Kennard, 1982) $(C-)H\cdots O$ contact

of 2·33 (3) Å between molecules related by the translation c. This interaction, $H(2)\cdots O(3)'$, must be regarded as repulsive, since in the z direction there are no other obviously repulsive contacts between the two molecules.

Of the three corresponding contacts in the low-temperature structure $H(32)\cdots O(23)$ is completely relieved, to 2·96 (4) Å, and $H(22)\cdots O(13)$ lengthened to 2·38 (4) Å, by the rotation of molecule (2). The third of these contacts, $H(12)\cdots O(33)$, is lengthened to 2·37 (4) Å by the mainly translational shift of molecules (1) and (3) in the x, y plane, by 0·36 Å relative to each other. Since the relevant methylene H atoms are in calculated, tetrahedral positions, the relative differences between these $H\cdots O$ distances tend to be more reliable than their absolute values.

The transformation from the high- to the low-temperature form is also accompanied by a slight tightening of the coordination of the O atoms to the Rb atoms. The mean Rb–O distance of the seven nearest O atoms is 3·015 Å in the high-temperature form; in the low-temperature structure the three corresponding means are 2·983, 3·001 and 2·976 Å.

Further study of this phase transition by calorimetric and dilatometric techniques, as well as by neutron diffraction, would be of interest. The exact temperature of the transition, and the possible dependence of the degree of disorder on the rate of passage through the transition, or on annealing, remain unsettled.

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