Calcium Hydrogen Citrate Trihydrate

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Abstract. $CaC_6H_6O_7.3H_2O$, prepared by slow precipitation from an aqueous mixture of calcium chloride and sodium citrate at a pH of 4·0, is monoclinic, $P2_1/c$, with $Z=4$, $a=8·7955$ (54), $b=5·5891$ (15), $c=23·8176$ (175) Å, $\beta=116·770$ (57)°, F.W. 284·2, $V=1045·35$ Å^3, $D_x=1·806$ g cm^{-3}, $D_m=1·79$ g cm^{-3}; λ(graphite monochromatized Cu $K\alpha_1$)$=1·54051$ Å. The final R, for 1317 reflexions, was 0·0756. Each calcium ion is surrounded by seven oxygen atoms, two of which form bridges to another symmetry-related calcium ion.

Introduction. There are three possible calcium citrate compounds with calcium to citrate ratios of 1:2, 1:1 and 3:2. The last type is found naturally in some insects (Parker & Rudall, 1955; Kenchington, 1974) and cell dimensions of the tetrahydrate have been published by Pogainis & Shaw (1957). The crystals of calcium hydrogen citrate (calcium to citrate ratio$=1:1$) were obtained as well faceted needles and a crystal with dimensions $0·2 \times 0·2 \times 0·5$ mm was selected for examination.

The data were collected on an Enraf–Nonius CAD-4 computer-controlled diffractometer by the moving-crystal moving-counter technique in the range $3° \leq \theta \leq 70°$. Of 1810 independent reflexions accessible in principle, 1317 were measured and used in the analysis. The systematic absences, $0k0$ for $k=2n+1$ and $h0l$ for $l=2n+1$, determined the space group $P2_1/c$ (No. 14). No correction for absorption was made. Lorentz and polarization factors were applied to the intensity data and approximate values of the temperature and scale factors were obtained from a Wilson plot.

The position of the calcium ion was established from a three-dimensional Patterson map and the carbon and oxygen atoms from a three-dimensional electron-density map calculated with the phases specified by the structure factors calculated from the coordinates of the calcium ion only.

The positional and anisotropic thermal parameters were refined by block-diagonal least-squares calculations on the 1906A computer of Leeds University Computing Laboratory, with modified versions of the programs of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961), to an R value of 0·0796. A difference synthesis was calculated and the coordinates of the hydrogen atoms were found. Refinement of the parameters was carried out, anisotropically for all atoms except the hydrogens, which were treated isotropically, to produce the final residual $R=0·0756$. The atomic scattering

factors used were those in *International Tables for X-ray Crystallography* (1962) and the weighting scheme used was $\sqrt{w} = 1/\{1+[(|F_o|-p_2)/p_1]^2\}^{1/2}$ with $p_1=F_{Max}/10·5$ and $p_2=F_{Max}/5·25$.*

Discussion. A diagram showing two symmetry-related molecules and the numbering of the atoms is given in Fig. 1. Atomic coordinates with their estimated stan-

Table 1. *Atomic coordinates and estimated standard deviations*

	x	y	z
Ca	0·13859 (17)	0·19611 (26)	0·22417 (6)
O(1)	0·26611 (62)	0·46091 (99)	0·17902 (22)
O(2)	0·65382 (59)	0·11815 (96)	0·38818 (23)
O(3)	0·94347 (60)	0·49727 (90)	0·37902 (21)
O(4)	0·09419 (62)	−0·02683 (87)	0·33678 (22)
O(5)	0·01175 (62)	0·32984 (97)	0·29228 (21)
O(6)	0·18182 (71)	0·12540 (99)	0·03794 (24)
O(7)	0·70440 (73)	0·32376 (104)	0·49096 (25)
O(8)	0·36312 (62)	0·37336 (114)	0·31401 (24)
O(9)	0·58118 (77)	0·25359 (102)	0·10672 (31)
O(10)	0·62937 (67)	0·42215 (103)	0·24741 (26)
C(1)	0·76833 (90)	0·05323 (118)	0·37367 (31)
C(2)	0·95306 (83)	0·09107 (126)	0·41983 (30)
C(3)	0·03946 (81)	0·27520 (127)	0·39603 (29)
C(4)	0·04753 (75)	0·18319 (131)	0·33692 (28)
C(5)	0·22230 (84)	0·32666 (143)	0·44529 (29)
C(6)	0·23140 (83)	0·45998 (135)	0·50160 (29)

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* A table of calculated and observed structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30482 (24 pp. 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
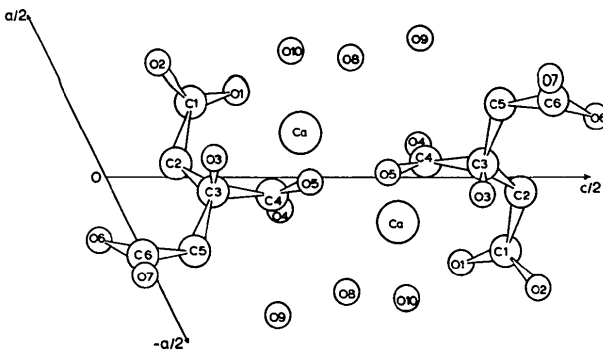

Fig. 1. The molecular arrangement and numbering scheme for calcium hydrogen citrate trihydrate.

Table 2. *Anisotropic temperature parameters* $(\times 10^4)$ *and estimated standard deviations*

Ca	125 (5)	81 (5)	119 (5)	−27 (12)	150 (9)	−38 (12)
O(1)	215 (26)	277 (30)	150 (22)	117 (44)	182 (42)	−12 (46)
O(2)	122 (23)	276 (28)	222 (24)	−104 (44)	201 (40)	10 (42)
O(3)	242 (26)	146 (24)	173 (22)	29 (40)	309 (41)	171 (42)
O(4)	210 (25)	124 (24)	222 (23)	17 (41)	274 (42)	109 (42)
O(5)	245 (25)	240 (29)	110 (21)	111 (43)	205 (39)	205 (47)
O(6)	376 (31)	254 (29)	214 (25)	128 (44)	467 (49)	171 (48)
O(7)	404 (31)	201 (28)	274 (26)	−190 (50)	403 (49)	−292 (54)
O(8)	121 (25)	441 (37)	232 (26)	−171 (50)	4 (42)	32 (48)
O(9)	356 (33)	216 (32)	484 (35)	66 (51)	454 (49)	54 (48)
O(10)	209 (27)	212 (29)	324 (28)	202 (50)	115 (47)	−42 (46)
C(1)	235 (35)	86 (32)	172 (31)	−10 (54)	241 (57)	−75 (57)
C(2)	151 (32)	168 (33)	121 (28)	80 (55)	166 (53)	−46 (57)
C(3)	160 (31)	135 (34)	130 (28)	17 (52)	173 (51)	75 (54)
C(4)	105 (28)	156 (33)	152 (29)	−4 (59)	190 (49)	42 (59)
C(5)	154 (30)	253 (41)	108 (28)	−154 (60)	92 (49)	−51 (63)
C(6)	137 (32)	214 (38)	120 (29)	−21 (56)	98 (53)	72 (57)

dard deviations are in Table 1 and the anisotropic thermal vibration parameters are in Table 2. Calculated bond lengths and bond angles are listed in Tables 3 and 4 respectively. Each calcium ion is octahedrally coordinated to oxygen atoms, four from a citrate ion and two from water molecules with two of the oxygen atoms, O(5) and O(5′), forming bridges between two calcium ions. The oxygen–calcium distances vary between 2·37 and 2·49 Å with an average of 2·42 Å, while the O–Ca–O angles are variable, probably due to the presence of the bridging atoms.

Table 3. *Bond lengths and estimated standard deviations* (Å)

C(1)–O(1)	1·262 (8)	C(3)–C(5)	1·534 (9)
C(1)–O(2)	1·257 (8)	C(4)–O(4)	1·242 (9)
C(1)–C(2)	1·514 (10)	C(4)–O(5)	1·265 (8)
C(2)–C(3)	1·531 (9)	C(5)–C(6)	1·505 (9)
C(3)–O(3)	1·451 (8)	C(6)–O(6)	1·228 (8)
C(3)–C(4)	1·531 (8)	C(6)–O(7)	1·310 (9)

Table 4. *Bond angles and estimated standard deviations* (°)

O(1)–C(1)–O(2)	121·9 (5)	C(3)–C(4)–O(4)	118·1 (5)
O(1)–C(1)–C(2)	118·7 (5)	C(3)–C(4)–O(5)	117·4 (5)
O(2)–C(1)–C(2)	119·5 (5)	O(4)–C(4)–O(5)	124·4 (5)
C(1)–C(2)–C(3)	112·0 (5)	C(3)–C(5)–C(6)	113·1 (5)
C(2)–C(3)–O(3)	110·7 (5)	C(5)–C(6)–O(6)	123·0 (6)
C(2)–C(3)–C(4)	110·6 (5)	C(5)–C(6)–O(7)	115·0 (5)
C(2)–C(3)–C(5)	111·5 (5)	O(6)–C(6)–O(7)	122·0 (5)

Of the remaining oxygen atoms, two, O(7) and O(2), are linked by a hydrogen bond of length 2·557 Å and O(6) and O(3) by a possible hydrogen bond of length

2·758 Å. The final oxygen, in a water molecule [O(9)], forms hydrogen bonds with O(4) (2·832 Å) and O(8) (2·735 Å).

A comparison of the bond lengths in this structure with those found in anhydrous citric acid (Nordman, Weldon & Patterson, 1960) and sodium dihydrogen citrate (Glusker, Van der Helm, Love, Dornberg & Patterson, 1960) shows that the C–O bond length of the hydroxyl group on C(3) is modified by the ionization of the carboxyl group attached to C(3) (1·415 Å unionized; 1·44 and 1·451 Å ionized). Other, slight, differences are not significant.

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