Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71133 (39 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1032]

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Structure of Dipotassium Hydrogen Citrate

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Abstract

Dipotassium hydrogen 2-hydroxy-1,2,3-propanetricarboxylate is shown by this crystal structure determination to be ionized at the central carboxyl group and one terminal carboxyl group. Each citrate ion forms an intramolecular hydrogen bond as well as an intermolecular hydrogen bond connecting it to an adjacent citrate ion. Each K ion is surrounded by eight O atoms from several citrate ions. The metal–oxygen distances range from 2.706 to 3.136 Å.

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Comment

The crystal structure of dipotassium hydrogen citrate was determined in order to compare the metal chelation with that found in tripotassium citrate monohydrate (Carrell, Glusker, Piercy, Stallings, Zacharias, Davis, Astbury & Kennard, 1987).

Each K ion is surrounded by eight O atoms. This compares with values of six to nine for other potassium citrates (Carrell *et al.*, 1987; Zacharias & Glusker, 1993). The citrate ion is shown by this study to have the central carboxyl group and one terminal carboxyl group ionized. The carboxyl group C(5), O(3), O(4) is shown by interatomic distances, O—C—O angles (Table 2) and the location of an H atom to be non-ionized. It takes part in an internal (intraionic) hydrogen bond from O(3) to O(5) (in the central carboxyl group). This is in line with previous evidence on the order of ionization of citric acid

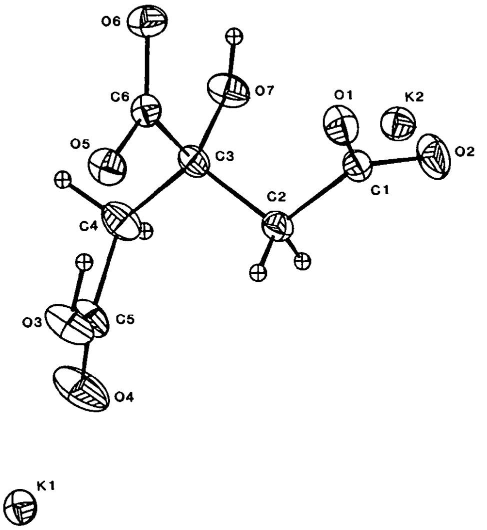

Fig. 1. *ORTEP* (Johnson, 1965) representation at 50% probability level of the thermal ellipsoids, showing atomic numbering.

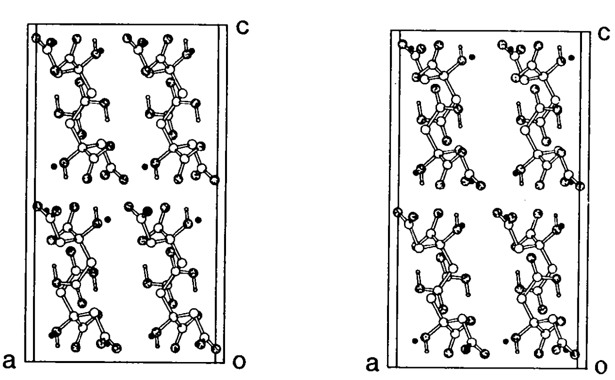

Fig. 2. Stereoview of the crystal packing projected down the *b* axis. Metal ions are black and O atoms are stippled.

(Glusker, van der Helm, Love, Dornberg & Patterson, 1960) in which the central carboxyl group is ionized first, followed by the terminal carboxyl groups. The K ion does not take part in tridentate chelation such as that found in many citrates with smaller cations (Glusker, 1980), in the potassium salt of a fluorodeoxycitrate (Carrell *et al.*, 1987) and in a double citrate salt (Zacharias & Glusker, 1993).

Experimental

Crystal data

$2K^+.C_6H_6O_7^{2-}$
M_r = 268.31
Monoclinic
$C2/c$
a = 10.757 (2) Å
b = 9.650 (2) Å
c = 18.918 (3) Å
β = 90.09 (1)°
V = 1963.8 (7) Å^3
Z = 8
D_x = 1.815 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 16 reflections with θ = 11.2-20.3°
μ = 0.9715 mm^{-1}
T = 293 K
Prism
0.32 × 0.21 × 0.20 mm
Colorless

Data collection

Siemens-Nicolet *P*3*m* diffractometer
Variable ω scans of rate 8.37-58.6° min^{-1}
Absorption correction: empirical
T_{min} = 0.855, T_{max} = 1.000
7435 measured reflections
7076 independent reflections
5794 observed reflections [$I \geq 3.0\sigma(I)$]
R_{int} = 0.021
θ_{max} = 42.5°
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 18$
$l = -35 \rightarrow 35$
4 standard reflections monitored every 92 reflections intensity variation: <1%

Refinement

Refinement on F
Final R = 0.040 (R_{all} = 0.051)
wR = 0.051 (wR_{all} = 0.060)
S = 2.18
5794 reflections
160 parameters
All H-atom parameters refined
$w = [\sigma^2(F)]^{-1}$; $\sigma(F) = (F/2)[\sigma^2(I)/(I)^2 + \delta^2]^{1/2}$, δ = 0.022 (instrumental uncertainty)
$(\Delta/\sigma)_{max}$ = 0.01 for K,O,C; = 0.03 for H
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2)

For non-H atoms U_{eq} = 1/3(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{iso}/U_{eq}
K(1)	0.09950 (1)	0.15838 (2)	0.05433 (1)	0.02226 (6)
K(2)	0.11809 (1)	0.45186 (2)	0.42158 (1)	0.02280 (7)
O(1)	0.47091 (7)	0.17182 (8)	0.45900 (4)	0.0262 (2)
O(2)	0.3816 (1)	0.37876 (8)	0.44567 (4)	0.0344 (3)
O(3)	0.35790 (9)	−0.0344 (1)	0.23426 (4)	0.0353 (3)
O(4)	0.2306 (1)	0.0959 (1)	0.17292 (4)	0.0476 (4)
O(5)	0.38391 (7)	−0.09826 (7)	0.36031 (3)	0.0250 (2)
O(6)	0.26882 (7)	−0.07047 (8)	0.45697 (3)	0.0270 (2)
O(7)	0.15748 (6)	0.15731 (8)	0.41045 (3)	0.0256 (2)
C(1)	0.40713 (8)	0.25795 (8)	0.42492 (4)	0.0200 (2)
C(2)	0.35323 (8)	0.21008 (8)	0.35418 (4)	0.0213 (2)
C(3)	0.25003 (7)	0.10113 (8)	0.36535 (3)	0.0186 (2)
C(4)	0.18244 (8)	0.0707 (1)	0.29494 (4)	0.0273 (3)
C(5)	0.2606 (1)	0.0463 (1)	0.22952 (4)	0.0279 (3)
C(6)	0.30416 (7)	−0.03302 (8)	0.39770 (4)	0.0190 (2)
H(O3)	0.371 (4)	−0.062 (4)	0.284 (2)	0.071 (9)
H(O7)	0.165 (2)	0.125 (3)	0.452 (1)	0.034 (5)

Table 2. *Geometric parameters* (Å, °)

For K—O distances all e.s.d.'s are 0.001 Å.

O(1)—C(1)	1.255 (1)	K(1)—O(2^{i})	2.706
O(2)—C(1)	1.261 (1)	K(1)—O(4)	2.716
O(3)—C(5)	1.308 (2)	K(1)—O(6^{ii})	2.728
O(4)—C(5)	1.216 (2)	K(1)—O(1^{iii})	2.801
O(5)—C(6)	1.278 (1)	K(1)—O(7^{iv})	2.845
O(6)—C(6)	1.238 (1)	K(1)—O(5^{v})	2.856
O(7)—C(3)	1.420 (1)	K(1)—O(6^{v})	2.983
C(1)—C(2)	1.529 (1)	K(1)—O(2^{iii})	3.136
C(2)—C(3)	1.544 (1)	K(2)—O(1^{vi})	2.730
C(3)—C(4)	1.545 (1)	K(2)—O(1^{vii})	2.742
C(3)—C(6)	1.545 (1)	K(2)—O(4^{v})	2.790
C(4)—C(5)	1.516 (1)	K(2)—O(5^{vii})	2.813
O(3)—H(O3)	1.00 (3)	K(2)—O(6^{vi})	2.839
O(7)—H(O7)	0.84 (2)	K(2)—O(7)	2.882
		K(2)—O(2)	2.955
		K(2)—O(3^{v})	2.963
O(1)—C(1)—O(2)	124.9 (1)	C(4)—C(3)—C(6)	111.0 (1)
O(1)—C(1)—C(2)	117.1 (1)	C(3)—C(4)—C(5)	118.2 (1)
O(2)—C(1)—C(2)	118.0 (1)	O(3)—C(5)—O(4)	120.4 (1)
C(1)—C(2)—C(3)	111.0 (1)	O(3)—C(5)—C(4)	118.8 (1)
O(7)—C(3)—C(2)	109.1 (1)	O(4)—C(5)—C(4)	120.8 (1)
O(7)—C(3)—C(4)	105.1 (1)	O(5)—C(6)—O(6)	124.4 (1)
O(7)—C(3)—C(6)	110.2 (1)	O(5)—C(6)—C(3)	116.5 (1)
C(2)—C(3)—C(4)	110.4 (1)	O(6)—C(6)—C(3)	119.1 (1)
C(2)—C(3)—C(6)	110.7 (1)		

O(1)—C(1)—C(2)—C(3)	69.5 (1)
O(2)—C(1)—C(2)—C(3)	−108.6 (1)
C(1)—C(2)—C(3)—O(7)	56.0 (1)
C(1)—C(2)—C(3)—C(4)	171.1 (1)
C(1)—C(2)—C(3)—C(6)	−65.5 (1)
O(7)—C(3)—C(4)—C(5)	163.8 (1)
C(2)—C(3)—C(4)—C(5)	46.3 (1)
C(6)—C(3)—C(4)—C(5)	−77.0 (1)
O(7)—C(3)—C(6)—O(5)	176.3 (1)
O(7)—C(3)—C(6)—O(6)	−3.7 (1)
C(2)—C(3)—C(6)—O(5)	−62.9 (1)
C(2)—C(3)—C(6)—O(6)	117.1 (1)
C(4)—C(3)—C(6)—O(5)	60.2 (1)
C(4)—C(3)—C(6)—O(6)	−119.9 (1)
C(3)—C(4)—C(5)—O(3)	44.7 (1)
C(3)—C(4)—C(5)—O(4)	−138.4 (1)
H(O7)—O(7)—C(3)—C(2)	−103 (2)
H(O7)—O(7)—C(3)—C(4)	139 (2)
H(O7)—O(7)—C(3)—C(6)	19 (2)

D—H···A	D—H	H···A	D···A	D—H···A
O(3)—H(O3)···O(5)	1.00 (3)	1.48 (4)	2.478 (1)	176 (4)
O(7)—H(O7)···O(2^{vi})	0.84 (2)	2.00 (2)	2.777 (1)	152 (2)

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

Equimolar amounts of potassium carbonate and citric acid monohydrate were dissolved in water and warmed with stirring.

Portions of the solution were placed in screw-capped vials, overlain with ethanol, closed and allowed to stand at room temperature. Small colorless prisms formed in about one week.

Diffraction data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied (North, Phillips & Mathews, 1968). The positions of the K atoms were obtained using the direct methods program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declerq & Woolfson, 1980) and a structure-factor calculation using these gave a Fourier map from which the remaining non-H atoms were located. Refinement of the structure on *F*, first with isotropic and then anisotropic thermal parameters, using a full-matrix least-squares procedure, gave parameters for the calculation of a difference Fourier map from which the locations of the H atoms were found. These H atoms were included in the final refinement cycles with isotropic thermal factors equivalent to those of the atoms to which they were bonded. All crystallographic calculations were made with in-house programs (Carrell, Shieh & Takusagawa, 1981). Thermal ellipsoid diagrams were produced with the program *SNOOPI* (Davies, 1983) and other diagrams with the program *VIEW* (Carrell, 1976).

This research was supported by grants GM-44360 and CA-06927 from the National Institutes of Health and by an appropriation from the Commonwealth of Pennsylvania.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances, bond angles and torsion angles involving H atoms, and direction cosines of non-H-atom thermal ellipsoids have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71070 (58 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1033]

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Structure of Strontium Citrate Pentahydrate

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Abstract

The crystal structure of tristrontium bis(2-hydroxy-1,2,3-propanetricarboxylate) pentahydrate has been determined. One Sr ion is coordinated with eight O atoms, another with nine and the third with ten at distances ranging from 2.498 (2) to 2.781 (2) Å. Two Sr ions are bound to citrate ions in a tridentate manner. Both citrate ions in the asymmetric unit are in an extended conformation. There are 11 hydrogen bonds in one asymmetric unit of the crystal structure.

Comment

The crystal structure of strontium citrate has been determined in order to establish the conformation of the citrate ion and the manner by which it is chelated by the metal ion, for comparison with data from other citrate ions (Glusker, 1980).

This crystal structure determination shows that the citrate ion is in an extended conformation. As in other citrates the plane of the central carboxyl group is almost perpendicular to the plane of the C-atom backbone [C(1) to C(5)]. The O atom of the hydroxyl group lies in the plane of the central carboxyl group [C(6), O(5), O(6) on C(3)]. Both citrate ions are chelated in a tridentate manner to an Sr cation; Sr(1) binds O(5*A*), O(7*A*) and O(4*A*) while Sr(3) binds O(5*B*), O(7*B*) and O(2*B*) (Table 2). Sr ions share both O atoms of the central carboxyl group [O(5) and O(6) bound by $\mathrm{Sr}(1^{\mathrm{ii}})$ and $\mathrm{Sr}(3^{\mathrm{viii}})$] and the carboxyl group not involved in tridentate chelation [O(1*A*) and O(2*A*) to $\mathrm{Sr}(3^{\mathrm{vii}})$ and O(3*B*) and O(4*B*) to $\mathrm{Sr}(1^{\mathrm{iii}})$]. This type of binding is particularly characteristic of divalent ions with metal–oxygen distances of approximately 2.6 Å (Carrell, Carrell, Erlebacher & Glusker, 1988), the range here being 2.650–2.772 Å. The hydroxyl group H atoms act as bridges between different citrate ions through hydrogen bonding (see Table 2 and Fig. 2).

The Sr—O distances vary from 2.498 (2) to 2.781 (2) Å, with average values of 2.58 Å for coordination number 8 [Sr(2)], 2.67 Å for coordination number 9 [Sr(1)], and 2.68 Å for coordination number 10 [Sr(3)]. These values are considerably

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