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Structure of a Citrate Double Salt: Potassium Dihydrogen Citrate–Lithium Potassium Hydrogen Citrate Monohydrate

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Abstract

The crystal structure of a double salt of potassium dihydrogen citrate and lithium potassium hydrogen citrate monohydrate has been determined. One potassium ion is coordinated with eight O atoms and the other with nine O atoms at *M*—O distances in the range 2.660 (1) to 3.139 (1) Å. Two of these O atoms are shared by both potassium ions. The lithium ion is tetrahedrally surrounded by four O atoms at distances in the range 1.870 (3) to 1.988 (3) Å. This crystal structure contains nine hydrogen bonds in the asymmetric unit. The water molecule connects different citrate ions along the **c** direction by hydrogen bonding.

Comment

The crystal structure of a double salt of citric acid, potassium dihydrogen citrate–lithium potassium hydrogen citrate monohydrate, was determined in order to compare the metal chelation with that found in other potassium and lithium citrates.

The asymmetric unit of this crystal structure contains one dihydrogen citrate ion (*B*) (Fig. 1) and one hydrogen citrate ion, two potassium ions, a lithium ion and a water molecule. Table 2 gives the dimensions of the citrate ions which are in the fully-extended conformation, along with selected torsion angles. Data on the metal coordination and hydrogen bonding in the crystal are given in Table 3. The potassium ion K(1) is surrounded by eight O atoms and K(2) by nine O atoms. The distances between the potassium ion and the O atoms are, in general, larger when the coordination number is higher. The minimum values are 2.660 (1) Å for a coordination number of eight and 2.729 (1) Å for a coordination number of nine. In both cases the potassium ion spans the α-hydroxycarboxylate group, and forms a tridentate chelate O(6*A*), O(7*A*), O(1*A*) and O(6*B*), O(7*B*), O(4*B*). Such chelation has been found in potassium deoxyfluorocitrate (Carrell, Glusker, Piercy, Stallings, Zacharias, Davis, Astbury & Kennard, 1987) but not in other potassium citrates to date. The location of the citrate H(O5*A*) atom, between O(5*A*) and O(2*A*) of another citrate ion, was checked by calculation of a difference electron-density map. The peak corresponding to this H atom in the map was elongated. Since the e.s.d. values for H atoms are somewhat high, particularly in view of the presence of potassium ions in the structure, it is assumed that either this H(O5*A*) atom is disordered between two positions or that its location is questionable. Therefore, the question as to which O atom [O(5*A*) or O(2*A*)] is involved in the ionization of this citrate ion (*A*) is uncertain in this crystal structure determination, although the C—O distances suggest that the carboxyl group containing O(5*A*) is not ionized (Table 2).

The lithium ion is surrounded by four O atoms from different citrate ions, as found in certain other crystal structures of other lithium citrates (Gabe, Glusker, Minkin & Patterson, 1967; Rossi, Rickles &

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Glusker, 1983) except for one that is isomorphous with the sodium salt and appears to have a coordination number of five (Glusker, van der Helm, Love, Dornberg, Minkin, Johnson & Patterson, 1965), and one lithium ion in trilithium citrate (Rossi *et al.*, 1983) which has a coordination number of six and Li—O distances of 1.998 to 2.222 Å. Li—O distances in the structure reported in this paper range from 1.870 (3) to 1.988 (3) Å compared with values of 1.882 to 1.960 Å for the tetracoordinated lithium ions in trilithium citrate (Rossi *et al.*, 1983).

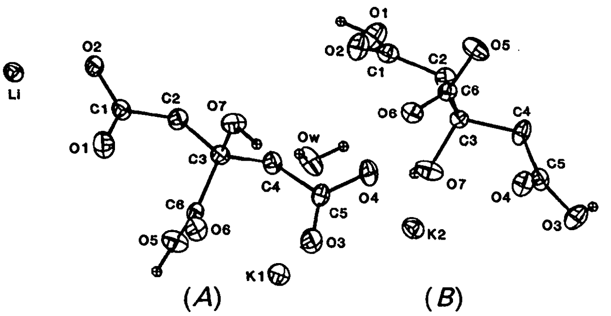

Fig. 1. *ORTEP* (Johnson, 1965) representation (50% probability) showing the atomic numbering. Citrate (*B*) is monoionized.

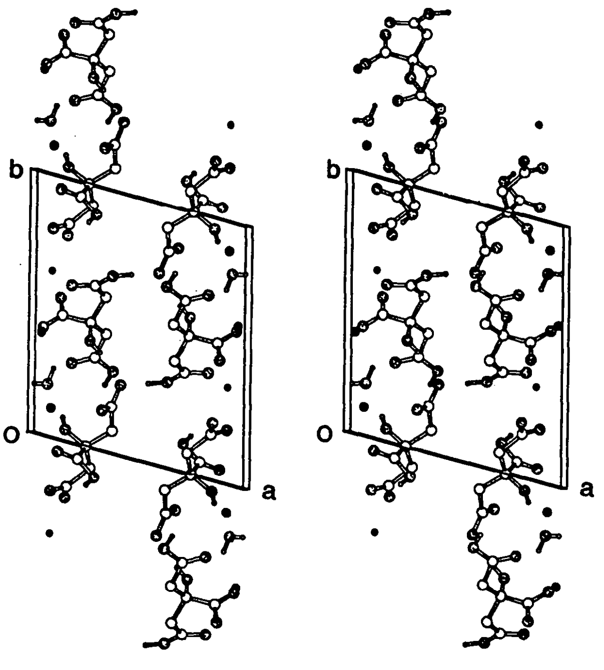

Fig. 2. Stereoview of the packing diagram projected down **c**. Metal ions are black, O atoms are stippled.

Experimental

Crystal data

Li$^+$.2K$^+$.C$_6$H$_6$O$_7^{2-}$.C$_6$H$_7$O$_7^-$.H$_2$O
$Z = 2$
$D_x = 1.79$ Mg m^{-3}
$M_r = 484.39$
Triclinic
$P\bar{1}$
$a = 11.343$ (3) Å
$b = 13.078$ (3) Å
$c = 6.272$ (1) Å
$\alpha = 89.79$ (2)°
$\beta = 94.36$ (2)°
$\gamma = 104.20$ (2)°
$V = 899.3$ (4) Å^3
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 16 reflections with
$\theta = 6.5$–17.3°
$\mu = 0.601$ mm^{-1}
$T = 293$ K
Irregularly shaped
0.35 × 0.21 × 0.08 mm
Colorless

Data collection

Siemens-Nicolet *P*3*m* diffractometer
Variable ω scans of rate 1.0–58.6° min^{-1}
Absorption correction: empirical
$T_{min} = 0.854$, $T_{max} = 1.000$
4504 measured reflections
4126 independent reflections
3657 observed reflections [$I \geq 3.0\sigma(I)$]
$R_{int} = 0.017$
$\theta_{max} = 27.5$°
$h = -14 \rightarrow 14$
$k = -16 \rightarrow 16$
$l = -8 \rightarrow 0$
4 standard reflections monitored every 92 reflections
intensity variation: <1%

Refinement

Refinement on *F*
Final $R = 0.039$
$wR = 0.049$
$S = 0.68$
3657 reflections
331 parameters
All H-atom parameters refined
$w = [\sigma^2(F)]^{-1}$
$(\Delta/\sigma)_{max} = 0.3$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
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)	0.08402 (3)	0.10900 (3)	0.77364 (6)	0.0256 (1)
K(2)	0.03944 (3)	0.38767 (3)	0.69062 (6)	0.0253 (1)
Li	0.1120 (3)	−0.3638 (2)	−0.1600 (5)	0.021 (1)
O*w*	0.0798 (1)	0.1989 (1)	0.3716 (2)	0.0367 (7)
O(1*A*)	0.1041 (1)	−0.2034 (1)	0.1740 (2)	0.0321 (6)
O(2*A*)	0.1803 (1)	−0.21245 (9)	−0.1382 (2)	0.0269 (5)
O(3*A*)	0.3247 (1)	0.1521 (1)	0.6379 (2)	0.0326 (6)
O(4*A*)	0.4164 (1)	0.26937 (9)	0.4101 (2)	0.0269 (5)
O(5*A*)	0.2921 (1)	−0.1104 (1)	0.5554 (2)	0.0289 (6)
O(6*A*)	0.1258 (1)	−0.04700 (9)	0.5433 (2)	0.0263 (5)
O(7*A*)	0.1702 (1)	0.0463 (1)	0.1687 (2)	0.0292 (6)
C(1*A*)	0.1811 (2)	−0.1699 (1)	0.0438 (3)	0.0219 (7)
C(2*A*)	0.2875 (2)	−0.0754 (1)	0.1020 (3)	0.0243 (7)
C(3*A*)	0.2635 (1)	0.0019 (1)	0.2662 (3)	0.0208 (7)
C(4*A*)	0.3826 (2)	0.0873 (1)	0.3152 (3)	0.0240 (7)
C(5*A*)	0.3728 (1)	0.1756 (1)	0.4670 (3)	0.0205 (7)
C(6*A*)	0.2187 (1)	−0.0553 (1)	0.4704 (3)	0.0201 (7)
O(1*B*)	0.3960 (1)	0.3158 (1)	−0.0975 (2)	0.0329 (6)
O(2*B*)	0.2016 (1)	0.3052 (1)	−0.0457 (2)	0.0295 (6)
O(3*B*)	0.3655 (1)	0.6716 (1)	0.7142 (2)	0.0301 (6)
O(4*B*)	0.1808 (1)	0.5969 (1)	0.5788 (2)	0.0259 (5)
O(5*B*)	0.1453 (1)	0.5414 (1)	0.0463 (2)	0.0312 (6)
O(6*B*)	0.0602 (1)	0.41115 (9)	0.2568 (2)	0.0235 (5)
O(7*B*)	0.2716 (1)	0.4055 (1)	0.4585 (2)	0.0287 (5)
C(1*B*)	0.3085 (2)	0.3490 (1)	−0.0158 (3)	0.0219 (7)
C(2*B*)	0.3571 (1)	0.4501 (1)	0.1107 (3)	0.0210 (7)

C(3*B*)	0.2795 (1)	0.4758 (1)	0.2838 (2)	0.0172 (6)
C(4*B*)	0.3442 (2)	0.5874 (1)	0.3667 (3)	0.0247 (8)
C(5*B*)	0.2909 (1)	0.6187 (1)	0.5608 (3)	0.0211 (7)
C(6*B*)	0.1505 (1)	0.4755 (1)	0.1885 (3)	0.0182 (6)
H1(O*w*)	0.018 (3)	0.186 (2)	0.342 (5)	0.079 (9)
H2(O*w*)	0.108 (2)	0.264 (2)	0.332 (4)	0.054 (7)
H1(O5*A*)	0.253 (3)	−0.148 (2)	0.665 (5)	0.072 (9)
H1(O7*A*)	0.155 (2)	0.088 (2)	0.263 (4)	0.040 (6)
H1(O1*B*)	0.362 (2)	0.258 (2)	−0.172 (4)	0.046 (7)
H1(O3*B*)	0.453 (3)	0.697 (3)	0.677 (5)	0.09 (1)
H1(O7*B*)	0.319 (2)	0.370 (2)	0.454 (3)	0.041 (6)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

	(*A*)	(*B*)
O(1)—C(1)	1.241 (2)	1.314 (2)
O(2)—C(1)	1.270 (2)	1.208 (2)
O(3)—C(5)	1.243 (2)	1.309 (2)
O(4)—C(5)	1.266 (2)	1.224 (1)
O(5)—C(6)	1.312 (2)	1.246 (2)
O(6)—C(6)	1.209 (2)	1.257 (2)
O(7)—C(3)	1.425 (2)	1.422 (2)
C(1)—C(2)	1.524 (2)	1.505 (2)
C(2)—C(3)	1.530 (2)	1.535 (2)
C(3)—C(4)	1.538 (2)	1.536 (2)
C(3)—C(6)	1.537 (2)	1.537 (2)
C(4)—C(5)	1.529 (2)	1.502 (2)
O(5)—H1(O5)	0.92 (2)	
O(7)—H(1O7)	0.86 (2)	0.79 (2)
O*w*—H1(O*w*)	0.70 (2)	
O*w*—H2(O*w*)	0.87 (3)	
O(1)—H1(O1)		0.88 (2)
O(3)—H1(O3)		1.01 (2)
O(1)—C(1)—O(2)	123.8 (1)	123.7 (2)
O(1)—C(1)—C(2)	120.2 (1)	111.9 (1)
O(2)—C(1)—C(2)	116.0 (1)	124.4 (1)
C(1)—C(2)—C(3)	115.4 (1)	117.7 (1)
O(7)—C(3)—C(2)	106.4 (1)	112.9 (1)
O(7)—C(3)—C(4)	111.0 (1)	108.5 (1)
O(7)—C(3)—C(6)	109.1 (1)	109.5 (1)
C(2)—C(3)—C(4)	107.9 (1)	105.9 (1)
C(2)—C(3)—C(6)	111.1 (1)	110.8 (1)
C(4)—C(3)—C(6)	111.2 (1)	109.3 (1)
C(3)—C(4)—C(5)	114.9 (1)	112.8 (1)
O(3)—C(5)—O(4)	123.9 (2)	119.6 (1)
O(3)—C(5)—C(4)	119.1 (1)	118.2 (1)
O(4)—C(5)—C(4)	117.0 (1)	122.2 (1)
O(5)—C(6)—O(6)	124.9 (1)	125.3 (1)
O(5)—C(6)—C(3)	113.3 (1)	115.3 (1)
O(6)—C(6)—C(3)	121.8 (1)	119.3 (1)
C(6)—O(5)—H1(O5)	107 (1)	
C(3)—O(7)—H1(O7)	107 (1)	111 (2)
C(1)—O(1)—H1(O1)		108 (1)
C(5)—O(3)—H1(O3)		114 (2)
H1(O*w*)—O*w*—H2(O*w*)	106 (3)	
O(1)—C(1)—C(2)—C(3)	−27.1	−156.4
O(2)—C(1)—C(2)—C(3)	155.3	26.1
C(1)—C(2)—C(3)—O(7)	−64.4	67.5
C(1)—C(2)—C(3)—C(4)	176.4	−173.9
C(1)—C(2)—C(3)—C(6)	54.2	−55.6
O(7)—C(3)—C(4)—C(5)	60.1	−49.8
C(2)—C(3)—C(4)—C(5)	176.3	−171.2
C(6)—C(3)—C(4)—C(5)	−61.6	69.4
O(7)—C(3)—C(6)—O(5)	171.4	173.8
O(7)—C(3)—C(6)—O(6)	−9.8	−6.2
C(2)—C(3)—C(6)—O(5)	54.4	−61.2
C(2)—C(3)—C(6)—O(6)	−126.8	118.9
C(4)—C(3)—C(6)—O(5)	−65.8	55.1
C(4)—C(3)—C(6)—O(6)	113.0	−124.9
C(3)—C(4)—C(5)—O(3)	49.5	140.1
C(3)—C(4)—C(5)—O(4)	−131.3	−40.3
H1(O5)—O(5)—C(6)—O(6)	8	
H1(O5)—O(5)—C(6)—C(3)	−173	
H1(O7)—O(7)—C(3)—C(2)	178	−12
H1(O7)—O(7)—C(3)—C(4)	−65	−105
H1(O7)—O(7)—C(3)—C(6)	58	136
H1(O1)—O(1)—C(1)—O(2)		−1
H1(O1)—O(1)—C(1)—C(2)		−178
H1(O3)—O(3)—C(5)—O(4)		−170
H1(O3)—O(3)—C(5)—C(4)		10

Table 3. *Metal–oxygen contact distances* (Å) *and hydrogen-bond geometry* (Å, °)

K(1)—O(6*A*)	2.660 (1)	K(2)—O(4*B*)	2.925 (1)
K(1)—O(1A^{i})	2.754 (1)	K(2)—O(4B^{iii})	2.956 (1)
K(1)—O*w*	2.780 (1)	K(2)—O(5B^{ii})	2.983 (1)
K(1)—O(2B^{ii})	2.785 (1)	K(2)—O(7*B*)	3.063 (1)
K(1)—O(7A^{ii})	2.789 (1)	K(2)—O(5B^{iii})	3.077 (1)
K(1)—O(3*A*)	2.844 (1)	K(2)—O(6B^{iii})	3.135 (1)
K(1)—O(6A^{i})	2.936 (1)	Li—O(5B^{iv})	1.870 (3)
K(1)—O(7A^{i})	3.139 (1)	Li—O(2*A*)	1.942 (3)
K(2)—O(1A^{i})	2.729 (1)	Li—O(6B^{v})	1.949 (2)
K(2)—O(6*B*)	2.758 (1)	Li—O(4B^{vi})	1.988 (3)
K(2)—O(2B^{ii})	2.789 (1)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*w*—H1···O(6A^{i})	0.70 (2)	2.28 (3)	2.753 (2)	127 (3)
O*w*—H2···O(6*B*)	0.87 (3)	2.17 (2)	2.922 (2)	145 (2)
O*w*—H2···O(7*B*)	0.87 (3)	2.37 (2)	3.046 (2)	135 (2)
O(5*A*)—H···O(2A^{ii})	0.92 (3)	1.65 (3)	2.569 (2)	178 (2)
O(7*A*)—H···O*w*	0.86 (2)	1.99 (2)	2.806 (2)	156 (2)
O(7*A*)—H···O(6*A*)	0.86 (2)	2.47 (2)	2.669 (2)	93 (2)
O(1*B*)—H···O(3A^{vii})	0.87 (2)	1.78 (2)	2.640 (2)	166 (2)
O(3*B*)—H···O(4A^{viii})	1.01 (2)	1.58 (2)	2.584 (2)	173 (2)
O(7*B*)—H···O(4*A*)	0.79 (2)	1.95 (2)	2.734 (2)	171 (2)

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

An aqueous solution of tripotassium citrate and trilithium citrate in the approximate molar ratio 1:1 was warmed with stirring. Portions of the cooled solution were placed in test tubes, overlain with ethanol and sealed. Crystals formed in about 14 d.

Diffraction data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied (North, Phillips & Mathews, 1968). Weights were derived from counting statistics using the relation $\sigma(F) = (F/2)[\sigma^2(I)/I^2 + \delta^2]^{1/2}$ in which δ (= 0.029) is an instrumental uncertainty based on the variation in the intensities of the standard reflections monitored during the data collection.

The positions of the K atoms were obtained using the direct-methods computer program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). A structure-factor calculation gave a Fourier map from which the remaining non-H atoms were located. Refinement of the structure, first with isotropic and then anisotropic thermal parameters, using a full-matrix least-squares procedure followed by calculation of a difference Fourier map, revealed the positions of the H atoms. These were included in the final refinement cycles with isotropic thermal parameters equivalent to those of the atoms to which they are bonded. All crystallographic calculations were made using 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).

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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.

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

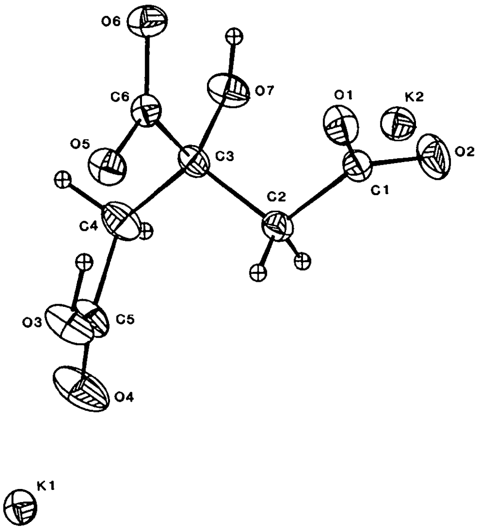

Fig. 1. *ORTEP* (Johnson, 1965) representation at 50% probability level of the thermal ellipsoids, showing atomic numbering.

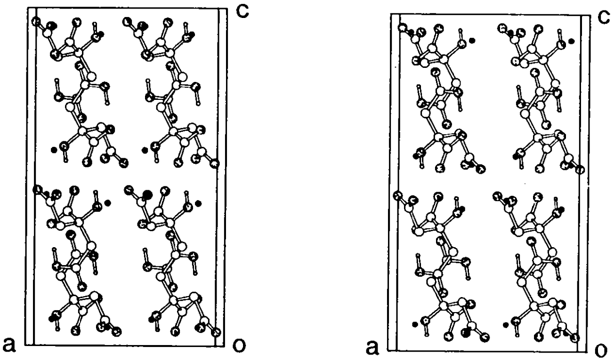

Fig. 2. Stereoview of the crystal packing projected down the *b* axis. Metal ions are black and O atoms are stippled.