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The Crystal Structure of Ca-Malate-dihydrate, $CaC_4H_4O_5 \cdot 2H_2O$

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The crystal structure of $CaC_4H_4O_5 \cdot 2H_2O$ has been determined and refined from three-dimensional X-ray data. The crystals are orthorhombic (space group $P2_12_12_1$) with four molecules in a unit cell with the dimensions $a = 6.728$ Å, $b = 8.448$ Å and $c = 13.413$ Å. The structure comprises double chains of calcium ions linked together along the a-axis by one of the carboxyl groups of the malate ions. Each calcium ion has eight ligands arranged in an irregular way. The mean bond lengths are: Ca–O = 2.46 Å and C–C = 1.51 Å.

Chelate formation between calcium ions and the dicarboxylic acids of the Krebs cycle probably plays an important role in the transportation of calcium ions in plants. Many studies[1] have been made on solutions of metal ions and these acids in order to determine the compositions and stabilities of the complexes formed. Since very little was known about the structure of these complexes, an X-ray investigation of Ca-malate-dihydrate was undertaken.

EXPERIMENTAL

Calcium-malate-dihydrate was prepared by adding solid $Ca(OH)_2$ to an aqueous solution of L-malic acid in equivalent amounts.[2] Suitable crystals for X-ray studies were obtained by recrystallization from warm dilute HNO_3. The pH of the solution was adjusted to about 5 with K_2CO_3.

The unit-cell dimensions of the orthorhombic crystals were determined from powder patterns recorded in a Guiner-type focussing camera using Cr$K\alpha$-radiation and with silicon as internal standard. A value of 2.2896 Å was assumed for the Cr$K\alpha_1$ wavelength.

A crystal with dimensions approximately 0.2 × 0.2 × 0.2 mm was used for the single crystal studies. Equi-inclination Weissenberg photographs for the six zones $0 \leq h \leq 5$ were recorded using Cu$K\alpha$-radiation. In order to correlate the individual layer-lines a second crystal was mounted and zone $l = 0$ was recorded in a similar way. The relative intensities were estimated visually using the multiple-film technique and comparison with a calibrated intensity scale. The data were corrected for Lorentz and polarization effects. No corrections were made for absorption. 764 independent reflexions were used for the structure determination.

STRUCTURE DATA

Cell symmetry: Orthorhombic; space group $P2_12_12_1$.
Dimensions: $a = 6.728 \pm 0.001$ Å, $b = 8.448 \pm 0.001$ Å, $c = 13.413 \pm 0.003$ Å.
Volume of unit cell: 762 Å^3.
Density (observed by the flotation method): 1.8 g/cm^3.
Density: (calculated) 1.81 g/cm^3 for a cell content of four formula units.

DETERMINATION AND REFINEMENT OF ATOMIC PARAMETERS

The positions of the calcium and five oxygen atoms of the asymmetric unit were determined from a three-dimensional Patterson synthesis. These positions were used to compute phase angles for a three-dimensional electron density map from which the remaining two oxygen and four carbon atoms were located. All Fourier and structure-factor calculations were made on the Swedish computer FACIT EDB using programmes devised by Liminga and Olovsson.[3]

The atomic parameters were first refined by the least-squares method employing the programme devised by Åsbrink and Brändén [4] for the computer FACIT. The parameters refined were the atomic coordinates (hydrogen atoms excluded), individual isotropic temperature factors and six scale factors, one for each set of Weissenberg multiple-films. The weights, w, were calculated according to an equation suggested by Cruickshank *et al.*[5] $w = 1/(a + |F_o| + c|F_o|^2)$, final constants being $a = 1.6724$ and $c = 0.03228$. Atomic scattering factors were obtained from the *International Tables*.[6] After ten cycles of refinement the conventional R-value was 0.091.

Further refinement was achieved on the computer IBM 7090 using the programme OR—FLS,[7] modified by Brändén to accommodate more parameters. The parameters now refined were atomic coordinates (hydrogen atoms excluded), individual anisotropic temperature factors, and one scale factor. The eight hydrogen atoms of the asymmetric unit were included in the calculation of structure-factors at this stage of the refinement. The arrangement of H-atoms in the structure was obtained from a difference synthesis based on the final parameters from the isotropic refinement. The H-atom parameters used in the structure-factor calculation were computed from the positions of the oxygen and carbon atoms, assuming regular tetrahedral bond angles and O—H and C—H distances of 1.0 and 1.1 Å, respectively. After three cycles of anisotropic refinement the R-value was 0.076. No attempt was made to solve the anisotropy of the crystal from the anisotropic temperature factors, since data were collected only at room temperature.[8] Final atomic parameters are listed in Table 1 and a comparison of $|F_{obs}|$ and $|F_{calc}|$ is made in Table 2. Planar arrangements in the structure were calculated according to Blow [9] and are listed in Table 3.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Interatomic distances, bond angles and hydrogen bond lengths are given in Table 4 together with approximate standard deviations calculated from the correlation matrix obtained in the last cycle of anisotropic refinement.[7]

Table 1. Final atomic coordinates and their estimated standard deviations.

Atoms	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Ca(1)	0.0424	0.0003	0.1887	0.0002	0.0727	0.0001
O(2)	0.3093	0.0011	0.0243	0.0007	0.6739	0.0004
O(3)	0.2475	0.0013	0.2266	0.0009	0.3857	0.0005
O(4)	0.0734	0.0014	0.4763	0.0008	0.0772	0.0005
O(5)	0.3846	0.0011	0.2343	0.0008	0.0882	0.0004
O(6)	0.0439	0.0012	0.4316	0.0007	0.5041	0.0004
O(7)	0.0599	0.0010	0.2474	0.0008	0.2510	0.0004
O(8)	0.2039	0.0013	0.2889	0.0009	0.8991	0.0005
C(9)	0.1949	0.0016	0.1842	0.0010	0.3001	0.0005
C(10)	0.0327	0.0015	0.3201	0.0009	0.8686	0.0005
C(11)	0.3014	0.0017	0.0410	0.0009	0.2554	0.0005
C(12)	0.0103	0.0017	0.4238	0.0011	0.7775	0.0006
H(13)	0.2937		0.4919		0.5520	
H(14)	0.4454		0.4848		0.6474	
H(15)	0.1181		0.3569		0.4609	
H(16)	0.4378		0.1241		0.4565	
H(17)	0.4001		0.1079		0.7018	
H(18)	0.1938		0.0443		0.8182	
H(19)	0.0964		0.3755		0.7152	
H(20)	0.4073		0.4633		0.2886	

Thermal parameters of non-hydrogen atoms and their estimated standard deviations. β, as given here, is defined by

$$T = \exp\{-10^{-4}(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$$

Atoms	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca(1)	88(6)	66(2)	25(1)	0(2)	− 2(2)	3(1)
O(2)	174(19)	89(8)	36(3)	−47(10)	− 6(7)	2(4)
O(3)	224(23)	138(11)	38(3)	41(14)	−17(8)	−16(5)
O(4)	239(26)	101(9)	61(5)	−10(13)	12(10)	−10(5)
O(5)	127(23)	121(9)	32(4)	17(11)	−13(6)	21(4)
O(6)	205(21)	92(7)	38(3)	−25(12)	8(7)	− 4(4)
O(7)	185(24)	129(9)	35(3)	53(13)	− 2(8)	− 8(4)
O(8)	106(24)	155(12)	42(3)	26(12)	− 4(7)	− 8(5)
C(9)	157(28)	76(10)	30(4)	−23(15)	6(8)	12(6)
C(10)	134(28)	89(10)	23(3)	25(15)	−24(8)	− 1(5)
C(11)	206(30)	72(10)	24(3)	− 1(13)	− 1(9)	10(5)
C(12)	131(27)	114(12)	32(4)	−37(16)	−12(9)	19(6)

The structure comprises double chains of calcium ions linked together along the a-axis by one of the carboxyl groups of the malate ions as shown in Fig. 1. These chains are linked together by a network of hydrogen bonds.

Each calcium ion has eight ligands arranged in an irregular configuration. Five of the ligands are carboxyl-oxygen atoms from three different malate ions. These oxygen atoms and the calcium ion are approximately coplanar. A hydroxyl-oxygen and a water molecule on one side of this plane and another

Table 2. Observed and calculated structure factors.

H	K	L	|Fo|	|Fc|	H	K	L	|Fo|	|Fc|	H	K	L	|Fo|	|Fc|	H	K	L	|Fo|	|Fc|
0	0	2	12.2	5.0	0	7	11	3.7	2.5	1	3	1	43.7	43.1	2	0	14	33.6	32.5
0	0	4	18.1	19.2	0	7	10	9.5	9.5	1	3	0	5.6	5.8	2	0	16	6.8	7.8
0	0	6	93.4	94.8	0	7	9	8.5	8.3	1	4	14	20.0	18.9	2	1	16	9.2	9.0
0	0	8	8.7	7.2	0	7	8	15.1	13.6	1	4	13	11.7	12.4	2	1	15	14.8	15.7
0	0	10	14.3	14.4	0	7	7	14.5	13.1	1	4	12	22.8	20.5	2	1	14	8.9	7.6
0	0	12	38.1	35.2	0	7	6	4.4	5.0	1	4	11	8.6	7.7	2	1	13	12.1	10.3
0	0	14	13.9	13.7	0	7	5	25.5	28.3	1	4	10	12.5	13.3	2	1	12	12.4	12.9
0	0	16	14.9	15.2	0	7	4	17.2	19.3	1	4	9	18.8	19.5	2	1	11	4.4	4.0
0	1	17	2.9	4.2	0	7	3	8.4	9.5	1	4	8	24.9	24.6	2	1	10	7.7	8.1
0	1	15	10.3	9.1	0	7	2	11.9	13.1	1	4	7	12.2	11.6	2	1	9	10.3	10.8
0	1	13	31.4	27.3	0	7	1	22.3	23.8	1	4	6	28.9	29.5	2	1	8	16.2	16.1
0	1	12	6.2	6.8	0	8	10	3.3	3.5	1	4	5	12.3	11.2	2	1	7	34.3	35.4
0	1	11	12.4	10.8	0	8	9	10.1	10.3	1	4	4	23.7	21.5	2	1	6	17.9	18.8
0	1	10	11.3	11.1	0	8	8	12.8	11.3	1	4	3	15.2	14.5	2	1	5	29.4	31.8
0	1	9	18.0	17.7	0	8	6	9.8	9.8	1	4	2	27.3	27.4	2	1	4	10.1	11.2
0	1	7	56.8	54.8	0	8	3	17.3	15.4	1	4	1	17.6	21.0	2	1	3	29.6	25.5
0	1	6	2.9	2.7	0	8	2	13.7	13.4	1	4	0	80.2	69.6	2	1	2	6.5	4.4
0	1	5	80.7	85.6	0	8	1	12.8	10.8	1	5	15	4.8	5.4	2	1	1	53.6	53.8
0	1	4	21.9	20.8	0	8	0	28.1	28.0	1	5	14	4.6	4.2	2	1	0	53.4	53.8
0	1	3	5.3	5.8	0	9	9	8.0	7.9	1	5	13	14.2	14.0	2	2	16	8.3	9.7
0	1	2	30.3	27.0	0	9	7	11.1	11.0	1	5	12	5.2	5.6	2	2	15	11.1	11.4
0	1	1	73.0	78.3	0	9	5	10.6	9.7	1	5	10	9.2	9.9	2	2	14	4.6	4.6
0	2	16	5.1	4.3	0	9	4	5.4	5.3	1	5	9	17.9	18.5	2	2	13	8.9	9.0
0	2	15	8.3	7.2	0	9	3	4.8	4.7	1	5	8	15.4	13.3	2	2	12	19.4	20.6
0	2	14	6.6	6.3	0	9	2	4.9	4.7	1	5	7	37.8	34.8	2	2	11	15.5	16.4
0	2	13	8.6	7.8	0	9	1	16.8	12.7	1	5	6	7.8	7.4	2	2	10	26.6	28.8
0	2	11	8.2	7.8	0	10	6	5.8	6.1	1	5	5	11.5	14.4	2	2	9	7.5	8.6
0	2	10	7.6	8.2	0	10	5	3.8	4.3	1	5	4	7.7	7.6	2	2	8	16.9	19.8
0	2	9	13.8	13.2	0	10	4	8.4	8.5	1	5	3	3.4	2.7	2	2	7	11.4	11.2
0	2	7	23.5	21.7	0	10	3	6.9	7.6	1	5	2	11.6	12.6	2	2	6	18.7	19.8
0	2	6	73.4	75.7	0	10	2	8.8	9.0	1	5	1	12.1	11.5	2	2	5	18.4	16.9
0	2	5	36.5	35.3	0	10	1	10.9	9.8	1	5	0	25.8	24.5	2	2	4	27.3	25.5
0	2	4	55.9	59.3	0	10	0	9.1	8.3	1	6	14	6.6	7.8	2	2	3	34.8	31.9
0	2	3	39.3	38.2	1	0	2	8.3	7.2	1	6	13	9.2	7.8	2	2	2	23.2	22.5
0	2	2	26.1	23.7	1	0	3	36.5	39.8	1	6	12	5.6	5.8	2	2	1	19.5	17.8
0	2	1	71.2	70.2	1	0	4	16.6	16.0	1	6	11	8.1	8.9	2	2	0	9.6	11.2
0	2	0	71.7	65.7	1	0	5	45.9	51.5	1	6	10	6.8	6.1	2	3	15	13.2	12.7
0	3	16	12.3	14.5	1	0	6	22.9	24.2	1	6	9	22.9	24.2	2	3	14	6.8	5.8
0	3	15	3.5	3.8	1	0	7	7.2	8.8	1	6	8	16.8	16.4	2	3	13	6.9	6.8
0	3	14	5.9	4.9	1	0	8	14.1	14.5	1	6	7	4.8	5.3	2	3	12	11.6	10.7
0	3	13	14.9	14.9	1	0	9	31.6	30.8	1	6	6	11.4	13.8	2	3	11	11.2	10.5
0	3	12	22.7	22.6	1	0	10	33.9	33.2	1	6	5	17.3	18.1	2	3	10	25.9	25.6
0	3	11	23.4	20.6	1	0	11	43.5	48.8	1	6	4	6.4	5.4	2	3	9	9.4	11.8
0	3	10	24.8	22.2	1	0	12	11.6	9.6	1	6	3	38.1	33.7	2	3	8	7.4	7.7
0	3	9	5.8	5.2	1	0	14	11.8	8.5	1	6	2	9.3	10.1	2	3	7	16.7	15.2
0	3	8	23.2	23.7	1	0	16	7.2	6.0	1	6	1	16.1	15.1	2	3	6	13.8	13.7
0	3	7	5.1	5.0	1	0	17	18.4	14.9	1	6	0	3.7	2.2	2	3	5	24.8	24.3
0	3	6	2.9	2.9	1	1	17	4.9	7.8	1	7	13	5.6	7.2	2	3	4	24.7	23.8
0	3	5	11.2	9.1	1	1	16	18.7	18.6	1	7	12	8.1	9.8	2	3	3	38.1	35.8
0	3	4	89.3	91.2	1	1	15	4.7	5.1	1	7	11	7.7	6.9	2	3	2	65.8	62.8
0	3	3	26.4	22.7	1	1	14	6.6	6.7	1	7	10	19.7	19.8	2	3	1	37.6	37.1
0	3	2	61.0	56.7	1	1	13	7.8	6.7	1	7	9	6.1	5.7	2	3	0	7.8	9.7
0	3	1	56.4	54.9	1	1	12	16.5	16.6	1	7	8	16.5	15.4	2	4	15	4.5	4.3
0	4	15	6.3	6.8	1	1	11	16.4	14.8	1	7	6	14.6	13.4	2	4	14	5.5	4.7
0	4	14	13.3	10.3	1	1	10	29.2	30.7	1	7	5	16.2	14.3	2	4	13	8.5	7.6
0	4	13	7.1	7.3	1	1	9	11.4	10.7	1	7	4	28.6	30.5	2	4	12	6.8	6.6
0	4	12	16.2	16.4	1	1	8	10.1	8.4	1	7	3	12.9	13.5	2	4	11	26.2	26.9
0	4	11	12.6	14.5	1	1	7	21.1	18.2	1	7	2	20.3	18.0	2	4	10	15.5	13.7
0	4	9	39.9	40.6	1	1	6	25.1	25.8	1	7	1	16.0	13.3	2	4	9	8.3	7.9
0	4	8	3.6	3.3	1	1	5	27.5	28.9	1	7	0	5.3	4.7	2	4	8	5.3	5.4
0	4	7	4.8	5.5	1	1	4	45.6	47.6	1	8	11	8.9	10.9	2	4	7	5.8	6.7
0	4	6	33.7	32.6	1	1	3	37.3	33.5	1	8	10	3.8	3.4	2	4	6	8.8	9.3
0	4	5	8.2	8.7	1	1	2	44.2	47.4	1	8	9	20.7	20.2	2	4	5	25.7	28.3
0	4	4	20.4	20.2	1	1	1	47.1	46.4	1	8	8	3.4	2.5	2	4	4	24.6	26.7
0	4	3	85.4	86.7	1	1	0	34.4	32.9	1	8	5	14.3	13.1	2	4	3	35.3	32.4
0	4	2	9.2	8.6	1	2	16	6.7	6.5	1	8	4	10.7	9.3	2	4	2	26.6	25.9
0	4	1	55.0	52.4	1	2	15	5.2	4.5	1	8	3	24.5	23.8	2	4	1	6.1	7.2
0	4	0	79.5	79.3	1	2	14	10.0	8.8	1	8	0	3.4	3.2	2	4	0	18.8	15.7
0	5	15	4.4	5.9	1	2	13	8.8	8.4	1	9	9	7.5	7.7	2	5	14	6.2	5.8
0	5	14	5.5	4.6	1	2	12	15.6	16.6	1	9	8	3.6	3.7	2	5	13	5.4	5.2
0	5	13	4.3	3.8	1	2	11	20.6	17.2	1	9	7	9.5	11.1	2	5	12	8.6	7.8
0	5	12	8.8	9.0	1	2	10	9.5	8.3	1	9	6	5.2	5.7	2	5	11	6.8	5.3
0	5	10	22.6	24.8	1	2	9	9.7	8.9	1	9	5	4.8	4.5	2	5	10	10.7	11.1
0	5	9	4.9	3.3	1	2	8	33.7	34.4	1	9	4	14.2	15.7	2	5	9	9.4	9.1
0	5	8	4.8	3.6	1	2	7	4.9	5.8	1	9	3	8.1	7.4	2	5	8	9.7	10.4
0	5	7	15.5	17.5	1	2	6	32.3	31.5	1	9	2	9.1	9.9	2	5	6	4.2	5.2
0	5	5	7.3	8.0	1	2	5	49.1	47.9	1	9	1	10.0	8.8	2	5	4	23.1	26.2
0	5	4	33.7	34.1	1	2	4	26.4	26.1	1	10	6	9.6	12.0	2	5	3	16.0	18.6
0	5	3	3.1	2.0	1	2	3	57.4	49.8	1	10	5	7.0	7.4	2	5	2	20.0	20.7
0	5	2	36.3	35.8	1	2	2	50.4	52.8	1	10	4	6.3	5.9	2	5	1	16.5	15.7
0	5	1	14.1	14.4	1	2	1	24.0	22.5	1	10	3	12.5	11.9	2	5	0	9.7	9.8
0	6	14	9.1	10.9	1	2	0	22.7	22.4	1	10	2	4.9	6.0	2	6	13	10.8	10.4
0	6	11	6.4	6.2	1	3	15	11.2	9.9	1	10	1	7.7	7.3	2	6	12	5.3	5.5
0	6	10	5.9	6.2	1	3	14	14.0	11.9	1	10	0	8.8	8.8	2	6	11	15.3	13.9
0	6	9	9.0	9.6	1	3	13	17.0	18.3	2	0	1	31.0	33.0	2	6	9	10.5	9.9
0	6	8	33.3	30.8	1	3	12	11.9	12.2	2	0	2	44.2	48.0	2	6	8	11.5	11.8
0	6	7	20.9	19.8	1	3	11	8.3	7.2	2	0	3	20.9	22.2	2	6	7	13.2	12.6
0	6	6	5.3	4.4	1	3	10	8.2	9.3	2	0	4	37.6	35.7	2	6	6	19.3	16.8
0	6	5	19.9	21.3	1	3	9	21.3	22.0	2	0	5	25.9	24.6	2	6	5	10.5	11.8
0	6	4	18.4	20.8	1	3	8	13.7	13.8	2	0	6	35.0	35.8	2	6	4	24.8	27.6
0	6	3	24.2	26.0	1	3	7	41.8	47.3	2	0	7	19.4	19.8	2	6	3	18.8	18.3
0	6	2	10.5	10.9	1	3	6	22.6	20.6	2	0	8	14.3	13.9	2	6	2	19.4	20.8
0	6	1	25.4	25.8	1	3	5	34.4	31.7	2	0	9	17.5	20.1	2	6	1	23.0	23.4
0	6	0	10.3	10.2	1	3	4	7.2	8.3	2	0	10	14.6	13.9	2	6	0	6.2	5.7
0	7	13	8.2	9.9	1	3	3	26.3	25.9	2	0	12	18.4	17.4	2	7	12	6.8	5.9
0	7	12	7.5	8.1	1	3	2	26.5	24.3	2	0	13	9.4	9.5	2	7	11	4.7	3.4

H	K	L	|Fo|	|Fc|	H	K	L	|Fo|	|Fc|	H	K	L	|Fo|	|Fc|	H	K	L	|Fo|	|Fc|
2	7	10	8.7	8.1	3	3	1	36.7	38.0	4	2	14	5.2	4.0	5	0	3	8.3	8.1
2	7	9	10.4	11.2	3	3	0	43.9	44.8	4	2	13	10.4	8.9	5	0	4	37.1	38.9
2	7	8	15.3	14.1	3	4	14	15.7	14.3	4	2	12	11.3	9.8	5	0	5	6.2	5.6
2	7	7	18.6	18.2	3	4	13	7.9	7.6	4	2	11	5.2	4.2	5	0	6	21.2	22.8
2	7	6	11.2	12.1	3	4	12	14.2	13.2	4	2	10	11.1	12.4	5	0	7	18.5	18.6
2	7	5	8.9	8.7	3	4	11	7.6	7.8	4	2	9	11.2	11.9	5	0	8	8.0	7.8
2	7	4	13.0	13.6	3	4	10	5.2	4.8	4	2	8	4.7	4.9	5	0	9	14.9	15.8
2	7	3	10.4	8.9	3	4	9	8.6	8.2	4	2	7	10.0	9.1	5	0	10	28.0	25.2
2	7	2	20.0	21.7	3	4	8	15.7	17.1	4	2	6	14.0	12.4	5	0	11	4.1	3.6
2	7	1	20.1	22.4	3	4	7	33.2	30.1	4	2	5	15.4	17.1	5	0	12	13.0	12.4
2	7	0	14.9	14.7	3	4	6	28.9	26.7	4	2	4	18.4	19.8	5	1	13	5.1	4.2
2	8	10	3.6	2.7	3	4	5	38.7	35.8	4	2	3	13.1	11.7	5	1	12	7.1	6.8
2	8	9	4.6	3.3	3	4	4	19.3	19.9	4	2	2	24.0	22.4	5	1	11	20.5	19.2
2	8	8	7.5	7.1	3	4	3	4.9	4.7	4	2	1	26.2	26.4	5	1	10	11.4	10.1
2	8	7	9.9	9.5	3	4	2	41.1	39.6	4	2	0	12.2	13.0	5	1	9	15.8	15.3
2	8	6	6.6	6.6	3	4	1	34.8	31.6	4	3	14	4.1	3.9	5	1	8	10.4	9.9
2	8	5	18.7	17.6	3	4	0	28.7	28.6	4	3	13	7.1	6.8	5	1	7	7.3	6.7
2	8	4	7.3	6.9	3	5	13	8.6	9.6	4	3	12	6.1	6.7	5	1	6	11.5	12.0
2	8	3	9.1	7.3	3	5	12	13.7	13.7	4	3	11	20.2	21.0	5	1	5	27.8	24.8
2	8	2	17.6	17.6	3	5	11	4.6	4.7	4	3	10	13.6	13.1	5	1	4	14.9	14.2
2	8	1	9.5	7.8	3	5	9	3.6	2.7	4	3	9	15.7	16.2	5	1	3	28.5	28.0
2	8	0	18.8	19.5	3	5	8	11.9	12.3	4	3	8	5.7	5.6	5	1	2	5.9	4.8
2	9	8	6.3	6.6	3	5	7	34.5	28.9	4	3	7	7.3	7.7	5	1	1	17.1	18.4
2	9	7	13.8	13.8	3	5	6	15.9	19.4	4	3	6	12.7	12.8	5	1	0	6.6	7.1
2	9	6	3.9	5.1	3	5	5	14.5	15.7	4	3	5	12.0	10.4	5	2	13	11.4	10.8
2	9	5	7.4	7.3	3	5	3	5.1	5.4	4	3	4	11.3	11.4	5	2	12	9.8	9.6
2	9	4	4.0	3.3	3	5	2	19.1	19.5	4	3	3	35.1	35.3	5	2	11	8.1	9.1
2	9	3	5.9	5.8	3	5	1	21.5	21.5	4	3	2	14.1	12.0	5	2	10	17.3	16.2
2	9	2	8.1	7.2	3	5	0	15.0	15.1	4	3	1	13.2	13.5	5	2	9	11.6	11.4
2	9	1	8.9	8.4	3	6	12	12.9	15.3	4	3	0	11.5	10.0	5	2	8	9.2	10.5
2	9	0	17.1	14.9	3	6	11	12.4	10.6	4	4	13	3.8	2.3	5	2	7	12.8	13.0
2	10	4	6.1	6.6	3	6	10	13.8	12.1	4	4	12	15.1	12.9	5	2	6	14.9	15.8
2	10	3	11.6	11.8	3	6	9	6.2	5.7	4	4	11	4.7	4.3	5	2	5	17.9	16.4
2	10	2	9.7	9.2	3	6	8	10.7	9.7	4	4	10	13.6	12.3	5	2	4	10.1	8.7
2	10	1	10.4	9.8	3	6	7	9.9	10.5	4	4	9	5.7	5.4	5	2	3	14.9	13.2
2	10	0	7.6	8.0	3	6	6	23.2	22.4	4	4	8	9.6	11.1	5	2	2	5.7	6.4
3	0	1	6.5	6.4	3	6	5	13.9	16.5	4	4	7	3.1	3.5	5	2	1	18.4	17.1
3	0	2	68.7	72.9	3	6	4	11.8	10.9	4	4	6	13.9	13.0	5	3	13	4.7	6.2
3	0	3	45.8	48.8	3	6	3	8.9	8.3	4	4	5	4.1	2.5	5	3	12	13.2	13.8
3	0	4	59.3	63.3	3	6	2	4.6	4.5	4	4	4	23.4	23.5	5	3	11	7.1	6.6
3	0	5	46.6	43.7	3	6	1	21.6	21.5	4	4	3	22.6	24.3	5	3	10	3.7	4.8
3	0	6	3.2	2.4	3	6	0	18.9	19.8	4	4	2	22.8	22.9	5	3	9	3.9	4.9
3	0	7	30.3	31.1	3	7	11	10.5	12.5	4	4	1	9.2	9.8	5	3	8	21.8	19.5
3	0	8	40.6	37.6	3	7	10	14.4	13.8	4	4	0	2.6	1.8	5	3	7	7.5	7.8
3	0	9	16.9	15.8	3	7	9	15.1	13.8	4	5	12	7.1	6.2	5	3	6	21.7	20.9
3	0	10	21.0	21.5	3	7	8	10.6	11.8	4	5	11	16.1	16.3	5	3	5	11.9	12.6
3	0	11	24.7	25.2	3	7	7	8.1	5.5	4	5	10	6.6	7.7	5	3	4	3.2	3.1
3	0	13	6.8	7.3	3	7	6	16.4	16.7	4	5	9	3.5	3.1	5	3	3	11.4	13.4
3	0	14	5.8	5.2	3	7	5	7.5	8.5	4	5	8	10.9	9.6	5	3	2	21.3	19.2
3	0	15	4.0	3.9	3	7	4	11.0	9.4	4	5	7	4.4	3.9	5	3	1	15.3	14.6
3	1	15	10.7	11.2	3	7	3	24.4	21.7	4	5	6	4.4	4.6	5	3	0	27.5	29.7
3	1	14	5.2	5.2	3	7	2	14.5	13.2	4	5	5	19.0	18.5	5	4	12	5.9	6.2
3	1	13	9.8	7.1	3	7	1	15.5	15.7	4	5	4	21.2	21.5	5	4	11	4.4	3.5
3	1	12	4.7	3.1	3	7	0	6.0	6.5	4	5	3	16.8	15.4	5	4	9	15.3	16.1
3	1	11	26.8	28.0	3	8	9	9.2	8.8	4	5	2	17.4	16.2	5	4	8	6.7	7.2
3	1	10	25.7	26.2	3	8	8	4.6	4.8	4	5	1	15.2	17.3	5	4	7	26.2	29.4
3	1	9	21.8	22.1	3	8	6	9.7	10.0	4	5	0	12.8	11.6	5	4	6	5.3	5.8
3	1	8	20.5	23.9	3	8	5	15.6	13.4	4	6	11	3.2	3.3	5	4	5	13.4	14.1
3	1	7	13.8	12.1	3	8	4	11.6	11.1	4	6	10	12.1	11.9	5	4	4	12.7	12.1
3	1	6	17.6	15.6	3	8	3	13.2	13.1	4	6	8	6.8	7.2	5	4	3	5.4	4.5
3	1	5	43.2	45.5	3	8	2	10.3	9.5	4	6	7	13.1	13.2	5	4	2	10.7	10.5
3	1	4	40.1	36.6	3	8	1	11.7	9.5	4	6	6	9.4	10.4	5	4	1	15.0	12.4
3	1	3	47.3	44.5	3	9	6	5.4	5.6	4	6	5	11.3	10.4	5	4	0	17.2	16.9
3	1	2	48.2	44.6	3	9	5	6.1	6.5	4	6	4	9.6	8.4	5	5	11	3.8	3.2
3	1	1	26.5	26.2	3	9	4	9.8	11.4	4	6	3	11.2	10.3	5	5	10	3.6	3.1
3	1	0	26.2	34.2	3	9	3	9.6	9.8	4	6	2	11.8	13.5	5	5	9	11.7	11.1
3	2	15	8.6	9.1	3	9	2	5.5	5.8	4	6	1	21.6	24.7	5	5	8	9.4	9.5
3	2	13	10.0	9.7	4	0	1	15.9	19.5	4	6	0	6.2	6.1	5	5	7	8.3	8.7
3	2	12	16.5	14.3	4	0	2	2.0	1.8	4	7	10	3.8	4.8	5	5	6	15.1	16.3
3	2	11	16.3	16.2	4	0	3	2.7	2.5	4	7	9	2.9	2.8	5	5	5	6.0	4.9
3	2	10	13.3	14.9	4	0	4	4.0	3.6	4	7	8	13.2	11.7	5	5	3	7.2	7.8
3	2	9	16.1	19.1	4	0	5	24.8	25.4	4	7	7	6.3	6.2	5	5	2	12.5	13.6
3	2	8	21.8	25.1	4	0	6	10.1	9.1	4	7	6	13.6	12.8	5	5	1	7.2	5.3
3	2	7	16.9	15.4	4	0	7	32.4	36.1	4	7	5	15.7	14.4	5	5	0	19.4	18.1
3	2	6	23.2	24.9	4	0	8	5.9	5.7	4	7	4	10.6	10.1	5	6	10	8.3	9.4
3	2	5	14.7	15.7	4	0	9	17.7	15.7	4	7	3	4.7	4.1	5	6	9	7.3	7.0
3	2	4	28.3	24.1	4	0	11	6.4	5.8	4	7	2	16.2	14.8	5	6	8	11.5	12.3
3	2	3	33.3	32.0	4	0	13	10.2	10.8	4	7	1	12.9	12.6	5	6	7	10.4	10.8
3	2	2	40.2	44.8	4	0	14	6.3	6.6	4	7	0	25.2	21.4	5	6	6	8.5	7.5
3	2	1	40.0	43.4	4	0	15	15.9	18.5	4	8	8	5.4	5.2	5	6	4	14.4	15.5
3	2	0	8.8	9.6	4	1	14	11.9	13.0	4	8	7	13.1	14.6	5	6	3	9.3	9.2
3	3	15	6.5	5.8	4	1	13	8.3	7.8	4	8	6	7.1	7.6	5	6	2	13.5	12.3
3	3	14	11.1	10.4	4	1	12	18.5	16.1	4	8	5	9.4	8.9	5	6	1	14.9	12.3
3	3	13	13.8	11.8	4	1	11	9.8	7.8	4	8	4	5.3	4.9	5	7	8	5.0	6.4
3	3	12	19.3	19.9	4	1	10	19.4	18.3	4	8	3	6.1	5.2	5	7	7	3.0	2.7
3	3	11	18.7	17.9	4	1	9	15.1	11.5	4	8	2	5.7	5.3	5	7	6	8.7	8.2
3	3	10	3.7	3.8	4	1	8	9.4	8.2	4	8	1	15.3	13.2	5	7	5	11.7	12.3
3	3	9	9.7	12.6	4	1	7	12.3	14.4	4	8	0	17.7	17.9	5	7	4	9.3	8.8
3	3	8	28.5	30.7	4	1	6	21.3	21.9	4	9	4	4.2	4.6	5	7	3	17.3	17.5
3	3	7	31.9	34.6	4	1	5	19.4	16.5	4	9	3	6.5	7.3	5	7	2	7.7	7.3
3	3	6	31.2	30.1	4	1	4	11.1	11.8	4	9	2	13.6	15.6	5	7	0	5.8	7.0
3	3	5	28.0	29.9	4	1	3	6.9	4.7	4	9	1	11.1	10.5	5	8	6	5.4	6.9
3	3	4	16.2	15.6	4	1	2	15.9	13.4	4	9	0	3.9	3.9	5	8	4	12.8	12.6
3	3	3	11.8	12.2	4	1	1	3.7	3.9	5	0	1	2.3	2.8	5	8	2	10.2	11.8
3	3	2	30.5	31.2	4	1	0	38.7	38.0	5	0	2	9.1	10.2	5	8	0	3.7	2.9

Table 3. Least-squares planes.

Plane 1.

$0.67430x + 0.61372y - 0.41069z - 0.17359 = 0$

Atoms comprising the plane	Displacements (Å)	Atoms comprising the plane	Displacements (Å)
O(3A)	−0.003	C(9A)	0.010
O(7A)	−0.003	C(11A)	−0.002

Plane 2.

$-0.02705x - 0.80950y - 0.58649z + 2.36559 = 0$

Atoms comprising the plane	Displacements (Å)	Atoms comprising the plane	Displacements (Å)
O(5A)	−0.001	C(10A)	0.003
O(8A)	−0.001	C(12A)	0.000

Plane 3.

$0.05132x - 0.99469y - 0.08926z + 2.05974 = 0$

Atoms comprising the plane	Displacements (Å)	Atoms comprising the plane	Displacements (Å)
O(7A)	−0.299	Ca(1A)	0.401
O(8B)	−0.176	O(5A)	0.117
O(8C)	0.062	O(5B)	−0.106

Plane 4.

$0.83283x - 0.00951y - 0.55345z + 0.23781 = 0$

Atoms comprising the plane	Displacements (Å)	Atoms comprising the plane	Displacements (Å)
O(4A)	0.036	Ca(1A)	−0.080
O(6A)	0.027	O(2A)	0.015

water molecule on the other constitute the remaining ligands. Each calcium ion thus binds to three different malate ions with three, two, and one bond, respectively. Similarly each malate ion is coordinated to three calcium ions.

An interesting feature of the structure is that the malate ion acts as a tridentate chelate agent towards one calcium ion. Two carboxyl oxygen atoms, one from each end of the molecule, and the hydroxyl-oxygen are coordinated to the same calcium ion with bond distances 2.34, 2.45, and 2.47 Å, respectively. In this way three different chelate rings are obtained with five, six, and seven atoms, respectively. Measurements of the stability constants in solution shows that the complex of calcium with malic acid ($\log \beta_2 = 2.66$) is somewhat more stable than the corresponding complex with succinic acid ($\log \beta_2 = 2.00$).[10] This indicates that chelate formation involving the hydroxyl-oxygen may exist not only in the solid state but also in solution. One of the carboxyl groups is bonded to two different calcium ions besides being involved in the previously described chelate formation involving a third calcium ion. This carboxyl group acts as a bidentate ligand towards one of those calcium ions, the Ca—O bond distances being 2.49 and 2.71 Å. The second Ca-ion is bonded to the carboxyl oxygen atom that forms a very strong bond of length 2.32 Å in the chain-direction. Each oxygen atom of this carboxyl group is thus bonded to two different Ca-ions whereas only one oxygen atom of the other carboxyl group of the malate ion is bonded to calcium.

Table 4. Interatomic distances and angles.

Atoms	Distances (Å)	σ(Å)	Atoms	Distances (Å)	σ(Å)
Ca(1A)—O(2A)	2.465	0.007	C(10A)—O(8A)	1.251	0.013
Ca(1A)—O(4A)	2.439	0.007	C(10A)—O(5A)	1.241	0.012
Ca(1A)—O(5A)	2.344	0.008	C(11A)—O(2A)	1.434	0.010
Ca(1A)—O(5B)	2.494	0.006	C(9A) —C(11A)	1.529	0.013
Ca(1A)—O(6A)	2.474	0.006	C(10A)—C(12A)	1.512	0.010
Ca(1A)—O(7A)	2.448	0.006	C(11A)—C(12A)	1.503	0.017
Ca(1A)—O(8B)	2.708	0.007	O(6B) —O(3C)	2.721	0.010
Ca(1A)—O(8C)	2.317	0.009	O(6B) —O(3B)	2.820	0.010
C(9A) —O(3A)	1.256	0.010	O(4A) —O(6B)	2.863	0.012
C(9A) —O(7A)	1.243	0.011	O(2C) —O(7B)	2.754	0.009

Atoms	Angle (°)	σ(°)	Atoms	Angle (°)	σ(°)
O(7A) —C(9A) —O(3A)	124.8	0.9	Ca(1B)—O(6B) —O(3B)	118.0	0.4
O(7A) —C(9A) —C(11A)	118.3	0.7	Ca(1B)—O(6B) —O(3C)	115.7	0.3
O(3A) —C(9A) —C(11A)	116.9	0.8	Ca(1B)—O(6B) —O(4A)	96.6	0.3
O(5A) —C(10A)—O(8A)	120.5	0.7	O(3B) —O(6B) —O(4A)	125.8	0.3
O(5A) —C(10A)—C(12A)	120.9	0.9	O(3B) —O(6B) —O(3C)	111.2	0.2
O(8A) —C(10A)—C(12A)	118.6	0.9	O(3C) —O(6B) —O(4A)	85.5	0.3
C(9A) —C(11A)—O(2A)	111.1	0.8	O(8C) —Ca(1A)—O(7A)	82.6	0.2
C(9A) —C(11A)—C(12A)	113.4	0.8	O(7A) —Ca(1A)—O(5A)	80.4	0.2
C(12A)—C(11A)—O(2A)	109.7	0.7	O(5A) —Ca(1A)—O(8B)	68.3	0.2
C(11A)—C(12A)—C(10A)	116.5	0.8	O(8B) —Ca(1A)—O(5B)	48.9	0.2
C(11A)—O(2A) —Ca(1A)	110.5	0.4	O(5B) —Ca(1A)—O(8C)	72.6	0.2
C(11A)—O(2A) —O(7D)*	107.9	0.5	O(2A) —Ca(1A)—O(4A)	132.7	0.3
Ca(1A)—O(2A) —O(7D)*	117.7	0.3	O(4A) —Ca(1A)—O(6A)	154.8	0.2
Ca(1A)—O(4A) —O(6B)	109.8	0.3	O(6A) —Ca(1A)—O(2A)	71.6	0.2

The Ca—O bond distances, ranging from 2.32 Å to 2.71 Å with an average of 2.46 Å, found in this structure agree quite well with those reported in the literature. Clark [11] found an average distance of 2.47 Å (2.37—2.59) for the eight Ca—O bonds in $CaB_3O_3(OH)_5 \cdot 4H_2O$ and MacLennan and Beevers [12] reported the average values 2.48 Å (2.40—2.58) and 2.44 Å (2.29—2.61) in $CaHPO_4$, where different calcium ions are coordinated to eight and seven oxygen atoms, respectively. In a recent structure determination of calcium-5-keto-D-gluconate [13] a coordination of eight oxygen atoms to calcium at the vertices of a regular triakis-tetrahedron has been observed. The Ca—O distances vary between 2.39 and 2.47 Å.

The chains of calcium and malate ions are held together by hydrogen bonds, which are shown in Fig. 2. The hydroxyl-oxygen is bonded to a carboxylic oxygen of an adjacent malate ion by a hydrogen bond of length 2.75 Å.

* Molecule D (not shown in the figures) is hydrogen bonded to molecule A.

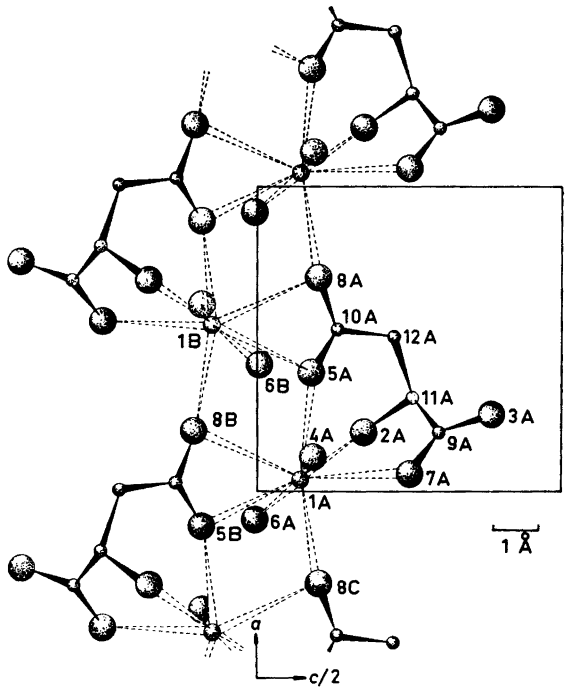
8A
10A
12A
1B
6B
5A
11A
3A
8B
4A
2A
9A
7A
1A
5B
6A
1 Å
8C
a
c/2

Fig. 1.

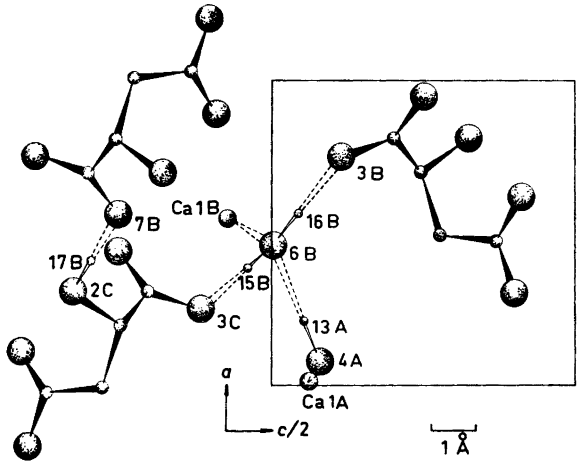
3B
Ca1B
7B
16B
17B
6B
15B
2C
3C
13A
4A
a
Ca1A
c/2
1 Å

Fig. 2.

One of the water molecules links two adjacent chains by hydrogen bonds of lengths 2.72 and 2.82 Å to two symmetry-related carboxyl oxygen atoms (O(3)). O(3) is the only oxygen atom of the malate ion that is not coordinated to calcium. Finally there is one hydrogen bond within the chain between two adjacent water molecules.

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