Acta Cryst. (1972). B28, 135

The Crystal Structure of Calcium Fumarate Trihydrate, $CaC_4H_2O_4.3H_2O$

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(*Received* 10 *September* 1970 *and in revised form* 23 *March* 1971)

The crystal structure of calcium fumarate trihydrate has been solved from three-dimensional X-ray data, and refined by the method of least-squares with anisotropic temperature factors for each atom. The crystals are orthorhombic, $a=6{\cdot}62$, $b=17{\cdot}63$, $c=6{\cdot}97$ Å, space group $Pna2_1$ with four molecules in the cell. Chains of fumarate ions lie parallel to [010] and are in two layers at $Z\simeq 0{\cdot}0$ and $Z\simeq c/2$. The structure is held together by ionic Ca···O linkages with eightfold coordination round Ca (average Ca···O = 2·45 Å), and by ten hydrogen bonds (ranging from 2·70 to 2·93 Å) linking the oxygen atoms of the fumarate ion via the three water molecules. Two of the water molecules form bifurcated hydrogen bonds.

Fumaric acid, $C_4H_4O_4$, is a dicarboxylic acid, and the crystal structures of several of its salts have been studied in this laboratory (Gupta & Roy, 1967, 1969; Gupta & Sahu (R.G.), 1970; Gupta & Sahu (B.N.), 1970). Its calcium salt is of unusual interest since, calcium being divalent, one calcium atom is expected to ionize both the carboxyl groups in the acid molecule. The relative disposition of the Ca ion and the oxygen atoms of the fumarate ions and water molecules is, therefore, of considerable interest.

Experimental technique and crystal data

The crystals were prepared by adding $CaCO_3$ in stoichiometric proportions to an aqueous solution of the acid. The crystals were lath-like, colourless, with [001] as the direction of elongation and (010) as the platy face. They are orthorhombic with $a=6{\cdot}62$, $b=17{\cdot}63$, $c=6{\cdot}97$ Å. These lattice parameters were determined from high $\sin\theta$ reflexions on zero level Weissenberg photographs on which silver lines had been superposed as internal standards. The unit cell gives $a:b:c=0{\cdot}375:1:0{\cdot}395$. The density is 1·71 g. cm^{-3}, giving a unit cell content of 836·6 a.m.u. which may be compared with 832 a.m.u. expected for four formula units of $CaC_4H_2O_4.3H_2O$. There is a previous reference (Wherry & Hann, 1922) to a so-called calcium fumarate dihydrate, $CaC_4H_2O_4.2H_2O$, which is described as 'Orthorhombic with $a:b:c=0{\cdot}397:1:0{\cdot}377$; crystals (101) tablets with [110], [011]'. It seems very probable that what the above workers called a *dihydrate* is really a *trihydrate*. The unit cell of Wherry & Hann is the same as ours with a and c interchanged. We have confirmed the water content by gravimetric analysis.

Space group absences (hkl, none; $0kl$, $k+l\neq 2n$; $h0l$, $h\neq 2n$) give two possibilities, $Pna2_1$ and $Pnam$. The latter requires eight asymmetric formula units per cell compared with the four observed. Our studies of the fumarate ion lead us to rule out the possibility of their occupying special positions. We therefore assumed the space group to be $Pna2_1$, a choice which was subsequently confirmed by successful refinement.

Intensities were collected from normal and equi-inclination Weissenberg photographs of a small single crystal (0·20 × 0·15 × 0·10 mm) with unfiltered Cu K radiation ($\mu=45{\cdot}4$ cm^{-1} for Cu $K\alpha$) and the multiple-film technique. A total of 424 reflexions with non-zero intensity were collected, the number expected theoretically being 808. The intensities were estimated visually with a standard intensity scale made with crystal-reflected spots, corrected for Lorentz–polarization and spot-shape factors in the normal way, and brought on to an approximate absolute scale by statistical methods.

Determination of the structure

Patterson sections at $Z=0$, $\frac{1}{8}$, $\frac{1}{4}$, $\frac{3}{8}$, and $\frac{1}{2}$ were computed with all the observed data and gave a possible site for the calcium atom at $X\sim 0{\cdot}058$, $Y\sim 0{\cdot}20$, $Z\sim 0{\cdot}0$. The projection down [001] being centrosymmetric, a Fourier synthesis for the $hk0$ data was calculated phased on the calcium alone. This revealed a gross position for the fumarate ion and one water molecule. Packing considerations were applied to deduce reasonable positions for the other two water molecules. The structure converged to $R(hk0)=0{\cdot}21$,

Table 1. *Fractional coordinates* (× 10⁴) *with their e.s.d's*

	x	y	z
C(1)	0714 (42)	3642 (12)	0011 (76)
C(2)	0906 (43)	4495 (14)	0024 (79)
C(3)	−0751 (49)	4950 (15)	0000 (00)
C(4)	−0496 (42)	5770 (13)	0115 (78)
O(1)	2308 (24)	3244 (17)	−0051 (63)
O(2)	−1015 (31)	3345 (10)	0042 (60)
O(3)	−2199 (27)	6152 (11)	0035 (61)
O(4)	1139 (33)	6105 (14)	0120 (72)
$(H_2O)_I$	0496 (42)	0908 (11)	2633 (67)
$(H_2O)_{II}$	0541 (47)	1496 (18)	−2335 (70)
$(H_2O)_{III}$	3064 (38)	2473 (13)	3330 (61)
Ca	0589 (07)	2034 (03)	0730 (46)

Table 2. *The observed and calculated structure factor magnitudes*

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
2	0	0	68.0	66.8	5	6	0	31.9	31.5	3	9	1	21.1	23.3	1	15	2	33.3	28.7	7	7	2	21.1	23.1	6	7	3	23.2	23.5
6	0	0	52.5	56.6	5	7	0	14.2	14.7	3	10	1	17.9	18.9	1	17	2	26.6	26.7	7	10	2	8.0	3.2	6	8	3	23.2	21.0
8	0	0	22.5	25.4	5	8	0	24.7	21.4	3	11	1	35.0	38.9	1	18	2	13.1	16.4	8	0	2	16.0	16.2	7	1	3	10.0	7.8
0	2	0	52.2	63.2	5	16	0	33.0	30.2	3	13	1	16.7	16.2	1	19	2	8.8	10.5	8	2	2	12.6	11.8	7	2	3	13.9	14.4
0	4	0	63.8	61.5	5	16	0	27.4	28.0	3	15	1	16.7	18.1	2	0	2	38.0	37.7	8	4	2	8.0	9.9	7	3	3	10.0	13.0
0	6	0	12.0	7.9	6	1	0	45.0	49.0	3	16	1	14.8	19.6	2	1	2	32.0	35.8	0	1	3	59.5	64.8	7	4	3	21.3	21.0
0	8	0	7.8	7.9	6	2	0	11.6	12.8	4	2	1	33.4	30.4	2	2	2	35.0	38.1	0	3	3	65.5	70.6	7	5	3	13.1	15.0
0	10	0	35.7	39.7	6	3	0	14.6	12.0	4	4	1	20.3	18.7	2	3	2	35.0	38.3	0	5	3	14.7	17.0	7	6	3	15.5	17.2
0	16	0	12.7	10.0	6	4	0	12.0	8.4	4	6	1	23.2	18.7	2	4	2	56.2	57.2	0	7	3	54.3	54.9	8	0	4	100.2	112.3
0	18	0	12.0	8.9	6	5	0	23.6	20.1	4	8	1	13.0	10.1	2	5	2	32.1	34.3	0	9	3	27.1	23.0	8	2	4	55.0	54.8
0	20	0	27.7	26.7	6	6	0	20.6	19.1	4	10	1	23.6	28.8	2	7	2	13.9	7.8	0	11	3	44.4	37.6	8	4	4	64.2	56.5
0	22	0	21.7	22.2	6	7	0	8.2	8.3	4	12	1	36.6	62.9	2	8	2	14.3	15.4	0	13	3	40.3	41.6	8	6	4	23.1	19.5
1	1	0	35.3	42.5	6	8	0	16.1	17.4	4	14	1	13.4	14.9	2	9	2	15.2	12.6	0	19	3	20.1	19.6	8	8	4	10.0	17.8
1	3	0	52.5	49.2	6	9	0	23.6	25.7	4	16	1	9.3	17.2	2	10	2	16.0	13.1	0	21	3	27.9	29.3	8	10	4	21.5	26.8
1	4	0	19.5	20.4	6	10	0	10.5	12.0	5	1	1	20.7	16.8	2	11	2	19.4	16.8	1	1	3	6.9	10.5	8	12	4	19.5	22.5
1	5	0	46.5	46.5	6	11	0	22.5	25.1	5	2	1	8.9	7.8	2	12	2	20.2	15.4	1	2	3	26.3	28.7	1	1	4	26.0	27.8
1	6	0	16.5	17.2	6	12	0	12.0	12.8	5	3	1	10.8	10.9	2	13	2	38.8	38.7	1	3	3	19.6	21.0	1	2	4	14.6	13.9
1	7	0	63.6	59.6	6	13	0	6.7	5.6	5	4	1	13.4	12.5	2	14	2	30.0	25.8	1	4	3	64.4	56.3	1	3	4	33.2	32.5
1	8	0	15.0	18.5	6	14	0	7.8	7.5	5	5	1	16.8	15.8	2	17	2	16.9	20.2	1	5	3	19.0	23.2	1	4	4	15.3	14.2
1	9	0	26.2	24.2	0	1	1	86.0	87.7	5	6	1	13.8	11.5	2	18	2	15.6	16.9	1	6	3	34.1	34.6	1	5	4	34.8	36.7
1	11	0	12.0	9.1	0	3	1	77.4	73.2	5	7	1	39.1	38.7	2	19	2	16.0	18.8	1	8	3	35.7	40.2	1	6	4	15.[illegible]	10.2
1	13	0	24.7	21.7	0	5	1	63.8	62.6	5	8	1	17.8	17.5	2	20	2	16.4	21.1	1	9	3	19.0	16.9	1	7	4	20.8	21.1
1	15	0	30.0	23.6	0	7	1	122.2	126.1	5	9	1	35.4	31.8	2	21	2	12.2	17.0	1	12	3	21.7	18.4	1	15	4	24.4	23.6
1	16	0	18.7	16.8	0	9	1	43.6	40.8	5	11	1	13.4	13.7	3	1	2	7.6	6.5	1	14	3	22.1	23.4	2	0	4	32.5	27.5
1	17	0	51.0	49.0	0	11	1	12.6	14.1	5	13	1	12.6	12.7	3	2	2	26.6	26.0	1	16	3	24.8	24.8	2	1	4	15.[illegible]	21.0
2	1	0	37.5	38.1	0	13	1	29.3	29.0	5	15	1	27.2	24.4	3	3	2	22.3	22.5	1	18	3	15.5	18.4	2	2	4	22.4	21.1
2	2	0	14.2	11.4	0	15	1	19.5	15.2	5	17	1	23.2	22.7	3	4	2	68.6	61.1	2	0	3	28.3	30.5	2	3	4	25.4	24.4
2	3	0	20.7	16.5	0	17	1	13.8	10.0	6	1	1	32.5	31.8	3	5	2	19.0	18.1	2	1	3	36.6	35.7	2	4	4	22.8	24.5
2	4	0	10.0	6.6	0	19	1	24.4	25.8	6	2	1	34.2	33.7	3	6	2	35.9	33.8	2	2	3	33.9	29.9	2	10	4	23.4	20.7
2	6	0	10.5	9.4	0	21	1	17.5	20.0	6	3	1	13.8	14.2	3	7	2	12.6	14.8	2	3	3	31.0	36.2	2	11	4	19.8	23.7
2	7	0	27.7	25.8	1	1	1	6.9	9.0	6	4	1	13.8	15.0	3	8	2	22.8	24.4	2	4	3	24.0	19.5	2	12	4	24.6	22.5
2	8	0	32.3	32.1	1	2	1	23.6	27.7	6	6	1	23.6	25.0	3	12	2	39.3	39.6	2	5	3	19.4	16.5	2	13	4	23.6	25.1
2	9	0	36.8	36.8	1	4	1	19.9	21.6	6	7	1	24.8	26.1	3	13	2	18.1	21.1	2	6	3	17.8	16.8	2	14	4	22.4	20.0
2	10	0	33.8	33.2	1	5	1	9.3	9.5	6	8	1	22.8	26.5	3	14	2	24.5	22.8	2	7	3	23.6	21.3	3	1	4	9.9	14.2
2	11	0	26.2	23.9	1	6	1	35.8	40.5	6	9	1	9.3	12.9	3	15	2	14.3	14.0	2	8	3	15.5	16.9	3	2	4	35.9	32.9
2	12	0	21.7	22.9	1	7	1	12.6	15.1	6	10	1	17.7	19.0	3	16	2	16.9	18.8	2	10	3	20.5	19.4	3	3	4	25.0	22.4
2	13	0	46.5	46.0	1	8	1	85.9	84.1	6	11	1	8.1	9.3	3	17	2	8.8	13.4	2	11	3	32.9	30.3	3	4	4	30.0	30.2
2	14	0	48.0	44.3	1	9	1	23.2	23.1	6	12	1	7.7	12.0	3	20	2	36.3	38.3	2	12	3	40.7	41.8	3	5	4	25.4	26.9
2	15	0	16.5	13.9	1	10	1	12.4	12.2	6	13	1	6.9	9.4	4	0	2	15.6	13.4	2	13	3	29.1	26.9	3	6	4	37.4	32.4
2	16	0	14.2	11.8	1	12	1	33.8	29.4	6	14	1	6.1	8.1	4	1	2	17.7	20.7	3	1	3	10.0	8.1	3	7	4	21.5	16.7
2	17	0	11.6	12.7	1	14	1	28.8	25.7	7	3	1	14.6	12.3	4	3	2	20.2	18.2	3	2	3	10.0	11.2	3	8	4	27.0	25.7
2	18	0	20.6	19.3	1	15	1	13.8	14.0	7	4	1	8.1	9.6	4	5	2	25.3	20.9	3	3	3	37.6	32.6	3	12	4	30.6	28.9
2	19	0	27.4	23.3	1	16	1	36.4	35.0	7	5	1	12.5	10.1	4	7	2	30.0	27.5	3	4	3	27.6	27.7	3	14	4	28.0	27.1
2	20	0	22.5	21.0	1	17	1	9.7	12.7	7	6	1	11.4	16.0	4	9	2	34.6	35.2	3	5	3	60.0	59.3	3	16	4	17.6	22.4
3	1	0	35.6	35.4	1	18	1	24.4	21.9	7	7	1	19.1	17.9	4	11	2	27.9	29.3	3	6	3	27.0	22.8	3	17	4	14.8	10.6
3	2	0	89.8	87.1	2	0	1	46.4	45.5	7	11	1	9.7	6.4	4	13	4	42.2	44.5	3	7	3	23.2	20.4	3	18	4	26.0	21.0
3	3	0	52.2	50.1	2	1	1	42.7	47.2	8	1	1	21.9	17.4	4	15	2	19.5	18.4	3	9	3	21.3	19.0	4	0	4	30.6	37.2
3	4	0	74.6	76.6	2	2	1	39.5	36.6	0	0	2	143.2	139.4	4	17	2	13.1	11.5	3	10	3	12.4	13.7	0	1	5	25.3	22.2
3	5	0	10.5	7.0	2	3	1	21.1	19.8	0	2	2	15.2	16.3	4	19	2	23.2	22.0	3	11	3	34.1	32.8	0	5	5	20.0	18.4
3	6	0	15.7	14.5	2	4	1	8.1	5.8	0	4	2	19.0	24.6	5	1	2	7.1	9.3	3	13	3	34.1	29.6	0	7	5	38.[illegible]	33.9
3	7	0	13.5	9.6	2	5	1	6.1	5.4	0	6	2	49.4	47.9	5	2	2	34.4	30.8	3	14	3	17.4	18.7	0	9	5	32.3	44.6
3	8	0	27.7	25.8	2	6	1	24.8	23.2	0	8	2	50.7	51.7	5	4	2	35.9	30.1	3	15	3	29.1	26.9	0	11	5	33.6	36.9
3	9	0	10.1	14.4	2	7	1	12.2	11.2	0	10	2	56.0	58.4	5	6	2	41.8	38.0	3	17	3	22.5	18.3	1	2	5	19.7	20.7
3	12	0	38.3	42.2	2	8	1	15.5	22.7	0	12	2	50.2	45.2	5	8	2	21.1	19.9	3	19	3	14.3	9.8	1	4	5	29.4	24.6
3	13	0	16.5	16.3	2	9	1	39.7	38.0	0	14	2	25.3	27.3	5	16	2	25.7	21.7	4	0	3	41.1	39.5	1	6	5	31.5	31.7
3	18	0	18.7	17.6	2	10	1	30.1	33.6	0	16	2	17.7	18.2	6	0	2	40.1	47.3	4	2	3	39.1	40.0	1	8	5	24.4	27.3
3	19	0	13.9	14.7	2	11	1	41.1	43.2	0	18	2	23.6	19.5	6	1	2	39.3	37.2	4	4	3	12.4	9.6	2	0	5	29.3	29.5
3	20	0	28.5	26.3	2	12	1	46.8	47.7	0	20	2	10.9	17.0	6	2	2	14.7	17.1	4	6	3	30.6	28.8	2	1	5	17.0	19.5
4	1	0	67.6	56.7	2	13	1	32.9	28.0	0	22	2	16.0	21.5	6	3	2	17.7	16.9	4	8	3	28.7	25.8	3	3	5	17.0	17.6
4	2	0	9.7	13.8	2	18	1	15.4	15.1	1	1	2	98.8	95.8	6	4	2	10.5	7.9	4	10	3	17.8	17.3	3	5	5	21.0	20.4
4	3	0	20.6	17.0	2	19	1	22.8	18.6	1	2	2	34.2	34.0	6	5	2	10.5	10.2	4	12	3	39.5	37.5	3	7	5	36.7	33.0
4	5	0	31.5	30.1	2	20	1	26.0	23.8	1	3	2	34.6	30.8	6	8	2	13.5	10.6	4	14	3	15.9	19.6	3	9	5	29.3	25.0
4	9	0	30.0	24.6	3	1	1	13.4	9.5	1	4	2	17.3	19.5	6	10	2	12.2	11.4	4	18	3	14.7	12.2	3	11	5	20.0	21.4
4	13	0	31.1	32.2	3	2	1	9.7	11.0	1	5	2	74.5	73.0	6	11	2	17.7	19.0	5	3	3	31.4	27.1	3	13	5	33.0	30.0
4	15	0	18.7	20.3	3	3	1	37.8	35.1	1	6	2	18.5	19.5	6	14	2	25.3	23.8	5	5	3	36.8	30.4	3	15	5	21.1	19.4
4	17	0	19.1	18.9	3	4	1	27.7	25.6	1	7	2	46.0	51.8	7	1	2	21.9	17.2	5	7	3	17.8	19.0	6	0	5	19.2	20.1
4	19	0	31.1	41.8	3	5	1	87.8	89.5	1	8	2	10.9	8.5	7	2	2	6.3	7.2	5	9	3	17.4	19.5	6	1	5	12.9	15.2
5	3	0	13.5	11.1	3	6	1	35.8	36.3	1	9	2	20.2	21.6	7	3	2	15.2	13.5	6	0	3	24.0	22.5	2	0	6	25.0	27.0
5	4	0	33.8	28.4	3	7	1	40.3	44.4	1	11	2	16.0	9.4	7	4	2	12.2	13.3	6	1	3	24.8	24.7	2	1	6	22.2	26.6
															7	5	2	21.9	20.9	6	2	3	24.8	24.8	2	2	6	25.6	27.9
															7	6	2	16.0	17.9	6	6	3	20.5	22.1	2	3	6	17.9	15.1
																									2	0	7	27.2	20.6

$R(0kl) = 0{\cdot}20$. In the final stages the structure was refined by least-squares methods with anisotropic temperature factors for all the non-hydrogen atoms. The final R value was 0·095. The *SFLS* program of Busing, Martin & Levy (1962) as modified by Ha nilton, Ibers, Johnson & Srikanta was used on the CDC-3600 computer at TIFR, Bombay.

Table 3. *Bond lengths and angles with their e.s.d.'s*

O(1)–C(1)	1·26 (2) Å	O(1)–C(1)–O(2)	121·4 (1·5)°
O(2)–C(1)	1·25 (3)	O(1)–C(1)–C(2)	119·1 (1·8)
O(3)–C(4)	1·31 (3)	O(2)–C(1)–C(2)	119·9 (1·7)
O(4)–C(4)	1·23 (3)	C(1)–C(2)–C(3)	121·7 (1·7)
C(1)–C(2)	1·50 (3)	C(2)–C(3)–C(4)	119·9 (1·7)
C(2)=C(3)	1·35 (3)	C(3)–C(4)–O(3)	114·6 (1·7)
C(3)–C(4)	1·46 (3)	C(3)–C(4)–O(4)	125·7 (1·5)
		O(3)–C(4)–O(4)	120·4 (1·7)

The final atomic coordinates with their estimated standard deviations expressed as units in the last place are given in Table 1 and the observed and calculated structure factors are given in Table 2. The bond lengths and angles in the fumarate ion are given in Table 3, the labelling of the atoms being shown in Fig. 1. Table 4 gives the thermal parameters for the atoms and Table 5 the intermolecular contacts less than 4·0 Å.

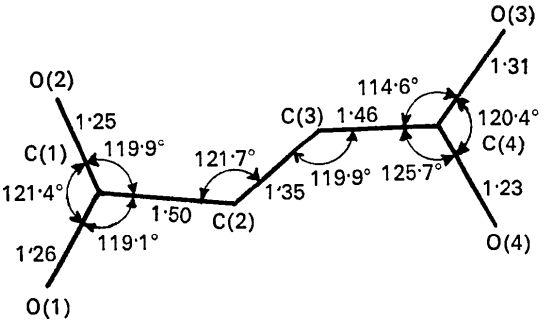

Fig. 1. Labelling scheme of the atoms, bond lengths, and bond angles.

Table 4. *Thermal parameters* ($\times 10^4$) *with their e.s.d.'s*

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

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	46 (54)	2 (54)	222 (185)	−23 (16)	116 (84)	59 (24)
C(2)	71 (60)	3 (6)	316 (197)	−12 (16)	25 (80)	−74 (28)
C(3)	201 (79)	10 (8)	84 (89)	36 (25)	77 (77)	12 (20)
C(4)	83 (57)	3 (7)	150 (182)	22 (21)	−53 (105)	−10 (23)
O(1)	56 (32)	12 (6)	415 (155)	−6 (11)	3 (48)	−67 (25)
O(2)	105 (47)	2 (5)	148 (114)	−20 (12)	−122 (54)	−7 (16)
O(3)	33 (41)	12 (6)	120 (103)	10 (13)	56 (51)	−2 (21)
O(4)	129 (58)	17 (7)	346 (167)	−36 (16)	110 (76)	−50 (28)
$(H_2O)_I$	237 (69)	9 (6)	135 (123)	−27 (20)	−3 (84)	38 (20)
$(H_2O)_{II}$	207 (76)	57 (14)	130 (101)	37 (32)	−158 (94)	00 (34)
$(H_2O)_{III}$	180 (54)	13 (6)	36 (85)	−25 (17)	43 (73)	−30 (25)
Ca	42 (10)	2 (1)	101 (80)	5 (4)	−100 (24)	3 (6)

Table 5. *Intermolecular contacts* (*up to* 4·0 Å)

Contact	Distance	Contact	Distance
O(1) ——$_b$O(3′)	3·70 Å	O(1)——^b_cO(3′)	3·59 Å
O(2) ——$_b$O(4′)	3·67	O(2)——^b_cO(4′)	3·56
O(3) ——$_b$C(1′)	3·62	O(3)——^b_cC(1′)	3·63
O(4) ——$_b$C(1′)	3·65	O(4)——^b_cC(1′)	3·79
$(H_2O)_I$—^a_bO(3″)	2·78	C(1)——$_b$C(4′)	3·71
$(H_2O)_I$—$_b$O(4″)	2·84	C(1)——^b_cC(4′)	3·57
$(H_2O)_{II}$ −$_a$O(1‴)	2·70	C(2)——$_b$C(4′)	3·59
$(H_2O)_{II}$ −$^{b}_{a}$O(3″)	2·93	C(2)——^b_cC(4′)	3·47
$(H_2O)_{II}$ −O(2‴)	2·83	C(2)——$_b$C(3′)	3·61
$(H_2O)_{II}$ −^c_bO(4″)	2·90	C(2)——^b_cC(3′)	3·63
$(H_2O)_{III}$−O(2‴)	2·77	C(3)——$_b$C(3′)	3·53
$(H_2O)_{III}$−O(1)	2·71	O(1)——O(2‴)	3·01
$(H_2O)_{III}$−$_b$O(4″)	2·77	$(H_2O)_I$−$_a$O(1‴)	3·19
$(H_2O)_{III}$−$_b$O(3′)	2·71	$(H_2O)_I$−O(2‴)	3·21

The labelling scheme for symmetry related atoms is:

Coordinates	Superscript
$x \quad y \quad z$	None
$\bar{x} \quad \bar{y} \quad \frac{1}{2}+z$	′
$\frac{1}{2}-x \quad \frac{1}{2}+y \quad \frac{1}{2}+x$	″
$\frac{1}{2}+x \quad \frac{1}{2}-y \quad z$	‴

A symbol such as $-_a$O(1‴) indicates the symmetry related atom O(1‴) displaced by a translation $-\mathbf{a}$, and so on.

Table 6 gives the Ca···O contacts, there being an eightfold coordination of the Ca by oxygen atoms (Fig. 5) with an average Ca···O distance of 2·45 Å.

Table 6. *Calcium ... oxygen contacts* (Å)

Ca...O_1	2·48
Ca...O_2	2·59
Ca...$(H_2O)_I$	2·39
Ca...$(H_2O)_{II}$	2·34
Ca...$(H_2O)_{III}$	2·56
Ca...O(2‴)	2·39
Ca...$-_a$O(1‴)	2·29
Ca...$-_a(H_2O‴)_{III}$	2·61

Planarity of the fumarate ion

The best plane passing through the atoms of the fumarate ion derived by the method of least-squares is given in equation (*A*). The deviations of the atoms from this plane are given in Table 7. The equation of the best plane through O(1), C(1), and O(2) is given by equation (*B*), and that through C(2), C(3), C(4), O(3), and O(4) by equation (*C*). Planes *B* and *C* make an angle of 3·2° with each other.

$$X+1\cdot552Y-48\cdot172Z-12\cdot081=0 \qquad (A)$$
$$X-0\cdot500Y+34\cdot920Z+2\cdot553=0 \qquad (B)$$
$$X+1\cdot071Y-30\cdot197Z-0\cdot006=0 \qquad (C)$$

Table 7. *Deviations of atoms from plane A with their e.s.d.'s*

Atom	Deviation
C(1)	−0·041 (52) Å
C(2)	0·000 (54)
C(3)	0·020 (01)
C(4)	−0·009 (53)
O(1)	0·000 (43)
O(2)	−0·103 (41)
O(3)	0·045 (41)
O(4)	0·027 (55)

Description of the structure

Figs. 2 and 3 show the crystal structure viewed down **c** and **a** respectively. Fumarate ions are aligned parallel to **b** forming chains which are in two layers at $Z\simeq 0\cdot0$ and $Z\simeq c/2$. The structure is held together by (i) van der Waals forces (Table 5), (ii) Ca···O ionic linkages (Table 6), and (iii) hydrogen bonds of which there are ten (Table 8).

Hydrogen bonding scheme

Fig. 4 shows the environement of each water molecule in the structure, and Fig. 2 the hydrogen bonding in the crystal structure as a whole. The bond lengths in the fumarate ion (Table 3) suggest that one of the

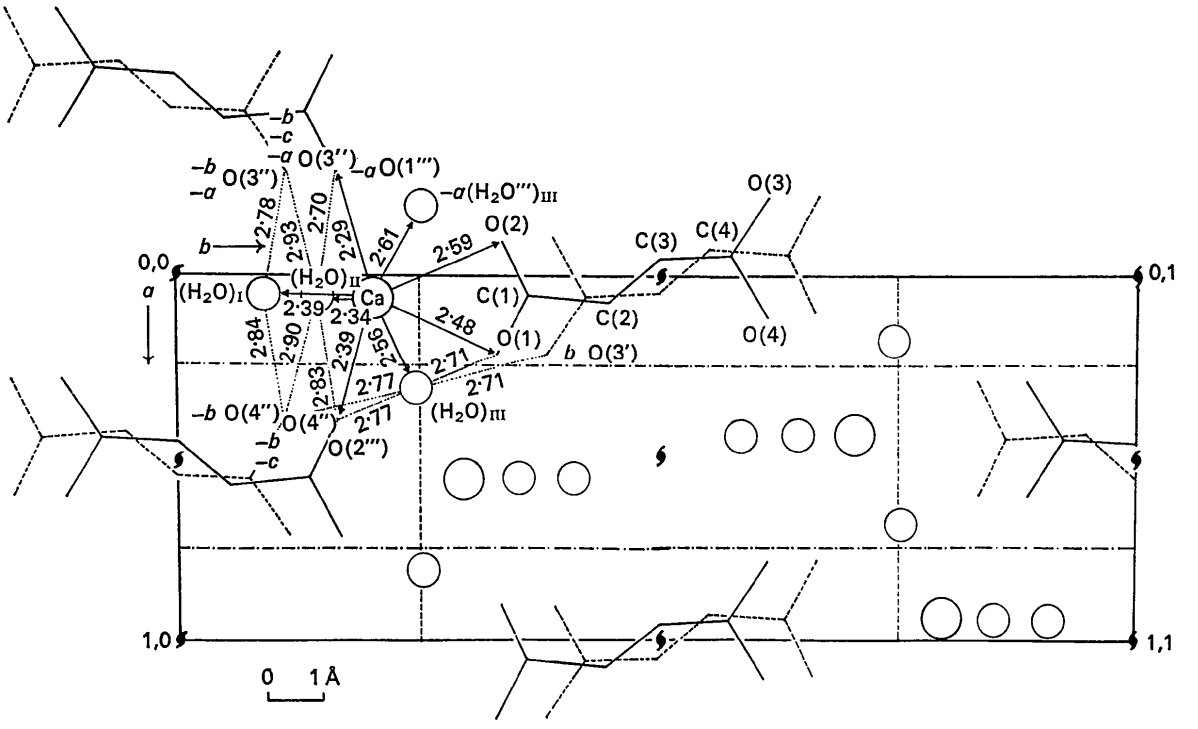

Fig. 2. The crystal structure, looking down the [001] axis.

carboxyl groups (C(4), O(3), O(4)) is not ionized because of the lack of equality of the C–O bonds (1·31, 1·24 Å). This may well, however, be due to inadequacy of the data. It may be noted that none of the oxygen atoms of this carboxyl group makes any significant contact with the Ca ions. There are altogether six hydrogen atoms of the three water molecules available for hydrogen bonding, but Table 8 shows that there are ten short distances, ranging from 2·70 to 2·93 Å, each of which must be regarded as a hydrogen bond. A tentative assignment of the hydrogen bonding is given below.

Table 8. *Details of proposed hydrogen bonding scheme*

Hydrogen bond			Angle
Donor	Acceptor	Distance	(O–H_2O–O)
$(H_2O)_I$	$_bO(4'')$	2·84 Å	102·6°
$(H_2O)_I$	$^{a}_{b}O(3'')$	2·78	
$(H_2O)_{II}$	$_aO(4'')$	2·90 (*p*)	78·0 (*pq*)
$(H_2O)_{II}$	$^{c}_{b}O(2''')$	2·83 (*q*)	106·2 (*qr*)
$(H_2O)_{II}$	$_aO(1''')$	2·70 (*r*)	79·5 (*rs*)
$(H_2O)_{II}$	$^{b}_{c}O(3'')$	2·93 (*s*)	98·0 (*ps*)
	$^{}_{a}$		
$(H_2O)_{III}$	O(1)	2·71 (*t*)	86·3 (*tu*)
$(H_2O)_{III}$	$_bO(3')$	2·71 (*u*)	
$(H_2O)_{III}$	O(2''')	2·77 (*v*)	83·2 (*vw*)
$(H_2O)_{III}$	$_bO(4'')$	2·77 (*w*)	

(*a*) $(H_2O)_I$ links the chain of fumarate ions, unit translation **a** apart, both chains being at the same height $Z \simeq c/2$, through hydrogen bonds $(H_2O)_I \cdots {}^{b}_{a}O(3'') =$ 2·78 and $(H_2O)_I \cdots {}_bO(4'') = 2{\cdot}84$ Å, the angle subtended at the water molecule by these two hydrogen bonds being 102·6°.

(*b*) $(H_2O)_{II}$ forms four hydrogen bonds

$(H_2O)_{II} \cdots {}_aO(1''') = 2{\cdot}70$ $(H_2O)_{II} \cdots {}^{b}_{a}O(3'') = 2{\cdot}93$ Å.

$(H_2O)_{II} \cdots O(2''') = 2{\cdot}83$ $(H_2O)_{II} \cdots {}^{c}_{b}O(4''') = 2{\cdot}90$ Å.

As there are only two hydrogen atoms available from this water molecule, this system of four hydrogen bonds must be regarded as a system of bifurcated hydrogen bonds. The angles between the various hydrogen bonds subtended at $(H_2O)_{II}$ are given in Fig. 4(*b*). The linkages provided by these four hydrogen bonds bind chains of fumarate ions, again unit translation **a** apart, but now in two different layers $Z \simeq 0{\cdot}0$ and $Z \simeq c/2$.

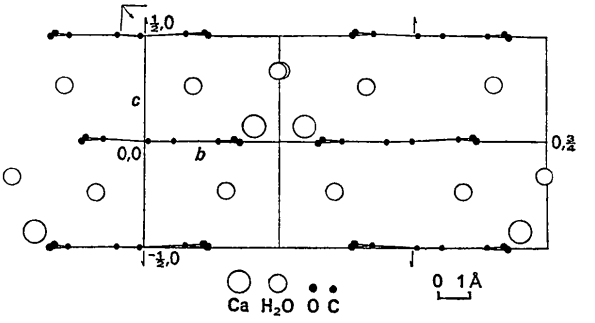

Fig. 3. The crystal structure, looking down the [100] axis.

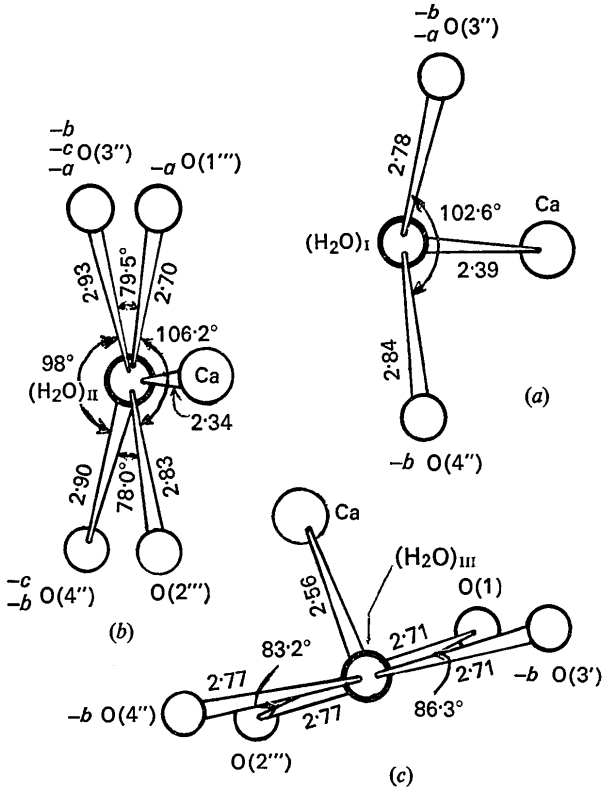

Fig. 4. Environment of the individual water molecule.

(*c*) $(H_2O)_{III}$ binds the chains of fumarate ions in the [010] direction, both in the same layer, $Z \simeq 0{\cdot}0$.

$(H_2O)_{III}\cdots O(2''') = 2{\cdot}77$ and $(H_2O)_{III}\cdots O(1) = 2{\cdot}71$ Å

as well as the layer displaced by $c/2$.

$(H_2O)_{III}\cdots {}_bO(3') = 2{\cdot}71$ $(H_2O)_{III}\cdots {}_{-b}O(4'') = 2{\cdot}77$ Å.

Again these four hydrogen bonds must be regarded as a bifurcated system. Such bifurcated hydrogen bonds involving one water molecule have been reported previously (Ambady, 1968; Parry, 1951).

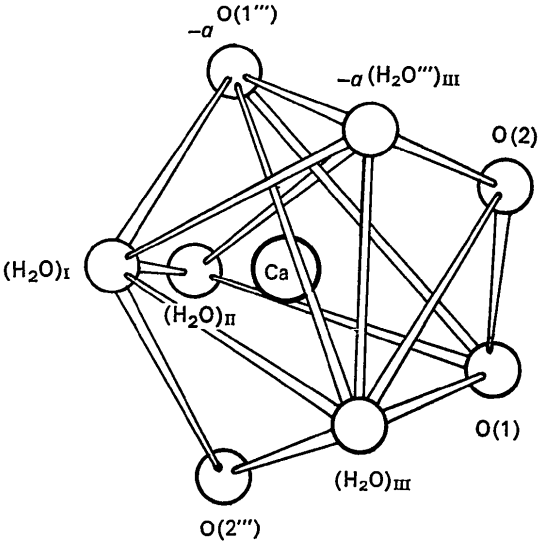

Fig. 5. The coordination polyhedron of calcium.

Grateful acknowledgement is made for the computer facilities made available to us at the Computer Centre, TIFR, Bombay for the *SFLS* refinement on the CDC-3600.

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