

The Crystal Structure of the Calcium and Strontium Salts of Arabonic Acid

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The crystal structures of the calcium and strontium salts of arabonic acid have been determined by X-ray crystallographic methods, using the isomorphous replacement technique. The carbon atoms of the arabonate anion form a nearly planar zig-zag chain. The bond C_2-O_2 is approximately coplanar with the carboxyl group. The cations are surrounded by eight oxygen atoms which lie in the corners of a distorted Archimedean antiprism. The structures of the two isomorphous compounds are compared.

As part of a program of investigations of the conformations of simple sugars, we have determined the crystal structure of arabonic acid, $CH_2OH(CHOH)_3COOH$, in the form of its calcium and strontium salts. Amongst earlier crystal structure analysis related to the structure of this compound should be mentioned those of β -arabinose² and potassium gluconate¹. A comparison of the open-chain structure of arabonic acid with the ring structure of the parent sugar would appear to be of interest.

EXPERIMENTAL. CRYSTAL DATA

A sample of the Ca-D-arabonate, $Ca(C_3O_6H_9)_2 \cdot 5H_2O$, was supplied by Fluka AG. In order to prepare the strontium salt, the calcium ions were first removed as oxalate. Subsequent addition of $SrCO_3$ and alcohol yielded big, well-developed crystals. The crystals had the same habit for the two salts, being elongated along the b axis and bounded by $\{100\}$, $\{101\}$ and $\{001\}$.

Oscillation and Weissenberg photographs were taken about the b and c axes using filtered copper radiation ($\lambda = 1.542 \text{ \AA}$). They showed the crystals to be monoclinic, with unit cell dimensions $a = 14.74 \text{ \AA}$, $b = 5.82 \text{ \AA}$, $c = 11.40 \text{ \AA}$, $\beta = 99^\circ$ for the Ca salt and $a = 14.79$, $b = 5.83$, $c = 11.78 \text{ \AA}$, $\beta = 99^\circ$ for the Sr salt (all $\pm 0.5\%$). The compounds are thus isomorphous. Reflections are absent for odd values of $h + k$, and the lattice is therefore C -centered. As the compounds are optically active, the space group must be $C2$. By flotation in mixtures of CCl_4 and $CHBr_3$ the density was found to be 1.59 g/cm^3 for the Ca salt and 1.69 g/cm^3 for the Sr salt, which gives two (calc. 2.01 for both salts) molecules $Ca(Sr)(C_3O_6H_9)_2 \cdot 5H_2O$ in the unit cell.

The intensities were measured on integrated Weissenberg diagrams by means of a Hilger Watts photometer and corrected for Lorentz-polarization effects. Small crystals of cross-section about 0.1×0.1 mm were used and no correction for absorption applied.

For the calcium salt 163 reflections were observed in the b projection and 53 in the c projection, the numbers obtainable by copper radiation being 210 and 60, respectively. In the two corresponding projections of the strontium salt only six reflections were not observed with measurable intensity.

DETERMINATION OF THE STRUCTURE OF CALCIUM ARABONATE

The data given above show that the calcium ion, as well as one molecule of water, must lie on two-fold axes. The position of the ion was chosen as origin and the structure solved by the isomorphous replacement method.

The b projection. This projection is centrosymmetric, and the difference between the structure factors for the two salts should be given simply by the difference in the scattering power of the calcium and strontium ions corrected for thermal vibrations. This was borne out by the experimental values after their reduction to absolute scale, and the signs of the structure factors were directly deduced. In general, the signs were positive, as was to be expected, but surprisingly, the sign of the very strongest reflection, $60\bar{1}$, was found to be negative. Because of this our first attempts to solve the structure by the heavy atom method were unsuccessful. The corresponding Fourier map showed clearly the positions of the carbon and oxygen atoms, and the calculated structure factors agreed well with the observed ones, the value of the reliability

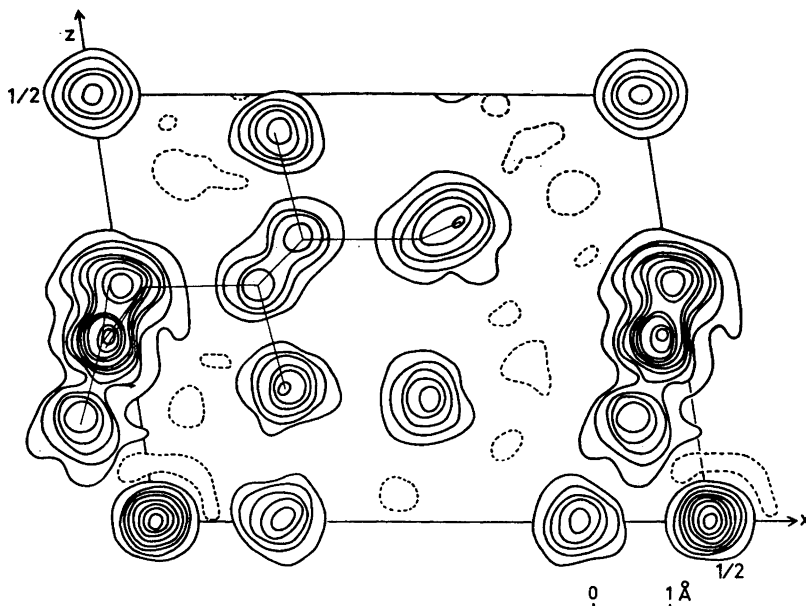


Fig. 1. Electron density projection in direction of b axis. Contours at 0, 2, 4, ... $e \cdot \text{\AA}^{-2}$, the zero line being dotted. For the calcium ion every second contour is omitted.

Table 1. Atomic coordinates of Ca-arabonate as fractions of the corresponding cell edge.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{hol}
Ca	0.0000	0.000	0.0000	1.1
C ₁	-0.0248	-0.322	0.218	2.5
C ₂	0.0195	-0.094	0.2741	2.0
C ₃	0.1249	-0.110	0.2765	2.0
C ₄	0.1718	0.111	0.3335	2.0
C ₅	0.2763	0.120	0.3261	2.5
O ₀	-0.0550	-0.321	0.1117	2.2
O ₁	-0.0096	-0.506	0.2825	2.0
O ₂	-0.0170	0.091	0.2051	2.2
O ₃	0.1355	-0.110	0.1536	2.0
O ₄	0.1620	0.132	0.4552	2.2
O ₅	0.3169	0.338	0.3495	2.8
O ₆	0.1145	0.303	0.0012	3.0
O ₇	0.2618	-0.427	0.1414	2.6
O ₈	0.0000	-0.333	0.5000	2.5
H ₁	0.010	-0.05	0.362	3.0
H ₂	0.138	-0.25	0.293	—
H ₃	0.158	0.27	0.317	—
H ₄	0.303	0.02	0.387	—
H ₅	0.285	0.02	0.235	—
H ₆	0.495	-0.40	0.415	—
H ₇	0.483	0.22	0.234	—
H ₈	0.405	0.45	0.035	—
H ₉	0.163	0.40	0.047	—
H ₁₀	0.278	0.43	0.208	—
H ₁₁	0.300	-0.38	0.095	—
H ₁₂	0.175	-0.22	0.150	—
H ₁₃	0.330	0.43	0.480	—
H ₁₄	0.378	0.28	0.400	—

index, $R = \Sigma ||F_c| - |F_o|| / \Sigma |F_o|$, being 0.21. The structure was further refined by least squares calculations and difference syntheses. The final value of R for all reflections obtainable by copper radiation is 0.09. In the calculation of R non-observed reflections are only taken into account when F_c exceeds the observable limit of intensity. The atoms C₁ and O₂ overlap and their coordinates are less certain than those of the other atoms. The positions of the hydrogen atoms were derived partly from the difference maps, partly by stereochemical considerations. The atomic scattering curve of Forsyth and Wells⁴ was used for the Ca ion, and those of Berghuis *et al.*⁵ for the other atoms. In the temperature factor, $\exp(-B \sin^2 \theta / \lambda^2)$, B is 1.1 for the Ca ion and 2.0–3.0 for the other atoms. The final difference map, from which the atomic coordinates given in Table 1 are derived, indicates clearly that the vibrations of a number of atoms are anisotropic, but this has not been taken into account in the structure factor calculations. Fig. 1 shows the electron density map and in Table 3 observed and calculated values of the structure factors are compared.

The c projection. This non-symmetrical projection was solved by applying the isomorphous replacement procedure described by Bokhoven *et al.*³, the resulting double Fourier synthesis being interpreted by means of the known b projection of the structure. For the two water molecules several positions

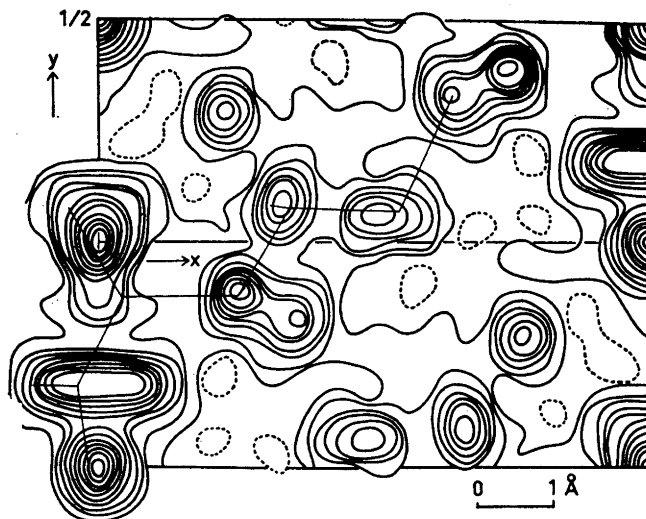


Fig. 2. Electron density projection in direction of c axis. Contours as in Fig. 1.

were suggested by the maps. The correct ones were deduced by comparing observed and calculated structure factors. The y coordinates were then refined by least squares calculations, maintaining the x coordinates derived from the b projection unchanged. The resolution is very poor in this projection and no really efficient refinement could be carried out. The final value of R is 0.09. The electron density map is shown in Fig. 2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE OF CALCIUM ARABONATE

The bond lengths and bond angles calculated from the coordinates in Table 1 are given in Table 2 and Fig. 3. The Cruickshank formulae⁶ give the following values for the standard deviations of the atomic coordinates: $\sigma(x) = \sigma(z) = 0.008$ Å, $\sigma(y) = 0.012$ Å for the carbon atoms, and $\sigma(x) = \sigma(z) = 0.006$ Å, $\sigma(y) = 0.009$ Å for the oxygen atoms. The corresponding standard deviation in the bond lengths lie in the range 0.011–0.015 Å for the C–C bonds and 0.009–0.013 Å for C–O bonds. However, lack of resolution makes the uncertainty considerably greater for most bonds and we do not consider deviations less than 0.05 Å significant. The limit of error in the bond angles is estimated to be about 3° for most angles.

The arabonate ion. The carbon atoms form an extended, nearly planar zig-zag chain with the oxygen atoms lying above and below this plane (Fig. 3), as was found in the gluconate ion¹. Certain chemical properties of sugars have also been explained by this arrangement⁸ and it appears reasonable to assume that it is the preferred conformation of all open-chain sugars. One might

Table 2. Bond lengths (in Å units) and bond angles in Ca-arabonate. Primes indicate atoms in neighbouring molecules.

C ₁ -C ₂	1.57	C ₁ -C ₂ -C ₃	108°
C ₂ -C ₃	1.55	C ₂ -C ₃ -C ₄	110°
C ₃ -C ₄	1.55	C ₃ -C ₄ -C ₅	113°
C ₄ -C ₅	1.56	O ₀ -C ₁ -O ₁	125°
C ₁ -O ₀	1.29	O ₀ -C ₁ -C ₂	118°
C ₁ -O ₁	1.23	O ₁ -C ₁ -C ₂	117°
C ₂ -O ₂	1.39	C ₁ -C ₂ -O ₂	108°
C ₃ -O ₃	1.43	C ₃ -C ₃ -O ₃	111°
C ₄ -O ₄	1.42	C ₂ -C ₃ -O ₃	104°
C ₅ -O ₅	1.41	C ₄ -C ₃ -O ₃	107°
Ca-O ₀	2.47	C ₃ -C ₄ -O ₄	112°
Ca-O ₂	2.45	C ₅ -C ₄ -O ₄	108°
Ca-O ₃	2.52	C ₄ -C ₅ -O ₅	114°
Ca-O ₅	2.44	C ₃ -O ₃ -O ₆	124°
O ₃ -O ₆	2.95	C ₃ -O ₃ -O ₇	104°
O ₇ -O ₆	2.95	C ₅ -O ₅ -O ₇	103°
O ₆ -O ₀	2.62	C ₄ -O ₄ -O ₅	135°
O ₃ -O ₇	2.64	O ₅ -O ₇ -O ₃	115°
O ₄ -O ₅	2.79	O ₇ -O ₆ -O ₀	107°
O ₅ -O ₇	2.75	C ₅ -O ₅ -O ₈	97°
O ₁ -O ₈	2.66	O ₃ -O ₇ -O ₆	86°
O ₃ -O ₁	2.50	C ₂ -O ₂ -O ₁	122°
O ₆ -O ₇	2.94		
O ₅ -O ₈	3.13		

expect non-planar carbon chains for sugars in which a planar chain gives unfavourable O—O distances. Glucose is such a sugar, but in spite of this the chain is planar, favourable O—O contacts being obtained by widening some of the angles at the carbon atoms. From the data given on the gluconate ion the O₂—O₄ distance is calculated to be 2.97 Å, whereas a structure based on tetrahedral angles gives 2.52 Å.

The plane of the carboxyl ion is roughly co-planar with the plane C₁C₂O₂ containing the α-hydroxyl oxygen O₂, the angle between the planes being about 20°. The distance O₀—O₂ is somewhat smaller (2.64 Å) than normal van der Waals approach and could be extended by rotation about the C₁—C₂

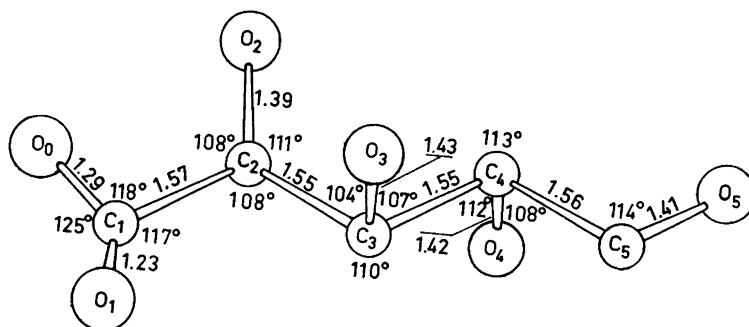


Fig. 3. The structure of the arabonate ion.

bond. This structural feature appears to be common to all compounds containing the groups $C(OH)COOH$ and $C(OH)COO^-$ and has been discussed by Jeffrey and Parry ⁷.

The two C—O bonds in the carboxyl group are found to have lengths 1.23 Å and 1.29 Å, respectively. A symmetrical structure is to be expected ⁹. The difference is probably mainly due to inaccuracy in the structure analysis, as the atom C_1 is unresolved in both projections. Part of it may, however, be caused by crystal forces, the external bonding being different for the two oxygen atoms.

The C—C and C—O bond lengths do not deviate significantly from the normal values of about 1.53 Å and 1.43 Å, respectively. The mean C—C—C angle is 110° and the mean C—C—OH angle 109°.

The open-chain structure derived in the present work can be transformed into the pyranose form of arabinose by a rotation of 120° around the bonds C_2-C_3 , C_3-C_4 and C_4-C_5 . This places O_5 near O_1 (or O_0) and the structure corresponds to one of the two chair conformations characteristic of arabopyranose ($2e3e4a \rightleftharpoons 2a3a4e$), dependent on the direction of rotation.

The ionic environment. Each calcium ion is surrounded by eight oxygen atoms related in pairs by the operation of the two-fold axis on which the ion is situated. They lie in the corners of a distorted square Archimedean antiprism.

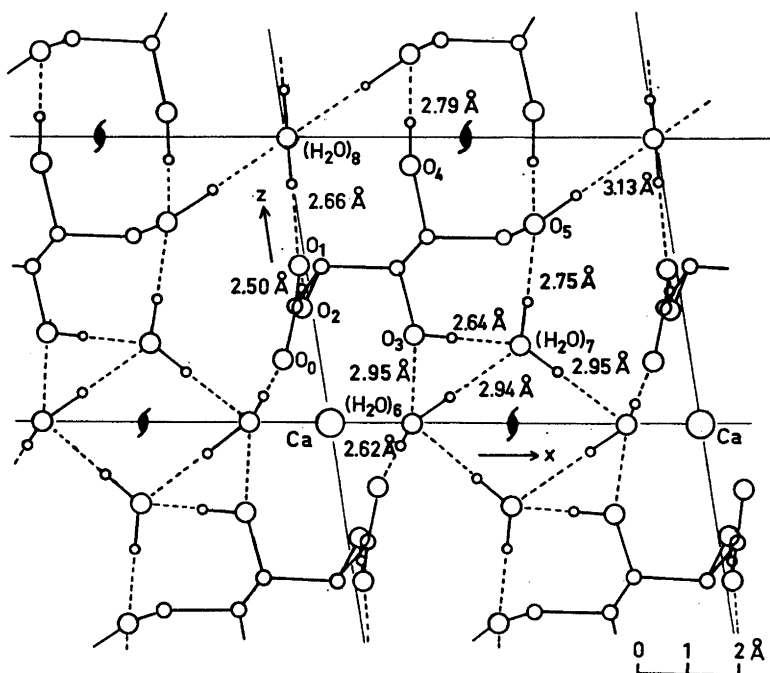


Fig. 4. The b -projection of the structure. Short contacts are shown by broken lines. The smallest circles indicate the proposed positions of the oxygen-bonded hydrogen atoms.

Table 3. Observed (F_o) and calculated (F_c) structure factors for Ca arabonate.

$h k l$	F_o	F_c	$h k l$	F_o	F_c
00 1	41	43	40 0	77	75
00 2	51	— 54	40 1	38	36
00 3	31	31	40 2	5	— 1
00 4	42	41	40 3	12	11
00 5	14	— 10	40 4	5	4
00 6	74	71	40 5	22	21
00 7	52	48	40 6	13	— 10
00 8	38	33	40 7	6	— 1
00 9	35	33	40 8	6	3
00 10	14	14	40 9	6	4
00 11	24	22	40 10	35	33
00 12	6	6	40 11	< 8	11
00 13	< 6	5	40 12	< 6	2
00 14	24	24	40 13	< 6	— 0
20 $\bar{1}$ 4	24	23	60 $\bar{1}$ 4	17	19
20 $\bar{1}$ 3	< 6	— 0	60 $\bar{1}$ 3	12	10
20 $\bar{1}$ 2	< 6	— 4	60 $\bar{1}$ 2	< 6	5
20 $\bar{1}$ 1	13	15	60 $\bar{1}$ 1	18	20
20 $\bar{1}$ 0	36	39	60 $\bar{1}$ 0	< 8	4
20 $\bar{0}$ 9	13	11	60 $\bar{0}$ 9	7	8
20 $\bar{0}$ 8	50	46	60 $\bar{0}$ 8	< 6	6
20 $\bar{0}$ 7	40	33	60 $\bar{0}$ 7	< 6	— 4
20 $\bar{0}$ 6	49	— 51	60 $\bar{0}$ 6	39	39
20 $\bar{0}$ 5	45	46	60 $\bar{0}$ 5	38	38
20 $\bar{0}$ 4	88	89	60 $\bar{0}$ 4	63	69
20 $\bar{0}$ 3	8	— 8	60 $\bar{0}$ 3	29	30
20 $\bar{0}$ 2	17	— 18	60 $\bar{0}$ 2	38	— 35
20 $\bar{0}$ 1	73	80	60 $\bar{0}$ 1	126	— 129
20 0	75	70	60 0	106	110
20 1	42	37	60 1	54	45
20 2	6	— 1	60 2	19	17
20 3	8	6	60 3	30	26
20 4	121	120	60 4	45	46
20 5	9	16	60 5	6	— 3
20 6	22	17	60 6	13	12
20 7	10	5	60 7	6	5
20 8	8	6	60 8	< 8	— 0
20 9	9	— 3	60 9	14	14
20 10	60	58	60 10	12	16
20 11	31	31	60 11	23	24
20 12	< 6	1	60 12	6	6
20 13	< 6	0	80 $\bar{1}$ 3	20	22
40 $\bar{1}$ 4	14	15	80 $\bar{1}$ 2	< 6	5
40 $\bar{1}$ 3	< 6	— 1	80 $\bar{1}$ 1	< 6	— 2
40 $\bar{1}$ 2	< 6	— 0	80 $\bar{1}$ 0	18	21
40 $\bar{1}$ 1	10	— 11	80 $\bar{0}$ 9	< 8	2
40 $\bar{1}$ 0	26	24	80 $\bar{0}$ 8	32	31
40 $\bar{0}$ 9	17	18	80 $\bar{0}$ 7	63	67
40 $\bar{0}$ 8	29	29	80 $\bar{0}$ 6	< 6	— 1
40 $\bar{0}$ 7	11	— 4	80 $\bar{0}$ 5	14	17
40 $\bar{0}$ 6	27	27	80 $\bar{0}$ 4	68	68
40 $\bar{0}$ 5	15	— 17	80 $\bar{0}$ 3	25	21
40 $\bar{0}$ 4	58	61	80 $\bar{0}$ 2	21	— 21
40 $\bar{0}$ 3	18	— 21	80 $\bar{0}$ 1	54	51
40 $\bar{0}$ 2	85	— 92	80 0	71	71
40 $\bar{0}$ 1	12	— 10	80 1	34	36

$h k l$	F_o	F_c	$h k l$	F_o	F_c
8 0 2	14	16	14 0 $\bar{1}0$	9	12
8 0 3	15	— 12	14 0 $\bar{9}$	< 6	3
8 0 4	49	47	14 0 $\bar{8}$	< 6	— 2
8 0 5	33	30	14 0 $\bar{7}$	12	13
8 0 6	49	46	14 0 $\bar{6}$	< 7	1
8 0 7	27	27	14 0 $\bar{5}$	7	7
8 0 8	15	14	14 0 $\bar{4}$	20	20
8 0 9	22	— 18	14 0 $\bar{3}$	19	19
8 0 10	21	19	14 0 $\bar{2}$	< 7	0
8 0 11	23	24	14 0 $\bar{1}$	< 7	0
8 0 $\bar{1}2$	12	11	14 0 0	< 7	10
10 0 $\bar{1}3$	< 5	6	14 0 1	24	23
10 0 $\bar{1}2$	23	23	14 0 2	17	19
10 0 $\bar{1}1$	8	12	14 0 3	12	— 12
10 0 $\bar{1}0$	6	9	14 0 4	< 7	8
10 0 $\bar{9}$	16	15	14 0 5	< 6	0
10 0 $\bar{8}$	35	36	14 0 6	12	13
10 0 $\bar{7}$	15	— 13	14 0 7	15	16
10 0 $\bar{6}$	7	10	16 0 $\bar{9}$	8	10
10 0 $\bar{5}$	19	19	16 0 $\bar{8}$	32	29
10 0 $\bar{4}$	61	63	16 0 $\bar{7}$	12	10
10 0 $\bar{3}$	49	53	16 0 $\bar{6}$	< 6	5
10 0 $\bar{2}$	8	11	16 0 $\bar{5}$	< 6	— 7
10 0 $\bar{1}$	9	— 4	16 0 $\bar{4}$	10	9
10 0 0	21	19	16 0 $\bar{3}$	17	21
10 0 1	20	16	16 0 $\bar{2}$	16	19
10 0 2	10	5	16 0 $\bar{1}$	15	16
10 0 3	38	35	16 0 0	17	20
10 0 4	29	29	16 0 1	13	15
10 0 5	25	23	16 0 2	< 6	1
10 0 6	24	23	16 0 3	< 5	5
10 0 7	21	19	16 0 4	< 5	55
10 0 8	8	— 4	16 0 5	11	11
10 0 9	6	— 3	18 0 $\bar{5}$	< 5	3
10 0 10	34	32	18 0 $\bar{4}$	16	16
10 0 11	14	17	18 0 $\bar{3}$	15	15
12 0 $\bar{1}2$	6	7	18 0 2	13	17
12 0 $\bar{1}1$	6	7	18 0 1	< 6	1
12 0 $\bar{1}0$	6	10	18 0 0	13	15
12 0 $\bar{9}$	16	16	1 1 0	82	74
12 0 $\bar{8}$	13	11	3 1 0	49	52
12 0 $\bar{7}$	< 7	5	5 1 0	43	44
12 0 $\bar{6}$	< 7	0	7 1 0	52	57
12 0 $\bar{5}$	< 7	1	9 1 0	13	7
12 0 $\bar{4}$	31	34	11 1 0	19	16
12 0 $\bar{3}$	21	21	13 1 0	13	15
12 0 $\bar{2}$	19	21	15 1 0	15	15
12 0 $\bar{1}$	14	— 17	17 1 0	12	12
12 0 0	23	22	0 2 0	53	58
12 0 1	< 7	1	2 2 0	34	28
12 0 2	14	14	4 2 0	106	103
12 0 3	7	2	6 2 0	35	33
12 0 4	< 8	1	8 2 0	51	47
12 0 5	< 7	10	10 2 0	31	26
12 0 6	29	28	12 2 0	30	37
12 0 7	10	11	14 2 0	20	21
12 0 8	7	2	16 2 0	20	17
12 0 9	< 5	9	1 3 0	30	24

<i>h k l</i>	<i>F</i> _o	<i>F</i> _c	<i>h k l</i>	<i>F</i> _o	<i>F</i> _c
3 3 0	65	60	3 5 0	<10	10
5 3 0	31	30	5 5 0	<10	13
7 3 0	13	10	7 5 0	16	15
9 3 0	39	34	9 5 0	< 9	10
11 3 0	13	13	11 5 0	15	15
13 3 0	15	14	13 5 0	12	11
15 3 0	18	16	0 6 0	10	17
0 4 0	35	40	2 6 0	25	23
2 4 0	46	47	4 6 0	19	13
4 4 0	32	29	6 6 0	14	18
6 4 0	< 9	9	8 6 0	< 7	3
8 4 0	15	14	10 6 0	13	16
10 4 0	20	25	1 7 0	9	8
12 4 0	16	14	3 7 0	10	8
14 4 0	16	16	5 7 0	13	12
1 5 0	42	39			

In any one molecule, the carboxyl oxygen (O_0) and the hydroxyl oxygens O_2 and O_3 are coordinated to the same calcium ion. A water molecule completes the scheme. Each cation is thus coordinated to only two anions. The four Ca—O distances are nearly equal, lying in the range 2.44–2.52 Å, in agreement with the values found in other structures containing eight-coordinated calcium ions.

The hydrogen bonds. In the structure there are ten different intermolecular O—O distances shorter than 3.2 Å. The number of oxygen-bonded hydrogen atoms is nine. It appears reasonable to assume that these all are involved in hydrogen bond formation, although the refinement is not so complete that the hydrogen atoms appear clearly on the difference map. The one short contact which is not a hydrogen bond, might be O_5 — O_8 as this distance is considerably longer (3.13 Å) than the other O—O distances (Table 2). However, in the isomorphous strontium compound all short O—O contacts are unchanged to

Table 4. Atomic coordinates of Sr arabonate as fractions of the corresponding cell edge.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Sr	0.000	0.000	0.000
C ₁	-0.023	-0.315	0.219
C ₂	0.018	-0.090	0.280
C ₃	0.124	-0.119	0.283
C ₄	0.170	0.094	0.333
C ₅	0.277	0.108	0.331
O ₀	-0.059	-0.323	0.121
O ₁	-0.009	-0.499	0.287
O ₂	-0.019	0.082	0.210
O ₃	0.139	-0.120	0.163
O ₄	0.160	0.128	0.456
O ₅	0.315	0.337	0.352
O ₆	0.122	0.313	-0.006
O ₇	0.260	-0.429	0.147
O ₈	0.000	-0.344	0.500

Table 5. Bond lengths (in Å units) and bond angles in Sr arabonate.

C ₁ -C ₂	1.58	C ₁ -C ₂ -C ₃	103°
C ₂ -C ₃	1.57	C ₂ -C ₃ -C ₄	108°
C ₃ -C ₄	1.49	C ₃ -C ₄ -C ₅	115°
C ₄ -C ₅	1.59	O ₀ -C ₁ -O ₁	124°
C ₁ -O ₀	1.34	O ₀ -C ₁ -C ₂	124°
C ₁ -O ₁	1.19	O ₁ -C ₁ -C ₂	113°
C ₂ -O ₂	1.35	C ₁ -C ₂ -O ₂	106°
C ₃ -O ₃	1.46	C ₃ -C ₂ -O ₂	115°
C ₄ -O ₄	1.49	C ₂ -C ₃ -O ₃	106°
C ₅ -O ₅	1.45	C ₄ -C ₃ -O ₃	105°
Sr-O ₀	2.59	C ₃ -C ₄ -O ₄	113°
Sr-O ₁	2.60	C ₅ -C ₄ -O ₄	105°
Sr-O ₃	2.68	C ₄ -C ₅ -O ₅	114°
Sr-O ₆	2.58	C ₃ -O ₃ -O ₇	126°
O ₃ -O ₆	3.20	C ₃ -O ₃ -O ₇ '	107°
O ₇ -O ₆ '	3.04	C ₄ -O ₄ -O ₅	133°
O ₆ -O ₀	2.68	O ₅ -O ₇ -O ₃	113°
O ₃ -O ₇	2.57	O ₇ -O ₆ '-O ₀	103°
O ₄ -O ₅ '	2.81		
O ₅ -O ₇	2.78		
O ₁ -O ₈	2.65		
O ₂ -O ₁ '	2.55		
O ₆ -O ₇	2.86		
O ₅ -O ₈	3.12		

within 0.10 Å except O₃-O₆, which is increased from 2.95 Å to 3.20 Å. We therefore prefer to consider O₃-O₆ to be the one contact which is not a hydrogen bond. The appearance of the difference map lends some support to this view. However, other distributions of the hydrogen atoms cannot be ruled out, and it is also possible that the hydrogen bond system is different in the two compounds. The proposed positions of the hydrogen atoms is shown in Fig. 4 and in Table 1. The hydrogen bonds conform well to the general stereochemistry of the molecules and link them together in a three-dimensional network. Three short hydrogen bonds of lengths 2.50, 2.62, and 2.66 Å are associated with the carboxyl oxygens. The water molecule (H₂O)₇ is linked to the hydroxyl oxygens O₃ and O₅ in different molecules by bonds of lengths 2.64 and 2.75 Å, and appears also to be connected with two different (H₂O)₆ molecules by weaker bonds of lengths 2.95 and 2.94 Å. These four bonds are roughly tetrahedrally distributed, whereas the arrangements around (H₂O)₆ and (H₂O)₈ are rather irregular.

THE STRUCTURE OF STRONTIUM ARABONATE

Refinements were carried out in two projections also on this compound, mainly by least squares calculations. The final value obtained for *R* was 0.10 for both projections. The atomic coordinates are given in Table 4, and the corresponding interatomic distances and bond angles in Table 5. The accuracy of the data is lower than for the calcium compound and we do not consider the differences in molecular dimensions significant although the deviation

from a symmetrical carboxyl ion is surprisingly large. The four Sr—O distances vary between 2.58 and 2.68 Å corresponding to a difference of 0.14 Å in the ionic radii of eight-coordinated strontium and calcium ions.

A comparison of the atomic coordinates (Tables 1 and 4) shows what happens when the calcium ion is substituted by the larger strontium ion. The x and y coordinates of the arabonate ion are nearly unchanged, but all the atoms have moved 0.12–0.18 Å in direction of the positive z axis (mean value 0.16 Å). The water molecules $(\text{H}_2\text{O})_7$ and $(\text{H}_2\text{O})_8$ follow the movement of the arabonate ion. On the other hand, $(\text{H}_2\text{O})_6$, which is linked to the cation, moves away from the cation principally in the direction of x (by 0.12 Å), but also considerably (0.08 Å) in direction of the negative z axis. This latter movement is evidently due to the strong hydrogen bond (2.62 Å) between $(\text{H}_2\text{O})_6$ and O_9 . Consequently, the distance O_3 — O_6 is much longer (by 0.25 Å) in the strontium compound (see Fig. 4), as mentioned above. It is notable that the hydrogen bonds are changed only to a small extent by the expansion of the structure, the largest difference being 0.09 Å. The mean length of the hydrogen bonds in the calcium compound is 2.78 Å, in the strontium compound 2.79 Å.

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