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The Crystal Structure of Rinkite

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Rinkite, $(Ti,Nb,Al,Zr)(Na,Ca)_3(Ca,Ce)_4(Si_2O_7)_2(O,F)_4$ approximately, is a silicate crystallizing in the monoclinic system, space group $P2_1/c$ with $a=7{\cdot}437$, $b=5{\cdot}664$, $c=18{\cdot}843$ Å, $\beta=101°23'$ and $Z=2$. The structure was refined with anisotropic thermal parameters by the least-squares method to a final R value of 5·5% for observed reflexions. The choice of the centrosymmetric space group was made at the end of the isotropic refinement in both space groups $P2_1$ and $P2_1/c$. The structure is based on sheets of octahedra parallel to the (001) plane with the Si_2O_7 groups and some metal ions between them. There are two symmetrically dependent octahedral sheets in the unit cell, containing gaps which are only statistically occupied. There are also two independent cations in sevenfold coordination. All interatomic distances and bond angles are within the limits given in the literature.

Introduction

The crystallography of the silicate rinkite has been studied by many authors, and different symmetries (from triclinic to orthorhombic) have been ascribed. Gottardi (1966) has suggested how the monoclinic pseudo-orthorhombic character of the mineral could produce such disparate results: he proposed two types of monoclinic cell (space group $P2_1/m$ *or* $P2_1$), both with

$$a=18{\cdot}83,\ b=5{\cdot}66,\ c=7{\cdot}44\ \text{Å and } \beta=101°22'\,.$$

The two may be distinguished by diffraction from the (005) and ($\bar{5}$05) planes: in the first monoclinic setting the diffraction from the (005) plane is the stronger; in the second setting the indexing of the two diffractions is reversed and the ($\bar{5}$05) diffraction becomes the stronger.

There have been several determinations of the crystal structure of rinkite: the first by Kheirov, Mamedov & Belov (1963) is based on the triclinic cell of Sahama & Hytönen (1957) in space group $P\bar{1}$; the second by Li Tê-Yü, Simonov & Belov (1965) is topologically equivalent to the first but is based on a monoclinic (pseudo-orthorhombic) cell in space group $P2_1$ with $\beta\simeq 90°$; the third, by Simonov & Belov (1967) in space group $P2_1$ with $\beta=101°$, is topologically equivalent to the other two structures.

Experimental

The rinkite studied was from Kangerdluarsuk, Greenland (specimen N·94: 0075 of Naturhistoriska Riksmuseets, Stockholm). The chemical formula assumed in this investigation was that of Semenov (Li Tê-Yü, Simonov & Belov, 1965):

$$Ca_{3{\cdot}35}Na_{2{\cdot}11}K_{0{\cdot}06}Ce_{1{\cdot}05}Th_{0{\cdot}04}Nb_{0{\cdot}33}Zr_{0{\cdot}07}Ti_{0{\cdot}52}\ Fe_{0{\cdot}09}Mg_{0{\cdot}08}Al_{0{\cdot}09}[Si_2O_7]_2OF_3\,.$$

This analysis was preferred to that of Christensen (Bøggild, 1953) because it is the more recent. In fact the two analyses are nearly the same. The only important difference is that Semenov's analysis gives Nb(0·33) and Zr(0·07) instead of only Zr(0·42) found by Christensen.

This difference is chemically but not structurally important because Zr and Nb have atomic numbers 40 and 41 respectively.

The crystal data determined by Gottardi (1966) have been confirmed from back-reflexions Weissenberg photographs to be:

$$\begin{aligned} a &= 7{\cdot}437 \pm 0{\cdot}002\ \text{Å}\\ b &= 5{\cdot}664 \pm 0{\cdot}002\\ c &= 18{\cdot}843 \pm 0{\cdot}003\\ \beta &= 101°23' \pm 1'\\ U &= 778{\cdot}11\ \text{Å}^3\\ Z &= 2 \end{aligned}$$

Space group $P2_1/c$

The density, measured with a torsion microbalance was

$$D_{\text{exp}}=3{\cdot}44\pm 0{\cdot}02\ \text{g.cm}^{-3}$$

which compares favourably with the calculated value,

$$D_{\text{calc}}=3{\cdot}45\ \text{g.cm}^{-3}\,.$$

Here the values of a and c are interchanged with respect to those given by Li Tê-Yü *et al.* (1965), Gottardi (1966) and Simonov & Belov (1967). An attempt to obtain the first monoclinic setting of Gottardi (1966) involved a comparison of the intensities of the 500 and 50$\bar{5}$ reflexions but the latter was missing, as were all $h0l$ reflexions with h odd: this systematic absence implies the presence of a glide plane, the true space group being $P2_1/c$ and not $P2_1/m$. This error by Gottardi (1966) and Simonov & Belov (1967) could be explained by their measurements having been made on a twin.

The crystal was ground by hand to a sphere of 0·042 cm diameter before mounting. It was rotated about its b axis, and the intensity data were collected for reciprocal lattice levels from $k=0$ to $k=4$, using Ni-filtered

Cu $K\alpha$ radiation and a Stoë-Güttinger automatic Weissenberg goniometer. In all 1306 independent reflexions were collected, which constitute approximately 80% of the total number of reflexions in the Cu $K\alpha$ limiting sphere.

Only those reflexions which simultaneously satisfied the following two conditions were assumed to have been observed:

(*a*) The area of the peak (corrected for background) was larger than 1/10 of the background area.

(*b*) The area of the peak (corrected for background) was larger than the area of the background oscillations.

The validity of these conditions was confirmed by the variation in the values of some groups of reflexions measured twice.

In all, 239 reflexions (about 18% of the total) were considered to be unobserved.

Corrections were made for Lorentz and polarization factors and for absorption ($\mu R=8{\cdot}97$ cm^{-1} for Cu $K\alpha$ radiation) using IBM 1620 computer programs.

Refinement

An earlier examination of single-crystal Weissenberg photographs of rinkite clearly showed the space group to be $P2_1/c$ owing to the absence of systematic extinctions of the type $h0l$ with $l=2n+1$ and $0k0$ with $k=2n+1$. However, we also refined the structure in the non-centrosymmetric space group $P2_1$, as used by Simonov & Belov (1967), in order to compare the results in these two space groups.

Before refinement the $23\bar{1}$ and $44\bar{l}$ reflexions were ignored because the background was anomalously high.

The atomic scattering curves used in the calculations of structure factors were taken from Hanson, Herman, Lee & Skillman (1964).

The atomic positions determined by Simonov & Belov (1967) provided the initial coordinates, which were refined by the full-matrix least-squares program of Busing, Martin & Levy (1962) with individual temperature factors and unit weights.

After four least-squares refinement cycles the reliability index R defined as $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, was 9·5% for space group $P2_1/c$ and 8·0% for $P2_1$. In the next three least-squares cycles Hughes's (1941) weighting scheme was used:

$$w=\frac{1}{80}\text{ if }|F_o|\le 80$$

$$w=\frac{80}{F_o^{\,2}}\text{ if }|F_o|>80;$$

with this scheme the average $w(F_o-F_o)^2$ was approximately constant over the whole range of F_o values. At this point the R index reached the value of 9% for the centrosymmetric space group and of 7·1% for the non-centrosymmetric space group while the weighted R_w values, defined as $[\Sigma w||F_o|-|F_c||^2/\Sigma w|F_o|^2]^{1/2}$, were respectively 10·7% for space group $P2_1/c$ and 8·9% for $P2_1$.

At the end of the isotropic refinement the interatomic distances were computed by the *ORFFE* program of Busing, Martin & Levy (1964) for both space groups. In Table 1 the Si–O distances within the Si_2O_7 groups are listed. Comparison of the distances obtained for the two space groups was not decisive in choosing the correct space groups, but it did not invalidate the choice of $P2_1/c$ principally because of the higher standard, errors in the distances obtained for $P2_1$. Moreover, during this stage of the refinement it was seen that, notwithstanding the slight convergence in the non-centrosymmetric space group, almost all the atoms, and particularly the heaviest, tend to group in centrosymmetric pairs. At this point the crystallographic R_w factors were tested after Hamilton (1965), searching for an indication of the correct space group. The result of the test was that the centrosymmetric space group should be rejected at the 0·5% significance level.

Table 1. *Interatomic distances* (Å) *within* Si_2O_7 *groups at the end of the isotropic refinement*

Space group $P2_1$		Space group $P2_1/c$	
Si_2O_7 group 1			
Tetrahedron 1*A*		Both tetrahedra	
Si(1)–O(1)	1·61 ± 0·03	Si(1)–O(1)	1·63 ± 0·01
Si(1)–O(3)	1·66 ± 0·03	Si(1)–O(3)	1·63 ± 0·01
Si(1)–O(5)	1·64 ± 0·04	Si(1)–O(5)	1·61 ± 0·01
Si(1)–O(7)	1·63 ± 0·03	Si(1)–O(7)	1·65 ± 0·01
Average	1·635	Average	1·63
Tetrahedron 1*B*			
Si(1)–O(1)	1·65 ± 0·03		
Si(1)–O(3)	1·61 ± 0·03		
Si(1)–O(5)	1·59 ± 0·04		
Si(1)–O(7)	1·68 ± 0·03		
Average	1·63		
Si_2O_7 group 2			
Tetrahedron 2*A*		Both tetrahedra	
Si(2)–O(2)	1·62 ± 0·03	Si(2)–O(2)	1·61 ± 0·01
Si(2)–O(4)	1·63 ± 0·04	Si(2)–O(4)	1·60 ± 0·01
Si(2)–O(6)	1·61 ± 0·03	Si(2)–O(6)	1·61 ± 0·01
Si(2)–O(7)	1·65 ± 0·03	Si(2)–O(7)	1·64 ± 0·01
Average	1·63	Average	1·615
Tetrahedron 2*B*			
Si(2)–O(2)	1·60 ± 0·03		
Si(2)–O(4)	1·61 ± 0·04		
Si(2)–O(6)	1·62 ± 0·04		
Si(2)–O(7)	1·65 ± 0·03		
Average	1·62		

However, we believe that for the crystal structure of rinkite the Hamilton test is not reliable enough to be accepted. In fact the full-matrix refinement shows, in the $P2_1$ space group, a slight convergence and very high standard deviations in the atomic parameters (about three times higher than in $P2_1/c$). Furthermore,

Table 2. *Observed and calculated structure factors*

A minus sign for Fo means 'less than'. An asterisk indicates reflexions omitted from the least-squares refinement.

H	L	FO	FC
K = 0			
1	0	-51	132
2	0	305	383
3	0	-52	72
4	0	537	-538
5	0	559	588
6	0	305	-351
7	0	202	-242
8	0	401	394
9	0	441	437
0	2	467	-588
1	2	615	654
2	2	-53	-131
3	2	151	-112
4	2	351	342
5	2	751	753
6	2	835	831
7	2	239	226
8	2	965	925
1	-2	-52	313
2	-2	391	427
3	-2	-52	14
4	-2	3094	4112
5	-2	-52	47
6	-2	729	695
7	-2	346	335
8	-2	401	-381
9	-2	233	218
0	4	-54	157
1	4	741	741
2	4	1176	1148
3	4	514	456
4	4	1897	1861
5	4	279	-269
6	4	571	-555
7	4	621	611
8	4	628	-597
1	-4	769	796
2	-4	-53	-58
3	-4	-52	46
4	-4	620	-635
5	-4	162	168
6	-4	692	663
7	-4	370	35
8	-4	1497	1451
9	-4	-22	-28
0	6	2426	2548
1	6	-52	-66
2	6	1129	-1176
3	6	711	755
4	6	951	-1116
5	6	391	-391
6	6	81	-75
7	6	-35	22
8	6	1119	1197
1	-6	451	391
2	-6	1179	1137
3	-6	283	289
4	-6	349	329
5	-6	935	958
6	-6	371	-375
7	-6	-43	-27
8	-6	398	-305
9	-6	-22	21
0	8	1013	-1089
1	8	125	-74
2	8	239	214
3	8	167	174
4	8	1376	1411
5	8	535	507
6	8	667	652
7	8	69	-64
1	-8	368	-317
2	-8	1082	-1124
3	-8	631	628
4	-8	1931	1917
5	-8	197	184
6	-8	795	753
7	-8	91	63
8	-8	451	439
9	-8	559	532
0	10	1484	1442
1	10	346	372
2	10	1238	1376
3	10	71	19
4	10	-48	-26
5	10	194	187
6	10	549	-556
7	10	379	301
1	-10	94	95
2	-10	219	192
3	-10	615	631
4	-10	897	-937
5	-10	652	-634
6	-10	631	-627
7	-10	437	427
8	-10	971	945
0	12	-52	-148
1	12	206	229
2	12	798	-827
3	12	371	386
4	12	145	136
5	12	141	-147
6	12	658	642
1	-12	260	253
2	-12	1271	1279
3	-12	-51	-58
4	-12	1327	1348
5	-12	316	297
6	-12	-44	-38
7	-12	411	412
8	-12	553	-525
0	14	475	499
1	14	94	96
2	14	477	458
3	14	188	185
4	14	1557	1611
5	14	207	275
6	14	275	277
1	-14	165	172
2	-14	943	-957
3	-14	115	173
4	-14	-49	-25
5	-14	421	447
6	-14	721	699
7	-14	226	-216
8	-14	1167	1116
0	16	2141	2157
1	16	-46	65
2	16	[illegible]	386
3	16	331	-321
4	16	583	-503
5	16	431	431
1	-16	274	275
2	-16	479	460
3	-16	393	387
4	-16	229	210
5	-16	-42	-81
6	-16	567	-529
7	-16	162	143
0	18	752	-729
1	18	273	276
2	18	107	-88
3	18	-39	27
4	18	571	553
1	-18	91	95
2	-18	477	401
3	-18	205	-255
4	-18	1496	1513
5	-18	119	121
6	-18	647	629
7	-18	544	524
0	20	735	712
1	20	131	139
2	20	339	330
3	20	337	350
1	-20	244	221
2	-20	111	-50
3	-20	-35	-65
4	-20	689	-650
5	-20	325	316
6	-20	284	328
0	22	717	697
1	22	81	-73
1	-22	75	90
2	-22	300	268
3	-22	283	278
4	-22	594	570
K = 1			
1	0	121	112
2	0	2200	2220
3	0	-55	-55
4	0	540	548
5	0	415	394
6	0	340	-322
7	0	-45	57
8	0	532	-532
1	1	482	387
2	1	1573	1560
3	1	154	133
4	1	593	580
5	1	638	629
6	1	491	473
7	1	-44	21
8	1	283	-257
1	-1	297	265
2	-1	748	-788
3	-1	-55	149
4	-1	-55	13
5	-1	204	218
6	-1	997	999
7	-1	123	112
8	-1	492	491
9	-1	355	370
0	2	452	246
1	2	319	242
2	2	196	122
3	2	319	334
4	2	813	-830
5	2	473	-402
6	2	276	-274
7	2	347	338
8	2	669	649
1	-2	439	-271
2	-2	2282	-2297
3	-2	-55	-28
4	-2	-55	29
5	-2	154	145
6	-2	993	1011
7	-2	219	-211
8	-2	575	547
9	-2	331	323
0	3	744	662
1	3	613	574
2	3	1159	988
3	3	129	139
4	3	570	-592
5	3	166	204
6	3	163	152
7	3	312	337
8	3	359	357
1	-3	591	539
2	-3	1099	1599
3	-3	215	214
4	-3	-55	1
5	-3	74	111
6	-3	115	-104
7	-3	274	204
8	-3	113	-113
9	-3	-22	51
0	4	1393	-1250
1	4	293	-234
2	4	257	-276
3	4	467	473
4	4	1415	1443
5	4	347	-305
6	4	838	835
7	4	-49	16
8	4	-28	-41
1	-4	-55	19
2	-4	163	-107
3	-4	-55	-53
4	-4	516	-535
5	-4	421	-380
6	-4	968	-998
7	-4	69	69
8	-4	-36	-34
9	-4	51	49
0	5	895	-923
1	5	220	274
2	5	462	396
3	5	446	453
4	5	741	745
5	5	257	-269
6	5	985	998
7	5	321	330
8	5	344	342
1	-5	379	413
2	-5	1036	1010
3	-5	119	79
4	-5	552	542
5	-5	491	476
6	-5	981	980
7	-5	252	246
8	-5	123	-85
9	-5	49	20
0	6	1964	2019
1	6	207	-227
2	6	1487	1548
3	6	-55	-18
4	6	361	-379
5	6	307	332
6	6	757	-769
7	6	276	-277
8	6	359	-342
1	-6	292	266
2	-6	286	331
3	-6	489	-519
4	-6	741	748
5	-6	163	149
6	-6	350	352
7	-6	228	222
8	-6	559	-554
9	-6	379	-304
0	7	923	969
1	7	-55	-87
2	7	1759	1795
3	7	378	383
4	7	477	-485
5	7	117	112
6	7	-40	1
7	7	-34	-77
1	-7	96	37
2	-7	454	378
3	-7	336	345
4	-7	535	-561
5	-7	376	381
6	-7	453	443
7	-7	67	-47
8	-7	487	496
9	-7	281	293
0	8	680	-685
1	8	149	150
2	8	396	-944
3	8	259	-232
4	8	787	-818
5	8	244	244
6	8	320	324
7	8	156	152
1	-8	-55	117
2	-8	1488	-1508
3	-8	223	-218
4	-8	1445	-1456
5	-8	404	419
6	-8	283	281
7	-8	339	-352
8	-8	504	511
9	-8	-21	42
0	9	471	479
1	9	-55	64
2	9	442	398
3	9	-54	5
4	9	466	-498
5	9	318	333
6	9	512	513
7	9	192	189
1	-9	-55	-44
2	-9	1743	1743
3	-9	502	493
4	-9	806	810
5	-9	120	-108
6	-9	124	118
7	-9	221	207
8	-9	250	-232
0	10	1014	-1070
1	10	258	250
2	10	109	113
3	10	139	101
4	10	875	910
5	10	168	-170
6	10	-35	37
7	10	136	138
1	-10	273	-279
2	-10	906	945
3	-10	290	291
4	-10	425	436
5	-10	-52	3
6	-10	817	-841
7	-10	167	-180
8	-10	661	-635
0	11	768	-836
1	11	318	342
2	11	950	963
3	11	264	270
4	11	591	565
5	11	-43	25
6	11	436	426
1	-11	133	172
2	-11	441	399
3	-11	-55	79
4	-11	478	462
5	-11	-52	-103
6	-11	942	948
7	-11	432	424
8	-11	407	403
0	12	1332	1383
1	12	119	-100
2	12	480	-470
3	12	-51	5
4	12	635	-635
5	12	-39	13
6	12	422	-410
1	-12	183	-160
2	-12	106	-96
3	-12	-54	-1
4	-12	809	816
5	-12	454	-442
6	-12	698	698
7	-12	340	337
8	-12	115	120
0	13	700	700
1	13	139	128
2	13	387	362
3	13	283	285
4	13	-38	33
5	13	-36	46
6	13	100	-85
1	-13	299	295
2	-13	944	935
3	-13	173	197
4	-13	489	-523
5	-13	351	342
6	-13	67	47
7	-13	-36	-23
8	-13	316	310
0	14	604	-627
1	14	-52	-52
2	14	545	-558
3	14	228	-251
4	14	175	173
5	14	330	341
6	14	613	617
1	-14	-53	94
2	-14	469	455
3	-14	-52	-20
4	-14	907	-917
5	-14	-48	-4
6	-14	322	-313
7	-14	72	-63
8	-14	397	373
0	15	199	195
1	15	-51	64
2	15	230	-252
3	15	-44	-30
4	15	-37	1
5	15	304	327
1	-15	174	173
2	-15	360	338
3	-15	227	251
4	-15	597	581
5	-15	226	232
6	-15	531	529
7	-15	100	91
0	16	96	75
1	16	170	172
2	16	993	1012
3	16	-40	-54
4	16	281	267
5	16	91	-13
1	-16	-51	-44
2	-16	485	484
3	-16	147	161
4	-16	649	641
5	-16	227	229
6	-16	-37	3
7	-16	183	-173
1	17	-45	-32
1	17	223	232
2	17	967	941
3	17	-35	-44
4	17	297	298
1	-17	189	165
2	-17	178	-206
3	-17	-47	48
4	-17	-44	29
5	-17	-39	-14
6	-17	401	387
7	-17	274	287
0	18	284	276
1	18	-43	-47
2	18	498	-495
3	18	257	286
4	18	275	-251
1	-18	-46	-0
2	-18	1024	-1019
3	-18	99	98
4	-18	103	-109
5	-18	331	-308
6	-18	379	355
7	-18	94	104
0	19	391	302
1	19	-37	87
2	19	59	-16
3	19	130	131
1	-19	162	156
2	-19	1001	979
3	-19	-49	5
4	-19	67	-63
5	-19	236	233
6	-19	70	-42
0	20	240	-239
1	20	-32	-33
2	20	80	68
1	-20	-37	34
2	-20	551	543
3	-20	110	-111
4	-20	301	-289
5	-20	-27	-54
6	-20	606	-605
0	21	-31	9
1	21	-27	26
2	21	63	46
1	-21	88	84
2	-21	-32	-26
3	-21	-31	-4
4	-21	258	262
5	-21	232	245
0	22	484	471
1	-22	-27	-43
2	-22	-27	-42
3	-22	280	-255
4	-22	189	190
1	-23	61	55
2	-23	-21	22
K = 2			
1	0	100	218
2	0	206	-289
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1	-17	103	-77
2	-17	76	-71
3	-17	240	-235
*4	-17	352	350
5	-17	-15	46
0	18	704	742
1	18	36	43
1	-18	118	106
2	-18	-20	-26
3	-18	276	262
*4	-18	223	-197
0	19	353	-367
1	-19	42	-8
2	-19	216	-209
3	-19	-15	-24

an inspection of the correlation matrix showed that all correlation terms between corresponding parameters of pairs of atoms, taken to be independent in $P2_1$ but symmetry-related in $P2_1/c$, are very large (always larger than |0·5|, sometimes larger that |0·9|). This large correlation in the non-centrosymmetric space group between all the pairs of atoms occurs because of the presence of 'inverse overlap'. Parthasarathy, Sime & Speakman (1969) showed that under these conditions the reliability of the Hamilton test is severely compromised. We confirmed this by means of the following test: first a hypothetical structure was built consisting of two mod-

Table 3. *Atomic coordinates with their standard errors*

	x/a	y/b	z/c
M(1)	0·0000	0·0000	0·0000
M(2)	0·5000	0·0000	0·0000
M(3)	0·7500 ± 0·0005	0·5012 ± 0·0009	0·0004 ± 0·0002
M(4)	0·0938 ± 0·0002	0·6605 ± 0·0003	0·1918 ± 0·0001
M(5)	0·5969 ± 0·0002	0·6630 ± 0·0003	0·1902 ± 0·0001
Si(1)	0·3515 ± 0·0004	0·1541 ± 0·0007	0·1403 ± 0·0002
Si(2)	0·7831 ± 0·0004	0·1530 ± 0·0007	0·1379 ± 0·0001
O(1)	0·2172 ± 0·0011	0·1488 ± 0·0017	0·0609 ± 0·0004
O(2)	0·8306 ± 0·0011	0·1410 ± 0·0019	0·0578 ± 0·0004
O(3)	0·3379 ± 0·0011	0·3971 ± 0·0017	0·1849 ± 0·0005
O(4)	0·8436 ± 0·0012	0·3949 ± 0·0018	0·1797 ± 0·0005
O(5)	0·3355 ± 0·0011	0·9311 ± 0·0018	0·1918 ± 0·0004
O(6)	0·8559 ± 0·0011	0·9365 ± 0·0017	0·1903 ± 0·0004
O(7)	0·5581 ± 0·0011	0·1413 ± 0·0020	0·1206 ± 0·0005
OF(1)	0·0308 ± 0·0010	0·7052 ± 0·0017	0·0617 ± 0·0004
OF(2)	0·5303 ± 0·0011	0·6546 ± 0·0016	0·0642 ± 0·0004

where M(1) is Ti(51·5%), Nb(32·7%), Al(8·9%), Zr(6·9%)
M(2) is Na(66·0%), Ca(19·0%), K(2·0%), and vacancies (13%)
M(3) is Na(75·9%), Ca(21·9%), K(2·2%)
M(4) and M(5) are Ca(68·5%), Ce(26·2%), Fe(2·3%), Mg(2·0%), Th(1·0%)
OF(1) and OF(2) are F(75·0%), O(25·0%)

Table 4. *Anisotropic thermal parameters* ($\times 10^4$) *with their standard deviations*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M(1)	27 ± 3	286 ± 36	13 ± 1	−23 ± 4	6 ± 1	−40 ± 2
M(2)	99 ± 11	162 ± 45	4 ± 2	2 ± 13	1 ± 3	−6 ± 5
M(3)	86 ± 7	97 ± 40	21 ± 1	6 ± 8	10 ± 2	16 ± 3
M(4)	38 ± 2	113 ± 34	10 ± 1	0 ± 2	3 ± 1	4 ± 1
M(5)	54 ± 2	190 ± 34	11 ± 1	3 ± 3	5 ± 1	3 ± 1
Si(1)	39 ± 5	132 ± 38	6 ± 1	−3 ± 6	1 ± 1	−1 ± 2
Si(2)	41 ± 5	109 ± 37	6 ± 1	−7 ± 6	3 ± 1	1 ± 2
O(1)	93 ± 14	122 ± 51	11 ± 2	−19 ± 17	−8 ± 4	1 ± 7
O(2)	88 ± 14	289 ± 55	8 ± 2	15 ± 19	7 ± 4	9 ± 7
O(3)	86	16	21	5	15	−15
O(4)	89 ± 15	125 ± 54	22 ± 3	−16 ± 18	13 ± 5	−22 ± 8
O(5)	87 ± 14	139 ± 59	11 ± 2	14 ± 17	7 ± 4	3 ± 7
O(6)	87 ± 15	116 ± 51	12 ± 2	6 ± 17	3 ± 5	5 ± 7
O(7)	70 ± 14	324 ± 57	15 ± 3	2 ± 2	7 ± 5	−14 ± 8
OF(1)	115 ± 14	296 ± 53	14 ± 2	−41 ± 18	6 ± 4	0 ± 7
OF(2)	156 ± 16	155 ± 51	14 ± 2	17 ± 19	8 ± 5	3 ± 7

erately anisotropic atoms and structure factors were calculated assuming the space group $P2_1/c$. Isotropic refinement of this hypothetical structure was then carried out, taking as observed structure factors the calculated structure factors from the anisotropic structure, in the two space groups $P2_1$ and $P2_1/c$.

The transition from the space group $P2_1/c$ to $P2_1$ was effected by splitting up the atoms which are single in the centrosymmetric space group into those that are double in the non-centrosymmetric space group. The results, as expected, showed:

(*a*) very large correlation terms (about $|0{\cdot}95|$) between corresponding parameters of the two pairs of symmetry-related atoms;

(*b*) higher standard deviations for the atomic parameters in the space group $P2_1$ than for the corresponding parameters in $P2_1/c$ (about 5 times higher);

(*c*) very poor convergence in the full-matrix refinement of the $P2_1$ space group.

In addition, at the end of the refinement the atomic coordinates in the $P2_1$ space group were far removed from the corrected coordinates (up to 0·025 Å).

According to Hamilton's tables the hypothesis that the trial structure is centrosymmetric should be rejected at the 10% significance level. Obviously this result cannot be accepted because the correct starting structure is centrosymmetric. Therefore, for the reasons given above, we feel justified in deciding to ignore the result of the Hamilton test.

At this point, because there was no valid argument favouring the $P2_1$ rather than the $P2_1/c$ space group, we considered that the correct space group was that of higher symmetry. Anisotropic refinement was therefore carried out only in the space group $P2_1/c$. Anisotropic temperature factors were introduced in the form

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

Three further least-squares cycles reduced the reliability index for observed reflexions to $R=5{\cdot}5\%$ and $R_w=7{\cdot}4\%$. The reliability index for observed and non-observed reflexions, which were given half of the minimum observable value, was $R=7{\cdot}5\%$.

The observed and calculated structure factors are listed in Table 2. Tables 3 and 4 respectively give the final positional and thermal parameters with their standard deviations. The final distribution of atoms

Table 5. *Interatomic distances* (Å) *with their standard errors*

The superscripts refer to the symmetry code

	x	y	z
i	$x-1$	y	z
ii	x	$y-1$	z
iii	$1-x$	$y-\frac{1}{2}$	$\frac{1}{2}-z$
iv	$1-x$	$y+\frac{1}{2}$	$\frac{1}{2}-z$
v	$1-x$	$1-y$	$-z$
vi	$-x$	$1-y$	$-z$
vii	$1-x$	$-y$	$-z$
viii	$-x$	$-y$	$-z$
ix	$x+1$	y	z
x	x	y	$z-1$

Interatomic distances which are symmetrically dependent are bracketed

Si(1) - tetrahedron

Si(1)—O(1)	1·63 ± 0·01
Si(1)—O(3)	1·63 ± 0·01
Si(1)—O(5^{ii})	1·61 ± 0·01
Si(1)—O(7)	1·65 ± 0·01
Average	1·63

O(1)—O(3)	2·72 ± 0·01
O(1)—O(5^{ii})	2·74 ± 0·01
O(1)—O(7)	2·56 ± 0·01
O(3)—O(5^{ii})	2·64 ± 0·01
O(3)—O(7)	2·65 ± 0·01
O(5^{ii})-O(7)	2·62 ± 0·01

Si(2) - tetrahedron

Si(2)—O(2)	1·62 ± 0·01
Si(2)—O(4)	1·60 ± 0·01
Si(2)—O(6^{ii})	1·60 ± 0·01
Si(2)—O(7)	1·64 ± 0·01
Average	1·615

O(2)—O(4)	2·70 ± 0·01
O(2)—O(6^{ii})	2·73 ± 0·01
O(2)—O(7)	2·54 ± 0·01
O(4)—O(6^{ii})	2·60 ± 0·01
O(4)—O(7)	2·62 ± 0·01
O(6^{ii})-O(7)	2·61 ± 0·01

M(2) - polyhedron

M(2) -O(1)	2·72 ± 0·01
M(2) -O(1^{vii})	
M(2) -O(2)	2·61 ± 0·01
M(2) -O(2^{vii})	
M(2) -O(7)	2·37 ± 0·01
M(2) -O(7^{vii})	
M(2) -OF(2^{ii})	2·29 ± 0·01
M(2) -OF(2^{v})	
Average	2·50

M(4) - polyhedron

M(4) -O(3)	2·37 ± 0·01
M(4) -O(4^{i})	2·37 ± 0·01
M(4) -O(4^{iv})	2·72 ± 0·01
M(4) -O(5)	2·36 ± 0·01
M(4) -O(6^{i})	2·36 ± 0·01
M(4) -O(6^{iii})	2·52 ± 0·01
M(4) -OF(1)	2·42 ± 0·01
Average	2·45

M(1) - octahedron

M(1)—O(1)	1·98 ± 0·01
M(1)—O(1^{viii})	
M(1)—O(2^{i})	1·99 ± 0·01
M(1)—O(2^{vii})	
M(1)—OF(1^{ii})	2·02 ± 0·01
M(1)—OF(1^{vi})	
Average	2·00

O(1)—O(2^{i})	2·86 ± 0·01
O(1^{viii})-O(2^{vii})	
O(1)—OF(1^{ii})	2·87 ± 0·01
O(1^{viii})-OF(1^{vi})	
O(1)—O(2^{vii})	2·74 ± 0·01
O(1^{viii})-O(2^{i})	
O(1)—OF(1^{vi})	2·78 ± 0·01
O(1^{viii})-OF(1^{ii})	
OF(1^{ii})-O(2^{i})	2·88 ± 0·01
OF(1^{vi})-O(2^{vii})	
OF(1^{ii})-O(2^{vii})	2·79 ± 0·01
OF(1^{vi})-O(2^{i})	

M(3) - octahedron

M(3)—O(1^{v})	2·33 ± 0·01
M(3)—OF(2^{v})	2·37 ± 0·01
M(3)—OF(2)	2·38 ± 0·01
M(3)—O(2)	2·33 ± 0·01
M(3)—OF(1^{v})	2·48 ± 0·01
M(3)—OF(1^{ix})	2·47 ± 0·01
Average	2·39

OF(2)—OF(2^{v})	2·95 ± 0·02
O(2)—OF(2^{v})	3·38 ± 0·01
O(1^{v})—OF(1^{v})	3·44 ± 0·01
O(1^{v})—OF(2^{v})	3·69 ± 0·01
O(2)—OF(1^{v})	3·47 ± 0·01
O(1^{v})—OF(1^{ix})	2·78 ± 0·01
OF(2)—O(1^{v})	2·79 ± 0·01
O(2)—OF(2)	3·69 ± 0·01
OF(2)—OF(1^{ix})	3·79 ± 0·01
O(2)—OF(1^{ix})	3·52 ± 0·01
OF(1^{v})-OF(1^{ix})	3·26 ± 0·02
OF(1^{v})-OF(2^{v})	3·72 ± 0·01

M(1)—M(2)	3·72
M(1)—M(3^{v})	3·38 ± 0·01
M(2)—M(3)	3·38 ± 0·01
M(3)—M(3^{v})	3·72 ± 0·01

Table 5 (*cont.*)

M(5) – polyhedron	
M(5) –O(3)	2·43 ± 0·01
M(5) –O(3^{iv})	2·66 ± 0·01
M(5) –O(4)	2·42 ± 0·01
M(5) –O(5)	2·47 ± 0·01
M(5) –O(5^{iii})	2·54 ± 0·01
M(5) –O(6)	2·47 ± 0·01
M(5) –OF(2)	2·33 ± 0·01
Average	2·47

among the sites of Table 3 was chosen, after many trials, so as to give a low value of *R*. During the refinement the occupancy factors of the cations M and anions OF were treated as variables. At the end all occupancy factors reached values near to 1. Only the M(2) cation exhibited an occupancy factor of 87%.

The β_{22} coefficient of the O(3) atom, which persisted in being negative during the two first cycles, was forced to become slightly positive each time, but even in the last cycle it did not reach a positive value, and was held at a near zero value.

Description of the structure

Fig. 1 gives a general view of the structure in (010) projection and Fig. 2 shows the structure in greater detail. It is based on octahedral sheets parallel to (001), between which are Si_2O_7 groups and additional metal cations. Of the five types of cation site listed in Table 3 M(1), M(2) and M(3) occur in the octahedral sheets, while M(4) and M(5) occur between them.

Fig. 3 shows an octahedral sheet in (001) projection. The anions are O and (F,O). In the latter case they were assumed to be F(75%) and O(25%) statistically distributed. The smaller octahedra contain the M(1) cations; they are regular, with cation–anion distances of 1·98–2·02 Å and edge lengths of 2·74–2·88 Å (Table 5). They were assumed to contain Ti(51·5%), Nb(32·7%), Al(8·9%) and Zr(6·9%). The larger octahedra contain the M(3) cations. They are less regular, with cation–anion distances of 2·33–2·48 Å and edge lengths of 2·78–3·79 Å, and were assumed to contain Na(75·9%), Ca(21·9%), and K(2·2%). The M(2) cations, which are 8-coordinated, occur in the gaps in the octahedral sheets. By least-squares refinement only 87% of these sites were found to be occupied, and the occupancy was assumed to be Na(66·0%), Ca(19·0%), K(2·0%) and vacancies (13%), the Na:Ca:K ratios thus being the same as for M(3). This is in sufficient agreement both with the chemical formula (occupancy 78%) and with the results of Simonov & Belov (1967), who found an occupancy of 75%. The cation–anion distances in this polyhedron range from 2·29 to 2·72 Å.

Each gap is closed on both sides by Si_2O_7 groups at different heights and related by a centre of symmetry (see Fig. 1). These tetrahedra are regular with interatomic distances varying from 1·61 to 1·65 Å with an average value of 1·63 Å in the Si(1) tetrahedron, and from 1·60 to 1·64 Å with an average value of 1·62 Å in the Si(2) tetrahedron.

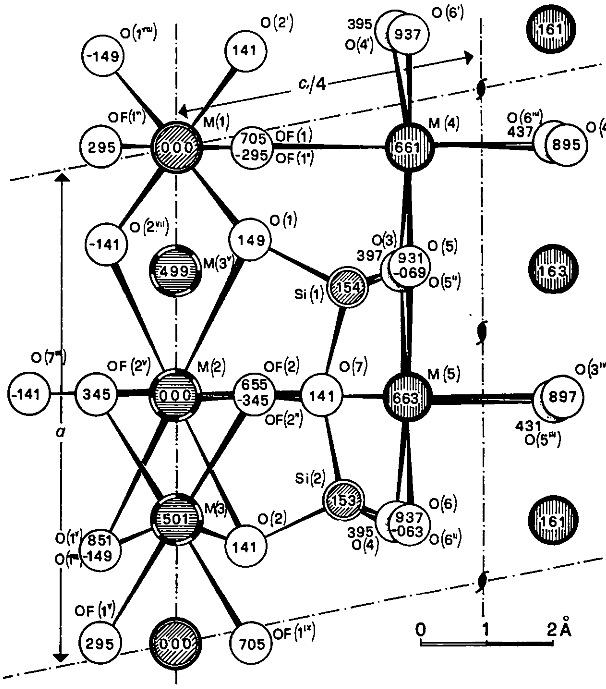

Fig. 2. A projection of the structure of rinkite on the (010) plane. Numbers inside the circles give the heights of the atoms in thousandths of the cell edge.

The O–Si–O bond angles are also regular with an average value of 109°, while the Si(1)–O(7)–Si(2) angle has a value of 155°5′ (Table 6).

Table 6. *Bond angles with their standard errors*

Superscripts refer to the symmetry code of Table 5.

Si(1)–tetrahedron	Bond angle
O(1)—Si(1)–O(3)	113·6 ± 0·5°
O(1)—Si(1)–O(5^{ii})	115·7 ± 0·5
O(1)—Si(1)–O(7)	102·8 ± 0·4
O(3)—Si(1)–O(5^{ii})	109·5 ± 0·5
O(3)—Si(1)–O(7)	108·0 ± 0·5
O(5^{ii})–Si(1)–O(7)	106·5 ± 0·5
Average	109·3

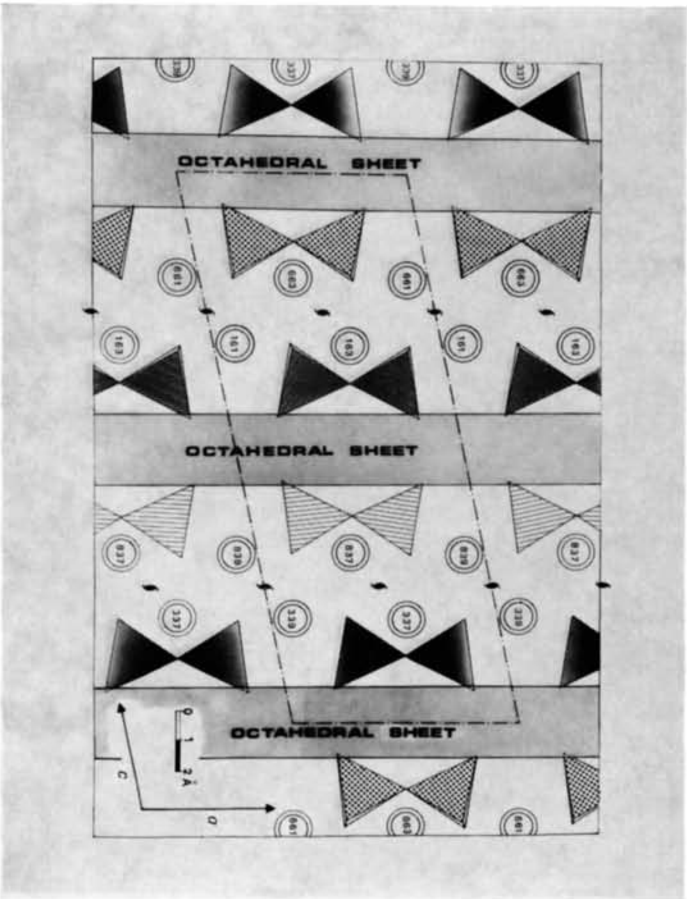

Fig. 1. The distribution of larger cations (mainly Ca and rare earth) and Si_2O_7 groups between the octahedral sheets viewed along the *b* axis. Numbers inside the circles give the heights for the M(4) and M(5) cations in thousandths of the cell edge. Also the Si_2O_7 groups may have four different *y*/*b* values as shown by the four different shadings.

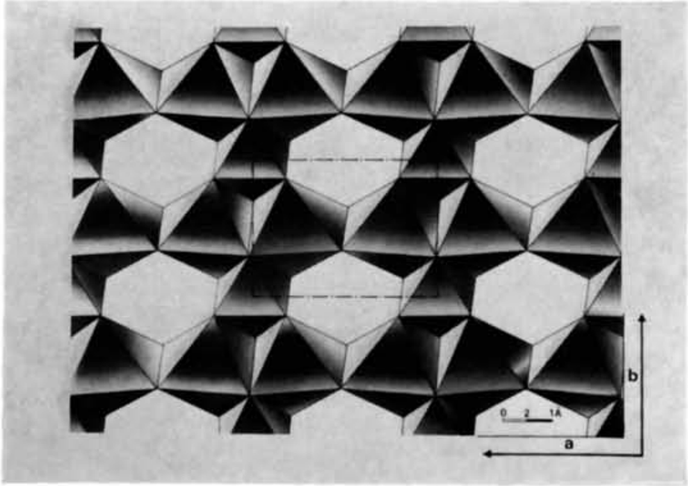

Fig. 3. Orthogonal view of the octahedral sheet parallel to the (001) plane. Smaller and regular octahedra are occupied by M(1) cations. Larger and irregular octahedra are occupied by M(3) cations. The gaps are statistically occupied by M(2) cations which reach coordination number eight.

Table 6 (*cont.*)

Si(2)–tetrahedron	
O(2)—Si(2)–O(4)	113·8 ± 0·5
O(2)—Si(2)–O(6^{ii})	115·7 ± 0·5
O(2)—Si(2)–O(7)	102·4 ± 0·4
O(4)—Si(2)–O(6^{ii})	109·0 ± 0·5
O(4)—Si(2)–O(7)	108·0 ± 0·5
O(6^{ii})–Si(2)–O(7)	107·4 ± 0·5
average	109·3
Si(1)—O(7)–Si(2)	155·5 ± 0·6

In the asymmetric unit there are two regular polyhedra labelled M(4) and M(5) with Ca (68·5%), Ce(26·2%), Fe(2·3%), Mg(2·0%), and Th(1·0%) in sevenfold coordination.

The coordination of seven anions around these cations is quite simple: M(4) is at the centre of a square [O(3), O(4′), O(5), O(6′)] which is almost parallel to the *ab* plane; two other oxygen atoms, O(4^{IV}) and O(6^{III}), lie close to the cation M(4) on one side, and the anion OF(1) on the other. The same situation prevails for M(5) which is placed in a square [O(3), O(4), O(5), O(6)] with two oxygen atoms O(3^{IV}) and O(5^{III}), on one side and the OF(2) anion on the other.

The 14 cation–anion distances average 2·45 ± 0·10 Å. Table 7 gives for each atom the root mean-square displacements along the principal axes of the thermal ellipsoid and the angles which they make with the axes of a cartesion system. The latter is defined as follows: axis 1 is in the direction of vector $\overleftarrow{M(1^{I})\,M(1)}$; axis 2 is in the direction of [axis 1] × [M(1) M(1^{X})]; axis 3 is in the direction of [axis1] × [axis 2].

Table 7. *Analysis of anisotropic thermal parameters*

θ_1, θ_2 and θ_3 are the angles of the principal axes of the thermal ellipsoids with respect to axes 1, 2 and 3 of the cartesian system defined in the text.

Atom	Principal axis	R.m.s. displacement	θ_1	θ_2	θ_3
	1	0·082	11°	84°	81°
M(1)	2	0·102	79	120	148
	3	0·242	90	150	60
	1	0·037	91	23	67
M(2)	2	0·098	95	67	157
	3	0·167	5	87	94
	1	0·112	92	160	70
M(3)	2	0·151	178	89	92
	3	0·197	91	70	20
	1	0·101	10	90	80
M(4)	2	0·124	82	54	142
	3	0·141	96	36	54
	1	0·120	3	91	88
M(5)	2	0·139	87	83	173
	3	0·176	89	7	83
	1	0·097	51	86	39
Si(1)	2	0·110	39	89	129
	3	0·147	93	4	92
	1	0·099	102	95	13
Si(2)	2	0·103	163	101	103
	3	0·134	102	12	88
	1	0·111	100	97	12
O(2)	2	0·153	168	83	100
	3	0·219	84	10	82
	1	0·115	57	74	37
O(1)	2	0·139	86	22	111
	3	0·189	147	76	61
	1	0·011	99	16	77
O(3)	2	0·147	167	101	83
	3	0·196	81	102	15
	1	0·120	87	26	64
O(4)	2	0·151	175	89	85
	3	0·212	86	116	26
	1	0·136	93	110	20
O(5)	2	0·143	44	132	101
	3	0·162	46	48	73
	1	0·130	76	141	55
O(6)	2	0·149	113	128	132
	3	0·160	152	87	62
	1	0·136	7	94	95
O(7)	2	0·153	96	104	165
	3	0·234	87	15	104
	1	0·157	78	85	13
OF(1)	2	0·167	26	68	103
	3	0·228	113	23	90
	1	0·152	85	131	41
OF(2)	2	0·161	81	137	131
	3	0·208	11	80	88

The M(1) and M(2) atoms exhibit very marked anisotropy, the maximum displacements being mutually perpendicular, but the vibrations of many of the atoms are not significantly anisotropic. There is no favoured direction for the major axes of the thermal ellipsoids.

At the end of the anisotropic refinement it was thought that the statistical occupancy of the site at $\frac{1}{2}$,0,0 might influence the positions of its neighbours. In particular it was thought that when the position at $\frac{1}{2}$,0,0 was unoccupied, the OF(2) ion might tend to occupy a site nearer to $\frac{1}{2}$,0,0. This hypothesis would have been confirmed by strong anisotropy in the motion of the ions along the OF(2)–M(2) direction, about the normal to **a**. This was not in fact verified by the results of the anisotropic refinement; the major axes of the thermal ellipsoids of these two atoms are almost parallel to one another and to the *a* axis.

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The Structure and Absolute Configuration of the Calcium Salt of Garcinia Acid, the Lactone of (–)-Hydroxycitric Acid

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The calcium salt of the lactone of (–)-hydroxycitric acid crystallizes in the orthorhombic system as a tetrahydrate. Unit-cell dimensions are $a=8{\cdot}680$, $b=17{\cdot}299$, $c=7{\cdot}135$ Å. The space group is $P2_12_12$ with four units of $Ca(C_6O_7H_4).4H_2O$ per cell. 1371 independent data, of which 97 were below the threshold of measurement, were collected on a manual diffractometer with Cu $K\alpha$ radiation (to $2\theta=160°$). The structure was solved by heavy-atom techniques and was refined by the full-matrix least-squares method to an R value of 0·050. All hydrogen atoms were found from a difference map and their parameters were refined. The absolute configuration of the free (–)-hydroxycitric acid, determined from anomalous dispersion measurements on the lactone salt, is (1*S*:2*S*)-1,2-hydroxy-1,2,3-propanetricarboxylic acid. The two carboxyl groups are *cis* with respect to the plane of the lactone ring and the two $-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{COO}^-$ groupings are each almost planar. The lactone forms a bidentate chelate with the calcium ion. The calcium ion is surrounded by eight oxygen atoms in a square antiprism arrangement, with Ca–O distances of 2·39–2·52 Å, and with one face of the coordination polyhedron shared with that of another calcium ion.

Crystals of the calcium salt of garcinia acid, the lactone of (–)-hydroxycitric acid, were provided by Dr Y. S. Lewis of the Central Food Technological Research Institute, Mysore, India; the acid had been isolated from the fruits of *Garcinia cambogia* Desr. (Lewis & Neelakantan, 1965). There are two asymmetric carbon atoms in hydroxycitric acid and hence four isomers exist. Therefore, an X-ray crystallographic study was undertaken to determine the absolute configuration of this isomer that is accumulated by plants. It is the enantiomorph of a hydroxycitrate which is a substrate of isocitric dehydrogenase in the Krebs cycle (Martius & Maué, 1941). It had also been found (Watson, Fang & Lowenstein, 1969) that garcinia acid inhibits citrate cleavage enzyme more powerfully than does (+)-*allo*-hydroxycitrate, another hydroxycitrate accumulated by plants. This crystallographic study was also made to determine the nature of the packing around the calcium ion and of the hydrogen bonding in the crystal.

Experimental

The crystals are orthorhombic with cell dimensions $a=8{\cdot}680\pm0{\cdot}004$, $b=17{\cdot}299\pm0{\cdot}015$, $c=7{\cdot}135\pm0{\cdot}005$ Å which were measured on the General Electric XRD-5 diffractometer with copper radiation [$\lambda(\mathrm{Cu}\,K\alpha_1)=1{\cdot}5405$ Å]. The space group is $P2_12_12$ (from the systematic absences $h00$, h odd and $0k0$, k odd) with $Z=4$. The observed density is 1·88 g.cm^{-3}, measured by flotation in a mixture of methylene iodide and carbon tetrachloride. The density calculated for four units of $Ca\,(C_6O_7H_4).4H_2O$ is 1·86 g.cm^{-3}. The crystals became slightly damp on standing in air for long periods of time (a year or more), presumably due to a tendency to deliquescence.

Data were collected on a crystal of size $0{\cdot}28\times0{\cdot}28\times0{\cdot}13$ mm. Intensities were measured on a General Electric XRD-5 diffractometer with the θ–2θ scan technique and with nickel-filtered copper radiation. 1371 independent reflections were scanned to $2\theta=160°$, and of these 97 were below the threshold of measurement (judged from the diffractometer trace). The data were corrected for the Lorentz and polarization factors.

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