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A Refinement of the Crystal Structure of $CaHPO_4$ (Synthetic Monetite)

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$CaHPO_4$, synthetic monetite, crystallizes in the triclinic unit cell $a=6{\cdot}910\,(1)$, $b=6{\cdot}627\,(2)$, $c=6{\cdot}998\,(2)$ Å, $\alpha=96{\cdot}34\,(2)°$, $\beta=103{\cdot}82\,(2)°$, $\gamma=88{\cdot}33\,(2)°$ at 25 °C with cell contents of 4[$CaHPO_4$]. The structure has been refined in space-group $P\bar{1}$ by the method of least-squares to $R_w=0{\cdot}032$, $R=0{\cdot}031$ using 3738 observed X-ray reflections measured on a diffractometer. Corrections were made for absorption, anomalous dispersion and isotropic secondary extinction.

The structure may be considered to consist of $CaHPO_4$ chains bonded together by Ca· · ·O bonds and three types of hydrogen bonds. One type of hydrogen bond, O(1)–H(1)· · ·O(5), is normal but is at the short end of the normal range with O(1)· · ·O(5) = 2·565 (1) Å; one, O(7)–H(2)· · ·O(7′), is very short with O(7)· · ·O(7′) = 2·458 (2) Å and is across a nominal center of symmetry; and one, O(6)–H(3)· · ·O(8) where O(6)· · ·O(8) = 2·669 (1) Å, is in the normal range but is presumed to be statistically disordered, with hydrogen covalently bonded to half of the O(6) atoms on average. The P–O distances support the choice of these hydrogen positions. Ca(1) is coordinated to seven oxygen atoms in an approximately pentagonal bipyramid with Ca(1)· · ·O distances ranging from 2·2951 (9) Å to 2·763 (1) Å. Ca(2) is coordinated to eight oxygen atoms with Ca(2)· · ·O distances ranging from 2·379 (1) Å to 2·5718 (9) Å, which all indicate strong Ca· · ·O bonding. The Ca coordinations in several calcium phosphates and related compounds are compared.

Introduction

The general features of the crystal structure of $CaHPO_4$ were determined by McLennan & Beevers (1955), who refined the structure to $R=0{\cdot}20$ using $hk0$, $h0l$ and $0kl$ photographic data. The standard deviations (> 0·05 Å) of the interatomic distances were too large to allow reasonable assumptions about the hydrogen bonding to be made.

The structure was refined to $R=0{\cdot}15$ by Jones & Cruickshank (1961) using 790 reflections collected and measured by MacLennan & Beevers but uncorrected for high absorption. Possible positions for the hydrogen atoms given by Jones & Cruickshank were based on the P–O and O· · ·O distances they obtained. Curry, Denne & Jones (1968) measured 381 neutron diffraction data of $CaHPO_4$ at room temperature and refined the occupational parameters of possible hydrogen sites while keeping the parameters of the heavier atoms fixed at the fairly imprecise and ambiguous values obtained earlier by Jones & Cruickshank (1961). They assigned hydrogens to the O(1) atoms and to half of the O(6) and O(7) atoms in the structure. This work has been continued by Denne & Jones (1969).

Egan & Wakefield (1964) observed an abnormal broad hump beginning at 223 °K with a maximum at 273 °K in the heat capacity versus temperature curve of $CaHPO_4$. This anomaly can be plausibly interpreted by rapid hydrogen motion, although the nuclear magnetic resonance line width and the second moment of $CaHPO_4$ did not change significantly on cooling from room temperature to liquid-nitrogen temperature (Jones & Cruickshank, 1961). Alternatively the anomaly could arise from an order–disorder process. After the X-ray refinement reported here, we intend to study $CaHPO_4$ at two or more temperatures by neutron diffraction.

Data collection and structure refinement

The crystal used in the collection of X-ray data was colorless and approximately rhombic in shape with an edge of about 0·15 mm and a volume of 0·004 mm³. It was taken from a sample of $CaHPO_4$ grown by cyclic dilution and concentration of the supernatant aqueous solution over a mixture of $CaHPO_4$ and $Ca_5(PO_4)_3OH$ in the lower chamber of a Soxhlet apparatus. It was attached to the goniometer head in our usual way Dickens & Bowen, 1971*a*).

Formula (ideal): $CaHPO_4$; cell at 25 °C: triclinic; $a=6{\cdot}910(1)$, $b=6{\cdot}627(2)$, $c=6{\cdot}998(2)$ Å; $\alpha=96{\cdot}34(2)°$, $\beta=103{\cdot}82\,(2)$, $\gamma=88{\cdot}33\,(2)$; volume = 390·27 Å³; space group $P\bar{1}$ assumed; cell contents 4[$CaHPO_4$]; calculated density 2·933 g.cm^{-3}; observed density 2·929 g·cm^{-3} (de Schulten, 1901).

The X-ray data were measured using the general procedure given by Dickens & Bowen (1971*b*). θ–2θ scans were done at 1° min^{-1} for 2θ, and the backgrounds were counted for 10 sec each. 8849 reflections were collected from two hemispheres of the reciprocal lattice; hkl and $\bar{h}\bar{k}\bar{l}$ pairs were merged into a unique set of 3861 reflections, of which 3738 were 'observed

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and 123 were 'unobserved'. After correction for absorption, symmetrically equivalent F_{hkl}'s agreed within 2% on average. Unobserved reflections were those less than $2\sigma(I)$ above background. The intensities were corrected for absorption as described by Dickens & Bowen (1971*a*, *b*). μ(Mo) was taken to be 21·3 cm^{-1}. The maximum and minimum transmission factors were 0·796 and 0·701, respectively. 2θ for the highly oriented graphite monochromator crystal was 12·32°.

The structure as given by Jones & Cruickshank was refined isotropically using the program *RFINE* (written by L. W. Finger of the Carnegie Institute of Washington) to $R_w = 0{\cdot}086$, $R = 0{\cdot}089$ in two cycles (average shift/error for second cycle $= 0{\cdot}91$) and then to $R_w = 0{\cdot}035$, $R = 0{\cdot}032$ in two cycles of anisotropic refinement. The scattering factors were those of the neutral atoms and were taken from Cromer & Mann (1968). The hydrogen atoms were found in a difference electron-density synthesis as peaks of 0·75, 0·77 and 0·34 e.Å^{-3} for the hydrogen atoms H(1), H(2) and H(3) on O(1), O(7) and O(6), respectively. H(3) is a hydrogen atom disordered over two widely separated sites, while H(2) is either in a centered hydrogen bond or in two sites which are very close to each other. The highest peak in the map which did not correspond to atoms was ~0·50 e.Å^{-3}; the 'half' hydrogen H(3) was found by taking the highest peak within 1·2 Å of O(6). The structure was refined for (i) two more cycles with these hydrogen atoms included with fixed isotropic thermal parameters of 1 Å², and with H(2) fixed at the origin, (ii) two cycles in which the isotropic extinction parameter, *r* in the notation of Zachariasen (1967), was also varied, and (iii) three cycles in which allowance was also made for the anomalous scattering of Ca, P and O. The values for f' and f'' were taken from Cromer (1965).

In these cycles, R_w decreased from 0·035 to 0·032, R changed from 0·032 to 0·031. The extinction parameter value of $1{\cdot}8(6) \times 10^{-6}$ cm indicates that secondary extinction is negligible in this case. The largest correlation coefficient was 0·46 between the extinction and scale parameters. The next largest was 0·40 between x and z of O(8). The position of H(3) was not well defined in any of the refinements. It wandered from 1·24 Å to 1·58 Å from O(6), with O(6)–H···O(8) angles of about

Table 1. *Atomic parameters in* CaHPo₄

The figures in parentheses are standard deviations calculated in the final least-squares refinement.

	x	y	z	B_{11}*	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca(1)	0·29479 (4)	0·43386 (4)	0·27252 (4)	0·757 (7)	1·198 (8)	1·067 (7)	−0·002 (6)	0·145 (6)	−0·263 (6)
Ca(2)	0·17564 (4)	0·83738 (3)	0·66528 (4)	1·194 (8)	0·586 (7)	1·010 (8)	−0·090 (5)	−0·047 (6)	0·146 (5)
P(1)	0·20800 (4)	0·37900 (4)	0·72135 (4)	0·560 (8)	0·443 (8)	0·638 (8)	−0·042 (6)	0·098 (6)	0·047 (6)
P(2)	0·29581 (4)	0·94245 (4)	0·20824 (4)	0·851 (9)	0·732 (9)	0·689 (9)	0·171 (7)	0·092 (7)	0·048 (7)
O(1)	0·3226 (1)	0·3325 (1)	0·9380 (1)	1·04 (3)	1·23 (3)	0·66 (2)	0·23 (2)	0·09 (2)	0·27 (2)
O(2)	0·3518 (1)	0·4924 (1)	0·6332 (1)	0·74 (3)	0·91 (3)	0·89 (3)	−0·16 (2)	0·22 (2)	0·25 (2)
O(3)	0·1387 (1)	0·1810 (1)	0·5958 (1)	1·09 (3)	0·49 (2)	1·07 (3)	−0·13 (2)	0·05 (2)	−0·14 (2)
O(4)	0·0398 (1)	0·5237 (1)	0·7459 (1)	0·71 (3)	0·76 (3)	1·36 (3)	0·17 (2)	0·27 (2)	0·02 (2)
O(5)	0·3329 (1)	0·8363 (1)	0·0155 (1)	0·99 (3)	1·60 (3)	0·88 (3)	0·33 (2)	0·10 (2)	−0·31 (2)
O(6)	0·4592 (1)	0·1024 (2)	0·3019 (2)	0·96 (3)	1·40 (3)	1·69 (3)	−0·41 (2)	−0·09 (2)	−0·54 (3)
O(7)	0·0995 (1)	0·0660 (1)	0·1639 (1)	0·91 (3)	1·35 (3)	0·83 (2)	0·51 (2)	0·02 (2)	0·03 (2)
O(8)	0·2874 (2)	0·7896 (2)	0·3514 (2)	2·24 (4)	1·24 (4)	1·64 (3)	0·62 (3)	0·96 (3)	0·86 (3)

* Thermal parameters have the form $\exp\left[-\tfrac{1}{4}(a^{*2}B_{11}h^2 + b^{*2}B_{22}k^2 + c^{*2}B_{33}l^2 + 2a^*b^*B_{12}hk + 2a^*c^*B_{13}hl + 2b^*c^*B_{23}kl)\right]$.

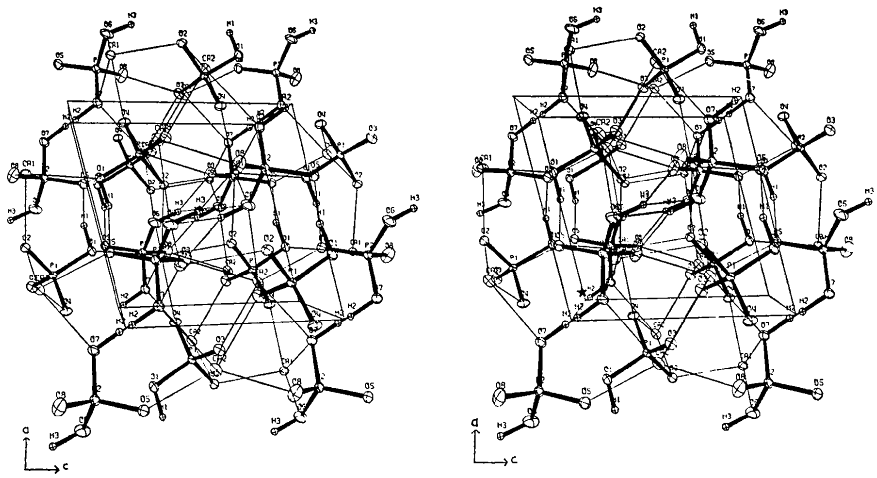

Fig. 1. A stereo illustration of the crystal structure of CaHPO₄, viewed along [010]. The origin of the crystallographic coordinate system is marked by *. The CaHPO₄ chains are seen nearly end on. Two sites for H(2) are very close together. Only one of these sites may be occupied at any given time. The same is truc for the two adjacent H(3) sites.

Table 2. *Calculated and observed structure factors for* $CaHPO_4$

Columns are k, $10F_o$ and $10F_c$. F_o and F_c are on an absolute scale. These values do not include corrections for extinction or anomalous dispersion. Unobserved reflections are those less than $2\sigma(I)$ and are marked by *.

0,K,0		
1	7	-22
2	295	299
3	495	-481
4	267	-270
5	153	155
6	78	78
7	65	-66
8	154	-159
9	201	-207
10	100	-107
11	22	30
0,K,1		
-12	36	32
-11	161	-172
-10	39	40
-9	15	10
-8	28	26
-7	76	77
-6	461	-470
-5	73	-70
-4	359	-372
-3	579	565
-2	229	228
-1	135	140
0	196	-211
1	94	87
2	149	-130
3	132	122
4	347	340
5	152	-153
6	319	323
7	146	-147
8	75	-73
9	85	85
10	96	-98
11	90	93
0,K,2		
11	119	124
10	60	67
-9	92	97
-8	62	-59
-7	71	-72
-6	242	303
-5	7	-2
-4	105	107
-3	74	-78
-2	611	-631
-1	78	71
0	854	-937
1	318	306
2	385	-360
3	215	209
4	122	113
5	158	-154
6	74	71
7	135	133
8	159	157
9	101	102
10	77	78
11	132	-136
0,K,3		
-11	67	95
-10	91	-90
-9	17	16
-8	126	128
-7	16	-15
-6	479	487
-5	111	112
-4	109	112
-3	443	-456
-2	196	-185
-1	418	-408
0	650	651
1	12	-15
2	270	-265
3	415	-399
4	492	-493
5	234	229
6	45	-45
7	261	258
8	19	-13
9	112	-110
10	90	89
11	11*	6
0,K,4		
-11	121	-121
-10	60	-65
-9	15	-9
-8	129	128
-7	174	174
-6	272	-276
-5	132	135
-4	244	-247
-3	330	333
-2	583	595
-1	160	-154
0	198	202
1	355	-363
2	82	-81
3	9	-1
4	26	22
5	31	-35
6	95	-93
7	118	-115
8	112	-110
9	82	82
10	25	-21
0,K,5		
-11	23	23
-10	106	107
-9	97	-97
-8	230	-232
-7	155	-150
-6	117	-121
-5	160	163
-4	61	53
-3	53	-56
-2	135	-141
-1	95	97
0	94	-91
1	473	476
2	206	205
3	25	24
4	292	292
5	333	-333
6	167	164
7	94	-91
8	21	19
9	37	-33
10	123	-123
0,K,6		
-11	69	65
-10	100	-95
-9	24	-28
-8	11	3
-7	126	-128
-6	152	153
-5	212	-213
-4	46	-47
-3	285	-297
-2	271	-277
-1	185	191
0	23	22
1	421	422
2	31	28
3	11	-6
4	24	-19
5	159	158
6	44	44
7	138	140
8	18	-17
9	160	-160
0,K,7		
-10	45	-44
-9	60	59
-8	157	156
-7	91	84
-6	69	-70
-5	47	-45
-4	160	-158
-3	15	15
-2	182	181
-1	127	-127
0	34	30
1	265	-286
2	102	-103
3	38	43
4	114	-108
5	253	252
6	154	-154
7	74	75
8	17	-16
9	54	51
0,K,8		
-9	45	-42
-8	46	-48
-7	27	29
-6	46	-44
-5	327	329
-4	183	186
-3	24	13
-2	44	46
-1	242	-246
0	20	-17
1	77	-78
2	61	59
3	179	-177
4	45	-41
5	251	-252
6	51	50
7	21	15
8	99	98
0,K,9		
-9	77	-72
-8	33	-28
-7	78	81
-6	112	112
-5	27	26
-4	79	76
-3	46	-45
-2	92	-90
-1	258	263
0	72	-72
1	207	207
2	62	-64
3	162	-162
4	23	20
5	99	-98
6	73	75
7	42	-41
0,K,10		
-8	23	19
-7	39	-44
-6	26	-28
-5	172	-170
-4	35	-34
-3	21	22
-2	18	13
-1	120	122
0	14	-10
1	28	25
2	41	36
3	108	109
4	36	-29
5	163	162
0,K,11		
-6	91	-90
-5	41	37
-4	14	10
-3	73	-76
-2	30	-23
-1	216	-215
0	88	87
1	52	-53
2	161	158
3	86	83
4	40	-37
0,K,12		
-3	80	-82
-2	93	-87
-1	31	29
0	18	-1
1	31	27
-1,K,-12		
1	18	-8
2	83	80
-1,K,-11		
-3	14	-8
-2	88	88
-1	80	-82
0	110	-110
1	50	-51
2	76	-76
3	178	174
4	23	-14
5	49	49
-1,K,-10		
-5	142	141
-4	155	153
-3	59	-60
-2	29	-34
-1	95	-96
0	36	-36
1	26	25
2	23	-19
3	126	-129
4	134	-132
5	62	-64
6	10*	6
7	108	105
-1,K,-9		
-6	65	69
-5	46	-47
-4	45	-43
-3	150	149
-2	11	0
-1	204	207
0	14	10
1	180	-180
2	83	82
3	193	-195
4	62	64
5	40	-37
6	52	-51
7	33	-33
8	84	-81
-1,K,-8		
-7	187	-189
-6	51	-48
-5	96	-94
-4	22	-21
-3	177	178
-2	9*	7
-1	83	86
0	16	-12
1	20	-17
2	47	27
3	256	261
4	18	13
5	73	71
6	91	-90
7	205	-202
8	84	82
9	13	-2
-1,K,-7		
-8	146	-148
-7	16	-15
-6	96	-94
-5	22	-20
-4	101	104
-3	244	-243
-2	26	-23
-1	314	-314
0	60	58
1	213	216
2	50	54
3	232	233
4	111	-108
5	45	40
6	209	209
7	73	77
8	92	94
9	55	-44
10	116	-118
-1,K,-6		
-9	104	106
-8	8*	4
-7	256	260
-6	9*	8
-5	152	-149
-4	193	-193
-3	127	-129
-2	8*	6
-1	74	73
0	54	-50
1	286	-294
2	31	-28
3	86	-85
4	259	264
5	94	97
6	45	43
7	101	97
8	178	-177
9	109	107
10	8*	-1
-1,K,-5		
-10	95	98
-9	70	69
-8	133	135
-7	173	-175
-6	25	25
-5	65	67
-4	11	-9
-3	533	529
-2	195	-195
-1	181	182
0	142	-139
1	197	-201
2	9	-6
3	62	-58
4	41	-42
5	122	-119
6	229	-231
7	104	-108
8	19	20
9	142	137
10	122	126
11	49	47
-1,K,-4		
-10	31	-31
-9	176	-178
-8	21	22
-7	177	-180
-6	137	138
-5	98	99
-4	282	282
-3	176	176
-2	312	305
-1	225	-214
0	208	199
1	164	165
2	118	-125
3	93	91
4	405	-411
5	260	-270
6	89	87
7	153	-154
8	171	174
9	163	-160
10	33	-34
11	51	-56
-1,K,-3		
-11	61	-62
-10	170	-173
-9	22	20
-8	146	-147
-7	251	252
-6	45	-45
-5	146	-137
-4	128	-127
-3	372	-370
-2	538	529
-1	69	70
0	214	212
1	98	-99
2	394	-395
3	208	207
4	272	276
5	177	176
6	75	74
7	49	-46
8	283	-290
9	35	-26
10	46	-50
11	23	23
-1,K,-2		
-11	10*	10
-10	85	84
-9	292	296
-8	15	-2
-7	82	-83
-6	326	-332
-5	90	-89
-4	274	-263
-3	359	343
-2	480	-469
-1	152	-141
0	515	-488
1	65	-86
2	350	363
3	158	150
4	480	488
5	40	37
6	166	-168
7	183	185
8	79	-78
9	240	244
10	51	51
11	78	-77
-1,K,-1		
-11	112	111
-10	114	112
-9	169	-174
-8	255	258
-7	202	-204
-6	262	261
-5	47	36
-4	206	-202
-3	70	64
-2	236	-268
-1	350	-333
0	167	-170
1	133	-146
2	21	-34
3	183	-183
4	65	-64
5	68	-46
6	235	240
7	111	113
8	272	284
9	85	-81
10	40	47
11	14	-11
-1,K,0		
-11	43	-50
-10	76	-77
-9	68	-72
-8	114	120
-7	188	189
-6	153	152
-5	28	30
-4	39	40
-3	409	-402
-2	831	819
-1	41	32
0	13	9
1	27	1
2	847	-940
3	201	206
4	59	-66
5	148	145
6	66	61
7	183	-184
8	78	-80
9	122	-124
10	41	41
11	125	126
-1,K,1		
-11	83	-87
-10	88	-93
-9	231	237
-8	186	-191
-7	76	77
-6	406	-416
-5	35	-36
-4	284	285
-3	265	258
-2	706	701
-1	144	131
0	75	-70
1	161	157
2	373	365
3	99	93
4	310	314
5	249	-252
6	451	-462
7	122	-124
8	228	-237
9	159	162
10	49	47
11	76	-78
-1,K,2		
-11	80	81
-10	26	-15
-9	197	-206
-8	97	-102
-7	204	-206
-6	25	20
-5	88	82
-4	216	-221
-3	218	216
-2	231	-261
-1	499	507
0	263	293
1	203	212
2	508	519
3	518	-515
4	42	41
5	64	-62
6	15	13
7	174	174
8	28	-28
9	108	-109
10	83	-78
11	41	-40
-1,K,3		
-11	25	-17
-10	39	36
-9	125	-128
-8	277	288
-7	7*	3
-6	49	50
-5	86	-89
-4	341	-340
-3	111	-107
-2	20	13
-1	248	244
0	448	-466
1	211	-204
2	572	-587
3	234	236
4	56	59
5	393	386
6	202	203
7	62	-58
8	139	139
9	119	-121
10	25	26
11	96	96
-1,K,4		
-11	19	-16
-10	98	104
-9	214	216
-8	81	83
-7	176	178
-6	108	-109
-5	106	-105
-4	355	363
-3	377	-382
-2	305	312
-1	483	-511
0	375	-384
1	260	-257
2	211	-213
3	174	170
4	115	120
5	44	45
6	52	-52
7	97	-95
8	78	76
9	159	160
10	143	145
-1,K,5		
-11	54	55
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2	329	-332
3	74	74
4	268	-270
5	20	16
6	82	82
7	20	18
8	125	122
-9,K,2		
-8	32	-33
-7	129	127
-6	74	74
-5	44	-42
-4	174	178
-3	126	-129
-2	225	229
-1	54	-53
0	71	76
1	103	-101
2	178	-179
3	131	-129
4	22	-18
5	25	24
6	13	9
7	17	12
8	152	-145
-9,K,3		
-8	37	-34
-7	66	-68
-6	43	-48
-5	14	9
-4	8*	-2
-3	194	197
-2	71	-72
-1	18	-18
0	39	38
1	66	-63
2	319	318
3	54	-55
4	112	106
5	140	-134
6	90	-89
7	41	40
-9,K,4		
-8	7*	-8
-7	87	-86
-6	30	30
-5	85	84
-4	255	-259
-3	9*	3
-2	204	-206
-1	118	119
0	128	127
1	181	177
2	18	-18
3	66	65
4	17	-15
5	42	40
6	142	140
7	37	-30
-9,K,5		
-8	71	71
-7	15	8
-6	28	-24
-5	114	-110
-4	32	31
-3	178	-181
-2	126	125
-1	111	-113
0	43	-41
1	96	92
2	213	-211
3	131	129
4	20	-15
5	106	105
6	109	108
7	15	5
-9,K,6		
-8	50	-47
-7	59	57
-6	9*	0
-5	10*	7
-4	120	120
-3	17	-13
-2	52	54
-1	116	-117
0	92	-91
1	74	-71
2	64	60
3	54	-53
4	11	8
5	71	-71
6	140	-135
-9,K,7		
-7	23	-22
-6	93	93
-5	173	173
-4	67	-63
-3	93	90
-2	114	-114
-1	101	99
0	148	144
1	20	-17
2	80	77
3	260	-248
4	39	-39
5	110	-107
6	10*	0
-9,K,8		
-6	40	-41
-5	28	-22
-4	33	-32
-3	54	51
-2	97	96
-1	57	56
0	12	-2
1	78	78
2	96	-95
3	64	61
4	30	-21
5	12	1
-9,K,9		
-5	33	-33
-4	62	62
-3	128	-119
-2	32	33
-1	67	-69
0	100	-100
1	120	114
2	21	-18
3	150	144
4	10*	-1
-9,K,10		
-4	13	-5
-3	110	-105
-2	110	-106
-1	47	-45
0	53	48
1	46	-40
2	125	118
-10,K,-4		
-3	60	60
-2	111	115
-1	78	-80
0	80	80
1	183	-186
2	36	35
3	106	103
-10,K,-3		
-4	37	-33
-3	26	21
-2	134	-139
-1	133	-138
0	75	-76
1	22	23
2	22	-21
3	25	22
4	13	6
5	46	-43
-10,K,-2		
-5	104	-108
-4	14	2
-3	64	-62
-2	34	-35
-1	109	106
0	121	-122
1	31	30
2	129	-128
3	67	-71
4	69	66
5	55	-55
-10,K,-1		
-6	35	33
-5	114	-117
-4	69	66
-3	60	62
-2	155	161
-1	33	25
0	69	71
1	90	-102
2	9*	-2
3	51	50
4	16	-10
5	44	44
6	157	-154
-10,K,0		
-6	159	-164
-5	179	186
-4	56	-56
-3	104	104
-2	38	36
-1	116	-119
0	153	155
1	54	55
2	109	109
3	88	90
4	71	-65
5	9*	-6
6	61	-58
-10,K,1		
-7	79	84
-6	13	-1
-5	24	-27
-4	145	-148
-3	93	-98
-2	17	-5
-1	109	109
0	37	-36
1	84	85
2	67	-66
3	37	-37
4	184	193
5	40	-39
6	154	149
-10,K,2		
-7	92	-87
-6	71	74
-5	173	-176
-4	95	95
-3	19	-18
-2	19	-13
-1	46	47
0	216	-218
1	28	-32
2	100	-95
3	8*	-4
4	71	70
5	21	16
6	43	-41
-10,K,3		
-7	11*	2
-6	23	22
-5	115	119
-4	62	64
-3	39	43
-2	32	32
-1	155	-160
0	37	39
1	126	-125
2	14	-12
3	41	-40
4	109	-102
5	63	61
6	108	-101
-10,K,4		
-7	130	133
-6	42	-46
-5	134	132
-4	110	-110
-3	38	-35
-2	115	113
-1	18	19
0	137	136
1	43	-41
2	18	-18
3	67	-84
4	55	51
5	13	-6
6	64	61
-10,K,5		
-7	46	-46
-6	98	-98
-5	123	-125
-4	12	2
-3	43	39
-2	16	-10
-1	195	196
0	164	-163
1	157	148
2	24	23
3	86	84
4	179	174
5	44	-41
6	20	-17
-10,K,6		
-6	70	65
-5	107	-101
-4	57	59
-3	70	-70
-2	78	-80
-1	15	9
0	13	-9
1	55	50
2	61	56
3	28	26
4	43	-37
5	110	103
-10,K,7		
-6	20	20
-5	45	45
-4	56	-56
-3	75	-75
-2	79	74
-1	117	-113
0	128	124
1	196	-181
2	27	-17
3	63	-58
4	63	-62
-10,K,8		
-5	79	75
-4	11*	-13
-3	99	94
-2	32	30
-1	62	63
0	93	-91
1	57	-53
2	70	-72
3	37	-32
-10,K,9		
-4	101	103
-3	29	24
-2	75	-74
-1	118	111
0	54	-49
1	113	106
2	14	4
-11,K,-3		
-1	38	-36
0	71	69
1	106	103
-11,K,-2		
-3	38	33
-2	36	-38
-1	18	20
0	30	-28
1	167	-159
2	85	82
3	108	-107
-11,K,-1		
-4	14	-1
-3	71	76
-2	132	-130
-1	81	-85
0	141	-144
1	26	25
2	18	9
3	80	80
4	33	-35
-11,K,0		
-5	18	19
-4	93	96
-3	134	-138
-2	93	96
-1	20	-18
0	29	30
1	134	135
2	92	-89
3	34	33
4	138	-132
5	48	-45
-11,K,1		
-5	57	-60
-4	45	43
-3	20	17
-2	121	120
-1	117	117
0	66	66
1	44	-40
2	62	60
3	95	-89
4	45	47
5	36	36
-11,K,2		
-5	41	34
-4	22	-23
-3	172	174
-2	138	-137
-1	7*	-6
0	55	-52
1	40	-38
2	224	223
3	21	23
4	56	53
5	57	-52
-11,K,3		
-6	72	72
-5	8*	1
-4	29	-30
-3	138	-135
-2	61	-60
-1	57	-57
0	9*	2
1	43	41
2	80	-80
3	62	55
4	49	-47
5	17	11
-11,K,4		
-6	33	-33
-5	51	-49
-4	84	79
-3	74	-70
-2	76	76
-1	34	-33
0	90	-89
1	26	-26
2	144	-144
3	17	17
4	72	-63
5	69	66
-11,K,5		
-5	41	29
-4	58	57
-3	153	153
-2	42	-38
-1	12	-7
0	42	-45
1	118	-112
2	158	155
3	38	-33
4	27	24
-11,K,6		
-5	29	29
-4	61	-62
-3	26	23
-2	76	-73
-1	53	52
0	150	147
1	42	37
2	84	82
3	15	-9
4	13	8
-11,K,7		
-4	18	-17
-3	27	-23
-2	86	79
-1	9*	0
0	26	-23
1	106	96
2	85	-83
3	175	157
-11,K,8		
-3	25	-20
-2	19	16
-1	78	-74
0	64	-66
1	58	-54
-12,K,0		
-1	122	122
0	120	-122
1	47	45
-12,K,1		
-3	26	28
-2	16	-11
-1	17	16
0	22	-21
1	29	-26
2	48	-47
-12,K,2		
-3	22	22
-2	100	96
-1	126	-127
0	216	215
1	50	-47
2	104	95
3	45	-40
-12,K,3		
-3	10*	2
-2	10*	7
-1	106	106
0	39	39
1	48	47
2	54	-47
3	65	-58
-12,K,4		
-3	22	19
-2	116	-113
-1	52	52
0	166	-161
1	86	79
2	40	-37
-12,K,5		
-3	72	-68
-2	16	-17
-1	148	-148
0	63	60
1	47	-42
2	11*	11
-12,K,6		
-2	73	68
-1	47	-44
0	108	103

150–160°. From the P–O bond lengths observed here (see below) and from the findings of Curry, Denne & Jones (1968), H(3) is believed to be covalently bonded to O(6).

The structural parameters obtained in the refinements which included corrections for extinction and anomalous dispersion are given in Table 1. In general, the precision is improved by a factor of 15 to 20 over the previous determinations. The structural details in the PO_4 groups are more consistent with the observed chemistry and hence are also considered to be more accurate than earlier values. The observed and calculated structure factors are given in Table 2. Three sets of hydrogen atom positions from (i) the Fourier difference synthesis, (ii) the least-squares refinements and (iii) calculations to idealize the HPO_4^{2-} geometry (see below) are given in Table 3.

Discussion

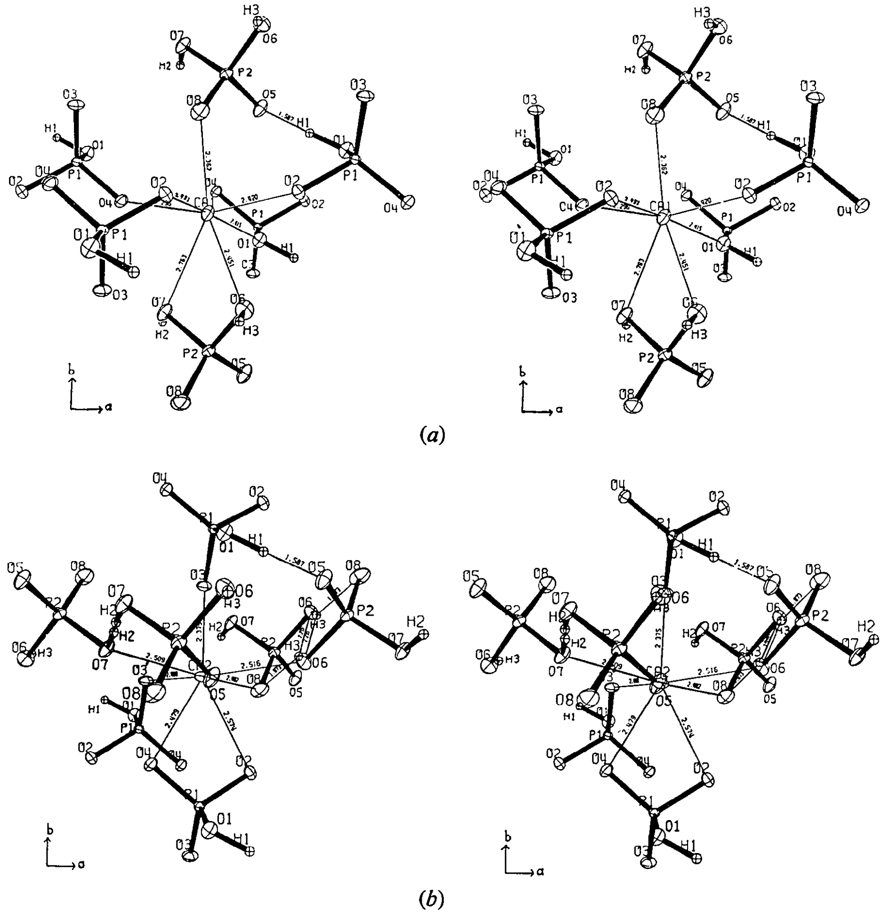
The structure of $CaHPO_4$ (Fig. 1) contains, parallel to [010], distorted versions of the Ca–XO_4 chains found in several other calcium phosphates and related compounds, *e.g.* $Ca(H_2PO_4)_2.H_2O$ (Dickens & Bowen 1971*b*; Jones & Cruickshank, 1961; MacLennan & Beevers, 1956); $CaHPO_4.2H_2O$ (Curry & Jones, 1970; Jones & Smith, 1962; Beevers, 1958); $CaSO_4.2H_2O$ (Atoji & Rundle, 1958) and $CaSO_4$ (Hohne, 1962; Cheng & Zussmann, 1963). In $CaHPO_4$, one set of chains consists of the Ca(1) and $P(2)O_4$ ions, and the other set consists of the Ca(2) and $P(1)O_4$ ions. The usual chain linkage of two XO_4 edges to each Ca ion has been reduced to one PO_4 edge and a PO_4 apex in $CaHPO_4$.

Table 3. *Hydrogen positions in* $CaHPO_4$

A = electron density difference synthesis
B = least-squares refinements (calculated standard deviations ~0·003)
C = calculated

		A	*B*	*C*
H(1)	*x*	0·43	0·44	0·455
	y	0·29	0·27	0·267
	z	0·96	0·95	0·944
H(2)	*x*	0	0	0·010
	y	0	0	0·023
	z	0	0	0·034
H(3)	*x*	0·54	0·56	0·522
	y	0·14	0·17	0·090
	z	0·43	0·48	0·443

The calculated hydrogen positions were used to obtain distances mentioned in Table 4 and the text.


(*a*)

(*b*)

Fig. 2. The calcium ion coordinations in: (*a*) $CaHPO_4$ [Ca(1)], (*b*) $CaHPO_4$ [Ca(2)].

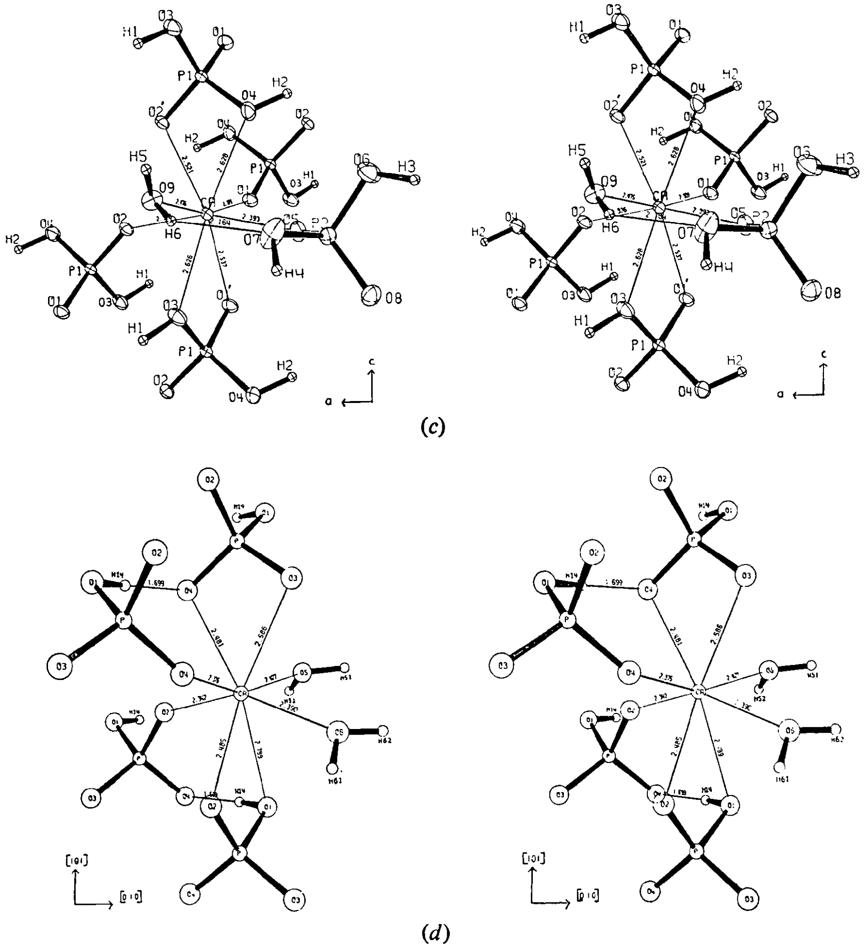


Fig. 2 (*cont.*). (*c*) Ca(H$_2$PO$_4$)$_2$.H$_2$O, (*d*) CaHPO$_4$.2H$_2$O. The direction of the Ca–PO$_4$ chain runs from the top to the bottom of the drawing in each case. The similarities in the structures can be seen from the PO$_4$–Ca–PO$_4$ sequences in the centers of the drawings and from the two PO$_4$ groups to the left of each of these sequences [in (*c*) these two PO$_4$ groups are shown behind rather than to the left of the chain sequence]. The latter PO$_4$ groups define the positions of the two chains in the corrugated sheet which are adjacent to the chain that is shown.

The Ca ion environments

The details of the environments of the two crystallographically different Ca ions in the structure are given in Table 4 and Fig. 2(*a*) and (*b*). Ca(1) is coordinated [Fig. 2(*a*)] to seven oxygen atoms, six [O(4), O(8), O(1), O(2), O(2′) and O(6)] with Ca···O distances in the range 2·295 to 2·450 Å, which denote strong Ca···O bonding, and one [O(7)] at 2·763 Å, which is at the upper end of the normal range. The O(6), O(7) PO$_4$ edge and the PO$_4$ apexes O(2), O(8) and O(4) are arranged in an approximately planar pentagon; O(1) and O(2′) are the apexes of an approximately pentagonal bipyramid. This type of coordination is common in calcium phosphates. As is the case in other compounds where Ca–XO$_4$ chains are found, the coordination of the O(6), O(7) P(2)O$_4$ edge to Ca(1) in the Ca(1)–P(2)O$_4$ chain involves the longest Ca···O distances, which is in accord with Pauling's rule (Pauling, 1960) concerning repulsion between (in this case) Ca and P. Only the apex O(8) of the opposite P(2)O$_4$ edge O(5), O(8) is coordinated to Ca(1) and is involved in the second shortest Ca···O bond. The Ca(1)···P(2) distances along the direction of the Ca(1)–P(2)O$_4$ chain are 3·2380 (4) Å for edge coordination of the P(2)O$_4$ group to Ca(1) and 3·4496 (4) Å for apex coordination, which show that, as judged from the Ca···P distances in this and other calcium phosphates, the Ca(1)···P(2) repulsion is normal in both cases.

Ca(2) is coordinated [Fig. 2(*b*)] to eight oxygen atoms [O(3), O(5), O(4), O(3′), O(8), O(7), O(6), O(2)] with Ca···O distances in the range 2·379 to 2·572 Å. All these bonds are strong. In the Ca(2) coordination geometry, O(8), O(6), O(5), O(7) and O(3′) lie in an approximate pentagon. O(3) lies at one apex of an approximate pentagonal bipyramid, and the center of the O(2), O(4) edge of the P(1)O$_4$ group lies at the remaining apex position. The chain involving Ca(2) includes the P(1)O$_4$ group coordinated in a manner very similar to the coordination of the P(2)O$_4$ group to

Ca(1). Both chain directions are vertical in Fig. 2(*a*) and (*b*). The Ca(2)···P(1) distances for the O(2), O(4) edge and the O(3) apex coordination in the Ca–P(1)O$_4$ chain are 3·1005 (4) and 3·5750 (4) Å, respectively.

Table 4. *Interatomic distances and angles in* $CaHPO_4$

			Distance (Å) or angle (°)*	
P(1),	O(1)		1·5925 (9) Å	
P(1),	O(2)		1·5397 (8)	
P(1),	O(3)		1·5177 (9)	
P(1),	O(4)		1·5147 (9)	
O(1),	P(1),	O(2)	108·10 (5)°	
O(1),	P(1),	O(3)	109·40 (5)	
O(1),	P(1),	O(4)	106·59 (5)	
O(2),	P(1),	O(3)	111·23 (5)	
O(2),	P(1),	O(4)	107·45 (5)	
O(3),	P(1),	O(4)	113·81 (5)	
O(1),	O(2)		2·536 (1) Å	
O(1),	O(3)		2·539 (1)	
O(1),	O(4)		2·492 (1)	
O(2),	O(3)		2·523 (1)	
O(2),	O(4)		2·463 (1)	
O(3),	O(4)		2·540 (1)	
P(2),	O(5)		1·5244 (9)	
P(2),	O(6)		1·5459 (10)	
P(2),	O(7)		1·5482 (9)	
P(2),	O(8)		1·5125 (10)	
O(5),	P(2),	O(6)	110·43 (6)°	
O(5),	P(2),	O(7)	109·59 (5)	
O(5),	P(2),	O(8)	110·64 (6)	
O(6),	P(2),	O(7)	104·78 (6)	
O(6),	P(2),	O(8)	110·58 (7)	
O(7),	P(2),	O(8)	110·70 (6)	
O(5),	O(6)		2·522 (1) Å	
O(5),	O(7)		2·511 (1)	
O(5),	O(8)		2·497 (1)	
O(6),	O(7)		2·451 (1)	
O(6),	O(8)		2·514 (1)	
O(7),	O(8)		2·518 (1)	
Environments				
O(1),	H(1)		0·992	assumed
O(6),	H(3)		0·992	
O(7),	H(2)		0·992	
O(1),	Ca(1)		2·4142 (9)	
O(1),	O(5)		2·565 (1)†	
H(1),	O(5)		1·58‡	
O(1),	H(1),	O(5)	172°	
P(1),	O(1),	O(5)	118·52 (5)	
O(2),	Ca(1)		2·4223 (9) Å	
O(2),	Ca(1′)		2·4482 (9)	
O(2),	Ca(2)		2·5718 (9)	
O(3),	Ca(2)		2·379 (1)	
O(3),	Ca(2′)		2·4785 (9)	
O(4),	Ca(1)		2·2951 (9)	
O(4),	Ca(2)		2·4796 (9)	
O(5),	Ca(2)		2·433 (1)	
O(5),	H(1)		1·58	
O(5),	O(1)		2·565 (1)†	
O(6),	Ca(1)		2·450 (1)	
O(6),	Ca(2)		2·518 (1)	
O(6),	H(3)		2·28	
O(6),	O(8′)		2·669 (1)†	
H(3),	O(8′)		1·83	
O(6),	H(3),	O(8′)	140°	
Table 4 (*cont.*)				
P(2),	O(6),	O(8′)	139·53 (7)°	
O(7),	Ca(1)		2·5098 (9) Å	
O(7),	Ca(1′)		2·763 (1)	
O(7),	O(7′)		2·458 (2)†	
O(7),	H(2)		1·47	
O(7),	2(1),	O(7′)	171°	
P(2),	O(7),	O(7′)	108·29 (6) Å	
O(8),	Ca(1)		2·363 (1)	
O(8),	Ca(2)		2·483 (1)	
O(8),	O(6′)		2·669 (1)†	
O(8),	H(3′)		1·87	

* The figures in parentheses are standard deviations in the last digit of the interatomic distances and angles, and were calculated from the standard deviation in the atomic positional parameters and the unit-cell parameters. They include terms from the variance-covariance matrix.

† Hydrogen bond between these two oxygen atoms.

‡ Distances and angles involving hydrogen were obtained using the calculated hydrogen positions.

The PO$_4$ *groups and their environments*

The details of the two unique PO$_4$ groups and their environments are given in Table 4. In the P(1)O$_4$ group the O(2), O(4) edge is the only edge coordinated to Ca. The O(2)–P(1)–O(4) angle is less than the tetrahedral angle, in accord with Pauling's rule. Two other O–P(1)–O angles less than the tetrahedral angle involve oxygen O(1), which is covalently bonded to hydrogen. Such P–O bonds contain less double bond character than when the oxygen is 'terminal' (Cruickshank, 1961). O–P–O angles with one or both oxygens of this type are expected to be less than tetrahedral (see Table 11 of Baur & Khan, 1970). Similar angles have been observed in the recent refinements of $Ca(H_2PO_4)_2.H_2O$ (Dickens & Bowen, 1971*b*) and $CaPO_3F.2H_2O$ (Perloff, 1971). The O(1)–P(1)–O(3) angle in $CaHPO_4$ is not significantly less than this tetrahedral angle, presumably because it is 'opposite' the O(2)–P(2)–O(4) angle which is contracted by coordination to the Ca ion.

The P(1)–O distances (Table 4) overwhelmingly point to O(1) as being covalently bonded to hydrogen. (P(1)–O(2) is the second longest, 1·5397 Å, of the P(1)–O bonds; this apparent lengthening compared to P(1)–O(3) and P(1)–O(4) is probably due to the influence of the three Ca ions bonded to O(2)). O(1) is the donor in the hydrogen bond of H(1) to O(5); the O(1)···O(5) distance, 2·565 Å, is very short, and the H(1)···O(5) distance of 1·58 Å, Table 4, indicates that there is a strong hydrogen bond between these two atoms.

In the P(2)O$_4$ group, P(2)–O(6) and P(2)–O(7) are the longest P–O distances and are about equal with an average value of 1·547 Å. This value is close to being halfway (1·554 Å) between (i) the average (1·516 Å) of the P(1)–O(3) and P(1)–O(4) distances, which are the P(1)–O distances least disturbed by cationic and hydrogen bonding, and (ii) the P(1)–O(1) distance of

1·5925 Å, where the extension is due mainly to the presence of a covalently bonded hydrogen. Thus the P(2)–O distances support the assignment of half a covalently bonded hydrogen atom on average to each O(6) and O(7).

O(5) has the next longest P–O distance after O(6) and O(7). Although O(5) is bonded only to one Ca ion, where O(6) and O(7) and O(8) are all bonded to two, it is the acceptor in the strong 'normal' hydrogen bond involving H(1) on O(1), which probably serves to lengthen the P(2)–O(5) bond. The results of Curry, Denne & Jones (1968) suggest that there is no covalent bond between O(5) and hydrogen. The shortest P(2)···O distance is P–O(8), which is the acceptor in the hydrogen bond involving the statistically affected hydrogen atom H(3) covalently bonded to O(6). Because on average O(8) enters into only half a hydrogen bond, P(2)···O(8) is not expected to be as long as P(2)···O(5) (the effect of the two Ca ions bonded to O(8) and one Ca ion to O(5) is expected to be subordinate to the effect of hydrogen bonds). Thus, the observed P(2)···O distances are compatible with the environments of the oxygen atoms.

The only O–P–O angle less than 109·5° in the $P(2)O_4$ group involves O(6) and O(7), which are both covalently bonded to hydrogen. This edge is also shared with Ca, so that in the case of the $P(2)O_4$ group, the two angle-decreasing effects are working together.

The hydrogen positions

The four hydrogen atoms in the unit cell of $CaHPO_4$ have an unusual distribution as found by Curry, Denne & Jones (1968) and indicated here by the P–O distances and, in the case of H(1) and H(2), by the difference electron density synthesis. The shortest interphosphate O···O distance, 2·458 (2) Å, is between the centrosymmetrically related atoms O(7) and O(7′). Only one of the four hydrogen atoms, H(2), can be placed in this hydrogen bond, and is either on the center of symmetry or disordered about that center. The next shortest interphosphate O···O distance, 2·565 (1) Å, is between O(1) and O(5). Two hydrogen atoms, H(1) and H(1′), in general positions, can be accommodated in hydrogen bonds of this type. The fourth, H(3), seems to occupy a hydrogen bonding position between O(6) and O(8′), where O(6)···O(8′) = 2·669 Å. This hydrogen atom can fill only half of the two available sites and must, therefore, be disordered. When an idealized position is generated for H(3) according to the rationale given below, H(3) occupies a site where it also appears to form a very weak bond [H(3)···O(6′) = 2·28 Å] between O(6) and O(6′), which have a separation of 3·144 (2) Å. In this bond, the disorder would be with respect to a center of symmetry analogous to that in the H(2) hydrogen bond. Full occupancy of the H(3) sites would bring pairs of hydrogen atoms improbably close together, *i.e.* about 1·58 Å. Thus, it would appear that all the H(3) sites could not be filled even if hydrogen atoms were available.

Because hydrogen atom positions are imprecisely determined by X-ray methods, probable positions of the hydrogen atoms in $CaHPO_4$ were calculated assuming the O–H distance and the P–O–H angle to be 0·992 Å and 113·7° respectively. These latter values are the average of 4 'normal' hydrogen bonds as elucidated by neutron diffraction for $CaHPO_4.2H_2O$ (Curry & Jones, 1970) and $Ca(H_2PO_4)_2$ (Dickens, Prince, Schroeder & Brown, unpublished). The hydrogen atoms were assumed to lie in the same plane as the heavy atoms in the system P–O–H···O. This will give the shortest possible H···O distance, which in general is a realistic approximation. H(3), however, forms a hydrogen bond between two oxygen atoms in the Ca(2) coordination and its position may be affected by repulsion from Ca.

The distance O(7)···O(7′) of 2·458 (2) Å in the hydrogen bond O(7)–H(2)···O(7′) implies a very strong hydrogen bond. Whether or not this hydrogen bond and indeed the whole structure is truly or only nominally centrosymmetric is not yet known, although Denne & Jones (1969) give a personal communication from W. G. Perdok that a very weak piezo-electric effect has been found in $CaHPO_4$. In the opinion of the present authors, the R_w factor reported here is close to or at the limit of the data and testing the centrosymmetry of the whole structure by refining in space-group $P1$ and subsequently applying the ratio test (Hamilton, 1965) would not be worthwhile. The distance O(7)···O(7′) reported here is comparable to the O···O separations of 2·459 (9) Å in potassium hydrogen malonate, $KOOC.CH_2.COOH$ (Sime & Speakman, 1970), 2·40 Å in potassium hydrogen chloromaleate, $KOOC.CH=CCl.COOH$ (Ellison & Levy, 1965), 2·437 (4) Å in potassium hydrogen maleate $KOOC.CH=CH.COOH$ (Darlow & Cochran, 1961), and 2·49 (2) Å in $HCrO_2$ (Hamilton & Ibers, 1963) where centered hydrogen bonds are probable in all cases.

The maximum r.m.s. amplitudes of apparent vibration for O(6) and O(8) are 0·175 Å in each case. In our experience more typical values in the absence of positional disorder are ~0·10 Å. The maximum amplitude of O(8) is more or less along the O(6)···O(8′) vector; that for O(6) is roughly perpendicular to this vector. The O(6)···O(8′) separations with and without H(3) intervening can be estimated by Pythagoras's rule from the 'excess' thermal motion and the average O(6)···O(8′) distance to be ~2·593 Å when O(6) and O(8′) are hydrogen bonded and ~ 2·745 Å when they are not. The former distance indicates a strong hydrogen bond, and the latter is comparable with the closest O···O non-bonded contact distance of ~2·76 Å usually observed. O(6) and O(8′) therefore seem to be exhibiting positional disorder depending on the occupancy of the H(3) site, as would be expected because the average O(6)···O(8′) separation of 2·669 Å is too small to be realistic in those cases where there is no H(3) between O(6) and O(8′). This positional disorder is corroborated by the apparent thermal motion of Ca(2), which is bonded to both O(6) and O(8), and which has apparent thermal amplitudes of 0·138 Å and 0·132 Å toward O(6) and O(8), respectively.

The distance of ~1·58 Å between the occupied and unoccupied sites for H(3) is probably too large for a rapid interchange of occupancy to take place. Thus, H(3) seems to be firmly attached to O(6), and probably forms a hydrogen bond which is abnormal only in its statistical disorder. The O(7)–H(2)–O(7′) hydrogen bond may, therefore, be non-centered, because local electroneutrality arguments suggest that when H(3) is covalently bonded to O(6), H(2) will not be covalently bonded to O(7) in the same P(2)O$_4$ group. In this case, the structure would really be acentric unless the cell volume is doubled.

Relationship of $CaHPO_4$ *to other calcium phosphates and related compounds*

The crystal structures of $CaHPO_4.2H_2O$ and $Ca(H_2PO_4)_2.H_2O$ contain corrugated sheets made up of $(CaHPO_4)^0$ and $(CaH_2PO_4)^+$ chains, respectively. In $CaSO_4.2H_2O$, there are corresponding $CaSO_4$ chains and sheets. In $Ca(H_2PO_4)_2.H_2O$, the $(CaH_2PO_4)^+$ sheets are separated by $H_2PO_4^-$ ions and water molecules. Sheets similar to those in the above compounds may also be present in $Ca_2(NH_4)H_7(PO_4)_4.2H_2O$, $Ca_2KH_7(PO_4)_4.2H_2O$, and $CaCl(H_2PO_4).H_2O$ (Brown, Smith, Lehr & Frazier, 1958). The widespread occurrence of the corrugated sheet feature speaks for its stability. The structures of $CaHPO_4$ and $CaHPO_4.2H_2O$ are closely related if allowance is made for the water molecules; corrugated sheets in $CaHPO_4$ may be imagined parallel to several planes, *e.g.* (101), $(10\bar{1})$ and (001), with the Ca–PO$_4$ chains running parallel to [010] (see Fig. 1).

Comparison of the sheets in $CaHPO_4$, $CaSO_4$, $CaHPO_4.2H_2O$, $CaSO_4.2H_2O$, and $Ca(H_2PO_4)_2.H_2O$ may be made in terms of the Ca coordinations in the five compounds. In $Ca(H_2PO_4)_2.H_2O$ [Fig. 2(*c*); Dickens & Bowen (1971*b*)] the shortest Ca···O bonds (2·309, 2·326 Å) are between chains in the same layer; the next shortest (2·393, 2·475 Å) are from the surface of the layer to the interlayer $H_2O/H_2PO_4^-$ network; the next longest bonds (2·521, 2·538 Å) are to PO$_4$ oxygens which are in the same chain as the Ca ion but which have no covalently bonded hydrogen atoms; the longest (2·626, 2·628 Å) are to the oxygens in the same chain which have covalently bonded hydrogens. The pattern is the same in $CaHPO_4.2H_2O$ [Fig. 2(*d*)], $CaSO_4$ and $CaSO_4.2H_2O$ though actual distances are a little different.

For Ca(1) in $CaHPO_4$, Ca(1)···O(7) is the longest bond, and Ca(1) is so far away from O(5) (3·427 Å) that Ca(1) and O(5) are not considered to be bonded. This is to be expected from the above descriptions, because these atoms are in the same chain and O(5) and O(7) are covalently bonded to hydrogen. The other Ca···O distances do not follow the previous pattern, however. In particular, the Ca(1)···O(6) distance, which is within the chain and where half of the O(6) atoms in the structure are considered to be covalently bonded to hydrogen, is relatively short, 2·451 Å. (However, as was remarked earlier, the position of O(6) is believed to be an average of two slightly different positions depending on the occupancy of the H(3) site.) In the case of Ca(2) in $CaHPO_4$, O(1), which is covalently bonded to hydrogen and is within the chain, is so far away that it is not considered to be bonded to Ca(2); on the other hand, O(3), the other member of the PO$_4$ edge, O(1), O(3), has the shortest Ca(2)···O bond. $CaSO_4$ conforms to the general pattern; the formally analogous compound $CaHPO_4$ does not probably because of the deforming power of the hydrogen bonds, two of which are very strong, and partly because of the averaged effects of hydrogen disorder. Much of the disruptive effect on the Ca–PO$_4$ coordinations can be traced to H(1) which, in forming the bond O(1)–H(1)···O(5), apparently breaks up two edge sharings by pulling O(1) away from Ca(2) and O(5) from Ca(1). Two other possible factors in the non-conformity of $CaHPO_4$ are Ca···H repulsions and the size of the oxygen coordination polyhedron round Ca. From detailed comparison with other structures, neither of these seems dominant in $CaHPO_4$. The deforming power of hydrogen bonds in calcium phosphates is of interest if PO_4^{3-} groups in the structures become HPO_4^{2-} or $H_2PO_4^-$ groups to restore electroneutrality if some Ca^{2+} ions are missing. In cases such as these, the structure probably undergoes some local distortion, and in extreme cases, may even be so distorted that it remains amorphous.

Note added in proof: – Two formulae are given incorrectly in Dickens & Bowen (1971*b*). The corrected formulae are:

$$\sigma(F)=[\sigma(I)/2]\ \{(\mathrm{LP}/I)\}^{1/2}$$

$$\beta=(-1{\cdot}58883\times10^6)\ [\lambda^2(\cos^2 2\theta_m+\cos^4 2\theta_c)\mathrm{d}A/\mathrm{d}\mu]/\\ [AV^2\sin 2\theta_c(\cos^2 2\theta_m+\cos^2 2\theta_c)]\ .$$

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Etude Cristallochimique d'Hydrates Intermédiaires de la Série des Aluns. Cas du Dihydrate $CsTl^{III}(SO_4)_2.2H_2O$

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$CsTl^{III}(SO_4)_2.2H_2O$ crystallizes in space group $C2/c$ with $a=9{\cdot}320$, $b=14{\cdot}610$, $c=7{\cdot}121$ Å; $\beta=106{\cdot}50°$ and $Z=4$. The structure has been determined from Patterson and Fourier syntheses using three-dimensional data collected by the equi-inclination Weissenberg technique with Mo $K\alpha$ radiation. The structure was refined by the method of least squares. The final R value for 515 observed structure factors is 0·065. The crystal structure consists of infinite chains parallel to [101] of composition $[Tl^{III}(SO_4)_2(H_2O)_2]^-$ linked together by Cs^+ cations. Each Cs^+ is surrounded by ten nearest oxygen neighbours at an average distance of 3·36 Å. In the infinite chains, thallium is coordinated to four separate SO_4 tetrahedra and 2 water molecules (average distance $Tl^{III}\text{–}O=2{\cdot}24$ Å). The oxygen atoms with bond lengths of 2·64 and 2·66 Å are probably hydrogen-bridged.

Introduction

Dans le cadre d'une étude sur la déshydratation des sulfates doubles hydratés de formule générale $A^IB^{III}(SO_4)_2.nH_2O$, nous nous sommes intéressés au cas des sels à degré d'hydratation élevé formant la série des aluns. Lipson (1935) a montré que les aluns ne pouvaient pas être considérés comme isotypes mais appartenaient à trois types suivant la taille du cation alcalin monovalent. Dans le cas où le cation est petit (Na^+), ce sont les aluns γ; l'alun de type β se forme si le cation est de grosse taille (Cs^+), alors que pour les cations de rayon ionique intermédiaire (K^+, Rb^+, NH_4^+), l'alun est de type α; ce dernier est de loin le plus commun.