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Table 9. *Shortest intermolecular distances*

$S(1)\cdots S(1^{iii})$	3·60 Å
$S(1)\cdots O^{ii}$	3·59
$S(1)\cdots C(2^{ii})$	3·85
$S(1)\cdots C(3^{ii})$	3·86
$S(2)\cdots C(2^{vi})$	3·78
$S(2)\cdots C(3^{vi})$	3·81
$O\cdots O^{ii}$	3·89
$O\cdots C(2^{v})$	3·52
$O\cdots C(3^{iv})$	3·94
$C(1)\cdots C(3^{iv})$	3·92

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On the Crystal Structure of Pumpellyite

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(*Received* 18 *November* 1968)

Pumpellyite, $Ca_8Al_8(Mg, Fe^{II}, Fe^{III}, Al)_4$ $[(SiO_4)_4/(Si_2O_7)_4/(OH)_8(H_2O, OH)_4]$ is a mixed-group silicate, like epidote, which crystallizes in the monoclinic system, space group $A2/m$, with $a = 8·83$, $b = 5·90$, $c = 19·17$ Å, $\beta = 97°7'$ and $Z = 1$. The structure was refined, with isotropic thermal parameters, by the least-squares method to an R value of 12·3% for observed reflexions. Pumpellyite is characterized by the presence of two types of symmetrically independent chains of octahedra. The first type, through the point (a/2, c/4), is made up of Al (50%), Mg (35%), Fe (15%), the second of Al only. Both types of chain are united by isolated tetrahedra, SiO_4, and double tetrahedra, Si_2O_7. Finally, in the crystal structure there are two independent calcium atoms in sevenfold coordination. An interesting feature is the distorted coordination of one tetrahedron of the group Si_2O_7. All other bond distances are within the limits given in the literature.

Introduction

The silicate mineral pumpellyite, like epidote, is characteristic of low grade metamorphic rocks. Pumpellyite probably occurs in nature more frequently than is usually believed; it is easily mistaken for epidote.

This is a report of the refinement of the crystal structure of the mineral. A description of the unrefined structure has been given by Gottardi (1965).

Experimental

The pumpellyite studied was from Hicks Ranch, Sonoma County, California, U.S.A.

The unit-cell data, $a = 8·83 \pm 0·01$, $b = 5·90 \pm 0·01$, $c = 19·17 \pm 0·02$, $\beta = 97°7' \pm 5'$ were determined, and are similar to those given by Coombs (1953). These data were obtained by a least-squares method starting from the lattice spacings measured on a Guinier–De Wolff powder diagram (Cu radiation) calibrated with 10% silicon powder. The space group was confirmed as $A2/m$.

The density was measured, on small splinters weighing a few milligrams, with a torsion microbalance; the result was $D_{exp} = 3·18 \pm 0·03$ g.cm^{-3}.

A chemical analysis was performed by A. Alietti; the results of this analysis allows the calculation of the following formula, on the basis of 56 oxygen atoms:

$$(Ca_{7·60}Mg_{0·40})_{tot=8·00}(Mg_{1·20}Fe^{II}{}_{0·77}Fe^{III}{}_{0·18}Al_{10·00})_{tot=11·97}[Si_{11·20}Al_{0·80})_{tot=12·00}O_{44}/\{(OH)_{9·29}(H_2O)_{2·71}\}_{tot=12·00}],$$

$Z = 1$.

The above formula and unit-cell constants lead to a calculated density of $D_{calc} = 3·20$.

The different atoms are grouped following the crystallochemical rules, to reach totals of atomic coefficients near to multiples of 4 (positions with a multiplicity number smaller than 4 are improbable in space group *A*2/*m*).

Intensities of 588 reflexions were obtained by visual estimation from Weissenberg photographs of the zero, first, second and third layers, around **b** (Cu *Kα* radiation). The total number of possible reflexions in these layers was 793. Although the exposure time was as high as 120 hours for some films, the high number of non-observed reflexions, 205 or 26%, is a result of the distortion of single crystals of pumpellyite, resulting in the comet-like appearance of diffraction spots in the Weissenberg photographs (see Coombs, 1953). This particular appearance of the diffraction spots not only prevents the measurement of low intensity diffraction spots, but also lowers the precision of intensity measurements and, hence, of the refinement.

An absorption correction was applied by the Alberti & Gottardi (1966) method, the crystal dimensions be-

Table 1. *Observed and calculated structure factors*

A minus sign for Fo means 'less than'.

H	L	FO	FC
K = 0			
1	0	222	-156
2	0	732	-717
3	0	1401	-1455
4	0	1124	1075
5	0	489	-446
6	0	-107	99
7	0	511	-511
8	0	1254	1227
9	0	1063	-1075
10	0	897	-1008
11	0	-65	155
0	2	152	56
1	2	124	346
2	2	1371	-1570
3	2	846	715
4	2	1278	-1276
5	2	718	672
6	2	1427	-1416
7	2	417	-484
8	2	-124	175
9	2	1220	1034
10	2	683	-763
11	2	-56	-182
1	-2	221	246
2	-2	419	431
3	-2	1163	1389
4	-2	1481	-1544
5	-2	222	-138
6	-2	-107	-126
7	-2	1128	1071
8	-2	1017	1096
9	-2	-119	62
10	-2	433	-529
11	-2	214	296
0	4	688	829
1	4	482	-422
2	4	1291	-1179
3	4	-77	16
4	4	517	-380
5	4	905	-852
6	4	399	-381
7	4	900	826
8	4	618	584
9	4	555	-568
10	4	-88	-238
1	-4	396	-476
2	-4	714	-793
3	-4	270	-292
4	-4	1150	1268
5	-4	333	-309
6	-4	256	163
7	-4	-119	-223
8	-4	1080	1226
9	-4	427	-395
10	-4	-100	103
11	-4	431	-517
0	6	417	-374
1	6	317	283
2	6	270	-380
3	6	238	214
4	6	1567	1350
5	6	510	424
6	6	1016	-1053
7	6	-124	-130
8	6	336	341
9	6	-105	-29
10	6	-77	89
1	-6	343	430
2	-6	1772	-2303
3	-6	454	329
4	-6	1192	1327
5	-6	494	571
6	-6	1289	-1260
7	-6	-121	-161
8	-6	-124	16
9	-6	756	748
10	-6	-98	-332
11	-6	235	278
0	8	158	-161
1	8	606	-479
2	8	247	-264
3	8	1073	-954
4	8	2499	2231
5	8	657	673
6	8	587	-546
7	8	543	-534
8	8	739	716
9	8	-96	-97
1	-8	636	-658
2	-8	2226	-2317
3	-8	383	365
4	-8	616	674
5	-8	739	-858
6	-8	-116	57
7	-8	954	1000
8	-8	517	-516
9	-8	543	-693
10	-8	452	-655
11	-8	809	1052
0	10	904	-985
1	10	459	-490
2	10	1982	1814
3	10	1369	1152
4	10	606	565
5	10	-121	96
6	10	888	-994
7	10	-119	317
8	10	-105	30
1	-10	-88	53
2	-10	-91	9
3	-10	825	821
4	-10	1397	910
5	-10	515	-436
6	-10	613	-588
7	-10	608	-701
8	-10	492	-470
9	-10	-109	317
10	-10	751	-825
0	12	2816	2713
1	12	445	334
2	12	341	-328
3	12	700	-748
4	12	954	903
5	12	-124	-124
6	12	876	-560
7	12	-112	36
8	12	-91	247
1	-12	492	-505
2	-12	975	-1018
3	-12	541	-449
4	-12	2110	2224
5	-12	-119	-131
6	-12	-123	109
7	-12	529	-468
8	-12	567	600
9	-12	548	-653
10	-12	399	-349
0	14	793	-624
1	14	700	604
2	14	2058	-2018
3	14	-123	-14
4	14	289	-328
5	14	853	719
6	14	984	-997
7	14	294	-264
8	14	-70	-117
1	-14	457	416
2	-14	-114	-349
3	-14	956	891
4	-14	-119	-148
5	-14	-123	138
6	-14	555	-455
7	-14	1192	1035
8	-14	501	560
9	-14	-88	-179
0	16	-121	428
1	16	-123	119
2	16	756	-745
3	16	494	-554
4	16	410	344
5	16	494	-606
6	16	322	440
7	16	186	216
1	-16	254	-185
2	-16	534	524
3	-16	299	-327
4	-16	-124	115
5	-16	851	-687
6	-16	492	-291
7	-16	475	468
8	-16	580	646
9	-16	429	-524
0	18	301	-104
1	18	-123	268
2	18	1016	-881
3	18	-116	13
4	18	664	626
5	18	252	-156
6	18	-74	99
1	-18	266	158
2	-18	904	-760
3	-18	-123	91
4	-18	-121	181
5	-18	263	251
6	-18	1973	-1809
7	-18	445	399
8	-18	259	317
0	20	1315	1214
1	20	-112	327
2	20	525	-595
3	20	1215	-1088
4	20	981	1019
5	20	476	463
1	-20	630	-566
2	-20	487	-317
3	-20	-114	-298
4	-20	459	416
5	-20	777	-806
6	-20	266	-209
7	-20	348	444
0	22	-96	-3
1	22	-91	7
2	22	583	476
3	22	697	737
1	-22	-98	60
2	-22	679	600
3	-22	389	414
4	-22	228	117
5	-22	550	-534
0	24	793	777
1	-24	-67	-426
2	-24	-67	-774
3	-24	-60	240
4	-24	-44	795
K = 1			
1	1	1270	1090
2	1	497	-475
3	1	625	496
4	1	316	-348
5	1	-71	-38
6	1	313	-399
7	1	511	-535
8	1	188	-87
9	1	289	-287
10	1	-71	-203
1	-1	501	457
2	-1	350	307
3	-1	1704	1878
4	-1	726	787
5	-1	165	-135
6	-1	434	-328
7	-1	639	649
8	-1	497	563
9	-1	-87	-123
10	-1	466	-428
11	-1	393	-480
0	3	-37	14
1	3	343	364
2	3	716	656
3	3	1415	-1207
4	3	998	-936
5	3	507	-420
6	3	595	633
7	3	474	-418
8	3	259	-351
9	3	208	-316
10	3	383	314
1	-3	541	-412
2	-3	313	-272
3	-3	-54	3
4	-3	319	-265
5	-3	1122	976
6	-3	504	412
7	-3	-87	28
8	-3	891	-1058
9	-3	407	410
10	-3	447	431
11	-3	413	634
0	5	208	167
1	5	2762	-2614
2	5	602	-594
3	5	487	451
4	5	1294	1218
5	5	-77	-114
6	5	-87	73
7	5	-91	-152
8	5	188	281
9	5	-61	43
10	5	356	306
1	-5	497	540
2	-5	551	613
3	-5	904	-1010
4	-5	548	-510
5	-5	-74	-57
6	-5	403	315
7	-5	376	272
8	-5	591	504
9	-5	444	341
10	-5	333	-355
0	7	259	-261
1	7	339	383
2	7	-60	6
3	7	175	140
4	7	662	-608
5	7	-84	120
6	7	602	-593
7	7	521	538
8	7	407	419
9	7	565	546
10	7	514	-694
1	-7	1479	-1672
2	-7	245	-246
3	-7	800	830
4	-7	985	1126
5	-7	581	-609
6	-7	450	-300
7	-7	454	-443
8	-7	625	562
9	-7	175	-164
10	-7	239	221
0	9	202	-135
1	9	494	542
2	9	175	195
3	9	178	179
4	9	296	-215
5	9	1233	1165
6	9	628	736
7	9	-91	9
8	9	551	-678
9	9	-64	-91
1	-9	-64	-1
2	-9	-64	-59
3	-9	444	-328
4	-9	723	-920
5	-9	505	-516
6	-9	-87	-35
7	-9	682	-537
8	-9	447	-435
9	-9	376	-308
10	-9	464	400
0	11	208	168
1	11	-74	-23
2	11	-77	42
3	11	756	698
4	11	272	240
5	11	269	-254
6	11	-91	-52
7	11	-84	73
8	11	235	306
9	11	366	-452
1	-11	1344	1304
2	-11	155	-103
3	-11	-77	-6
4	-11	229	-195
5	-11	659	808
6	-11	-91	66
7	-11	497	-327
8	-11	501	-449
9	-11	-77	-59
10	-11	-57	-59
0	13	403	223
1	13	171	-121
2	13	339	-315
3	13	477	-444
4	13	-91	119
5	13	481	-365
6	13	615	-678
7	13	447	-453
8	13	-57	96
1	-13	655	569
2	-13	383	310
3	-13	914	1016
4	-13	192	217
5	-13	343	-286
6	-13	390	-390
7	-13	833	894
8	-13	487	505
9	-13	-67	220
0	15	-87	-14
1	15	195	165
2	15	985	940
3	15	1314	-1114
4	15	780	-533
5	15	339	-309
6	15	565	557
7	15	-60	152
1	-15	958	-1020
2	-15	185	-201
3	-15	-91	-246
4	-15	202	241
5	-15	-91	-76
6	-15	302	340
7	-15	195	-11
8	-15	423	-365
9	-15	481	485
0	17	225	100
1	17	840	-796
2	17	581	-531
3	17	-87	3
4	17	195	139
5	17	215	212
1	-17	629	776
2	-17	198	167
3	-17	954	-1025
4	-17	296	-260
5	-17	-87	-39
6	-17	662	718
7	-17	-74	32
8	-17	249	265
0	19	326	-276
1	19	376	476
2	19	-84	-66
3	19	524	512
4	19	-71	21
5	19	-57	23
1	-19	306	-251
2	-19	370	-467
3	-19	-87	27
4	-19	218	220
5	-19	511	-474
6	-19	326	-390
7	-19	-60	-131
0	21	255	-268
1	21	565	640
2	21	276	353
3	21	-60	11
4	21	-47	150
1	-21	178	-128
2	-21	-77	-31
3	-21	-77	156
4	-21	302	-339
5	-21	269	-188
6	-21	181	-224
0	23	-57	8
1	23	239	179
2	23	-44	122
1	-23	423	451
2	-23	-60	88
3	-23	-57	9
K = 2			
1	0	1351	894
2	0	1356	1026
3	0	939	-789
4	0	378	-288
5	0	556	619
6	0	550	639
7	0	411	-425
8	0	945	-1000
9	0	-172	-137
10	0	-139	-233
0	2	811	-783
1	2	973	-716
2	2	1956	1519
3	2	-128	16
4	2	511	-525
5	2	-167	-182
6	2	811	-897
7	2	817	-843
8	2	-189	-203
9	2	395	565
10	2	495	690
1	-2	878	-739
2	-2	539	567
3	-2	811	731
4	-2	350	-233
5	-2	900	-926
6	-2	1701	1709
7	-2	-189	394
8	-2	-195	200
9	-2	350	-324
10	-2	-139	289
0	4	1868	-2006
1	4	322	249
2	4	1940	1772
3	4	889	726
4	4	3201	-3345
5	4	-172	94
6	4	-189	-180
7	4	900	944
8	4	428	-563
9	4	-161	135
10	4	472	588
1	-4	734	608
2	-4	900	-859
3	-4	-128	86
4	-4	1462	-1396
5	-4	1195	1124
6	-4	1862	1839
7	-4	-195	-389
8	-4	400	-449
9	-4	345	454
10	-4	-139	60
0	6	1395	1315
1	6	511	-452
2	6	1195	1223
3	6	-150	-174
4	6	-167	139
5	6	422	-425
6	6	461	184
7	6	472	-497
8	6	667	702
9	6	-150	-453
10	6	428	856
1	-6	878	-745
2	-6	1251	-1271
3	-6	445	-407
4	-6	-156	146
5	-6	-167	119
6	-6	572	650
7	-6	634	-635
8	-6	406	196
9	-6	-172	184
10	-6	-133	274
1	8	1593	-1581
2	8	-150	172
3	8	-161	-132
4	8	745	-798
5	8	873	1049
6	8	761	876
7	8	-189	-189
8	8	-167	-434
9	8	-128	497
1	-8	656	563
2	-8	328	-326
3	-8	-150	-31
4	-8	2273	-2549
5	-8	661	628
6	-8	495	531
7	-8	967	992
8	-8	1156	-1273
9	-8	-167	149
10	-8	-128	-259
0	10	1034	-711
1	10	1028	-928
2	10	1984	1869
3	10	528	401
4	10	673	568
5	10	867	-867
6	10	595	758
7	10	-178	166
8	10	-150	-348
9	10	-100	-281
1	-10	345	-349
2	-10	2257	2399
3	-10	350	-239
4	-10	428	422
5	-10	1000	-1004
6	-10	-195	38
7	-10	995	-921
8	-10	422	-442
9	-10	606	89
0	12	361	-361
1	12	456	444
2	12	-183	121
3	12	-189	-191
4	12	-195	-327
5	12	-195	329
6	12	-183	385
7	12	528	540
8	12	1534	-1454
1	-12	1045	1145
2	-12	528	597
3	-12	506	-561
4	-12	623	691
5	-12	623	752
6	-12	517	110
7	-12	650	-573
8	-12	750	-796
9	-12	489	541
10	-12	-78	316
0	14	1162	-1394
1	14	561	-427
2	14	500	-524
3	14	428	-448
4	14	-189	123
5	14	-183	311
6	14	-161	-291
7	14	461	-405
1	-14	[illegible]	[illegible]
2	-14	711	819
3	-14	511	497
4	-14	556	355
5	-14	450	-511
6	-14	667	620
7	-14	-178	265
8	-14	-150	-145
9	-14	-117	-118
0	16	1595	-1579
1	16	-195	-192
2	16	539	583
3	16	528	382
4	16	1401	-1064
5	16	-161	-191
6	16	489	580
1	-16	639	804
2	-16	495	577
3	-16	-195	-112
4	-16	1006	-1011
5	-16	534	505
6	-16	567	480
7	-16	-156	-133
8	-16	723	-668
0	18	-189	14
1	18	434	-435
2	18	445	525
3	18	-167	94
4	18	-150	178
5	18	539	-663
1	-18	456	-475
2	-18	-189	-162
3	-18	-183	-341
4	-18	-178	-145
5	-18	-172	307
6	-18	-156	-309
7	-18	389	-331
0	20	-167	274
1	20	495	432
2	20	-150	8
3	20	-133	-142
4	20	445	-598
1	-20	-172	118
2	-20	-167	63
3	-20	656	-674
4	-20	1234	-1097
5	-20	522	521
6	-20	-117	262
7	-20	-72	216
0	22	-128	118
2	22	989	952
1	-22	-133	-122
2	-22	1734	1639
3	-22	545	-469
4	-22	395	-357
5	-22	534	-535
K = 3			
0	1	-46	53
1	1	1220	818
2	1	553	-444
3	1	169	-73
4	1	-63	-122
5	1	-72	88
6	1	477	-457
7	1	776	-779
8	1	-72	37
9	1	249	-200
10	1	241	-257
1	-1	443	-318
2	-1	316	186
3	-1	2009	1788
4	-1	511	573
5	-1	-72	63
6	-1	460	-334
7	-1	502	486
8	-1	506	488
9	-1	295	-282
10	-1	350	-358
0	3	-51	39
1	3	629	400
2	3	595	462
3	3	819	-600
4	3	802	-727
5	3	819	-731
6	3	515	533
7	3	460	-435
8	3	287	-301
9	3	-59	-167
1	-3	662	-555
2	-3	333	-289
3	-3	304	-244
4	-3	-63	3
5	-3	1194	1223
6	-3	295	220
7	-3	-76	57
8	-3	705	-874
9	-3	219	205
10	-3	359	333
0	5	186	128
1	5	1426	-1417
2	5	667	-513
3	5	152	131
4	5	1084	1093
5	5	325	-310
6	5	-76	-57
7	5	-76	-106
8	5	304	331
9	5	245	214
1	-5	316	217
2	-5	511	419
3	-5	1072	-1076
4	-5	426	-333
5	-5	[illegible]	[illegible]
6	-5	367	314
7	-5	587	507
8	-5	477	390
9	-5	266	190
10	-5	295	-328
0	7	122	-80
1	7	409	424
2	7	224	44
3	7	-68	-72
4	7	532	-460
5	7	-76	-65
6	7	574	-568
7	7	734	737
8	7	485	405
9	7	439	492
1	-7	975	-940
2	-7	485	-472
3	-7	291	227
4	-7	895	1055
5	-7	722	-654
6	-7	397	-294
7	-7	198	-224
8	-7	637	581
9	-7	-59	-89
10	-7	-38	59
0	9	-63	-14
1	9	523	489
2	9	-68	118
3	9	279	-189
4	9	232	-182
5	9	1148	1229
6	9	544	560
7	9	-68	109
8	9	409	-516
1	-9	207	273
2	-9	169	-96
3	-9	-68	-133
4	-9	705	-863
5	-9	684	-791
6	-9	186	68
7	-9	485	-387
8	-9	295	-359
9	-9	177	-160
0	11	321	333
1	11	354	-321
2	11	-72	-69
3	11	662	632
4	11	266	188
5	11	-68	-90
7	11	-59	123
8	11	257	322
1	-11	1101	1288
2	-11	215	-193
3	-11	198	190
4	-11	224	-151
5	-11	565	600
6	-11	177	-75
7	-11	557	-435
8	-11	279	-227
9	-11	-46	63
0	13	283	248
1	13	165	-225
2	13	397	-412
3	13	333	-342
4	13	219	178
5	13	160	-123
6	13	494	-601
7	13	452	-593
1	-13	279	275
2	-13	367	382
3	-13	1017	1175
4	-13	-76	122
5	-13	312	-247
6	-13	414	-428
7	-13	616	686
8	-13	388	499
0	15	-76	-3
1	15	198	70
2	15	684	680
3	15	802	-746
4	15	466	-364
5	15	350	-350
6	15	329	511
1	-15	886	-1072
2	-15	198	-153
3	-15	166	-173
4	-15	405	379
5	-15	219	111
6	-15	186	118
7	-15	-59	-68
8	-15	228	-277
0	17	-72	-20
1	17	654	-511
2	17	591	-480
3	17	152	35
4	17	295	241
5	17	101	113
1	-17	536	419
2	-17	-72	168
3	-17	840	-966
4	-17	160	-127
5	-17	-63	52
6	-17	557	630
7	-17	-46	105
0	19	246	-228
1	19	456	551
2	19	-59	-46
3	19	435	448
4	19	-42	106
1	-19	152	-190
2	-19	561	-601
3	-19	143	-128
4	-19	308	376
5	-19	447	-418
6	-19	241	-378
0	21	211	-213
1	21	565	698
1	-21	-51	-61
2	-21	135	-129
3	-21	169	116
4	-21	266	-337

Table 2. *Atomic coordinates with their standard errors*

	Number of atoms in unit cell	x/a	y/b	z/c	B (Å^2)
Al, Mg, Fe	4	0·5000	0·2500	0·2500	0·57 ± 0·14
Ca(1)	4	0·2502 ± 0·0001	0·5000	0·3395 ± 0·0003	0·35 ± 0·12
Ca(2)	4	0·1895 ± 0·0007	0·5000	0·1550 ± 0·0003	0·95 ± 0·13
Si(1)	4	0·0484 ± 0·0009	0·0000	0·0907 ± 0·0004	0·33 ± 0·16
Si(2)	4	0·1674 ± 0·0009	0·0000	0·2482 ± 0·0004	0·38 ± 0·15
Si(3)	4	0·4661 ± 0·0008	0·0000	0·4021 ± 0·0004	0·11 ± 0·14
Al	8	0·2541 ± 0·0005	0·2454 ± 0·0020	0·4964 ± 0·0003	0·08 ± 0·10
O(1)	8	0·1360 ± 0·0013	0·2218 ± 0·0050	0·0685 ± 0·0006	0·56 ± 0·23
O(2)	8	0·2674 ± 0·0014	0·2318 ± 0·0047	0·2444 ± 0·0006	0·86 ± 0·25
O(3)	8	0·3684 ± 0·0013	0·2220 ± 0·0050	0·4209 ± 0·0006	0·58 ± 0·23
O(4)	4	0·1304 ± 0·0023	0·5000	0·4448 ± 0·0010	0·27 ± 0·38
O(5)	4	0·1283 ± 0·0023	0·0000	0·4558 ± 0·0011	0·38 ± 0·41
O(6)	4	0·3695 ± 0·0023	0·5000	0·0445 ± 0·0011	0·37 ± 0·41
O(7)	4	0·3665 ± 0·0022	0·0000	0·0338 ± 0·0010	0·07 ± 0·37
O(8)	4	0·0376 ± 0·0021	0·0000	0·1779 ± 0·0009	0·31 ± 0·36
O(9)	4	0·4746 ± 0·0023	0·5000	0·1764 ± 0·0010	0·40 ± 0·40
O(10)	4	0·0667 ± 0·0021	0·0000	0·3152 ± 0·0010	0·40 ± 0·38
O(11)	4	0·4992 ± 0·0022	0·5000	0·3129 ± 0·0010	0·24 ± 0·38

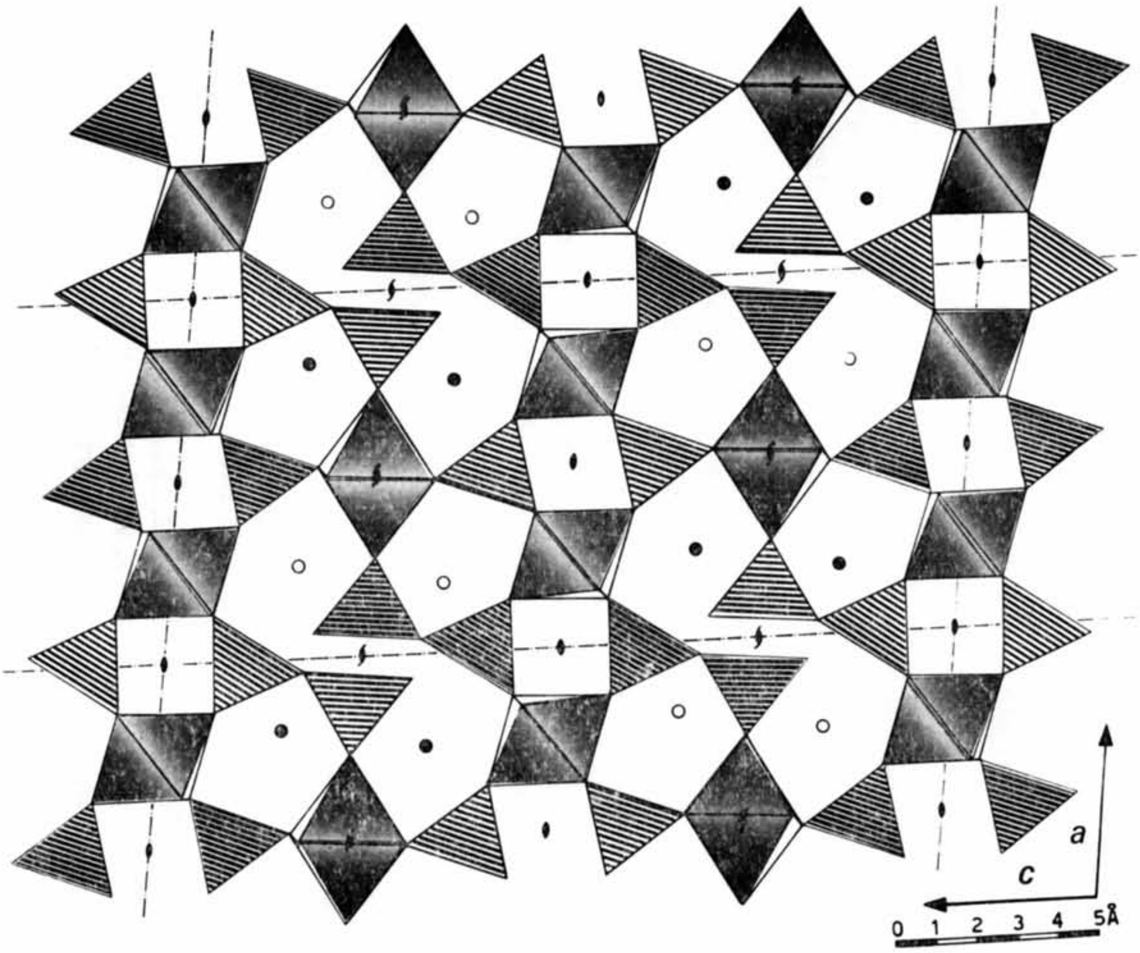

Fig. 1. A plane view, along the *b* axis of the arrangement of the tetrahedra and octahedra in the structure of pumpellyite. The Ca atoms at $y/b=0$ are represented by white circles if and by black circles at $y/b=\frac{1}{2}$. Tetrahedra at $y/b=0$ are marked by light stripes and those at $y/b=\frac{1}{2}$ by heavier stripes.

ing 0·09 × 0·18 × 0·04 mm and $\mu = 186{\cdot}7$ cm^{-1} for Cu $K\alpha$ radiation.

Refinement

The refinement was carried out by the least-squares program of Busing, Martin & Levy (1962) with the atom form factors for neutral atoms given in *International Tables for X-ray Crystallography* (1962). During refinement the (isotropic) temperature factor of atom Si(3) became negative after each cycle, so it was necessary to fix it at $B = 0{\cdot}11$ Å^2, a value obtained by adding the calculated negative value to its positive standard deviation. The lowest residual obtained was as high as 12·3% without non-observed reflexions, and 15·9% with non-observed reflexions taking half of the minimum observable value. This lack of precision in the intensity measurements made further refinement pointless.

Table 3. *Interatomic distances* (Å) *with their standard errors*

The superscripts refer to the symmetry code

–	x	y	z
′	x	$-y$	z
″	x	$\frac{1}{2}-y$	$z-\frac{1}{2}$
‴	$-x$	$\frac{1}{2}-y$	$\frac{1}{2}-z$
iv	$1-x$	$\frac{1}{2}-y$	$\frac{1}{2}-z$
v	x	$1-y$	z
vi	$1-x$	y	$-z$
vii	$1-x$	$\frac{1}{2}-y$	$1-z$

Interatomic distances and bond angles which are symmetrically dependent are bracketed.

	Distances
Si(1)–tetrahedron	
Si(1)–O(1)	1·60 ± 0·03
Si(1)–O(1′)	
Si(1)–O(4‴)	1·64 ± 0·02
Si(1)–O(8)	1·69 ± 0·02
Average	1·64
O(1)—O(1′)	2·62 ± 0·06
O(1)—O(4‴)	2·68 ± 0·02
O(1′)—O(4‴)	
O(1)—O(8)	2·70 ± 0·02
O(1′)—O(8)	
O(4‴)–O(8)	2·62 ± 0·03
Si(2)–tetrahedron	
Si(2)–O(2)	1·63 ± 0·02
Si(2)–O(2′)	
Si(2)–O(8)	1·66 ± 0·02
Si(2)–O(10)	1·65 ± 0·02
Average	1·65
O(2) –O(2′)	2·73 ± 0·06
O(2) –O(8)	2·64 ± 0·02
O(2′)–O(8)	
O(2) –O(10)	2·73 ± 0·02
O(2′)–O(10)	
O(8) –O(10)	2·61 ± 0·03
Si(3)–tetrahedron	
Si(3)–O(3)	1·63 ± 0·02
Si(3)–O(3′)	
Si(3)–O(6$^{\mathrm{iv}}$)	1·67 ± 0·02
Si(3)–O(9$^{\mathrm{iv}}$)	1·65 ± 0·02
Average	1·65
O(3) —O(3′)	2·62 ± 0·06
O(3) —O(6$^{\mathrm{iv}}$)	2·67 ± 0·02
O(3′)—O(6$^{\mathrm{iv}}$)	
O(3) —O(9$^{\mathrm{iv}}$)	2·79 ± 0·02
O(3′)—O(9$^{\mathrm{iv}}$)	
O(6$^{\mathrm{iv}}$)–O(9$^{\mathrm{iv}}$)	2·58 ± 0·03

Table 3 (*cont.*)

	Distances
Al, Mg, Fe–octahedron	
Al, Mg, Fe–O(2)	2·04 ± 0·01
Al, Mg, Fe–O(2$^{\mathrm{iv}}$)	
Al, Mg, Fe–O(9)	2·03 ± 0·01
Al, Mg, Fe–O(9$^{\mathrm{iv}}$)	
Al, Mg, Fe–O(11)	1·90 ± 0·01
Al, Mg, Fe–O(11$^{\mathrm{iv}}$)	
Average	1·99
O(2)—O(9)	2·85 ± 0·02
O(2$^{\mathrm{iv}}$)–O(9$^{\mathrm{iv}}$)	
O(2)—O(9$^{\mathrm{iv}}$)	2·92 ± 0·02
(2$^{\mathrm{iv}}$)–O(9)	
O(2)—O(11)	2·78 ± 0·02
O(2$^{\mathrm{iv}}$)–O(11$^{\mathrm{iv}}$)	
O(2)—O(11$^{\mathrm{iv}}$)	2·81 ± 0·02
O(2$^{\mathrm{iv}}$)–O(11)	
O(9)—O(11)	2·60 ± 0·02
O(9$^{\mathrm{iv}}$)–O(11$^{\mathrm{iv}}$)	
O(9)—O(11$^{\mathrm{iv}}$)	2·96 ± 0·01
O(9$^{\mathrm{iv}}$)–O(11)	
Al–octahedron	
Al″–O(1)	1·84 ± 0·01
Al″–O(3″)	1·87 ± 0·01
Al″–O(4″)	2·04 ± 0·02
Al″–O(5″)	1·93 ± 0·02
Al″–O(6)	1·94 ± 0·02
Al″–O(7)	1·89 ± 0·02
Average	1·92
O(1)—O(4″)	2·70 ± 0·02
O(1)—O(5″)	2·71 ± 0·03
O(1)—O(6)	2·72 ± 0·03
O(1)—O(7)	2·57 ± 0·02
O(3″)–O(4″)	2·75 ± 0·02
O(3″)–O(5″)	2·65 ± 0·03
O(3″)–O(6)	2·71 ± 0·03
O(3″)–O(7)	2·72 ± 0·02
O(4″)–O(5″)	2·96 ± 0·01
O(4″)–O(7)	2·53 ± 0·03
O(5″)–O(6)	2·55 ± 0·03
O(6)—O(7)	2·96 ± 0·01

	Distances
Ca(1)–polyhedron	
Ca(1)–O(2)	2·43 ± 0·02
Ca(1)–O(2$^{\mathrm{v}}$)	
Ca(1)–O(3)	2·41 ± 0·02
Ca(1)–O(3$^{\mathrm{v}}$)	
Ca(1)–O(4)	2·39 ± 0·02
Ca(1)–O(8‴)	2·52 ± 0·02
Ca(1)–O(11)	2·32 ± 0·02
Average	2·42
Ca(2)–polyhedron	
Ca(2)–O(1)	2·34 ± 0·02
Ca(2)–O(1$^{\mathrm{v}}$)	
Ca(2)–O(2)	2·37 ± 0·02
Ca(2)–O(2$^{\mathrm{v}}$)	
Ca(2)–O(6)	2·80 ± 0·02
Ca(2)–O(9)	2·50 ± 0·02
Ca(2)–O(10‴)	2·40 ± 0·02
Average	2·44
Ca(1‴)–Si(1)	3·10 ± 0·01
Ca(1)—Si(2)	3·46 ± 0·01
Ca(1)—Si(3)	3·63 ± 0·01
Ca(2)—Si(1)	3·37 ± 0·01
Ca(2)—Si(2)	3·47 ± 0·01
Ca(2)—Si(3$^{\mathrm{iv}}$)	3·36 ± 0·01

The observed and calculated structure factors are shown in Table 1 and the coordinates of the atoms in Table 2.

Description of the structure

The crystal structure of pumpellyite (see Fig. 1) is characterized by the presence of cation–oxygen coordination octahedra which share edges to form chains parallel to **b**. There are two symmetrically independent chains: in the first, the coordinating cations are Al (50%), Mg(35%) and Fe (15%), in the second only Al atoms are present. In the unit cell there are two symmetrically equivalent chains of the first type, and four of the second type. All magnesium and iron ions were set at the centres of the first chains, going through the point (*a*/2, *c*/4), because such distributions gave the lowest sum of $|F_o - F_c|^2$. Bond distances in the chains (see Table 3) are quite normal, with an average value of 1·99 Å in the first, and of 1·92 Å in the second. The O–O distances are also normal, with an average of 2·80 Å; smallest O–O distances were measured for the pairs O(5″)–O(6), 2·55; O(7)–O(4″), 2·53; O(11)–O(9), 2·60 Å. In each of these pairs the first oxygen atom is not bound to the silicon atom, and this fact strongly supports the hypothesis that the unbound oxygen atoms are in fact hydroxyl groups (or even water molecules), so that these three distances are shortened as a result of the presence of a hydrogen atom (see Fig. 2).

All the other oxygen atoms are also coordinated by silicon atoms, to form both double tetrahedra, Si_2O_7 [with Si(1) and Si(2)], and isolated tetrahedra, SiO_4

Table 4. *Bond angles with their standard errors*

Superscripts refer to the symmetry code of Table 3.

	Bond angle		Bond angle		Bond angle
O(1)—Si(1)–O(1′)	109·3 ± 1·5°	O(2) –Si(2)–O(2′)	113·6 ± 1·3°	O(3) —Si(3)–O(3′)	106·7 ± 1·4°
O(1)—Si(1)–O(4‴)	111·2 ± 0·7	O(2) –Si(2)–O(8)	106·6 ± 0·7	O(3) —Si(3)–O(6^{iv})	107·9 ± 0·7
O(1′)—Si(1)–O(4‴)		O(2′)–Si(2)–O(8)		O(3′)—Si(3)–O(6^{iv})	
O(1)—Si(1)–O(8)	110·5 ± 0·7	O(2) –Si(2)–O(10)	112·4 ± 0·7	O(3) —Si(3)–O(9^{iv})	115·9 ± 0·7
O(1′)—Si(1)–O(8)		O(2′)–Si(2)–O(10)		O(3′)—Si(3)–O(9^{iv})	
O(4‴)–Si(1)–O(8)	103·9 ± 1·0	O(8) –Si(2)–O(10)	104·4 ± 1·0	O(6^{iv})–Si(3)–O(9^{iv})	102·0 ± 1·0
Average	109·4°	Average	109·3°	Average	109·4°
Si(1) —O(8)–Si(2)	133·5 ± 1·2°				

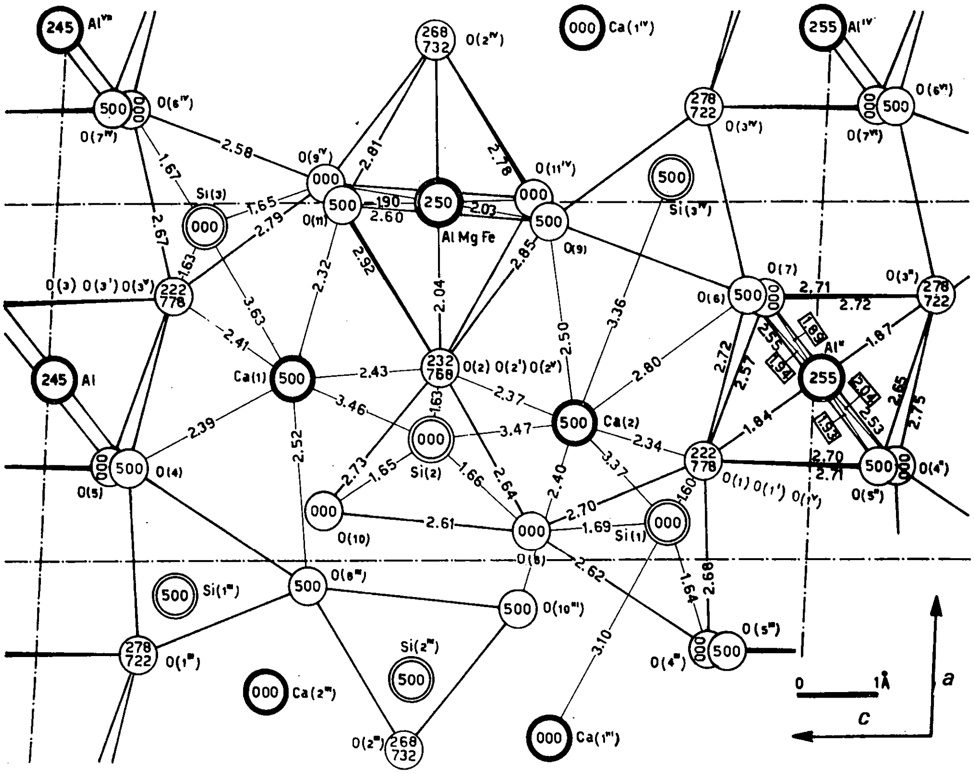

Fig. 2. A projection of the structure on the *xz* plane. Numbers inside the circles give the heights of the atoms in thousandths of the cell edge. The bond lengths are also shown.

[with Si(3)]. Most Si–O bond distances are normal, with an average value of 1·65 Å. Also the O–Si–O bond angles (see Table 4) are quite normal with an average value of 109°4′. The Si(1)–O(8)–Si(2) bond angle is 133°. In the tetrahedron containing Si(1) there is some deviation from the normal value: the Si(1)–O(8) distance is somewhat higher (1·69–0·02 Å) and Si(1)–O(1) lower (1·60 ± 0·03 Å).

The experimental error alone seems an inadequate explanation for this deviation. To obtain a regular tetrahedron around Si(1) it would be necessary to admit a 2σ error in both Si–O distances, and this is highly improbable. We think that the rather short distance Ca(1‴)–Si(1) (3·10 Å), the shortest distance Ca–Si in this structure, could explain the shortening of the Si(1)–O(1) bond. It should be noted also that the distance Al″–O(1) is the shortest of its kind (see Fig. 2). Besides, a lateral shift of Si(1) towards O(8) would be prohibited by two atoms Ca(2) and by Ca(1‴).

The coordination of seven oxygen atoms around the calcium atoms is quite simple: Ca(1) is at the centre of a square [O(2), O(2^{v}), O(3), O(3^{v})] parallel to **b**; two other oxygen atoms, O(4) and O(8‴), lie close to the calcium atom at one side, and one oxygen atom, O(11), at the other.

The same situation holds for Ca(2); it is placed in a square [O(1), O(1^{v}), O(2), O(2^{v})] with two oxygen atoms at one side [O(6), O(9)], and one at the other [O(10″)].

The 14 Ca–O distances average 2·43 ± 0·12 Å which is smaller than usual.

It is worth noting that, although the whole refinement was carried out with isotropic temperature factors, some trials with difference syntheses revealed qualitatively strong anisotropic movements of calcium atoms in the direction normal to the coordination square. The low precision of intensity measurement mentioned above discouraged us from attempting any quantitative measurement of this anisotropic temperature factor.

This work was made possible through financial support of Centro Nazionale di Cristallografia del C.N.R., Roma. The authors would like to thank Professor Glauco Gottardi for assistance and for a critical review of the manuscript.

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The Crystal and Molecular Structure of μ-Oxobis[bis(diethyldithiophosphato)oxomolybdenum(V)] 1,2-Dichlorobenzene, $Mo_2O_3[S_2P(OC_2H_5)_2]_4.2C_6H_4Cl_2$

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(*Received* 13 *January* 1969)

$Mo_2O_3[S_2P(OC_2H_5)_2]_4.2C_6H_4Cl_2$ crystallizes in space group $P\bar{1}$ with $a = 11·36 \pm 0·01$, $b = 13·96 \pm 0·01$, $c = 8·66 \pm 0·01$ Å, $\alpha = 94·9 \pm 0·2°$, $\beta = 103·8 \pm 0·2°$, $\gamma = 81·7 \pm 0·2°$ and with $Z = 1$. Least-squares refinement with anisotropic temperature factors gave an R index of 0·117 for 3200 non-zero photographic data. The diamagnetic binuclear molecule consists of two distorted octahedra which share a linear bridging oxygen atom situated at an inversion centre. The molybdenum to bridging oxygen atom bond length is 1·863 Å and to the terminal oxygen atom, 1·647. The Mo–S bond *trans* to the terminal oxygen atom is 2·801 Å and the other Mo–S bonds have a mean length of 2·496 Å.

Introduction

Oxidation of square-pyrimidal $MoO(S_2P(OC_2H_5)_2]_2$ (Jowitt & Mitchell, 1966) gives $Mo_2O_3[S_2P(OC_2H_5)_4]_4$, the structure of which we now report.

Experimental

A compound with the formulation $MoO(dtp)_2$, where $dtp = S_2P(OC_2H_5)_2$, diethyldithiophosphate anion was supplied by R. N. Jowitt and P. C. H. Mitchell of Reading University. Recrystallization under nitrogen with 1,2-dichlorobenzene produced ligth-brown transparent crystals. When dried in air they became opaque and

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