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The Crystal Structure of Phosphoric Acid Hemihydrate, $H_3PO_4 . \frac{1}{2}H_2O$

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The crystal structure of phosphoric acid hemihydrate, $H_3PO_4.\frac{1}{2}H_2O$, was determined from three-dimensional Weissenberg data. Its crystals are monoclinic, with $a=7·922 \pm 0·010$, $b=12·987 \pm 0·020$, $c=7·470 \pm 0·010$ Å, $\beta=109·9 \pm 0·1$°, space group $P2_1/a$, and $Z=8$. The structure was solved by vector methods and was then refined by full-matrix least-squares analysis. The two crystallographically independent phosphoric acid molecules are geometrically very similar to each other. Each is approximately tetrahedral with the P–O bond length significantly shorter than the P–OH bonds. Each phosphoryl oxygen atom, moreover, is the acceptor in two strong hydrogen bonds. The phosphoric acid and water molecules are linked into a three-dimensional network by hydrogen bonding, with each oxygen atom participating in at least one relatively strong intermolecular hydrogen bond.

Experimental

Orthophosphoric acid crystallizes in an anhydrous form, H_3PO_4, and as a hemihydrate, $H_3PO_4.\frac{1}{2}H_2O$. The crystal structure of the anhydrous form has been reported by Furberg (1955) and by Smith, Brown & Lehr (1955). Orthophosphoric acid is commercially important and the orthophosphate ion is of great biological significance. Thus the crystal structure of the hemihydrate was determined to provide more information about hydrogen bonding in orthophosphates and to learn more about the bond lengths in the PO_4 group. Crystallographic data extant on $H_3PO_4.\frac{1}{2}H_2O$ are the unit-cell constants and morphological and optical properties reported by Smith, Brown & Lehr (1955) and the X-ray powder pattern by Lehr, Brown, Frazier, Smith & Thrasher (1967).

Introduction

Phosphoric acid hemihydrate was triply crystallized from reagent-grade phosphoric acid. Because of its chemical reactivity and hygroscopic character, the X-ray data were collected from a single crystal grown in a thin-walled glass capillary. The space group and preliminary unit-cell dimensions were determined from a set of Weissenberg photographs. The final cell dimensions were calculated by least-squares refinement of powder pattern data ($\lambda=1·5418$). The powder pattern was taken on a powder diffractometer and the sample was enclosed in an air-tight water-free container. The density was determined by flotation in a mixture of ethylene dibromide and chloroform. These data are reported in Table 1.

Table 1. *Crystal data for* $H_3PO_4.\frac{1}{2}H_2O$

$a=7·922 \pm 0·010$ Å*	Space group $P2_1/a$
$b=12·987 \pm 0·020$	$Z=8$
$c=7·470 \pm 0·010$	$\varrho_c=1·97$ g.cm^{-3}
$\beta=109·9 \pm 0·10$°	$\varrho_o=1·99$ g.cm^{-3}

* The errors in the cell parameter are the standard errors obtained from a least-square refinement of these parameters using twenty experimental 2θ values.

For intensity data, a crystal was grown from its melt in a capillary of diameter 0·30 mm. The *a* axis of the crystal was parallel to both the length of the capillary and to the rotation axis of the camera. Eight levels of integrated data, with three films per level, were collected (using Cu $K\alpha$ radiation) by the equi-inclination Weissenberg method. The intensities were measured on a densitometer; however, those too weak to be accurately measured were estimated by the eye against a standard strip. The data were corrected for absorption (cylindrical correction), spot extension, Lorentz and polarization factors. Equivalent spots were averaged. Of 1390 unique reflections on the films, 1085 were considered to be observed. Reflections which were difficult to determine accurately were considered as unobserved and are indicated by an asterisk in Table 4.

Determination and refinement

A three-dimensional Patterson map was calculated from the observed data. Analysis of the large peaks in

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the Patterson map revealed the electron-density coordinates for the two independent phosphorus atoms. Vector techniques, similar to those outlined in a paper on vector verification (Mighell & Jacobson, 1964) were then used to locate the remaining nine oxygen atoms in the asymmetric unit.

Full-matrix isotropic least-squares refinement on all atoms except the hydrogen atoms was carried out on the trial model using scattering factors for neutral phosphorus, and singly negative oxygen from *International Tables for X-ray Crystallography* (1962). The quantity minimized was $\Sigma\, w(F_o - F_c)^2$ with the following weighting scheme: $w=1$ for $|F_o|<26$ and $w=26/F_o$ for $|F_o|>26$. Unobserved reflections were given zero weight in the refinement unless the value of F_c exceeded that of F_o. The reflections for which this occurred were given unit weight. The trial model refined readily.

As a result of this refinement the agreement factor

$$R=\Sigma\, ||F_o|-|F_c||/\,\Sigma\, |F_o|\;,$$

based on 1074 observed reflections, was 8·7%. The resulting atomic positional and thermal parameters are given in Table 2. The thermal parameters are unexpectedly low, as the intensity data were taken at room temperature which is only slightly below the melting point of this compound (29·3 °C). The explanation for this fact is probably related to the strong hydrogen bonding discussed later.

In general, the R values for the various subsets of reflections were low. However, a number of F_o's (with large I_o's, low $\sin\theta/\lambda$, and occurring near the rotation axis) were considerably lower in magnitude than the corresponding calculated structure factors. This effect is almost certainly caused by extinction. Two additional cycles of refinement were carried out excluding these reflections (marked by an 'E' in Table 4). Although the R value decreased to 7·5%, no significant changes in atomic parameters were noted.

After the isotropic refinement, a difference-Fourier (F_o-F_c) synthesis was calculated. Analysis of the resultant map revealed tentative positions for two of the three OH-hydrogen atoms for each crystallographically independent H_3PO_4 molecule. All four of these hydrogen atoms are involved in strong hydrogen bonding (average $-$O...O$-$ separation of 2·58 Å) to the phosphoryl type oxygen atoms (*i.e.* oxygen atoms without hydrogens) of neighboring molecules. Selection of atoms O(1) and O(5) as the phosphoryl oxygens is based primarily on their short P–O bond distances (Table 3) and is substantiated by the locations of these four hydrogen atoms.

The hydrogen atoms near the water oxygen atom were obscured by a few spurious peaks and by poor resolution. In part, this lack of resolution may be attributable to the extinction in some low order reflections and to errors in the absorption correction introduced by the assumption of a cylindrical crystal. However, the approximate locations of two hydrogen atoms

Table 2. *Atomic parameters for phosphoric acid hemihydrate*

	X/a	Y/b	Z/c	B
P(1)	0·44526 (20)*	0·39800 (10)	0·25203 (18)	0·86 (3)
O(1)	0·59475 (60)	0·36947 (31)	0·43166 (58)	1·72 (7)
O(2)	0·44726 (61)	0·33646 (34)	0·07428 (60)	2·03 (8)
O(3)	0·25746 (68)	0·38271 (34)	0·26803 (64)	2·18 (8)
O(4)	0·45885 (58)	0·51288 (29)	0·19678 (56)	1·53 (7)
P(2)	0·58025 (19)	0·13649 (9)	0·64062 (18)	0·80 (3)
O(5)	0·74440 (58)	0·10139 (32)	0·60719 (57)	1·69 (7)
O(6)	0·54629 (58)	0·07118 (30)	0·79738 (58)	1·60 (7)
O(7)	0·42137 (61)	0·12621 (31)	0·44902 (60)	1·82 (8)
O(8)	0·58611 (56)	0·24968 (31)	0·71008 (56)	1·55 (7)
O(9)	0·86427 (60)	0·36588 (32)	0·01954 (58)	1·81 (8)

* The numbers in parentheses are standard errors (from least-squares) in the last significant figures.

Table 3. *Bond distances and angles*

H_3PO_4 (*A*)		H_3PO_4 (*B*)	
P(1)–O(1)	1·503 (4) Å	P(2)–O(5)	1·477 (5) Å
P(1)–O(2)	1·554 (5)	P(2)–O(6)	1·542 (5)
P(1)–O(3)	1·545 (6)	P(2)–O(7)	1·557 (5)
P(1)–O(4)	1·561 (5)	P(2)–O(8)	1·554 (5)
O(1)–P(1)–O(2)	113·7 (3) °	O(5)–P(2)–O(6)	110·5 (3) °
O(1)–P(1)–O(3)	112·7 (3)	O(5)–P(2)–O(7)	107·5 (3)
O(1)–P(1)–O(4)	111·6 (2)	O(5)–P(2)–O(8)	114·9 (3)
O(2)–P(1)–O(3)	106·9 (3)	O(6)–P(2)–O(7)	110·8 (3)
O(2)–P(1)–O(4)	104·1 (3)	O(6)–P(2)–O(8)	105·0 (3)
O(3)–P(1)–O(4)	107·3 (3)	O(7)–P(2)–O(8)	108·1 (2)

The numbers in parentheses are the standard errors in the last significant figure.

Table 4. *Observed and calculated structure factors for* $H_3PO_4.\frac{1}{2}H_2O$

The columns are l, $10F_o$ and $10F_c$, respectively. Unobserved reflections are indicated with * and reflections affected by extinction are indicated by E.

0,K,0		
2	207	187
4	1044E	-1726
6	245	-222
8	1015	1010
10	72*	20
12	82	-115
14	63*	-6
0,K,1		
0	461	-522
1	31	44
2	72	65
3	372	-408
4	476	541
5	507	513
6	264	245
7	227	239
8	394	-408
9	303	300
10	72*	4
11	286	-302
12	222	218
13	180	-195
14	61*	-31
15	111	125
16	84	-83
0,K,2		
0	571E	-616
1	415	-466
2	345	-333
3	96	50
4	346	-302
5	320	325
6	516	558
7	121	115
8	123	-106
9	223	-190
10	269	-290
11	126	104
12	197	-176
13	83	64
14	177	183
15	47*	-28
0,K,3		
0	377	367
1	111	-87
2	434	-426
3	450	453
4	422	-427
5	99	-72
6	64*	3
7	433	-414
8	340	319
9	258	-243
10	240	-209
11	319	307
12	140	-129
13	112	126
0,K,4		
0	299	294
1	117	95
2	135	102
3	195	-190
4	66*	-11
5	155	-132
6	367	-342
7	248	-226
8	74*	56
9	251	242
10	260	276
11	68*	10
12	113	100
13	148	-152
14	232	-245
0,K,5		
0	301	304
1	643	-655
2	298	296
3	629	-663
4	219	-202
5	541	528
6	74*	50
7	395	389
8	91	71
9	221	-225
10	65*	57
11	196	-214
12	96	-75
13	81	80
0,K,6		
0	312	-272
1	220	215
2	74*	-29
3	435	422
4	238	243
5	216	-205
6	228	226
7	111	-98
8	65*	-37
9	102	105
10	222	-249
11	139	123
12	63	-65
0,K,7		
0	123	-117
1	71	63
2	70	-79
3	117	125
4	90	84
5	96	98
6	182	-169
7	113	-99
8	57	39
9	122	-110
10	69	73
0,K,8		
0	170	177
1	77	-81
2	52*	16
3	159	-164
4	277	-287
5	149	136
6	123	-117
7	30*	12
1,K,0		
1	80	133
2	534E	611
3	271	281
4	272	248
5	319	255
6	221	-213
7	75	-67
8	248	-245
9	221	209
10	73*	-20
11	442	482
12	101	104
13	95	-91
14	62*	43
15	371	-393
1,K,1		
1	197	225
2	905E	-1254
3	137	-133
4	284	-275
5	163	138
6	554	593
7	213	201
8	263	263
9	102	87
10	95	-80
11	83	85
12	73*	17
13	68*	-41
14	60*	22
15	108	-94
1,K,2		
1	45*	40
2	450	-447
3	328	-329
4	119	-135
5	57*	32
6	167	128
7	104	93
8	236	222
9	254	-298
10	152	125
11	252	-243
12	103	-100
13	141	140
14	56*	-4
15	190	199
1,K,3		
1	720	-719
2	340	343
3	441	458
4	362	374
5	358	376
6	237	-230
7	547	-564
8	403	-409
9	406	-411
10	74*	55
11	226	217
12	220	222
13	99	94
14	48*	21
15	126	-126
1,K,4		
1	400	417
2	248	-234
3	266	-280
4	211	231
5	435	-413
6	197	164
7	99	86
8	257	-271
9	272	268
10	190	-170
11	65*	42
12	65	72
13	102	-98
1,K,5		
1	72*	57
2	73*	-42
3	92	82
4	76	-85
5	74*	13
6	74*	-48
7	73*	71
8	200	177
9	194	167
10	104	94
11	79	68
12	234	-251
1,K,6		
1	416	-432
2	288	-319
3	395	411
4	72*	-48
5	396	414
6	196	179
7	149	-137
8	70	63
9	153	-156
10	47*	-7
11	37	50
1,K,7		
1	65*	41
2	108	95
3	64	-64
4	141	119
5	67	-81
6	54*	-58
7	48*	33
8	164	-171
1,K,8		
1	46*	42
2	259	279
3	42*	13
4	39*	-2
5	169	-182
6	174	-198
1,K,-1		
1	235	233
2	707E	838
3	318	-337
4	93	101
5	99	79
6	320	-299
7	279	270
8	190	-173
9	138	-121
10	100	-84
11	224	-196
12	73*	-20
13	112	104
14	62*	-9
15	145	150
1,K,-2		
1	765E	-835
2	833E	-961
3	303	298
4	50	-43
5	428	445
6	668	735
7	377	-342
8	81	-53
9	505	-534
10	485	-507
11	96	-89
12	91	75
13	154	157
14	190	187
15	118	114
16	143	-150
1,K,-3		
1	361	344
2	130	104
3	239	-217
4	412	-422
5	550	-556
6	134	-92
7	255	-234
8	466	463
9	198	195
10	203	174
11	168	152
12	208	-216
13	112	-141
14	60	-71
15	126	-137
1,K,-4		
1	153	141
2	60*	-28
3	62*	-22
4	123	-80
5	154	-122
6	69*	29
7	168	141
8	74*	25
9	241	212
10	73*	42
11	70*	-5
12	187	173
13	55*	-27
14	107	85
1,K,-5		
1	270	-256
2	69*	12
3	351	341
4	268	251
5	289	309
6	136	120
7	74*	6
8	364	-351
9	72*	22
10	217	-222
11	62*	41
12	265	292
1,K,-6		
1	249	-195
2	93	97
3	244	206
4	76	-94
5	191	158
6	92	-83
7	73	-58
8	204	159
9	65	-73
10	57*	23
11	50	-41
12	252	-271
1,K,-7		
1	193	183
2	453	-440
3	220	-216
4	69*	-23
5	261	-256
6	303	303
7	86	86
8	54*	21
9	77	61
10	139	-162
1,K,-8		
1	59*	-4
2	80	55
3	100	93
4	100	78
5	136	-152
6	74	-70
7	239	-261
8	107	-115
2,K,0		
0	646E	1110
1	124	-114
2	98	101
3	268	255
4	81	-102
5	273	-255
6	123	104
7	79	-33
8	211	185
9	295	-310
10	83	-74
11	177	171
12	98	79
13	197	205
14	57	59
15	46	-59
16	30*	14
2,K,1		
0	937E	1192
1	587	591
2	145	133
3	66	58
4	162	-144
5	286	-271
6	235	-212
7	93	81
8	173	132
9	523	559
10	121	115
11	200	-176
12	211	191
13	352	-350
14	91	-103
15	80	70
16	46	-59
2,K,2		
0	417	-457
1	209	212
2	108	-83
3	125	115
4	54*	7
5	210	213
6	299	310
7	64*	5
8	253	-249
9	89	88
10	69*	-49
11	69	-61
12	63*	-19
13	57*	-17
14	46*	-1
15	35*	15
2,K,3		
0	323	-321
1	374	-360
2	345	-338
3	59*	29
4	129	-147
5	108	107
6	356	364
7	68*	52
8	69*	11
9	273	-260
10	318	-323
11	127	102
12	157	-145
13	104	111
14	172	173
2,K,4		
0	328	345
1	429	407
2	72	-87
3	420	407
4	108	-125
5	449	-465
6	253	-248
7	399	-439
8	111	107
9	245	250
10	100	112
11	192	207
12	105	106
13	175	-180
2,K,5		
0	133	123
1	246	-246
2	156	172
3	364	-386
4	69*	38
5	234	251
6	98	-114
7	82	67
8	62*	-36
9	58*	-32
10	146	174
11	118	-92
12	74	65
2,K,6		
0	118	119
1	83	-87
2	67	80
3	65*	-43
4	130	-115
5	61*	-0
6	208	206
7	131	129
8	113	84
9	101	94
10	135	-146
2,K,7		
0	181	-211
1	159	175
2	71	-63
3	293	324
4	164	182
5	104	-92
6	41*	-1
7	124	-137
2,K,-1		
0	918E	-1141
1	345E	478
2	190	157
3	229	269
4	365	384
5	541	-607
6	170	154
7	235	-228
8	494	-526
9	66*	-3
10	172	145
11	78	75
12	135	130
13	79	71
14	67	-68
15	45*	-16
16	110	-104
2,K,-2		
0	276	-281
1	400	455
2	439	-486
3	411	-447
4	326	-345
5	282	-260
6	262	237
7	201	189
8	210	212
9	458	467
10	305	-304
11	301	-292
12	238	-268
13	228	-239
14	146	135
15	43*	20
16	101	127
2,K,-3		
0	137	-60
1	191	181
2	240	-234
3	270	254
4	173	143
5	57	62
6	311	-299
7	235	193
8	123	90
9	94	-80
10	69*	33
11	76	-46
12	64*	59
13	68	62
14	146	-137
15	37*	4
2,K,-4		
0	116	-83
1	257	231
2	459	461
3	447	464
4	197	197
5	297	-260
6	403	-385
7	67*	10
8	239	-218
9	69*	35
10	435	449
11	73	81
12	175	178
13	52*	-33
14	195	-197
15	110	103
2,K,-5		
0	62*	-30
1	272	254
2	201	172
3	66	54
4	66*	39
5	151	-125
6	291	281
7	253	-220
8	74	68
9	105	91
10	207	-209
11	58*	40
12	181	-167
13	42	49
14	324	322
2,K,-6		
0	322	-301
1	222	-262
2	70	-70
3	326	-316
4	330	330
5	138	130
6	111	-87
7	67*	40
8	64*	-46
9	61	-72
10	55*	-23
11	53	-53
12	37*	27
2,K,-7		
0	198	-176
1	68*	-23
2	68*	-44
3	67*	21
4	66*	31
5	263	-231
6	224	-200
7	123	103
8	53*	-36
9	220	211
10	170	153
2,K,-8		
0	103	105
1	59	52
2	57*	26
3	184	178
4	235	-252
5	123	104
6	46*	16
7	121	-116
8	48	68
2,K,-9		
0	136	-146
1	37*	4
2	36*	39
3	33*	22
4	200	213
5	150	175
3,K,0		
1	294	304
2	93	50
3	105	-119
4	60	-40
5	55*	3
6	75	69
7	207	188
8	69*	5
9	162	158
10	180	-182
11	120	101
12	125	-106
13	64*	-32
14	66	78
15	106	-107
3,K,1		
1	132	152
2	62	29
3	124	100
4	67	-51
5	106	91
6	64*	32
7	68*	-35
8	72*	34
9	189	164
10	75*	4
11	359	358
12	59	83
13	62	-49
14	51*	14
15	309	-303
3,K,2		
1	265	248
2	603	-641
3	516	-524
4	180	-179
5	66*	20
6	348	361
7	490	498
8	231	217
9	166	-137
10	74*	-32
11	416	-415
12	64*	-5
13	97	81
14	44	39
3,K,3		
1	219	-181
2	295	294
3	68*	25
4	70*	15
5	104	85
6	251	-260
7	239	-233
8	75*	3
9	251	-264
10	169	185
11	63*	42
12	55*	-17
13	73	73
14	36	-51
3,K,4		
1	167	150
2	165	-152
3	189	-172
4	276	316
5	185	-173
6	181	179
7	73*	-15
8	389	-418
9	66*	30
10	234	-247
11	52*	26
12	238	243
3,K,5		
1	199	187
2	170	-173
3	130	-122
4	72*	-26
5	102	-88
6	91	78
7	129	143
8	80	66
9	99	109
10	45*	-19
3,K,6		
1	67	-79
2	65*	-43
3	118	127
4	68	-63
5	118	125
6	54*	-33
7	48*	10
8	104	111
9	31	39
3,K,7		
1	142	-144
2	220	-251
3	71	77
4	96	100
5	117	148
3,K,-1		
1	175E	279
2	602	655
3,K,-1		
3	531	-583
4	161	173
5	122	-114
6	191	-193
7	437	456
8	291	-283
9	166	-144
10	171	-166
11	477	-512
12	155	136
13	81	67
14	77	55
15	376	379
3,K,-2		
1	370	-404
2	393	-426
3	288	306
4	265	-258
5	55*	-22
6	311	311
7	547	-557
8	263	230
9	237	-222
10	168	-147
11	186	183
12	102	-83
13	64*	36
14	54*	23
15	100	-98
3,K,-3		
1	328	342
2	103	90
3	346	-356
4	384	-396
5	403	-391
6	156	-141
7	223	223
8	434	449
9	229	218
10	254	249
11	158	-157
12	170	-188
13	87	-76
14	62	-76
15	73	75
3,K,-4		
1	111	119
2	59*	3
3	89	81
4	218	218
5	75	-58
6	120	99
7	163	135
8	303	-309
9	271	249
10	162	-133
11	69*	27
12	331	354
13	74	-51
14	213	214
3,K,-5		
1	123	-110
2	88	90
3	225	202
4	115	88
5	182	170
6	74*	-39
7	76	62
8	108	-89
9	90	58
10	68*	-45
11	62*	-39
12	54*	-23
13	70	-56
3,K,-6		
1	92	-77
2	173	166
3	75*	-31
4	91	-67
5	75*	66
6	181	-167
7	135	105
8	145	131
9	141	-137
10	115	112
11	240	-230
12	255	-254
3,K,-7		
1	245	218
2	516	-498
3	158	-154
4	71*	33
5	367	-353
6	348	336
7	144	-113
8	77	-62
9	128	129
10	169	-167
11	83	68
3,K,-8		
1	63*	-26
2	249	262
3	61*	32
4	58*	23
5	55*	-39
6	255	-246
7	92	-94
8	37*	-13
3,K,-9		
1	43*	19
2	74	82
3	108	-100
4	76	77
5	107	108
4,K,0		
0	39*	-6
1	114	-126
2	276	309
3	145	113
4	57	77
5	62	-83
6	184	-162
7	120	-96
8	189	-187
9	421	-405
10	320	305
11	193	172
12	137	136
13	310	314
14	137	-143
15	75	-83
4,K,1		
0	817E	969
1	53*	29
2	57	63
3	59*	15
4	236	-251
5	127	-111
6	81	-74
7	159	159
8	337	316
9	76*	36
10	74*	-27
11	71	-78
12	63*	35
13	55	-44
14	41*	24
4,K,2		
0	424	-414
1	83	94
2	65*	2
3	239	-236
4	461	460
5	72*	73
6	74*	-16
7	222	235
8	340	-358
9	302	306
10	79	63
11	214	-228
12	246	240
13	178	-186
14	100	-98
4,K,3		
0	363	-390
1	72*	-9
2	140	-129
3	164	151
4	75*	-10
5	170	170
6	239	262
7	109	-93
8	149	-141
9	199	-212
10	129	-133
11	113	106
12	111	-85
13	181	186
4,K,4		
0	130	127
1	76*	55
2	139	-155
3	208	207
4	174	-174
5	185	-190
6	73	61
7	140	-146
8	104	114
9	58*	-22
10	115	-107
11	113	123
4,K,5		
0	72	84
1	71*	-23
2	88	90
3	111	-128
4	118	114
5	64*	-32
6	269	-284
7	55*	-35
8	86	-95
9	77	92
4,K,6		
0	56*	19
1	140	-184
2	61	72
3	187	-213
4	49*	20
5	147	192
6	114	128
7	85	96
4,K,-1		
0	857E	-976
1	332	395
2	140	-157
3	100	-107
4	295	304
5	347	-334
6	297	279
7	141	-116
8	247	-239
9	304	266
10	174	-156
11	75	-83
12	94	-93
13	98	-91
14	80	90
4,K,-2		
0	384	-395
1	117	118
2	361	-379
3	136	-115
4	165	165
5	90	84
6	64*	-55
7	196	170
8	100	91
9	84	76
10	243	-227
11	187	-159
12	73	-60
13	60*	-38
14	50	57
4,K,-3		
0	46*	40
1	519	-579
2	243	215
3	272	-225
4	59*	52
5	417	379
6	553	-504
7	536	509
8	74*	-50
9	322	-309
10	425	410
11	137	-119
12	153	131
13	119	115
14	280	-283
4,K,-4		
0	59*	-11
1	520	523
2	378	373
3	572	559
4	66*	19
5	345	-315
6	72*	-4
7	405	-395
8	76*	-35
9	181	161
10	160	145
11	211	292
12	61	-64
13	50*	-25
14	94	77
4,K,-5		
0	115	-108
1	202	-185
2	70*	14
3	291	-294
4	223	223
5	284	289
6	130	130
7	156	-121
8	75*	20
9	209	-193
10	202	-203
11	60*	18
12	51*	-38
13	219	224
4,K,-6		
0	442	-414
1	357	-352
2	120	-125
3	352	-343
4	382	347
5	76*	13
6	121	-114
7	241	240
8	145	-116
9	64*	47
10	57*	29
11	78	-97
12	91	76
4,K,-7		
0	80	65
1	74*	-7
2	74*	7
3	154	132
4	290	-274
5	70*	-37
6	108	-99
7	62*	-4
8	57*	49
9	50*	18
10	144	136
11	23*	20
4,K,-8		
0	238	224
1	64*	-29
2	63*	34
3	63	50
4	249	-235
5	326	297
6	51*	5
7	150	-130
8	85	94
4,K,-9		
0	326	-310
1	43*	52
2	42*	-22
3	39*	49
4	439	444
5,K,0		
1	145	160
2	707E	843
3	204	-171
4	172	149
5	71*	-38
6	436	-450
7	266	248
8	261	-216
9	80*	34
10	77*	29
11	221	-191
12	63*	55
13	51*	21
5,K,1		
1	172	131
2	217	256
3	90	95
4	132	-128
5	76*	-36
6	161	-146
7	80*	-50
8	158	145
9	264	235
10	73*	61
11	282	290
12	116	-106
13	123	-115
5,K,2		
1	256	228
2	542	-525
3	214	-206
4	151	-152
5	85	-92
6	393	384
7	196	189
8	188	176
9	72*	79
10	169	-140
11	57*	-45
12	46*	6
5,K,3		
1	232	-196
2	311	316
3	80*	-56
4	100	-116
5	272	239
6	273	-272
7	86	84
8	184	167
9	302	-319
10	238	227
11	202	-217
5,K,4		
1	77*	-5
2	169	163
3	75*	-19
4	132	128
5	70*	-63
6	98	-95
7	134	-145
8	178	-185
9	46*	-46
10	33*	-9
5,K,5		
1	227	270
2	63*	-56
3	204	-215
4	83	99
5	198	-210
6	49	68
7	111	119
5,K,-1		
1	215	-238
2	92	-107
3	78	70
4	62	-53
5	123	93
6	186	146
7	124	-113
8	79*	-7
9	264	-249
10	184	-171
11	171	-154
12	65*	13
13	97	102
5,K,-2		
1	290	-319
2	142	-118
3	264	254
4	333	-365
5	67*	1
6	72*	18
7	361	-347
8	461	458
9	80*	-74
10	127	115
11	140	117
12	273	-288
13	55*	-28
14	61	-73
5,K,-3		
1	471	553
2	251	240
3	363	-356
4	65*	-21
5	506	-542
6	188	-185
7	266	255
8	80*	26
9	430	432
10	173	176
11	89	-76
12	116	97
13	177	-145
5,K,-4		
1	228	-246
2	127	122
3	325	355
4	189	195
5	269	273
6	78*	-49
7	80*	-41
8	266	-254
9	78*	42
10	74*	-22
11	86	91
12	220	220
5,K,-5		
1	306	-337
2	305	312
3	290	290
4	78*	32
5	316	349
6	260	-238
7	80*	-39
8	77*	24
9	191	-181
10	92	97
11	58*	-64
12	185	-195
5,K,-6		
1	265	240
2	354	-363
3	254	-242
4	82	-88
5	276	-282
6	238	-202
7	74*	62
8	124	129
9	64*	51
10	57	-68
11	92	-112
5,K,-7		
1	78*	-0
2	79	-71
3	76*	44
4	74*	50
5	172	-154
6	68*	4
7	241	-248
8	82	-78
9	69	66
5,K,-8		
1	65*	-29
2	410	405
3	62*	-13
4	61	64
5	56	69
6	337	-324
7	44	50
8	54	-59
5,K,-9		
1	79	-62
2	178	-187
3	37*	-4
6,K,0		
0	652E	-827
1	132	126
2	71*	69
3	98	75
4	501	527
5	122	-111
6	119	107
7	216	-184
8	386	-415
9	110	-101
10	76*	44
11	99	86
12	130	112
13	114	145
6,K,1		
0	766E	840
1	131	-121
2	166	155
3	84*	40
4	471	-510
5	87*	0
6	94	-112
7	86*	35
8	352	350
9	261	-226
10	122	106
11	75	88
12	84	-80
6,K,2		
0	191	224
1	89	79
2	87*	19
3	88*	-68
4	87*	44
5	86*	-50
6	86	-99
7	183	168
8	74*	30
9	199	182
10	57*	33
11	160	-156
6,K,3		
0	339	-378
1	106	-90
2	84*	-71
3	217	-191
4	227	193
5	199	186
6	121	147
7	170	155
8	204	-187
9	50*	-6
6,K,4		
0	73*	-12
1	73*	-37
2	92	-102
3	123	120
4	148	-153
5	93	63
6	154	161
7	107	-86
6,K,5		
0	108	121
1	171	147
2	47*	-14
3	162	153
6,K,-1		
0	46*	-76
1	50*	68
2	202	-231
3	226	-217
4	153	-140
5	80*	0
6	145	129
7	97	78
8	206	194
9	150	135
10	281	-255
11	185	-187
12	208	-209
13	62	-58
6,K,-2		
0	149	163
1	219E	-334
2	77	-95
3	241	-228
4	184	-157
5	228	210
6	214	-218
7	359	362
8	204	193
9	87	-88
10	80*	33
11	104	-103
12	61*	-57
13	46	-35
6,K,-3		
0	53*	-32
1	56*	34
2	255	280
3	283	297
4	76*	21
5	81*	63
6	269	-221
7	89	-84
8	106	-104
9	161	-139
10	296	315
11	104	120
12	58*	56
13	84	103
6,K,-4		
0	269	263
1	293	290
2	121	132
3	213	182
4	133	-130
5	123	-103
6	159	157
7	323	-337
8	152	137
9	139	120
10	152	-137
11	140	124
12	105	-109
6,K,-5		
0	295	-274
1	445	-509
2	122	-137
3	466	-519
4	345	347
5	311	330
6	98	104
7	218	209
8	81*	-38
9	241	-212
10	197	-197
11	82	-108
12	36*	17
6,K,-6		
0	110	83
1	88*	-28
2	88*	-41
3	87*	65
4	264	-211
5	173	-190
6	145	-129
7	77*	38
8	97	86
9	129	140
10	130	140
6,K,-7		
0	281	233
1	82*	46
2	82*	9
3	107	104
4	346	-365
5	107	94
6	69*	14
7	70	-86
8	88	94
6,K,-8		
0	68*	-49
1	67*	4
2	66*	-29
3	65	52
4	143	148
5	215	224
6	58	69
7	116	-117
7,K,0		
1	94*	-29
2	99	112
3	100*	-50
4	103*	48
5	104*	36
6	104*	-24
7	126	114
8	96	-95
9	100	-82
10	100	-100
11	218	-207
7,K,1		
2	412	460
3	116	115
4	104*	45
5	102*	-8
6	306	-274
7	93*	-72
8	85*	-61
9	119	118
10	58*	53
7,K,2		
1	102*	-15
2	182	-176
3	143	118
4	96*	-82
5	92*	24
6	121	134
7	101	-79
8	104	100
9	103	99
7,K,3		
1	90	81
2	158	-138
3	181	-172
4	144	-139
5	73*	-25
6	113	84
7	166	167
7,K,4		
1	248	-228
2	252	272
3	135	137
7,K,-1		
1	350	-395
2	272	-300
3	299	311
4	97*	-65
5	200	171
6	238	219
7	335	-326
8	99*	63
9	214	-189
10	134	-122
11	74	70
7,K,-2		
1	154	198
2	141	152
3	104	-96
4	195	-184
5	342	-333
6	217	-195
7	104*	-65
8	299	266
9	232	217
10	269	259
11	71	65
12	132	-154
7,K,-3		
1	66*	-31
2	105	-116
3	89	100
4	119	143
5	101*	46
6	104*	93
7	104*	34
8	224	-191
9	93*	90
10	82*	-38
11	68*	39
7,K,-4		
1	257	-250
2	93*	86
3	303	303
4	185	181
5	291	276
6	104*	-26
7	102*	-81
8	231	-204
9	88*	-39
10	96	-60
7,K,-5		
1	102*	-27
2	103*	-10
3	104*	-4
4	104*	-87
5	103*	44
6	101*	-57
7	96*	30
8	181	154
7,K,-6		
1	104*	105
2	393	-401
3	102*	-119
4	100*	38
5	197	-179
6	272	266
7,K,-7		
1	94*	-51
2	221	220
3	91	93
4	86*	44
5	80*	-40
6	183	-195
7	187	-226
7,K,-8		
1	71*	-30
2	69*	-3
3	81	-65
4	58*	25

in the vicinity of the water oxygen are strongly indicated by two short separations (2·71 and 2·67 Å) from phosphate OH-oxygen atoms O(2) and O(6) to the water oxygen O(9). The phosphate OH-oxygen atoms are believed to be the donors in these two hydrogen bonds because (1) the water protons are needed to account for the closeness of approach of the five additional oxygens (each at a distance of $\simeq 3$ Å) in the immediate environment of the water molecule, and (2) the –O···O– separation tends to be shorter when the hydroxyl group, rather than water molecule, is the donor in a hydrogen bond (Baur, 1965).

Description of the structure

The asymmetric unit in phosphoric acid hemihydrate contains one water and two phosphoric acid molecules. In the following discussion, the two independent phosphoric acid molecules are referred to as $H_3PO_4(A)$ and $H_3PO_4(B)$; where the phosphorus atoms P(1) and P(2) are in $H_3PO_4(A)$ and $H_3PO_4(B)$ respectively.

The H_3PO_4 *molecules*

The two crystallographically independent phosphoric acid molecules are geometrically very similar to each other. Each is approximately tetrahedral, but in each the P–O bond is significantly shorter than the P–OH bonds. Considering both $H_3PO_4(A)$ and $H_3PO_4(B)$, the average P–O and P–OH bond lengths are 1·490 and 1·552 Å, respectively. The bond angles show small deviations from the tetrahedral angle. Bond angles and distances are listed in Table 3.

The three-dimensional structure

The phosphoric acid and water molecules are linked together into a three-dimensional network by hydrogen bonding. Each of the nine oxygen atoms is involved in at least one relatively strong intermolecular hydrogen bond. Fig. 1 shows a projection of the structure along the *c* axis; the intermolecular (–O···O–) distances less than 2·72 Å are also shown.

Each $H_3PO_4(A)$ molecule is connected by hydrogen bonding with one water and four H_3PO_4 (*B*) molecules (Fig. 1). Specifically, the phosphoryl oxygen atom, O(1), of $H_3PO_4(A)$ is the focus of the strongest hydrogen bonding; it is the acceptor and is linked to OH-oxygen atoms, O(7) and O(8), from two separate H_3PO_4 (*B*) molecules with (–O···O–) distances of 2·55 and 2·62 Å, respectively. The angle formed by these three oxygen atoms, with O(1) at the apex is 106°. In contrast to the phosphoryl oxygen atom, each of the three OH-oxygen atoms in $H_3PO_4(A)$ is involved in only one strong hydrogen bond (*i.e.* –O···O– less than 2·72 Å). Thus OH-oxygen atoms O(3) and O(4) are linked to the phosphoryl type oxygen atoms, O(5) of two separate $H_3PO_4(B)$ molecules, each with an

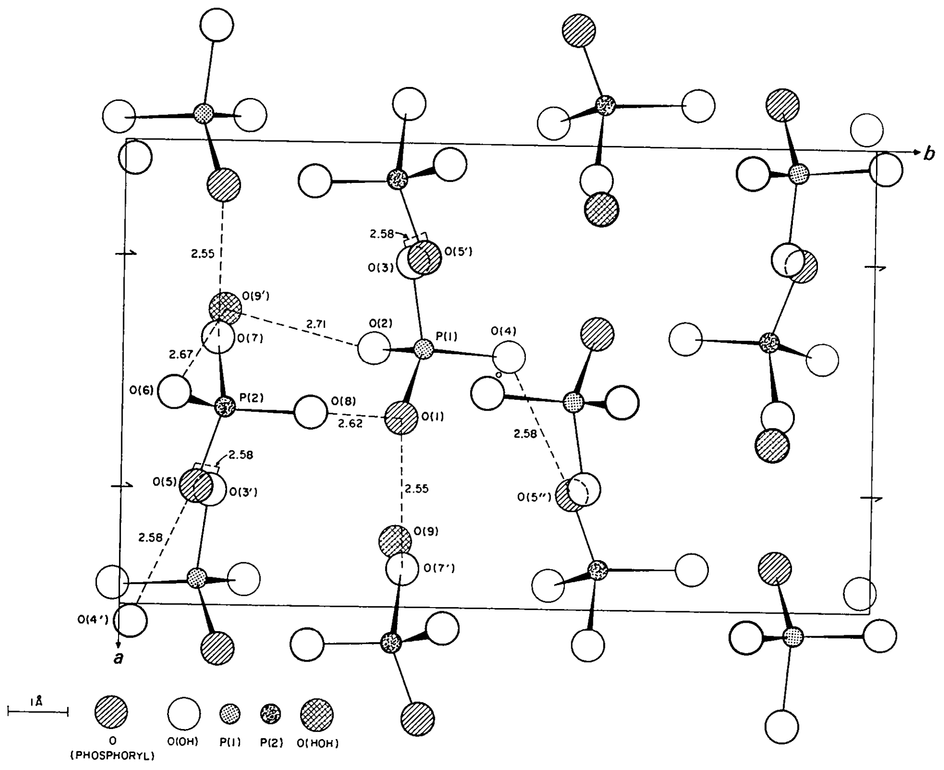

Fig. 1. Projection of the structure $H_3PO_4.\frac{1}{2}H_2O$ along the *c* axis. Oxygen atoms which are hydrogen bonded are connected by dashed lines.

–O···O– separation of 2·58 Å. A total of four H_3PO_4 (*B*) molecules are hydrogen bonded to one $H_3PO_4(A)$. The third P–OH oxygen atom, O(2), is hydrogen bonded to the water oxygen atom, O(9), at a distance of 2·71 Å.

Each $H_3PO_4(B)$, in an analogous manner, is hydrogen bonded to one water and four $H_3PO_4(A)$ molecules (Fig. 1). Thus the phosphoryl oxygen O(5) is linked to the OH-oxygen atoms O(3) and O(4) from two $H_3PO_4(A)$ molecules. The phosphoryl oxygen is the acceptor in the formation of two hydrogen bonds, both having an (–O···O–) separation of 2·58 Å; the angle formed by these three oxygen atoms with O(5) at the apex is 105°. Each of the three OH-oxygen atoms in $H_3PO_4(B)$ is involved in only one relatively strong hydrogen bond (*i.e.* less than 2·68 Å). As noted above, the oxygen atoms O(7) and O(8) are linked (as donors) to the phosphoryl type O(1) oxygen atoms of two separate $H_3PO_4(A)$ molecules with –O···O– distances of 2·55 and 2·62 Å, respectively. The third OH-oxygen atom, O(6), is hydrogen-bonded to the water oxygen atom, O(9), at a distance of 2·67 Å.

Environment about the water molecule

As indicated above, the water oxygen atom, O(9), is hydrogen bonded to OH-oxygen atoms O(2) in $H_3PO_4(A)$ and O(6) in $H_3PO_4(B)$ at distances of 2·71 and 2·67 Å, respectively. The angle involving these three oxygen atoms, with O(9) at the apex, is 104°. For reasons given above, the P–OH type oxygen atoms are tentatively assigned as the donors in these two hydrogen bonds.

In addition, five phosphate oxygen atoms, all of the OH type, and all from different phosphate groups are between 2·96 and 3·09 Å away from the water oxygen (Fig. 2). To explain the closeness of these five oxygen atoms, it is reasonable to assume that the water protons are involved in a type of 'multiple' hydrogen bond.

Comparison with anhydrous H_3PO_4

The crystal structure of anhydrous H_3PO_4 (Furberg, 1955) is similar in several ways to the one described above for the hemihydrate. Again, hydrogen bonding plays an important role in the crystal structure; each H_3PO_4 is associated with five neighboring molecules. As in the hemihydrate, the P–O bond is significantly shorter than the P–OH bonds. The phosphoryl oxygen atom, moreover, is again the focus of the strongest hydrogen bond formation. This oxygen atom is attached to two OH-oxygen atoms from separated H_3PO_4 molecules by strong hydrogen bonds with distances of 2·52 and 2·53 Å. The angle, involving these three oxygen atoms, with the phosphoryl oxygen at the apex is 95°. The average corresponding angle in the hemihydrate is 105°.

Many of the computer calculations on this structure were performed using the X-ray 63 system of programs developed at the University of Maryland and at the

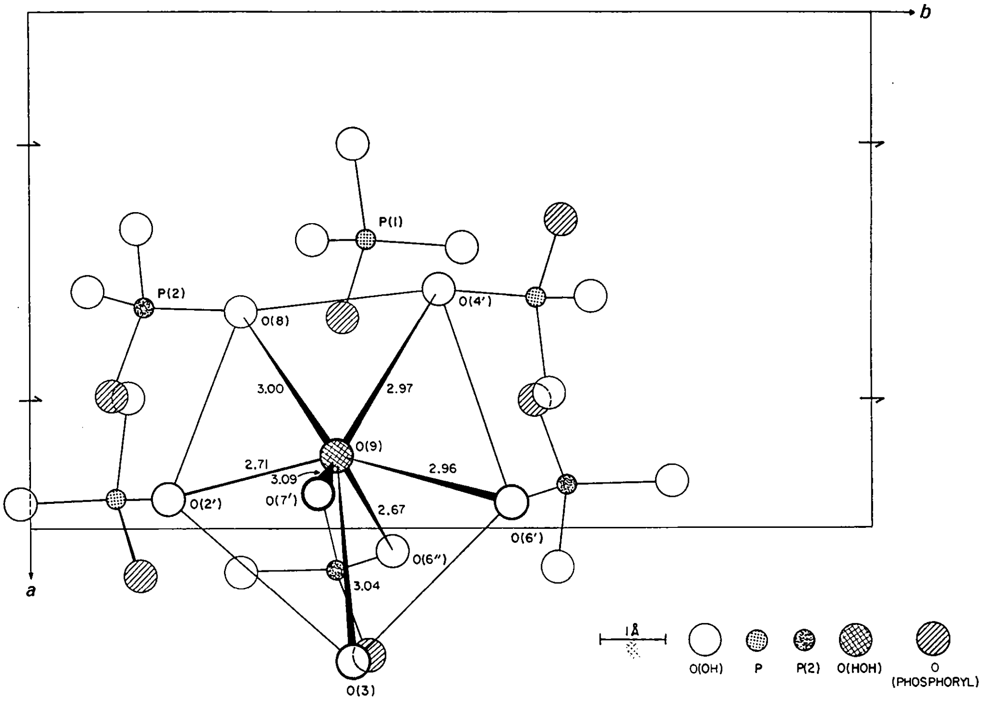

Fig. 2. The water oxygen atom [O(9)] in $H_3PO_4.\frac{1}{2}H_2O$. The seven oxygen atoms which are between 2·67 and 3·09 Å distant from O(9) are connected to this water oxygen atom by heavy solid lines. For clarity, O(7′) has been moved slightly to the viewer's left.

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Preparation, Properties and Crystal Structure of Barium Vanadium Sulfide, $BaVS_3$*

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Barium vanadium sulfide, $BaVS_3$, has been prepared and single crystals have been grown from a barium chloride flux. The crystal structure of $BaVS_3$ at room temperature has been determined by single-crystal analysis and the space group is $P6_3/mmc$ with two formula units per unit cell. The hexagonal cell dimensions are $a=6{\cdot}724\pm0{\cdot}005$ Å and $c=5{\cdot}610\pm0{\cdot}005$ Å. The calculated density is $4{\cdot}30$ g.cm^{-3} and the observed density is $4{\cdot}22$ g.cm^{-3}. The structure has been refined by least-squares techniques to a final R value on F of 7·5% for 192 independent reflections above background. The structure is based on hexagonal close-packed BaS_3 layers with the vanadium cations occupying one quarter of the octahedral voids between these layers. These are all the voids that are bounded exclusively by anions. The vanadium cations form chains parallel to the c axis with a V–V distance of $2{\cdot}805\pm0{\cdot}002$ Å. Low temperature powder X-ray studies indicate that a crystallographic distortion begins to occur near 185°K and this distortion gradually increases as the temperature is decreased. At liquid nitrogen temperature the distortion is considerable, but its exact nature is unknown. A plot of resistivity as a function of temperature indicates a change in the slope at approximately 130°K. This change is associated with a transition from the metallic to the semiconducting state. The electrical properties of $BaVS_3$, in the metallic state, are discussed in terms of direct interactions between the vanadium cations.

Introduction

Katz & Ward (1964) have recently described the structures of a number of mixed metal oxides in terms of the stacking sequence of essentially close-packed metal-oxygen layers. The concept of structure in terms of stacking sequences permits the correlation of a large number of structure types. In addition, it is possible to utilize these ideas in order to predict the existence of new compounds.

Compounds of the type ABX_3 where A is a large cation, B a small cation, and X is an anion, can be described as an essentially close-packed array of A and X ions, provided A and X are approximately the same size. In such an array, one quarter of the octahedral voids are bounded exclusively by the anions; these are the octahedra occupied by the B cations. The well known perovskite-type structure may be described in terms of cubic close-packing of the AX_3 layers. If the stacking sequence of the close-packed layers is hexagonal, then a different structure-type results. In addition, other structure-types can be described in terms of different sequences of hexagonal and cubic layers. The structure of compounds with a common packing sequence has usually been classified according to the crystal structures of minerals or specific compounds, *e.g.* perovskite, spinel, nickel arsenide, *etc.* This may at times lead to confusion because many such compounds often show marked differences in their crystallographic properties; a common packing sequence does not necessarily imply a common crystal structure. In this study it is preferred to designate the compounds according to the packing sequence rather than by association with the structure of a particular class of minerals or compounds.

In ABX_3 compounds with a cubic close-packed arrangement of ions, the octahedra occupied by B cations share corners; in the hexagonal close-packed structure these octahedra share faces and form continuous chains parallel to the c axis of the crystal. The ternary transition metal sulfides and selenides $BaTiS_3$ (Hahn & Mutschke, 1956; Clearfield, 1963; Aslanov & Kovba, 1964), $BaTiSe_3$ (Aslanov, 1964), $SrTiS_3$ (Hahn &

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