strained by hydrogen bonding and packing requirements; however, this may be in part a reflection of absorption errors.

The dihedral angles that completely specify the orientation of the thiourea groups relative to the planes defined by Ni and S atoms are given in Table III. Three factors contribute to these orientations: (a) hydrogen bonding to the bromide ion, (b) steric requirements that restrict the thiourea groups, and (c) electrostatic interactions between electrons in the S–C pπ molecular orbitals and the metal d_{xz}, d_{yz}, d_{xy} orbitals, all of which are filled. Obviously all three factors contribute to the specific orientation of a thiourea group and studies are currently underway in this laboratory to determine which factor(s) predominate(s). Preliminary photographic data indicate that $Ni(tu)_6Br_2$ and $Ni(tu)_6I_2$ are isomorphous and a comparison of the specific orientations of thiourea groups in this series to the orientation of thiourea groups in $Pt(tu)_4Cl_2$,[20] $Pd(tu)_4Cl_2$,[19] and the isomorphous series $Mn(tu)_4Cl_2$, $Fe(tu)_4Cl_2$, $Cd(tu)_4Cl_2$, and $Co(tu)_4Cl_2$[18,42] is being made.

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(42) J. E. O'Connor and E. L. Amma, to be submitted for publication.

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The Crystallography and Structure of α-Zirconium Bis(monohydrogen orthophosphate) Monohydrate[1]

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The crystal structure of α-zirconium bis(monohydrogen orthophosphate) monohydrate, $Zr(HPO_4)_2 \cdot H_2O$, has been determined from integrated precession data (568 nonzero reflections). The crystals are monoclinic, space group $P2_1/c$, with cell dimensions $a = 9.076 \pm 0.003$ Å, $b = 5.298 \pm 0.006$ Å, $c = 16.22 \pm 0.02$ Å, and $\beta = 111.5 \pm 0.1°$. The calculated density with $Z = 4$ is 2.76 g/cm^3 compared to an observed density of 2.72 ± 0.04 g/cm^3. The structure was refined to an R factor of 8.4% by least-squares methods. The structure is a layered one, each layer consisting of planes of zirconium atoms bridged through phosphate groups which alternate above and below the metal atom planes. Each phosphate group bonds to three different zirconium atoms producing octahedral coordination about the zirconium atoms. The Zr–O bond distances range from 2.04 to 2.11 Å. The fourth phosphate oxygen bears the hydrogen and points toward an adjacent layer. The layers are arranged relative to each other in such a way as to form zeolitic-type cavities. A water molecule resides in the center of each cavity and is hydrogen bonded to phosphate groups. The relation between structure and ion-exchange properties of the crystals is discussed in this and a forthcoming paper.

Introduction

Preparations commonly called zirconium phosphate are of interest because they function as ion exchangers. These phosphates have been prepared in both amorphous and crystalline forms. When solutions containing phosphate ion and Zr(IV) salts are mixed, amorphous gels of variable composition result.[2] These gels are transformed into microcrystals by refluxing them in various phosphate-containing solutions. If the refluxing medium is phosphoric acid, the resultant crystals are the normal or α phase.[3] However, refluxing in a mixture of phosphoric acid and sodium dihydrogen phosphate produces the β and γ phases.[4]

The α phase (α-ZrP) has been shown to be zirconium bis(monohydrogen orthophosphate) monohydrate, $Zr(HPO_4)_2 \cdot H_2O$, on the basis of its composition, dehydration, and ion-exchange behavior.[3] Crystals large enough for a single-crystal X-ray diffraction study were prepared from the microcrystals as described below. An attempt to solve the structure by two-dimensional methods was only partially successful.[5]

Severe overlap of several oxygen atom peaks in the Fourier projections prevented a complete solution of the structure. A three-dimensional study has now been carried out, the details of which are reported here.

Experimental Section

Preparation.—Single crystals were prepared by heating a mixture of gel and 12 M phosphoric acid in a sealed quartz tube for several weeks at 170–180°. Very thin hexagonal or triangular platelets were obtained.

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(1) Portions of this paper were taken from the Ph.D. thesis of G. D. Smith presented to the Chemistry Department, Ohio University, June 1968. This work was supported by the National Science Foundation under Grant No. GP-6433.

(2) C. B. Amphlett, "Inorganic Ion-Exchangers," Elsevier Publishing Co., Amsterdam, 1964, pp 84–136.

(3) A. Clearfield and J. A. Stynes, *J. Inorg. Nucl. Chem.*, **26**, 117 (1964).

(4) A. Clearfield, R. H. Blessing, and J. A. Stynes, *ibid.*, **30**, 2249 (1968).

(5) A. Clearfield and G. D. Smith, *J. Colloid Interface Sci.*, **28**, 325 (1968).

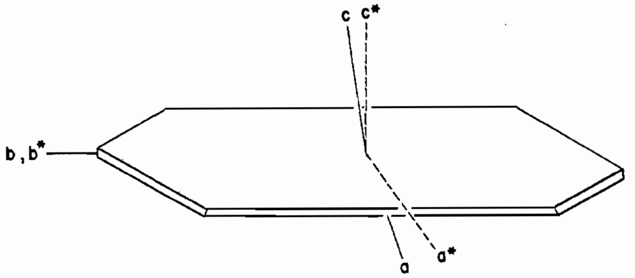

Figure 1.—Schematic drawing on an α-ZrP hexagonal platelet. The real axes are indicated by solid lines and the reciprocal axes by dashed lines.

X-Ray Data.—A single crystal of α-ZrP (hexagonal platelet) is shown schematically in Figure 1. The unit cell was found to be monoclinic. The real and reciprocal axes are indicated in the figure by solid and dashed lines, respectively.

Accurate cell dimensions were obtained from precession photographs using Mo Kα radiation (0.7107 Å). The films were corrected for shrinkage by exposing pairs of fiducial spots along both the horizontal and the vertical directions of the film. The cell constants were found to be a = 9.076 ± 0.003 Å, b = 5.298 ± 0.006 Å, c = 16.22 ± 0.02 Å, and β = 111.5 ± 0.1°.

The unit cell volume of 725.7 Å^3 with four formula units per unit cell gives a density of 2.76 g/cm^3. This compares with an observed density, determined pycnometrically in cyclohexane, of 2.72 ± 0.04 g/cm^3 (average of four determinations).

A survey of $h0l$, $h1l$, $h2l$, $0kl$, $1kl$, $2kl$, $hk0$, $hk1$, and $hk2$ precession photogaphs (taken with zirconium-filtered Mo Kα radiation) revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. These absences are consistent with the space group P2$_1$/c. Since there are four formula units per unit cell, no symmetry restrictions need be imposed.

Intensity data were gathered from integrated precession photographs using Mo Kα radiation. Two crystals approximately 0.4 mm long by 0.2 mm wide by 0.025 mm thick were used to gather the intensity data. One was mounted so that its b^* axis coincided with the dial axis and nkl, n = 0–4, and hkn, n = 0–10, photographs were obtained. The other was mounted so that the dial axis coincided with the a^* axis and the precession axis was b. This setting was used to obtain $h0l$, $h1l$, and $h2l$ photographs. Long (24–48 hr) and short (2 hr) exposures of each layer were taken to ensure that all reflections were within the proportional response range of the film. The intensities of the integrated spots were read with a Joyce-Loebl Mark IIIC double-beam automatic recording microdensitometer (Joyce-Loebl and Co., Ltd.). The intensities were corrected for Lorentz and polarization factors and then placed on the same scale following the least-squares procedure of Monahan, Schiffer, and Schiffer.[6] No correction for absorption was applied (μ = 19.0 cm^{-1}). Since all of the intensity photographs were taken with the X-ray beam traversing the thin section of the crystal, the absorption correction varies only slightly from photograph to photograph. In all, 568 nonzero intensities were recorded.

TABLE I

X-RAY POSITIONAL AND THERMAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS[a]

Atom	X	Y	Z	B, Å^2
Zr$_1$	0.7606 (2)	0.250 (2)	0.5144 (1)	0.67 (2)
P$_2$	0.0008 (6)	0.752 (5)	0.6129 (4)	1.13 (8)
P$_3$	0.4711 (6)	0.255 (5)	0.1044 (4)	0.98 (8)
O$_4$	0.105 (2)	0.806 (5)	0.560 (1)	1.7 (3)
O$_5$	0.934 (3)	0.486 (6)	0.601 (2)	2.6 (4)
O$_6$	0.869 (2)	0.941 (5)	0.589 (4)	1.6 (4)
O$_7$	0.104 (2)	0.760 (9)	0.716 (1)	2.2 (3)
O$_8$	0.344 (3)	0.057 (5)	0.062 (1)	2.0 (4)
O$_9$	0.418 (2)	0.514 (5)	0.069 (1)	1.6 (3)
O$_{10}$	0.512 (2)	0.257 (9)	0.205 (1)	2.3 (3)
O$_{11}$	0.375 (2)	0.814 (5)	0.910 (1)	1.9 (4)
O$_{12}$	0.254 (2)	0.265 (8)	0.259 (1)	3.1 (4)

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digit.

Solution and Refinement of the Structure

The zirconium and phosphorus positional parameters were known fairly well from the previous two-dimemsional study.[5] These were further refined by least-squares and then a three-dimensional electron density map was prepared using signs calculated for these positions. Sections were taken perpendicular to the b axis every 0.25 Å. The atomic parameters obtained from this map were in good agreement with those derived from the two projections. However, the calculated structure factors for all reflections with l odd were in poor agreement with the observed data. This resulted from an ambiguity in location of the origin which could not be resolved in projection because of the small number of ($h0l$) and ($0kl$) reflections with l odd. On shifting the origin by $z = 1/4$, a marked improvement in agreement was observed.

The structural parameters obtained above were refined by the block-diagonal least-squares method.[7] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The atomic scattering factors for the neutral atoms were those tabulated in ref 8. Only the scattering factor for zirconium was corrected (real part only) for dispersion.[9] For the initial cycles of refinement a weighting scheme similar to that suggested by Hughes was employed.[10] The weights were $w = 1$ when $|F_o|/K \leq 4.8$ and $w = 4.8K/|F_o|$ when $|F_o|/K > 4.8$. K is the over-all scale factor which places $|F_o|$ on the absolute scale. Individual isotropic temperature factors were assigned for each atom.

The relaxation factors suggested by Hodgson and Rollet[11] were found to produce oscillations of the positional parameters. However, when a constant relaxation factor of 0.5 was employed, rapid convergence was obtained. In five cycles the residual, $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, was reduced from 0.184 to 0.109. At this point a new weighting scheme was introduced.[12] The new weights were $w = 1/(a +$

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(6) J. E. Monahan, M. Schiffer, and J. P. Schiffer, *Acta Cryst.*, **22**, 322 (1967).

(7) The programs used in this work were all locally modified for use on the Ohio University IBM 360 Model 44 computer: (a) C. Calvo, "Data Process for Precession Photographs," McMaster University, Hamilton, Ont., Canada; (b) F. R. Ahmed, "NRC-8 Fourier Program; NRC-10 Structure Factor Least Squares," National Research Council, Ottawa, Ont., Canada; (c) M. E. Pippy and F. R. Ahmed, "NRC-12 Scan of Interatomic Distances and Angles," National Research Council, Ottawa, Ont., Canada.

(8) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

(9) See ref 8, p 213.

(10) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

(11) L. I. Hodgson and J. S. Rollett, *Acta Cryst.*, **16**, 329 (1963).

(12) D. W. J. Cruickshank and D. E. Pilling in "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," Pergamon Press Inc., New York, N. Y., 1960, p 45.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS × 10 (IN ELECTRONS) FOR α-ZrP[a]

L	FO	FC
H= 0, K= 0		
6	855	-761
8	628	711
10	1150	1173
12	333*	307
14	347*	-49
16	352*	18
18	339*	260
H= 1, K= 0		
0	121*	110
2	317	251
4	221*	215
6	261	285
8	768	782
10	559	675
12	475	672
14	588	724
16	511	611
H= -1, K= 0		
2	137*	-171
4	441	-390
6	236*	-108
8	272*	-65
10	702	-745
12	920	-1036
14	701	-923
16	567	-501
18	345*	-340
H= 2, K= 0		
0	170*	-1
2	578	-552
4	1201	-1346
6	1329	-1378
8	343	-463
10	328*	87
12	344	-350
14	352*	-334
16	343*	-89
H= -2, K= 0		
2	1274	-1439
4	2588	-2900
6	1120	-1119
8	566	-566
10	427	354
12	903	-904
14	597	-652
16	351*	-177
18	348*	267
H= 3, K= 0		
0	288	-285
2	267	-296
4	725	-808
6	979	-925
8	361	-453
10	762	-802
12	349	-476
14	420	-488
16	330*	-229
H= -3, K= 0		
2	497	491
4	211*	-3
6	1191	795
8	594	652
10	375	448
14	378	397
16	632	682
18	620	709
20	399	486
H= 4, K= 0		
0	934	1063
2	693	734
4	690	701
6	311	312
8	720	735
10	472	523
12	351*	111
14	342*	-248
H= -4, K= 0		
2	232*	280
4	376	600
6	1437	1607
8	1815	1882
10	964	1029
12	319*	-79
14	337	-300
16	390	419
18	349*	403
20	333*	115
H= 5, K= 0		
0	273*	54
2	411	361
4	309*	94
6	807	841
8	837	903
10	463	537
12	347*	298
14	322*	285
16	433	515
H= -5, K= 0		
2	570	593
4	261*	-78
6	492	-476
8	285*	-319
10	599	-602
12	322*	-161
14	445	-508
16	365	-407
18	541	-616
20	531	-605
22	364	-448
H= 6, K= 0		
0	626	-559
2	313*	-260
4	667	-704
6	544	-527
8	349*	-255
10	349*	149
12	333*	-50
14	264*	-103
H= -6, K= 0		
2	1045	-1077
4	1419	-1493
6	623	-637
8	300*	-260
10	313	-360
12	1114	-980
14	720	-755
16	351*	-94
18	349*	142
20	330*	-89
H= 7, K= 0		
0	323*	-266
2	548	-556
4	756	-758
6	351*	-277
8	352*	-202
10	377	-451
12	490	-613
H= -7, K= 0		
2	315*	67
4	311*	-39
6	348	-358
8	316*	170
10	327	314
12	627	660
14	697	517
16	353*	371
18	348*	418
20	323*	264
22	388	418
H= 8, K= 0		
0	989	982
2	629	660
4	354*	330
6	353*	5
8	338*	110
10	290*	222
H= -8, K= 0		
2	344	299
4	334	301
6	493	480
8	1019	1024
10	768	769
12	348	323
14	353*	236
16	598	491
18	421	419
H= 9, K= 0		
0	701	560
2	357*	366
6	497	464
8	473	475
H= -9, K= 0		
2	443	398
4	352*	38
6	516	-349
8	352*	-41
10	354*	-41
12	357*	-161
14	518	-404
16	369	-456
18	333*	-252
20	270*	-309
H= 10, K= 0		
0	358*	-238
2	348*	-255
H= -10, K= 0		
2	557	-517
4	644	-617
6	371	-347
8	496	-417
10	726	-480
12	801	-849
14	449	-454
16	340*	-109
18	301*	7
H= 11, K= 0		
0	329*	-104
2	495	-390
H= -11, K= 0		
2	347*	-97
4	356*	-307
6	354	-312
8	359*	53
10	357*	329
12	349*	181
14	339*	71
16	300*	105
18	399	404
H= -12, K= 0		
2	336	295
4	394	356
6	600	540
8	539	463
10	341	304
H= 0, K= 1		
2	254	-265
4	545	-479
6	428	-431
7	232*	121
8	477	-521
9	277*	92
10	361	-430
11	313*	-15
12	860	-898
13	342*	-81
14	674	-743
15	364*	-56
16	481	-618
17	379*	21
18	383*	-263
19	385*	62
H= 1, K= 1		
0	1093	1361
2	2765	2857
4	1205	1271
5	197*	-75
6	689	714
7	251*	-9
8	382	-301
9	292*	74
10	685	769
11	324*	46
12	531	575
13	351*	-1
14	361*	177
15	371*	0
16	377*	-263
17	382*	20
18	384*	-168
19	383*	18
H= -1, K= 1		
4	721	-688
6	1221	-1223
7	218*	92
8	1458	-1366
9	266*	46
10	387	-389
11	304*	-10
12	320*	89
13	334*	-42
14	426	-446
15	358*	-1
16	367	-355
17	375*	12
18	381*	-159
19	384*	-12
20	384*	347
H= 2, K= 1		
0	648	527
1	162	-133
2	232	257
3	241	-191
4	903	828
5	230*	-49
6	307	352
7	335	196
8	770	764
9	307*	223
10	613	625
11	336*	77
12	387	411
13	359*	-119
14	387	414
15	376*	-153
16	381	496
17	384*	-64
18	572	669
H= -2, K= 1		
4	325	291
5	159*	-71
6	241	292
7	214*	-4
8	1001	863
9	259*	8
10	777	744
11	297*	34
12	722	734
13	327*	45
14	356	400
15	353*	27
16	429	480
17	372*	-5
18	487	504
19	382*	-37
20	416	500
21	382*	-30
H= 3, K= 1		
0	539	-571
1	597	583
2	750	-751
3	292	312
4	630	-549
5	257*	-121
6	1231	-1200
7	292*	-255
8	866	-865
10	336*	-143
11	347*	16
12	358*	203
13	367*	17
14	375*	-14
15	380*	-7
16	383*	-159
H= -3, K= 1		
1	297	279
2	1895	1957
3	401	-334
4	491	515
5	505	-472
6	805	768
7	248	-234
8	634	614
9	258*	101
10	1232	1246
11	293*	147
12	952	977
13	323*	99
14	336*	1
15	348*	16
16	359*	-182
17	367*	-14
18	375*	17
19	380*	-24
20	383*	258
21	383*	-11
H= 4, K= 1		
0	213*	36
1	223*	95
2	338	-357
3	252*	-44
4	582	-574
5	282*	-172
6	1040	-1024
7	311*	-152
8	394	-439
9	337*	22
10	375	-351
11	359*	137
12	411	-503
13	375*	114
14	521	-600
15	382*	0
16	447	-529
H= -4, K= 1		
1	205*	69
2	201*	-8
3	200*	66
4	251	269
5	211*	120
6	520	-515
7	233*	109
8	414	-405
9	263*	-7
10	539	-593
11	293*	-131
12	431	-453
13	321*	-84
14	429	-428
15	345*	-6
16	559	-584
17	365*	60
18	403	-451
19	378*	46
20	502	-547
21	382*	15
22	416	-429
24	200	-348
H= 5, K= 1		
0	497	521
1	255*	146
2	993	1067
3	313	268
4	742	726
5	306*	151
6	317	290
7	329*	-46
8	340*	-18
9	351*	-63
10	360*	253
11	369*	-26
12	375*	319
13	379*	4
14	381*	46
15	381*	-16
H= -5, K= 1		
1	292	-226
2	617	-629
3	384	-395
4	1064	-1069
5	234	-179
6	1620	-1666
7	249*	132
8	669	-738
9	271*	224
10	284*	-245
11	297*	112
12	309*	23
13	322*	-29
14	747	-753
15	344*	-65
16	555	-597
18	371*	-108
19	377*	-14
20	380*	249
21	381*	8
22	379*	115
H= 6, K= 1		
0	502	508
1	283*	170
2	534	547
3	303*	178
4	315*	222
5	325*	-24
6	336*	42
7	345*	-199
8	644	701
9	363*	-183
10	663	758
11	376*	-15
12	504	621
13	380*	117
14	379*	184
H= -6, K= 1		
1	267*	35
2	318	-344
3	257*	-30
4	416	435
5	257*	19
6	262*	-71
7	267*	-3
8	274*	120
9	284*	-122
10	293*	147
11	236	-168
12	372	480
13	326*	-64
14	645	701
15	346*	81
16	485	523
17	363*	120
18	526	521
19	376*	67
20	495	359
21	380*	-23
22	471	302
H= 7, K= 1		
0	908	-955
1	308	-272
2	317*	-280
3	326*	-54
4	335*	-89
5	344*	86
6	353*	-300
7	360*	82
8	367	-400
9	373*	18
10	377*	-130
11	380*	-10
12	379*	157
H= -7, K= 1		
1	293*	-239
2	1292	1330
3	285*	41
4	615	625
5	356	361
6	284	268
7	287	293
8	308	319
9	299*	4
10	962	987
11	254	-208
12	725	746
13	333*	-172
14	347*	265
15	351*	-25
16	359*	18
17	365*	54
18	372	329
19	377*	55
20	379	335
21	379*	29
H= 8, K= 1		
0	325*	-216
1	331*	-25
2	339*	-116
3	346*	76
4	574	-575
5	360*	103
6	648	-640
7	372*	36
8	376	-369
9	379*	-53
10	379*	-178
11	377*	-71
12	371*	-297
13	358*	-22
14	410	-472
H= -8, K= 1		
1	319*	-67
2	319*	271
3	310*	-24
4	468	454
5	306*	1
6	307*	-42
7	309*	-30
8	400	-377
9	317*	-44
10	322*	-226
11	328*	35
12	336	-323
13	345*	113
14	349	-201
15	357*	84
16	531	-538
18	461	-399
19	378*	-87
H= 9, K= 1		
0	347*	225
1	354*	-100
2	506	566
3	364*	-88
4	419	423
5	374*	-12
6	377*	252
7	379*	29
8	379*	-91
9	377*	27
10	371*	23
11	360*	12
12	340*	8
H= -9, K= 1		
1	343*	17
2	339*	-197
3	335*	173
4	598	-630
5	330*	170
6	854	-857
7	330*	4
8	649	-678
9	336*	-171
10	355	-304
11	344*	-146
12	348	-337
13	354*	-23
14	643	-653
15	365*	81
16	417	-445
17	375*	65
18	378*	-113
19	379*	13
20	379*	108
21	376*	-17
22	370*	-99
23	357*	-17
H= 10, K= 1		
0	441	410
1	371*	-91
2	575	572
3	377*	-58
4	379	357
5	380*	26
6	380*	195
7	377*	79
8	370*	328
9	358*	45
10	398	429
11	302*	-9
12	247	307
H= -10, K= 1		
1	363*	-36
2	360*	-30
3	357*	33
4	355*	93
5	353*	16
6	353*	-114
7	352*	-18
8	353*	-219
9	355*	-1
10	357*	143
11	360*	70
12	390	335
13	366*	72
14	371*	317
15	374*	-25
16	377*	154
17	379*	-111
18	380*	203
19	380*	-93
20	411	444
21	372*	6
22	360	408
23	341*	76
24	307	356
H= 11, K= 1		
0	380	-320
1	382*	40
2	382*	-224
H= -11, K= 1		
1	379*	63
2	546	507
3	375*	13
4	374	232
5	372*	-72
6	437	402
7	371*	-107
8	585	542
9	372*	-34
10	747	707
11	374*	70
12	457	441
13	378*	101
14	380*	69
15	381*	37
16	382*	165
17	382*	-29
18	389	347
19	377*	-44
20	388	351
H= 12, K= 1		
0	382*	-132
1	379*	2
2	374*	-84
3	366*	-9
4	354*	-297
5	334*	-1
6	450	-472
H= -12, K= 1		
1	384*	10
2	384	368
3	384*	11
4	384	355
5	384*	-8
6	384*	21
7	383*	-4
8	383*	-165
9	384*	22
10	384*	-26
11	384*	26
12	384*	72
13	385*	-1
14	384*	-94
15	383*	-47
16	382	-347
17	378*	-76
18	456	-369
H= 0, K= 2		
0	2082	-2158
1	328	-277
2	511	-511
3	660	-602
4	912	-868
5	315	-297
6	590	-550
8	1090	-1130
10	867	-911
11	257*	96
12	285*	-18
13	307*	2
14	325*	168
15	340*	-46
16	351*	-3
17	358*	-13
18	362*	-231
19	340*	-12
20	352*	-36
H= 1, K= 2		
2	315	-298
4	726	-669
6	721	-682
8	577	-597
9	212*	144
10	250*	-190
11	279*	98
12	307*	-312
13	371*	4
14	657	-682
15	348*	-58
16	697	-767
17	361*	-54
18	513	-602
H= -1, K= 2		
6	511	486
8	740	731
9	141	-149
10	936	918
11	239*	-197
12	614	649
13	295*	-6
14	336	392
15	331*	96
16	344	272
17	355*	113
18	360	435
19	362*	20
20	521	571
21	345*	-45
22	319	443
H= 2, K= 2		
0	483	402
2	1631	1482
4	1841	1751
6	1135	1114
10	291	-261
11	301*	35
12	340	298
13	335*	19
14	346	353
15	356*	22
16	361*	114
17	361*	0
18	356	-274
H= -2, K= 2		
2	281	316
4	1178	1179
6	775	664
8	976	907
12	923	943
13	287*	-10
14	478	526
15	325*	12
16	339*	79
17	351*	9
18	358	-273
19	361*	16
20	360*	-182
21	352*	13
H= 3, K= 2		
0	409	392
2	661	548
4	693	663
6	407	444
7	231*	17
8	259*	138
9	284*	109
10	630	731
11	321*	81
12	603	645
13	346*	10
14	578	604
15	360*	-49
16	361*	239
17	356*	-45
H= -3, K= 2		
2	409	-395
6	290	-269
8	420	-402
10	682	-723
11	233*	-122
12	678	-722
13	285*	17
14	522	-544
15	327*	126
16	437	-423
17	347*	84
18	356	-355
19	360*	6
20	360	-336
21	355*	-65
22	361	-429
H= 4, K= 2		
0	1736	-1606
3	234	211
4	259	-280
5	225	172
6	290*	-16
7	273*	-15
8	544	-606
9	310*	-88
10	497	-552
11	338*	-49
12	348*	-168
13	356*	-5
14	360*	203
15	360*	5
16	354*	123
H= -4, K= 2		
2	1056	-988
4	521	-463
6	671	-656
8	1052	-1059
9	205	-254
10	913	-914
11	245*	-157
12	268*	-234
13	288*	18
14	306*	60
15	322*	62
16	335	-394
17	346*	18
18	354	-346
19	359*	-14
20	360*	-116
21	356*	-1
22	343*	311
H= 5, K= 2		
0	199	-142
1	191*	10
2	214	-258
3	234*	74
4	253*	-20
5	271*	103
6	677	-728
7	304*	56
8	760	-853
9	331*	-41
10	502	-521
11	351*	-81
12	357*	-284
13	360*	-51
14	358*	-274
15	351*	20
16	426	-488
H= -5, K= 2		
2	608	-533
6	437	438
7	176*	21
8	201*	118
9	222*	68
10	270	285
11	262*	30
12	279*	174
13	295*	-30
14	649	716
15	324*	-78
16	521	620
17	346*	-75
18	526	574
19	358*	-17
20	431	392
21	355*	42
22	344*	269
23	320*	57
24	282	243
H= 6, K= 2		
0	305	334
1	253*	26
2	266*	157
3	279*	11
4	625	664
5	304*	12
6	574	553
7	328*	2
8	339	265
9	347*	-9
10	354*	-127
11	358*	2
12	358*	25
13	355*	3
14	343*	59
15	321*	18
H= -6, K= 2		
1	232*	-28
2	1017	959
3	220*	-5
4	1605	1533
5	220*	-9
6	814	804
7	233*	50
8	244*	197
9	255*	2
10	267*	140
11	280*	38
12	785	768
13	306*	-11
14	721	729
15	329*	5
16	340*	159
17	348*	-6
18	355*	-117
19	358*	4
20	358*	66
H= 7, K= 2		
0	466	247
1	291*	-20
2	524	511
3	310*	16
4	700	677
5	329*	45
6	338*	224
7	346*	14
8	352*	160
9	356*	-15
10	377	434
11	356*	-49
12	507	619
13	330*	-21
14	408	484
H= -7, K= 2		
1	275*	30
2	270*	-12
3	266*	24
4	264*	89
5	263*	2
6	338	266
7	269*	27
8	274	-266
9	281*	41
10	321	-331
11	299*	48
12	481	-472
13	318*	0
14	347	-322
15	337*	-35
16	344	-344
17	351*	-50
18	522	-525
19	358*	-7
20	356*	-375
H= 8, K= 2		
0	868	-924
1	320*	11
2	594	-615
3	334*	-69
4	341*	-276
5	347*	-41
6	352*	12
7	356*	-22
8	357*	-89
9	355*	0
10	348*	-183
11	334*	-15
H= -8, K= 2		
1	307*	-98
2	330	-321
3	298*	-128
4	317	-287
5	294*	-20
6	480	-478
7	297*	121
8	974	-962
9	304*	137
10	671	-690
11	316*	36
12	323*	-233
13	330*	-66
14	337*	-185
15	344*	-91
16	495	-484
17	354*	-23
18	388	-434
19	356*	5
20	352*	-51
21	342*	14
H= 9, K= 2		
0	504	-468
1	341*	34
2	345*	-205
3	349*	-30
4	354*	-107
5	356*	-79
6	438	-446
7	353*	-41
8	519	-568
9	331*	19
10	372	-407
H= -9, K= 2		
1	331*	-87
2	414	-412
3	324*	-39
4	322*	-111
5	320*	1
6	279	246
7	320*	-2
8	322*	13
9	324*	-25
10	328*	58
11	333*	-28
12	357*	203
13	342*	34
14	379	402
15	351*	48
16	354	405
17	356*	23
18	355	215
19	352*	-38
20	343	300
21	327*	-52
22	363	353
H= 10, K= 2		
0	352*	153
1	354*	-27
2	355*	146
3	355*	7
4	353*	208
5	348*	19
6	339*	264
H= -10, K= 2		
1	348*	21
2	519	524
3	343*	8
4	688	710
5	340*	-34
6	434	440
7	339*	-26
8	410	377
9	341*	-23
10	365	362
11	345*	5
12	717	696
13	351*	21
14	406	393
15	355*	28
16	355*	123
17	354*	24
18	348*	49
19	340*	5
20	324*	244
21	295*	-7
22	283	269
H= 11, K= 2		
0	353*	6
1	351*	14
2	357	365
3	337*	-7
4	548	555
5	299*	-32
6	414	406
H= -11, K= 2		
1	354*	-23
2	355*	-5
3	354*	5
4	354*	250
5	353*	33
6	356	311
7	352*	16
8	352*	1
9	353*	-3
10	353*	-251
11	354*	-18
12	354*	-137
13	355*	15
14	354*	-73
15	352*	36
16	348*	-139
17	341*	21
18	460	-411
19	311*	-3
20	447	-394
H= 12, K= 2		
0	325	-263
1	309*	-33
2	283	-219
H= -12, K= 2		
1	335*	58
2	341*	-154
3	345*	24
4	348*	-227
5	349*	-23
6	562	-528
7	352*	-67
8	631	-577
9	352*	-45
10	445	-421
11	349*	1
12	347*	-148
13	344*	51
14	340*	-197
15	333*	43
16	452	-409
17	303*	7
18	330	-297
H= 0, K= 3		
4	425	349
5	330*	34
6	434	332
7	342*	13
8	428	361
9	357*	-6
10	364*	352
11	372*	-103
12	737	756
13	385*	-112
14	660	694
15	391*	1
16	499	555
H= 1, K= 3		
0	1208	-1093
1	349*	185
2	1877	-1752
3	357*	-92
4	841	-776
5	367*	-325
6	375*	-340
7	382*	-149
8	391*	149
9	399*	4
10	688	-690
11	418*	55
12	567	-552
13	437*	21
H= -1, K= 3		
1	492	423
2	452	363
3	352*	126
4	807	738
5	360*	-79
6	1039	955
7	373*	-198
8	993	905
9	388*	-56
10	397*	181
11	406*	8
12	415*	-64
13	426*	66
14	435*	408
15	444*	44
16	454*	335
17	460*	28
H= 2, K= 3		
0	395	-381
1	346*	75
2	352*	-171
3	359*	-40
4	367*	-361
5	376*	-138
6	385*	-164
7	396*	-93
8	602	-668
9	417*	107
10	693	-735
11	439*	119
H= -2, K= 3		
1	340*	77
4	348*	-284
5	355*	106
6	362*	-277
7	371*	173
8	531	-519
9	390*	141
10	481	-442
11	410*	-76
12	421	-526
13	432*	-177
14	444*	-428
15	455*	-71
16	571	-543
17	477*	57
18	487	-516
H= 3, K= 3		
0	667	632
1	369*	22
2	380*	277
3	393*	-1
4	408*	176
5	421*	-23
6	990	872
7	450*	0
8	838	806
9	479*	19
H= -3, K= 3		
1	353*	-6
2	1735	-1747
4	899	-834
5	369*	-8
6	617	-543
7	394*	62
8	409*	-307
9	423*	-43
10	826	-818
11	451*	-22
12	776	-757
13	480*	-41
14	493*	-57
15	508*	2
H= 4, K= 3		
4	479	447
5	229*	-247
6	903	862
7	294*	-118
8	480	475
9	335*	87
10	348*	364
11	360*	188
12	487	419
13	372*	88
14	452	465
H= -4, K= 3		
6	418	360
9	123*	68
10	424	426
11	258*	-6
12	353	345
13	311*	-131
14	355	381
15	345*	-71
16	483	530
17	366*	-16
18	372*	440
19	371*	41
20	468	492
21	337*	30
22	384	370
H= -5, K= 3		
4	952	841
6	1558	1481
H= -6, K= 3		
4	359	-326
H= -7, K= 3		
2	917	-872
4	363	-349
H= -8, K= 3		
4	365	-347
H= -9, K= 3		
4	578	537
6	767	623
8	552	468
H= -11, K= 3		
6	372	-323
H= 0, K= 4		
0	1821	1776
1	358*	-55
2	834	733
3	360*	-42
4	362	305
5	364*	-28
6	367*	110
7	371*	61
8	726	711
9	378*	54
10	780	757
11	384*	38
12	387*	122
13	387*	-13
H= 1, K= 4		
0	401*	38
1	402*	-12
2	405*	76
3	407*	-44
4	409*	197
5	412*	84
6	466	398
7	421*	79
8	639	637
9	431*	49
10	618	460
11	443*	-52
H= -1, K= 4		
4	406*	-230
5	408*	95
6	411*	-250
7	415*	130
8	419*	-267
9	425*	19
10	500	-493
11	435*	-22
12	638	-583
13	447*	-125
14	623	-517
15	455*	-50
H= 2, K= 4		
0	412*	-110
1	433	371
2	434	-407
3	420*	21
4	962	-881
5	430*	-183
6	893	-882
7	442*	-239
8	449*	-276
H= -2, K= 4		
1	472	-348
2	837	-786
3	413*	-37
4	1541	-1446
5	418*	296
6	857	-778
7	427*	278
8	432	-295
9	438*	66
10	445*	99
11	451*	-138
12	656	-586
13	466*	-127
H= 3, K= 4		
0	459*	-194
1	463*	112
2	468*	-348
3	474*	79
4	482*	-505
5	490*	-37
6	499*	-419
H= -3, K= 4		
1	455*	-17
2	263	225
3	456*	13
4	459*	78
5	463*	-105
6	468*	317
7	474*	-135
8	482*	316
9	490*	-70
10	499*	336
11	508*	99
12	518*	339
H= 4, K= 4		
0	1044	1045
1	258*	1
2	823	782
3	291*	36
4	392	374
H= -4, K= 4		
1	233*	-76
2	419	440
6	682	602
7	271*	27
8	1120	1031
9	303*	-19
10	809	797
11	331*	1
12	344*	126
13	355*	30
H= -5, K= 4		
2	360	353
H= -6, K= 4		
2	750	-728
4	989	-970
6	453	-480
H= -8, K= 4		
4	353	345
6	540	536
8	839	774
H= -10, K= 4		
4	520	-503
8	341	-299
H= 1, K= 5		
0	544	478
1	441*	138
2	1099	995
3	442*	116
4	694	676
5	445*	74
6	499	364
7	449*	-39
8	451*	49
9	452*	-22
10	454	458
H= -1, K= 5		
2	441*	-93
3	441*	-148
4	571	-539
5	443*	-157
6	1005	-871
7	446*	18
8	851	-768
9	450*	70
10	452*	-141
11	454*	68
12	455*	88
H= 2, K= 5		
0	463*	202
1	464*	-75
2	465*	155
3	467*	-46
4	469*	277
5	472*	-7
6	475*	235
7	479*	41
8	482*	495
H= -2, K= 5		
1	463*	-90
2	463*	42
3	463*	14
4	464*	186
5	466*	-15
6	468*	224
7	470*	0
8	473*	369
9	477*	-55
10	480*	353
11	484*	-27
12	537*	381
H= 3, K= 5		
0	661	-614
1	532*	136
2	534*	-350
3	538*	169
4	542*	-260
5	546*	47
6	730	-581
H= -3, K= 5		
1	528*	-51
2	968	1049
3	528*	-225
4	481	443
5	532*	-122
6	535*	196
7	538*	2
8	542*	259
9	546*	154
10	873	692
11	557*	83
12	712	629
H= -5, K= 5		
4	461	-444
6	780	-758
H= -6, K= 5		
4	212	193
H= -7, K= 5		
2	798	749
4	566	468
H= -8, K= 5		
4	295	288
H= -9, K= 5		
4	558	-517
8	463	-443
H= 0, K= 6		
0	928	-881
1	381*	-74
2	498	-438
3	379*	-180
4	378*	-255
5	375*	-105
6	372*	-253
7	366*	-3
8	538	-551
10	479	-497
H= 1, K= 6		
0	460*	-42
1	460*	-38
3	459*	-32
H= -1, K= 6		
1	460*	-74
2	460*	25
3	460*	-37
4	459*	165
5	459*	21
6	459*	242
7	457*	-7
8	454*	273
9	455*	-60
10	452*	331
11	449*	-135
12	443*	324
H= 2, K= 6		
0	497*	208
1	497*	13
2	497*	368
3	498*	17
4	629	576
5	499*	-26
6	523	513
7	500*	18
H= -2, K= 6		
1	496*	-35
2	580	556
3	497*	-3
4	948	855
5	497*	24
6	574	483
7	499*	40
8	499*	163
H= 3, K= 6		
0	579*	143
1	580*	-61
2	581*	229
3	582*	-93
4	585*	240
5	587*	-60
6	589*	171
7	591*	32
8	592*	181
H= -3, K= 6		
1	578*	1
2	137	-103
3	578*	16
4	579*	-48
5	580*	75
6	581*	-131
7	584*	19
8	585*	-161
9	587*	-43
10	589*	-256
11	591*	-71
12	592*	-338
H= 4, K= 6		
0	841	-756
1	378*	48
2	555	-481
3	377*	68
4	375*	-147
5	372*	70
6	366*	-49
7	356*	-25
8	340*	-306
9	311*	-72
10	376	-310
H= -4, K= 6		
1	377*	113
2	536	-481
4	446	-207
6	500	-361
8	660	-577
10	480	-479
H= -6, K= 6		
2	345	356
6	533	677
H= -8, K= 6		
8	666	-562
H= 1, K= 7		
0	500	-363
2	737	-619
H= -1, K= 7		
1	447*	79
2	447*	137
3	446*	-36
4	444*	376
5	441*	-57
6	617	597
7	431*	-49
8	519	467

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[a] Asterisks denote unobserved reflections.

TABLE III

BOND DISTANCES IN α-ZrP (ÅNGSTRÖM UNITS)

Zr_1–O_4	2.04 (2)	P_2–O_4	1.51 (2)	P_3–O_8	1.52 (3)
O_5	2.10 (3)	O_5	1.52 (4)	O_9	1.50 (3)
O_6	2.06 (3)	O_6	1.50 (3)	O_{10}	1.54 (2)
O_8	2.06 (3)	O_7	1.60 (2)	O_{11}	1.54 (2)
O_9	2.11 (2)	Av	1.53	Av	1.52
O_{11}	2.06 (2)				
Av	2.07				

TABLE IV

BOND ANGLES IN α-ZrP (DEGREES)

O_4–Zr_1–O_5	90.9 (1.0)	O_4–P_2–O_5	113.7 (1.7)	O_8–P_3–O_9	112.1 (1.6)
O_4–Zr_1–O_6	88.6 (0.9)	O_4–P_2–O_6	109.7 (1.6)	O_8–P_3–O_{10}	109.4 (1.8)
O_4–Zr_1–O_8	90.1 (0.9)	O_4–P_2–O_7	109.8 (1.7)	O_8–P_3–O_{11}	110.3 (1.6)
O_4–Zr_1–O_9	91.1 (0.9)	O_5–P_2–O_6	110.1 (1.7)	O_9–P_3–O_{10}	108.4 (1.8)
O_4–Zr_1–O_{11}	178.8 (1.0)	O_5–P_2–O_7	102.3 (1.8)	O_9–P_3–O_{11}	110.0 (1.5)
O_5–Zr_1–O_6	90.1 (1.0)	O_6–P_2–O_7	111.0 (1.8)	O_{10}–P_3–O_{11}	106.3 (1.8)
O_5–Zr_1–O_8	89.8 (1.1)				
O_6–Zr_1–O_9	89.9 (0.9)				
O_8–Zr_1–O_9	90.2 (1.0)				

$|F_o|K + b|F_o|^2K^2)$, where $a = 2|F_{\min}|K$ and $b = 2/|F_{\max}|K$. The final value of R was 0.084 and the weighted R was 0.089.

The final parameters together with their standard deviations are listed in Table I. Table II lists the observed and calculated structure amplitudes. The final difference map showed several positive regions the highest of which was 1.25 e/Å^3 in the vicinity of a zirconium atom. These peaks could not be assigned to hydrogen atoms and must arise from other factors, primarily absorption, thermal motion errors, and termination-of-series effects.

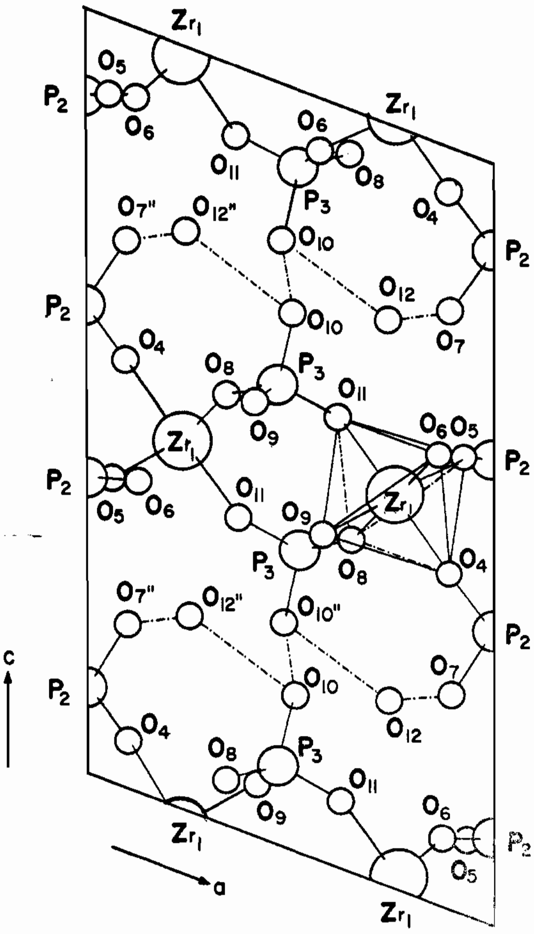

Figure 2.—Projection of the α-ZrP structure on (010). The glide plane is at $y = {}^1/_4, {}^3/_4$, and the 2_1 axes are at $x = 0, {}^1/_2$; $z = {}^1/_4, {}^3/_4$. The doubly primed atoms are related to similarly numbered unprimed atoms by the 2_1 axes. Broken lines indicate possible hydrogen bonding (Scheme I). The water molecular is O_{12}.

Description of the Structure

The structure of α-ZrP projected onto the *ac* plane is shown in Figure 2. The zirconium atoms are situated alternately slightly above and below the *ab* planes at $z = 0$ and ${}^1/_2$. These are bridged to phosphate groups located above and below the metal atom planes to form layers. One of the idealized layers is shown in more detail in Figure 3. Any three adjacent zirconium atoms in the same layer form a slightly distorted equilateral triangle. The phosphate groups are located such that the phosphorus atoms are in the centers of the equilateral triangles above and below the metal atom planes in alternate triangles. Three of the phosphate oxygens are bonded to the three metal atoms forming the triangle. The fourth oxygen bears the hydrogen and is directed nearly perpendicular to the *ab* plane.

The bond distances and bond angles are given in Tables III and IV. The coordination about the zirconium atoms is octahedral, the largest deviation from 90° angles being 2.3°. The phosphate tetrahedra are slightly distorted. In one phosphate group the P–O bond of the P–OH group is 1.60 Å while the other three P–O bonds average 1.51 Å. This same phosphate group has one bond angle (O_5–P_2–O_7) which deviates

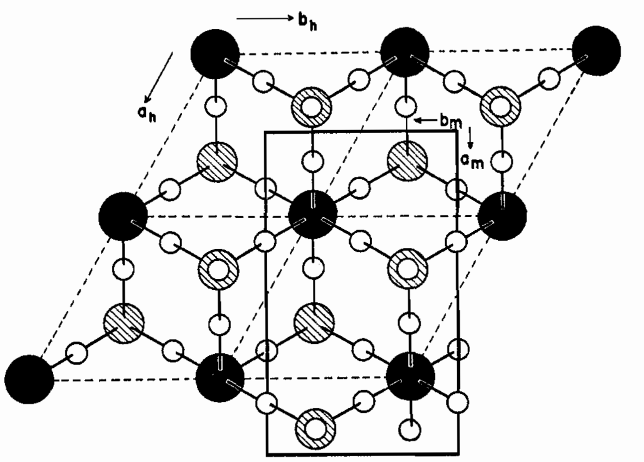

Figure 3.—Idealized layer in the α-ZrP structure showing relationship of the pseudo-hexagonal cell (broken lines) to the true, monoclinic unit cell.

significantly from tetrahedral. The other phosphate group is more regular, the bond lengths varying from 1.50 to 1.54 Å and the angles from 106 to 112°. These bond distances and angles are rather similar to those found in potassium dizirconium triphosphate.[13]

The most interesting features of the α-ZrP structure are those which make it possible for the crystals to exchange ions. The description of these features is facilitated by making use of a pseudo-hexagonal unit cell which is related to the true unit cell by

$$a_h = {}^1/_2 a_m/\cos 30° \cong 5.24\ \text{Å}$$

$$b_h = b_m = 5.298\ \text{Å}$$

$$c_h = 1.5 c_m \cos 21.5° = 22.62\ \text{Å}$$

The hexagonal c axis is coincident with the c^* axis of the monoclinic unit cell and hence is perpendicular to the hexagonal face (001) of the crystal. The origin of the new cell is placed at a zirconium atom as shown in Figure 3. The positions of the metal atoms in the pseudo-cell are very close to 0, 0, 0; $^1/_3$, $^2/_3$, $^1/_3$; $^2/_3$, $^1/_3$, $^2/_3$. The phosphorus atoms are (ideally) at 0, 0, $\pm ^1/_4$; $^1/_3$, $^2/_3$, $^1/_{12}$; $^1/_3$, $^2/_3$, $^7/_{12}$; $^2/_3$, $^1/_3$, $^5/_{12}$; $^2/_3$, $^1/_3$, $^{11}/_{12}$. Thus, any two adjacent layers are displaced relative to one another by $^1/_3$, $^2/_3$, $^1/_3$. This places the phosphorus atoms directly above the zirconium atom (and *vice versa*) in the layer below.

The arrangement of atoms described above results in the presence of cavities between layers of the type shown in Figure 4. The phosphorus and zirconium atoms in each layer from a six-membered ring (oxygens neglected) with a chair shape. However, one of the rings is rotated 60° relative to the other. The cavities are closed at the top and bottom by phosphate groups, respectively, above and below the centers of the six-membered rings. There is exactly one such cavity per formula unit of α-ZrP and the water molecule sits in the center of the cavity.

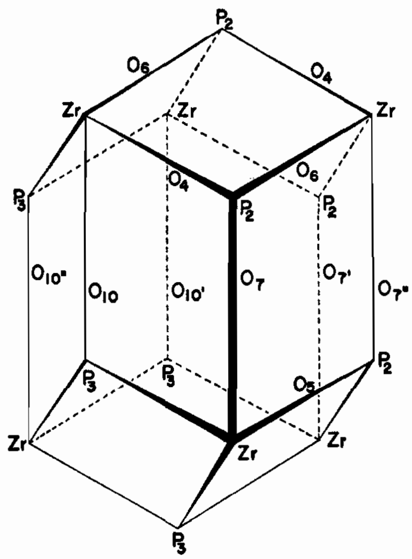

Figure 4.—Idealized picture of a cavity formed by two adjacent layers in α-ZrP. The symmetry of the cavity is D_{3d}-$\bar{3}2m$ with the water located in the center of the cavity and the $\bar{3}$ axis parallel to c^*. The singly primed atoms are related to unprimed atoms of the same number by one unit cell translation. To preserve clarity, not all of the oxygen atoms have been included.

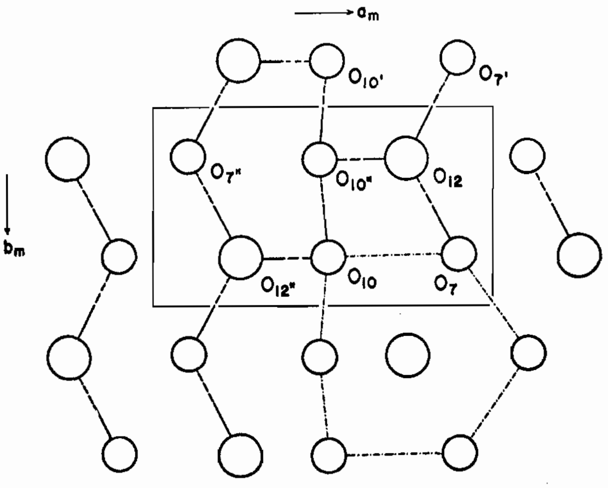

Figure 5.—Projection of oxygen atoms involved in hydrogen bonding by Scheme I onto (001). The water molcule is O_{12}. The dot–dashed line outlines one cavity and the solid line one unit cell. The half-solid, half-broken lines indicate hydrogen bonds with the solid portion representing the O–H bond.

The water molecule (O_{12}) is held in the cavity by hydrogen bonds. This is inferred from the oxygen–oxygen distances in Table V. There are three short O–O distances involving the water molecule (O_{12}–O_{10}'', O_{12}–O_7, and O_{12}–O_7'). One possible arrangement of hydrogen bonds is that in which one hydrogen atom of a phosphate group is directed toward the water molecule ($\mathrm{P_2{-}O_7{-}H{-}{-}{-}O{<}^{H}_{H}}$) and the water hydrogens are directed at O_{10}'' and O_7'. The disposition of these

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[13] B. Matcović, B. Prodić, and M. Sljukić, Abstracts, Summer Meeting of the American Crystallographic Association, Minneapolis, Minn., Aug 1967, No. VII.

TABLE V

POSSIBLE HYDROGEN BOND DISTANCES IN α-ZrP (ÅNGSTRÖM UNITS)

O_{12}–O_7	3.06 (6)
O_{10}''	2.78 (3)
O_7'	2.82 (6)
O_{10}''–O_{10}	3.07 (6)
O_{10}'	3.07 (6)[a]

[a] Next shortest distance is O_{10}–O_7 which is 3.24 (3) Å.

bonds in projection is shown in Figure 5. All three of these hydrogen bonds are intralayer bonds. The remaining hydrogen bonds form very weak interlayer bonds of the type P_3–O_{10}–H---O_{10}'' and P_3–O_{10}''–H---O_{10}'. These hydrogen bonds form a zigzag array running parallel to the *b* axis. All of the interlayer hydrogen bonds involve P_3-type phosphate groups whereas the P_2 type are all involved in intralayer hydrogen bonding.

An alternative hydrogen-bonding scheme involves the assumption that the shortest hydrogen bonds originate from the two P–OH groups with water as the acceptor atom for both these bonds. Thus, the bonding scheme would be P_2–O_7–H---O_{12} and P_3–O_{10}''–H---O_{12}. One hydrogen atom of the water forms a very long bond to O_7 and the other hydrogen forms no hydrogen bond in this scheme. There are no interlayer hydrogen bonds so that the layers are held together by van der Waals forces.

Both hydrogen-bonding schemes are speculative at present and the correct choice must await a neutron diffraction study. However, in either case the forces between layers are quite weak and one might expect cleavage parallel to the layers (001). This is in fact observed.

The zeolitic nature of the crystals and the weak forces between layers provide a basis for explaining their sieving behavior and the ready expansion of the lattice during exchange.[3] These aspects of the exchange mechanism will be discussed in a forthcoming paper.

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The Crystal Structure of Rhenium(VII) Oxide

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The crystal structure of rhenium(VII) oxide, Re_2O_7, has been determined from three-dimensional single-crystal X-ray data collected by film techniques. The least-squares refinement converges to a conventional *R* factor of 0.053 for 1126 nonzero reflections. The compound crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $a = 12.508$, $b = 15.196$, $c = 5.448$ Å, and $V = 1035.5$ Å^3. The unit cell contains 8 formula units. Measured and calculated densities are 6.14 and 6.214 g/cm^3, respectively. The structure consists of strongly distorted ReO_6 octahedra and fairly regular ReO_4 tetrahedra which are connected through corners to form polymeric double layers in the *ac* plane. The double layers have only van der Waals contacts to neighboring ones. Parallel zigzag chains of octahedra, every other chain being part of the upper or lower half of the double layer, are linked through corners of the tetrahedra in such a way that rings (o–t–o–t) (o, octahedron, t, tetrahedron) within the layers are formed. The octahedra contain three short (1.65–1.75 Å) and three long (2.06–2.16 Å) Re–O bonds, while in the tetrahedra the bond distances range from 1.68 to 1.80 Å. The structure is one of the relatively few known examples where metal atoms of the same oxidation number occur with coordination numbers 4 and 6 in the same structure. From the crystal structure the mechanisms of evaporation (to form $O_3ReOReO_3$ molecules) and of hydrolysis (where $Re_2O_7(OH_2)_2$ is formed) can be derived. In its structural and bond properties, rhenium(VII) oxide represents an intermediate between the polymeric oxides MoO_3 and WO_3 and the more covalently bonded OsO_4, which forms a molecular structure.

Introduction

The very simple crystal structure of rhenium(VI) oxide[1] has been known for a long time and has become the model for a basic structure type. Structure and bonding of solid rhenium(VII) oxide, on the other hand, have been completely unknown up to now and have been the object of speculation and controversy. A mass spectroscopic investigation[2] and vapor density measurements[3] have shown that the oxide in the gas phase consists of Re_2O_7 molecules which have to be formulated as O_3Re–O–ReO_3 with tetrahedrally coordinated rhenium. From the physical and spectroscopic properties of the compound there were

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(1) K. Meisel, *Z. Anorg. Allgem. Chem.*, **207**, 121 (1932).

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