In a recent study on the Raman spectra of metal complexes, Brintzinger and Plane[23] have concluded that metal binding by pyrophosphate is essentially electrostatic with *at least* one PCO_3 group coordinated through two O atoms to the metal ion. Because of steric effects, they have proposed that the pyrophosphate ion acts as a tridentate anion. It is reasonable to assume similar interactions by the isoelectronic methylenediphosphonates, with HEDP having an additional bonding site.

It is of interest to note that large deviations from linearity were obtained for plots of log $\beta_{\mathrm{MH}_i\mathrm{L}}$ against ionization potential. This is contrary to that reported[17] for the metal hydroxides where plots of log β against z^2/r or the ionization potential were linear. The similarity between the two plots could be fortuitous since for the alkali metal ions only Na^+ and Li^+ were included in the correlation.

The entropies of hydration of metal ions are proportional to the reciprocal of the crystal radii.[24] The excellent fit of log $\beta_{\mathrm{MH}_i\mathrm{L}}$ *vs.* $1/r$ suggests that the enthalpy changes accompanying alkali metal ion complexing by diphosphonates are either negligible or independent of alkali metal ion. Work is underway to measure the enthalpy change for metal ion complexing to determine the relative significance of the ΔH and ΔS terms to the stability of these ionic complexes.

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The Crystal and Molecular Structure of Dipotassium Phenyl Phosphate Sesquihydrate ($K_2C_6H_5PO_4 \cdot 1.5H_2O$)

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The structure of $K_2C_6H_5PO_4 \cdot 1.5H_2O$ has been determined by X-ray diffraction study. The crystals are orthorhombic (a = 5.91, b = 12.01, c = 30.80 A, space group Pbcn) with eight molecules per unit cell. The intensities of 728 independent reflections were recorded photographically and estimated with a densitometer. The structure was solved by a symbolic sign method and has been refined to a conventional R factor of 11%. The phosphate group is in the form of a distorted tetrahedron, with one long ester P–O distance of 1.64 A and three essentially equal P–O distances of 1.51, 1.53, and 1.53 A. The bond angles at the phosphorus atom vary from 101 to 114°. There are three different potassium ions in the cell, one in a general position and two in special positions. If the limit of potassium coordination is taken as 3 A, K(1) in a general position is coordinated to four oxygen atoms, K(2) in a special position is coordinated to six oxygen atoms, and K(3) also in a special position is coordinated to four oxygen atoms. Of the phosphate oxygen atoms two are coordinated or hydrogen bonded to three other atoms and one is coordinated or hydrogen bonded to four other atoms in addition to the covalent bond to the phosphorus atom. This has the effect of producing a tightly bonded crystal with small thermal vibrations, particularly evident in the phosphate group. This also appears to cause the three nonester oxygen atoms to be equidistant from the phosphorus atom.

Introduction

The hydrolysis of organic phosphates has been studied for a number of alkyl and aryl phosphates.[1-3] The structures of organic phosphates, in particular a comparison of the P–O–C linkages, should help in interpretation and understanding of the kinetic results, even though extrapolation from crystal structures to structures in solution is difficult. It is particularly interesting and informative to consider the effects of metal coordination and hydrogen bonding on the structures, inasmuch as in several instances the presence of a metal ion has appreciably effected the hydrolysis rates.[4] Such results suggest the possibility of a metal ion complex in solution in these cases. A complex between the monoanion, PO_4R^-, and a water molecule has been proposed to explain the structural requirements for hydrolysis of monoesters as well as cyclic phosphate esters.[5,6] Structural results[7,8] indicate a rather significant effect of hydrogen bonding and complex formation on P–O and PO–C distances which may be significant when considering various factors affecting the kinetics. The structure of dipotassium phenyl phosphate with 1.5 molecules of water of hydration is, to

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our knowledge, the only monoaryl phosphate structure published other than calcium naphthyl phosphate.[7]

Experimental Section

Crystals of dipotassium phenyl phosphate sesquihydrate were obtained by recrystallization from water. A crystal about 0.27 mm thick, 0.54 mm wide, and 1 mm long was selected and sealed in a glass capillary to prevent possible loss of water during the collection of the X-ray data.

Dipotassium phenyl phosphate sesquihydrate (mol wt 277.24) crystallizes in an orthorhombic space group, and systematic extinctions in the $0kl$ reflections, $k \neq 2n$, $h0l$ zone, $l \neq 2n$, and $hk0$ zone, $h + k \neq 2n$ indicate space group Pbcn (no. 60); d_m 1.735; d_c 1.683 g/cc. There are eight molecules per unit cell and the lattice parameters determined from Weissenberg and rotation photographs are: $a = 5.91 \pm 0.03$, $b = 12.01 \pm 0.05$, $c = 30.80 \pm 0.06$ A. For $K_2C_6H_5PO_4 \cdot 1.5H_2O$, the total number of electrons, $F(000)$, is 1128; the linear absorption coefficient for Cu Kα radiation is $\mu = 91.75$ cm^{-1}.

The crystal was mounted on the a axis and multiple-film Weissenberg photographs were taken using Cu Kα radiation from $h = 0$ to $h = 4$ for intensity measurements. Intensities of 728 independent reflections were measured by scanning with a densitometer reflections that had been integrated in a direction perpendicular to the direction of scanning. Areas under the densitometer tracings were measured with a planimeter and taken as proportional to the relative intensities since the recorder had a logarithmic response. Intensities were corrected for absorption using an absorption correction program written by Takeda.[9]

The intensities were reduced to F values and a Wilson plot obtained which gave initial level to level scaling and an over-all temperature factor.[10]

Structure Determination

The structure was solved by the symbolic addition procedure described by Karle and Karle,[11] after several attempts to interpret a three-dimensional Patterson map failed. Normalized structure factors were calculated and the signs of 120 reflections were determined initially by the Σ_2 relationship, *i.e.*, $sF_h \sim sF_{h-k}'sF_k''$. The first E map showed two potassium atoms, in special positions (c) in space group Pbcn, and indicated the positions of the other potassium atom, the phosphorus atom, and four oxygen atoms. A second E map, using an additional 120 signs derived from the Σ_2 relationship, showed all of these positions plus one molecule of water in a general position and one in a special position. The structure factors from these positions were used to calculate phases for the next Fourier synthesis which showed the phenyl group. These atomic positions were refined and another Fourier synthesis was calculated. It was not originally known how many molecules of water the crystal held but the crystallographic molecular weight indicated approximately two. This Fourier synthesis and a difference Fourier synthesis failed to show another half-molecule of water.

The refinement was entirely normal and was carried out using the least-squares refinement program of Busing, Levy, and Martin[12] using the Hughes[13] weighting scheme. Three cycles refining the positional parameters and scale factors brought the R to 18%. Three cycles refining positional and isotropic thermal parameters gave the final R of 11%. A final difference Fourier synthesis showed no significant features.

Results and Discussion

Table I shows the final atomic positions and thermal parameters with their standard deviations. Table II gives the final structure factors. The interatomic distances and bond angles are shown in Table III along with standard deviations. Figure 1 shows the [100] projection of the structure which has all of the essential features, inasmuch as the a axis is only 5.91 A. Table IV lists bond distances for other metal salts of phosphate monoesters.

TABLE I

ATOMIC PARAMETERS, TEMPERATURE FACTORS, AND THEIR STANDARD DEVIATIONS

Atom	x	y	z	B, A^3
K(1)	0.5865 (9)[a]	0.1229 (4)	0.1477 (1)	1.12 (8)
K(2)	0.0000 (–)	0.1172 (5)	0.2500 (–)	0.71 (10)
K(3)	0.5000 (–)	0.2960 (5)	0.2500 (–)	0.91 (11)
P(4)	0.0536 (10)	0.3057 (4)	0.1699 (1)	0.24 (8)
O(5)	0.0026 (28)	0.2672 (11)	0.1198 (4)	0.99 (24)
O(6)	−0.1761 (24)	0.2844 (10)	0.1912 (4)	0.23 (8)
O(7)	0.2399 (29)	0.2295 (11)	0.1858 (4)	0.77 (26)
O(8)	0.1169 (33)	0.4296 (14)	0.1703 (5)	2.59 (34)
O(9)	−0.0689 (31)	0.9772 (13)	0.1762 (5)	2.05 (31)
O(10)	0.5000 (–)	0.0421 (17)	0.2500 (–)	1.61 (39)
C(11)	0.1619 (45)	0.2398 (18)	0.0915 (7)	2.04 (41)
C(12)	0.15800 (47)	0.1458 (21)	0.0705 (8)	2.33 (49)
C(13)	0.3395 (56)	0.1158 (26)	0.0404 (8)	3.59 (58)
C(14)	0.5291 (55)	0.1797 (23)	0.0346 (8)	3.04 (54)
C(15)	0.5399 (66)	0.2753 (27)	0.0541 (10)	4.94 (75)
C(16)	0.3493 (44)	0.3144 (20)	0.0840 (7)	1.73 (43)

[a] The number in parentheses is the standard deviation and refers to the least significant digits.

The ester phosphorus–oxygen distance is 1.64 A, the other three P–O distances being 1.51, 1.53, and 1.53 A. This seems to indicate that the charge on the phosphate group is equally distributed between the three nonesterified oxygens and that there is about the same amount of π bonding to each of these oxygen atoms. (See Figure 2.)

The sum of the four P–O bond lengths seems to be important in indicating the total amount of π bonding. Cruikshank[14] has suggested that though the individual P–O bond lengths in any phosphate group may range from 1.40 to 1.69 A, their sum is nearly constant. This assumes a linear relationship between the bond length and the bond order and indicates a constant amount of π-bond character has been allocated between the four bonds. Examination of the sums of the four P–O bond lengths in a number of phosphates gives a mean value for this sum of 6.177 ± 0.03 A with

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(9) The program was written by H. Takeda to utilize the subroutines of C. W. Burnham and modified by J. Stewart for "Program System for X-ray Crystallography," University of Washington and University of Maryland, 1965.

(10) All programs used, except the least-squares refinement and absorption, were those from the Montana State University Library for Crystallographic Computing for the IBM 1620, written by C. T. Li, G. Svetich, C. N. Caughlan, R. D. Witters, and K. Watenpaugh.

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TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

0	0	L
4	118	-95
6	113	99
8	119	-98
12	245	252
14	223	-228
16	93	107
18	100	-103
20	60	48
22	45	-36
24	81	81
26	67	-57
28	93	97
30	82	-83
36	58	65
0	2	L
0	349	-324
1	39	-37
3	65	-57
4	63	50
5	103	-86
6	42	50
7	64	56
8	56	61
9	191	-207
10	47	-46
11	44	50
13	93	103
14	73	77
15	84	-82
16	64	-67
17	52	-44
18	38	40
19	155	164
21	73	-79
23	32	-30
24	44	-32
25	90	100
29	74	-90
31	47	56
36	38	-43
38	33	40
0	4	L
0	23	17
1	136	-136
2	46	-40
3	73	62
7	95	86
8	120	-109
9	57	-49
10	176	198
11	87	85
12	26	-17
13	60	-67
14	132	-133
15	80	65
16	89	101
17	39	-43
18	59	57
20	91	-95
21	56	-48
22	56	48
23	76	65
25	80	-81
28	61	-72
35	52	57
0	6	L
0	35	-37
1	266	280
2	28	25
4	33	25
5	62	-69
7	46	46
8	31	-31
9	102	100
10	28	-26
11	165	-170
12	38	41
13	73	77
15	48	-44
16	34	-37
17	32	30
19	42	-40
20	54	-41
21	57	56
23	57	-56
25	50	44
27	58	-51
29	61	68
30	39	39
32	39	-42
33	22	-16
35	19	-23
0	8	L
0	39	38
1	39	-47
4	43	-46
5	30	-26
6	33	-23
7	23	17
8	73	73
10	46	-38
12	62	-62
14	81	80
15	51	40
18	79	-75
20	87	95
23	58	49
26	57	60
0	10	L
0	75	87
1	73	-81
4	32	26
5	43	41
6	36	36
9	49	-46
10	60	-58
11	87	101
12	76	73
13	38	-35
14	54	-68
15	53	-51
19	44	55
24	55	57
26	47	-49
27	26	34
28	20	28
0	12	L
0	120	-125
1	36	32
5	33	-30
7	39	45
8	32	-36
9	62	-60
10	86	96
11	46	-44
12	58	-64
13	57	58
16	29	-32
18	43	55
19	46	43
20	76	-72
21	33	-39
22	31	40
1	0	L
4	79	-86
6	63	-59
8	56	53
10	83	102
12	50	-59
14	46	-48
16	59	61
18	42	-44
22	87	88
24	35	-33
26	40	-37
28	33	34
1	1	L
0	78	-76
1	70	-52
2	15	-17
3	27	21
4	86	102
5	140	135
6	135	-145
9	144	138
10	50	58
11	41	-46
12	36	33
13	72	-83
14	48	-51
15	71	80
16	85	90
19	137	-148
21	52	50
23	52	50
24	35	31
25	57	-63
29	56	64
31	51	-49
32	45	34
34	32	-39
1	2	L
2	87	74
3	106	-97
5	24	-16
7	89	105
8	28	-26
9	28	-23
10	58	-64
12	30	25
13	68	83
14	46	45
15	30	-33
17	38	-36
24	36	32
1	3	L
0	83	95
3	116	103
4	178	-170
5	182	-210
6	293	286
7	64	64
8	90	-104
11	58	60
12	42	-45
13	48	-46
15	54	59
16	78	-99
17	47	-47
18	77	85
20	70	-73
22	59	57
23	50	42
24	40	-36
25	53	-55
26	35	30
27	50	42
30	52	49
32	58	-68
33	45	-55
34	55	68
35	59	56
1	4	L
3	47	-45
4	48	51
5	59	44
6	77	73
8	21	-16
11	31	21
12	22	19
13	35	-34
14	41	-39
15	40	37
18	36	33
21	35	32
22	46	-37
23	39	-36
32	37	39
1	5	L
0	28	21
3	113	-99
4	42	-27
5	139	116
7	27	-22
10	60	-53
11	63	-62
13	51	54
14	71	80
15	65	-69
16	37	-29
17	35	35
18	51	-56
20	70	76
22	35	25
23	29	-28
24	59	-65
25	51	58
27	50	-49
30	57	-65
1	6	L
3	87	85
4	39	-32
5	46	-41
12	33	37
13	27	18
15	44	-44
17	25	30
21	61	-75
23	59	52
25	23	27
27	48	-45
29	47	42
1	7	L
0	39	36
1	29	25
2	36	-28
3	56	-54
4	24	-26
5	161	135
6	57	58
7	110	-121
8	70	-65
10	58	54
11	26	23
13	59	61
14	84	-68
15	86	-91
17	83	85
18	64	69
19	52	-44
20	82	-94
23	53	-55
24	54	46
25	44	37
29	38	27
30	54	52
31	59	-65
32	27	-27
33	46	60
1	8	L
2	41	43
4	45	-46
5	30	30
6	45	-38
8	50	49
12	44	-39
13	52	-48
14	50	42
21	52	46
1	9	L
1	46	51
2	33	-38
4	103	105
5	138	-133
6	70	-73
7	117	127
11	45	-45
12	59	64
14	71	-85
16	49	47
17	64	-67
19	60	59
21	34	-30
22	29	-30
23	30	28
24	57	65
26	65	-74
[illegible]	25	27
2	0	L
2	128	-137
4	31	37
6	23	-29
8	171	183
12	127	122
14	106	-121
16	49	48
20	37	40
22	89	-108
26	100	-104
28	83	79
30	33	-38
36	49	58
2	1	L
1	106	-91
2	17	-12
3	87	107
4	41	-48
6	57	63
7	84	-85
8	25	23
9	88	93
10	41	-51
12	71	83
13	74	-88
15	40	50
16	92	-110
18	42	49
19	32	-35
20	28	28
22	60	-75
24	33	40
25	34	30
26	32	37
28	40	-48
29	45	-43
2	2	L
2	36	-42
3	40	29
5	33	-28
6	39	37
7	55	62
8	79	-95
9	67	-84
10	75	93
11	18	17
13	23	19
15	39	-38
16	20	9
17	42	-41
18	54	-62
19	88	102
21	41	-49
22	58	61
24	65	-80
25	41	38
26	37	38
29	34	-41
31	39	47
2	3	L
1	39	-26
2	82	101
3	138	118
4	19	-16
5	43	-37
6	20	-15
7	61	-59
9	43	44
10	28	-27
12	37	-30
13	41	-44
15	33	-37
16	64	77
20	34	-47
21	31	-27
22	49	52
23	49	51
26	39	-45
27	43	-49
28	47	53
2	4	L
0	44	-32
1	138	-117
2	89	66
3	80	60
4	16	-15
6	32	-29
7	58	48
9	51	-53
10	16	12
11	89	100
12	38	-38
13	69	-80
15	70	75
18	79	84
20	68	-70
21	50	-37
23	62	54
24	48	48
25	65	-78
27	53	50
32	34	-31
2	5	L
2	62	49
3	34	-22
4	83	-69
6	79	-58
7	56	39
8	77	85
11	59	-54
12	57	-65
13	35	33
14	46	43
15	45	48
17	41	-37
20	40	41
23	53	-58
27	46	43
28	30	-22
30	39	41
32	26	-24
2	6	L
0	45	36
1	149	158
2	31	-27
3	52	-47
5	47	-38
6	81	66
8	73	-67
9	84	78
11	112	-111
12	38	34
13	84	88
14	[illegible]	[illegible]
15	65	-56
21	47	40
23	46	-42
25	77	68
27	52	-64
29	51	52
2	7	L
2	47	-55
4	27	24
5	51	-59
6	46	35
8	70	-69
12	67	65
13	71	53
14	49	-45
15	40	42
17	71	-79
20	55	-40
21	64	59
23	58	-43
27	39	35
29	40	-42
30	36	-37
2	8	L
1	44	-41
8	77	63
12	44	-36
14	64	57
15	49	39
18	46	-37
20	60	48
24	37	-37
25	31	-28
26	37	35
2	9	L
2	48	-49
4	44	61
5	34	37
6	29	25
8	39	-28
11	18	15
13	32	-24
17	62	56
18	26	20
21	50	-55
22	38	-45
23	39	39
27	37	-46
29	31	36
2	10	L
3	36	39
9	40	-38
10	47	-51
11	65	56
14	43	-52
19	36	35
21	39	-44
2	11	L
2	57	51
3	44	48
4	44	-47
7	46	-55
9	26	32
2	12	L
5	34	-30
6	31	22
8	47	-48
3	0	L
6	28	-22
8	39	50
10	40	46
12	51	-56
14	44	-35
16	81	82
18	56	-48
20	63	-69
22	110	111
26	86	-87
28	87	86
3	1	L
1	24	19
2	51	-49
3	36	-33
4	35	37
5	60	70
7	26	24
8	20	20
9	32	-40
10	33	-35
12	23	16
14	43	-44
16	33	27
17	45	49
19	68	-69
20	47	37
23	49	40
25	31	-35
28	29	20
31	28	-25
3	2	L
1	79	83
2	34	29
3	140	-137
4	40	-38
5	35	32
7	81	97
9	68	-82
10	40	-38
13	56	65
14	39	44
15	38	-28
16	24	-31
17	40	-38
22	46	-45
28	37	-38
30	30	25
31	35	-35
3	3	L
1	46	-41
2	104	80
3	71	59
4	112	-104
5	94	-102
6	69	64
10	45	52
11	27	23
13	30	-31
14	31	39
15	33	34
16	53	-68
17	44	-52
18	65	74
19	114	117
20	104	-101
21	42	-44
[illegible]	40	34
30	40	51
31	43	47
32	47	-54
33	45	-54
34	43	48
3	4	L
1	41	-34
2	56	-42
3	67	59
5	54	-48
6	83	77
8	58	-57
9	45	47
10	40	-42
11	48	-53
12	81	86
14	43	-41
15	45	43
16	56	-58
17	45	-34
18	63	71
22	57	-44
23	41	-37
24	32	25
28	19	-20
29	21	-26
3	5	L
0	64	-61
1	70	65
3	59	-50
5	37	25
10	33	25
11	54	-49
12	39	-29
13	60	68
14	30	28
16	42	40
19	64	-56
20	41	40
24	51	-55
25	50	41
3	6	L
5	55	42
11	95	83
13	46	-51
17	70	78
21	75	-64
23	72	59
27	60	-57
3	7	L
1	31	37
3	45	-50
4	37	-38
5	53	64
7	53	-55
9	82	97
15	68	-66
16	40	-34
17	59	48
18	40	34
19	62	-45
20	45	-29
21	58	48
23	51	-46
3	8	L
2	96	114
3	52	62
4	82	-98
5	34	-38
6	22	-24
8	79	89
9	33	36
10	57	-61
11	46	-40
12	33	-28
3	9	L
2	35	-43
3	39	42
5	27	-32
6	28	-38
7	37	38
10	43	-49
11	15	-15
12	30	37
14	42	-40
15	40	42
16	42	42
17	33	-36
19	38	44
20	45	52
21	37	-40
22	24	-28
3	10	L
7	34	35
10	30	39
11	44	-38
13	24	23
15	37	40
16	27	36
17	47	-54
22	28	33
23	53	-55
4	0	L
4	98	111
6	88	-85
8	87	89
12	23	25
14	113	-131
16	104	122
18	33	-32
20	29	21
22	61	-65
24	72	74
26	57	-57
28	45	36
4	1	L
1	63	-73
4	22	-25
6	31	35
7	45	-50
12	43	52
15	41	37
16	51	-48
18	58	57
22	54	-49
4	2	L
2	45	39
3	40	47
5	41	-49
6	28	-35
13	41	-54
14	52	59
15	51	47
16	38	-45
4	3	L
1	17	-11
2	17	-16
5	32	28
6	32	-31
7	35	-39
10	53	66
11	35	38
12	35	-39
16	47	39
17	48	53
18	50	-45
20	26	-28
21	48	-41
22	58	48
4	4	L
0	91	67
1	77	-59
3	54	42
4	81	-61
6	62	51
9	53	-50
11	64	63
13	47	-50
15	52	49
4	5	L
2	110	119
4	110	-91
7	42	37
8	83	70
10	74	-74
4	6	L
3	50	-55
5	78	69
7	85	-84
4	7	L
2	59	-71
4	57	60
7	33	23
8	38	-45
11	64	-73
15	44	55
17	49	-51

[a] The columns reading from left to right contain the values of l, F_o, and F_c.

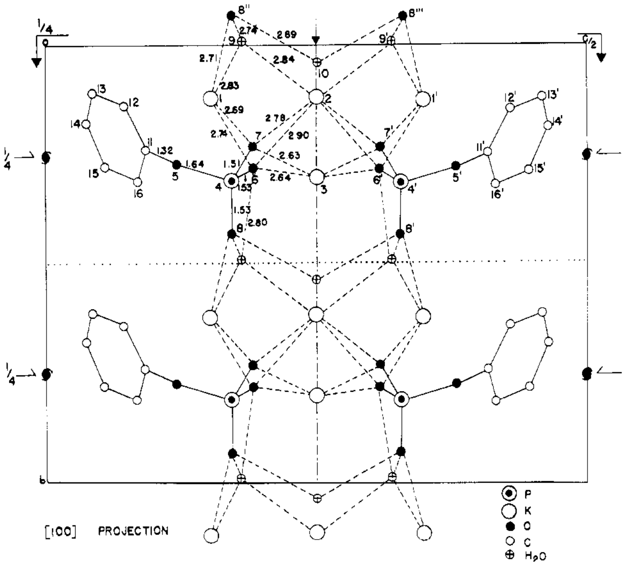

Figure 1.—Projection of the structure of dipotassium phenyl phosphate sesquihydrate projected down the *a* axis.

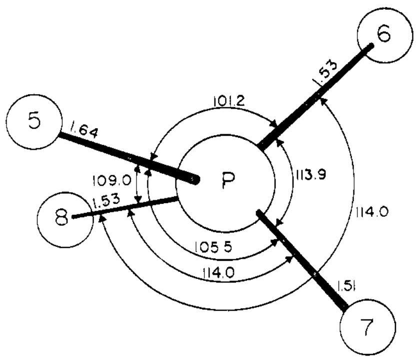

Figure 2.—The phosphate bond distances and angles in dipotassium phenyl phosphate sesquihydrate.

a rather remarkable constancy for the sum.[15] Examination of the sum of the four P–O bond lengths in Table IV shows that dipotassium phenyl phosphate has one of the largest sums although the difference may not be significant considering the standard deviations of the bond distances.

The C–O(P) bond of 1.32 A is characteristic of C–O bonds in which the oxygen is attached to an aromatic group and indicates partial double-bond character. The dihedral angle between the phenyl ring and P–O–C plane is 51.7°.

The potassium ions are four and six coordinated if the limit of coordination is taken as 3 A. K(1) is coordinated to O(6) from one phosphate group, O(7 from the one directly above it, O(8) from another phosphate group, and water oxygen O(9). K(2) is coordinated to O(6) and O(7) from the same phosphate group, water oxygen O(9), and the three oxygen atoms related to these by the twofold axis. K(3) is coordinated to O(7) from one phosphate group, O(6) from a phosphate group directly above, and the two atoms related to these by the twofold axis. Thus, with this limit of coordination, K(1) is coordinated to

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[15] M. Calleri and J. C. Speakman, *Acta Cryst.*, **17**, 1097 (1964).

TABLE III

INTERATOMIC DISTANCES AND ANGLES

Interatomic Distances

Atoms	Bond, A
P(4)–O(5)	1.64 (2)[a]
P(4)–O(6)	1.53 (2)
P(4)–O(7)	1.51 (2)
P(4)–O(8)	1.53 (2)
O(5)–C(11)	1.32 (4)
C(11)–C(12)	1.30 (5)
C(12)–C(13)	1.46 (6)
C(13)–C(14)	1.37 (6)
C(14)–C(15)	1.30 (6)
C(15)–C(16)	1.52 (7)
C(16)–C(11)	1.44 (5)
K(1)–O(6)	2.74 (2)
K(1)–O(7)	2.69 (3)
K(1)–O(8″)	2.71 (3)
K(1)–O(9″)	2.83 (3)
K(2)–O(6)	2.90 (2)
K(2)–O(7)	2.78 (2)
K(2)–O(9)	2.84 (2)
K(3)–O(6)	2.64 (2)
K(3)–O(7)	2.63 (2)
O(6)–O(9)	2.80 (3)
O(8)–O(9)	2.74 (3)
O(8)–O(10)	2.89 (3)

Some Nonbonded Contacts Less Than 4 A

Atoms	Bond, A
K(1)–O(5)	3.12 (2)
K(1)–O(10)	3.34 (1)
K(1)–C(11)	3.36 (4)
K(1)–C(12)	3.49 (4)
K(1)–C(13)	3.61 (4)
K(1)–C(14)	3.57 (4)
K(1)–C(15)	3.43 (4)
K(1)–C(16)	3.33 (4)
K(2)–P(4)	3.36 (1)
K(2)–O(10)	3.09 (2)
K(3)–O(9)	3.68 (2)
K(3)–O(10)	3.05 (2)
O(5)–O(9)	3.44 (3)
O(6)–O(9)	3.77 (3)
O(7)–O(9)	3.09 (3)
O(7)–O(10)	3.37 (3)
O(9)–O(10)	3.41 (2)

Bond Angles

Atoms	Angle, deg
O(5)–P(4)–O(6)	101.2 (3)[a]
O(5)–P(4)–O(7)	105.5 (3)
O(5)–P(4)–O(8)	109.0 (4)

Bond Angles (*Continued*)

Atoms	Angle, deg
O(6)–P(4)–O(7)	113.9 (3)
O(6)–P(4)–O(8)	112.0 (4)
O(7)–P(4)–O(8)	114.0 (4)
P(4)–O(5)–C(11)	124.0 (11)
O(5)–C(11)–C(12)	122.0 (18)
O(5)–C(11)–C(16)	119.9 (18)
C(12)–C(11)–C(16)	118.1 (18)
C(11)–C(12)–C(13)	121.0 (19)
C(12)–C(13)–C(14)	123.0 (21)
C(13)–C(14)–C(15)	118.4 (21)
C(14)–C(15)–C(16)	120.9 (25)
C(15)–C(16)–C(11)	118.2 (16)
O(6)–K(1)–O(7)	80.8 (2)
O(6)–K(1)–O(8″)	135.1 (2)
O(6)–K(1)–O(9)	75.6 (2)
O(7)–K(1)–O(9)	133.3 (2)
O(6)–K(2)–O(6′)	92.3 (1)
O(6)–K(2)–O(7)	53.3 (1)
O(6)–K(2)–O(7′)	85.7 (2)
O(6)–K(2)–O(9)	72.5 (3)
O(6)–K(2)–O(9′)	156.3 (3)
O(7)–K(2)–O(7′)	122.0 (1)
O(7)–K(2)–O(9)	70.7 (3)
O(7)–K(2)–O(9′)	139.5 (3)
O(9)–K(2)–O(9′)	127.3 (4)
O(6′)–K(3)–O(6″)	173.9 (1)
O(6′)–K(3)–O(7)	94.4 (1)
O(6′)–K(3)–O(7″)	83.8 (1)
O(7)–K(3)–O(7″)	144.6 (1)
K(1)–O(6)–K(2)	89.9 (4)
K(1)–O(6)–K(3)	90.1 (5)
K(1)–O(6)–P(4)	111.3 (8)
K(2)–O(6)–K(3)	82.4 (4)
K(2)–O(6)–P(4)	93.7 (7)
K(3)–O(6)–P(4)	158.4 (8)
K(1)–O(7)–K(2)	117.9 (5)
K(1)–O(7)–K(3)	91.6 (5)
K(1)–O(7)–P(4)	134.6 (9)
K(2)–O(7)–K(3)	84.9 (5)
K(2)–O(7)–P(4)	98.8 (8)
K(3)–O(7)–P(4)	119.0 (9)
K(1)–O(8)–P(4)	136.0 (10)
K(1)–O(8)–O(9)	95.5 (6)
K(1)–O(8)–O(10)	73.2 (5)
P(4)–O(8)–O(9)	126.8 (9)
P(4)–O(8)–O(10)	113.7 (9)
O(9)–O(8)–O(10)	88.9 (6)
K(1)–O(9)–K(2)	103.3 (6)
O(8)–O(10)–O(8″)	124.2 (3)

[a] The number in parentheses is the standard deviation and refers to the least significant digits.

four oxygen atoms, K(2) to six, and K(3) to four oxygen atoms. These potassium–oxygen distances range from 2.63 to 2.90 A.

The next closest contacts to K(1) are O(5) from the cell directly above, which is 3.13 A, and O(10) which is 3.34 A. Also the phenyl group is oriented in a manner that the perpendicular from K(1) to the plane is almost in the center of the ring, the K(1) to ring distance being 3.2 A. It seems that the π cloud of the phenyl ring is coordinated to K(1), thus satisfying the unsymmetric coordination and charge around this ion. The next closest contact to K(3) is O(10) which is 3.05 A from K(3) and might be considered coordinated to this ion. The next closest contact to K(2) is also O(10) which is 3.09 A from this ion. A list of some nonbonded contacts is given in Table III. The oxygen coordination around the potassium ions at the 3-A limit and some distances and angles are shown in Figures 3–5.

Examination of the interatomic distances indicates that water oxygen atom O(9) is hydrogen bonded to O(6) above and O(8) while being coordinated to K(1) and K(2); water oxygen atom O(10) appears to be hydrogen bonded to O(8) and the atom related to O(8) by the twofold axis, but O(10) does not appear to be coordinated to a potassium ion. The nonbonded contacts in the direction of the *c* axis between phenyl car-

Table IV

Comparison of Bond Distances for Metal Salts of Phosphate Monoesters

	P=O	P—O	P—OR	ΣD
Dipotassium phenyl phosphate		1.51 1.53 1.53	1.64	6.21
Calcium thymidylate[a]	1.474	1.514 1.486	1.587	6.061
Barium uridine 5-phosphate[b]	1.51	1.52 1.55	1.64	6.22
Disodium β-glycerol phosphate[c]	1.46	1.52 1.53	1.62	6.13
Dipotassium glucose 1-phosphate[d]	1.48	1.52 1.53	1.59	6.12

[a] K. N. Trueblood, P. Horn, and V. Luzzati, *Acta Cryst.*, **14,** 965 (1961). [b] E. Shefter and K. N. Trueblood, *ibid.*, **18,** 1067 (1965). [c] See ref 8. [d] C. A. Beevers and G. H. Maconachie, *Acta Cryst.*, **18,** 232 (1965).

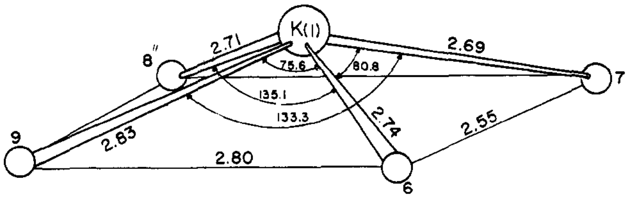

Figure 3.—Coordination around K(1) in dipotassium phenyl phosphate sesquihydrate.

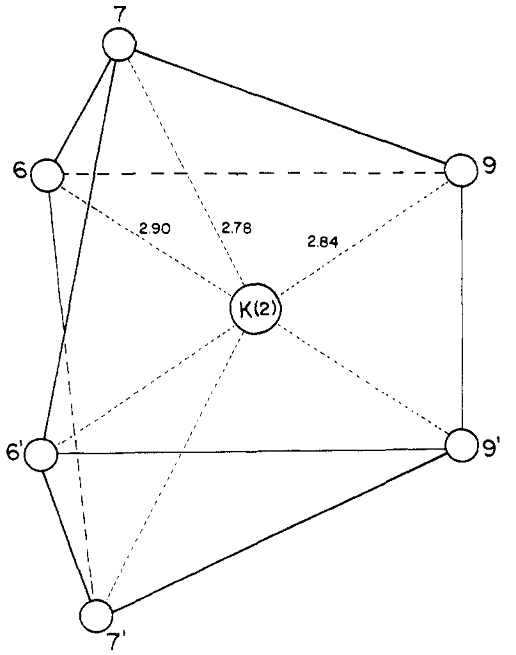

Figure 4.—Coordination around K(2) in dipotassium phenyl phosphate sesquihydrate.

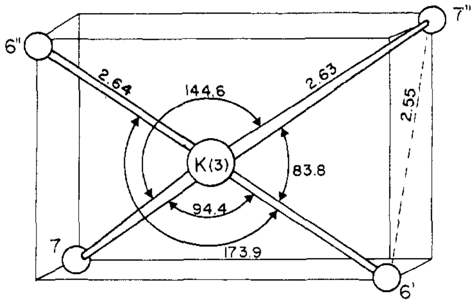

Figure 5.—Coordination around K(3) in dipotassium phenyl phosphate sesquihydrate.

bons are greater than 4 A. Thus, there is a very strong network of bonds among potassium ions, the water molecules, and the phosphate oxygen atoms in the direction of the *a* axis and the *b* axis but only van der Waals contacts between phenyl groups in the *c* direction.

The very low temperature factors observed in Table I appear to be the result of a very tightly knit structure which is evident from Figure 1 considering the hydrogen bonding and potassium ion coordination. In this respect there is a similarity to sodium β-glycerol phosphate pentahydrate.[8] We know of no systematic error in the data which would cause the temperature factors to be too low, unless the applications of absorption corrections were inadequate owing to uncertainty in measuring the crystal size.

Several results seen in this structure may be important in considering the hydrolysis of monosubstituted organic phosphates. The identity of the phosphoryl oxygen has apparently disappeared since all of the nonesterified oxygens are nearly equidistant from phosphorus. There is apparently a strong tendency for all of the phosphate oxygen atoms to coordinate with the positive potassium ion and to form hydrogen bonds with water molecules. This may be important in considering the proposed intermediate in the hydrolysis of monosubstituted organic phosphates.[4,5] The phosphate tetrahedron is quite distorted, the O(5)–P–O(6) angle of 101° being only a few degrees from the small angle at phosphorus (98.4°) in cyclic organic phosphate molecules.[16,17] The angle at O(5) is 124° which confirms the suggestion that this is normally close to 120°.[17]

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(16) T. A. Steitz and W. N. Lipscomb, *J. Am. Chem. Soc.*, **87,** 2488 (1965).

(17) M. G. Newton, J. R. Cox, Jr., and J. A. Bertrand, *ibid.*, **88,** 1503 (1966).