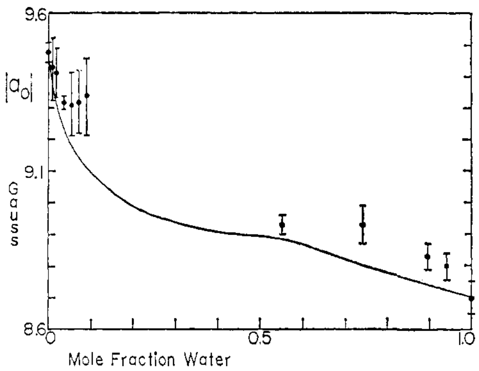

Figure 4. Variation of a_O with mole fraction of water added to acetonitrile. Points represent experimental values and the heights of the lines indicate the 95% confidence level of the measurements. The solid curve indicates the calculated solvent dependence of the oxygen coupling constants (see text).

oxygen and carbon atoms, a statement which is formulated as eq 10. We have chosen to evaluate the two

$$a_O = Q_{OC}{}^{O}\rho_7{}^{\pi} + Q_{CO}{}^{O}\rho_1{}^{\pi} \qquad (10)$$

constants in eq 10 using the calculated spin densities and observed oxygen coupling constants for PBSQ in water and acetonitrile. The values are $Q_{OC}{}^{O} = -40.41$ gauss and $Q_{CO}{}^{O} = -16.69$ gauss.[52] Having fixed the extreme conditions of pure water and pure acetonitrile, values of a_O were calculated for intermediate conditions and are given in Table III. A graphic comparison of calculated and observed oxygen-17 coupling constants is presented in Figure 4.

It is far too early to assess the validity of eq 10 as a description of oxygen-17 coupling constants. There is at least a strong indication that a_O is responsive to changes of spin density on the carbonyl carbon atom.

Exchange Reaction. As indicated previously, the rate constant for the exchange of the oxygen atoms in PBSQ with the water in an acetonitrile solution at 25°, 0.19 hr^{-1}, is significantly larger than the constant for the exchange of water with neutral *p*-benzoquinone in the same medium. Kinetic data for the exchange of *p*-benzoquinone with pure water are limited to the report[53] that *p*-benzoquinone undergoes 5.8% exchange in 5 min at 20°. Total exchange in 10 days has also been reported.[54] The rate constant for exchange of the oxygen atoms in hydroquinone with water[55] at 25° is 1.9×10^{-6} hr^{-1}. In view of the rapid exchange through the anion radical in acetonitrile we are surprised by the report[54] that the addition of *p*-benzoquinone does not influence the speed of exchange of hydroquinone in water.

The occurrence of the exchange reaction suggests that a_O in various semiquinones may be accessible without the necessity of synthesizing gross quantities of the corresponding quinone. Thus reduction of quinones in aprotic solvents containing small quantities of ^{17}O-enriched water should permit the occurrence of the "back-exchange" reaction with the anion and eventual observation of a_O.

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[52] While the individual spin densities are substantially dependent on the particular choice of $Q_{CH}{}^{H}$, the values of $Q_{OC}{}^{O}$ and $Q_{CO}{}^{O}$ only change to -44.56 and -15.99 gauss when $Q_{CH}{}^{H}$ is changed to -26 gauss.

[53] E. Adler, I. Falkehag, and B. Smith, *Acta Chem. Scand.*, **16**, 529 (1962).

[54] V. V. Fesenko and I. P. Gragerov, *Dokl. Akad. Nauk SSSR*, **101** 695 (1955).

[55] This value was estimated from the data in ref 54.

The Crystal and Molecular Structure of Disodium β-Glycerolphosphate Pentahydrate ($Na_2PO_4C_3H_5(OH)_2 \cdot 5H_2O$)

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Contribution from the Department of Chemistry, Montana State University, Bozeman, Montana. *Received May 5, 1966*

Abstract: The structure of disodium β-glycerolphosphate has been determined by X-ray diffraction study. The crystals are monoclinic, $a = 7.943$, $b = 12.104$, $c = 6.167$ A, $\beta = 107°$, space group $P2_1$ with one molecule in the asymmetric unit. The first Fourier synthesis was based on phosphorus phases; the rest of the structure emerged gradually from four more Fouriers. The phosphorus–oxygen distances are normal and are 1.62, 1.53, 1.52, and 1.46 A. Each of the phosphate oxygens is involved in hydrogen bonding or coordinated to sodium. Both sodium atoms are six coordinated. A strong network of hydrogen bonding and sodium coordination holds the crystal together.

Glycerolphosphates are involved in the biosynthesis and degradation of phospholipids, the synthesis of fats from fatty acids, the exchange of hydrogen in biological systems, as well as in a variety of other biologically important processes. Since most of these functions involve hydrolysis of the P–O–C bond at one step or another, precise structural information is significant in understanding the processes. Thus, in

Table I. Atomic Parameters, Temperature Factors, and Their Standard Deviations

Atom	x/a	$\sigma(x/a)$	y/b	$\sigma(y/b)$	z/c	$\sigma(z/c)$	B	(σB)
Na(1)	0.2008	0.0007	0.2893	0.0006	0.7782	0.0012	0.95	0.11
Na(2)	0.8447	0.0007	0.2984	0.0006	0.3919	0.0012	0.97	0.11
P(3)	0.1674	0.0004	0.0000	...	0.0026	0.0007	0.08	0.07
O(4)	0.2284	0.0012	−0.1142	0.0009	−0.0409	0.0021	0.63	0.17
O(5)	−0.0119	0.0010	0.0262	0.0008	0.8608	0.0019	0.23	0.16
O(6)	0.1878	0.0012	0.0215	0.0009	0.2535	0.0019	0.53	0.18
O(7)	0.2795	0.0012	0.0926	0.0008	0.9173	0.0019	0.47	0.17
O(8)	0.7174	0.0016	0.1347	0.0011	0.2432	0.0025	1.93	0.24
O(9)	0.4899	0.0012	0.2656	0.0009	0.8071	0.0019	0.63	0.17
O(10)	0.1212	0.0014	0.2296	0.0010	0.3932	0.0022	1.35	0.20
O(11)	0.0637	0.0013	0.4554	0.0009	0.5789	0.0021	1.02	0.19
O(12)	0.2565	0.0013	0.3803	0.0009	0.1399	0.0021	1.01	0.19
O(13)	0.5821	0.0015	0.3839	0.0011	0.4537	0.0024	1.61	0.22
O(14)	0.9201	0.0012	0.2491	0.0009	0.7796	0.0020	0.98	0.19
C(15)	0.5135	0.0021	0.1483	0.0015	0.7908	0.0035	1.43	0.28
C(16)	0.4588	0.0017	0.0819	0.0012	0.9651	0.0030	0.70	0.23
C(17)	0.5433	0.0021	0.1186	0.0014	0.2023	0.0036	1.43	0.28

a program to study the structure of organic phosphates in the hope of relating these structures to rates of hydrolysis, we have been interested in glycerolphosphates. The only other glycerolphosphate which has been studied is L-α-glycerolphosphorylcholinecadmium chloride trihydrate, the structure of which has been determined by Sundralingam and Jensen.[1]

Experimental Section

Crystals of disodium β-glycerolphosphate (E. H. Sargent and Co.) were obtained by slow recrystallization from water. Preliminary investigation indicated that these were pentahydrate, and thus, in order to prevent possible loss of water during the collection of the X-ray data, a small crystal of uniform cross section 0.2 mm in diameter and 1.0 mm long was sealed in a capillary tube and used for the X-ray data.

X-Ray diffraction photographs showed this to be monoclinic with lattice dimensions $a = 7.943$, $b = 12.104$, $c = 6.167$ A, $\beta = 107°$, $Z = 2$. Systematic extinctions existed for the $0k0$ zone when $k \neq 2n$; thus the space group was either $P2_1$ or $P2_1/m$ and the final structure proved to be $P2_1$. For $Na_2PO_4C_3H_5(OH)_2 \cdot 5H_2O$ the total number of electrons in the unit cell is $F(000) = 320$; the linear absorption coefficient for Cu Kα radiation is $\mu = 23$ cm^{-1}.

Multiple-film Weissenberg photographs were taken with Cu Kα radiation for $l = 0$ to 4; 830 intensities were measured by scanning with a densitometer reflections that had been integrated in a direction perpendicular to the direction of scanning, and measuring the areas under the densitometer tracings with a planimeter. No absorption corrections were applied, since the crystal was uniform in cross section and small enough that the absorption corrections were assumed negligible. Lorentz and polarization corrections were applied using Montana State University's data reduction program,[2] which also gives a Wilson plot for preliminary scale and temperature factors.

Structure Determination

The phosphorus positions were found from a sharpened Patterson, using F_s^2 modified according to the function

$$F_s^2 = \frac{(F_o)^2(K)^2(\Sigma Z_i)^2}{(\Sigma f_i)^2 \exp(-2B \sin^2 \theta/\lambda^2)}$$

The temperature factor B was set at zero in as much as experience has shown that use of the temperature factor found from the Wilson plot in this sharpening function produces a much oversharpened Patterson map. The phosphorus position found from the Harker section was $x/a = 0.1675$, $y/b = 0.0000$, $z/c = 0.0000$. Phases from the partial structure factors calculated from this position were used for the first Fourier map. Although a pseudo-plane of symmetry existed in this map and many peaks existed which seemingly were extraneous, it was possible to choose four oxygens making some chemical sense. The Fourier, the Patterson, and a minimum function used for checking indicated the correctness of these, and a second Fourier was calculated from phases determined from these five atoms. This showed two more oxygens and two carbons of the glycerol group. These nine atoms were used to determine the phases for the next Fourier, which revealed all the atoms. Up to this point, it was not possible to distinguish between sodium and oxygen peaks in the Fourier map. The next two Fouriers showed the sodium atoms as distinguished from oxygens and gave reasonable atomic positions. At this stage, the R factor was 0.32, and the refinement of the structure was started.

The first three cycles of least-squares refinement using Busing, Levy, and Martin's[3] least-squares program (ORNL-TM-305) refined only positional parameters and reduced the R to 0.22. Six more cycles, using the Hughes weighting scheme and refining both positional parameters and isotropic temperature factors, reduced the R to 0.097.

The final positions with standard deviations are given in Table I. The final set of structure factors based on these positions are given in Table II. The interatomic distances and angles and their standard deviations are shown in Tables III and IV, and Figure 1 shows the [001] projection of the structure with the interatomic distances.

Discussion

The phosphate group does not appear significantly different from other organic phosphates for which structures are known.[4,5] The P–OC bond distance of 1.62 A is in good agreement with other P–O ester bonds, and the other three bonds of 1.52, 1.53, and 1.46 A are quite characteristic of monosubstituted organic phosphates.[4] The 1.46-A bond indicates a

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(1) M. Sundaralingam and L. H. Jensen, *Science*, 1035 (1965).

(2) C. T. Li and C. N. Caughlan, Data Reduction Program, Montana State University, 1964.

(3) W. R. Busing, K. D. Martin, and H. A. Levy, Least-Squares Program, U. S. Atomic Energy Commission Publication No. ORNL-TM-305, 1962.

(4) C.-T. Li and C. N. Caughlan, *Acta Cryst.*, **19**, 637 (1965).

(5) M. Sundralingam and L. H. Jensen, *J. Mol. Biol.*, **13**, 930 (1965).

Table II. Observed and Calculated Structure Factors[a]

	0 K 0		
2	65	57	316
4	411	421	55
6	208	170	241
8	519	526	32
10	277	282	287
12	89	63	180
14	243	242	71
	1 K 0		
0	254	248	270
1	369	408	178
2	307	305	328
3	326	322	177
4	712	709	1
5	341	328	117
6	197	185	11
7	108	82	139
8	65	46	127
9	189	201	79
10	161	154	65
11	265	264	174
13	112	106	160
14	104	113	84
15	103	110	109
	2 K 0		
0	192	190	90
1	172	192	162
2	260	237	165
3	171	154	111
4	288	249	310
5	345	363	89
6	133	142	182
7	191	173	169
8	120	105	229
9	262	244	144
10	313	322	102
11	127	115	148
12	90	77	49
13	116	116	63
14	120	136	215
15	112	117	173
	3 K 0		
1	222	220	268
2	269	272	29
3	328	301	264
4	438	434	212
5	76	59	156
6	233	226	149
7	125	119	203
8	241	227	233
9	111	104	167
10	262	264	106
11	109	111	296
12	103	73	123
13	75	50	32
14	185	199	191
	4 K 0		
0	274	262	0
1	403	444	357
2	172	153	48
3	336	368	225
4	328	320	103
5	207	196	310
6	121	103	98
7	247	236	350
8	142	142	58
9	125	116	319
10	109	104	231
11	130	112	242
12	103	112	136
14	61	79	92
	5 K 0		
0	79	73	270
1	241	271	263
2	317	349	316
3	71	62	258
4	227	213	48
5	332	355	259
6	244	275	27
7	163	146	231
8	200	209	88
9	220	229	309
10	208	225	1
12	93	85	120
13	54	51	306
	6 K 0		
0	160	161	0
1	77	59	209
2	120	132	47
3	53	64	9
4	395	419	28
5	138	140	334
6	293	311	294
7	270	294	149
8	172	170	83
10	156	177	29
11	88	87	198
12	116	126	35
	7 K 0		
0	95	78	270
1	122	112	37
2	170	172	35
3	167	172	179
4	122	99	140
5	128	138	146
6	97	110	31
7	131	132	177
8	82	64	325
9	75	57	86
10	149	170	27
	8 K 0		
0	88	86	90
1	132	143	56
2	105	109	91
3	98	87	95
4	111	112	197
5	174	188	76
6	106	125	145
7	101	98	0
	9 K 0		
0	154	178	180
1	71	56	348
2	79	88	187
4	87	120	105
5	53	57	81
6	136	168	137
	0 K 1		
3	347	343	93
4	215	213	169
5	400	440	33
6	166	159	68
7	99	95	345
8	303	304	7
9	88	98	172
10	211	200	292
11	170	190	225
12	227	235	20
13	103	73	55
14	83	87	270
	1 K 1		
2	82	90	349
3	356	362	75
4	290	231	137
5	154	139	317
6	241	240	317
7	215	191	87
8	216	211	75
9	178	206	4
10	197	210	285
11	188	185	178
13	139	157	81
14	82	103	293
15	86	116	119
	-1 K 1		
1	283	304	342
3	436	439	327
6	662	724	73
7	163	179	267
8	337	333	[illegible]
9	196	153	241
10	120	120	162
11	218	210	327
12	199	170	16
13	154	91	358
14	71	68	189
	2 K 1		
0	409	439	90
1	381	391	19
2	249	256	95
3	322	346	36
4	263	274	62
5	273	298	327
6	280	300	342
7	223	244	151
8	366	389	110
9	343	369	18
11	136	114	155
12	133	99	96
13	117	109	13
14	76	67	302
	-2 K 1		
0	109	103	90
1	400	415	338
2	541	586	165
3	370	365	251
4	400	243	18
5	277	197	256
6	181	156	145
9	194	176	284
10	313	319	135
12	128	119	35
13	117	78	350
14	97	91	217
	3 K 1		
0	266	231	180
1	222	220	255
2	145	142	267
3	94	99	274
4	201	199	109
5	235	241	285
6	91	104	158
7	185	180	20
8	200	212	91
9	265	282	348
10	54	71	139
11	71	78	8
12	184	199	97
13	88	92	270
14	122	155	111
	-3 K 1		
1	148	166	206
2	559	578	109
3	431	396	326
4	177	182	75
5	275	257	260
6	235	215	204
7	139	113	52
8	137	174	109
10	148	150	139
11	148	161	26
12	125	118	196
13	103	91	290
14	92	102	126
	4 K 1		
0	215	214	0
2	204	206	24
3	339	352	238
4	227	234	192
5	227	247	2
6	162	168	164
7	288	319	331
11	154	159	345
12	68	61	186
13	136	147	260
	-4 K 1		
3	200	188	128
4	284	278	170
5	203	203	73
6	337	313	186
7	124	104	88
8	145	132	179
9	150	133	167
10	190	174	323
11	120	116	175
12	173	175	196
13	152	168	71
14	111	121	145
	5 K 1		
0	118	97	270
2	219	215	23
3	185	197	246
	150	172	306
6	94	91	8
7	328	343	329
8	116	103	295
9	106	110	244
10	114	97	75
11	129	146	278
	-5 K 1		
2	218	181	357
3	224	165	78
4	272	242	0
5	199	175	151
6	204	188	24
7	247	247	163
8	101	133	78
9	163	143	144
11	120	134	79
13	110	117	150
	6 K 1		
0	69	84	0
1	99	95	7
2	154	153	312
3	179	202	282
4	256	271	293
6	135	134	4
7	102	61	102
8	105	80	2
9	116	113	85
10	86	59	317
11	72	90	326
	-6 K 1		
0	171	185	270
2	398	425	28
3	126	116	118
4	181	156	281
5	155	158	224
6	189	182	11
7	57	54	218
8	226	215	272
9	126	117	28
10	103	117	73
11	90	81	170
	7 K 1		
0	86	97	0
1	247	274	99
2	110	83	38
3	196	235	29
4	80	70	11
6	103	102	257
7	212	226	71
8	107	109	350
	-7 K 1		
1	298	298	228
2	420	460	26
3	207	279	333
5	170	203	354
6	175	179	24
8	76	70	345
9	140	178	242
10	68	99	173
11	60	89	266
	8 K 1		
1	135	153	208
3	114	128	79
4	117	129	199
	-8 K 1		
1	188	189	344
2	145	129	339
3	194	190	329
5	185	149	248
6	65	74	139
7	170	153	265
8	63	76	159
	9 K 1		
0	82	71	90
2	75	80	200
3	73	82	352
4	68	64	117
	-9 K 1		
2	136	134	228
3	71	76	261
5	63	58	88
6	49	60	201
7	90	102	295
	-10 K 1		
2	61	89	110
4	29	54	64
	0 K 2		
4	186	180	232
5	317	327	43
6	244	250	76
7	106	101	354
8	246	263	356
9	99	90	112
10	263	263	297
11	42	49	34
12	178	177	299
13	91	48	278
	1 K 2		
1	236	245	47
2	317	345	81
3	358	429	239
4	134	137	344
5	73	80	19
6	142	156	348
7	130	124	5
8	125	141	313
9	242	252	170
11	275	321	34
13	109	99	168
14	97	107	316
	-1 K 2		
2	164	204	347
3	186	157	125
4	144	140	347
6	360	346	307
7	116	80	265
8	130	111	65
9	333	349	352
11	134	89	114
12	102	72	212
	2 K 2		
0	164	177	90
1	128	125	281
2	73	42	218
3	127	134	303
4	122	116	218
5	100	80	91
6	145	153	173
9	249	273	69
10	86	67	115
11	141	164	53
12	125	116	194
13	113	111	83
	-2 K 2		
1	100	77	36
2	136	85	282
3	261	261	263
4	231	222	177
5	554	627	356
6	308	304	348
7	175	180	101
8	289	298	102
9	253	255	274
11	144	122	224
12	141	164	103
13	127	138	327
	3 K 2		
0	130	135	90
2	269	296	97
3	300	312	17
5	241	246	220
6	130	126	90
7	141	123	179
8	116	107	139
9	95	94	332
10	149	149	100
12	120	139	111
13	102	123	51
	-3 K 2		
0	170	188	270
1	181	182	231
2	189	157	190
3	200	202	288
4	150	138	378
5	233	220	323
6	328	292	237
7	119	76	173
8	246	235	127
9	158	123	295
10	145	123	205
12	163	203	124
13	119	112	19
14	100	131	104
	4 K 2		
0	220	247	180
2	91	40	205
3	127	112	22
4	170	170	109
5	77	76	249
6	153	142	136
7	113	86	300
8	152	156	216
9	192	203	260
10	100	51	296
11	191	202	220
12	120	43	332
	-4 K 2		
0	177	202	90
1	178	171	279
2	131	134	294
4	116	100	251
5	294	303	43
6	230	213	125
7	127	110	315
8	147	144	238
9	199	201	54
10	125	119	195
	5 K 2		
0	95	110	0
1	113	108	105
2	72	85	117
3	260	280	356
4	68	79	112
5	252	265	256
6	119	100	347
7	145	159	327
8	145	127	13
10	95	87	298
11	136	134	304
	-5 K 2		
0	91	103	270
2	89	105	313
3	194	161	40
4	393	362	260
5	271	251	79
6	217	199	83
7	169	189	275
8	280	309	275
9	102	60	63
10	175	165	182
11	120	130	54
12	119	112	318
13	94	113	171
	6 K 2		
0	94	56	180
1	256	266	281
2	95	77	344
3	114	141	330
4	145	128	6
5	106	94	85
6	169	187	282
7	144	137	350
8	80	78	26
9	67	83	81
	-6 K 2		
0	73	84	0
1	175	189	169
2	250	252	54
3	120	125	227
4	214	214	281
5	127	90	310
7	144	147	290
8	241	236	326
9	105	64	39
10	117	104	59
	7 K 2		
0	145	149	0
1	106	112	51
4	122	123	46
5	170	167	49
7	77	107	51
	-7 K 2		
0	233	254	270
1	105	105	338
2	92	84	94
3	233	265	294
4	247	295	24
5	139	136	255
10	69	83	6
	8 K 2		
0	99	130	180
1	23	39	82
2	73	87	147
3	119	154	173
5	94	118	48
	-8 K 2		
0	134	124	0
1	170	171	346
2	194	190	214
4	127	135	78
5	102	115	316
7	188	192	340
8	167	143	163
9	144	150	341
10	83	63	37
	-9 K 2		
2	125	136	188
3	58	69	298
5	64	86	335
6	67	78	125
	-10 K 2		
0	169	194	180
1	63	79	156
2	53	72	62
	0 K 3		
0	100	110	180
1	484	550	181
2	207	232	4
4	149	134	279
6	163	165	7
7	176	171	21
8	146	145	267
9	227	258	342
10	207	199	2
11	97	65	229
12	148	186	294
13	100	141	41
	1 K 3		
0	274	299	0
1	327	370	177
2	121	144	316
3	165	191	1
5	69	49	95
7	119	112	21
8	116	103	270
9	253	259	75
10	132	135	293
11	132	112	18
12	83	66	2
13	134	83	158
	-1 K 3		
1	254	375	222
3	181	186	4
4	162	158	263
5	307	343	352
6	153	161	327
7	160	176	310
8	172	189	18
9	264	279	320
11	146	151	233
12	91	77	254
13	86	77	295
	2 K 3		
0	149	152	180
1	376	406	76
2	61	82	232
3	119	85	214
5	220	238	173
6	137	119	262
7	83	98	25
8	174	178	189
9	264	273	146
10	67	55	194
11	193	183	18
12	146	93	188
13	104	124	99
	-2 K 3		
1	81	61	125
2	126	134	180
3	253	263	246
4	228	247	184
5	242	252	330
6	202	201	125
7	118	129	320
8	220	224	227
9	116	118	263
10	118	108	348
11	126	128	342
12	76	61	252
13	109	120	251
14	61	57	13
	3 K 3		
0	79	59	90
1	88	101	5
2	302	354	196
3	206	191	96
4	155	154	202
5	234	221	79
7	179	208	325
8	146	136	124
9	104	81	182
10	218	245	206
12	119	159	186
	-3 K 3		
0	381	410	180
2	188	289	127
3	134	153	257
4	176	109	181
5	93	111	79
6	195	202	93
7	156	183	215
8	137	106	209
9	162	149	173
10	153	115	101
11	116	139	275
12	104	72	146
	4 K 3		
0	220	239	180
1	258	275	357
3	128	134	292
4	93	101	232
5	128	88	356
6	192	210	207
7	56	39	237
8	197	210	235
9	214	259	263
10	114	110	225
11	37	74	267
	-4 K 3		
1	216	224	7
2	112	97	281
3	220	194	108
4	271	299	187
5	329	314	60
6	293	226	83
7	100	65	61
8	118	67	99
11	146	157	71
12	100	97	253
13	91	85	77
	5 K 3		
0	76	93	0
1	153	140	235
2	98	77	13
3	135	150	236
4	155	139	348
5	329	336	350
8	155	170	311
9	162	185	303
10	66	91	240
	-5 K 3		
1	102	113	245
2	88	70	186
3	193	197	155
4	95	86	55
5	144	151	26
6	204	202	306
7	149	141	46
8	162	170	52
9	110	115	6
10	79	70	17
11	207	198	156
	6 K 3		
0	130	123	270
1	91	26	318
2	144	162	290
3	123	76	284
4	148	156	330
5	132	125	265
6	151	146	30
7	132	132	133
8	167	206	286
	-6 K 3		
0	121	129	0
1	146	138	185
2	102	106	331
3	114	118	347
4	206	165	66
5	262	264	354
6	130	127	312
7	132	105	166
8	60	25	436
9	119	144	6
	-7 K 3		
0	104	77	270
1	279	304	345
2	135	129	182
3	167	185	299
4	151	149	21
5	141	113	234
6	172	170	264
7	169	164	215
8	65	54	24
9	91	77	319
10	112	88	327
11	141	114	359
	-8 K 3		
0	197	153	90
1	97	81	242
3	197	214	252
4	153	161	233
5	109	117	264
6	95	82	134
7	137	127	265
	-9 K 3		
0	58	53	180
1	102	99	247
2	77	77	105
3	51	61	200
5	49	70	176
	-10 K 3		
0	60	55	90
1	76	73	160
2	40	59	174
	0 K 4		
0	170	205	270
1	114	123	239
2	167	168	34
3	147	170	11
4	70	103	273
5	132	140	110
6	150	147	292
7	164	179	154
8	249	244	20
9	153	147	208
10	105	89	284
11	55	48	46
12	155	148	4
	1 K 4		
0	95	97	90
1	160	164	177
2	155	104	14
	-10 K 4		
2	122	129	151
	1 K 4		
3	260	317	177
4	72	70	255
5	133	127	95
6	142	156	164
7	272	289	143
8	172	160	302
9	168	156	55
11	208	297	143
12	174	165	2
	-1 K 4		
0	97	104	90
1	180	207	254
2	97	103	262
3	153	469	220
4	203	203	6
5	80	67	30
6	251	204	313
7	383	403	326
8	91	78	76
9	137	113	194
10	82	66	287
11	71	84	351
12	69	46	42
13	49	42	205
	2 K 4		
0	124	151	180
1	199	225	150
2	192	194	185
3	210	200	87
4	221	239	200
5	45	26	204
6	230	239	119
7	274	300	158
8	124	116	337
9	98	80	167
10	112	109	210
11	142	144	159
12	59	71	342
	-2 K 4		
1	129	132	345
2	144	132	190
3	334	400	348
4	195	174	110
5	174	179	200
6	177	157	226
7	272	263	344
8	239	255	210
9	169	133	162
10	133	133	266
11	241	227	290
12	40	32	259
13	137	139	233
	3 K 4		
1	85	65	10
3	163	163	183
5	103	92	4
6	148	151	216
7	88	92	254
8	190	203	190
9	66	56	28
10	165	161	106
11	49	55	214
	-3 K 4		
0	147	159	90
1	48	57	286
2	264	266	218
3	126	139	285
4	356	407	197
5	170	157	98
6	232	203	195
7	119	111	193
8	189	178	219
9	179	153	172
10	128	97	219
11	93	63	349
12	165	212	207
	4 K 4		
0	95	105	270
1	185	217	344
2	238	288	90
3	124	129	349
4	116	105	168
5	82	71	20
6	164	168	236
7	123	123	351
8	97	70	144
9	170	165	250
10	55	29	7
	-4 K 4		
0	149	147	180
1	301	365	107
2	122	114	108
3	344	351	59
4	166	163	232
5	175	136	101
6	93	114	255
7	314	326	171
8	197	164	199
10	159	119	93
11	150	140	142
12	146	130	237
	5 K 4		
0	144	162	270
1	103	102	270
2	98	78	324
3	101	112	260
4	117	102	57
5	101	165	252
6	65	58	64
7	149	172	260
8	62	46	11
	-5 K 4		
1	178	206	126
3	268	277	157
4	176	153	295
5	85	74	30
6	77	58	296
7	232	176	86
8	81	63	307
9	118	112	46
10	97	79	272
12	61	43	137
	6 K 4		
0	48	37	0
1	114	153	144
2	115	148	276
4	94	88	316
6	113	146	19
	-6 K 4		
0	178	166	270
1	75	71	304
2	202	224	15
3	41	44	114
4	146	129	281
5	101	49	11
6	148	98	284
7	59	64	315
8	147	118	327
9	77	81	331
10	111	132	302
11	80	72	47
	-7 K 4		
2	90	90	270
3	240	279	357
4	112	115	259
5	136	132	295
6	85	68	317
7	134	195	238
8	115	122	306
	-8 K 4		
0	207	210	90
1	36	42	326
2	71	88	221
3	199	182	236
4	219	232	214
5	132	139	325
7	157	159	326
8	95	99	199
9	105	134	357
	-9 K 4		
0	140	156	180
2	178	187	191
3	94	92	154
4	142	132	113
5	72	78	31
6	171	189	206
	-10 K 4		
1	126	133	141

[a] Within each group the columns reading from left to right contain the values of K, $10F_o$, $10F_c$, and α.

large amount of double-bond character, since a phosphorus–oxygen double bond is usually considered 1.43 A.[6] The structure of the phosphate group is shown in Figure 2 with bond angles and distances.

The C–O and the C–C bonds are somewhat shorter than generally accepted distances for single bonds of this type. An average single C–O bond is given as 1.43 A.[7] In sodium β-glycerolphosphate the C–O bond seems to depend upon the number of hydrogen bonds, sodium coordinations, or covalent bonds other than the C–O bond, that are formed. O(9) is involved in four other bonds and shows a C–O distance of 1.44 A; O(7) is involved in three other bonds and has a C–O distance of 1.37 A; O(8) has only two other bonds and has a C–O distance of 1.34 A. The last difference, *e.g.*, 1.34 compared to 1.37, is not significant, but the difference between 1.44 and these is significant. The C–O bond distance of 1.34 A corresponds to a partial double-bond character equivalent to that of an oxygen attached to an aromatic ring.[7] The C–C distances of 1.48 and 1.51 A are

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[6] D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

[7] "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 276.

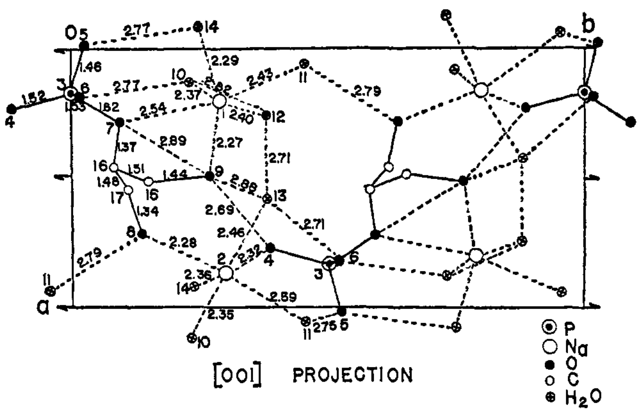

Figure 1. [001] projection of the structure of disodium β-glycerolphosphate pentahydrate. Dashed lines show hydrogen bonding or coordination to sodium.

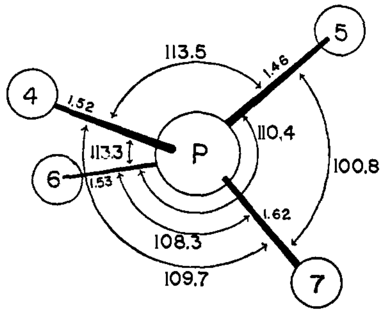

Figure 2. The bond angles and distance of the phosphate group in disodium β-glycerolphosphate pentahydrate.

Table III. Interatomic Distances

Atoms	Bond, A	Std dev, A
P(3)–O(4)	1.516	0.0089
P(3)–O(5)	1.457	0.0141
P(3)–O(6)	1.527	0.0160
P(3)–O(7)	1.618	0.0079
O(7)–C(16)	1.368	0.0197
C(16)–C(15)	1.509	0.0018
C(16)–C(17)	1.477	0.0452
C(15)–O(9)	1.439	0.0201
C(17)–O(8)	1.341	0.0300
Na(1)–O(7)	2.541	0.0039
Na(1)–O(9)	2.266	0.0105
Na(1)–O(10)	2.373	0.0227
Na(1)–O(11)	2.431	0.0017
Na(1)–O(12)	2.403	0.0221
Na(1)–O(14)	2.285	0.0137
Na(2)–O(4)	2.316	0.0110
Na(2)–O(8)	2.284	0.0264
Na(2)–O(10)	2.347	0.0066
Na(2)–O(11)	2.594	0.0245
Na(2)–O(13)	2.461	0.0021
Na(2)–O(14)	2.355	0.0143
O(5)–O(14)	2.767	0.0081
O(6)–O(10)	2.766	0.0176
O(7)–O(9)	2.888	0.0140
O(9)–O(13)	2.884	0.0023
O(12)–O(13)	2.709	0.0295
O(8)–O(11)	2.785	0.0325
O(13)–O(6)	2.709	0.0334
O(11)–O(5)	2.751	0.0146
O(10)–O(12)	2.821	0.0060
O(4)–O(9)	2.685	0.0289

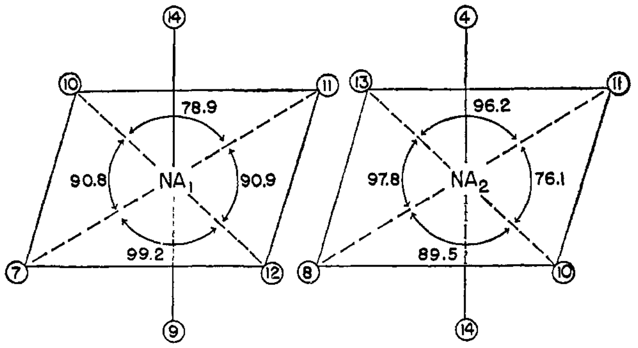

Figure 3. The sodium coordination bond angles in disodium β-glycerolphosphate pentahydrate. Other angles and distances are shown in Tables III and IV.

Table IV. Bond Angles

Atoms	Angle, deg	Std dev, deg
O(4)–P(3)–O(5)	113.50	0.51
O(4)–P(3)–O(6)	113.27	0.44
O(4)–P(3)–O(7)	109.67	0.49
O(5)–P(3)–O(6)	110.39	0.32
O(5)–P(3)–O(7)	100.83	0.38
O(6)–P(3)–O(7)	108.33	0.29
P(3)–O(7)–C(16)	120.28	0.84
Na(1)–O(7)–P(3)	131.02	0.57
Na(1)–O(7)–O(9)	48.83	0.31
O(9)–O(7)–C(16)	58.69	0.62
O(7)–C(16)–C(15)	107.79	1.10
O(7)–C(16)–C(17)	107.98	1.12
C(15)–C(16)–C(17)	113.70	1.14
O(9)–C(15)–C(16)	113.79	1.32
O(8)–C(17)–C(16)	110.89	1.31
O(7)–Na(1)–O(9)	73.52	0.26
O(7)–Na(1)–O(10)	90.81	0.34
O(10)–Na(1)–O(14)	88.87	0.42
O(11)–Na(1)–O(14)	83.84	0.40
O(11)–Na(1)–O(12)	90.88	0.36
O(9)–Na(1)–O(12)	95.38	0.33
O(4)–Na(2)–O(13)	82.46	0.28
O(8)–Na(2)–O(13)	97.76	0.33
O(4)–Na(2)–O(11)	91.19	0.32
O(10)–Na(2)–O(11)	76.11	0.39
O(8)–Na(2)–O(14)	97.43	0.38
O(10)–Na(2)–O(14)	87.85	0.42
P(3)–O(5)–O(10)	114.88	0.55
Na(2)–O(4)–P(3)	125.47	0.87
Na(2)–O(4)–O(9)	100.43	0.51
P(3)–O(4)–O(9)	131.14	0.82
P(3)–O(6)–O(10)	120.02	0.59
O(4)–O(9)–O(13)	76.88	0.37
O(4)–O(9)–C(15)	116.35	0.48
Na(1)–O(9)–O(13)	111.45	0.46
Na(1)–O(9)–O(7)	57.58	0.28
O(7)–O(9)–C(15)	53.06	0.55
Na(2)–O(8)–C(17)	120.32	0.96
Na(2)–O(8)–O(11)	111.90	0.63
C(17)–O(8)–O(11)	116.30	0.96
Na(1)–O(10)–O(6)	124.87	0.51
Na(1)–O(11)–O(8)	108.53	0.45
Na(2)–O(11)–O(5)	85.09	0.47
Na(1)–O(12)–O(10)	103.01	0.43
Na(1)–O(12)–O(13)	122.10	0.48
O(6)–O(13)–O(12)	141.64	0.59
O(9)–O(13)–O(12)	97.04	0.49
Na(2)–O(13)–O(6)	86.09	0.43
Na(2)–O(13)–O(9)	109.50	0.49
Na(1)–O(14)–O(5)	94.40	0.39

slightly shorter than the generally accepted C–C distance of 1.54, but the difference is probably not significant.

These are two other interesting and significant features about this structure. The first is the coordination of the sodium which is six coordinated in the form of a somewhat distorted octahedron. The details are indicated in Figure 3 with the pertinent angles shown. The Na–O distances are remarkably uniform, varying only from 2.28 to 2.59 A.

The second significant feature is the very elaborate network of hydrogen bonding, which, when combined with the sodium coordination, makes an extremely tightly bonded crystal. For example, O(9) is hydrogen bonded to O(7), O(4), O(13) in addition to being bonded to carbon and coordinated to sodium. The hydrogen-bond distances are all between 2.69 and 2.89 A, indicating a generally strong hydrogen bonding.

The very low-temperature factors observed in Table I are a result of this tightly knit structure. Whether or not these truly represent the thermal vibrations, one would expect low-temperature factors for oxygen and phosphorus atoms held as tightly as these, the oxygens being held in some cases by five neighboring atoms.[8]

Acknowledgment. We thank the National Institutes of Health for Grant GM-08392-04, which has made this work possible. We also thank Mr. Merlyn Gunsch, who did some of the preliminary work on the crystal; the Montana State University Computing Center and Western Data Processing Center of UCLA for grants of computing time. Also, we wish to thank the University of Washington and Professor Lyle Jensen for the use of the densitometer used in measuring the intensities.

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(8) The low-temperature factors were considered in some detail in the refinement. They do not appear owing to either level to level scaling or the absorption of the crystal. The only unknown factors seem to be the form factors or the absorption due to the capillary, which seemed unlikely. Thus, we must assume that they are real or that some other unknown systematic error is involved.

Complexes of Aluminum Bromide with Aromatic Hydrocarbons in Solution[1,2]

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Abstract: The interaction of aluminum bromide with aromatic hydrocarbons in solution has been studied by determining the apparent molecular weight of the aluminum bromide over a wide range of composition and temperature. The molecular weights were determined from the lowering of the vapor pressures and the depressions of the freezing point. At one extreme, aluminum bromide exhibits the dimeric molecular weight in benzene, with no evidence of dissociation over the concentration range examined. At the other extreme, the solute exhibits the monomeric molecular weight in mesitylene, the first clear case for dissociation of such a Lewis acid dimeric halide by a π donor. From variation in the apparent molecular weight with concentration, evidence was obtained as to the combination of the aromatic with aluminum bromide. The results of the present study indicate that at 70° aluminum bromide exists in the following forms in the respective aromatic solutions: Al_2Br_6 in benzene, a mixture of Al_2Br_6 and $ArH \cdot Al_2Br_6$ in toluene, $ArH \cdot Al_2Br_6$ in *m*-xylene, and a mixture of $ArH \cdot Al_2Br_6$ and $ArH \cdot Al_2Br_3$ in mesitylene. On the other hand, at 5°, the following species are indicated: $ArH \cdot Al_2Br_6$ in benzene, a mixture of $ArH \cdot Al_2Br_6$ and $ArH \cdot AlBr_3$ in toluene, and $ArH \cdot AlBr_3$ in either *m*-xylene or mesitylene. These results suggest that the equilibria, $Al_2Br_6(soln) + ArH(l) \rightleftharpoons ArH \cdot Al_2Br_6(soln)$ and $ArH \cdot Al_2Br_6(soln) + ArH(l) \rightleftharpoons 2ArH \cdot AlBr_3(soln)$, tend to shift to the right with the increasing basicities of the aromatics involved and with decreasing temperature of the solution. The order of increasing interaction of the aromatics with aluminum bromide at the temperatures examined is benzene < toluene < *m*-xylene < mesitylene.

In previous papers of this series,[6] we presented evidence for the existence of both 1:1 and 1:2 solid complexes, with the respective compositions $ArH \cdot AlBr_3$ and $ArH \cdot Al_2Br_6$, formed between aromatic hydrocarbons (ArH) and aluminum bromide. The fact that complexes of this composition exist in the solid phase does not ensure their existence in solution. Originally, we had become interested in these complexes while attempting to understand the part they played in the kinetics of the aluminum bromide catalyzed reaction of alkyl bromides with benzene and toluene in excess aromatic as the reaction medium.[7] Accordingly, we decided to explore the nature of the interaction of aluminum bromide with representative aromatic hydrocarbons in the aromatic as solvent.

In fact, the literature contains a number of conflicting reports as to the precise nature of the interaction of aluminum bromide with aromatic hydrocarbons in solution. For example, from molecular weight determinations by the freezing point depression method, Van Dyke[8] obtained a value of 534.0 for the molecular

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(1) The Catalytic Halides. XXX.

(2) Based on a thesis submitted by S. U. Choi in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Research Assistant (1953–1956) on Project No. AT(11-1)-170 supported by the Atomic Energy Commission.

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(6) (a) S. U. Choi and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 903 (1966); (b) H. C. Brown and W. J. Wallace, *ibid.*, **75**, 6265 (1953).

(7) H. C. Brown and H. Jungk, *ibid.*, **77**, 5584 (1955); **78**, 2182 (1956).

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