The Structures of Anhydrous Sodium Trimetaphosphate, Na₃P₃O₉, and the Monohydrate, Na₃P₃O₉.H₂O

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The two sodium trimetaphosphates, anhydrous and monohydrate, are orthorhombic with similar cell dimensions.

$$Na_3P_3O_9: \; a = 7\cdot928, \; b = 13\cdot214, \; c = 7\cdot708 \text{ Å}, \; V = 807\cdot5 \text{ Å}^3, \; D_x = 2\cdot516 \text{ g.cm}^{-3}$$
$$Na_3P_3O_9.H_2O: \; a = 8\cdot500, \; b = 13\cdot189, \; c = 7\cdot558 \text{ Å}, \; V = 847\cdot4 \text{ Å}^3, \; D_x = 2\cdot539\text{g.cm}^{-3}.$$

For both materials, $D_m = 2\cdot49$ g.cm^{-3}, $Z = 4$ and the space group is *Pmcn*. Weissenberg film data were collected, three-dimensional data for $Na_3P_3O_9$ and two-dimensional data for $Na_3P_3O_9.H_2O$. The structure of $Na_3P_3O_9$ was obtained from Patterson maps and refined by least squares. There is space in the structure on the mirror plane to accommodate the water molecule. Its position was confirmed in the hydrate. The two phases are isostructural with respect to the Na, P, and O positions.

The $P_3O_9^{3-}$ anion has the chair configuration of a six-membered ring and occupies a position on the mirror plane. In $Na_3P_3O_9$ the average P–O ring distance is $1\cdot615$ Å and the average P–O non-ring distance is $1\cdot484$ Å; the average ring O–P–O angle is $101\cdot1°$, and the average P–O–P angle is $126\cdot9°$. In $Na_3P_3O_9$ the two non-equivalent Na ions are fivefold coordinated. One coordination figure is a pyramid with a rectangular base, the other, a distorted trigonal bipyramid. In the hydrate, the water molecule provides sixfold octahedral coordination for both types of Na ion.

Although the two structures are extremely closely related, there is no evidence that the water can enter or leave the structure without breaking down the single crystal.

Introduction

Comparison of single-crystal data (Table 1) and indexed powder patterns (Fig. 1) of the anhydrous and monohydrate forms of sodium trimetaphosphate indicates that the two crystals have closely related structures. Above 60 °C the solid phase in contact with saturated aqueous solution is Na₃P₃O₉, and between approximately 40 and 60 °C it is Na₃P₃O₉.H₂O (Thilo & Wallis, 1953; Ondik & Gryder, 1960). There is no evidence that water enters or leaves the structure without breaking down the single crystal. Heating the monohydrate crystal at 60 °C produces powdered anhydrous material, although the aggregate may retain the exterior morphology of the single hydrate crystal.

Experimental

Pure Na₃P₃O₉.1·5H₂O was heated to about 650 °C (above the Na₃P₃O₉ melting point) and the melt cooled slowly, about 5–10 °C per hour. Cleavage fragments of Na₃P₃O₉ were isolated from the matrix for single-crystal study. The intensity data were collected for a roughly cylindrical crystal slightly less than 0·1 mm in cross-section.

Fig. 1. Comparison of the powder patterns of Na₃P₃O₉ and Na₃P₃O₉.H₂O taken with Cu $K\alpha_1$ radiation.

Table 1. *Single-crystal data*

	Na₃P₃O₉	Na₃P₃O₉.H₂O
a =	$7\cdot928 \pm 0\cdot002$ Å*	a = $8\cdot500 \pm 0\cdot001$ Å
b =	$13\cdot214 \pm 0\cdot003$	b = $13\cdot189 \pm 0\cdot001$
c =	$7\cdot708 \pm 0\cdot002$	c = $7\cdot558 \pm 0\cdot001$
V =	$807\cdot5$ Å³	V = $847\cdot4$ Å³
D_x =	$2\cdot516$ g.cm^{-3}	D_x = $2\cdot539$ g.cm^{-3}
D_m =	$2\cdot49$ g.cm^{-3}	D_m = $2\cdot49$ g.cm^{-3}

For both salts, $Z = 4$; the space group is *Pmcn*
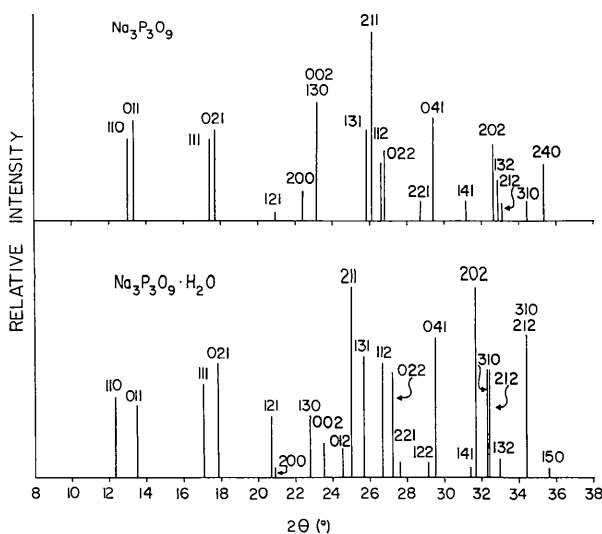
* The limits given are the standard deviations, σ.

Single crystals of the monohydrate were obtained from solid sodium trimetaphosphate kept under a saturated solution at 55 °C. After 24 hours, good single crystals (approximately 0·1 mm in largest cross-section) of the monohydrate found floating on the surface of the solution were removed by siphoning them onto filter paper with a medicine dropper.

The cell dimensions given in Table 1 were obtained from least-squares reduction of powder data recorded on a Geiger counter diffractometer with Cu $K\alpha_1$

Table 2. Observed and scaled calculated structure factors for Na3P3O9

Column 1

k	Fo	sFc
0k0		
2	14	-13
4	17	16
6	170	-174
8	69	-71
10	54	-52
12	78	71
14	104	-102
16	31	-34
1k0		
1	91	-94
3	150	-157
5	40	39
7	93	-96
9	21	-23
11	47	-48
13	62	-59
15	14	16
2k0		
0	150	148
2	77	-68
4	239	-252
6	83	-85
8	38	-43
10	40	45
12	188	177
14	13	-13
16	53	52
3k0		
1	145	-141
3	132	-122
5	194	188
9	132	130
11	39	38
13	50	-49
15	20	18
4k0		
0	278	294
2	92	95
4	123	114
6	114	-118
8	65	-70
10	52	-50
12	30	-27
14	21	15
5k0		
1	69	-67
3	138	-136
5	69	64
7	124	-126
9	21	21
11	18	-20
13	69	-68
6k0		
0	205	-203
2	69	72
4	56	-59
6	76	-77
10	47	43
12	17	20
7k0		
5	40	38
7	17	19
9	67	65
11	36	36
8k0		
0	25	31
2	103	106
4	56	57
6	73	-80
9k0		
1	33	31
3	27	-31
5	63	-67
7	5	0
10k0		
0	69	-72
2	24	19

Column 2

k	Fo	sFc
0k1		
1	>114	109
2	123	130
3	45	46
4	>236	-236
5	84	84
6	74	-77
7	13	9
8	41	41
9	16	21
10	28	-25
11	84	-85
12	72	71
13	57	-57
14	42	39
15	43	-42
16	91	-82
1k1		
1	76	76
2	30	-32
3	113	-108
4	82	-83
5	25	25
6	11	9
7	39	-40
8	77	-79
9	16	-13
10	23	-20
14	9	14
15	35	-31
16	6	13
2k1		
1	>218	-192
2	71	67
3	62	-60
4	79	-83
5	15	-13
6	29	-27
7	79	87
8	89	87
9	22	17
10	10	-7
11	42	44
12	68	66
14	14	17
15	33	33
16	60	-52
3k1		
1	88	82
2	21	-19
3	117	-111
4	66	65
5	16	18
6	36	35
7	73	72
8	80	84
9	60	-56
10	10	-10
11	86	85
12	27	27
15	61	-57
4k1		
1	12	9
2	84	-82
3	60	56
4	80	-84
5	108	111
6	31	-32
9	27	-25
10	48	46
11	70	-72
12	9	12
13	24	-25
15	27	-26
5k1		
1	62	60
2	16	18
3	104	-105
4	35	-37
5	48	43
6	23	-20
8	73	-75
9	38	-38
10	15	-19
11	20	24
12	18	-23
13	7	9
14	8	14

Column 3

k	Fo	sFc
6k1		
1	109	-110
2	103	-104
3	29	-24
4	37	32
7	37	40
10	71	72
11	35	33
13	28	26
7k1		
2	45	46
4	58	60
7	23	27
8	22	23
10	11	14
11	19	25
12	40	39
8k1		
1	35	36
2	81	-83
3	20	21
4	13	14
5	30	30
6	12	-19
8	40	-37
10	71	69
9k1		
1	16	-18
2	18	17
3	25	30
4	10	-14
5	7	-13
6	27	-29
7	23	-22
10k1		
1	26	-26
2	24	-29
0k2		
1	11	11
2	>173	179
3	29	35
4	26	-23
5	11	10
6	48	-48
7	44	-42
8	89	91
9	19	-20
10	54	55
11	40	-41
12	172	-168
15	8	-13
16	42	-42
1k2		
0	57	54
1	101	94
2	24	24
3	141	-135
4	24	-23
5	54	-54
6	32	-31
7	8	10
8	17	-21
9	53	-50
10	16	-14
11	34	-31
12	29	-28
15	37	35
2k2		
0	>228	-262
1	92	91
2	49	49
3	23	25
4	56	-56
5	127	126
7	14	10
8	82	85
10	84	84
11	47	-44
12	56	-55
13	28	-26
14	49	47

Column 4

k	Fo	sFc
3k2		
0	44	-46
1	43	-44
2	27	25
3	111	111
4	48	-44
5	118	-117
6	34	33
7	233	231
8	26	24
9	21	-22
10	39	36
11	50	-50
13	52	51
15	34	-34
4k2		
0	19	-17
1	45	-42
2	13	-21
4	48	50
5	8	14
6	67	64
7	28	29
9	31	-27
10	31	-30
11	54	-53
12	41	-39
13	8	-14
14	47	-42
15	13	10
5k2		
0	13	-11
1	81	81
2	17	18
3	52	-55
4	9	11
5	104	-101
7	56	56
8	30	-33
9	66	-66
10	23	-24
11	36	-37
12	32	-27
13	24	25
14	7	13
6k2		
0	9	-9
1	13	20
2	110	-111
3	17	19
4	10	-14
5	49	51
6	95	98
7	34	32
9	22	-23
10	9	-8
11	36	-34
12	73	75
13	22	-20
7k2		
0	57	-62
1	16	-19
2	83	83
4	15	20
5	10	-10
6	33	34
7	59	59
8	9	-10
11	6	10
8k2		
0	99	100
2	54	-54
3	42	42
4	18	18
5	67	68
8	18	-21
9	24	-26
9k2		
1	7	-13
3	21	-25
4	24	24
5	21	20
7	70	-74

Column 5

k	Fo	sFc
0k3		
1	>135	146
2	37	31
3	40	-36
4	>280	253
5	53	-51
6	118	-107
7	122	-123
8	103	-97
10	74	74
11	17	-15
12	40	35
13	27	24
14	41	-41
15	18	-22
16	42	39
1k3		
1	80	68
2	49	-48
3	68	65
4	75	-76
5	71	-64
6	27	-25
7	29	-27
8	46	-46
9	43	45
11	37	-40
13	31	-34
14	26	26
16	24	25
2k3		
1	126	115
2	54	49
3	30	28
4	106	94
5	117	-114
6	13	-11
7	39	-42
8	157	-153
9	39	-42
10	62	63
11	65	68
12	32	-33
13	44	40
15	42	39
3k3		
1	21	-22
2	13	-14
3	54	54
4	46	47
5	156	-149
6	36	41
7	24	-22
8	54	56
9	142	138
11	12	-13
12	9	-8
13	8	-14
14	28	-27
15	46	44
4k3		
1	90	88
2	11	12
4	41	46
5	18	-18
7	86	-90
8	42	44
10	42	-44
11	20	-22
12	18	17
13	20	20
5k3		
1	25	25
2	44	-46
3	98	93
4	62	-64
5	76	-77
6	21	-24
7	39	-39
8	29	-31
9	60	65
10	9	10
11	43	-44
13	31	-29

Column 6

k	Fo	sFc
6k3		
1	19	26
2	56	56
3	19	19
4	86	-85
5	51	-56
6	41	44
7	20	-21
8	18	18
9	22	-25
10	67	-67
11	37	38
12	23	-20
7k3		
4	28	-26
4	22	25
5	13	-17
6	20	24
8	38	37
9	11	16
10	10	13
11	14	14
8k3		
1	37	42
2	56	56
3	8	14
4	33	-34
7	35	-39
8	69	68
9k3		
1	31	35
2	16	-19
3	16	-21
4	37	-38
5	26	28
0k4		
1	45	-58
2	161	-167
3	26	29
4	89	87
5	73	-73
6	106	99
7	72	71
8	40	-38
9	61	60
10	74	-72
11	88	84
12	42	43
14	62	-59
15	30	-26
1k4		
1	142	140
2	33	-29
3	17	-18
4	40	-42
5	55	58
6	9	-7
7	20	-19
9	16	18
10	9	-9
11	18	15
12	27	-27
15	26	22
2k4		
0	15	-15
1	62	-55
2	52	-52
3	112	-109
4	15	-16
5	125	-119
6	86	88
7	20	-21
8	27	-31
10	31	-33
11	32	33
12	73	70
14	19	-21

Column 7

k	Fo	sFc
3k4		
0	28	-25
1	28	-27
2	32	-30
3	64	58
4	64	-61
5	144	136
6	12	-13
7	82	-77
8	31	28
9	48	48
11	43	46
12	25	30
13	45	-46
14	13	-16
4k4		
0	21	21
1	64	-60
2	26	-26
3	46	-48
4	56	56
6	9	-7
7	72	73
8	16	18
9	62	64
10	16	-16
11	33	30
12	37	-37
5k4		
0	76	77
1	40	-38
2	27	-31
3	26	-25
4	69	66
5	36	35
7	129	-129
8	22	22
10	27	-26
11	26	24
12	13	-15
13	17	-16
6k4		
0	119	-120
1	29	-31
2	53	50
3	105	-106
4	17	-15
5	32	-35
6	41	-39
7	24	-21
8	30	34
9	11	13
10	29	28
11	8	-9
7k4		
0	72	-72
1	9	13
2	21	-25
3	26	32
4	27	32
5	34	32
6	18	19
7	105	-103
8	25	27
9	15	-12
10	9	-9
12	10	-13
8k4		
0	42	-41
2	41	41
3	13	-15
4	30	32
5	11	17
6	15	-13
8	27	-25
9	31	-31
10	12	-15
12	17	-20
9k4		
1	24	25
3	14	-14
4	33	40

Column 8

k	Fo	sFc
0k5		
1	9	-11
2	148	158
3	30	34
4	14	18
5	37	37
6	49	47
7	35	34
8	83	83
9	13	13
10	63	-62
11	25	-22
12	30	33
13	49	-39
14	18	18
1k5		
1	72	69
3	36	-38
4	56	-56
5	56	58
6	30	-30
7	8	-8
8	52	-52
11	12	-15
12	11	-15
14	10	9
2k5		
1	74	-74
2	56	58
3	38	-36
4	76	-75
5	7	-8
6	27	-27
7	31	30
8	36	-26
9	39	38
10	71	-72
11	21	19
14	27	27
3k5		
1	24	26
2	29	28
3	100	-98
4	44	44
5	17	-15
6	22	18
7	39	38
8	56	55
9	67	-66
11	74	74
12	21	22
4k5		
1	18	17
2	15	17
4	71	72
5	18	17
6	54	52
7	34	32
8	38	34
9	18	19
11	16	-15
12	11	-9
13	47	-43
5k5		
1	64	63
2	19	-17
3	54	-54
4	49	-49
5	65	67
6	15	-13
8	27	-25
9	31	-31
10	12	-15
12	11	-20
6k5		
1	37	-38
2	63	-63
3	41	-41
4	20	24
6	19	-20
7	27	22
8	67	-64
9	30	27
10	10	11

Column 9

k	Fo	sFc
7k5		
1	21	-25
2	13	-8
3	16	-11
4	25	23
5	7	-8
6	32	33
7	6	8
8	49	48
8k5		
2	18	-20
3	6	9
4	77	81
5	27	26
6	18	21
0k6		
1	21	25
2	102	114
3	88	92
4	68	69
5	60	62
6	58	-61
7	8	-8
8	20	-16
9	8	13
10	28	-26
11	10	-9
12	62	-57
13	17	16
1k6		
0	33	29
1	44	45
2	19	19
3	14	-14
4	9	7
5	48	-48
7	19	-18
9	37	-35
11	16	-19
2k6		
0	88	-84
1	61	62
2	11	10
3	28	-30
5	21	23
6	63	-62
7	74	-77
9	32	-26
10	10	16
11	16	-15
3k6		
0	35	-34
1	69	65
2	27	26
3	57	54
4	53	-52
5	46	-50
6	8	-7
7	65	67
10	32	34
4k6		
0	82	84
2	54	53
3	72	69
5	31	32
6	8	-11
7	32	32
8	28	-27
10	13	-16
5k6		
0	20	16
1	53	52
2	30	34
3	11	-11
5	67	-63
7	7	13
8	7	-8
9	41	-37
10	10	12

Column 10

k	Fo	sFc
6k6		
0	57	59
1	15	13
2	40	-43
3	18	-18
4	52	-48
5	13	-14
6	13	-15
8	24	-23
9	33	-31
7k6		
0	17	-20
3	12	14
4	24	-22
8k6		
0	83	88
1	7	-10
0k7		
1	24	28
2	95	-101
3	17	18
4	40	43
5	32	35
6	6	-8
7	19	-19
8	25	21
9	29	-30
10	70	64
11	22	-21
1k7		
3	34	33
6	27	-26
7	16	-18
8	17	-15
9	14	14
10	8	-11
11	43	-36
2k7		
1	31	-28
2	89	-82
3	19	-19
4	39	-36
5	9	-7
6	16	-13
8	27	-31
10	66	56
11	25	24
3k7		
1	58	-58
2	16	17
3	53	53
4	17	14
5	30	-32
6	8	-10
9	47	43
10	37	33
11	13	-17
4k7		
1	45	42
2	21	-21
3	12	11
4	12	-10
7	13	-15
8	54	49
10	7	9
5k7		
1	19	-19
2	6	-9
3	51	53
5	15	-17
7	11	-14
8	11	-12
6k7		
1	10	-12
2	6	11
3	10	-12
4	78	-77
5	30	-29
7k7		
1	28	-28
2	4	-8

Scale factors, s

hk0	hk1	hk2	hk3	hk4	hk5	hk6	hk7
0·179	0·160	0·187	0·184	0·171	0·158	0·150	0·141

Table 3. *Structure parameters for* Na₃P₃O₉

	x	σ(x)	y	σ(y)	z	σ(z)	B	σ(B)
P(m)	0·250		0·0381	0·0001	−0·0232	0·0002	0·85	0·03
P	0·0676	0·0002	0·1713	0·0001	0·7466	0·0001	0·93	0·03
Na(m)	0·750		0·2241	0·0002	0·0356	0·0004	1·94	0·06
Na	0·4946	0·0003	0·0735	0·0002	0·3177	0·0003	1·73	0·04
O(1m)	0·250		0·0270	0·0004	0·1685	0·0007	1·43	0·09
O(2m)	0·750		0·0527	0·0004	0·1387	0·0007	1·43	0·09
O(3m)	0·250		0·2233	0·0004	0·7261	0·0006	1·15	0·08
O(1)	0·0926	0·0005	0·1094	0·0002	0·9272	0·0004	1·16	0·06
O(2)	0·0365	0·0005	0·0986	0·0003	0·6048	0·0005	1·83	0·07
O(3)	−0·0573	0·0005	0·2522	0·0003	0·7815	0·0004	1·47	0·07

radiation (1·5405 Å). The density and space group information in Table 1 were reported by Ondik & Gryder in 1960.

Three-dimensional data were collected for the anhydrous salt by taking films of levels hkl, where $l=0$ through 7, and $0kl$ with Cu $K\alpha$ radiation. An integrating Weissenberg camera was used with the usual multiple film techniques. The intensities were measured with a densitometer comparator and very weak spots were estimated visually. Lorentz and polarization corrections were applied. The same procedures were followed to obtain $hk0$ and $0kl$ data for the monohydrate.

Determination of the structures

Since the space group is not unequivocally determined by the diffraction aspect P^*cn, a Howells, Phillips & Rogers (1950) plot of $N(z)$ versus z (Lipson & Cochran, 1953) was calculated for the $hk0$ data for both salts. The graphs indicated a centric distribution for the intensities. Since for $P2_1cn$ the $hk0$ section is acentric and for $Pmcn$, centric, the structure was determined with $Pmcn$.

The general position of $Pmcn$ is eightfold. The special positions on mirror planes and centers of symmetry are both fourfold. If the centers were occupied, the reflections with $h=2n$, $k+l=2n$ would be more intense than the rest, corresponding to a pseudo-halving of a and of $b+c$, that is, of [011]. There were no indications that the centers were occupied. Since the atoms occur in multiples of 12, for every P, O and Na in a general position, there must be one in fourfold special position on the mirror plane. A two-dimensional Patterson map computed from the $hk0$ data of Na₃P₃O₉ provided x and y parameters for the P and Na. Approximate parameters for oxygen were established by considering the conformation of the P₃O₉³⁻ ring (Eanes & Ondik, 1962) and comparing trial positions with the Patterson map. After computing several sets of structure factors and electron density maps, the parameters were refined by the method of least squares. When $R(hk0)$ was reduced to 0·15, information from an $0kl$ Patterson map and from packing considerations were combined to give approximate z values. The complete set of hkl data ($l=0$ to 7), 729 observed reflections, was subjected

to least-squares treatment, varying a total of 43 parameters including 8 scale factors. The final $R(hkl)$ was 0·058 for the observed data, and 0·076 for all the data; 140 reflections were not included in the refinement. Most of these 140 were too weak to be observed and were entered as zero. A few were too intense to be measured with the densitometer, so a value corresponding to the maximum densitometer reading was arbitrarily assigned to them. These strong reflections are marked with > in the list of observed and scaled calculated structure factors in Table 2. The final parameters are given in Table 3, where the subscript m indicates the atoms on the mirror plane.

Examination of the Na₃P₃O₉ structure revealed a

Table 4. *Observed and scaled calculated structure factors for* Na₃P₃O₉.H₂O

hk0 data

k	F₀	sF_c	k	F₀	sF_c
0k			5k		
2	39	37	3	93	−93
4	52	−46	5	53	50
6	193	−202	7	107	−107
10	21	−16	9	17	−15
12	129	124	11	27	−25
14	38	−37	13	27	−27
16	123	−107	15	39	−38
1k			6k		
1	75	−79	0	248	−230
3	114	−118	6	56	−55
5	58	56	10	57	59
7	104	−103	12	27	−28
9	34	−35	14	24	23
11	43	−45	7k		
13	48	−48	1	60	62
15	32	−35	7	36	37
2k			9	48	48
0	34	36	11	11	17
2	103	−86	8k		
4	204	−209	0	68	71
6	61	−65	2	52	60
10	30	34	4	36	37
12	117	110	6	51	−52
3k			10	25	26
1	178	−168	9k		
3	195	−186	1	72	74
5	130	122	5	45	−50
7	54	57	7	7	−16
9	94	95	9	14	−16
11	119	115	10k		
13	45	−45	0	10	−15
15	24	−24	4	80	−80
4k			6-	12	14
0	218	214			
2	61	55			
4	153	145			
6	132	−128			
12	14	−20			

0kl data

k	F₀	sF_c	k	F₀	sF_c	k	F₀	sF_c
k0			k3			k6		
2	38	30	1	103	103	0	10	10
4	48	−37	2	33	−34	1	74	78
6	177	−165	3	26	26	2	72	70
10	16	−13	4	141	140	3	58	62
12	106	101	5	90	−88	4	26	31
14	28	−30	6	54	−53	5	17	−17
16	100	−88	7	63	−62	6	59	−62
k1			8	70	−73	7	30	−32
1	64	66	9	42	41	9	36	−35
2	101	106	11	22	27	10	35	31
3	27	27	12	69	68	11	38	−39
4	186	−184	13	13	−18	12	19	−23
5	101	97	14	36	−36	13	24	29
6	7	−7	15	19	−20	k7		
7	29	27	16	32	32	1	28	−23
8	42	42	k4			2	66	−71
10	9	−8	0	153	155	3	56	58
11	72	−65	1	100	−99	5	17	11
12	50	−50	2	78	−82	10	20	20
13	26	−27	3	24	23	11	18	−19
14	48	51	4	43	45	k8		
15	36	−38	5	29	−35	0	41	42
16	38	−37	6	77	73	1	31	−37
k2			7	13	16	3	46	48
0	95	−95	8	33	30	5	14	16
1	54	53	10	56	−57	6	41	39
2	142	136	11	56	55	7	28	−28
3	11	−6	13	15	−15	8	17	−19
4	12	16	14	34	−28	9	45	−39
5	41	−41	15	9	−14	k9		
6	73	−74	k5			1	40	32
7	49	−49	1	38	41	2	34	34
8	22	19	2	97	100	5	33	32
9	18	−18	4	32	−32			
10	42	44	5	82	78			
12	81	−72	6	25	−28			
13	25	25	7	33	32			
14	26	−30	10	31	−33			
16	15	18	11	35	−33			
			14	47	37			

Scale factors, s

hk0	0kl
0·159	0·130

Table 5. *Structure parameters for* $Na_3P_3O_9.H_2O$

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
P(m)	0·250		0·0317	0·0004	0·0075	0·0010	1·41	0·12
P	0·0831	0·0004	0·1614	0·0002	0·7666	0·0005	1·19	0·07
Na(m)	0·750		0·2340	0·0006	0·0289	0·0016	2·44	0·21
Na	0·4963	0·0012	0·0880	0·0004	0·3227	0·0008	2·28	0·12
O(1m)	0·250		0·0226	0·0013	0·2019	0·0029	2·03	0·36
O(2m)	0·750		0·0599	0·0011	0·1120	0·0031	2·29	0·38
O(3m)	0·250		0·2209	0·0009	0·7506	0·0027	1·23	0·28
O(1)	0·1034	0·0016	0·1015	0·0005	0·9541	0·0012	1·29	0·17
O(2)	0·0726	0·0019	0·0859	0·0005	0·6197	0·0012	1·62	0·18
O(3)	− 0·0434	0·0012	0·2365	0·0006	0·7910	0·0014	1·39	0·18
H_2O	0·750		0·0883	0·0011	0·4832	0·0028	2·26	0·34

possible position for the water molecule in the hydrate — a 'hole' on the mirror plane that would provide the necessary fourfold special position for the water. A difference synthesis was computed from the $hk0$ data for the hydrate compared with structure factors based on the position parameters of the anhydrous salt. This map indicated that the water molecule did indeed occupy the special position. The $hk0$ and $0kl$ data for the hydrate were subjected to least-squares treatment, varying 40 parameters including 2 scale factors. The final R equals 0·056 for the 167 observed reflections. The observed and scaled calculated structure factors are listed in Table 4, and the final parameters for $Na_3P_3O_9.H_2O$, in Table 5. Comparison of Tables 3 and 5 clearly indicates that the two salts share the same basic structure.

Form factors for P and Na^+ calculated by Tomiie & Stam (1958) and for O^- calculated by Freeman (1959) were used throughout. Film-to-film scaling, Lorentz and polarization corrections, structure factors and Fourier maps were computed on a high-speed digital computer with programs written at the National Bureau of Standards. Dr C. Burnham of the Geophysical Laboratory, Carnegie Institution of Washington wrote the least-squares program used to refine the cell dimensions of $Na_3P_3O_9$. A program written by Dr H. T. Evans, Jr., Dr D. Appleman, and Mr D. Handwerker of the U.S. Geological Survey was used to refine the cell dimensions of $Na_3P_3O_9.H_2O$. The structural parameters were refined and the interatomic distances and angles were computed with the programs written by Busing & Levy at Oak Ridge (1959a, b).

Discussion of the structures

A Raman study (Simon & Steger, 1954a, b) of sodium trimetaphosphate indicated that in solution the ring has $\bar{6}m2$ symmetry. In crystalline $Na_3P_3O_9$ the triangles formed by the P atoms and the O atoms are equilateral within experimental accuracy. The P–P distances are 2·887 ± 0·002 Å (2 ×) and 2·892 ± 0·003 Å. The O–O distances are all 2·495 ± 0·008 Å, where the limits are the standard deviations. The angle between the normals to these triangles is only 0·6°, but O(1) is 0·40 Å and O(3m), 0·38 Å from the plane of the P atoms. The ring is bisected by
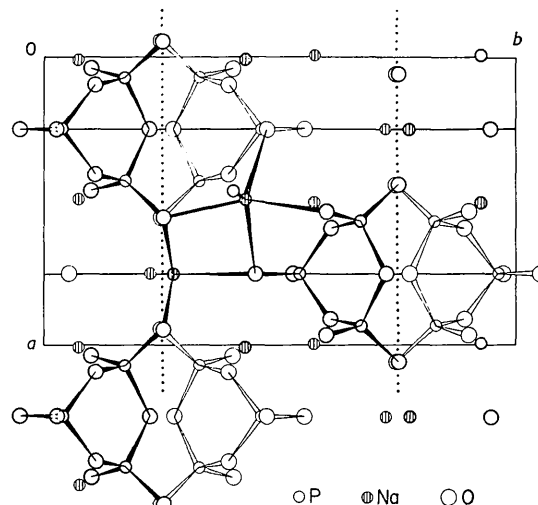
Fig. 2. The anhydrous structure viewed down c. The anions are shown, the heavier lines indicating the atoms with the higher z coordinate. The coordination of the Na ions is drawn in for one Na in general position and for one on the mirror plane.
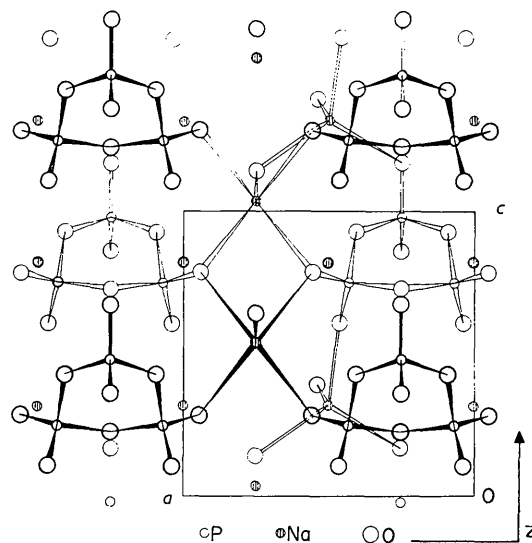
Fig. 3. The anhydrous structure viewed along b, but including the cell contents between approximately the origin and $\frac{1}{2}b$ only. The linkage of the Na(m) coordination pyramids along c and the coordination of the sodium ion in general position is indicated.

a mirror plane and also possesses pseudo $3m$ symmetry. As in LiK$_2$P$_3$O$_9$.H$_2$O (Eanes & Ondik, 1962) the trimetaphosphate anion has the chair configuration of a six-membered ring (Figs. 2 and 3). The bond distances and angles with their standard deviations are given in Table 6. These dimensions are consistent with values found in other condensed phosphates.

Table 6. P$_3$O$_9^{3-}$ *anion dimensions in* Na$_3$P$_3$O$_9$

P(m)–O(1)	1·609 ± 0·004 Å	(2 ×)
P(m)–O(1m)	1·485 ± 0·006	
P(m)–O(2m)	1·495 ± 0·005	
P–O(1)	1·627 ± 0·004	
P–O(3m)	1·609 ± 0·002	
P–O(2)	1·475 ± 0·004	
P–O(3)	1·482 ± 0·004	
O(1)–P(m)–O(1′)	101·7 ± 0·2°	
O(1m)–P(m)–O(2m)	120·9 ± 0·3	
O(1m)–P(m)–O(1)	107·1 ± 0·2	(2 ×)
O(2m)–P(m)–O(1)	109·2 ± 0·1	(2 ×)
P(m)–O(1)–P	126·3 ± 0·2	(2 ×)
P–O(3m)–P′	128·0 ± 0·3	
O(3m)–P–O(1)	100·9 ± 0·2	
O(2)–P–O(3)	119·5 ± 0·2	
O(1)–P–O(2)	109·1 ± 0·2	
O(1)–P–O(3)	106·8 ± 0·2	
O(3m)–P–O(2)	110·8 ± 0·2	
O(3m)–P–O(3)	108·1 ± 0·2	

Both Na ions in Na$_3$P$_3$O$_9$ are fivefold coordinated. The Na–O distances are given in Table 7. Na(m), the ion on the mirror plane, is coordinated to O atoms from five different rings. The oxygen atoms form a somewhat irregular pyramid with the base roughly parallel to (010). Na, the ion in general position, is surrounded by O atoms from four different rings which form a highly distorted trigonal bipyramid.

Table 7. *Comparison of* Na–O *distances in both structures*

In Na$_3$P$_3$O$_9$

Na(m)–O(2m)	2·400 ± 0·006 Å	
Na(m)–O(3)	2·454 ± 0·004	(2 ×)
Na(m)–O(3′)	2·511 ± 0·004	(2 ×)
Na–O(1m)	2·337 ± 0·004	
Na–O(2m)	2·466 ± 0·004	
Na–O(2)	2·252 ± 0·005	
Na–O(2′)	2·376 ± 0·004	
Na–O(3)	2·373 ± 0·004	

In Na$_3$P$_3$O$_9$.H$_2$O

Na(m)–O(2m)	2·38 ± 0·02 Å	
Na(m)–O(3)	2·68 ± 0·01	(2 ×)
Na(m)–O(3′)	2·51 ± 0·01	(2 ×)
Na(m)–H$_2$O	2·37 ± 0·02	
Na–O(1m)	2·44 ± 0·01	
Na–O(2m)	2·71 ± 0·02	
Na–O(2)	2·32 ± 0·01	
Na–O(2′)	2·42 ± 0·01	
Na–O(3)	2·36 ± 0·01	
Na–H$_2$O	2·47 ± 0·01	

The pyramids about Na(m) share basal edges with their own glide equivalents along c (Fig. 3). They also share an edge between the apex and the base with an Na bipyramid. The bipyramids share corners with their own equivalents across the mirror planes. This sharing of edges and corners forms a three-dimensional network of Na coordination polyhedra firmly linked with the anion.

The addition of water to form the monohydrate provides for sixfold coordination for both kinds of sodium ion. The water molecule occupies a position on the mirror plane opposite the apex of what is the pyramid in the anhydrous structure, changing the coordination figure to a skewed octahedron. The figure then formed about the Na ion in general position is very roughly octahedral also (Figs. 4 and 5).
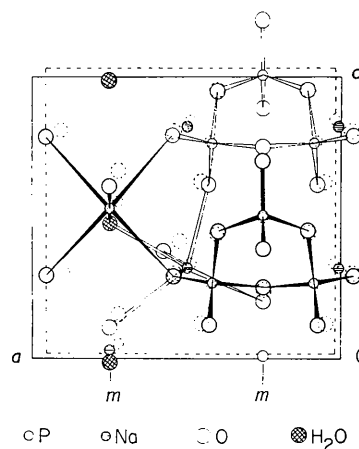
Fig. 4. The structure of the monohydrate is shown in solid lines. The dashed lines indicate the anhydrous structure. To make this comparison the P(m) atoms were superposed in both structures and the atoms which were appreciably shifted were drawn in.
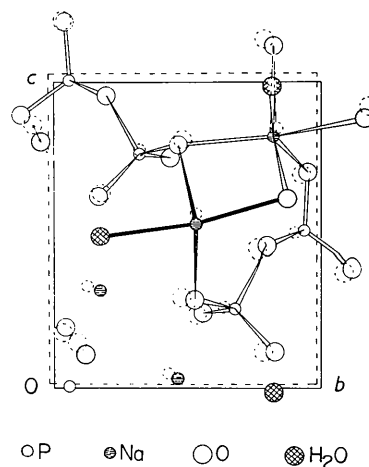
Fig. 5. The structure of the monohydrate is shown in solid lines. The dashed lines indicate the comparable atomic positions in the anhydrous structure. The comparison was made as in Fig. 4, by superposing P(m) in both structures.

The trimetaphosphate anion has changed shape slightly to accommodate the inclusion of the water molecule in the structure. Table 8 gives the dimensions of the ring in $Na_3P_3O_9 . H_2O$; comparison with Table 6 shows that most distances and angles are not drastically different in the two phosphates. The shifts of position undergone by some of the atoms has been indicated in Figs. 4 and 5. These shifts have the greatest effect on the $P-O(3m)-P$ bond angle, which is $128.0°$ in the anhydrous and $121.5°$ in the hydrate salt. The angle between the normals to the triangles of P and O atoms has also changed from $0.6°$ to $2.5°$. O(1) remains 0.40 Å from the plane of the P atoms but O(3m) is 0.49 Å in the hydrate. Also the triangles of P and O atoms are not quite so close to equilateral (distances: $P(m)-P$, 2.87 ± 0.01 Å $(2 \times)$, $P-P'$, $2.84 \pm$

Table 8. $P_3O_9^{3-}$ anion dimensions in $Na_3P_3O_9 . H_2O$

$P(m)-O(1)$	1.60 ± 0.01 Å	$(2 \times)$
$P(m)-O(1m)$	1.47 ± 0.02	
$P(m)-O(2m)$	1.51 ± 0.02	
$P-O(1)$	1.63 ± 0.01	
$P-O(3m)$	1.63 ± 0.01	
$P-O(2)$	1.49 ± 0.01	
$P-O(3)$	1.47 ± 0.01	
$O(1)-P(m)-O(1')$	$102.2 \pm 0.8°$	
$O(1m)-P(m)-O(2m)$	122.1 ± 1.0	
$O(1m)-P(m)-O(1)$	107.3 ± 0.6	$(2 \times)$
$O(2m)-P(m)-O(1)$	108.1 ± 0.6	$(2 \times)$
$P(m)-O(1)-P$	125.4 ± 0.8	$(2 \times)$
$P-O(3m)-P'$	121.5 ± 0.8	
$O(3m)-P-O(1)$	101.9 ± 0.8	
$O(2)-P-O(3)$	119.8 ± 0.7	
$O(1)-P-O(2)$	109.3 ± 0.4	
$O(1)-P-O(3)$	107.1 ± 0.6	
$O(3m)-P-O(2)$	108.6 ± 0.9	
$O(3m)-P-O(3)$	108.7 ± 0.5	

0.01 Å; $O(3m)-O(1)$, 2.53 ± 0.002 Å $(2 \times)$, $O(1)-O(1')$, 2.49 ± 0.03 Å). The symmetry of the ring remains unchanged.

The apparent reason for these shifts in the anion atom positions is the necessity that O(2) move away from the water molecule. In the anhydrous structure the smallest dimension of the 'hole' available to the water molecule is that distance between two O(2) atoms. Even taking into account the difference in z coordinates of the H_2O and O(2), the $H_2O-O(2)$ distance would be only of the order of 2.3 Å. The extra space needed for the water is provided both by expansion of the a dimension of the cell and by the shifting of the ring, so as to pull O(2) closer to the mirror plane bisecting the ring and away from the mirror plane containing the water. With these adjustments the $H_2O-O(2)$ distance is 2.93 Å. Other water–oxygen distances are $H_2O-O(1m)$, 2.79 Å, $H_2O-O(2m)$, 2.83 Å, and $H_2O-O(2')$, 2.86 Å. All but one of these, $H_2O-O(1m)$, are edges of sodium coordination figures. In fact, $H_2O-O(2m)$ is a shared edge. There is very

likely a hydrogen bond between H_2O and $O(1m)$, but little can be decided about a second bond. The other distance which would obey the mirror symmetry of the water position is the shared edge, and this seems highly unlikely as a position for a hydrogen bond. If there is a second hydrogen bond, the water is fivefold coordinated. The one hydrogen bond and the three sodium ions to which the water is coordinated form an approximately tetrahedral figure about it.

Thilo & Wallis (1953) have written that in the monohydrate the water molecules must be abnormally closely packed between the rings. This statement was made on the basis that the difference in mole volume between the anhydrous and the monohydrate salt is only about 5 ml per mole of H_2O compared with 14–16 ml per mole of H_2O usually found for simple hydrate salts. However, their computation did not take into account any available 'unused' space in the structure of the anhydrous phosphate. For instance, the difference in volume between the anhydrous and monohydrate compounds amounts to approximately 6 ml per mole of H_2O on the basis of the cell volumes reported in Table 1. Examination of a scale model of the anhydrous structure permits one to make a crude estimate of the space available to the water molecule. There is a volume 7–8 ml per mole of H_2O and this amount plus the 6 ml obtained by the expansion of the unit cell brings the volume available for the water to a reasonable range. Estimates of the volume occupied by the water in a hydrate should be based on knowledge of the anhydrous structure; if this knowledge is lacking, the conclusions drawn from such calculations must be qualified accordingly.

The anhydrous trimetaphosphate and monohydrate seem to be unusual in that they share the same structure. Possibly a similar situation exists for calcium sulfate hemihydrate and the dehydrated material. Powder work (Bunn, 1941) indicated that in $CaSO_4 . xH_2O$, for a variation in x between 0.02 and 0.65, the cell dimensions change slightly and only relatively minor changes occur in the structure. The similarity in the powder patterns of the two materials was also reported by Weiser, Milligan & Erholm (1936) and Weiser & Milligan (1937). They also showed that the hemihydrate is a true hydrate and not a zeolite. Flörke (1952) studied the structure of the dehydrated material and found that the calcium and sulfate ions were so arranged that channels exist which can accommodate the water. However, the water positions are not known exactly in the hemihydrate. There seem to be no other cases reported in the literature for an anhydrous material and its hydrate that share a common structure.

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The Crystal Structure of Dipotassium Glucose-1-phosphate Dihydrate

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A complete structure determination has been made of dipotassium glucose-1-phosphate dihydrate. The crystal is monoclinic, belonging to the space-group $P2_1$ and has the following cell dimensions:

$$a = 10\cdot44, \ b = 9\cdot025, \ c = 7\cdot518 \text{ Å}; \ \beta = 110°24'.$$

The observed density of 1·85 g.cm^{-3} agrees with that calculated for two units of $K_2 . C_6H_{11}O_5 . O . PO_3 . 2H_2O$ per unit cell.

The structure was determined primarily by vector methods, partly using the isomorphous diammonium glucose-1-phosphate dihydrate, and refined both by difference maps and by the method of least-squares. The α-configuration on carbon (1) has been confirmed, and the angles and dimensions of the esterified phosphate group found to agree generally with those of other sugar phosphates. The crystal is bound together both by electrostatic and by hydrogen bonds.

Introduction

Glucose-1-phosphate, the Cori ester, is found widely in both plants and animals. In plants it is the immediate precursor of starch, and in animals of glycogen, being also the first product in the breakdown and utilization of these substances. Though not classified as one of the high-energy phosphates, its heat of hydrolysis ($\sim$ 4800 cal.mole^{-1}) is appreciably higher than that of glucose-6-phosphate and the other low energy phosphates ($\sim$ 2500 cal.mole^{-1}). Kalckar (1941) considers this to be the energy which, loosely speaking, 'drives' the synthesis of these polysaccharides. In the presence of the appropriate enzyme and substrate the Cori ester also enters into the syntheses of a number of disaccharides, e.g. with fructose and in the presence of sucrose phosphorylase, sucrose is produced (Bonner, 1950). This enzyme, however, appears to be specific to glucose-1-phosphate only, as other disaccharides, some quite unknown in nature, can be produced by changing the sugar in the substrate.

The configuration of the molecule has been studied chemically both by Cori, Colowick & Cori (1937) and by Wolfrom & Pletcher (1941) who concluded from comparisons with a synthetic product, and from the high dextrorotation, that the natural ester was α-glucose-1-phosphate, which is confirmed by the present study.

Experimental

The potassium salt of glucose-1-phosphate can be obtained commercially in a very pure state. Crystals of this derivative, which is a dihydrate, are easily grown by slow cooling of a hot saturated aqueous