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References

AKSNES, O. & FOSS, O. (1954). *Acta Chem. Scand.* **8**, 1787.
BENT, H. A. (1961). *J. Inorg. Nucl. Chem.* **19**, 43.
BUERGER, M. J. (1942). *X-ray Crystallography.* p. 427. New York: Wiley.
EMERSON, K. (1960). Thesis, Univ. of Minnesota.
EMERSON, K. & BRITTON, D. (1963). *Acta Cryst.* **16**, 113.
FOSS, O. (1956). *Acta Chem. Scand.* **10**, 136.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
HYBL, A. (1961). Thesis, California Institute of Technology
International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.
OHLBERG, S. M. & VAUGHAN, P. A. (1954). *J. Amer. Chem. Soc.* **76**, 2649.
PAULING, L. (1959). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
ROSSMAN, M. G., JACOBSON, R. A., HIRSHFELD, F. & LIPSCOMB, W. N. (1959). *Acta Cryst.* **12**, 530.
SWANSON, H. E. & FUYAT, R. K. (1953). U.S. Nat. Bur. Stand. Circular 539. Vol. II, p. 41.

Acta Cryst. (1964). **17**, 1139

The Structure of the Triclinic Form of Sodium Tetrametaphosphate Tetrahydrate

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The cell dimensions of triclinic sodium tetrametaphosphate tetrahydrate, $Na_4P_4O_{12}.4H_2O$, are

$$a = 6.652 \pm 0.001,\ b = 9.579 \pm 0.002,\ c = 6.320 \pm 0.001\ \text{Å};$$
$$\alpha = 103^\circ\ 24' \pm 1',\ \beta = 106^\circ\ 59' \pm 1',\ \gamma = 93^\circ\ 17' \pm 1',$$

space group $P\bar{1}$, $Z = 1$.

The structure was determined from a three-dimensional Patterson function, and refined by complete-matrix least-squares. The R value for 1335 observed non-zero reflections is 0·086.

The tetrametaphosphate ring is on the center of symmetry at the origin of the unit cell. One of the two crystallographically different Na ions is fivefold coordinated, and the other is sixfold coordinated.

The fivefold coordinated Na ion links the rings along **c**, the sixfold coordinated ion links the rings along **a**. There are some similarities between the structures of the monoclinic and triclinic forms of this salt but the differences are too great to permit a transition between the two forms in the solid state. Such a transition, reported by other workers, has not been confirmed by this investigator.

Introduction

Bell, Audrieth & Hill (1952), in reporting the two crystalline modifications of $Na_4P_4O_{12}.4H_2O$, described a transition in the solid state from the monoclinic to the triclinic form. The transition was not observed by workers at The Johns Hopkins University (Gross, 1955). Preliminary chemical evidence (Gross, Gryder & Donnay, 1955) had indicated the possible existence of stereoisomers of the tetrametaphosphate anion ring. To establish the relationship between the two forms and learn whether the polymorphism is attributable to different stereoisomers, structure determinations were undertaken. The structure of the triclinic form is now given and compared with the monoclinic structure previously reported (Ondik, Block & MacGillavry, 1961).

Preparation

Pure sodium tetrametaphosphate was kindly provided by Dr J. W. Gryder of The Johns Hopkins University. The tetrametaphosphate was produced both by cold hydrolytic cleavage of α-P_4O_{10} (Bell, Audrieth & Hill, 1952) and by the Warschauer (1903) process from H_3PO_4 and CuO. The product of the latter procedure was purified of other phosphates by the ion-exchange method of Barney & Gryder (1955). Great care must be taken to avoid precipitating a mixture of the two modifications from solution. Approximately 97% pure triclinic material (by volume, as estimated during microscopic examination with a polarizing microscope) may be obtained by slowly adding 95% ethanol with rapid stirring to a solution of the sodium tetrametaphosphate kept at about 50 °C. Single crystals suitable for collecting intensity data were obtained by keeping some solid in a saturated solution at 60 °C for several days. At higher temperatures, large (up to 1 mm) crystals will form in a matter of hours but they often have bubbles and inclusions of mother liquor.

Experimental data

The crystals are usually precipitated from solution as clusters of poorly formed needles elongated along [001]. Crystals grown in solution at 60 °C or higher exhibit good faces, the three pinacoid forms {100}, {010}, {001} often being supplemented by small faces of other forms, {110}, {101}, {011}, {111}.

The indices of refraction measured in white light are $n_\alpha = 1{\cdot}440$, $n_\beta = 1{\cdot}458$, $n_\gamma = 1{\cdot}474$, all $\pm 0{\cdot}002$ (A. Van Valkenburg, private communication). The values reported by Bell *et al.* are 1·438, 1·459, and 1·468, all ±0·002. The material appears to be optically negative with a $2V$ very close to 90°. Since it is virtually impossible to obtain either of the crystalline modifications to the complete exclusion of the other, and since the indices of both forms are very close, great care had to be exercised. Each crystal used, usually acicular, had to be carefully examined to insure that the proper modification was being studied.

Precession films were taken to determine cell dimensions and the values obtained were subjected to a Delaunay reduction. Geiger counter powder data (Cu $K\alpha_1$, 1·5405 Å) were then indexed on the basis of these cell dimensions and subjected to a least-squares analysis. The final cell dimensions are

$$a=6{\cdot}652\pm0{\cdot}001,\ b=9{\cdot}579\pm0{\cdot}002,\ c=6{\cdot}320\pm0{\cdot}001\ \text{Å},$$
$$\alpha=103^\circ\ 24'\pm1',\ \beta=106^\circ\ 59'\pm1',$$
$$\gamma=93^\circ\ 17'\pm1',\ V=371{\cdot}3\ \text{Å}^3.$$

The density calculated on the basis of one formula weight per cell is 2·146 g.cm^{-3}; the observed value determined pycnometrically is 2·148 g.cm^{-3}; therefore $Z=1$. Pyroelectric (Gross, 1955) and piezoelectric tests were negative, indicating $P\bar{1}$ to be the more likely of the two triclinic space groups. The Raman and infrared spectroscopic work of Steger & Simon (1958) and Steger (1958) indicated that the tetrametaphosphate anion has $\bar{1}$ symmetry.

Integrating Weissenberg films of levels *hkl*, with $l=0, 1, 2, 3, 4, 5$, and 0*kl* were taken with Cu $K\alpha$ radiation, using the usual multiple film techniques. The intensities were measured with a densitometer comparator supplemented by visual estimation of very weak reflections. The data were corrected for Lorentz and polarization factors. No absorption corrections were considered necessary since crystals were chosen of suitable size and shape so that corrections were only of the order of 5%. The total number of independent reflections on the seven levels was 1435, 100 of these being too weak to be observed.

Determination of the structure

Since the space group was assumed to be $P\bar{1}$, and since there is only one tetrametaphosphate unit per unit cell, the ring anion must have a center of symmetry coinciding with that of the cell.

A three-dimensional Patterson function was computed and the set of peaks corresponding to P–P vectors within the ring readily identified. Trial coordinates for the Na ions, water molecules, and oxygen atoms were obtained from independent superpositions on the P–P peaks corresponding to vectors between centrosymmetrically related P atoms. Computation of structure factors and electron density maps from the *hk*0 and 0*kl* data indicated that these coordinates were valid. After several such sets of calculations the combined projection data were refined by least squares. When $R(hk0, 0kl)$ was 0·148, the complete set of data was refined. The final $R(hkl)$, for the non-zero reflections was 0·086. In the final refinement 55 parameters were varied, including seven scale factors, one for each level of data, and an x, y, z and isotropic B for each atom. The final parameters are listed in Table 1, the observed and scaled calculated structure factors in Table 2.

Table 1. *Final atomic coordinates*

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
P_I	0·2660	0·0003	0·0901	0·0002	0·2442	0·0003	0·75	0·03
P_{II}	0·8990	0·0003	0·2121	0·0002	0·9862	0·0003	0·83	0·03
O_I	0·8904	0·0008	0·2736	0·0005	0·7918	0·0008	1·46	0·08
O_{II}	0·8696	0·0008	0·3002	0·0005	0·1956	0·0007	1·32	0·08
O_{III}	0·1208	0·0007	0·1510	0·0005	0·0441	0·0007	1·15	0·08
O_{IV}	0·1570	0·0008	0·0788	0·0005	0·4132	0·0008	1·66	0·09
O_V	0·4803	0·0008	0·1713	0·0005	0·3181	0·0008	1·78	0·09
O_{VI}	0·7289	0·0008	0·0704	0·0005	0·9048	0·0008	1·59	0·08
Na_I	0·8210	0·0004	0·1256	0·0003	0·4217	0·0004	1·67	0·05
Na_{II}	0·5560	0·0005	0·4032	0·0003	0·2392	0·0004	1·78	0·05
$(H_2O)_I$	0·3481	0·0010	0·3556	0·0006	0·8186	0·0009	2·68	0·10
$(H_2O)_{II}$	0·2604	0·0009	0·4955	0·0006	0·3573	0·0008	1·86	0·09

Scale factors, *s*

*hk*0	*hk*1	*hk*2	*hk*3	*hk*4	*hk*5	0*kl*
2·78	2·50	2·44	3·53	3·50	3·54	2·72

Table 2. *Observed and scaled calculated structure factors*

$\underline{k}$	F_o	sF_c
	$0\underline{k}0$	
1	89	106
2	43	-41
3	80	-87
4	87	-93
5	65	-63
6	55	-53
7	49	-44
10	56	55
	$1\underline{k}0$	
0	70	64
1	109	128
2	104	-118
3	105	-114
4	33	27
5	25	-32
8	32	33
9	35	37
10	44	44
11	13	19
	$\bar{1}\underline{k}0$	
1	40	37
2	68	-65
3	64	56
4	98	98
5	78	-76
7	18	-8
8	41	-40
9	31	22
10	32	-35
11	34	-41
	$2\underline{k}0$	
0	98	-89
1	46	39
2	109	-102
3	88	-86
4	38	37
5	117	127
6	35	24
7	52	48
8	49	-49
9	19	-18
11	10	14
	$\bar{2}\underline{k}0$	
1	190	-205
2	104	-93
3	124	113
4	14	11
5	145	147
6	46	43
7	51	49
8	30	29
9	14	-13
10	31	-34
11	57	-63
	$3\underline{k}0$	
0	126	-121
1	35	35
2	21	17
3	39	38
4	17	18
5	40	46
6	17	18
7	73	-74
8	33	-36
9	42	-42
	$\bar{3}\underline{k}0$	
1	132	-131
2	90	86
3	86	79
4	41	37
5	60	-57
6	23	-19
8	39	38
9	56	63
10	17	-14
11	22	-19
	$4\underline{k}0$	
0	26	-29
1	8	1
2	109	117
3	74	-81
4	31	-28
5	17	-6
7	13	11
8	16	-15
9	25	-19
	$\bar{4}\underline{k}0$	
1	29	29
2	82	75
3	60	54
4	28	-22
5	77	-77
6	57	-59
7	66	-66
8	20	17
9	13	-5
10	18	21
11	35	30
	$5\underline{k}0$	
0	80	-84
1	36	-32
3	37	36
4	45	-48
5	14	-9
6	39	41
7	35	35
8	42	40
	$\bar{5}\underline{k}0$	
1	13	-10
2	93	98
3	14	5
4	14	-11
5	14	-10
6	36	-37
7	36	32
9	11	-12
10	24	-24
	$6\underline{k}0$	
0	41	-43
1	17	-21
2	45	49
3	41	45
4	15	-13
5	19	-24
	$\bar{6}\underline{k}0$	
1	17	20
2	57	-57
3	28	-22
4	35	-34
5	21	21
6	62	64
7	44	42
8	16	17
9	21	-19
	$7\underline{k}0$	
0	37	38
2	35	35
3	53	58
	$\bar{7}\underline{k}0$	
1	28	30
2	12	9
3	51	-55
4	36	-33
5	13	-12
6	10	0
7	23	24
	$8\underline{k}0$	
0	34	34
	$\bar{8}\underline{k}0$	
1	41	40
	$0\underline{k}1$	
0	54	64
1	63	-73
2	128	-164
3	75	-84
4	42	43
5	67	71
6	22	21
8	24	-25
9	55	53
10	16	13
11	17	-14
	$0\overline{\underline{k}}1$	
1	88	90
3	123	137
4	17	15
5	52	49
6	41	-39
7	62	-61
8	34	-31
9	33	-37
12	27	-24
	$1\underline{k}1$	
0	20	-17
1	23	-22
2	109	-133
3	6	-12
4	21	-19
5	140	166
6	100	113
7	24	26
9	29	-30
10	21	-23
	$\bar{1}\underline{k}1$	
0	120	137
1	92	97
2	24	-26
3	73	-68
4	20	-14
5	69	-70
6	52	-54
7	83	-85
8	26	25
9	24	23
10	32	30
11	16	14
	$1\overline{\underline{k}}1$	
1	112	-122
2	127	-125
3	24	19
4	47	45
5	25	17
7	45	45
9	63	65
10	16	13
11	47	-45
12	35	-38
	$1\underline{k}\bar{1}$	
1	69	79
3	112	-130
4	124	145
5	36	36
7	30	-27
8	82	-81
9	20	-22
10	32	26
11	26	25
	$2\underline{k}1$	
0	6	-5
1	49	49
2	32	31
3	78	-84
4	60	60
5	13	18
6	36	37
7	10	-12
8	69	-67
9	20	-18
10	20	13
	$\bar{2}\underline{k}1$	
0	75	73
1	103	-100
2	97	95
3	55	54
4	55	48
6	101	-106
7	35	-35
8	22	24
9	21	19
11	23	-22
	$2\overline{\underline{k}}1$	
2	25	-22
3	24	-21
4	55	-48
5	121	-121
6	15	9
7	26	24
8	103	104
9	78	73
10	26	24
11	45	-41
12	28	-30
	$2\underline{k}\bar{1}$	
1	22	-14
2	96	-106
3	71	-76
4	55	-53
5	57	61
6	78	80
7	29	25
8	36	34
9	19	-21
10	17	13
	$3\underline{k}1$	
0	99	103
1	102	110
2	72	77
4	91	-99
5	65	-62
6	22	-19
7	23	-23
9	15	-12
	$\bar{3}\underline{k}1$	
0	52	-49
1	81	77
2	41	-43
3	73	70
4	21	16
5	46	-49
7	44	44
8	51	55
9	21	19
10	60	-57
11	22	-26
	$3\overline{\underline{k}}1$	
1	69	-67
2	90	89
3	26	22
4	45	-45
5	49	-40
6	87	-80
7	41	-35
9	17	19
11	17	-14
	$3\underline{k}\bar{1}$	
1	30	29
2	35	-30
3	85	-90
4	32	-27
5	47	45
6	51	50
7	22	19
8	34	-25
9	20	-16
10	28	-22
	$4\underline{k}1$	
0	93	-95
1	18	16
2	36	39
4	20	-19
5	17	-24
7	20	16
	$\bar{4}\underline{k}1$	
1	49	-48
2	16	18
3	29	21
4	36	-28
5	46	-40
6	69	-69
7	47	47
8	38	40
10	7	10
	$4\overline{\underline{k}}1$	
1	23	21
2	26	18
3	69	69
4	18	14
5	19	-19
7	17	-17
8	17	-20
9	15	-17
10	73	-69
	$4\underline{k}\bar{1}$	
1	76	78
2	107	112
3	54	46
4	60	-59
5	39	-32
6	55	-56
8	37	-27
9	26	-18
	$5\underline{k}1$	
0	95	-99
1	45	-44
2	44	48
3	53	53
5	9	11
7	41	37
	$\bar{5}\underline{k}1$	
0	27	-27
1	16	-17
2	36	38
3	13	15
4	14	9
5	59	-56
6	22	20
8	17	-17
9	35	-35
	$5\overline{\underline{k}}1$	
1	77	-72
3	26	17
4	17	17
5	72	66
6	17	10
7	31	32
9	35	-30
10	13	-17
	$5\underline{k}\bar{1}$	
1	16	15
2	43	37
3	26	23
4	20	-20
5	70	-69
7	15	-15
8	12	13
	$6\underline{k}1$	
0	17	-19
1	27	-21
3	36	35
4	8	10
5	36	-35
	$\bar{6}\underline{k}1$	
0	78	-75
1	50	-44
2	20	19
3	69	67
4	26	23
5	42	34
6	44	41
7	12	12
8	29	-31
9	48	-42
	$6\overline{\underline{k}}1$	
1	27	24
2	41	34
3	36	-30
4	9	-10
5	32	-23
6	23	18
7	13	11
	$6\underline{k}\bar{1}$	
1	96	-98
2	17	16
3	22	18
7	50	45
	$7\underline{k}1$	
0	36	36
1	27	-29
3	10	-9
	$\bar{7}\underline{k}1$	
0	40	-44
3	33	-33
4	23	-19
5	19	21
6	44	44
7	32	34
	$7\overline{\underline{k}}1$	
1	55	55
2	25	20
4	19	-16
6	10	-11
	$7\underline{k}\bar{1}$	
2	30	-24
3	42	43
4	33	31
	$\bar{8}\underline{k}1$	
0	47	39
1	40	39
3	30	-31
4	55	-62
	$8\underline{k}\bar{1}$	
1	14	9
2	23	18
	$0\underline{k}2$	
0	66	-61
1	115	137
2	33	35
3	27	-28
4	48	45
5	45	41
6	41	40
7	26	-24
8	13	-15
9	33	31
10	28	-26
	$0\overline{\underline{k}}2$	
2	93	-95
3	131	-142
4	6	9
5	43	40
6	35	33
7	12	-11
8	23	25
9	34	31
10	13	-16
11	35	-34
12	44	-44
	$1\underline{k}2$	
0	98	99
1	36	-34
2	72	85
3	14	15
5	74	78
6	25	23
7	69	-75
8	60	-68
9	20	-19
10	26	27
	$\bar{1}\underline{k}2$	
0	111	117
1	57	48
2	85	-87
3	96	-108
4	71	-79
5	74	80
	$\bar{1}\underline{k}2$	
6	47	-46
7	14	-3
8	50	53
9	38	38
10	14	10
	$1\overline{\underline{k}}2$	
1	79	-80
2	67	-68
3	92	-94
4	50	-43
5	39	37
8	77	76
9	24	23
10	23	16
11	40	-33
	$1\underline{k}\bar{2}$	
1	122	144
2	35	40
3	48	-50
4	82	-91
5	48	51
8	59	-58
11	15	-17
	$2\underline{k}2$	
0	32	-37
1	14	17
2	15	13
3	22	-17
4	51	-50
5	39	-38
6	10	16
7	37	-43
8	33	-37
	$\bar{2}\underline{k}2$	
0	44	43
1	29	23
2	42	-40
3	80	-78
4	36	34
5	45	-45
6	37	-37
8	45	47
9	37	35
10	19	-23
	$2\overline{\underline{k}}2$	
1	53	52
2	47	39
3	77	75
4	130	138
5	62	-60
6	92	-91
7	61	-58
8	26	-21
9	36	37
10	13	-8
12	23	18
	$2\underline{k}\bar{2}$	
1	12	17
2	5	-4
3	15	12
4	54	-56
6	51	52
7	58	-60
8	10	-10
9	29	26
10	47	47
11	45	43
	$3\underline{k}2$	
0	16	-16
1	46	-49
2	47	-47
3	39	-40
4	47	-45
6	38	36
7	52	55
8	33	-29
	$\bar{3}\underline{k}2$	
0	37	-35
1	68	-59
2	71	-70
3	71	67
4	116	123
5	29	27
8	28	27
9	40	-40
10	27	-27
	$3\overline{\underline{k}}2$	
1	32	32
2	53	51
3	134	144
4	44	37
5	13	15
6	80	-80
7	27	-26
8	10	-7
9	40	-41
10	32	-28
11	9	-8
	$3\underline{k}\bar{2}$	
1	98	-101
2	46	47
3	68	-71
5	8	12
6	56	55
7	59	53
8	19	-20
9	9	-10
10	37	36
11	5	10
	$4\underline{k}2$	
0	63	-60
1	19	-20
3	57	56
6	44	44
7	35	39
	$\bar{4}\underline{k}2$	
0	65	-65
1	77	-76
2	28	27
3	56	53
4	49	44
5	36	-30
7	59	59
8	9	18
10	26	-24
	$4\overline{\underline{k}}2$	
1	74	-80
3	31	27
4	27	23
5	41	-35
7	54	47
8	38	35
9	22	21
10	21	-22
	$4\underline{k}\bar{2}$	
1	20	-17
2	40	-42
3	100	105
4	40	40
5	26	25
6	55	47
8	50	-48
9	58	-59
10	17	-14
	$5\underline{k}2$	
2	56	62
3	9	11
4	16	17
5	34	-36
	$\bar{5}\underline{k}2$	
2	30	-28
3	66	68
4	61	-58
5	86	-90
6	30	-29
8	8	13
9	9	15
	$5\overline{\underline{k}}2$	
1	14	-15
2	32	-33
3	39	-30
4	59	-54
5	50	-43
6	47	44
7	45	43
8	47	44
	$5\underline{k}\bar{2}$	
1	43	38
2	70	65
3	48	48
5	32	-31
6	27	-27
7	18	16
8	35	-34
9	40	-37
	$6\underline{k}2$	
0	9	10
1	21	21
2	7	9
3	25	23
4	21	-19
	$\bar{6}\underline{k}2$	
0	10	19
1	14	17
2	90	91
3	14	17
4	41	-34
5	51	-52
8	26	-29
	$6\overline{\underline{k}}2$	
1	12	8
2	43	45
4	28	-27
7	9	10
8	29	-30
	$6\underline{k}\bar{2}$	
1	10	-1
2	14	-13
4	30	-31
5	49	-45
6	33	-36
7	23	21
8	37	47
	$7\underline{k}2$	
0	14	-13
	$\bar{7}\underline{k}2$	
0	30	-33
2	27	29
3	9	13
5	30	31
6	61	65
	$7\overline{\underline{k}}2$	
1	27	27
4	6	-9
5	31	25
	$7\underline{k}\bar{2}$	
1	18	-17
2	12	-14
3	25	-26
5	43	-39
	$\bar{8}\underline{k}2$	
1	7	-6
2	19	-14
3	39	-38
4	33	-36
	$8\underline{k}\bar{2}$	
1	9	-15
2	6	9
3	28	29
	$0\underline{k}3$	
0	32	34
1	45	49
2	37	-48
3	71	-76
4	52	48
5	93	106
6	67	76
7	61	-61
8	34	-37
9	47	-49
	$0\overline{\underline{k}}3$	
1	27	21
2	38	35
3	195	-220
4	38	32
5	10	9
6	24	-21
7	27	-27
8	26	26
9	106	110
10	44	38
11	39	-36
	$1\underline{k}3$	
0	30	23
1	9	2
2	30	-30
3	97	-112
4	51	-54
6	13	18
7	17	-9
8	37	-37
9	45	47
	$\bar{1}\underline{k}3$	
0	31	32
1	93	-119
2	22	-10
3	58	-58
4	66	72
5	95	106
6	18	-17
7	18	-20
9	10	11
	$1\overline{\underline{k}}3$	
1	105	113
2	19	10
3	44	42
4	44	-40
6	122	-123
7	74	-68
8	119	127
9	87	83
12	29	-28
	$1\underline{k}\bar{3}$	
2	31	32
3	81	89
4	8	-7
5	104	110
6	65	63
7	124	-129
8	46	-43
9	19	-16
11	56	-54
12	30	-24
	$2\underline{k}3$	
0	32	36
2	45	-43
3	42	-39
4	132	-145
5	26	20
6	48	47
7	26	26
8	8	11
	$\bar{2}\underline{k}3$	
0	26	22
1	121	130
2	143	-155
3	14	-16
4	16	-11
5	52	-54
6	45	-46
7	31	-30
8	36	36
9	65	69
	$2\overline{\underline{k}}3$	
2	22	-14
3	48	42
4	105	101
5	50	45
6	87	-84
7	30	23
10	73	-73
11	43	-41
	$2\underline{k}\bar{3}$	
1	77	73
2	48	47
3	34	-31
5	95	103
6	83	86
7	53	-51
8	151	-168
9	45	-43
11	35	29
	$3\underline{k}3$	
0	102	-104
2	87	92
3	50	51
4	61	60
6	43	40
7	15	15
	$\bar{3}\underline{k}3$	
0	61	53
1	39	34
2	112	118
3	95	93
4	33	28
5	52	-58
6	124	-152
7	13	-12
8	28	35
9	25	27
	$3\overline{\underline{k}}3$	
1	82	-80
2	94	-95
3	32	20
4	88	89
5	54	-54
6	13	8
7	57	53
8	90	82
9	31	-28
10	51	-49
11	26	-27
	$3\underline{k}\bar{3}$	
1	45	-36
2	85	-81
3	71	-67
4	128	-140
5	21	-13
6	39	36
7	60	57
8	37	-34
10	90	84
11	32	35
	$4\underline{k}3$	
1	28	21
2	89	91
3	89	101
5	24	-25
	$\bar{4}\underline{k}3$	
2	68	64
3	92	89
4	84	84
5	40	-45
6	26	24
8	16	25
9	27	-29
	$4\overline{\underline{k}}3$	
1	123	-133
2	40	-38
4	19	-23
5	46	-39
6	30	-26
7	56	54
8	31	31
9	29	-19
10	39	39
	$4\underline{k}\bar{3}$	
1	36	-31
2	85	-89
3	100	-102
4	71	-70
5	84	-88
6	123	127
7	79	81
8	36	28
9	11	-7
10	20	17
	$5\underline{k}3$	
0	26	-23
2	11	-5
3	10	11
4	25	-20
	$\bar{5}\underline{k}3$	
0	61	-58
1	111	-107
2	40	-37
3	32	36
4	46	-37
5	13	-17
6	18	21
7	65	77
8	52	55
	$5\overline{\underline{k}}3$	
1	52	49
2	65	57
3	81	85
5	84	-86
6	11	-8
8	56	-54
	$5\underline{k}\bar{3}$	
1	39	-43
2	108	109
3	90	89
4	44	39
6	33	-31
7	49	48
9	66	-64
	$6\underline{k}3$	
1	30	-29
2	40	-35
	$\bar{6}\underline{k}3$	
0	64	-68
1	37	-38
2	35	-26
3	63	-59
4	54	-54
5	31	-33
6	16	11
7	43	[illegible]
8	[illegible]	-2
	$6\overline{\underline{k}}3$	
1	24	25
2	59	64
3	51	51
4	19	-18
5	31	27
6	25	26
	$6\underline{k}\bar{3}$	
1	87	90
2	64	58
3	111	113
4	44	42
5	47	-48
6	39	-50
7	10	-10
8	10	-6
	$\bar{7}\underline{k}3$	
0	12	-12
1	34	29
2	56	56
3	47	50
4	23	-29
5	10	0
	$7\underline{k}\bar{3}$	
1	55	-52
2	12	12
3	11	11
5	40	-36
6	60	-66
	$\bar{8}k3$	
1	28	26
2	43	44
3	11	-15
4	27	33
	$8\underline{k}\bar{3}$	
1	40	-44
2	41	-40
3	19	-18
	$0\underline{k}4$	
0	85	95
1	31	33
2	12	-14
3	26	28
4	15	13
5	61	60
6	52	-55
7	37	-43
8	35	-40
	$0\overline{\underline{k}}4$	
2	100	-103
3	62	-58
4	65	-66
5	19	18
6	61	-62
7	17	14
8	17	16
9	71	75
10	30	29
11	18	-18
	$1\underline{k}4$	
0	53	-59
1	52	51
2	79	-83
3	73	-73
6	36	33
7	14	7
	$\bar{1}\underline{k}4$	
0	82	100
1	53	62
2	24	21
3	27	19
4	73	75
6	24	20
7	37	-29
8	36	-35
	$1\overline{\underline{k}}4$	
1	11	-17
3	80	75
4	146	153
5	26	28
6	62	-58
7	86	-85
8	29	-25
9	12	14
10	34	-30
	$1\underline{k}\bar{4}$	
1	7	-5
2	120	-188
3	119	-149
4	48	-49
5	41	33
6	100	106
8	56	52
9	59	57
10	19	15
11	15	-18
	$2\underline{k}4$	
1	56	-58
3	29	-32
4	15	19
5	67	71
6	35	40
	$\bar{2}\underline{k}4$	
0	61	61
1	101	-104
2	119	-127
3	29	-32
4	14	-8
6	26	28
7	16	21
8	40	52
9	24	30
	$2\overline{\underline{k}}4$	
1	8	-80
2	45	44
3	104	104
4	48	41
6	63	-57
7	32	-30
8	69	64
9	21	-19
10	19	-28
11	40	-44
	$2\underline{k}\bar{4}$	
1	51	52
2	75	96
3	80	-95
4	41	41
5	80	81
6	61	61
7	56	47
8	41	-37
9	45	-38
11	75	-70
	$3\underline{k}4$	
0	32	-29
1	75	80
2	73	74
3	18	19
4	17	-16
5	11	-12
6	16	13
	$\bar{3}\underline{k}4$	
0	8	8
1	92	-89
2	45	-39
3	85	-83
4	69	-71
5	42	-41
6	24	-19
7	49	52
8	50	53
	$3\overline{\underline{k}}4$	
1	35	-31
4	15	15
5	111	-108
6	67	-62
7	21	22
8	43	42
9	57	56
10	8	9
	$3\underline{k}\bar{4}$	
1	165	177
2	25	20
3	63	63
5	29	29
6	40	36
7	71	-71
8	85	-85
9	49	-46
10	26	24
11	63	51
	$4\underline{k}4$	
1	25	24
2	35	38
3	11	-16
4	51	-60
	$\bar{4}\underline{k}4$	
0	48	-43
1	17	14
2	38	28
3	127	132
5	26	-27
6	47	-49
7	58	-61
	$4\overline{\underline{k}}4$	
1	35	30
2	38	28
3	53	47
4	63	-59
5	47	-42
6	38	-36
7	35	32
8	22	20
9	30	-33
	$4\underline{k}\bar{4}$	
1	38	33
2	89	87
3	41	-35
4	78	-82
5	50	-45
6	51	-42
7	12	6
8	44	-43
9	10	11
10	38	39
	$5\underline{k}4$	
0	44	-42
1	27	-25
	$\bar{5}\underline{k}4$	
0	88	-80
1	14	-7
2	140	143
3	66	59
4	65	62
6	29	-30
8	21	-21
	$5\overline{\underline{k}}4$	
1	24	-22
2	36	41
3	32	35
4	36	31
5	27	22
6	48	46
7	33	33
	$5\underline{k}\bar{4}$	
1	74	-71
2	12	-14
4	34	-34
5	12	11
6	45	39
7	30	26
8	10	12
9	46	-44
	$\bar{6}\underline{k}4$	
0	109	-98
1	15	-18
5	16	-14
6	14	16
7	14	14
	$6\underline{k}\bar{4}$	
1	64	-60
2	52	50
3	58	53
4	49	49
5	26	-25
6	43	38
7	39	32

Table 2 (*cont.*)

k	F_o	sF_c
	$\bar{7}k4$	
0	26	24
1	39	36
3	45	-40
4	58	-62
	$7k\bar{4}$	
1	23	-26
2	11	18
3	56	56
4	36	-28
5	20	-22
6	36	-41
	$\bar{8}k4$	
0	12	10
1	55	62
	$8k\bar{4}$	
2	20	-24
	$0k5$	
0	98	113
1	35	-35
2	71	-78
3	98	-102
4	34	-25
5	12	9
7	25	25
	$0\bar{k}5$	
1	52	44
2	23	-19
3	101	107
4	36	34
5	39	-32
6	58	-54
7	82	-76
10	30	27
11	35	-26
	$1k5$	
0	27	24
1	24	24
2	67	-70
3	73	-70
4	7	3
5	40	35
6	38	43
	$\bar{1}k5$	
0	97	120
1	67	72
2	89	-99
3	28	24
4	22	23
7	49	-50
	$1\bar{k}5$	
1	70	-72
4	94	93
5	10	6
6	26	27
7	57	49
10	33	-37
	$1k\bar{5}$	
1	97	123
2	22	-22
3	81	-89
4	31	-34
5	62	-65
6	96	-97
7	29	-25
8	34	-26
9	57	57
10	59	58
11	73	57
	$2k5$	
0	34	-35
1	80	84
2	75	74
3	12	11
4	27	25
	$\bar{2}k5$	
0	29	27
1	65	-65
2	44	43
3	64	69
4	66	69
5	46	44
6	32	-32
7	24	-25
	$2\bar{k}5$	
1	97	-91
2	65	-59
3	52	47
4	13	-18
	$2\bar{k}5$	
5	13	-17
8	66	63
9	40	41
10	11	-11
	$2k\bar{5}$	
1	24	20
2	86	-100
3	65	-76
5	68	73
7	8	6
10	51	48
11	17	11
	$3k5$	
0	28	-24
1	49	50
2	48	47
3	12	15
4	48	-46
	$\bar{3}k5$	
0	79	-71
1	106	-112
2	30	-34
3	21	21
4	44	44
6	34	37
	$3\bar{k}5$	
1	52	-50
2	24	22
3	43	31
4	24	-26
5	13	-18
6	46	-42
8	18	-13
9	11	15
	$3k\bar{5}$	
1	20	-18
2	28	-21
3	69	-81
4	60	64
5	91	96
6	133	146
7	8	10
8	29	-27
9	63	-61
10	60	-55
	$4k5$	
0	87	-95
1	31	-32
2	23	21
	$\bar{4}k5$	
0	24	-21
1	29	-25
2	35	34
3	24	21
4	57	-61
5	47	-54
6	44	-45
7	27	32
	$4\bar{k}5$	
1	14	-8
2	54	54
3	59	56
4	45	42
7	32	-17
	$4k\bar{5}$	
2	61	65
3	41	-38
4	43	-40
5	71	72
6	11	11
8	36	-32
9	56	-49
	$\bar{5}k5$	
0	41	-39
1	63	60
2	71	73
3	22	19
4	10	-13
5	49	-51
6	48	-53
	$5k\bar{5}$	
1	81	81
2	32	30
3	13	-17
4	99	-105
5	78	-72
6	13	14
7	14	14
8	8	5
9	20	21
	$\bar{6}k5$	
0	42	-41
2	25	28
3	29	31
4	24	-20
	$6k\bar{5}$	
1	67	-72
2	64	58
3	51	48
4	13	-21
5	14	-17
7	28	29
	$\bar{7}k5$	
0	49	-51
1	41	-36
2	26	-22
3	43	-50
	$7k\bar{5}$	
1	29	-35
2	51	48
3	94	95
4	41	36
5	27	-29
	$0k6$	
0	23	-28
1	26	-30
2	40	-47
3	29	-35
4	27	33
	$0\bar{k}6$	
1	41	-46
2	51	-54
3	22	22
4	78	81
5	48	49
6	44	44
7	17	-11
	$0k7$	
1	41	39
	$0\bar{k}7$	
2	22	-26
3	49	-48
4	11	-10
6	10	-15
7	13	21

Table 3. *Bond distances and angles in the tetrametaphosphate anion*

P_{I}–O_{IV}	1·475 Å	P_{II}–O_{I}	1·469 Å
P_{I}–O_{V}	1·473	P_{II}–O_{II}	1·468
P_{I}–O_{III}	1·602	P_{II}–O_{III}	1·592
P_{I}–O_{VI}	1·614	P_{II}–O_{VI}	1·596
	$\sigma = \pm 0{\cdot}005$ Å		
O_{III}–O_{IV}	2·533 Å	O_{III}–P_{I}–O_{IV}	110·8°
O_{III}–O_{V}	2·476	O_{III}–P_{I}–O_{V}	107·2
O_{III}–O_{VI}	2·443	O_{III}–P_{I}–O_{VI}	98·9
O_{IV}–O_{VI}	2·518	O_{IV}–P_{I}–O_{VI}	109·1
O_{IV}–O_{V}	2·560	O_{IV}–P_{I}–O_{V}	120·5
O_{V}–O_{VI}	2·501	O_{V}–P_{I}–O_{VI}	108·1
O_{I}–O_{II}	2·550 Å	O_{I}–P_{II}–O_{II}	120·6°
O_{I}–O_{III}	2·432	O_{I}–P_{II}–O_{III}	105·2
O_{I}–O_{VI}	2·510	O_{I}–P_{II}–O_{VI}	109·9
O_{II}–O_{III}	2·515	O_{II}–P_{II}–O_{III}	110·5
O_{II}–O_{VI}	2·447	O_{II}–P_{II}–O_{VI}	105·9
O_{III}–O_{VI}	2·506	O_{III}–P_{II}–O_{VI}	103·6
$\sigma = \pm 0{\cdot}007$ Å			
		P_{I}–O_{III}–P_{II}	137·6°
		P_{I}–O_{VI}–P_{II}	129·9
		$\sigma = \pm 0{\cdot}3°$	

Form factors for P^0 and Na^+ were taken from Tomiie & Stam and for O^0 from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). Values for O^{-1}, used for water, were obtained by interpolating between the values of Berghuis *et al.* for O^0 and O^{-2}. All computing was done on a high-speed digital computer.

Dr Charles W. Burnham of The Geophysical Laboratory, Carnegie Institution of Washington, wrote the program used for the least-squares refinement of the cell dimensions. The Busing & Levy (1959*a*, *b*) programs were used for the least-squares refinement of the structure and calculation of interatomic distances and angles.

Description of the structure

Interatomic distances and angles for the ring anion are listed in Table 3. (The numbering of atoms corresponds to that used for the monoclinic structure.) These distances and angles are consistent with those found in condensed phosphates. The ring can be seen in Figs. 1 and 2 along with the coordination figures for the Na ions.

Two types of Na ions connect the rings. Along **c**, the anion alternates with two Na_I ions related by a center of symmetry. The coordination is fivefold, including O_{II} and O_{IV} of one ring, O_I and O_{IV} of a second ring along **c** and O_V of a third ring along **a** (Na–O distances, 2·27–2·50 Å). The figure formed is an irregular pyramid. The atoms O_{II}, O_{IV}, O'_{IV} and O_V which form the base of the pyramid, and the Na_I ion are very close to being coplanar. O'_{IV} is only 0·127 Å from the plane formed by O_{II}, O_{IV} and O_V. Na_I is 0·207 Å from this same plane, just inside its coordination pyramid. The next nearest neighbor to Na_I is an O_{VI} of the second ring along **c** and although it would complete an irregular six-cornered figure it is at a large distance for Na–O coordination (3·05 Å). A similar situation occurs in $Na_5P_3O_{10}$, Phase I (Corbridge, 1960). In that structure, one Na ion has

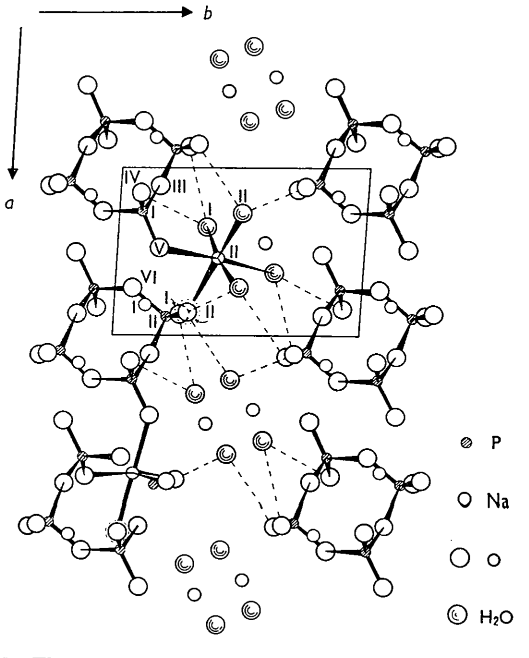

Fig. 1. The structure projected on the *ab* plane with one unit cell outlined. The numbering of the atoms is the same as that used in Table 1. The rings are completely outlined except where it would interfere with the drawing of the Na coordination. The coordination of one Na_I and one Na_{II} ion has been drawn. A dashed line encircling an atom indicates the atom in the cell beneath. The straight dashed lines indicate probable hydrogen bonds.

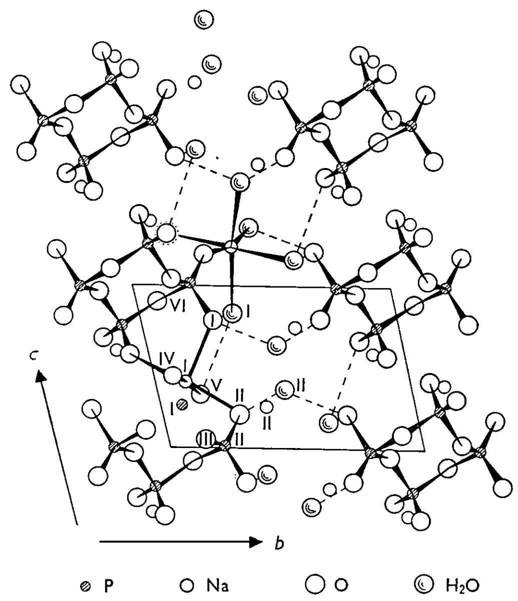

Fig. 2. The structure projected on the *bc* plane with one unit cell outlined. The anion at the origin is incomplete so that the $\mathrm{Na_{I}}$ coordination may be seen more easily. The dashed lines indicate probable hydrogen bonds and the dashed circle indicates the atom in the cell below.

a 'one-sided' fourfold coordination (distances 2·22 to 2·59 Å) with the next nearest oxygen neighbor at 3·05 Å. The Na–O distances are given in Table 4 with distances involving $\mathrm{O_{VI}}$ included in brackets for comparison with similar distances in the monoclinic structure.

Table 4. *Interatomic distances in the sodium–oxygen coordination polyhedra*

$\mathrm{Na_{I}}$–$\mathrm{O_{I}}$	2·335 Å	$\mathrm{Na_{II}}$–$\mathrm{O_{II}}$	2·444 Å
$\mathrm{Na_{I}}$–$\mathrm{O_{II}}$	2·501	$\mathrm{Na_{II}}$–$\mathrm{O_{V}}$	2·418
$\mathrm{Na_{I}}$–$\mathrm{O_{IV}}$	2·415	$\mathrm{Na_{II}}$–$\mathrm{(H_2O)_{I}}$	2·531
$\mathrm{Na_{I}}$–$\mathrm{O_{IV}'}$	2·318	$\mathrm{Na_{II}}$–$\mathrm{(H_2O)_{I}'}$	2·496
$\mathrm{Na_{I}}$–$\mathrm{O_{V}}$	2·266	$\mathrm{Na_{II}}$–$\mathrm{(H_2O)_{II}}$	2·440
[$\mathrm{Na_{I}}$–$\mathrm{O_{VI}}$	3·053]	$\mathrm{Na_{II}}$–$\mathrm{(H_2O)_{II}'}$	2·416
	$\sigma = \pm 0{\cdot}006$ Å		
$\mathrm{O_{I}}$–$\mathrm{O_{II}}$	3·799 Å	$\mathrm{O_{II}}$–$\mathrm{O_{V}}$	3·175 Å
$\mathrm{O_{I}}$–$\mathrm{O_{IV}}$	3·283	$\mathrm{O_{II}}$–$\mathrm{(H_2O)_{I}}$	3·736
$\mathrm{O_{I}}$–$\mathrm{O_{IV}'}$	3·626	$\mathrm{O_{II}}$–$\mathrm{(H_2O)_{I}'}$	3·685
$\mathrm{O_{I}}$–$\mathrm{O_{V}}$	3·306	$\mathrm{O_{II}}$–$\mathrm{(H_2O)_{II}'}$	3·410
$\mathrm{O_{II}}$–$\mathrm{O_{IV}'}$	3·213	$\mathrm{O_{V}}$–$\mathrm{(H_2O)_{I}}$	3·872
$\mathrm{O_{II}}$–$\mathrm{O_{V}}$	3·175	$\mathrm{O_{V}}$–$\mathrm{(H_2O)_{II}}$	3·495
$\mathrm{O_{IV}}$–$\mathrm{O_{IV}'}$	3·097	$\mathrm{O_{V}}$–$\mathrm{(H_2O)_{II}'}$	3·412
$\mathrm{O_{IV}}$–$\mathrm{O_{V}}$	3·819	$\mathrm{(H_2O)_{I}}$–$\mathrm{(H_2O)_{I}'}$	3·273
[$\mathrm{O_{II}}$–$\mathrm{O_{VI}}$	2·447]	$\mathrm{(H_2O)_{I}}$–$\mathrm{(H_2O)_{II}}$	3·586
[$\mathrm{O_{IV}}$–$\mathrm{O_{VI}}$	4·718]	$\mathrm{(H_2O)_{I}'}$–$\mathrm{(H_2O)_{II}}$	3·471
[$\mathrm{O_{IV}'}$–$\mathrm{O_{VI}}$	3·599]	$\mathrm{(H_2O)_{I}'}$–$\mathrm{(H_2O)_{II}'}$	3·397
[$\mathrm{O_{V}}$–$\mathrm{O_{VI}}$	3·469]	$\mathrm{(H_2O)_{II}}$–$\mathrm{(H_2O)_{II}'}$	3·156
	$\sigma = \pm 0{\cdot}010$ Å		

The $\mathrm{Na_{II}}$ ion further links rings along **a** by coordinating with $\mathrm{O_{II}}$ of one ring and $\mathrm{O_{V}}$ of another. The coordination is completed by the two water molecules and their centrosymmetric equivalents, forming an almost regular octahedron (Na–O dis-

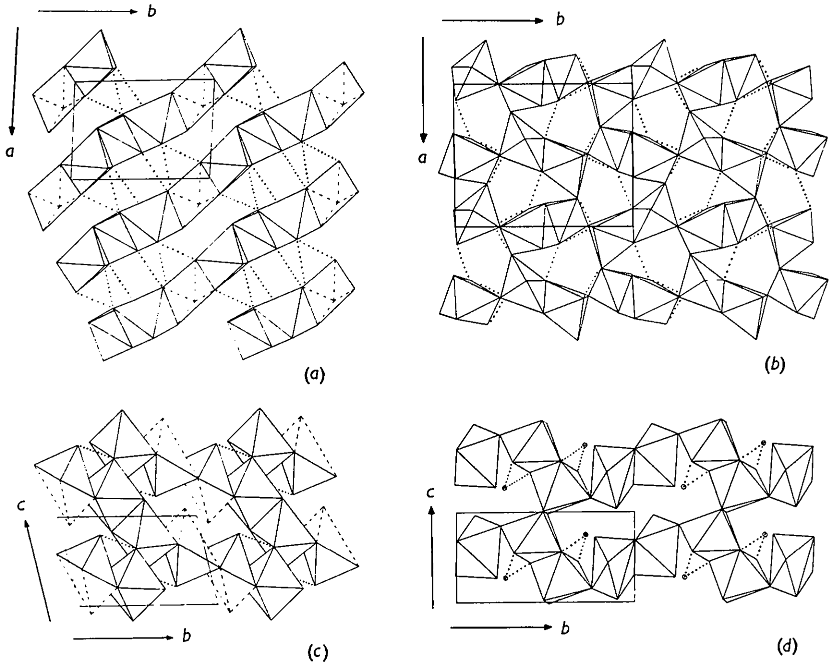

Fig. 3. The sodium coordination polyhedra. The dotted lines indicate probable hydrogen bonds. (*a*) and (*c*) The polyhedra in the triclinic form. The dashed lines are drawn to indicate the $\mathrm{O_{VI}}$ corner in order to facilitate comparison with the monoclinic form. (*b*) and (*d*) The polyhedra in the monoclinic form. The dotted lines in (*d*) indicate the hydrogen bonds to $\mathrm{O_{I}}$ of the phosphate tetrahedra.

tances, 2·42–2·53 Å). These octahedra serve to link rings along **b**. The Na_{II} octahedra share edges $(H_2O)_I$–$(H_2O)_I'$ and $(H_2O)_{II}$–$(H_2O)_{II}'$ to form chains along **c**. These chains share the edge O_{II}–O_V with the Na_I to form a sheet of Na coordination polyhedra. These sheets are parallel to (110) as shown in Fig. 3(*a*). The sheet itself is shown in Fig. 3(*c*). To facilitate comparison with the monoclinic structure the Na_I figure has been shown as a six-cornered polyhedron with the edges involving the O_{VI} drawn as dashed lines.

The major linkage between sheets is through the ring tetrahedra which fit between the Na_I polyhedra in one sheet and crosslink to the Na_{II} octahedra in adjacent sheets. The sheets may also be held together by hydrogen bonds. The shortest water–oxygen distances are $(H_2O)_{II}$–O_I (2·730 ± 0·007 Å), $(H_2O)_{II}$–O_{II} (2·883 ± 0·008 Å), $(H_2O)_I$–O_I (3·046 ± 0·008 Å), and $(H_2O)_I$–O_{IV} (3·127 ± 0·008 Å). Although the water–oxygen distances involving $(H_2O)_I$ are rather long for hydrogen bonds, they are suitably oriented and probably indicate the most likely hydrogen positions. The water–oxygen distances are shown as dotted lines in Fig. 3. Not only are the $(H_2O)_I$–oxygen distances long, but the Na–$(H_2O)_I$ distances are slightly longer than for $(H_2O)_{II}$. These longer distances are consistent with the fact that the B value for $(H_2O)_I$ is larger than that for $(H_2O)_{II}$.

Approximately tetrahedral figures are formed about $(H_2O)_I$ by two Na_{II} ions, O_{II} and O_{IV}, and about $(H_2O)_{II}$ by two Na_{II} ions and O_I and O_{II}. Three terminal oxygens of the ring also show roughly tetrahedral coordination: O_I is surrounded by Na_I, P_{II}, $(H_2O)_I$ and $(H_2O)_{II}$; O_{II} by Na_I, Na_{II}, P_{II} and $(H_2O)_{II}$; O_{IV} by two Na_I, P_I and $(H_2O)_I$.

Comparison of the monoclinic and triclinic structures

The rings in both structures are the same stereoisomer. Whereas in the monoclinic (M) form the anion has strong pseudosymmetry $2/m$, in the triclinic (T) form the ring is further skewed from this symmetry. In M the P–O–P angles are equal, 133·2°, although this equality is not required by space-group symmetry, but in T these angles are 137·6° and 129·9°. The O–P–O angles in both structures are much the same, as are the distances. However, the P–O ring bonds which had average values of 1·635 Å and 1·583 Å in M are 1·608Å and 1·594 Å in T. The difference in the ring bonds in T is much smaller (only $2{\cdot}8\sigma$ as compared with $3{\cdot}4\sigma$ in M).

The alternation of rings with Na_I ions along **c** is similar in both salts. However, in M the Na_I coordination is sixfold and in T it is fivefold. In M, one water molecule is coordinated to the Na_I ion but the comparable position in T is occupied by O_V. Na_{II} has similar coordination in both structures although the range of distances in T is smaller (2·42–2·53 Å) than in M (2·26–2·63 Å). Comparison of Figs. 3(*c*) and (*d*), shows the similarity of the *bc* planes in both structures with respect to the Na polyhedra. In M the sheet is formed by polyhedra sharing edges only with their centrosymmetric equivalents and sharing corners between Na_I and Na_{II} polyhedra. The sheet in T is formed by edge sharing between all polyhedra. That these sheets are linked forming a complete three-dimensional network of Na polyhedra in M and are separate sheets in T is clear from a comparison of Figs. 3(*a*) and (*b*).

The positions of the water molecules vary also. In M the water is located in layers parallel to (001), lying between the layers of rings. In T the water is also in layers but these are parallel to (010) and perpendicular to the plane of the rings. (See Fig. 3 of the paper on the monoclinic structure and Fig. 1 of this paper.)

It is interesting to compare these two polymorphic forms with Phases I and II of $Na_5P_3O_{10}$ (Davies & Corbridge, 1958; Corbridge, 1960). Differences in P–O chain distances were found and these differences are less in Phase I than in Phase II, a situation comparable to that in the T and M structures of the tetrametaphosphate.

In Phase II the tripolyphosphate chain is slightly distorted from $2m$ (C_{2v}) symmetry and this distortion is greater in Phase I, comparable to the increased distortion from $2/m$ (C_{2h}) symmetry of the tetrametaphosphate ring in T as compared with its pseudosymmetry in M. In Phase I one Na ion is only fourfold coordinated and all are sixfold coordinated in Phase II, also comparable to the fivefold coordination of Na_I in T and the sixfold coordination of Na_I in M.

Tests for a solid state transition

Attempts were made to observe a transition in the solid state at 54 °C as reported by Bell *et al.* Monoclinic crystals were placed on the heating stage of a polarizing microscope and observed as the stage was heated. No change in the crystalline form could be observed at 54 °C or indeed even to about 80 °C although the crystal was held at these elevated temperatures for several hours. Attempts by workers at The Johns Hopkins University (Gross, 1955) and by this worker to effect a change from monoclinic to triclinic by heating 1–2 g of the salt at temperatures as high as 80 °C for as long as 18 hours were unsuccessful. Powder patterns revealed no detectable amounts of the triclinic salt. The only change noted was the formation of the anhydrous material as the temperature was raised and the time of heating prolonged. The anhydrous salt was identified by the powder patterns reported by Bell *et al.* and by Corbridge & Tromans (1958).

By means of a small furnace-sample holder kindly loaned by Dr Robert S. Roth of the National Bureau of Standards, samples of both the monoclinic and triclinic forms were heated for varying periods of time ($\frac{1}{2}$ hour to about 16 hours) while the furnace was mounted on an X-ray diffractometer. Patterns could be taken at any temperature. No change from one polymorphic form to another could be detected. Only dehydration occurred, at temperatures as low as 50 °C if the sample was heated 12 or more hours and at 75 °C after 1 hour of heating. A transition in the solid state seems unlikely from a comparison of the two structures. Although the structures have similarities, major shifts in the relative positions of the anions, and in the sodium coordination would have to occur.

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References

Barney, D. L. & Gryder, J. W. (1955). *J. Amer. Chem. Soc.* **77**, 3195.

Bell, R. N., Audrieth, W. F. & Hill, O. F. (1952). *Ind. Engng Chem.* **44**, 568.

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Busing, W. R. & Levy, H. A. (1959*a*). *A Crystallographic Least Squares Refinement Program for the IBM* 704. Oak Ridge National Laboratory Report 59-4-37.

Busing, W. R. & Levy, H. A. (1959*b*). *A Crystallographic Function and Error Program for the IBM* 704. Oak Ridge National Laboratory Report 59-12-3.

Corbridge, D. E. C. (1960). *Acta Cryst.* **13**, 263.

Corbridge, D. E. C. & Tromans, F. R. (1958). *Anal. Chem.* **30**, 1101.

Davies, D. R. & Corbridge, D. E. C. (1958). *Acta Cryst.* **11**, 315.

Gross, R. J. (1955). Unpublished Dissertation, The Johns Hopkins University.

Gross, R. J., Gryder, J. W. & Donnay, G. (1955). *Abstracts of Papers*. 128th Meeting. Amer. Chem. Soc.

Ondik, H. M., Block, S. & MacGillavry, C. H. (1961). *Acta Cryst.* **14**, 555.

Steger, E. (1958). *Z. anorg. Chem.* **294**, 146.

Steger, E. & Simon, A. (1958). *Z. anorg. Chem.* **294**, 1.

Tomiie, Y. & Stam, C. H. (1958). *Acta Cryst.* **11**, 126.

Warschauer, F. (1903). *Z. anorg. Chem.* **36**, 137.

Acta Cryst. (1964). **17**, 1145

The Crystal Structure of Bisethylenediaminecopper(II) Nitrate

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The crystal structure of bisethylenediaminecopper(II) nitrate, $Cu(C_2N_2H_8)_2(NO_3)_2$, has been determined from three-dimensional X-ray diffraction data. The dimensions of the monoclinic ($P2_1/c$) cell are $a_0=8·30$, $b_0=10·05$, $c_0=8·07$ Å, $\beta=111° 6'$, $z=2$. The structure was refined by three-dimensional difference syntheses to $R=0·097$.

The copper ion has the usual distorted octahedral coordination with four N atoms at 2·03 Å and two O atoms at 2·59 Å. The ethylenediamine molecule is in the *gauche* configuration, with one C atom 0·39 Å from the CuN_4 plane and the other $-0·19$ Å

Introduction

As a part of a study of the coordination configuration of Cu^{2+}, we have determined the crystal structure of bisethylenediaminecopper(II) nitrate, $Cu(C_2N_2H_8)_2(NO_3)_2$, which was originally prepared and described as a dihydrate by Grossman & Schuck (1906), but later shown to be anhydrous by Johnson & Bryant (1934). A short report of preliminary work on this structure was reported by Watanabe & Atoji (1951). They report the cell to have dimensions $a=8·00$, $b=10·00$, $c=15·53$ Å, $\beta=97° 25'$, $Z=4$ molecules, space group $B2_1/a$. In *Structure Reports* (1951) it is erroneously suggested that this space group symbol is a misprint for $P2_1/a$. However, transformation of their cell to a primitive cell gives $a=8·00$, $b=10·00$, $c=8·27$ Å, $\beta=111° 19'$, in quite satisfactory agreement with our results.

Experimental

Bisethylenediaminecopper(II) nitrate was prepared by the method described by Grossman & Schuck (1906)

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