

The Structure of the Monoclinic Form of Sodium Tetrametaphosphate Tetrahydrate

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Crystals of monoclinic sodium tetrametaphosphate tetrahydrate, $\text{Na}_4\text{P}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$, are needlelike in habit, elongated along c . The unit cell dimensions are

$$a = 9.667 \pm 0.002, b = 12.358 \pm 0.002, c = 6.170 \pm 0.001 \text{ \AA}; \beta = 92^\circ 16' \pm 10';$$

space group $P2_1/a$, $Z = 2$. Two sets of three-dimensional X-ray diffraction data were collected with $\text{Cu } K\alpha$ radiation using Weissenberg multiple-film techniques, and the intensities were measured photometrically. The structure was determined by a combination of three-dimensional Patterson and electron-density syntheses, and a complete-matrix least-squares reduction of data. The final R value for 831 non-zero reflections is 0.108. Individual isotropic temperature factors were used.

The tetrametaphosphate rings are on centers of symmetry. The sodium ions are coordinated by six oxygen atoms in roughly octahedral configuration. One sodium ion links the rings in a network parallel to the ab plane. The other alternates with the rings linking them along c .

Introduction

Two crystalline modifications of sodium tetrametaphosphate exist: a monoclinic and a triclinic form (Bell, Audrieth & Hill, 1952). Preliminary chemical evidence (Gross, Gryder & Donnay, 1955) indicates that the polymorphism may be due to the existence of stereoisomers of the tetrametaphosphate ring. To investigate this possibility the two structure determinations were undertaken, beginning with the monoclinic form. Only one other tetrametaphosphate structure had been completely determined, that of ammonium tetrametaphosphate (Romers, Ketelaar & MacGillavry, 1951). An approximate structure for aluminum tetrametaphosphate was proposed by Pauling & Sherman in 1937 but not refined.

Experimental data

The pure monoclinic salt was kindly supplied by Dr John W. Gryder of The Johns Hopkins University. Cold hydrolytic cleavage of the phosphorus oxide $\alpha\text{-P}_4\text{O}_{10}$ which forms tetrametaphosphoric acid was followed by neutralization with NaOH . The product was salted out with NaCl and recrystallized several times from water and ethanol. The identity of the crystalline form was checked using indexed powder patterns. Suitable single crystals were grown by evaporation of 2–3 cm^3 of nearly-saturated aqueous solution at temperatures below 25 °C.

The crystals are needles elongated along $[001]$ with $\{110\}$ the predominant form. $\{100\}$ and $\{010\}$ are

usually small and occasionally cannot be seen at all. Cleavage is not pronounced in any direction, the crystals tending to fracture irregularly.

The indices of refraction measured in white light by oil immersion techniques are

$$n_\alpha = 1.440 \pm 0.002, n_\beta = 1.458 \pm 0.002, n_\gamma = 1.476 \pm 0.002.$$

These values agree well with those reported by Bell, Audrieth & Hill (1952). In white light the crystal appears to be slightly positive with a $2V$ extremely close to 90° . The plane of the optic axes is parallel to (010) . An extinction angle of 37° was measured from c with the crystals lying on one of the (110) faces. (The optical data were obtained by H. F. McMurdie and A. Van Valkenburg of the National Bureau of Standards.)

The cell data as reported by Barney & Gryder (1955) were used in the determination and refinement of the structure.

$$a = 9.65 \pm 0.04, b = 12.32 \pm 0.04, c = 6.17 \pm 0.04 \text{ \AA}, \\ \beta = 92^\circ 30' \pm 10';$$

$$\rho_c = 2.173 \pm 0.006, \rho_o = 2.18 \pm 0.01 \text{ g.cm.}^{-3}; \\ Z = 2; \text{ space group } P2_1/a.$$

After the structure had been determined, the cell dimensions were refined by a least-squares reduction of powder diffractometry data, using $\text{Cu } K\alpha_1$ radiation (1.5405 \AA). The refined values, used in calculating bond distances and angles, are

$$a = 9.667 \pm 0.002, b = 12.358 \pm 0.002, c = 6.170 \pm 0.001 \text{ \AA.}$$

$$\beta = 92^\circ 16' \pm 10'.$$

Two sets of Weissenberg films $hk0$, $hk1$, $hk2$, $hk3$, $hk4$, $hk5$, $h0l$, and $0kl$ were taken of different crystals with $\text{Cu } K\alpha$ radiation using multiple film techniques. The first set of intensities, obtained from unintegrated equi-inclination films, were used for the Patterson syntheses and electron density maps, after correction for Lorentz and Polarization factors and spot extension on upper layers (Phillips, 1956). The duplicate set, used for the refinement, was obtained from integrated films. The integrated intensities were measured with a densitometer-comparator and corrected for Lorentz and polarization factors on a high-speed digital computer. There was excellent agreement between the two sets. No absorption correction was made because the small crystals used necessitated a maximum correction of only 6%.

Extremely long-exposure precession films had been taken to verify the space-group assignment (Gross, 1955). Spots violating the criterion for space group $P2_1/a$ appeared. These same reflections could not be reproduced on long exposure Weissenberg films. Their intensities are extremely weak, and they are sharper and smaller than the other reflections. Such properties are characteristic of double reflections. The extra spots have been accounted for as double reflections involving strongly reflecting planes. Therefore, no change was made in the original space-group assignment by Andress, Gehring & Fischer (1949).

Determination of the structure

The general positions in $P2_1/a$ are fourfold; the only special positions, on centers of symmetry, are twofold. Because there are two tetrametaphosphate groups per unit cell, each group must have a center of symmetry. Since neither P nor O can be expected to have a centrosymmetric environment, these atoms must occupy fourfold general positions. Thus one special position is effectively blocked by the P_4O_{12} -group.

Because the sodium ions and water molecules occur in multiples of four, at the most only two of the remaining three special positions could be occupied. The assumption that no special positions are occupied was confirmed by the Patterson maps.

There are approximately twice as many reflections with $h+k=2n$ as $h+k=2n+1$, the former generally being far more intense than the latter. This distribution of the intensities corresponds to a pseudo-halving of $a+b$, that is, of $[110]$. This pseudo-halving combined with the space group $P2_1/a$ leads to a pseudo space group $C2/m$, which has these 'extra' symmetry elements: mirror planes $(010)_0$ and $(010)_{\frac{1}{2}}$, twofold axes $[010]$ through $x=0, z=0$, and $x=\frac{1}{2}, z=0$. Probably at least the P atoms, the heaviest scatterers, must conform approximately to this pseudosymmetry.

From a three-dimensional Patterson synthesis the P atoms were located, one P lying near the pseudo mirror plane, the other near the pseudo twofold axis. Independent superpositions on the Harker peaks of the two P atoms yielded positions for the O atoms and the Na^+ ions. Even in three dimensions there

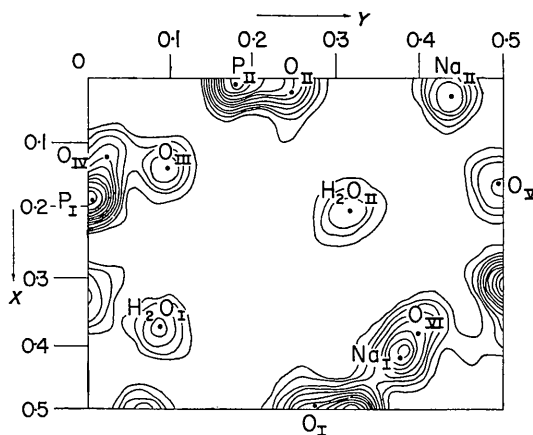


Fig. 1. Final electron density projection of cell contents along $[011]$. Contours are drawn at arbitrary intervals. Indicated atomic positions are those obtained from the final least-squares refinement.

Table 1. Final atomic coordinates

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
P_I	0.1874	0.0005	0.0033	0.0004	0.9032	0.0007	0.91	0.08
P_{II}	0.0080	0.0005	0.1778	0.0004	0.0457	0.0006	0.83	0.08
O_I	0.4972	0.0015	0.2730	0.0012	0.2663	0.0019	1.75	0.24
O_{II}	0.0192	0.0014	0.2455	0.0010	0.8501	0.0018	1.12	0.21
O_{III}	0.1361	0.0013	0.0987	0.0011	0.0661	0.0017	1.22	0.22
O_{IV}	0.1188	0.0013	0.0205	0.0010	0.6866	0.0017	0.98	0.21
O_V	0.1594	0.0014	0.4927	0.0012	0.0739	0.0019	1.56	0.22
O_{VI}	0.3851	0.0013	0.4017	0.0011	0.9764	0.0017	1.32	0.22
Na_I	0.4293	0.0009	0.3710	0.0007	0.5601	0.0011	2.03	0.15
Na_{II}	0.0265	0.0008	0.4385	0.0006	0.7636	0.0010	1.66	0.14
$(\text{H}_2\text{O})_I$	0.3786	0.0015	0.0853	0.0012	0.4461	0.0020	2.35	0.28
$(\text{H}_2\text{O})_{II}$	0.2005	0.0019	0.3174	0.0015	0.5552	0.0022	3.57	0.34

Scale factors

$hk0$	$hk1$	$hk2$	$hk3$	$hk4$	$hk5$
0.159	0.166	0.174	0.179	0.169	0.199

Table 2 (cont.)

h	$ F_o $	F_c	h	$ F_o $	F_c	h	$ F_o $	F_c	h	$ F_o $	F_c	h	$ F_o $	F_c	h	$ F_o $	F_c	h	$ F_o $	F_c																																																																																				
0	57	-59	0	47	29	4	24	-17	3	33	-32	1	24	27	5	81	-77	5	22	-20	5	39	-28	6	48	45	0	75	-17	0	22	-17	1	24	18	1	24	-18	2	46	-34	2	17	-26	3	49	47	4	48	47	4	40	-26	5	41	-31	7	26	29	0	85	-65	0	57	-65	2	22	-18	2	58	59	3	48	47	4	40	-26	4	35	-20	4	49	-46	6	49	-46	6	32	-35	6	49	-46	6	49	-46	6	32	-35	6	32	-35	6	32	-35

seven of the twelve atoms in the asymmetric unit lie very close to the axis and that there is considerable overlap. Refinement by the usual Fourier methods, or with a least-squares program using only a diagonal matrix, would have been extremely difficult.

The ambiguities in the 3-D electron-density map were resolved after obtaining the refined x and y parameters. The z coordinates were chosen by examination of a model and consideration of the coordination requirements of the sodium ions.

The structure was refined in three dimensions using the 831 observed reflections in the Cu sphere. Isotropic temperature factors of 1.5 were assumed for each atom. The 54 variables included the x , y , z , and B for each atom and an individual scale factor for each l level. The final R_{hkl} value is 0.108, and the final parameters are listed in Table 1. A comparison of the observed and calculated structure factors is listed in Table 2.

The atomic scattering factors for Na^+ and P^0 calculated by Tomiie & Stam (1958) and for O^0 calculated by McWeeny (1951) were used. The f_{O^0} were also used for water, rather than $f_{\text{O}^{2-}}$, since only approximately 2% of the non-zero reflections have a $\sin \theta$

value low enough to be affected by the difference in the two f curves.

Since there had been only one preliminary 3-D electron density synthesis, a 3-D difference synthesis was calculated to check the general features of the structure. The maximum background in this synthesis was approximately $0.7 \text{ e} \cdot \text{\AA}^{-3}$; therefore, all statements concerning electron distributions are subject to this error. Indicated shifts in parameters are extremely small. The largest shift was found to be 0.0003 of b for Na_1 , well within the estimated standard deviation of 0.0007.

Description and discussion of the structure

The tetrametaphosphate anion consists of rings of four phosphate tetrahedra sharing corners. These rings, besides having point group symmetry $\bar{1}$, show strong pseudosymmetry $2/m$. See Figs. 2 and 3. These pseudosymmetry elements are slightly inclined from (010) and [010], with the plane of the ring atoms being almost parallel to (001). In the ammonium tetrametaphosphate the ring does indeed possess $2/m$ symmetry.

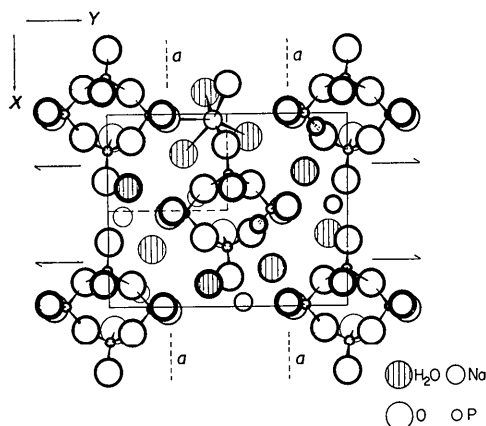


Fig. 2. The structure projected along c . In order to show complete rings, the limits of the cell are taken from $-\frac{1}{2}c$ to $+\frac{1}{2}c$. The unit cell is indicated by the solid black line, the asymmetric unit by the dashed line. The approximate z parameters have been indicated by the variation in line thickness.

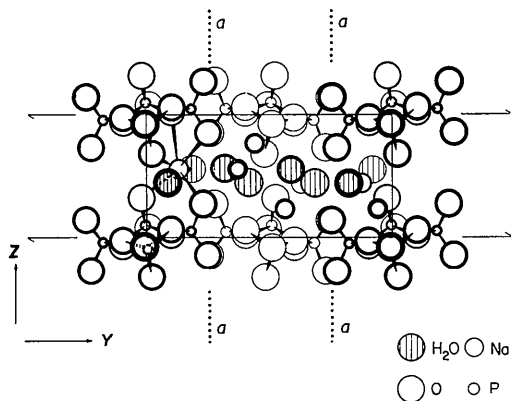


Fig. 3. The structure projected along a , from $-\frac{1}{2}a$ to $+\frac{1}{2}a$.

Interatomic distances and angles are given in Table 3 with the atom numbers as indicated in Fig. 4. These values are consistent with those found in other condensed phosphates. As pointed out by Davies & Corbridge (1958) a P-O single bond with the Schomaker-Stevenson covalency correction is 1.63 Å. Within the ring the P-O bonds are 1.635 and 1.584 Å, much larger than the terminal P-O bonds (1.487 Å). Examination of the possible resonance forms as given in the paper on the ammonium salt (Romers *et al.*, 1951) indicates that the P-O terminal bonds are primarily double whereas the P-O ring bonds are primarily single, agreeing with the observed lengths. In orthophosphates, the difference in lengths should disappear and each P-O bond be equal. The value found, 1.526 Å, (Posner, Perloff & Diorio, 1958) is, as expected, intermediate between 1.487 and 1.635 Å.

It is interesting that the bonds within the ring are not uniform; the bonds to P_I and those to P_{II} differ by 3.4σ . (σ is standard deviation.) The same magni-

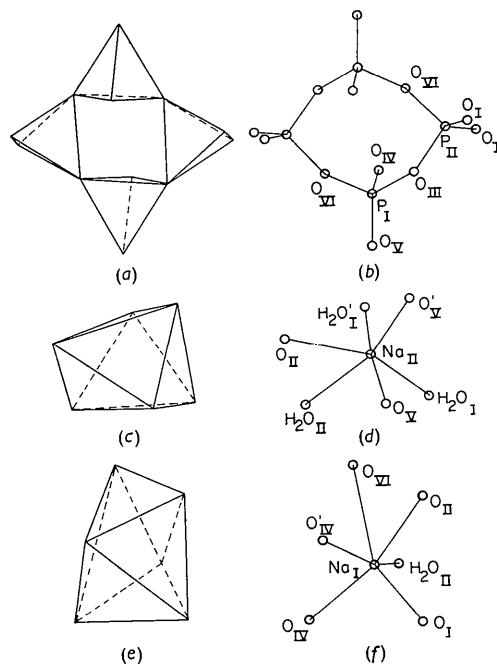


Fig. 4. Illustration of the anion tetrahedra and the sodium coordination polyhedra.

tude of difference was found also in the ammonium salt.

The average O-O distances for the two independent tetrahedra of the ring are 2.54 and 2.50 Å. The smallest distance, 2.383 Å between O_{II} and O_{VI} , is the only edge shared with a sodium coordination polyhedron.

The tetrametaphosphate rings are connected by two types of sodium coordination polyhedra. Two sodium

Table 3. *Interatomic distances and angles in tetrametaphosphate ring*

$P_I - O_{IV}$	1.484 Å	$P_{II} - O_I$	1.498 Å
$P_I - O_V$	1.488	$P_{II} - O_{II}$	1.476
$P_I - O_{III}$	1.639	$P_{II} - O_{III}$	1.579
$P_I - O_{VI}$	1.631	$P_{II} - O_{VI}$	1.587
$\sigma = \pm 0.016$			
$O_{III} - O_{IV}$	2.533 Å	$O_{III} - P_I - O_{IV}$	108.3°
$O_{III} - O_V$	2.551	$O_{III} - P_I - O_V$	109.3°
$O_{III} - O_{VI}$	2.456	$O_{III} - P_I - O_{VI}$	97.4°
$O_{IV} - O_{VI}$	2.547	$O_{IV} - P_I - O_{VI}$	109.6°
$O_{IV} - O_V$	2.578	$O_{IV} - P_I - O_V$	120.4°
$O_V - O_{VI}$	2.548	$O_V - P_I - O_{VI}$	109.5°
$O_I - O_{II}$	2.595 Å	$O_I - P_{II} - O_{II}$	121.5°
$O_I - O_{III}$	2.444	$O_I - P_{II} - O_{III}$	105.2°
$O_I - O_{VI}$	2.598	$O_I - P_{II} - O_{VI}$	114.7°
$O_{II} - O_{III}$	2.495	$O_{II} - P_{II} - O_{III}$	109.5°
$O_{II} - O_{VI}$	2.383	$O_{II} - P_{II} - O_{VI}$	102.1°
$O_{III} - O_{VI}$	2.467	$O_{III} - P_{II} - O_{VI}$	102.4°
$\sigma = \pm 0.021$			
$P_I - O_{VI} - P_{II}$	133.2°		
$P_I - O_{III} - P_{II}$	133.2°		
$\sigma = \pm 0.9°$			

ions of the first type (Na_{I}), related by a center of symmetry, alternate with the rings in the z direction. These ions are coordinated by O_{I} and O_{IV} of one ring and O_{II} , O'_{IV} , and O_{VI} of a second ring. See Figs. 3 and 4(e) and (f). A water molecule $(\text{H}_2\text{O})_{\text{II}}$ completes the irregular six-fold coordination. The two adjacent polyhedra share an edge across the center.

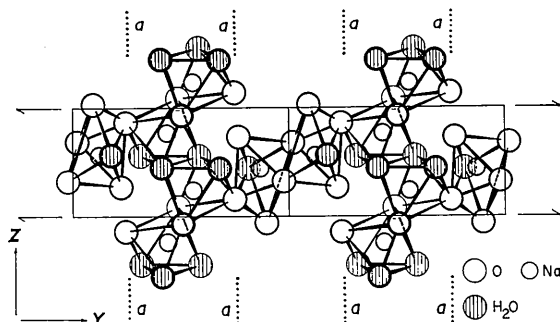


Fig. 5. Coordination polyhedra of the sodium ions showing the chains formed along z by the Na_{II} octahedra, and also how these chains are linked into the network parallel to x and y . Two unit cells are outlined.

The second type of sodium ion (Na_{II}) cross-links the rings in a network parallel to (001) . Three oxygens of the Na_{II} coordination polyhedra, O_{II} , O_{V} , and O'_{V} are contributed by three different anion rings. Water molecules $(\text{H}_2\text{O})_{\text{I}}$, $(\text{H}_2\text{O})'_{\text{I}}$, and $(\text{H}_2\text{O})_{\text{II}}$ complete the coordination as shown in Figs. 2 and 4(c) and (d). These $\text{Na}-\text{O}$ octahedra share edges $(\text{H}_2\text{O})_{\text{I}}-(\text{H}_2\text{O})'_{\text{I}}$ and $\text{O}_{\text{V}}-\text{O}'_{\text{V}}$ to form chains along $[001]$. See Fig. 5. The Na_{I} and Na_{II} polyhedra are linked by the corner O_{II} and by the corner $(\text{H}_2\text{O})_{\text{II}}$ to form a network of polyhedra alternately sharing edges and corners in the ab plane. See Fig. 6. The linkage of the polyhedra in three directions would account for the lack of cleavage.

The distances in the sodium polyhedra are given in

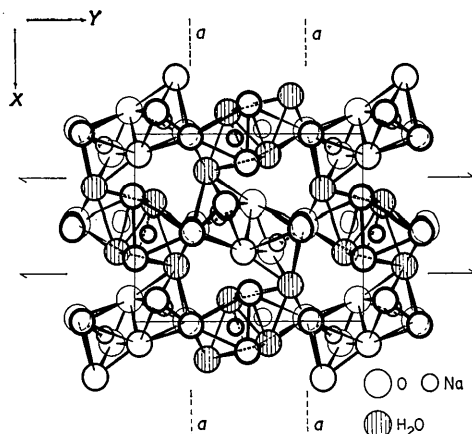


Fig. 6. Coordination polyhedra of the sodium ions showing the network formed in the x, y plane by the alternate sharing of edges and corners. The unit cell is outlined.

Table 4. The Na to non-ring oxygen distances vary from 2.258 to 2.446 Å. However, the distance $\text{Na}_{\text{I}}-\text{O}_{\text{VI}}$ (a ring oxygen) is much larger (2.648 Å) as is also the distance $\text{Na}_{\text{II}}-(\text{H}_2\text{O})_{\text{II}}$ (2.626 Å). The oxygen, O_{VI} , while contributing to the coordination of Na_{I} , does not serve to link adjacent Na polyhedra. This is not unexpected, since, from the point of view of Pauling's rules and the resonance forms, there are unsatisfied negative charges only on the non-ring oxygens.

Table 4. Interatomic distances in the sodium-oxygen coordination polyhedra

$\text{Na}_{\text{I}}-\text{O}_{\text{I}}$	2.297 Å	$\text{Na}_{\text{II}}-\text{O}_{\text{II}}$	2.446 Å
$\text{Na}_{\text{I}}-\text{O}_{\text{II}}$	2.430	$\text{Na}_{\text{II}}-\text{O}_{\text{V}}$	2.361
$\text{Na}_{\text{I}}-\text{O}'_{\text{IV}}$	2.427	$\text{Na}_{\text{II}}-\text{O}'_{\text{V}}$	2.258
$\text{Na}_{\text{I}}-\text{O}'_{\text{IV}}$	2.377	$\text{Na}_{\text{II}}-(\text{H}_2\text{O})_{\text{I}}$	2.429
$\text{Na}_{\text{I}}-\text{O}_{\text{VI}}$	2.648	$\text{Na}_{\text{II}}-(\text{H}_2\text{O})'_{\text{I}}$	2.397
$\text{Na}_{\text{I}}-(\text{H}_2\text{O})_{\text{II}}$	2.308	$\text{Na}_{\text{II}}-(\text{H}_2\text{O})_{\text{II}}$	2.626

$$\sigma(\text{Na}-\text{O}) = \pm 0.018 \text{ \AA}$$

$$\sigma(\text{Na}-\text{H}_2\text{O}) = \pm 0.021$$

$\text{O}_{\text{I}}-\text{O}_{\text{II}}$	3.607 Å	$\text{O}_{\text{II}}-\text{O}_{\text{V}}$	3.596 Å
$\text{O}_{\text{I}}-\text{O}'_{\text{IV}}$	3.275	$\text{O}_{\text{II}}-\text{O}'_{\text{V}}$	3.706
$\text{O}_{\text{I}}-\text{O}'_{\text{IV}}$	3.792	$\text{O}_{\text{II}}-(\text{H}_2\text{O})'_{\text{I}}$	3.488
$\text{O}_{\text{I}}-(\text{H}_2\text{O})_{\text{II}}$	3.480	$\text{O}_{\text{II}}-(\text{H}_2\text{O})_{\text{II}}$	2.725
$\text{O}_{\text{II}}-\text{O}'_{\text{IV}}$	3.123	$\text{O}_{\text{V}}-\text{O}'_{\text{V}}$	3.185
$\text{O}_{\text{II}}-\text{O}_{\text{VI}}$	2.383	$\text{O}_{\text{V}}-(\text{H}_2\text{O})_{\text{I}}$	3.413
$\text{O}_{\text{II}}-(\text{H}_2\text{O})_{\text{II}}$	3.600	$\text{O}_{\text{V}}-(\text{H}_2\text{O})_{\text{II}}$	3.899
$\text{O}_{\text{IV}}-\text{O}'_{\text{IV}}$	3.227	$\text{O}'_{\text{V}}-(\text{H}_2\text{O})_{\text{I}}$	3.750
$\text{O}_{\text{IV}}-\text{O}_{\text{VI}}$	4.345	$\text{O}'_{\text{V}}-(\text{H}_2\text{O})'_{\text{I}}$	3.209
$\text{O}_{\text{IV}}-(\text{H}_2\text{O})_{\text{II}}$	3.433	$(\text{H}_2\text{O})_{\text{I}}-(\text{H}_2\text{O})'_{\text{I}}$	3.205
$\text{O}'_{\text{IV}}-\text{O}_{\text{VI}}$	3.090	$(\text{H}_2\text{O})_{\text{I}}-(\text{H}_2\text{O})_{\text{II}}$	3.398
$\text{O}'_{\text{IV}}-(\text{H}_2\text{O})_{\text{II}}$	3.264	$(\text{H}_2\text{O})'_{\text{I}}-(\text{H}_2\text{O})_{\text{II}}$	3.379

$$\sigma = \pm 0.025 \text{ \AA}$$

The shortest polyhedral edge around Na_{I} is that edge shared with the P_{II} tetrahedron, a sharing found also in sodium triphosphate II (Davies & Corbridge, 1958). The shortest edge about Na_{II} is most likely due to hydrogen bonding between $(\text{H}_2\text{O})_{\text{II}}$ and O_{II} (2.725 Å). Other short distances between H_2O and O possibly attributable to hydrogen bonds which would link polyhedra are $(\text{H}_2\text{O})_{\text{II}}-\text{O}_{\text{I}}$ (2.970), $(\text{H}_2\text{O})_{\text{I}}-\text{O}_{\text{I}}$ (2.845), and $(\text{H}_2\text{O})_{\text{I}}-\text{O}_{\text{IV}}$ (3.073). The oxygen, O_{I} , which does not link the Na polyhedra, is the only oxygen acting as acceptor to two hydrogen bonds, with $(\text{H}_2\text{O})_{\text{I}}$ and $(\text{H}_2\text{O})_{\text{II}}$. The difference synthesis shows positive areas consistent with the short $\text{H}_2\text{O}-\text{O}$ distances although accurate hydrogen positions could not be determined because of the high background of that map.

Tetrahedral coordination of water and oxygen in inorganic structures has been discussed by Bernal & Fowler (1933) and Bernal & Megaw (1935) and more recently by Gillespie & Nyholm (1957). In this salt approximately tetrahedral figures are formed about the two waters and three of the terminal oxygens. $(\text{H}_2\text{O})_{\text{I}}$ is coordinated to two Na_{II} ions, O_{I} and O_{IV} ;

(H₂O)_{II} to Na_I, Na_{II}, O_I, and O_{II} forming very skewed tetrahedral figures. The three tetrahedral oxygens are: O_I surrounded by P_{II}, Na_I, (H₂O)_I and (H₂O)_{II}; O_{II} by P_{II}, Na_I, Na_{II}, and (H₂O)_{II}; and O_{IV} by two Na_I ions, P_I and (H₂O)_I. In all these cases, the oxygens act as acceptors in hydrogen bonding. The tetrahedra about the oxygens are reasonably undistorted considering the presence of the P–O bonds, which are, of course, much shorter than the Na–O or O–H–O distances.

Examination of the P peaks in the difference synthesis indicates that the P–O bonds are predominantly covalent, as in the ammonium salt. The P positions of the least-squares refinement are in positive areas of the difference synthesis indicating that the f_p was a good choice. The water positions are in positive areas indicating that, as could be expected, f_{O^-} is a better choice than the f_p actually used.

There is still no crystallographic evidence for the existence of stereoisomers of the tetrametaphosphate ring. The distortion of the anion from the $2/m$ symmetry in the ammonium salt to the $\bar{1}$ symmetry in this salt is small. In solution, there should be no distinction between the two. In order to determine whether the polymorphism of the sodium compound is due to stereoisomerism of the ring or merely to differences in packing, work has been begun on the triclinic sodium salt.

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