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The Crystal Structure of Sodium Pyrophosphate Decahydrate, $Na_4P_2O_7 . 10\,H_2O$

By D. M. MacArthur and C. A. Beevers

Chemistry Department, University of Edinburgh, Scotland

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A complete structure determination has been made of sodium pyrophosphate decahydrate, which is monoclinic, with space group $I2/c$ and cell dimensions $a = 17{\cdot}93$, $b = 6{\cdot}96$, $c = 14{\cdot}85$ Å, $\beta = 118° \,31'$.

The atomic parameters were found by the analysis of the three-dimensional Patterson function, using the short P–O vectors as the starting point. It was refined by difference maps of electron density, to a residual error factor of 0·20–0·23. The P_2O_7 ion consists of two PO_4 groups sharing an oxygen, with a P–O–P angle at the central oxygen of 134°. The sodium ions have octahedral groups of water molecules together with some of the oxygens atoms from the P_2O_7 groups, and the structure is described in terms of the sharing of oxygens and waters by these groups.

Introduction

Previous investigations of compounds containing a pyro-ion, X_2O_7, have confirmed that, except in the case of the pyro-antimonates, the ion exists as a discrete unit consisting of two XO_4 tetrahedra sharing a common oxygen. On the contrary, however, evidence regarding the X–O–X angle at the common oxygen is conflicting, with values ranging from 128° in Cl_2O_7 (Fonteyne, 1938), to 180° in ZrP_2O_7 (Levi & Peyronel, 1935) and in $Sc_2Si_2O_7$ (Zachariasen, 1930). This structure determination was undertaken, therefore, primarily to ascertain the configuration of the P_2O_7 group. As yet, the only work reported on the structure analysis of pyrophosphates has been by Levi & Peyronel, who investigated by the powder method the structure of cubic zirconium pyrophosphate, ZrP_2O_7, and its isomorphs. At the outset they based their selection of the space group on the assumption that the oxygen atom of the P–O–P must lie on a centre of symmetry, while they gave no evidence to support this except the final agreement of observed and calculated intensities. In our investigation the possibility of this atom being either on a centre of symmetry or a twofold axis was borne in mind, so that while the sequence P–O–P must be linear if on a centre of symmetry, it is not necessarily so if on a twofold axis. More recently Barclay, Cox & Lynton (1956), who have carried out a structure analysis of potassium pyrosulphate which has a non-linear S–O–S at 123°, have suggested that present evidence favours non-linear X–O–X bonds in all pyro-compounds with the possible exception of the pyrophosphates.

Experimental

According to Groth (1906–19), sodium pyrophosphate decahydrate crystallizes in the monoclinic holohedral class. The crystals obtained from saturated aqueous solution grow along the b axis with $(\bar{1}01)$, (101) and (001) as prominent faces. Oscillation and Weissenberg photographs about the principal axes were obtained, using filtered Cu $K\alpha$ radiation and a 5 cm.-radius normal-beam Weissenberg camera. The unit-cell dimensions were obtained from high-order $h0l$, $hk0$ and $0kl$ reflexions. In this investigation the a axis and the shorter diagonal of Groth's a–c face were taken as the a and c axes respectively. The results were:

$$a = 17{\cdot}93\pm0{\cdot}03,\quad b = 6{\cdot}96\pm0{\cdot}01,\quad c = 14{\cdot}85\pm0{\cdot}03 \text{ Å},$$
$$\beta = 118°\,31'\pm3'.$$

The absent spectra found were: $h0l$ when h and l are both odd; $0k0$ when k is odd; hkl when $h+k+l$ is odd; so that the space group is $I2/c$. The other possibility, Ic, was discarded because the crystal class is regarded as $2/m$ (Groth).

The unit-cell dimensions are in close agreement with the values published by Rao & Nampoothiri (1955), but we fail to agree with their conclusion as to the space group, which they give as $C2/c$. For the cell to be C face-centred Groth's axes would have to be chosen. Our cell, given above, contains four molecules of $Na_4P_2O_7 . 10\,H_2O$, giving a calculated specific gravity of 1·820 compared with the observed value of 1·817.

The reflexion intensities were estimated by visual comparison, using multiple exposures, and were corrected for Lorentz and polarization factors.

Structure determination

Since the general positions are eightfold and the special positions fourfold in the space group $I2/c$, at least one oxygen must lie on a special position; in order to maintain our conception of the pyrophosphate ion, this special oxygen must be that of the P–O–P linkage.

An attempt was first made to solve the structure using only two-dimensional data and calculating the Patterson projections down the three principal axes. However, this attempt proved unsuccessful owing to poor resolution and to the fact that the P–P vectors are not outstanding. It must be remembered that in a structure with one heavy atom H and one light atom L the Patterson peaks are $(H+L)^2 = H^2+2HL+L^2$, i.e. the HL peaks are all doubled in weight whereas the H^2 peak is single. Thus for the 'heavy atom' peak to be outstanding it must be much more than twice the atomic number of the light atom, and this of course does not obtain in the case of phosphorus and oxygen. Thus the identification of the P × P vector is not as easy as might appear at first sight.

The Patterson function in three dimensions was then calculated, using an electrical analogue computer of the Hägg–Laurent type, built by Dr F. Stern. The intervals used were $a/60$, $c/60$ and $b/30$. The first step taken in its interpretation was the determination of the orientation of the unique PO_4 group. A value of 1·5 Å was assumed for the P–O distance and a sphere of this radius was constructed around the origin. Any peaks on this sphere must be those due to P–O vectors, since all others are too long. In this way it was possible to identify the P–O vectors with some certainty, and it was only necessary to identify the P–P vector in order to deduce the complete orientation of the P_2O_7 groups. In this space group the two PO_4 groups forming the pyro ion can be related to each other by a centre of symmetry or by a twofold axis. If they are related by a centre the P–P vector will be twice that of one of the known P–O vectors. There were two possible peaks for this vector, giving two possible orientations of the P_2O_7 group. In each case the probable absolute coordinates of all the atoms of the P_2O_7 group were found from considerations of the Harker peaks, and all the vectors for the P_2O_7 groups were calculated. The agreement of the vectors with the Patterson map was invariably poor, however, and consideration was then given to the grouping of the two PO_4's around a twofold axis. In this case, if the coordinates of a known P–O peak are (x, y, z) then the P–P vector must be at $(2x, 0, 2z)$. One such vector existed, thus giving the orientation of the P_2O_7 group. From considerations of the centres of symmetry at $y = \frac{1}{2}$ and $y = \frac{1}{4}$ the absolute values of the coordinates of the phosphorus atoms were found. The vectors for the P_2O_7 groups now gave excellent agreement. For the further completion of the analysis of the structure the superposition method (Beevers & Robertson, 1950) was carried through for each contour level. This is equivalent to the minimum function method (Buerger, 1951) and the heavy atoms were used as searchers for the positions of the other atoms in the cell. The coincidence of vectors at once revealed again the oxygens of the pyro ion, thus giving an immediate indication of the peak heights to be expected for the remaining atoms. On inspection of the superposition map the Na atoms were unambiguously recognized, leaving only the five oxygen atoms of the water molecules. There were nine possible peaks for these but by means of packing considerations four were ruled out, leaving the correct number of positions. All the vectors between the sodium and oxygen atoms were then calculated and compared with the original Patterson function, to ensure that not only all the peaks were present but that no significant peaks remained unaccounted for. This was confirmed, and small alterations were applied to the atomic positions to obtain the best overall fit.

Refinement of the structure

The atomic positions obtained were used to calculate structure factors for the $(h0l)$ zone. This gave encouraging agreement, the factor $R = \Sigma||F_o|-|F_c|| \div |F_o|$ being 0·42, and this value was further reduced to 0·25 by the use of (F_o-F_c) syntheses. At this stage the (F_o-F_c) map indicated that a suitable temperature factor should be applied to the sodium and oxygen atoms, and when this procedure was adopted R was 0·20 (the differences from the reflexions 600 and $60\bar{4}$ were omitted as they were considered to be mainly due to extinction). Using the refined x and z parameters along with the y parameters from the Patterson superposition, the a- and c-axis projections were refined. Because of poor resolution these projections are not as accurate as the b-axis projection, the reliability factor R being 0·22 and 0·23 for the $(0kl)$ and $(hk0)$ zones respectively. All these values of R include contributions from unobserved reflexions, and no correction has been applied for extinction. Table 1 shows the agreement between observed and calculated values of F.

The final atomic coordinates are listed in Table 2. The scattering curves used for sodium (James & Brindley, 1931) and oxygen (Hoerni & Ibers, 1954) were modified by a temperature factor of $\exp(-B\sin^2\theta/\lambda^2)$, the value of B being 2·07 Å² in each case. A two-dimensional Fourier synthesis for the final structure, projected down the b axis, is shown in Fig. 1.

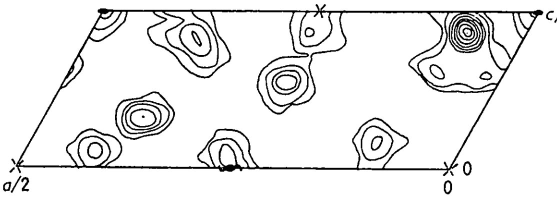


Fig. 1. Fourier synthesis of electron density projected down the b axis. Contours at 4, 8, 12, ..., 32 e.Å^{-2}.

Estimation of accuracy

The standard deviations of the electron density and the atomic coordinates were estimated by the method of Cruickshank (1949). The values obtained were:

Table 1. *Observed and calculated structure factors for the* $(h0l)$, $(hk0)$ *and* $(0kl)$ *planes of* $Na_4P_2O_7 . 10\,H_2O$

h	l	Fo	Fc	h	l	Fo	Fc	h	l	Fo	Fc	h	l	Fo	Fo	h	l	Fo	Fc	h	l	Fo	Fc
0	0	-	840	4	$\bar{2}$	51	54	6	2	139	$\overline{136}$	10	$\bar{8}$	75	86	14	$\bar{2}$	0	9	18	$\bar{4}$	41	$\overline{54}$
0	2	118	$\overline{143}$	4	$\bar{4}$	112	$\overline{137}$	6	4	49	38	10	$\overline{10}$	33	$\overline{26}$	14	$\bar{4}$	69	44	18	$\bar{6}$	59	$\overline{38}$
0	4	105	88	4	$\bar{6}$	118	141	6	6	12	$\overline{26}$	10	$\overline{12}$	67	59	14	$\bar{6}$	26	$\overline{16}$	18	$\bar{8}$	58	$\overline{51}$
0	6	27	22	4	$\bar{8}$	126	119	6	8	55	53	10	$\overline{14}$	77	$\overline{67}$	14	$\bar{8}$	0	$\overline{21}$	18	$\overline{10}$	83	$\overline{77}$
0	8	0	$\overline{13}$	4	$\overline{10}$	36	$\overline{44}$	6	10	7	$\overline{12}$	10	$\overline{16}$	8	12	14	$\overline{10}$	25	$\overline{13}$	18	$\overline{12}$	55	$\overline{56}$
0	10	18	$\overline{17}$	4	$\overline{12}$	74	$\overline{70}$	6	12	81	82	10	$\overline{18}$	0	$\bar{2}$	14	$\overline{12}$	55	$\overline{62}$	18	$\overline{14}$	32	28
0	12	34	$\overline{39}$	4	$\overline{14}$	38	22	8	0	120	109	10	2	87	90	14	$\overline{14}$	11	$\bar{2}$	18	$\overline{16}$	0	1
0	14	54	65	4	$\overline{16}$	0	$\bar{2}$	8	$\bar{2}$	8	1	10	4	8	6	14	$\overline{16}$	16	$\overline{28}$	18	2	27	$\overline{35}$
0	16	66	$\overline{70}$	4	$\overline{18}$	40	$\overline{40}$	8	$\bar{4}$	0	$\bar{2}$	10	6	22	19	14	$\overline{18}$	18	28	20	0	14	$\overline{23}$
2	0	47	46	4	2	133	$\overline{136}$	8	$\bar{6}$	46	$\overline{38}$	10	8	70	$\overline{61}$	14	2	85	$\overline{84}$	20	$\bar{2}$	14	13
2	$\bar{2}$	77	$\overline{92}$	4	4	67	74	8	$\bar{8}$	23	41	10	10	10	$\bar{1}$	14	4	36	38	20	$\bar{4}$	21	$\overline{33}$
2	$\bar{4}$	38	$\overline{19}$	4	6	0	6	8	$\overline{10}$	0	$\overline{17}$	12	0	82	67	14	6	60	40	20	$\bar{6}$	40	45
2	$\bar{6}$	58	$\overline{32}$	4	8	88	87	8	$\overline{12}$	71	76	12	$\bar{2}$	81	$\overline{56}$	16	0	49	57	20	$\bar{8}$	4	0
2	$\bar{8}$	0	0	4	10	55	$\overline{52}$	8	$\overline{14}$	34	25	12	$\bar{4}$	82	103	16	$\bar{2}$	55	$\overline{47}$	20	$\overline{10}$	24	14
2	$\overline{10}$	25	29	4	12	17	17	8	$\overline{16}$	74	59	12	$\bar{6}$	24	29	16	$\bar{4}$	21	6	20	$\overline{12}$	4	13
2	$\overline{12}$	40	$\overline{40}$	4	14	0	$\bar{3}$	8	$\overline{18}$	51	$\overline{44}$	12	$\bar{8}$	163	193	16	$\bar{6}$	52	$\overline{46}$	20	$\overline{14}$	22	$\overline{20}$
2	$\overline{14}$	10	$\overline{11}$	6	0	211	$\overline{269}$	8	2	45	42	12	$\overline{10}$	120	$\overline{117}$	16	$\bar{8}$	10	18	20	$\overline{16}$	41	40
2	$\overline{16}$	72	$\overline{42}$	6	$\bar{2}$	129	149	8	4	85	$\overline{75}$	12	$\overline{12}$	27	34	16	$\overline{10}$	14	29	22	$\bar{4}$	14	$\bar{7}$
2	2	53	$\overline{67}$	6	$\bar{4}$	141	$\overline{223}$	8	6	18	$\overline{10}$	12	$\overline{14}$	27	$\overline{14}$	16	$\overline{12}$	54	$\overline{46}$	22	$\bar{6}$	42	27
2	4	102	90	6	$\bar{6}$	30	28	8	8	7	$\bar{3}$	12	$\overline{16}$	39	$\overline{52}$	16	$\overline{14}$	124	113	22	$\bar{8}$	12	$\bar{6}$
2	6	19	$\overline{25}$	6	$\bar{8}$	127	$\overline{135}$	8	10	23	$\overline{25}$	12	$\overline{18}$	20	33	16	$\overline{16}$	11	$\overline{32}$	22	$\overline{10}$	27	2
2	8	56	$\overline{49}$	6	$\overline{10}$	0	$\bar{3}$	8	12	18	20	12	2	0	12	16	$\overline{18}$	10	0	22	$\overline{12}$	0	8
2	10	62	$\overline{47}$	6	$\overline{12}$	39	44	10	0	26	$\overline{29}$	12	4	22	$\overline{28}$	16	2	64	$\overline{62}$				
2	12	73	64	6	$\overline{14}$	32	$\overline{32}$	10	$\bar{2}$	59	15	12	6	42	50	16	4	18	25				
2	14	29	29	6	$\overline{16}$	87	89	10	$\bar{4}$	55	49	12	8	70	$\overline{58}$	18	0	5	4				
4	0	29	$\overline{26}$	6	$\overline{18}$	28	$\overline{39}$	10	$\bar{6}$	148	$\overline{155}$	14	0	0	18	18	$\bar{2}$	38	22				

k	l	Fo	Fc	k	l	Fo	Fo	k	l	Fo	Fo	k	l	Fo	Fo	k	l	Fo	Fc	k	l	Fo	Fc
1	1	66	$\overline{88}$	2	4	40	$\overline{37}$	3	5	150	124	4	8	12	6	5	11	24	$\overline{36}$	7	3	21	$\overline{23}$
1	3	136	154	2	6	21	21	3	7	25	$\overline{11}$	4	10	33	36	5	13	29	32	7	5	16	$\overline{19}$
1	5	29	14	2	8	37	$\overline{31}$	3	9	81	$\overline{78}$	4	12	54	$\overline{55}$	6	2	14	$\bar{6}$	7	7	16	$\bar{5}$
1	7	40	$\overline{48}$	2	10	21	$\overline{28}$	3	11	30	36	4	14	52	54	6	4	28	$\overline{34}$	7	9	4	1
1	9	41	40	2	12	66	53	3	13	25	$\overline{31}$	5	1	13	$\overline{47}$	6	6	27	18	8	2	16	$\overline{24}$
1	11	9	$\overline{16}$	2	14	48	$\overline{44}$	3	15	24	29	5	3	10	25	6	8	14	20	8	4	41	44
1	13	6	9	2	16	10	23	4	2	180	$\overline{158}$	5	5	0	7	6	10	17	$\overline{11}$	8	6	10	$\overline{14}$
1	15	27	$\overline{32}$	3	1	19	20	4	4	48	51	5	7	20	$\bar{9}$	6	12	13	14				
2	2	161	166	3	3	13	14	4	6	42	$\overline{37}$	5	9	28	$\bar{3}$	7	1	12	18				

h	k	Fo	Fo	h	k	Fo	Fo	h	k	Fo	Fo	h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc
1	1	59	$\overline{63}$	4	2	59	54	9	3	7	5	12	4	0	2	17	5	0	$\bar{3}$	7	7	26	$\overline{30}$
3	1	0	22	6	2	40	44	11	3	66	$\overline{58}$	14	4	8	25	0	6	75	$\overline{89}$	9	7	11	$\overline{15}$
5	1	52	48	8	2	50	52	13	3	23	25	16	4	36	34	2	6	68	$\overline{62}$	11	7	5	$\bar{6}$
7	1	116	$\overline{106}$	10	2	35	46	15	3	0	1	18	4	12	16	4	6	69	58	0	8	0	19
9	1	16	$\overline{20}$	12	2	22	$\overline{17}$	17	3	15	23	1	5	19	$\overline{25}$	6	6	73	60	2	8	22	29
11	1	4	2	14	2	42	$\overline{52}$	19	3	8	8	3	5	7	12	8	6	26	40	4	8	21	$\overline{18}$
13	1	72	70	16	2	44	$\overline{58}$	0	4	3	2	5	5	4	11	10	6	22	$\overline{13}$	6	8	36	$\overline{37}$
15	1	0	2	18	2	13	$\overline{10}$	2	4	6	3	7	5	73	66	12	6	13	3	8	8	48	$\overline{46}$
17	1	0	4	1	3	14	$\overline{19}$	4	4	53	38	9	5	72	59	14	6	0	$\overline{14}$				
19	1	12	$\overline{14}$	3	3	74	$\overline{70}$	6	4	0	5	11	5	22	19	1	7	72	57				
0	2	52	$\overline{61}$	5	3	4	5	8	4	23	41	13	5	77	$\overline{67}$	3	7	7	6				
2	2	48	$\overline{49}$	7	3	16	$\overline{14}$	10	4	68	44	15	5	22	$\overline{32}$	5	7	14	$\overline{20}$				

$$\sigma(\varrho) = 0{\cdot}87\ \text{e.Å}^{-2} \text{ for the (010) projection,}$$
$$\sigma(\varrho) = 1{\cdot}38\ \text{e.Å}^{-2} \text{ for the (001) projection,}$$
$$\sigma(\varrho) = 1{\cdot}85\ \text{e.Å}^{-2} \text{ for the (100) projection;}$$

$$\sigma(x) = \sigma(z) = 0{\cdot}011\ \text{Å},\quad \sigma(y) = 0{\cdot}020\ \text{Å for P},$$
$$\sigma(x) = \sigma(z) = 0{\cdot}020\ \text{Å},\quad \sigma(y) = 0{\cdot}034\ \text{Å for Na},$$
$$\sigma(x) = \sigma(z) = 0{\cdot}029\ \text{Å},\quad \sigma(y) = 0{\cdot}050\ \text{Å for O}.$$

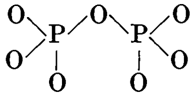
As the atomic parameters are estimated to the nearest 240th of the corresponding cell edges, the actual x, y and z parameters may be in doubt by as much as 0·04, 0·01 and 0·03 Å respectively. Therefore, in this case, the estimation of accuracy by the method of Cruickshank is not very meaningful, but is included to give some objective measure of the accuracy.

Table 2. *Atomic parameters*

	$\frac{240\,x}{a}$	$\frac{240\,y}{b}$	$\frac{240\,z}{c}$		$\frac{240\,x}{a}$	$\frac{240\,y}{b}$	$\frac{240\,z}{c}$
P	16	64	52	W_1	24	140	12
Na_1	58	166	33	W_2	57	4	52
Na_2	92	218	20	W_3	64	98	6
O_1	0	42	60	W_4	94	176	54
O_2	6	106	38	W_5	100	148	6
O_3	18	26	38				
O_4	86	46	44				

Discussion of the structure

The structure of $Na_4P_2O_7.10\,H_2O$ consists of $P_2O_7^{4-}$ ions, Na^+ ions and water molecules, arranged as in Fig. 2. The configuration of the pyrophosphate ion may be represented thus:



The centre P–O bonds lie at an angle of 133° 48′ to one another, each making 66° 54′ to the twofold axis passing through the oxygen atom. The values of the P–O bond lengths are:

$$P\text{–}O_1 = 1{\cdot}63\ \text{Å},\ P\text{–}O_2 = 1{\cdot}48\ \text{Å},\ P\text{–}O_3 = 1{\cdot}45\ \text{Å},\ P\text{–}O_4 = 1{\cdot}48\ \text{Å}.$$

Viewed in a direction down the P–P vector, the two groups of oxygens are staggered with respect to each other. The O–P–O angles for the ion are:

O_1–P–O_2 = 105° O_2–P–O_3 = 116°
O_1–P–O_3 = 99° O_2–P–O_4 = 113°
O_1–P–O_4 = 103° O_3–P–O_4 = 116°

Both of the two types of sodium atoms lie within octahedra made up of water molecules in the one case, and water molecules and oxygen atoms in the other case. All the water molecules take part in the sodium coordination, whereas only two of the three 'free' oxygen atoms are involved. The bond distances within the two types of octahedron are:

Na_1–W_1 = 2·36 Å Na_2–O_2 = 2·47 Å
W_2 = 2·65 O_4 = 2·63
W_2' = 2·40 W_1 = 2·46
W_3 = 2·78 W_3 = 2·41
W_3' = 2·76 W_4 = 2·38
W_4 = 2·38 W_5 = 2·39

The Na_1 octahedra (involving the water molecules 1, 2, 3 and 4) share edges and corners with each other so as to build up sheets of linked octahedra. These sheets lie parallel to the *b–c* plane at $x = \frac{1}{4}$ and $x = \frac{3}{4}$, and they are formed by the continued repetition of one octahedron by the screw axes and by the centres of symmetry of the space group. Any one octahedron shares one edge with an equivalent one related to it by a centre of symmetry (see the octahedra drawn in thin continuous lines in Fig. 3(*a*)), and in addition to this the edge opposite to the shared edge has each of its corners shared with another equivalent octahedron related to the first by a screw axis. In this way a continuous sheet is formed which is shown in a slightly idealized form by the thin continuous lines of Fig. 3(*a*). The accurate structure deviates from Fig. 3 by a slight rotation of the octahedra which causes the equivalent water molecules W_2 to be not exactly over the centres of symmetry in the *b*-axis projection (Fig. 2) and the water molecules W_3 to be not exactly on the screw axes.

Each Na_2 octahedron involves W_1, W_3 and W_4 molecules, which are also in the Na_1 octahedron, i.e. the Na_2 octahedron shares two edges with the Na_1 octahedra. Na_2 also coordinates W_5 and two oxygens O_2 and O_4 of the pyrophosphate group. Thus the Na_2 octahedra are closely linked to the sheets of Na_1 octahedra and the pyrophosphate groups are anchored to the Na_2 octahedra by the sharing of O_2 and O_4. O_3 does not take part in a sodium coordination octahedron. Fig. 3(*a*) shows the Na_2 octahedron in front of the sheets, in thick lines, and the Na_2 octahedron behind the sheets, in broken lines, and illustrates the sharing of edges between the octahedra. Fig. 3(*b*) shows an idealized projection down the *b* axis, and illustrates how the octahedra fit together and how they link up with the pyrophosphate ions. The latter

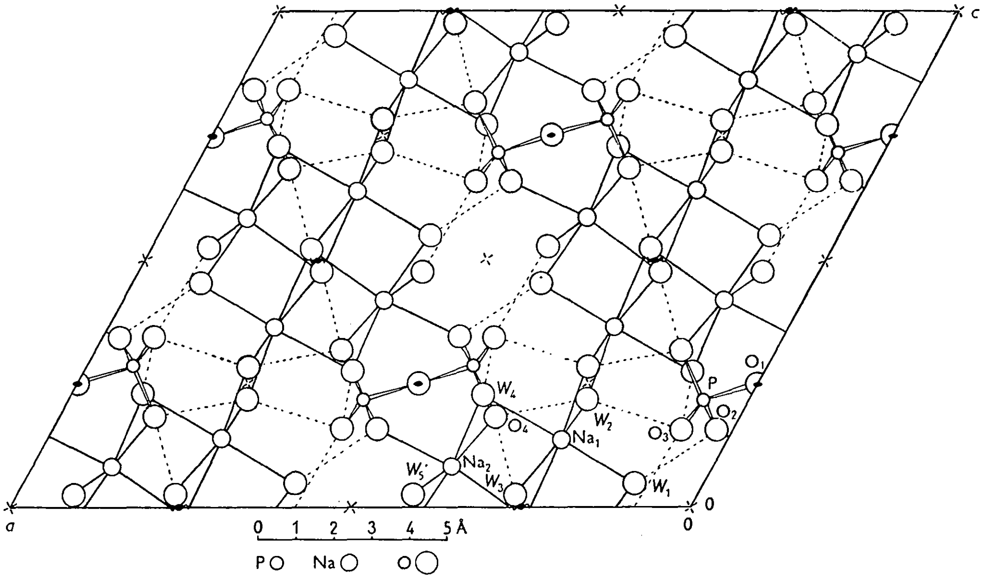


Fig. 2. Drawing of complete unit cell of the structure projected down the *b* axis.

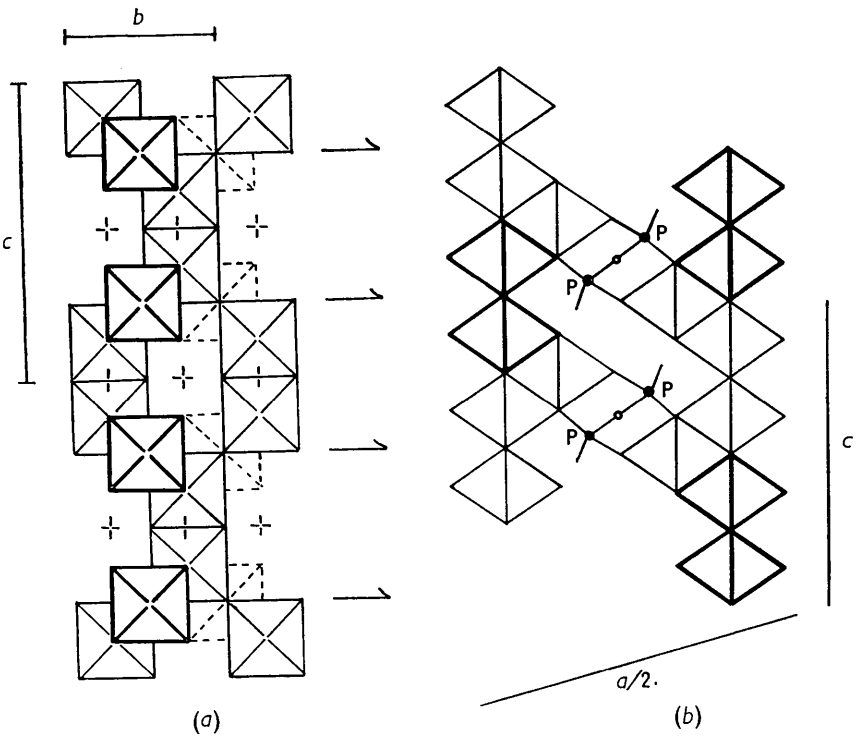


Fig. 3. Diagrams of the octahedra in the idealized structure.

are of course on the twofold axes and thus tie together adjacent sheets of octahedra.

In addition to the bonds from sodium atoms to oxygens and water molecules direct, there are a number of undoubted hydrogen bonds, although of course no attempt has been made in this work to detect the hydrogen atoms directly. Such hydrogen bonds are shown in Fig. 1 by broken lines, and the values for the distances are:

$W_1\text{–}O_2 = 2{\cdot}73$ Å
$W_2\text{–}O_4 = 2{\cdot}74$
$W_2\text{–}O_3 = 2{\cdot}77$
$W_3\text{–}O_4 = 2{\cdot}61$
$W_4\text{–}O_2 = 2{\cdot}81$ Å
$W_4\text{–}O_3 = 2{\cdot}84$
$W_5\text{–}O_3 = 2{\cdot}80$

Thus the W–O distances lie between 2·61 and 2·84 Å, and all the water molecules except W_5 have either three or four bonds. W_5 has only two bonds of this length, but if the bond $W_5\text{–}O_3$ is permitted (it has a length 3·01 Å) then W_5 also can be regarded as having three bonds.

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