Tableau 12. *Liaisons hydrogène*

1 2 3	d_{12}	d_{23}	d_{13}	∠123
O(3)—H(7)····O(1)	1,06 (18) Å	1,67 (18)	2,705 (22)	165 (16)°
O(3)—H(8)····O(9′′′)	1,04 (18)	1,90 (18)	2,853 (24)	151 (15)
O(6)—H(15)···O(4)	0,99 (21)	2,03 (20)	2,781 (22)	131 (14)
O(6)—H(16)···O(12^{v})	0,91 (19)	1,97 (22)	2,847 (22)	161 (16)
O(9)—H(23)···O(7)	1,17 (19)	1,96 (20)	3,092 (27)	163 (15)
O(9)—H(24)···O(6)	1,02 (18)	1,90 (18)	2,879 (22)	160 (14)
O(12)-H(31)···O(10)	0,99 (18)	2,06 (20)	2,904 (26)	143 (15)
O(12)-H(32)···O(3′)	1,13 (17)	1,72 (20)	2,774 (20)	153 (15)

Grenoble à l'aide de programmes précédemment cités (Quagliéri, Loiseleur & Thomas, 1972).

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Refinement of the Structure of Sodium Hexametaphosphate Hexahydrate, $Na_6(P_6O_{18}).6H_2O$

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A full-matrix least-squares refinement using Jost's [*Acta Cryst.* (1965). **19**, 555] data has reduced $R(hkl)$ for 828 observed reflexions to 0·084. The refined bond lengths of the $(P_6O_{18})^{6-}$ ring, P–O (bridge) 1·613 (4) Å and P–O (terminal) 1·471 (4) Å, agree with the dimensions found in the tetrametaphosphate $Na_4P_4O_{12}.4H_2O$.

The crystal structure of sodium hexametaphosphate hexahydrate, $Na_6(P_6O_{18}).6H_2O$, was determined by Jost (1965) and originally refined by means of electron-density difference syntheses to an R value of 0·16 for the 1244 unique reflexions estimated from Weissenberg photographs of the layers *hk*0–7, and 0–7*kl*.

Crystal data

$H_{12}Na_6O_{24}P_6$, F.W. 719·9, orthorhombic, $a=11·58$ (2), $b=18·54$ (4), $c=10·48$ (2) Å, $U=2249$ Å^3, $D_m=2·10$, $Z=4$, $D_c=2·12$. Space group *Ccmb* (No. 64).

In order to determine the structure more accurately, and, if possible, to locate the hydrogen atoms, a full-matrix least-squares refinement was carried out (in Glasgow) on the 828 non-zero reflexions recorded by Jost. Initial coordinates and isotropic temperature factors were taken from the original paper, and the non-standard space group setting used there has been retained. Five cycles of refinement of the positional and isotropic vibrational parameters reduced R to 0·097. A subsequent difference electron-density map did not reveal any unique positions for the hydrogen atoms of the water molecules. Repetition of the calculation using only low-order data was no more successful. Therefore refinement of the non-hydrogen atoms was continued, the vibrational parameters of all atoms

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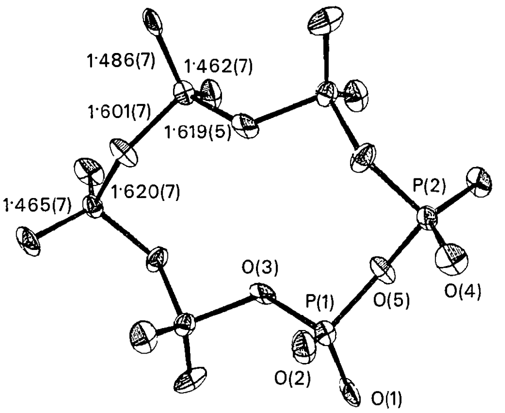


Fig. 1. The hexametaphosphate unit.

being allowed to vary anisotropically. Convergence occurred after 3 cycles of refinement, the final values of $R\,(=\sum|\Delta|/\sum|F_o|)$ and $R'\,(=\sum w\Delta^2/\sum w|F_o|^2)$ being 0·084, and 0·0120 respectively. The weighting scheme used in the final cycles was of the form:

$$\sqrt{\omega}=[\{1-\exp[-15\sin(\theta/\lambda)^2]\}/(1+0{\cdot}15|F_2|)]^{1/2}.$$

The final fractional coordinates and vibrational parameters for all atoms are given in Table 1. In order to comply with the modern practice that all the coordinates listed in Table 1 should refer to the atoms of the crystal-chemical unit (c.c.u.), several changes in coordinates have been made from those quoted by Jost. The equivalent positions referred to in the tables are listed in Table 2. The bond lengths and angles in the $(P_6O_{18})^{6-}$ ring are given in Table 3, and a drawing of the ring is shown in Fig. 1. This shows the numbering of the atoms and a representation of the 50% probability ellipsoids for thermal motion. The ring has symmetry $2/m$. The P–O distances do not differ significantly from those determined previously, but the estimated standard deviations have been reduced considerably. The lengths of the crystallographically distinct P–O (peripheral) and P–O (bridge) bonds are within about 0·01 Å of their respective mean values of 1·471 (4) and 1·613 (4) Å. These are very similar to the values of 1·479 (3) and 1·610 (3) Å found in the polyphosphate chain in Kurrol's salt (McAdam, Jost & Beagley, 1968) and the values of 1·471 (3) and 1·601 (3) Å found in the triclinic form of the tetrametaphosphate, $Na_4P_4O_{12}.4H_2O$ (Ondik, 1964).

Table 2. *Equivalent positions of space group Ccmb referred to in Tables* 1, 3 *and* 4

c.c.u.	x	y	z	v	$\frac{1}{2}-x$	y	$\frac{1}{2}+z$
ii	$-x$	y	$-z$	vi	$-\frac{1}{2}+x$	y	$\frac{1}{2}-z$
iii	$-x$	$-y$	$-z$	vii	$\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$
vi	x	$-y$	z	viii	$-\frac{1}{2}+x$	$-y$	$\frac{1}{2}-z$

Table 3. *Principal interatomic distances and angles in the* $(P_6O_{18})^{6-}$ *ring*

P–O (peripheral)		P–O (bridging)	
P(1)–O(1)	1·486 (7) Å	P(1)–O(3)	1·619 (5) Å
P(1)–O(2)	1·462 (7)	P(1)–O(5)	1·601 (7)
P(2)–O(4)	1·465 (7)	P(2)–O(5)	1·620 (7)
Mean	1·471 (4)	Mean	1·613 (4)
P(1) tetrahedron		**P(2) tetrahedron**	
O(1)–P(1)–O(2)	120·4 (4)°	$O(4)–P(2)–O(4^{ii})$	121·0 (4)°
O(1)–P(1)–O(3)	108·7 (4)	O(4)–P(2)–O(5)	110·8 (4)
O(1)–P(1)–O(5)	106·3 (4)	$O(4)–P(2)–O(5^{ii})$	105·9 (4)
O(2)–P(1)–O(3)	109·6 (4)	$O(5)–P(2)–O(5^{ii})$	100·8 (4)
O(2)–P(1)–O(5)	111·8 (4)		
O(3)–P(1)–O(5)	97·6 (4)		

Bridging oxygen atoms

P(1)–O(5)–P(2)	131·3 (4)°
$P(1)–O(3)–P(1^{iv})$	124·9 (4)

The interatomic distances pertaining to the coordination spheres of the two sodium ions are listed in Table 4.

Examination of the vibrational parameters of Table 1 suggested that there might be some disordering of O(7), the oxygen atom of one of the water molecules,

Table 1. *Fractional atomic coordinates* ($x,y,z\times10^4$) *and vibrational parameters* ($Å^2\times10^4$)

Standard deviations are given in parentheses.

$$f=f_o\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{31}lhc^*a^*+2U_{12}hka^*b^*)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Na(1)	1226 (3)	1720 (2)	3083 (4)	366 (22)	189 (17)	262 (19)	17 (30)	5 (35)	39 (30)
Na(2)	1114 (5)	0	3166 (30)	360 (30)	245 (25)	231 (27)	0	108 (50)	0
P(1)	1883 (2)	774 (1)	213 (2)	214 (11)	171 (10)	173 (10)	11 (17)	−6 (19)	22 (17)
P(2)	0	1827 (2)	0	234 (15)	153 (13)	180 (15)	0	−90 (27)	0
O(1)	3020 (6)	908 (4)	−402 (7)	253 (32)	287 (32)	308 (38)	209 (59)	46 (62)	108 (57)
O(2)	1758 (7)	832 (4)	1597 (7)	402 (40)	212 (30)	256 (34)	44 (54)	−75 (65)	−2 (61)
O(3)	1401 (9)	0	−263 (9)	245 (44)	261 (42)	205 (44)	0	−185 (85)	0
O(4)	423 (7)	2216 (4)	1123 (7)	392 (37)	285 (32)	239 (33)	−109 (58)	−208 (63)	5 (61)
O(5)	968 (6)	1270 (3)	−524 (6)	294 (33)	227 (29)	202 (29)	−30 (51)	−71 (59)	119 (55)
O(6)*	4614 (7)	922 (5)	1669 (9)	341 (41)	423 (42)	456 (48)	−54 (72)	−45 (79)	9 (69)
O(7)*	2922 (12)	2500	2500	439 (73)	550 (74)	870 (104)	626 (75)	0	0
O(7′)*	2918 (14)	2400 (18)	2351 (47)	478 (28)	89 (184)	547 (232)	−126 (202)	146 (208)	49 (136)

* O(6) and O(7) are oxygen atoms of water molecules.

Table 4. *Interatomic distances in the coordination spheres of the sodium ions*

Standard deviations are given in parentheses.

Na(1) polyhedron

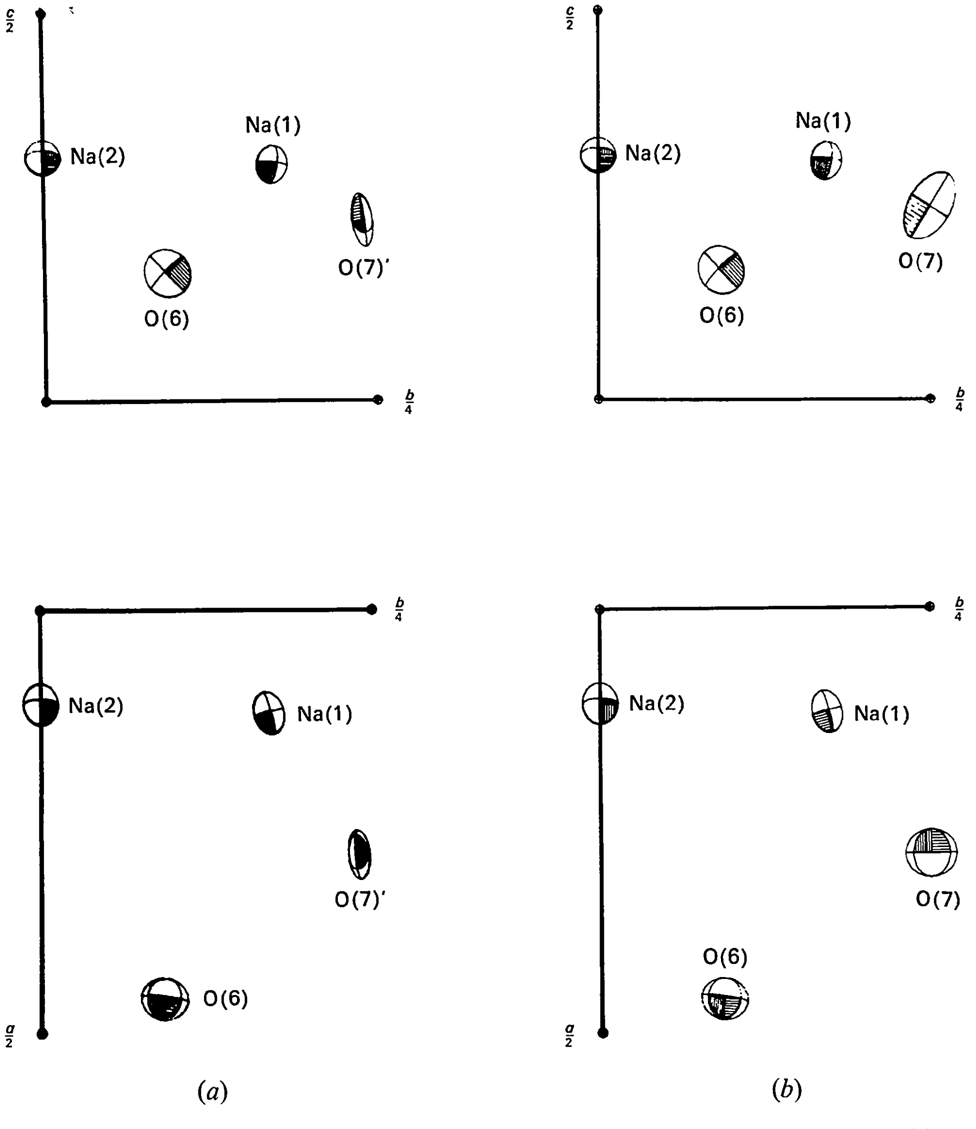
Na(1)···O(4^{ii})	2·334 (8) Å
Na(1)···O(2)	2·349 (8)
Na(1)···O(1^{v})	2·355 (8)
Na(1)···O(6^{vi})	2·396 (8)
Na(1)···O(4)	2·436 (8)
Na(1)···O(7)	2·514 (11)

Na(2) polyhedron

Na(2)···O($2^{\mathrm{i,\,iv}}$)	2·374 (8) Å
Na(2)···O($6^{\mathrm{vi,\,viii}}$)	2·444 (9)
Na(2)···O($1^{\mathrm{v,\,vii}}$)	2·469 (8)

which lies on a twofold axis perpendicular to the (100) plane. Consequently this atom was split into two 'half atoms' O(7)′ and allowed to refine off the twofold axis to which it had previously been constrained. This least-squares refinement of all the parameters converged to R and R' values of 0·082 and 0·0094 respectively. The only parameters which changed significantly were those associated with this atom. These adjusted parameters are also listed in Table 1.

A Hamilton R index Ratio Significance Test (Hamilton, 1964), carried out on the two values obtained for R', suggests that the decrease in R' is significant at the 99·995% level. However the e.s.d.'s obtained for the vibrational parameters of O(7) are so large that this conclusion must be treated with some caution. In



(*a*) (*b*)

Fig. 2. 50% probability vibrational ellipsoids for (*a*) O(7)′ and (*b*) O(7). [For clarity only one of the positions for O(7)′ has been drawn.]

Fig. 2 we plot the 50% probability vibrational ellipsoids for O(6) and O(7) in the two refinements. Inspection of these again suggests the disordered model to be more physically meaningful, but neither model is entirely convincing. The shortest contact between the oxygen atoms of the water molecules and those of the metaphosphate rings, is one of 2·849 (12) Å between O(6) and O(1). No other oxygen atom is within 3·0 Å of either O(6) or O(7). Since no hydrogen atoms were found in the difference syntheses, this lack of interaction rather suggests that the water molecules may be randomly oriented. A list of observed structure amplitudes and calculated structure factors can be obtained from one of us upon request.

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Structure Cristalline et Moléculaire de $Mn_2Cl_4.3C_2H_5OH$

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The solvate $Mn_2Cl_4.3C_2H_5OH$ forms triclinic crystals with lattice constants $a=10·80$, $b=9·57$, $c=7·95$ Å, $\alpha=107·33$, $\beta=81·37$, $\gamma=102·04°$. The space group is $P\bar{1}$. The observed density $d=1·70$ is in good agreement with the calculated density $d=1·698$ for $Z=2$. The peak height data were collected with an automated diffractometer. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations. The final R index based on F for 1334 reflexions above $4\sigma(I)$ was 0·089. The manganese atoms are octahedrally coordinated. The crystal is built up of chains of octahedra linked together parallel to [010]. The existence of hydrogen bonds between the chains gives slabs contained in the (100) planes. The structural cohesion is achieved by van der Waals forces between the slabs. An important deformation of the ethanol molecules has been found in this compound.

Introduction

Les solvates du chlorure de manganèse ont été étudiés presque exclusivement par spectrographie infrarouge ou réflectance diffuse. Tous les auteurs s'accordent pour donner à l'atome de manganèse un environnement octaédrique, sauf dans le cas du complexe, de couleur blanche, formé avec la bis-(2-diméthylaminométhyle)méthylamine où le spectre de réflectance diffuse s'explique par une coordinance 5 de l'atome de manganèse (Ciampolini & Speroni, 1966). Une étude structurale récente du composé $MnBr_2$.tris-(2-diméthylaminoéthyle)amine a permis de mettre à nouveau en évidence ce type d'hybridation (Di Vaira & Orioli, 1968); le manganèse se trouve au centre d'une bipyramide trigonale dont quatre sommets sont occupés par des atomes d'azote, le cinquième par un atome de brome. Outre cette étude, on ne connaît la structure cristalline que d'un nombre restreint de solvates. Zalkin, Forrester & Templeton (1964) et Baur (1968) ont étudié le tétrahydrate $MnCl_2.4H_2O$: celui-ci présente des octaèdres isolés, les atomes de chlore ayant une configuration *cis*. Ces groupes discrets se retrouvent dans le composé $MnCl_2.4$thiourée (Flint & Goodgame,