

On the Crystal Chemistry of Salt Hydrates.
VII. The Crystal Structures of Pseudo Trisodium Orthoarsenate Dodecahydrate
and the Isomorphous Phosphate and Vanadate Salts

BY EKKEHART TILLMANN* AND WERNER H. BAUR

Department of Geological Sciences, University of Illinois at Chicago, Chicago, Illinois, 60680, U.S.A.

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The pseudo-12-hydrate of trisodium orthophosphate $\text{Na}_3\text{PO}_4 \cdot (\text{NaOH})_{0-0.25} \cdot 12\text{H}_2\text{O}$ and the isomorphous vanadate and arsenate salts crystallize in space group $P\bar{3}c1$, $Z=4$ with $a=11.890$ (6), 12.038 (7), 12.017 (5) Å and $c=12.671$ (7), 12.833 (8) and 12.783 (6) Å (the numerical values are given in the sequence P, V, and As compound). The crystal structures were solved and refined using three-dimensional X-ray diffractometer data to $R=0.056, 0.070, 0.046$ for 556, 468, 534 F_{obs} . The crystal structures show that the compounds should be formulated as $[\text{Na}_{12-13}(\text{OH})_{0-1}(\text{OH}_2)_{48}](\text{XO}_4)_4$. The prominent geometrical feature of the structure is a two-dimensionally infinite sheet with composition $\text{Na}(\text{OH}_2)_4$ of Na-coordination octahedra which share edges and corners with each other. The connection between these layers is through hydrogen bonds formed mostly to the tetrahedral groups sandwiched between them. The Na^+ and OH^- ions of the excess NaOH occupy one site (*A*-site). This unusual statistical occupation is made possible by the flexibility of the hydrogen bonding arrangement.

Introduction

A hydrogen bond and its immediate surrounding can be schematically represented as $(\text{M})_n - D - \text{H} \cdots A - (\text{X})_m$, where *D* is an anion donating the bond, *A* an anion accepting the bond, while both *M* and *X* are one or more other cations to which *D* and *A* are bonded as well. It has been shown (Baur, 1961) that in hydrates the length of the hydrogen bond varies inversely with the electrostatic bond strength (Pauling, 1960, p. 547) received by the donor atom *D*, that is the cation(s) *M* influence the lengths of the hydrogen bonds. Furthermore it has been shown (Baur, 1970) that the length of the hydrogen bond also depends on the bond strength received by the acceptor atom of the hydrogen bond. These relationships have been summarized in a rule which states that the length of a hydrogen bond ($D - \text{H} \cdots A$) = $(a + b\Delta p)$ Å, where Δp is the difference between the electrostatic bond strengths received by the donor and acceptor atoms ($\Delta p = p_D - p_A$) and where *a* and *b* are empirically derived constants. For the case of both the donor and the acceptor being an oxygen atom $a=2.85(1)$ and $b=-0.38(2)$ (Baur, 1970). Values of Δp from -0.5 to $+0.8$ have been observed and found to correspond to hydrogen bond lengths of about 3.05 to 2.55 Å.

In the previous paper in this series (Baur & Khan, 1970) the crystal structures of $[\text{Na}_2(\text{OH}_2)_7][\text{PO}_3\text{OH}]$ and the corresponding arsenate salt were investigated in order to study the effect of different atoms *X* on the hydrogen bonds. In this case of isostructural compounds the Δp of course were identical in both salts;

therefore any differences in hydrogen bond lengths could be attributed either to the effect of the different X–O bond lengths (P–O = 1.54, As–O = 1.67 Å), or to the different electronegativities of the X-atoms. The result was negative; no significant differences between the hydrogen bond lengths in $\text{Na}_2 - \text{O}(\text{w})_D - \text{H} \cdots \text{O}_A - \text{X}$ were found for the case of X being P or As. Since the difference in electronegativities between P and As is small (2.1 *vs.* 2.0), it was thought worthwhile to study a series of compounds which included a vanadium salt, since the value of the electronegativity of V (1.6) is clearly different from the values of P or As, while the V–O distance (1.69 Å) is similar to the As–O distance. We chose $\text{Na}_3\text{XO}_4 \cdot 12\text{H}_2\text{O}$, where X can be P, V, Mn or As and investigated the P, V and As salts. From Menzel & von Sahr's (1937) work it is known that these compounds actually are non-stoichiometric because they usually contain excess NaOH. The composition can be expressed as $\text{Na}_3\text{XO}_4(\text{NaOH})_{0-0.25} \cdot 12\text{H}_2\text{O}$ (Tillmanns & Baur, 1970).

Experimental

A crystal of commercial sodium phosphate (tribasic crystal, Baker, 3836) was used for data collection. Crystals of the vanadate and arsenate compounds were grown from aqueous solutions at about 30°C. Crystal data are given in Table 1. They are in good agreement with those reported by Clark & Gross (1937). The densities measured by us do not agree with the values given by Rémy & Guérin (1970); their values are in error. The unit cell constants are based on the refinement of the setting of 20 reflections which had been centered on an automatic 4-circle X-ray diffractometer. Systematic extinctions ($h\bar{k}0l$) present only with

* Present address: Ruhr-Universität Bochum, Institut für Mineralogie, Bochum, Deutschland.

$l=2n$) are consistent with space groups $P\bar{3}c1$ and $P3c1$. The centric space group was confirmed by the successful solution and refinement of the structures. Intensity

data for all three compounds were collected on an automatic four-circle X-ray diffractometer following generally the methods described by Corfield, Doedens &

Table 1. *Crystal data, details of data collection and R values for refinement with anisotropic temperature factor*

Estimated standard deviations here and throughout the paper in parentheses following each value.

	Phosphate	Vanadate	Arsenate
a (Å)	11.890 (6)	12.038 (7)	12.017 (5)
c (Å)	12.671 (7)	12.833 (8)	12.783 (6)
V (Å ³)	1551 (1)	1611 (1)	1599 (1)
Z	4	4	4
D_x (g.cm ⁻³)	1.652	1.673	1.786
D_m (g.cm ⁻³)	1.64	1.66	1.76
F.W.	385.9	405.9	429.9
Space group	$P\bar{3}c1$	$P\bar{3}c1$	$P\bar{3}c1$
μ (Ag K α) (cm ⁻¹)	1.9	4.3	12.7
Diameter of crystal (mm)	0.34 -0.41	0.32 -0.39	0.31 -0.37
Volume of crystal (mm ³)	0.049	0.033	0.036
Mass of crystal (mg)	0.081	0.055	0.064
μR	0.032-0.039	0.07 -0.083	0.20 -0.24
Number of non-unique I_{hkl}	1878	2176	3798
Number of unique I_{hkl}	726	757	749
Number of $I_{hkl}=0$	170	289	215
Number of I_{hkl} used in refinement	556	468	534
$2\theta_{\max}$ (°)	36	36	36
$\sin \theta_{\max}/\lambda$ (Å ⁻¹)	0.55	0.55	0.55
$R_1 = \sum F_o - F_c / \sum F_o $	0.056	0.070	0.046
$R_2 = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$	0.058	0.063	0.050

Table 2. *Positional parameters in fractional coordinates ($\times 10^4$) and thermal parameters ($\times 10$) with their standard deviations*

The definition of the Debye-Waller temperature factor is

$$\exp [-\frac{1}{4}(h^2a^2B_{11} + k^2b^2B_{22} + l^2c^2B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})].$$

(a) [Na₁₂₋₁₃(OH)₀₋₁(OH₂)₄₈] (PO₄)₄

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	$\frac{1}{3}$	$\frac{2}{3}$	7161 (2)	15 (1)	15	12 (1)	8	0	0
Na	3455 (3)	-0199 (3)	0259 (2)	39 (2)	29 (2)	29 (2)	14 (1)	7 (1)	2 (1)
O(1)	$\frac{1}{3}$	$\frac{2}{3}$	5967 (5)	31 (3)	31	18 (2)	15	0	0
O(2)	4612 (4)	6810 (4)	7566 (3)	20 (2)	22 (2)	22 (2)	12 (2)	-2 (2)	-1 (2)
O(w3)	4600 (4)	2145 (4)	0392 (3)	25 (2)	24 (2)	29 (2)	12 (2)	-2 (1)	-3 (1)
O(w4)	-0066 (4)	5251 (4)	3755 (3)	26 (2)	33 (3)	21 (2)	13 (1)	-1 (2)	-2 (2)
O(w5)	1083 (4)	3220 (4)	1869 (3)	29 (3)	30 (3)	32 (3)	13 (2)	6 (2)	0 (2)
O(w6)	0209 (5)	1873 (5)	9033 (4)	44 (3)	59 (4)	81 (4)	21 (2)	-14 (2)	-4 (3)
$A \times 0.67$ (2)	0	0	0	24 (3)	24	46 (6)	12	0	0

(b) [Na₁₂₋₁₃(OH)₀₋₁(OH₂)₄₈] (VO₄)₄

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
V	$\frac{1}{3}$	$\frac{2}{3}$	7146 (2)	16 (1)	16	15 (1)	8	0	0
Na	3470 (4)	-0205 (4)	0285 (3)	46 (2)	37 (3)	32 (3)	18 (2)	10 (1)	2 (2)
O(1)	$\frac{1}{3}$	$\frac{2}{3}$	5839 (8)	47 (5)	47	18 (5)	23	0	0
O(2)	4748 (6)	6860 (6)	7585 (5)	24 (3)	30 (3)	25 (3)	14 (3)	-1 (3)	0 (3)
O(w3)	4554 (6)	2112 (6)	0414 (4)	30 (3)	19 (4)	32 (3)	13 (3)	-6 (3)	-5 (3)
O(w4)	-0070 (6)	5279 (7)	3763 (4)	28 (3)	31 (3)	23 (2)	13 (3)	1 (3)	-5 (3)
O(w5)	1025 (7)	3165 (7)	1831 (5)	33 (4)	34 (4)	28 (3)	16 (3)	2 (3)	-2 (3)
O(w6)	0190 (8)	1844 (9)	9069 (7)	49 (5)	77 (8)	109 (10)	32 (4)	-8 (4)	2 (4)
$A \times 0.62$ (3)	0	0	0	16 (7)	16	37 (7)	8	0	0

(c) [Na₁₂₋₁₃(OH)₀₋₁(OH₂)₄₈] (AsO₄)₄

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As	$\frac{1}{3}$	$\frac{2}{3}$	7126 (1)	17 (1)	17	14 (1)	9	0	0
Na	3473 (4)	-0201 (3)	0275 (3)	44 (2)	33 (2)	29 (1)	16 (1)	8 (1)	0 (1)
O(1)	$\frac{1}{3}$	$\frac{2}{3}$	5820 (6)	33 (3)	33	17 (3)	17	0	0
O(2)	4727 (5)	6861 (5)	7568 (4)	25 (3)	23 (3)	29 (3)	14 (3)	1 (2)	0 (2)
O(w3)	4543 (5)	2107 (6)	0403 (4)	31 (3)	24 (3)	29 (3)	14 (3)	-2 (3)	-2 (3)
O(w4)	-0061 (6)	5278 (6)	3778 (4)	27 (3)	38 (4)	20 (2)	13 (3)	1 (3)	-1 (3)
O(w5)	1041 (6)	3176 (6)	1817 (4)	34 (3)	32 (3)	32 (3)	14 (3)	2 (3)	-1 (3)
O(w6)	0177 (9)	1872 (9)	9140 (7)	68 (6)	84 (6)	125 (6)	38 (5)	-24 (5)	-12 (5)
$A \times 0.52$ (3)	0	0	0	36 (9)	36	73 (14)	18	0	0

Ibers (1967). The details of the data collection are listed in Table 1. Experimental procedures, if not stated and a list of computer programs used in the course of the work are the same as given by Baur & Khan (1970). In addition *ORFFE* II, the version of *ORFFE* (Busing, Martin & Levy, 1964) compatible with an IBM 360 computer, was used to calculate the shape and orientation of the thermal ellipsoids. All three compounds decomposed rapidly when exposed to air. They were mounted inside a Lindemann-glass capillary filled with kerosene. In this way the decomposition rate could be greatly reduced. The decrease in intensity was monitored by repeatedly measuring three standard reflections. The phosphate compound lost about 10% of its scat-

tering power during data collection, the vanadate and arsenate showed a decrease of 11 and 9% respectively. The measured intensities were corrected accordingly. Because of the small μR values of the crystals an absorption correction was not necessary. After correction for Lorentz-polarization effects equivalent reflections were sorted together and the individual values of the squared structure amplitudes and their standard deviations σ were averaged. Any intensity measurement was considered to be zero.

The crystal structure of the arsenate compound was solved by Patterson, Fourier and least-squares methods. The As and O(1) atoms were placed in special position

Table 3. $[\text{Na}_{12-13}(\text{OH})_{0-1}(\text{OH}_2)_4]_n(\text{XO}_4)_m$, observed and calculated structure factors for (a) the P salt, (b) the V salt, and (c) the As salt. Unobserved F are omitted

(a) P salt			(b) V salt			(c) As salt		
h	k	l	h	k	l	h	k	l
0	0	0	0	0	0	0	0	0
0	0	1	0	0	1	0	0	1
0	0	2	0	0	2	0	0	2
0	0	3	0	0	3	0	0	3
0	0	4	0	0	4	0	0	4
0	0	5	0	0	5	0	0	5
0	0	6	0	0	6	0	0	6
0	0	7	0	0	7	0	0	7
0	0	8	0	0	8	0	0	8
0	0	9	0	0	9	0	0	9
0	1	0	0	1	0	0	1	0
0	1	1	0	1	1	0	1	1
0	1	2	0	1	2	0	1	2
0	1	3	0	1	3	0	1	3
0	1	4	0	1	4	0	1	4
0	1	5	0	1	5	0	1	5
0	1	6	0	1	6	0	1	6
0	1	7	0	1	7	0	1	7
0	1	8	0	1	8	0	1	8
0	1	9	0	1	9	0	1	9
0	2	0	0	2	0	0	2	0
0	2	1	0	2	1	0	2	1
0	2	2	0	2	2	0	2	2
0	2	3	0	2	3	0	2	3
0	2	4	0	2	4	0	2	4
0	2	5	0	2	5	0	2	5
0	2	6	0	2	6	0	2	6
0	2	7	0	2	7	0	2	7
0	2	8	0	2	8	0	2	8
0	2	9	0	2	9	0	2	9
0	3	0	0	3	0	0	3	0
0	3	1	0	3	1	0	3	1
0	3	2	0	3	2	0	3	2
0	3	3	0	3	3	0	3	3
0	3	4	0	3	4	0	3	4
0	3	5	0	3	5	0	3	5
0	3	6	0	3	6	0	3	6
0	3	7	0	3	7	0	3	7
0	3	8	0	3	8	0	3	8
0	3	9	0	3	9	0	3	9
0	4	0	0	4	0	0	4	0
0	4	1	0	4	1	0	4	1
0	4	2	0	4	2	0	4	2
0	4	3	0	4	3	0	4	3
0	4	4	0	4	4	0	4	4
0	4	5	0	4	5	0	4	5
0	4	6	0	4	6	0	4	6
0	4	7	0	4	7	0	4	7
0	4	8	0	4	8	0	4	8
0	4	9	0	4	9	0	4	9
0	5	0	0	5	0	0	5	0
0	5	1	0	5	1	0	5	1
0	5	2	0	5	2	0	5	2
0	5	3	0	5	3	0	5	3
0	5	4	0	5	4	0	5	4
0	5	5	0	5	5	0	5	5
0	5	6	0	5	6	0	5	6
0	5	7	0	5	7	0	5	7
0	5	8	0	5	8	0	5	8
0	5	9	0	5	9	0	5	9
0	6	0	0	6	0	0	6	0
0	6	1	0	6	1	0	6	1
0	6	2	0	6	2	0	6	2
0	6	3	0	6	3	0	6	3
0	6	4	0	6	4	0	6	4
0	6	5	0	6	5	0	6	5
0	6	6	0	6	6	0	6	6
0	6	7	0	6	7	0	6	7
0	6	8	0	6	8	0	6	8
0	6	9	0	6	9	0	6	9
0	7	0	0	7	0	0	7	0
0	7	1	0	7	1	0	7	1
0	7	2	0	7	2	0	7	2
0	7	3	0	7	3	0	7	3
0	7	4	0	7	4	0	7	4
0	7	5	0	7	5	0	7	5
0	7	6	0	7	6	0	7	6
0	7	7	0	7	7	0	7	7
0	7	8	0	7	8	0	7	8
0	7	9	0	7	9	0	7	9
0	8	0	0	8	0	0	8	0
0	8	1	0	8	1	0	8	1
0	8	2	0	8	2	0	8	2
0	8	3	0	8	3	0	8	3
0	8	4	0	8	4	0	8	4
0	8	5	0	8	5	0	8	5
0	8	6	0	8	6	0	8	6
0	8	7	0	8	7	0	8	7
0	8	8	0	8	8	0	8	8
0	8	9	0	8	9	0	8	9
0	9	0	0	9	0	0	9	0
0	9	1	0	9	1	0	9	1
0	9	2	0	9	2	0	9	2
0	9	3	0	9	3	0	9	3
0	9	4	0	9	4	0	9	4
0	9	5	0	9	5	0	9	5
0	9	6	0	9	6	0	9	6
0	9	7	0	9	7	0	9	7
0	9	8	0	9	8	0	9	8
0	9	9	0	9	9	0	9	9

coordination octahedra of water molecules around the Na^+ ions in the general equivalent position (Fig. 1). These layers are parallel (0001) at height $z=0$ and $z=0.5$. Six octahedra joined by O(w3) serving as a common corner are arranged in a circlet around the A site. The circlets are connected by common edges [formed by two O(w4) atoms] to neighboring circlets. An additional octahedron is formed within the circlet by the six O(w6) atoms surrounding the A site. Only one hydrogen bond is formed directly between two neighboring layers [O(w5)–O(w5)]. Apart from that the only cohesion between the layers is provided by hydrogen bonds which are formed by the water molecules to the oxygen atoms of the tetrahedral groups sandwiched between the layers (Fig. 2). A schematic representation of this arrangement is given in Fig. 3.

The statistical occupation of the A site by a cation (Na^+) and an anion (OH^-) seems unusual but nevertheless it appears to be the only rational explanation of all the pertinent observations. It seems to be made possible by the flexibility of the arrangement of hydrogen bonds in this crystal structure. We have to distinguish three cases (a) OH^- in A [see Fig. 4(a)] (b) Na^+ in A [see Fig. 4(b)], and (c) A not occupied at all [see Fig. 4(c)]. In each case a likely hydrogen bonding scheme can be constructed.

All three cases have in common that O(w6) is bonded to Na^+ , and that the hydrogen atom pointing down in the drawing is not involved in a hydrogen bond since in its direction no likely acceptor atom is available at a hydrogen bonding distance. In case (a) oxygen atom O(w6) is receiving a hydrogen bond from O(w5) and donates one to $A(\text{OH}^-)$. While $A(\text{OH}^-)$ is surrounded by six O(w6) atoms it also has its own hydrogen atom which it most likely donates to a hydrogen bond to O(w6). Therefore it will be able to accept only five hydrogen bonds from the six surrounding O(w6) atoms, thus introducing additional statistical disorder [which is ignored in the schematic representation of Fig. 4(a)]. Hydroxide groups receiving five hydrogen bonds and donating one have been found in $[\text{Na}_2(\text{OH})_2](\text{OH})_2$ (Wunderlich, 1958) and in $[\text{Na}(\text{H}_2\text{O})_4](\text{OH})$ (Beurskens & Jeffrey, 1964). However in these cases no disorder has to be assumed since the site symmetry of the OH^- group is 1. In case (b) oxygen atom O(w6) is bonded to $A(\text{Na})$ and is donating a hydrogen bond to O(w5). In case (c) it is assumed that the edges O(w6)–O(w6') and O(w6)–O(w6'') of the octahedron around $A(\square)$ are

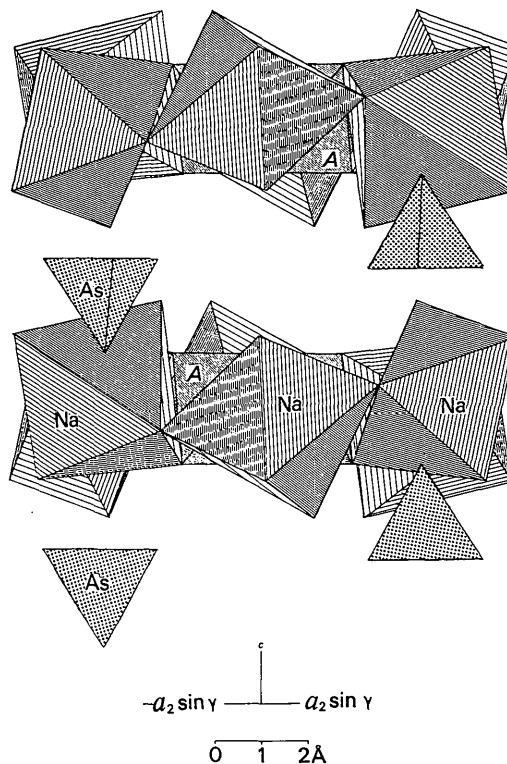


Fig. 2. $[\text{Na}_{12-13}(\text{OH})_{0-1}(\text{OH}_2)_{48}](\text{XO}_4)_4$, partial view parallel [1000]. The coordination octahedron around the A site is partly hidden inside the circlet of Na -coordination octahedra.

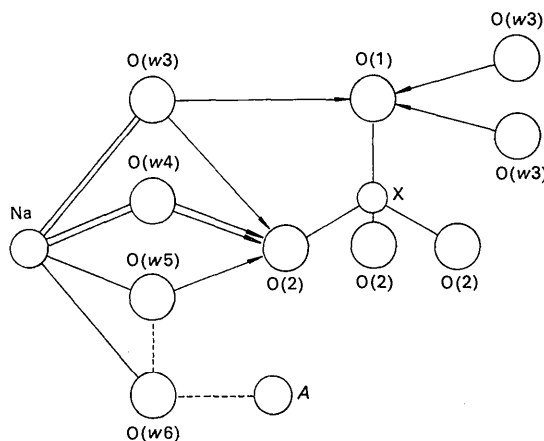


Fig. 3. $[\text{Na}_{12-13}(\text{OH})_{0-1}(\text{OH}_2)_{48}](\text{XO}_4)_4$, hydrogen bonds. X and O(1) are located on the threefold axis.

Table 4. Coordinates of hydrogen atom positions in the As salt

	From difference synthesis			Calculated		
	x	y	z	x	y	z
H(31)	0.530	0.270	0.990	0.535	0.259	0.003
H(32)	0.485	0.245	0.110	0.466	0.238	0.113
H(42a)	0.060	0.583	0.336	0.068	0.582	0.334
H(42b)	0.930	0.540	0.335	0.915	0.502	0.339
H(52)	0.175	0.400	0.200	0.175	0.394	0.212
H(55) $\times 0.5$	—	—	—	0.031	0.281	0.229
H(56) $\times 0.5$	—	—	—	0.137	0.267	0.148

hydrogen bonds. Since only six such edges are available for the 12 hydrogen atoms which are coordinated to the six O(*w*6) atoms and since all O(*w*6) atoms are symmetrically equivalent, the assumed statistical distribution is the only one consistent with the existing symmetry and the available sites.

A composite of the three cases is shown in Fig. 4(*d*). It is based on an occupancy factor of $\frac{2}{3}$ for the *A* site, that is Na⁺, OH⁻ and a void are occupying statistically the *A* site $\frac{1}{3}$ each. The bond strength distribution for the structure (Table 6) is based on this model. The following arguments can be made in order to support the claim that the *A* site is statistically occupied and

that the hydrogen bonds are distributed as shown before:

(*a*) Analytical evidence

This type of compound always has excess NaOH (Menzel & von Sahr, 1937, and many others as quoted by Tillmanns & Baur, 1970). There is only one site available in the structure for both Na⁺ and OH⁻. The occupancy factor of the *A* site refined for the phosphate compound to essentially the same value as required by the chemical analysis [Na₃PO₄·(NaOH)_{0.17}·12H₂O from the site refinement, Na₃PO₄·(NaOH)_{0.155}·12H₂O from the chemical analysis of the supplier].

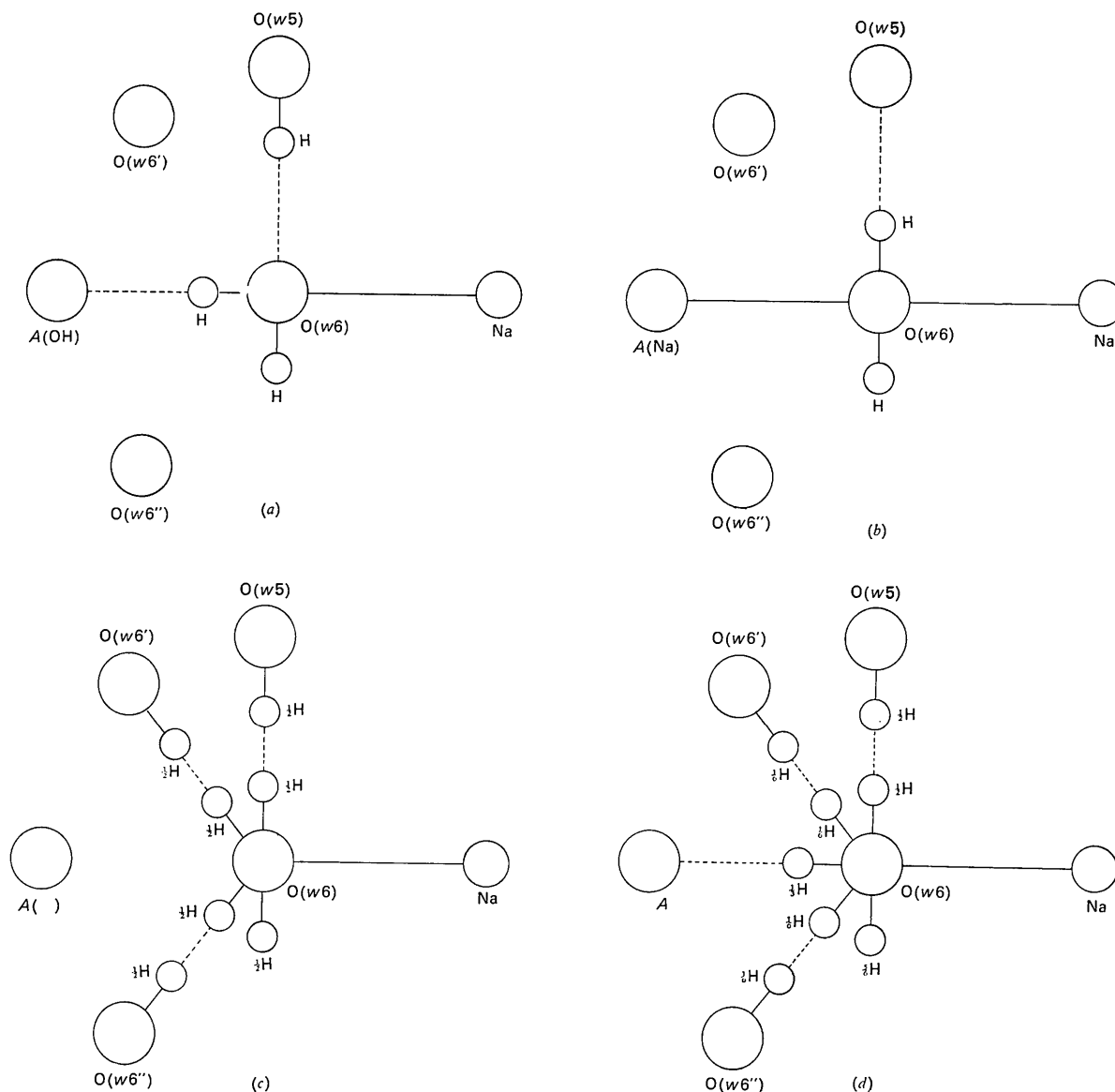


Fig. 4. Bonding around O(*w*6) when (*a*) *A* site is occupied by OH⁻, (*b*) *A* site is occupied by Na⁺, (*c*) *A* site is not occupied, and (*d*) composite of cases *a*, *b* and *c* assuming that each case has an equal probability. The symmetry of the *A* site is $\bar{3}$, only three of the six O(*w*6) atoms surrounding *A* are shown.

(b) 'Thermal ellipsoid' of O(w6)

The high temperature factor of O(w6) and the highly anisotropic nature of its thermal ellipsoid (Table 7) are supporting evidence for the statistical occupations of the *A* site by atoms of different sizes, because they reflect the statistical disorder of O(w6) over three different positions. When *A* is occupied by the OH⁻ group the distance O(w6)-*A* is largest because the hydrogen bond formed from O(w6) to OH⁻ should be about 2.7 Å long. When *A* is occupied by Na the distance O(w6)-*A* should be about 2.45 Å, and when *A* is not occupied at all the distance O(w6)-*A* should be approximately 2.2 Å. The value of 2.2 Å is calculated on the assumption that the O(w6) octahedron collapses to the point that its O(w6)-O(w6') edges are 2.8 Å long and correspond to hydrogen bonds. It is consistent with this interpretation that we observe a decrease in the O(w6)-*A* and O(w6)-O(w6') distances from the P salt, through the V salt to the As salt [Table 5(g)]. That is, the values decrease in the order which is to be

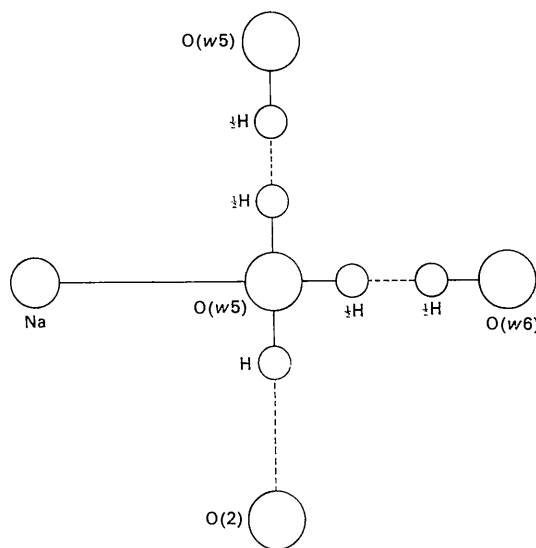


Fig. 5. Bonding around O(w5).

Table 5. Interatomic distances and bond angles

(a) Coordination around Na⁺

	P salt	V salt	As salt
Na-O(w3)	2.419 (5) Å	2.423 (8) Å	2.410 (7) Å
Na-O(w3)	2.475 (5)	2.516 (8)	2.500 (7)
Na-O(w4)	2.369 (4)	2.386 (6)	2.354 (5)
Na-O(w4)	2.411 (3)	2.431 (5)	2.416 (5)
Na-O(w5)	2.454 (4)	2.429 (7)	2.422 (6)
Na-O(w6)	2.631 (5)	2.693 (7)	2.595 (7)
Average:	2.462	2.480	2.450

Range of the 'right' angles O(w)-Na-O(w)

74.3-107.8°

72.9-109.3°

73.5-109.4°

Range of the 'straight' angles O(w)-Na-O(w)

162.6-174.3

169.8-173.7

161.1-174.4

Range of lengths of O(w)-O(w) edges in the Na-coordination octahedron

3.086-3.946 Å

3.097-4.036 Å

3.050-4.013 Å

Na-Na (over common edge)

3.524 (3)

3.539 (4)

3.526 (3)

Na-Na (over common corner) (2 ×)

4.282 (3)

4.368 (6)

4.356 (5)

(b) Tetrahedral coordination

	P salt	V salt	As salt
X-O(1)	1.512 (6) Å	1.677 (11) Å	1.670 (8) Å
X-O(2) (3 ×)	1.531 (4)	1.696 (6)	1.669 (5)
Average:	1.526	1.691	1.669
O(1)-X-O(2) (3 ×)	109.6 (2)°	109.4 (2)°	109.8 (2)°
O(2)-X-O(2) (3 ×)	109.3 (2)	109.5 (3)	109.2 (2)
O(1)-O(2) (3 ×)	2.487 (6) Å	2.753 (10) Å	2.731 (8) Å
O(2)-O(2) (3 ×)	2.498 (4)	2.770 (7)	2.721 (6)

(c) Hydrogen bonds donated to oxygen atoms in the tetrahedral groups

	P salt	V salt	As salt
O(w3) → O(1)	2.743 (5) Å	2.735 (8) Å	2.715 (6) Å
O(w3) → O(2)	2.821 (5)	2.791 (8)	2.819 (7)
O(w4) → O(2)	2.807 (4)	2.805 (7)	2.821 (6)
O(w4) → O(2)	2.822 (4)	2.794 (8)	2.820 (7)
O(w5) → O(2)	2.691 (5)	2.708 (9)	2.698 (8)
Average of 5 bonds	2.777	2.767	2.775
O(1)-O(w3)-O(2)	109.5 (2)°	108.1 (3)°	106.9 (2)°
O(2)-O(w4)-O(2)	107.2 (2)	103.9 (3)	104.0 (2)

(d) Distances involving the hydrogen atoms in the As salt (the positions taken from the difference synthesis are used)

O(w3) — H(31)	1.05 Å	H(42a) ··· O(2)	1.92 Å
H(31) ··· O(1)	1.70	O(w4) — H(42b)	1.01
O(w3) — H(32)	0.97	H(42b) ··· O(2)	1.90
H(32) ··· O(2)	1.85	O(w5) — H(52)	0.96
O(w4) — H(42a)	0.91	H(52) ··· O(2)	1.76
H(31) — O(w3) — H(32)	105°	H(42a) — O(w4) — H(42b)	91°
O(w3) — H(31) — O(1)	162	O(w4) — H(42a) — O(2)	170
O(w3) — H(32) — O(2)	173	O(w4) — H(42b) — O(2)	150
		O(w5) — H(52) — O(2)	165

Table 5 (cont.)

(e) Coordination around O(w6) (see Fig. 4). All distances and angles involving O(w6) represent only an average over the three likely positions of O(w6)

	P salt	V salt	As salt
O(w6)–O(w5)	2.711 (6) Å	2.722 (9) Å	2.727 (9) Å
O(w6)–Na	2.631 (5)	2.693 (7)	2.595 (7)
O(w6)–A	2.443 (5)	2.429 (9)	2.416 (9)
O(w6)–O(w6') [= O(w6)–O(w6'')]	3.237 (7)	3.190 (12)	3.076 (10)
Na—O(w6)–A	113.5 (2)°	115.0 (4)°	118.8 (4)°
Na—O(w6)–O(w5)	96.3 (2)	97.3 (2)	98.1 (2)
Na—O(w6)–O(w6')	76.5 (2)	78.2 (3)	81.5 (3)
Na—O(w6)–O(w6'')	82.2 (2)	82.9 (3)	85.8 (3)
O(w5)–O(w6)–O(w6')	80.4 (2)	79.8 (3)	78.7 (3)
O(w5)–O(w6)–O(w6'')	148.8 (2)	149.2 (4)	152.1 (4)
O(w6')–O(w6)–O(w6'')	68.9 (2)	70.1 (3)	74.6 (3)
O(w5)–O(w6)–A	106.1 (2)	105.6 (4)	105.3 (3)

(f) Coordination around O(w5) (see Fig. 5)

	P salt	V salt	As salt
O(w5)–O(w5')	2.745 (5) Å	2.741 (8) Å	2.782 (7) Å
O(w5)–O(w6)	2.711 (6)	2.722 (9)	2.727 (9)
O(w5)–Na	2.465 (4)	2.429 (7)	2.422 (6)
O(w5)–O(2)	2.691 (5)	2.708 (9)	2.698 (8)
Na—O(w5)–O(2)	111.2 (2)°	111.7 (3)°	111.7 (3)°
Na—O(w5)–O(w6)	97.1 (2)	98.7 (3)	97.5 (3)
Na—O(w5)–O(w5)	100.5 (2)	103.7 (3)	103.3 (2)
O(2)–O(w5)–O(w6)	108.5 (2)	106.6 (2)	107.1 (2)
O(2)–O(w5)–O(w5)	117.6 (2)	114.3 (3)	114.0 (3)
O(w6)–O(w5)–O(w5)	119.3 (2)	120.7 (4)	121.9 (3)

(g) Coordination around the A-site (see Fig. 4)

	P salt	V salt	As salt
A—O(w6) (6x)	2.443 (6) Å	2.429 (9) Å	2.416 (9) Å
O(w6)–O(w6') (6x)	3.237 (7)	3.190 (12)	3.076 (12)
O(w6')–O(w6'') (6x)	3.661 (8)	3.662 (12)	3.726 (12)
O(w6)–A–O(w6') (6x)	83.0 (2)°	82.1 (3)°	79.1 (3)°
O(w6')–A–O(w6'') (6x)	97.1 (2)	97.9 (3)	100.9 (3)

Table 6. Electrostatic bond strengths p_O (Baur, 1970; Pauling, 1960, p. 547) in the pseudo-12-hydrates

	Na	A(Na)	X	H(D)	H(A)	$\Sigma = p_O$
O(1)	—	—	1.25	—	3×0.17	1.75
O(2)	—	—	1.25	—	4×0.17	1.92
O(w3)	2×0.17	—	—	2×0.83	—	2.00
O(w4)	2×0.17	—	—	2×0.83	—	2.00
O(w5)	0.17	—	—	2×0.83	0.17	2.00
O(w6)	0.17	$\frac{1}{3} \times 0.17$	—	2×0.83	0.17	2.06
A(OH)	—	—	—	0.83	5×0.17	1.67

expected from the decrease of the occupancy factors in this sequence.

(c) Hydrogen bonding

The fact that no electron densities which could be interpreted as hydrogen atoms were found in the difference maps near O(w6), while they were found near O(w3), O(w4) and (partly) O(w5) indicates that the hydrogen atoms coordinated to O(w6) may be disordered. All the bond distances and bond angles for the three different cases of A site occupancy have reasonable values which fall into the expected range [Table 5(e)]. The assumption that the O(w6)–O(w5) hydrogen bond is statistically disordered so that both O(w6) and O(w5) can be both donor and acceptor atoms means that O(w5) must be also involved in a second disordered

bond. This is indeed the case since each O(w5) is within hydrogen bonding distance from another O(w5) atom, related to it by a twofold axis. For reasons of symmetry this hydrogen bond must also be disordered [see Fig. 5 and Table 5(f)].

(d) Other possibilities

The only alternative to the explanation given above would be to assume a disproportionation of H₂O into H₃O⁺ and OH[−], so that H₃O⁺ and Na⁺ would occupy statistically the A site. The OH[−] groups would have to partly replace water oxygen atoms, which is very unlikely, because it would mean that these OH[−] groups would have the same coordination and would receive the same small electrostatic bond strength as the water oxygen atoms.

Table 7. $[\text{Na}_{12-13}(\text{OH})_{0-1}(\text{OH}_2)_{48}](\text{AsO}_4)_4$, root mean square thermal displacements along principal axes

	Axis 1	Axis 2	Axis 3
As	0.130 (3) Å	0.146 (2) Å	0.146 (2) Å
Na	0.175 (6)	0.204 (6)	0.252 (6)
O(1)	0.130 (20)	0.206 (13)	0.206 (13)
O(2)	0.157 (10)	0.173 (11)	0.188 (10)
O(w3)	0.170 (10)	0.186 (11)	0.197 (9)
O(w4)	0.158 (10)	0.177 (10)	0.246 (10)
O(w5)	0.168 (12)	0.214 (9)	0.232 (9)
O(w6)	0.273 (12)	0.317 (13)	0.408 (11)
A	0.242 (31)	0.242 (31)	0.332 (31)

The maximum deviations between corresponding O(w) → O hydrogen bonds [see Table 5(c)] in the three salts are 0.028 Å, which means that these individual differences are significant. The average of the O(w) → O distances in the vanadium salt is 0.009 Å smaller than in the other two compounds. However this difference is too small to be interpreted as the effect of the tetrahedrally coordinated atom X on the length of the hydrogen bond. Therefore the result of this study is negative. The correlation between Δp and the hydrogen bond length however is clearly visible. The difference between the p_{O} values (see Table 6) received by the atoms (Ow3) and O(1) is $\Delta p = 0.25$ valence units (v.u.), which means that the calculated bond length is 2.75₅ Å (= 2.85 - 0.38 × 0.25; see the Introduction) while the observed average of the O(w3) → O(1) bonds in the three compounds is 2.73 Å. The Δp of all hydrogen bonds accepted by atom O(2) is 0.08 v.u., the calculated bond length is 2.82 Å, while the average length of all the observed hydrogen bonds accepted by the atoms O(2) [O(w3) → O(2), O(w4) → O(2) and O(w5) → O(2)] in the three salts is 2.78 Å. Thus the agreement between calculated hydrogen bond lengths and observed average hydrogen bond lengths is here as satisfactory as it was found in a survey of a large number of such bonds (Baur, 1970), where the mean difference between observed and calculated values was 0.08 Å (for 392 cases).

Of the small differences between the X-O(1) and X-O(2) bond lengths [Table 5(b)] only the one in the phosphate salt is possibly significant. The value of the observed difference is comparable with the difference calculated from the p_{O} -values (Table 6) of the oxygen atoms. Since $p_{\text{O}(1)} = 1.75$ v.u. and $p_{\text{O}(2)} = 1.92$ v.u., the average p_{O} for the phosphate group is 1.88 v.u. According to rule 3 (Baur, 1970) we can now calculate the corresponding expected deviations of the individual bond lengths from the mean for both O(1) and O(2). In the expression $d(\text{P-O}) = d(\text{P-O})_{\text{mean}} + b\Delta p_{\text{O}}$ we use here for $d(\text{P-O})_{\text{mean}}$ the observed mean distance in the tetrahedral group, for b the empirically derived value 0.109 Å/v.u. (Baur, 1970), while Δp_{O} is the difference between the p_{O} of the

individual oxygen atoms and the mean p_{O} for the whole tetrahedral group. The resulting calculated values $d[\text{P-O}(1)] = 1.512$ and $d[\text{P-O}(2)] = 1.530$ Å agree well with the observed ones. In view of the standard deviations of the observed values the good agreement must be accidental. Since values of the slope b have not been derived yet for the vanadate and the arsenate group we cannot make the same comparison for these tetrahedra, but it can be expected reasonably that these b values are similar to the one for the phosphate group. Therefore the difference between the V-O bonds is of the right magnitude. Since however the errors in the V-O and As-O bonds are larger than in the phosphate group, this agreement is of little consequence as the lack of it in the arsenate tetrahedron. The Na-O bond lengths and the angles O-Na-O in the octahedral coordination around the Na atom show the usual distortions expected for such weak bonds. The average Na-O distances are close to the mean of 2.44 Å of 116 Na-O distances in octahedral coordination (Baur, 1970).

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References

- BAUR, W. H. (1961). *Naturwissenschaften*, **44**, 549.
 BAUR, W. H. (1970). *Trans. Amer. Cryst. Assoc.* **6**, 129.
 BAUR, W. H. & KHAN, A. A. (1970). *Acta Cryst.* **B26**, 1584.
 BEURSKENS, G. & JEFFREY, G. A. (1964). *J. Chem. Phys.* **41**, 924.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. ORNL-TM-306, Oak Ridge National Laboratory, Tennessee.
 CLARK, G. L. & GROSS, S. T. (1937). *Z. Kristallogr.* **98**, 107.
 CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197.
International Tables for X-ray Crystallography (1962), Vol. III, Birmingham: Kynoch Press.
 MENZEL, H. & VON SAHR, E. (1937). *Z. Elektrochem.* **43**, 104.
 PAULING, L. (1960). *The Nature of the Chemical Bond*. 3rd ed. Ithaca: Cornell Univ. Press.
 RÉMY, F. & GUÉRIN, H. (1970). *Bull. Soc. chim. Fr.* 2073.
 TILLMANN, E. & BAUR, W. H. (1970). *Inorg. Chem.* **9**, 1957.
 WUNDERLICH, J. A. (1958). *Bull. Soc. Franç. Minér. Crist.* **81**, 287.