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On the Crystal Chemistry of Salt Hydrates.
VI. The Crystal Structures of Disodium Hydrogen Orthoarsenate Heptahydrate and of Disodium Hydrogen Orthophosphate Heptahydrate.

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The isomorphous pair of hydrated salts $Na_2HAsO_4.7H_2O$ and $Na_2HPO_4.7H_2O$ crystallizes in space group $P2_1/n$, $Z=4$ with $a=9{\cdot}40$ (9·26), $b=11{\cdot}03$ (11·01), $c=10{\cdot}67$ (10·44) Å and $\beta=95{\cdot}5$ (95·6)° (the values for the phosphate compound are in parentheses). The crystal structures have been determined and refined with the use of three-dimensional counter diffractometer data to $R=0{\cdot}048$ (0·081) for 1162 (1252) F_{hkl}. The most prominent feature of the structure is a column of face and edge sharing coordination octahedra which has the composition $[Na_2(OH_2)_7]^{2+}$ and is hydrogen bonded to the tetrahedral groups AsO_3OH (or PO_3OH). The salts should therefore be formulated as $[Na_2(OH_2)_7]$ $[XO_3OH]$. A plausible hydrogen bonding scheme which accounts for all hydrogen atoms has been established from steric considerations. The average Na–O(*w*) distances differ in the two compounds significantly: in the arsenate salt Na–O(*w*) it is 2·437 Å, in the phosphate it is 2·418 Å. The shapes of the orthoarsenate and orthophosphate groups in these two structures as well as in other phosphate and arsenate compounds display a systematic deviation from the ideal tetrahedral angles: the 'tetrahedral' angles are the larger the shorter the bonds are, which form their sides, and *vice versa*, while the O–O distances (the edges of the tetrahedra) stay relatively constant.

Introduction

The crystal structure of the isomorphous pair of hydrated salts $Na_2HPO_4.7H_2O$ and $Na_2HAsO_4.7H_2O$ was investigated in order to study the effect of the anion on the geometry of the hydrogen bond. An oxygen atom af a phosphate group and an oxygen atom in an arsenate group might influence the hydrogen bond differently when acting as the acceptor atoms. The effect, if any, would be expected to be less pronounced than the effect which the cation, to which the donor atom is coordinated, has on the length and strength of the hydrogen bond. It has been pointed out previously (Baur, 1961) that in hydrates the length of the hydrogen bond varies inversely with the electrostatic bond strength received by the donor atom (Baur, 1962; Pauling, 1960). This relationship has since been confirmed by the results of numerous new studies of hydrate structures. This is part six of a series of papers on the crystal chemistry of salt hydrates. The previous paper in the series is by Zahrobsky & Baur (1968).

Experimental

Crystals of both compounds were grown from aqueous solutions at about 40 °C. Preliminary information about the unit-cell parameters and the space group was gathered by film methods on a precession camera. The unit-cell data which are listed, together with other pertinent information, in Table 1 are based on the least-squares

Table 1. *Crystal data*

D_x and D_m refer to the calculated and the measured densities.

	$[Na_2(OH_2)_7]$ $[AsO_3OH]$	$[Na_2(OH_2)_7]$ $[PO_3OH]$
a	9·401 (4) Å	9·258 (3) Å
b	11·025 (4) Å	11·007 (3) Å
c	10·674 (4) Å	10·437 (3) Å
β	95·50 (1)°	95·61 (1)°
V	1101·3 (7) Å^3	1058·6 (7) Å^3
Z	4	4
D_x	1·882 (1) g.cm^{-3}	1·682 (1) g.cm^{-3}
D_m (Dufet, 1887)	1·8825 g.cm^{-3}	1·6789 g.cm^{-3}
F.W.	312·01	268·08
Space group	$P2_1/n$	$P2_1/n$
a:b:c	0·8527:1:0·9488	0·8411:1:0·9482
a:b:c (Dufet, 1887)	1·2294:1:1·3526	1·2047:1:1·3272
β	82°46′	83°3′
a:b:c (Dufet, transformed)	0·8547:1:0·9695	0·8405:1:0·9486
β	95·50°	95·58°
μ(Ag $K\alpha$)	18·0 cm^{-1}	2·1 cm^{-1}

refinement of 18 carefully set high angle reflections measured on a four-circle diffractometer. The matrix for expressing the unit cell corresponding to Dufet's (1887) setting in terms of our unit cell is (101, 010, $\bar{1}$01). The agreement between the $a{:}b{:}c$ measured by Dufet on an optical goniometer and measured by us by X-ray diffraction is satisfactory. The space group $P2_1/n$ was proved by the systematic extinctions ($h0l$ reflections only present when $h+l=2n$; $0k0$ reflections only present when $k=2n$) and by the successful refinement of the crystal structures. The estimated standard deviations are given in Table 1, as well as elsewhere in this paper, in parentheses following the value. They correspond to the last significant digits of these values.

The diffraction data for both compounds were collected on an automatic four-circle diffractometer using Ag $K\alpha$ radiation with Pd filter. The procedures used in aligning the diffractometer and adjusting the crystals were very similar to those described by Corfield, Doedens & Ibers (1967) and Doedens & Ibers (1967). The moving-counter, moving-crystal method was used with a 2θ scan rate of 2°. min^{-1}. Stationary-counter, stationary-crystal background counts of 10 sec each were taken at both ends of the scan. The performance of the system and the crystallinity of the sample were monitored by measuring three reference reflections at regular intervals. The standard deviation of one measurement was computed according to the expression: $\sigma(I)=[CT+0{\cdot}25(t_c/t_b)^2(B_1+B_2)+(pI)^2]^{1/2}$ (Corfield *et al.*, 1967). Here CT is the total integrated count in time t_c, while B_1 and B_2 are the background counts in time t_b. The value of p was chosen arbitrarily as 0·03; the intensity is $I=[CT-0{\cdot}5(t_c/t_b)\,(B_1+B_2)]$. In the case of the phosphate compound any intensity measured to be less than twice the standard deviation was considered to be zero; in the case of the arsenate compound all reflections which had an intensity $I>0$ were used. Data for the phosphate were gathered in the complete reciprocal sphere: intensities in all four quadrants, I_{hkl}, $I_{\bar{h}\bar{k}\bar{l}}$, $I_{h\bar{k}l}$ and $I_{\bar{h}k\bar{l}}$ were measured. The data collection for the As compound covered less than two quadrants because of a diffractometer malfunction. After the diffractometer was repaired it was not felt worthwhile to collect the remaining data since the crystal structure had meanwhile been determined and refined to a very acceptable R value. The collection of intensity data for the P compound was troubled by the fact that the crystals tended to decompose while in the X-ray beam. After some trial and error we found that the crystals survived best in kerosine. Therefore, we mounted a specimen with kerosine inside a Lindemann-glass capillary. In the course of two weeks of data collection this sample lost only 7% of its scattering power. The decomposition was monitored by measuring the standard reflections. The

Table 2. *Information regarding the collection of intensity data*

	$[Na_2(OH_2)_7]$ $[AsO_3OH]$	$[Na_2(OH_2)_7]$ $[PO_3OH]$
Diameter of crystal	0·28–0·37 mm	0·45–0·54 mm
Volume of crystal	0·017 mm^3	0·065 mm^3
Mass of crystal	0·032 mg	0·11 mg
μR	0·25–0·33	0·047–0·057
No. of quadrants searched	2	4
No. of non-unique I_{hkl} measured	3906	4779
No. of unique I_{hkl}	1177	2664
No. of $I_{hkl}=0$	15	1394
No. of I_{hkl} used in refinement	1162	1252
$2\theta_{\max}$	30° (in part 40°)	44°
$\sin\theta_{\max}/\lambda$	0·46 Å^{-1} (in part 0·61 Å^{-1})	0·67 Å^{-1}

Table 3. $[Na_2(OH_2)_7]$ $[AsO_3OH]$ *positional parameters in fractional coordinates* (× 10^4) *and thermal parameters* (× 10), *both with their standard deviations.*

The definition of the Debye–Waller temperature factor is:

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

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As	1025 (1)	2656 (1)	8962 (1)	14 (1)	17 (1)	15 (1)	1 (1)	1 (1)	1 (1)
Na(1)	1461 (3)	1015 (2)	4782 (2)	28 (2)	24 (1)	31 (1)	−1 (1)	6 (1)	0 (1)
Na(2)	6358 (3)	1040 (2)	9796 (2)	26 (2)	24 (1)	28 (1)	−2 (1)	4 (1)	2 (1)
O(1)	2657 (6)	2542 (3)	8517 (5)	16 (3)	26 (2)	26 (2)	1 (1)	−5 (2)	−3 (1)
O(2)	976 (6)	2471 (3)	510 (5)	23 (3)	29 (2)	16 (2)	−1 (1)	−4 (2)	1 (1)
O(3)	9831 (4)	1788 (3)	8137 (3)	19 (2)	27 (2)	23 (2)	−9 (2)	−1 (1)	−3 (1)
O(*h*4)	5589 (4)	849 (3)	3626 (3)	31 (2)	21 (2)	27 (2)	−2 (2)	6 (1)	−6 (2)
O(*w*5)	4813 (7)	2550 (3)	559 (5)	23 (3)	31 (2)	29 (3)	0 (1)	−1 (2)	1 (1)
O(*w*6)	8073 (6)	2498 (3)	937 (5)	26 (4)	39 (2)	22 (2)	2 (1)	3 (2)	−1 (1)
O(*w*7)	1959 (6)	2498 (3)	3153 (5)	25 (3)	26 (2)	16 (2)	1 (1)	10 (2)	1 (1)
O(*w*8)	9302 (5)	233 (4)	3518 (4)	26 (2)	33 (2)	29 (2)	7 (2)	1 (2)	−1 (2)
O(*w*9)	3017 (5)	9844 (3)	3654 (4)	23 (2)	18 (2)	28 (2)	1 (2)	7 (2)	1 (1)
O(*w*10)	4134 (5)	369 (4)	8628 (4)	35 (3)	27 (2)	27 (2)	2 (2)	−4 (2)	2 (1)
O(*w*11)	1814 (5)	61 (4)	1125 (4)	24 (2)	30 (2)	30 (2)	4 (2)	8 (2)	4 (1)

measured intensities were corrected accordingly. Nevertheless, the quality of the data set of the phosphate compound is inferior compared with the data set of the arsenate. For the details of the data collection see Table 2.

The data were corrected for Lorentz-polarization effects, but not for absorption, and the equivalent reflections and their standard deviations were averaged. In the structure factor calculations the scattering factors from *International Tables for X-ray Crystallography* (1962), were used. The crystal structure of $Na_2HAsO_4 \cdot 7H_2O$ was solved by a combination of Patterson, Fourier and least-squares methods. All atoms reside in the general equivalent position $\pm(x,y,z;\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$. The initial R value (for As only) was 0·42. Inclusion of additional atoms and refinement brought it down to 0·061. Refinement with anisotropic temperature factors lowered it further to 0·058. When the 23 strongest reflections (which were given zero weight in the refinement because they are suspected to be affected by extinction) are left out the final R is 0·048. We attempted to locate the hydrogen atoms in the final difference synthesis but were not successful. The resulting parameters are listed in Table 3, the F_o and F_c in Table 6. The phosphate compound was refined to an R value of 0·081. The final difference synthesis did not show any conspicuous features. Extinction effects could not be observed. Some of the largest structure factors have considerable deviations between F_o and F_c but these deviations are not systematic. The parameters are listed in Table 5, the F_o and F_c in Table 7.

Table 4. $[Na_2(OH_2)_7]$ $[AsO_3OH]$: *probable positions of the hydrogen atoms (fractional coordinates* $\times 10^3$)

Each hydrogen atom is identified by two numbers. The first one is the number of the oxygen atom to which it is covalently bonded, the second one is the number of the oxygen atom to which it forms the hydrogen bond.

	x	y	z
H(4, 9)	465	048	364
H(5, 1)	386	258	013
H(5, 3)	477	270	145
H(6, 1)	808	248	185

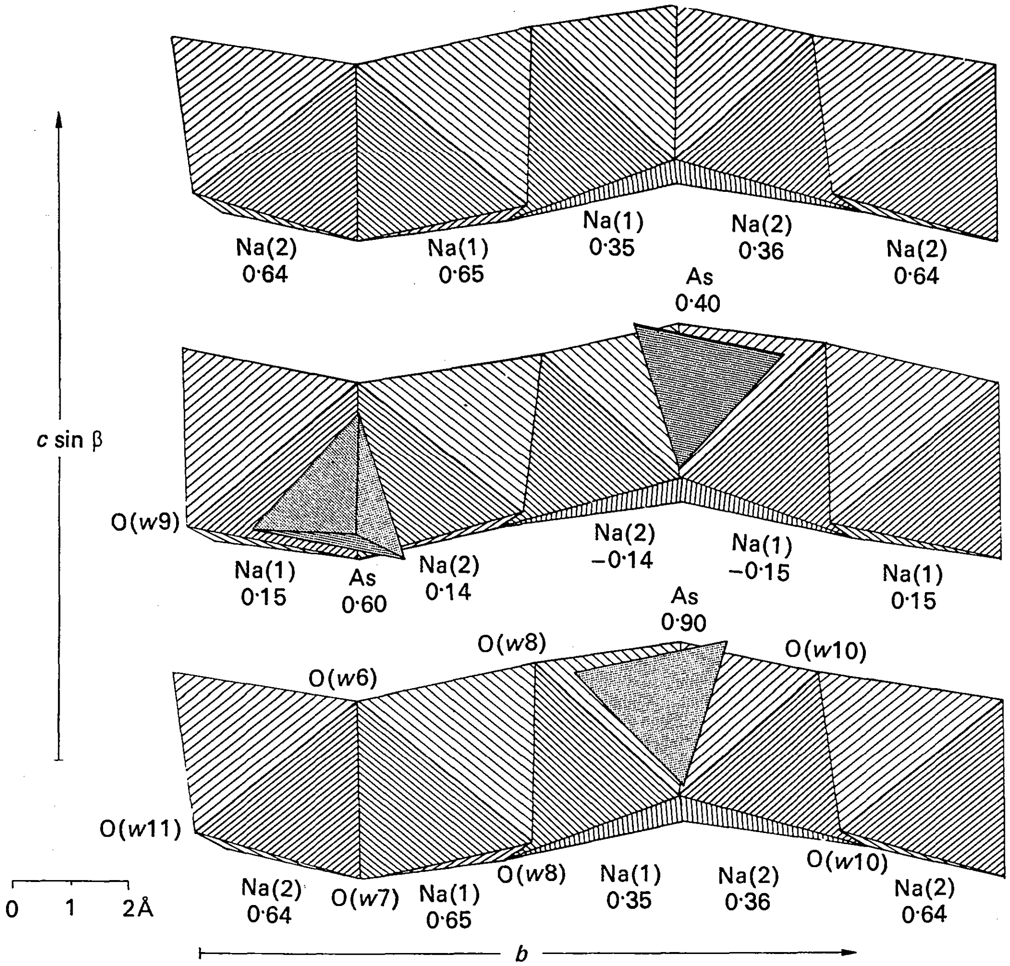

Fig. 1. $[Na_2(OH_2)_7]$ $[AsO_3OH]$, view parallel [100]. Polyhedral representation, the central atoms of the coordination polyhedra are identified and their height is given in fractional coordinates. Only some of the water oxygen atoms are identified.

Table 4 (*cont.*)

	x	y	z
H(6, 2)	905	249	071
H(7, 2)	132	236	239
H(7, 3)	290	271	293
H(8, 1)	870	091	324
H(8, 3)	943	971	281
H(9, 2)	329	905	398
H(9, 11)	257	976	280
H(10, 1)	357	110	847
H(10, 4)	419	994	784
H(11, 2)	177	088	078
H(11, 3)	085	978	122

All computations were performed on an IBM 360/50 computer. The following computer programs, in their local modifications, were used in the course of the work:

(1) Zalkin's Fourier program *FORDAP.*

(2) Busing, Martin & Levy's least-squares program *ORFLS.* This and the previous program were used in the versions modified by Hamilton and Ibers at Brookhaven National Laboratory and Northwestern University. Both these programs were adapted to IBM 360-FORTRAN-IV by Doedens.

(3) Ibers's unit-cell parameter and orientation-refinement program *NUPICK*, as adapted to the IBM 360/50 by Eisenberg.

(4) Baur's data reduction program *OUTPICK.* This program is based on Ibers & Doedens' *PICKOUT* written for a CDC 3400-computer. Since a program of this kind naturally is very machine dependent it proved easier to write it anew, than to try and adapt it to an IBM 360/50 computer.

(5) Baur's bond distance and angle program *SADIAN*69. This program calculates the standard deviations according to the formulas by Darlow (1960) and Ahmed & Cruickshank (1953), prepares printer plots of the three main projections of the crystal structure and presents scaled orthogonal coordinates for the execution of structure drawings.

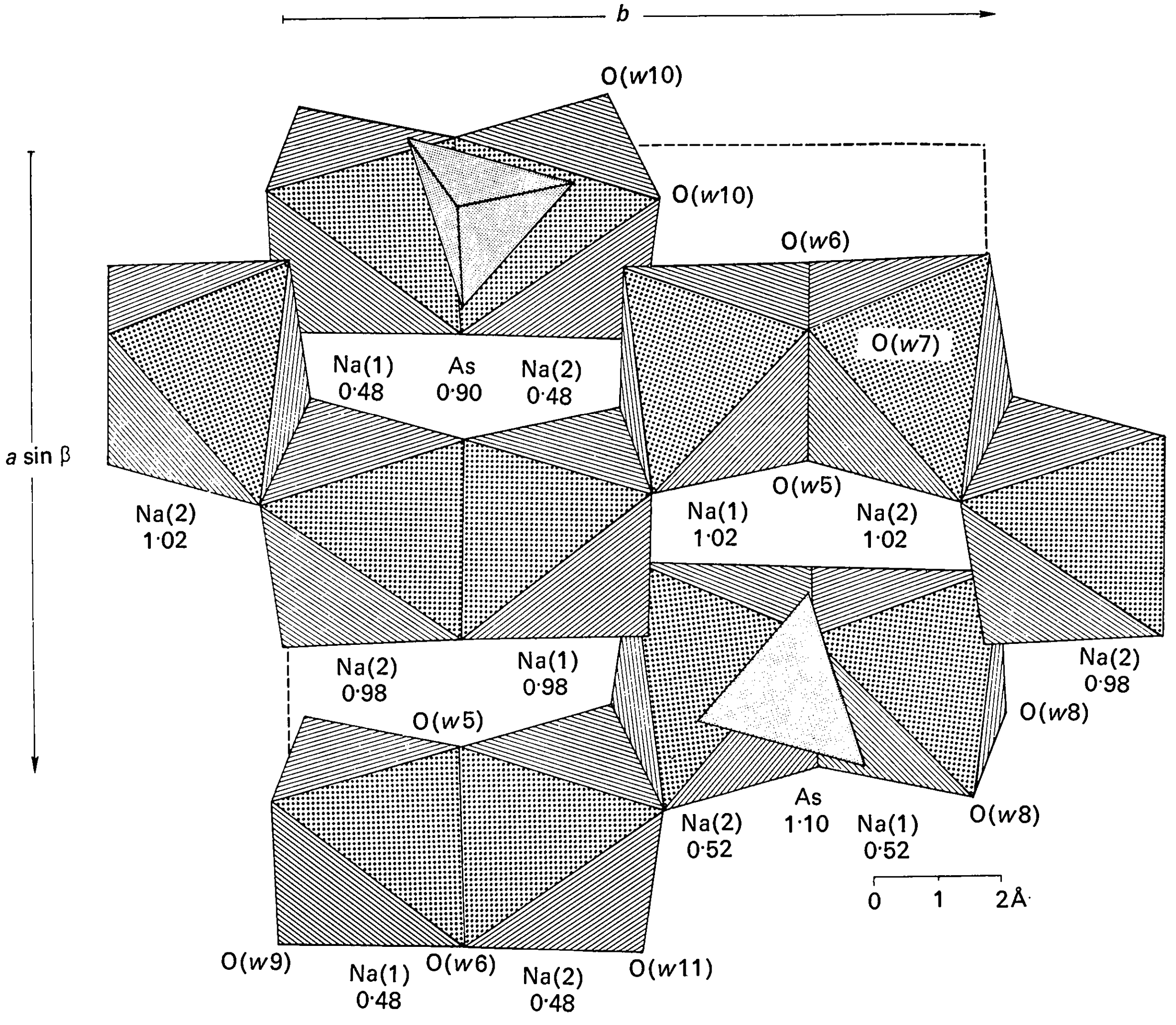

Fig. 2. $[Na_2(OH_2)_7]$ $[AsO_3OH]$, view parallel [001].

Table 5. $[Na_2(OH_2)_7]$ $[PO_3OH]$ *positional and thermal parameters*

For explanations see Table 3.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	1024 (2)	2633 (2)	8955 (2)	12 (1)	14 (1)	12 (1)	1 (1)	0 (1)	2 (1)
Na(1)	1404 (4)	1043 (3)	4756 (3)	25 (2)	20 (2)	28 (2)	−2 (1)	9 (1)	−1 (1)
Na(2)	6338 (4)	1053 (3)	9771 (3)	23 (2)	24 (2)	21 (2)	0 (1)	5 (1)	2 (1)
O(1)	2564 (5)	2522 (5)	8540 (5)	13 (2)	28 (3)	20 (2)	−3 (2)	4 (2)	−1 (2)
O(2)	997 (6)	2492 (5)	403 (5)	25 (3)	26 (3)	15 (2)	4 (2)	3 (2)	2 (2)
O(3)	9899 (6)	1832 (6)	8190 (5)	19 (3)	31 (3)	23 (3)	−4 (2)	−2 (2)	1 (2)
O(*h*4)	5613 (6)	968 (5)	3612 (6)	28 (3)	25 (3)	23 (3)	−6 (2)	9 (2)	−7 (2)
O(*w*5)	4759 (6)	2542 (5)	572 (6)	21 (2)	26 (3)	24 (3)	1 (2)	2 (2)	0 (2)
O(*w*6)	8041 (6)	2507 (5)	951 (6)	24 (3)	34 (3)	23 (3)	−1 (2)	4 (2)	2 (2)
O(*w*7)	1944 (6)	2503 (5)	3098 (6)	27 (3)	28 (3)	18 (2)	3 (2)	0 (2)	4 (2)
O(*w*8)	9212 (7)	232 (6)	3518 (6)	26 (3)	39 (4)	27 (3)	−2 (3)	2 (2)	−1 (3)
O(*w*9)	3063 (6)	9872 (6)	3680 (5)	21 (2)	26 (3)	20 (3)	3 (2)	0 (2)	−2 (2)
O(*w*10)	4082 (6)	347 (6)	8618 (6)	33 (3)	25 (3)	23 (3)	−1 (2)	−3 (2)	4 (2)
O(*w*11)	1781 (6)	46 (6)	1085 (6)	30 (3)	27 (3)	22 (3)	5 (2)	6 (2)	−1 (2)

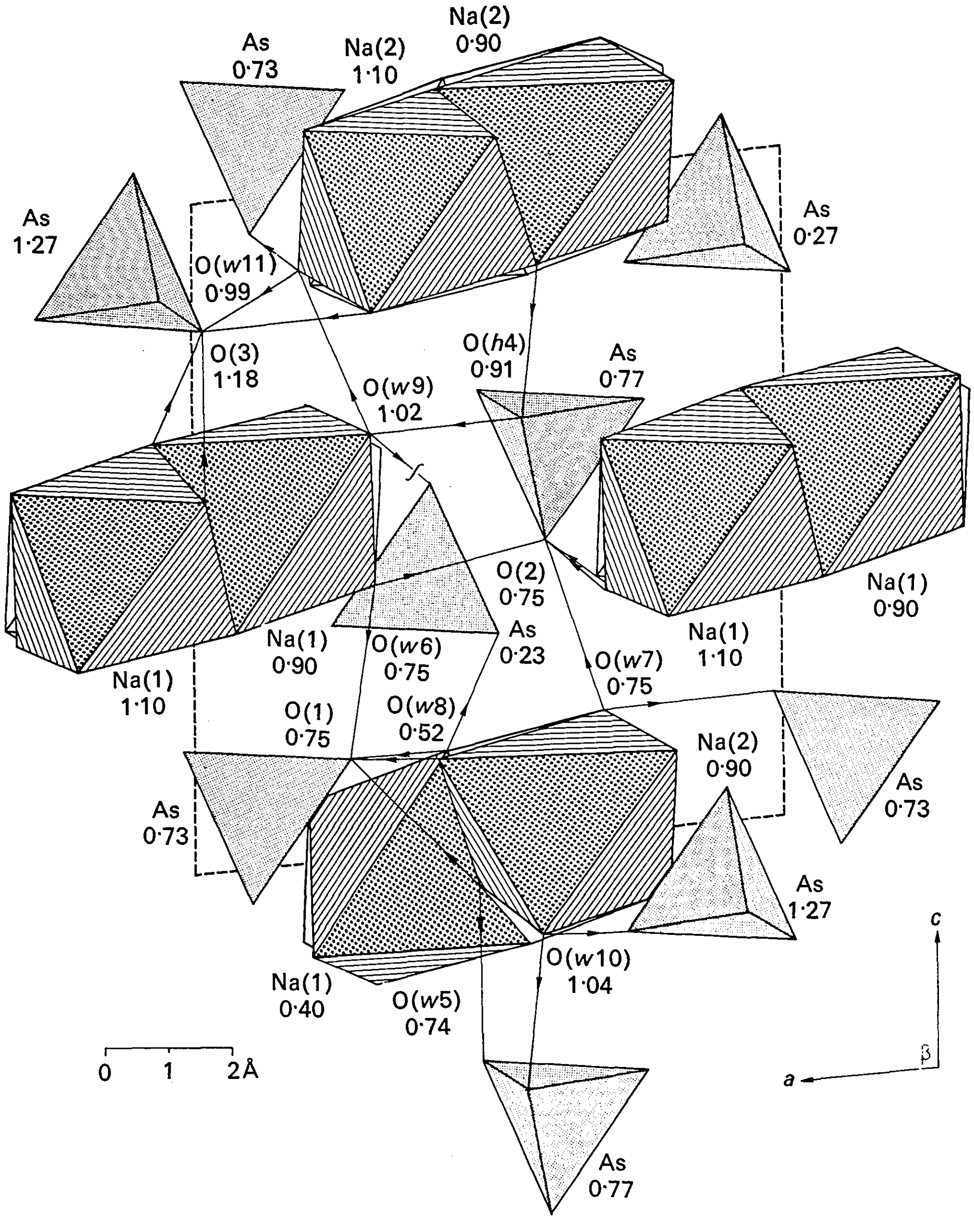

Fig. 3. $[Na_2(OH_2)_7]$ $[AsO_3OH]$, view parallel [010]. The hydrogen bonds are indicated by arrows pointing towards the acceptor atoms. Each oxygen atom is identified once in a position where its complete hydrogen bonding coordination is displayed.

Description and discussion of the crystal structures

Figs. 1, 2 and 3 show the three main projections of the arsenate compound. The atomic positions in the phosphate are so similar to those in the arsenate that the drawings can also be taken as representing the phosphate. The most pronounced feature of the structure are the chains of Na-coordination octahedra extending parallel [010]. The chains are formed by alternate face and edge sharing between the octahedra. At *y* values of about $\frac{1}{4}$ and $\frac{3}{4}$ the Na(1) and Na(2) octahedra are joined through a face formed by the O(*w*5), O(*w*6) and O(*w*7) atoms. Such pairs of octahedra $[Na_2(OH_2)_9]^{2+}$ share the edge O(*w*8)–O(*w*8) between two Na(1)-octahedra, and the edge O(*w*10)–O(*w*10) between two Na(2)-octahedra, thus forming an infinite column of composition

Table 6. $[Na_2(OH_2)_7]$ $[AsO_3OH]$ *observed and calculated structure factors* (× 4)

The 23 *F* which were given zero weight in the least-squares refinement are marked by an asterisk. Unobserved structure factors are omitted.

H	K	L	FO	FC
0	0	2	*318	368
0	0	4	*548	-633
0	0	6	4	6
0	0	8	201	187
0	0	10	152	156
0	0	12	38	-29
0	1	1	87	-73
0	1	2	*459	567
0	1	3	98	92
0	1	4	199	-197
0	1	5	29	35
0	1	6	228	-230
0	1	7	69	-65
0	1	8	100	-106
0	1	9	17	10
0	1	10	90	84
0	1	11	45	25
0	1	12	202	203
0	2	0	*430	-503
0	2	1	24	-25
0	2	2	146	-140
0	2	3	125	-125
0	2	4	141	150
0	2	5	23	24
0	2	6	278	309
0	2	7	86	87
0	2	8	110	105
0	2	9	0	-14
0	2	10	182	-204
0	2	11	14	-15
0	2	12	31	-29
0	3	1	70	66
0	3	2	118	-122
0	3	3	67	61
0	3	4	187	202
0	3	5	189	-196
0	3	6	297	311
0	3	7	32	-34
0	3	8	294	302
0	3	9	85	92
0	3	10	42	43
0	3	11	20	27
0	3	12	135	-135
0	4	0	*628	820
0	4	1	7	-9
0	4	2	36	-31
0	4	3	140	142
0	4	4	*552	-652
0	4	5	20	16
0	4	6	271	-278
0	4	7	143	-137
0	4	8	60	52
0	4	9	19	-16
0	4	10	106	112
0	4	11	42	44
0	4	12	24	-15
0	5	1	83	-83
0	5	2	315	329
0	5	3	11	8
0	5	4	92	-84
0	5	5	128	132
0	5	6	292	-285
0	5	7	8	6
0	5	8	118	-121
0	5	9	66	-69
0	5	10	54	50
0	5	11	29	-36
0	5	12	103	104
0	6	0	*512	-562
0	6	1	65	-64
0	6	2	273	-285
0	6	3	148	-145
0	6	4	104	96
0	6	5	8	-8
0	6	6	102	114
0	6	7	126	124
0	6	8	58	-53
0	6	9	43	47
0	6	10	96	-106
0	6	11	55	-56
0	7	1	187	186
0	7	2	196	-202
0	7	3	67	-65
0	7	4	62	-70
0	7	5	177	-176
0	7	6	107	111
0	7	7	21	-23
0	7	8	51	56
0	7	9	108	110
0	7	10	91	-89
0	7	11	56	61
0	8	0	435	445
0	8	1	173	178
0	8	2	159	156
0	8	3	183	190
0	8	4	161	-170
0	8	5	62	-68
0	8	6	96	-93
0	8	7	132	-130
0	8	8	57	63
0	8	9	25	-21
0	8	10	73	75
0	9	1	158	-165
0	9	2	98	92
0	9	3	112	116
0	9	4	45	-46
0	9	5	123	134
0	9	6	133	-129
0	9	7	11	6
0	9	8	81	-84
0	9	9	74	-72
0	10	0	94	-89
0	10	1	106	-103
0	10	2	35	35
0	10	3	118	-120
0	10	4	146	147
0	10	5	16	7
0	10	6	105	105
0	10	7	99	97
0	10	8	24	24
0	11	1	117	113
0	11	2	77	-78
0	11	3	46	-51
0	11	4	49	46
0	11	5	119	-118
0	11	6	106	102
0	11	7	46	-50
0	12	0	166	165
0	12	1	103	101
0	12	2	23	25
0	12	3	120	121
0	12	4	74	-75
0	12	5	21	-24
0	13	1	117	-117
0	13	2	52	53
0	13	3	64	63
1	0	-11	102	99
1	0	-9	268	275
1	0	-7	184	203
1	0	-5	186	-203
1	0	-3	*421	-498
1	0	-1	46	30
1	0	1	284	244
1	0	3	126	-125
1	0	5	*538	-591
1	0	7	421	-443
1	0	9	78	79
1	0	11	117	110
1	1	-12	32	39
1	1	-11	81	-76
1	1	-10	0	0
1	1	-9	38	41
1	1	-8	100	-101
1	1	-7	233	242
1	1	-6	13	-4
1	1	-5	379	411
1	1	-4	123	113
1	1	-3	56	-44
1	1	-2	16	14
1	1	-1	368	-362
1	1	0	74	-61
1	1	1	123	130
1	1	2	80	-80
1	1	3	376	408
1	1	4	51	49
1	1	5	214	212
1	1	6	23	27
1	1	7	248	-257
1	1	8	28	-25
1	1	9	206	-197
1	1	10	12	8
1	1	11	99	97
1	1	12	23	-10
1	2	-12	0	7
1	2	-11	30	23
1	2	-10	59	58
1	2	-9	179	-164
1	2	-8	12	1
1	2	-7	269	-290
1	2	-6	110	-110
1	2	-5	130	141
1	2	-4	19	19
1	2	-3	*461	568
1	2	-2	104	97
1	2	-1	123	-124
1	2	0	105	98
1	2	1	*482	-592
1	2	2	117	-110
1	2	3	244	-247
1	2	4	147	-147
1	2	5	275	290
1	2	6	89	89
1	2	7	275	275
1	2	8	33	40
1	2	9	141	-136
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4	6	5	63	-55
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4	7	0	190	196
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5	5	5	96	92
5	6	-6	125	121
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5	6	-4	38	-40
5	6	-3	193	-201
5	6	-2	175	-183
5	6	-1	308	309
5	6	0	19	17
5	6	1	234	239
5	6	2	151	154
5	6	3	174	-173
5	6	4	47	45
5	6	5	164	-150
5	7	-4	139	146
5	7	-3	47	-50
5	7	-2	47	-49
5	7	-1	54	-49
5	7	0	174	-175
5	7	1	287	302
5	7	2	13	-14
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5	8	-2	127	119
5	8	-1	153	-151
5	8	0	14	-10
5	8	1	94	-94
6	0	-6	34	7
6	0	-4	369	373
6	0	-2	240	250
6	0	0	162	-153
6	0	2	189	-196
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6	0	6	217	213
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6	1	2	76	-72
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6	2	4	112	-112
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6	3	-3	96	95
6	3	-2	163	-188
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6	3	1	16	-16
6	3	2	172	177
6	3	3	12	5
6	3	4	391	397
6	3	5	16	-8
6	4	-6	200	-203
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6	4	-4	89	92
6	4	-3	49	49
6	4	-2	61	64
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6	4	0	253	-252
6	4	1	11	-6
6	4	2	231	-229
6	4	3	80	-78
6	4	4	110	112
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6	5	-5	21	-18
6	5	-4	77	-68
6	5	-3	130	-138
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6	5	-1	28	27
6	5	0	166	159
6	5	1	167	168
6	5	2	172	-175
6	5	3	52	55
6	5	4	178	-163
6	6	-4	262	-277
6	6	-3	63	-70
6	6	-2	37	-37
6	6	-1	149	-152
6	6	0	148	157
6	6	1	15	-15
6	6	2	18	12
6	6	3	100	100
6	7	-2	247	-257
6	7	-1	29	-29
6	7	0	222	-207
6	7	1	97	-91
7	0	-5	86	-69
7	0	-3	73	61
7	0	-1	60	67
7	0	1	433	-434
7	0	3	370	-385
7	0	5	144	140
7	1	-6	21	-14
7	1	-5	180	-177
7	1	-4	64	-65
7	1	-3	142	-129
7	1	-2	15	15
7	1	-1	216	215
7	1	0	56	55
7	1	1	297	307
7	1	2	22	-27
7	1	3	178	-182
7	1	4	7	-7
7	2	-6	44	42
7	2	-5	63	-64
7	2	-4	18	13
7	2	-3	142	-134
7	2	-2	97	-98
7	2	-1	123	-123
7	2	0	35	-31
7	2	1	188	188
7	2	2	16	-9
7	2	3	160	156
7	2	4	18	-15
7	3	-5	262	270
7	3	-4	70	72
7	3	-3	182	181
7	3	-2	100	99
7	3	-1	210	-225
7	3	0	26	-28
7	3	1	294	-297
7	3	2	66	-63
7	3	3	88	102
7	3	4	58	-61
7	4	-5	44	39
7	4	-4	113	-122
7	4	-3	252	250
7	4	-2	25	32
7	4	-1	241	245
7	4	0	81	85
7	4	1	169	-164
7	4	2	8	4
7	4	3	176	-180
7	5	-3	127	-111
7	5	-2	79	-84
7	5	-1	153	153
7	5	0	12	18
7	5	1	224	228
7	5	2	82	83
7	6	-1	48	53
8	0	-4	114	102
8	0	-2	234	234
8	0	0	82	73
8	0	2	20	-17
8	1	-4	233	-240
8	1	-3	41	-35
8	1	-2	80	-79
8	1	-1	34	42
8	1	0	201	217
8	1	1	24	20
8	1	2	152	154
8	2	-4	105	122
8	2	-3	25	23
8	2	-2	224	-221
8	2	-1	42	-37
8	2	0	170	-176
8	2	1	0	7
8	2	2	187	187
8	3	-3	45	44
8	3	-2	27	-23
8	3	-1	35	37
8	3	0	285	-304
8	3	1	7	-8

$[Na_2(OH_2)_7]^{2+}$. These chains parallel [010] are arranged in $x=0$, $z=\frac{1}{2}$ and $x=\frac{1}{2}$, $z=0$ in such a way that they lie approximately in layers parallel (101). Between these sodium–water layers are layers containing the AsO_3OH (or PO_3OH) groups (Fig. 3). The tetrahedral groups and the sodium–water columns are linked through hydrogen bonds alone. Consequently the compounds can be formulated as $[Na_2(OH_2)_7][AsO_3OH]$ and $[Na_2(OH_2)_7][PO_3OH]$.

Inspection of Figs. 1 and 2 reveals that the planes at $y=\frac{1}{4}$ and $y=\frac{3}{4}$ (where the glide planes are situated) also are pseudo-mirror planes. The atoms As(or P), O(1),

Table 7. $[Na_2(OH_2)_7]$ $[PO_3OH]$ *observed and calculated structure factors* (× 5)

Unobserved structure factors are omitted.

H	K	L	FO	FC
0	0	2	408	402
0	0	4	571	-529
0	0	6	188	192
0	0	8	149	158
0	0	12	71	-71
0	1	1	70	-60
0	1	2	492	474
0	1	3	120	104
0	1	4	406	-361
0	1	6	124	-112
0	1	7	60	-82
0	1	8	50	41
0	1	10	56	69
0	1	12	133	119
0	2	0	461	-397
0	2	2	130	-102
0	2	3	105	-88
0	2	4	66	-66
0	2	6	151	165
0	2	7	64	63
0	2	8	183	183
0	2	10	93	-109
0	3	1	36	36
0	3	2	170	105
0	3	3	108	96
0	3	4	365	383
0	3	5	154	-159
0	3	6	232	244
0	3	8	251	253
0	3	9	62	70
0	3	10	92	97
0	3	12	62	-55
0	4	0	793	752
0	4	1	87	-78
0	4	2	126	-106
0	4	3	61	66
0	4	4	520	-572
0	4	6	186	-191
0	4	7	91	-93
0	5	2	165	165
0	5	3	68	-62
0	5	4	226	-223
0	5	6	233	-225
0	5	8	55	-59
0	5	9	44	-32
0	6	0	470	-483
0	6	1	45	51
0	6	2	286	-290
0	6	4	60	-60
0	6	7	55	59
0	7	1	57	89
0	7	2	107	-106
0	7	5	96	-100
0	7	9	63	68
0	7	10	98	-102
0	7	12	90	-94
0	8	0	477	482
0	8	1	92	114
0	8	2	167	178
0	8	3	101	102
0	8	4	110	-111
0	8	5	58	-67
0	8	7	72	-72
0	8	8	63	63
0	9	1	90	-106
0	9	3	99	91
0	9	4	99	-107
0	9	6	119	-110
0	10	0	131	-18
0	10	2	64	54
0	10	3	49	-43
0	10	4	95	103
0	10	6	98	94
0	11	4	73	74
0	11	5	92	100
0	11	7	52	-51
0	11	8	87	91
0	12	4	67	-68
0	13	1	69	-62
0	13	2	58	58
0	13	6	48	-13
0	14	2	57	-51
1	0	-11	160	152
1	0	-9	177	176
1	0	-7	187	200
1	0	-3	395	-382
1	0	-1	52	-50
1	0	1	67	70
1	0	3	264	-233
1	0	5	529	-531
1	0	7	320	-330
1	0	13	62	-64
1	1	-11	53	65
1	1	-9	88	102
1	1	-8	100	-104
1	1	-7	67	81
1	1	-5	333	345
1	1	-4	116	109
1	1	-3	60	60
1	1	-1	264	-234
1	1	0	51	-53
1	1	1	193	167
1	1	2	64	-62
1	1	3	276	253
1	1	4	37	38
1	1	5	66	82
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1	1	8	40	-33
1	1	9	110	-111
1	1	11	58	49
1	2	-13	70	83
1	2	-10	53	50
1	2	-9	51	-42
1	2	-7	306	-319
1	2	-6	79	-76
1	2	-5	58	-50
1	2	-3	582	505
1	2	-2	77	72
1	2	-1	101	-92
1	2	0	96	85
1	2	1	509	-469
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1	2	3	282	-247
1	2	4	110	-113
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1	2	6	97	99
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1	3	11	97	-91
1	3	13	61	-74
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1	4	-5	97	-88
1	4	-4	99	-102
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1	5	-3	49	-47
1	5	-2	33	-28
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1	5	1	289	-290
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1	5	4	76	-78
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1	5	7	208	-215
1	5	8	45	36
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1	6	-10	47	32
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1	6	4	114	-124
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1	9	5	129	124
1	9	7	111	-117
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1	10	-2	81	83
1	10	0	57	58
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1	10	3	232	-227
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7	7	-5	85	100
7	7	-4	52	62
7	7	-2	66	55
7	7	-1	121	-121
7	7	2	46	-51
7	7	3	100	102
7	8	-7	73	-80
7	8	-6	57	-48
7	8	-5	61	-57
7	8	-4	51	-45
7	8	0	63	72
7	8	1	175	-163
7	8	3	92	-97
7	8	4	47	-42
7	8	5	50	48
7	8	7	56	61
7	9	-3	99	-96
7	9	1	125	123
7	9	2	58	65
7	9	5	56	-50
7	10	-3	52	-57
7	10	-1	90	-88
7	11	-5	68	78
7	11	-3	49	40
7	11	-2	55	52
7	11	1	65	-68
7	11	2	55	-64
8	0	-8	174	-191
8	0	-6	67	-65
8	0	-4	114	108
8	0	-2	137	135
8	0	0	65	67
8	0	2	87	93
8	0	4	128	117
8	0	6	128	113
8	0	8	123	131
8	1	-7	55	70
8	1	-6	47	-52
8	1	-4	113	-121
8	1	-3	45	-43
8	1	-2	73	-84
8	1	-1	52	63
8	1	0	102	117
8	1	2	116	118
8	1	3	53	-52
8	1	6	100	-106
8	2	-6	112	96
8	2	-5	63	64
8	2	-4	159	173
8	2	-2	118	-110
8	2	0	128	-138
8	2	2	132	132
8	2	4	97	102
8	2	6	102	-104
8	2	7	51	28
8	2	8	107	-106
8	3	-11	58	-13
8	3	-8	85	-92
8	3	-6	153	-146
8	3	0	222	-234
8	3	2	185	-179
8	3	6	144	143
8	4	-8	78	-86
8	4	-6	76	-81
8	4	0	90	-88
8	4	2	91	-91
8	4	3	54	48
8	4	4	80	-86
8	4	5	50	-28
8	4	8	74	79
8	4	9	52	33
8	5	-10	47	22
8	5	-8	48	40
8	5	-5	41	19
8	5	-3	50	-46
8	5	-1	50	-30
8	5	0	99	101
8	5	2	97	110
8	5	6	133	-138
8	6	-6	109	101
8	6	-2	134	-126
8	6	-1	45	-37
8	6	0	93	-97
8	6	1	51	-56
8	6	6	89	-88
8	6	8	122	-132
8	7	-4	155	150
8	7	-1	56	55
8	7	0	56	-64
8	7	2	46	-33
8	7	3	54	-62
8	7	6	80	68
8	8	-8	62	-67
8	8	-6	77	-71
8	8	-2	85	84
8	9	-7	65	60
8	9	-5	57	23
8	9	-2	43	16
8	9	2	84	88
8	10	-4	67	67
8	10	1	62	-68
8	11	-1	75	77
8	11	0	68	-84
9	0	-9	62	55
9	0	-5	47	44
9	0	-3	99	102
9	0	-1	91	88
9	0	3	126	-115
9	0	5	83	-92
9	1	-9	108	105
9	1	-7	105	108
9	1	-3	42	20
9	1	1	92	98
9	1	3	101	100
9	1	6	43	17
9	2	-7	111	111
9	2	-5	57	49
9	2	-4	52	50
9	2	-1	111	-111
9	2	1	99	-101
9	2	3	118	110
9	2	5	103	100
9	2	7	76	-71
9	3	-10	52	26
9	3	-6	56	-39
9	3	-4	43	37
9	3	-3	82	92
9	3	-1	192	191
9	3	1	57	57
9	3	3	51	-60
9	3	5	75	79
9	3	7	92	99
9	3	8	49	13
9	4	-7	98	-95
9	4	-5	51	-56
9	4	-1	62	57
9	4	0	42	-17
9	4	1	74	85
9	4	4	45	26
9	4	5	61	-46
9	4	6	70	-49
9	5	-9	60	66
9	5	-7	99	92
9	5	-4	54	48
9	5	-3	63	-61
9	5	4	83	67
9	6	-7	66	69
9	6	-3	105	-109
9	6	-1	74	-65
9	6	2	55	-48
9	6	3	83	82
9	6	5	114	110
9	7	-7	70	-78
9	7	-3	79	-80
9	7	-2	47	34
9	7	3	135	-138
9	9	-2	52	-42
9	9	0	51	-57
9	10	-2	57	57
10	0	-6	117	-112
10	0	-4	198	-198
10	0	-2	80	-76
10	0	0	123	119
10	0	4	47	-48
10	1	-8	55	63
10	1	-6	58	49
10	1	-2	84	-72
10	2	-6	75	93
10	2	-4	62	51
10	2	-2	91	-100
10	2	0	114	-107
10	3	-3	40	11
10	3	0	63	-72
10	3	2	100	-101
10	3	4	52	-55
10	4	-8	77	70
10	4	-4	55	-50
10	4	0	198	183
10	4	2	117	102
10	4	3	48	48
10	4	4	48	-49
10	4	6	59	-70
10	5	-6	48	34
10	5	1	59	-65
10	6	-6	142	146
10	6	-4	74	70
10	7	-3	47	-11
10	7	2	49	28
10	8	-4	74	-74
10	8	0	52	50
11	0	-7	91	98
11	0	-5	61	-57
11	0	-1	167	168
11	0	1	92	95
11	0	3	58	50
11	1	-3	91	-90
11	1	-1	55	-65
11	2	-7	98	-68
11	2	-3	80	83
11	2	1	81	-65
11	3	-5	122	-125
11	3	-1	68	72
11	4	-5	88	-104
11	4	-3	90	-87
11	5	-5	55	47
11	6	-1	58	-57
11	6	1	66	-72
12	0	-4	84	-76
12	0	-2	89	-76
12	1	-4	81	74
12	2	-4	49	35
12	2	-2	116	111
12	3	-2	79	63

O(2), O(*w*5), O(*w*6) and O(*w*7) are in or close to these planes, while Na(1) and Na(2), O(*w*8) and O(*w*10), O(*w*9) and O(*w*11) are arranged in pairs to both sides of them. Only O(3) and O(*h*4) definitely do not obey this pseudo-symmetry. This is understandable in view of the fact that these two oxygen atoms serve chemically different functions in this structure: to one of them, to O(*h*4), the acidic hydrogen atom is attached, the other one serves only as acceptor of hydrogen bonds. It is tempting to speculate that in a similar structure where all the oxygen atoms of the tetrahedral anion are equivalent this plane would be a true mirror plane. This might conceivably be the case in $Na_2SO_4.7H_2O$, the crystal structure of which however is not known.

The following criteria were used to decide if a particular oxygen–oxygen contact corresponds to a hydrogen bond:

(*a*) The distance should be smaller than 3·1 Å.

(*b*) The contact should not be the edge of a coordination polyhedron.

(*c*) The bond angle geometry should be within acceptable limits (specifically the angle Na–O(*w*)–O(acceptor) should be larger than 95°, and the angle O(acceptor)–O(*w*)–O(acceptor) should not deviate by more than 35° from the tetrahedral angle).

Fifteen distances in the asymmetric unit satisfied these criteria, that is as many as there are hydrogen atoms available [see Fig. 3 and Table 8(*c*)]. In the tetrahedral group O(1), O(2) and O(3) are acceptor atoms for four hydrogen bonds each. The coordination of these atoms resembles a tetrahedral pyramid, the base of which is formed by the four hydrogen bond donors and the apex is the P (or As) atom. To the best of our knowledge such an arrangement has not been found in other crystal structures. However one would expect it to be common in highly hydrated orthophosphate, orthovanadate and orthoarsenate salts, because the bond strength received (Baur, 1962; Pauling, 1960) by an oxygen atom in these groups from the central cation is $\frac{5}{4}$ and therefore four (or five) long hydrogen bonds are needed to balance the charge of the oxygen atom (see Table 9 and Fig. 4). Atom O(*h*4) is involved in two hydrogen bonds. This, and the fact that the X–O(*h*4) distance in both compounds is significantly longer than the average of the tetrahedral bonds makes it certain that O(*h*4) is the oxygen atom linked to the acidic hydrogen atom. The O(*h*4) → O(*w*9) bond lengths are almost identical in both salts [see Table 8(*c*)]. While they are longer than the O(*h*) → O hydrogen bond of 2·48 Å in KH_2PO_4 (Bacon & Pease, 1955) they nevertheless are the shortest hydrogen bonds in both the $[Na_2(OH_2)_7]$ $[XO_3OH]$ compounds. Of the water oxygen atoms all but O(*w*9) and O(*w*11) are bonded to the two Na^+ ions each. These two water molecules accept one hydrogen bond each: O(*w*9) from O(*h*4), and O(*w*11) from O(*w*9). The water molecules which are coordinated to two Na^+ ions do not accept any hydrogen bonds. The O(*w*11) → O(*w*9) hydrogen bond is the only one which connects the sodium-water columns directly with each other. All other hydrogen bonds are between the tetrahedral groups on one side, and the water molecules of the octahedral chains on the other side. The water molecules are tetrahedrally surrounded by four bonds: the two hydrogen bonds which they donate, and by two Na^+ atoms (in five cases), or by one Na^+ atom and one hydrogen bond which they receive (in the case of the other two water molecules, O(*w*9) and O(*w*11)).

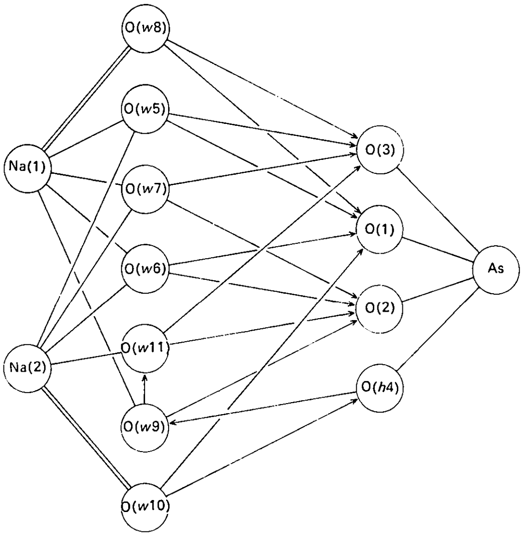

Fig. 4. $[Na_2(OH_2)_7]$ $[AsO_3OH]$, hydrogen bonding scheme.

Based on this hydrogen bonding scheme probable hydrogen atom positions were calculated for $[Na_2(OH_2)_7]$ $[AsO_3OH]$ (see Table 4). The following assumptions were made in the calculation:

(1) The O–H distance is 0·97 Å.

(2) The H–O(*w*)–H angle is 109·5°.

(3) The hydrogen bond formed by the acidic hydrogen atom is linear.

(4) The plane of the water molecule (which contains the oxygen atom and the two hydrogen atoms) is halfway between the plane defined by the water oxygen atom and the two acceptor oxygen atoms on one side, and the vector bisecting the angle M–O(*w*)–M on the other side (where M is either a Na^+ atom or a hydrogen bond donor). This condition makes the surroundings of the water oxygen atoms more 'tetrahedral' than they would be otherwise.

(5) The hydrogen atoms are positioned as far as possible away from the M atoms.

The hydrogen atoms thus placed result in H–O(acceptor) distances ranging from 1·69 to 2·09 Å. None of the H–H distances is shorter than 2·05 Å (except for hydrogen atoms belonging to the same water molecule) and none of the Na–H distances is shorter than 2·80 Å. Therefore, the postulated positions of the hydrogen atoms seem plausible and are believed to be within 0·2

Å of their true positions as one could determine them by neutron diffraction methods. After the foregoing discussion it seems reasonably certain that the hydrogen bonding scheme as explained above and illustrated in Figs. 3 and 4 and in Table 8(*c*) is correct even though we were not able to find direct proof of the hydrogen atom positions in the difference syntheses.

The corresponding individual hydrogen bond distances in the two salts deviate up to 0·046 Å from each other. Some of the differences are highly significant. The average distances however are nearly identical. Therefore the result of this investigation is negative. The bond distances do not reflect an influence of the anion on the lengths of the hydrogen bonds in the case of this pair of isomorphous arsenate and phosphate salts.

The range of the lengths of the hydrogen bonds donated by the water molcecules is 2·72 to 3·05, or 0·33 Å. This is similar to the spread found for example in $MgSO_4 \cdot 7H_2O$: 2·70 to 2·98 Å (Baur, 1964). Such a range appears to be typical of hydrated structures which are held together solely by hydrogen bonds, and where therefore the hydrogen donor and acceptor interactions determine the distances. This spread is small when compared with the one found in less hydrated compounds where the cohesion of the structure is provided by a framework of coordination polyhedra around the cations. In such structures the hydrogen

Table 8. *Interatomic distances and bond angles*

(*a*) Coordination around Na^+

	As salt	P salt
Na(1)–O(*w*5)	2·416 (5) Å	2·392 (6) Å
Na(1)–O(*w*6)	2·479 (5)	2·456 (7)
Na(1)–O(*w*7)	2·464 (5)	2·449 (7)
Na(1)–O(*w*8)	2·439 (5)	2·396 (7)
Na(1)–O(*w*8)	2·482 (5)	2·465 (6)
Na(1)–O(*w*9)	2·365 (5)	2·370 (6)
Averages of 6 Na–O(*w*) bonds	2·441 Å	2·421 Å
Range of the 'right' angles O(*w*)–Na(1)–O(*w*)	76·4–108·1°	76·9–104·5°
Range of the 'straight' angles O(*w*)–Na(1)–O(*w*)	158·3–171·3	159·6–174·7
Na(2)–O(*w*5)	2·402 (5) Å	2·400 (6) Å
Na(2)–O(*w*6)	2·509 (5)	2·486 (7)
Na(2)–O(*w*7)	2·486 (5)	2·466 (7)
Na(2)–O(*w*10)	2·368 (5)	2·341 (7)
Na(2)–O(*w*10)	2·444 (5)	2·434 (7)
Na(2)–O(*w*11)	2·391 (5)	2·366 (6)
Averages of 6 Na–O(*w*) bonds	2·433 Å	2·416 Å
Averages of 12 Na–O(*w*) bonds	2·437	2·418
Range of the 'right' angles O(*w*)–Na(2)–O(*w*)	75·4–104·5°	76·1–106·1
Range of the 'straight' angles O(*w*)–Na(2)–O(*w*)	157·0–178·1	157·3–176·4
Range of O(*w*)–O(*w*) distances in the Na-coordination octahedra	3·053–3·890 Å	3·025–3·837 Å
Na(1)–Na(1)	3·608 (3) Å	3·543 (5) Å
Na(1)–Na(2)	3·249 (3)	3·197 (5)
Na(2)–Na(2)	3·490 (3)	3·460 (5)

(*b*) Tetrahedral coordination

	As salt	P salt
X–O(1)	1·654 (5) Å	1·535 (5) Å
X–O(2)	1·669 (5)	1·522 (6)
X–O(3)	1·662 (4)	1·529 (6)
X–O(*h*4)	1·728 (4)	1·618 (6)
Averages of 3 short bonds	1·662 Å	1·529 Å
Averages of 4 X–O bonds	1·678	1·551
O(1)–O(2)	2·770 (7) Å	2·537 (7) Å
O(1)–O(3)	2·776 (6)	2·573 (7)
O(1)–O(*h*4)	2·642 (6)	2·462 (8)
O(2)–O(3)	2·760 (6)	2·537 (8)
O(2)–O(*h*4)	2·732 (5)	2·522 (8)
O(3)–O(*h*4)	2·738 (5)	2·538 (9)
O(1)–X–O(2)	113·0 (2)°	112·2 (3)°
O(1)–X–O(3)	113·7 (2)	114·2 (3)
O(1)–X–O(*h*4)	102·7 (2)	102·7 (3)
O(2)–X–O(3)	111·9 (2)	112·5 (3)
O(2)–X–O(*h*4)	107·0 (2)	106·9 (3)
O(3)–X–O(*h*4)	107·7 (2)	107·5 (3)

Table 8 (*cont.*)

(*c*) Hydrogen bond geometry

	As salt	P salt
O(*h*4) → O(*w*9)	2·662 (5) Å	2·658 (8) Å
O(*w*5) → O(1)	2·831 (8)	2·790 (8)
O(*w*5) → O(3)	2·845 (6)	2·809 (8)
O(*w*6) → O(1)	2·818 (7)	2·781 (8)
O(*w*6) → O(2)	2·809 (7)	2·850 (7)
O(*w*7) → O(2)	2·884 (7)	2·864 (8)
O(*w*7) → O(3)	2·815 (6)	2·825 (7)
O(*w*8) → O(1)	2·899 (6)	2·907 (9)
O(*w*8) → O(3)	3·004 (6)	3·050 (9)
O(*w*9) → O(2)	2·894 (5)	2·894 (8)
O(*w*9) → O(*w*11)	2·835 (6)	2·855 (8)
O(*w*10) → O(1)	2·767 (6)	2·773 (8)
O(*w*10) → O(*h*4)	2·789 (6)	2·779 (8)
O(*w*11) → O(2)	2·831 (5)	2·861 (8)
O(*w*11) → O(3)	2·720 (5)	2·737 (8)
Averages of 14 bonds donated by water molecules	2·839 Å	2·841 Å
Range of distances H---O (acceptor)	1·69–2·09 Å	
X—O(*h*4)—O(*w*9)	126·3 (2)°	128·0 (3)°
O(1)-O(*w*5)—O(3)	133·1 (2)	134·6 (3)
O(1)-O(*w*6)—O(2)	112·8 (2)	116·2 (3)
O(2)-O(*w*7)—O(3)	102·4 (2)	103·7 (2)
O(1)-O(*w*8)—O(3)	143·3 (2)	144·1 (3)
O(2)-O(*w*9)—O(*w*11)	117·3 (2)	117·3 (3)
O(1)-O(*w*10)-O(*h*4)	117·9 (2)	121·2 (3)
O(2)-O(*w*11)-O(3)	128·1 (2)	130·0 (3)
Range of angles Na–O(*w*)–Na	81·3–94·3°	80·6–93·6°
Range of other angles in the 'tetrahedral' water coordination	81·2–128·6°	83·2–129·0°
Range of angles O(*w*)–H---O (acceptor)	131–177°	

bonding is relatively unimportant for the lattice energy of the compound. Consequently the hydrogen bonding distances will be influenced by the steric requirements of the framework. Examples for this are: metavauxite, $[AlPO_4OHOH_2]_2[Fe(OH_2)_6]$ (Baur & Rama Rao, 1967) and vauxite, $FeAl_2(PO_4)_2(OH)_2\cdot 6H_2O$ (Baur & Rama Rao, 1968) where the lengths of the hydrogen bonds vary over a range of 0·58 Å, from 2·58 to 3·16 Å.

An unexpected difference is apparent between the Na–O(*w*) distances in the two compounds. The average of the Na–O(*w*) bonds in the arsenate salt is 0·019 Å longer than in the phosphate salt; with one exception (which is not significant) the individual bond distances are also longer, many of them significantly so. The effect appears to be real; a cause for it is not known. Since no analogous pairs of salts have been determined with comparable accuracy it is not known if this effect occurs in other cases as well. The difference in Na–O(*w*) bond lengths is reflected in the *b* cell length of the phosphate compound which is 0·2% shorter than the corresponding unit-cell edge of the arsenate. The length of *b* is determined by the repeat distance of the sodium–water columns. The *a* and *c* cell edges are influenced by the dimensions of the tetrahedral group as well. Therefore they differ in the two salts by 1·5 and 2·2%.

Chains of sodium–water coordination octahedra similar to those found here have been described by Wunderlich (1958) in $[Na_2(OH_2)_7]\,[OH]_2$. The octahedra are also sharing alternately faces and edges but they are topologically distinct from the columns in $[Na_2(OH_2)_7]\,[XO_3OH]$ and the chains do not posses pseudo-mirror planes. The different arrangement of the coordination octahedra causes the repeat distance in the direction of the chain to be distinctly longer (11·64 Å) in $[Na_2(OH_2)_7]\,[OH]_2$ than it is in the $[Na_2(OH_2)_7]\,[XO_3OH]$ compounds.

The sums of electrostatic bond strengths ζ (Pauling, 1960), shown in Table 9, are calculated under the assumption that each hydrogen bond contributes $\frac{1}{6}$ of one bond strength to the acceptor atom [column H(*a*)]. The remaining $\frac{5}{6}$ of the bond strength are counted towards the sum of the bond strengths of the atom donating the hydrogen bond [column H(*d*)]. This was found to be a reasonable assumption in many salt hydrates studied previously (Baur, 1962). It is apparent from Table 9 that the charges of the water molecules are balanced by the ζ's received. Despite this perfect balance we see from Table 8(*a*) that the spread of Na–O(*w*) distances is 0·15 Å, from 2·37 to 2·51 Å in the arsenate salt, from 2·34 to 2·49 Å in the phosphate salt. This probably is correlated with the distortions of the coordination octahedra due to the sharing of the faces and the edges. This distortion is also reflected in the spread of the bond angles subtended at the sodium atoms. Ideally these angles should be 90° and 180°, but instead they deviate from these values up to 23°. The oxygen atoms of the tetrahedral anion are partly undersaturated [O(1), O(2) and O(3)] and one is clearly oversaturated [O(*h*4)]. Consequently the bond distances X–O(1), X–O(2) and X–O(3) are significantly shorter, while X–O(*h*4) is significantly longer than the average for the tetrahedral group, thus maintaining an effective balance of electrostatic bond strength versus charge for the oxygen atoms. This conforms with the extended electrostatic valence rule (Baur, 1961).

The shape of orthophospate and orthoarsenate groups

An inspection of Table 8(*b*) reveals that all the bond angles in both tetrahedral anions deviate significantly from the values expected for a tetrahedral angle (109·5°). The angles fall into two classes: those involving O(*h*4) are smaller than the tetrahedral angle, the other ones are larger than the tetrahedral angle. We looked at the dimensions of similar anions in other crystal structures and found that the same was true not only for XO_3OH, but also for $XO(OH)_3$ and $XO_2(OH)_2$ groups. Two representative examples are detailed in Table 10. In order to show the prevailing pattern we have compiled in Table 11 the pertinent averaged data for 16 different tetrahedral groups. The estimated standard deviations of the individual bond lengths which were used for the averages presented in Table 11 are with one exception better than 0·01 Å. The exception is $H_3AsO_4\cdot\frac{1}{2}H_2O$ the bond lengths for which have standard deviations of about 0·02 Å. With one exception all longer bonds [X–O(*l*)] in this Table are X–O(*h*) bonds, that is bonds to oxygen atoms which have acidic hydrogen atoms attached to them. The exception is the phosphate group in di-*p*-chlorophenyl hydrogen phosphate: in this case the short P–O bond is the one to which the hydrogen atom is linked, while the long P–O bond leads to the oxygen atom which is bonded covalently to a carbon atom. This serves to show that the distortions of the angles are primarily not correlated with the O(*h*) atoms in the tetrahedral groups, but with the atoms which form the longer bonds to the central atom. The preponderance in Table 11 of tetrahedral groups which contain oxygen atoms linked to hydrogen atoms is simply caused by the fact that in such groups we observe the largest differences between individual X–O distances.

It should be observed that within each group the averaged O–O distances in Table 11 differ only about 1 or

Table 9. *Electrostatic bond strengths in* $[Na_2(OH_2)_7]$ $[AsO_3OH]$ (Baur, 1962; Pauling, 1960)

	Na(1)	Na(2)	As	H(*d*)	H(*a*)	ζ
O(1)			1·25		4 × 0·17	1·92
O(2)			1·25		4 × 0·17	1·92
O(3)			1·25		4 × 0·17	1·92
O(*h*4)			1·25	0·83	0·17	2·25
O(*w*5)	0·17	0·17		2 × 0·83		2·00
O(*w*6)	0·17	0·17		2 × 0·83		2·00
O(*w*7)	0·17	0·17		2 × 0·83		2·00
O(*w*8)	2 × 0·17			2 × 0·83		2·00
O(*w*9)	0·17			2 × 0·83	0·17	2·00
O(*w*10)		2 × 0·17		2 × 0·83		2·00
O(*w*11)		0·17		2 × 0·83	0·17	2·00

Table 10. *Geometry of an* $H_2PO_4^-$ group $[N_2H_6(H_2PO_4)_2]$ (Liminga, 1966) and of an H_3PO_4 group $[H_3PO_4]$ (Cole & Peterson, 1964)

(*a*) $H_2PO_4^{1-}$ group			
P–O(1)	1·504 (3) Å		
P–O(*h*2)	1·572 (3)		
P–O(*h*3)	1·556 (3)		
P–O(4)	1·515 (3)		
O(1)—P–O(*h*2)	110·4 (1)°	O(1)—O(*h*2)	2·525 (4) Å
O(1)—P–O(*h*3)	108·4 (2)	O(1)—O(*h*3)	2·482 (4)
O(1)—P–O(4)	115·5 (2)	O(1)—O(4)	2·554 (4)
O(*h*2)–P–O(*h*3)	106·5 (2)	O(*h*2)–O(*h*3)	2·506 (4)
O(*h*2)–P–O(4)	107·2 (1)	O(*h*2)–O(4)	2·484 (3)
O(*h*3)–P–O(4)	108·5 (2)	O(*h*3)–O(4)	2·492 (3)
(*b*) H_3PO_4 group			
P–O(1)	1·496 (3) Å		
P–O(*h*2)	1·545 (2)		
P–O(*h*3)	1·548 (2)		
P–O(*h*4)	1·545 (3)		
O(1)—P–O(*h*2)	112·0 (1)°	O(1)—O(*h*2)	2·522 (3) Å
O(1)—P–O(*h*3)	113·2 (1)	O(1)—O(*h*3)	2·543 (3)
O(1)—P–O(*h*4)	113·0 (1)	O(1)—O(*h*4)	2·537 (3)
O(*h*2)–P–O(*h*3)	105·6 (1)	O(*h*2)–O(*h*3)	2·464 (3)
O(*h*2)–P–O(*h*4)	107·3 (1)	O(*h*2)–O(*h*4)	2·489 (3)
O(*h*3)–P–O(*h*4)	104·9 (1)	O(*h*3)–O(*h*4)	2·453 (3)

2% while the corresponding angles differ by 5 to 8%. From this it can be concluded that we are dealing with a steric effect: the larger the 'tetrahedral' angles, the shorter the bonds, which form their sides, and *vice versa*, while the O–O distances (the edges of the tetrahedra) stay relatively constant. One could also say that since the oxygen atoms stay more or less in place, the central P or As atom is displaced within the tetrahedron toward the sides which display the larger tetrahedral angles. This is demonstrated by the numbers shown in Table 11 in three independent ways: (1) by the comparison of the data for the PO_3OH groups with those for the $PO(OH)_3$ groups, (2) the same for the arsenates and (3) by the angles of the $PO_2(OH)_2$ groups, which fall neatly into three categories, greater than the tetrahedral angle, about equal to the tetrahedral angle, and smaller than the tetrahedral angle. This steric effect should be best displayed when the tetrahedral group is not engaged in strong links to other elements of the crystal structure. A case in point is haidingerite, $CaHAsO_4.H_2O$, where the smallest of the group of the large angles actually is smaller than the average of the small angles; this shows even in the average, because the angle O(*s*)–X–O(*s*) of haidingerite is the smallest of these angles in Table 11. The reason for this seems to be that the O–O tetrahedral edge corresponding to this angle is a shared one with the Ca^{2+}-coordination polyhedron and therefore is shortened.

The average P–O bond distance for all the phosphate groups in the Table is 1·539 Å, the As–O distance (disregarding the less accurate $H_3AsO_4\cdot\frac{1}{2}H_2O$ determination) is 1·680 Å. There is no doubt that some of the averages of individual phosphate groups are significantly different from the overall average. This shows that the common assumption (Cruickshank, 1961) that the average P–O distance in tetrahedral groups is constant, is not strictly true. This is in contrast to the case of the sulfate group for which the average value of the S–O bond length of 1·473 Å (Baur, 1964) has since been confirmed by numerous new determinations (one example is $CuSO_4.3H_2O$ with S–O = 1·472 Å, Zahrobsky & Baur, 1968). Similarly there are unexplained, but significant, differences in individual P–O distances. The largest spread is observed for the P–O(*h*) distance in the PO_3OH groups: it ranges from 1·563 to 1·618 Å. Therefore one cannot expect the average values for the different $XO(s)_nO(l)_{4-n}$ groups to represent an 'ideal' shape for these groups.

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After the paper was submitted for publication we learned that Ferraris & Chiari (1970) had independently solved the crystal structure of the arsenate com-

Table 11. *Average interatomic distances and angles of phosphate and arsenate groups in accurately determined crystal structures*

O(*s*) and O(*l*) mean the oxygen atoms which form the shorter and longer bonds to the central atom of the tetrahedral group. The number of individual values used in averaging is indicated in square brackets following the value. X–O(*s*), O(*l*) refers to the average of all four tetrahedral bonds in the group.

Compound	Reference	X–O(*s*), O(*l*)	X–O(*s*)
$[Na_2(OH_2)_7][PO_3OH]$	This work	1·551 Å [4]	1·529 Å [3]
Newberyite, $MgHPO_4.3H_2O$	Sutor (1967)	1·544	1·522
Spermidine phosphate trihydrate	Huse & Iitaka (1969)	1·533	1·523
		1·534	1·511
		1·541	1·520
Averages for $PO(s)_3O(l)_1$ group:		1·541 Å	1·521 Å
Di-*p*-chlorophenyl hydrogen phosphate	Calleri & Speakman (1964)	1·539 Å [4]	1·498 Å [2]
$N_2H_6(H_2PO_4)_2$	Liminga (1966)	1·537	1·510
$N_2H_5(H_2PO_4)$	Liminga (1965)	1·534	1·506
KH_2PO_4	Bacon & Pease (1955)	1·546	1·502
Averages for $PO(s)_2O(l)_2$ group:		1·539 Å	1·504 Å
H_3PO_4	Cole & Peterson (1964)	1·534 Å [4]	1·496 Å [1]
$H_3PO_4.\frac{1}{2}H_2O$	Mighell, Smith & Brown (1969)	1·541	1·503
		1·533	1·477
Averages for $PO(s)_1O(l)_3$ group:		1·536 Å	1·492 Å
$[Na_2(OH_2)_7][AsO_3OH]$	This work	1·678 Å [4]	1·662 Å [3]
Haidingerite, $CaHAsO_4.H_2O$	Calleri & Ferraris (1967)	1·682	1·653
Averages for $AsO(s)_3O(l)_1$ group:		1·680 Å	1·658 Å
$H_3AsO_4.\frac{1}{2}H_2O$	Worzala (1968)	1·651 Å [4]	1·594 Å [1]
		1·675	1·621
Averages for $AsO(s)_1O(l)_3$ group:		1·663 Å	1·608 Å

Table 11 (*cont.*)

X–O(*l*)	O(*s*)–X–O(*s*)	O(*s*)–O(*s*)	O(*s*)–X–O(*l*)	O(*s*)–O(*l*)	O(*l*)–X–O(*l*)	O(*l*)–O(*l*)
1·618 Å [1]	114·2° [3]	2·549 Å [3]	105·7° [3]	2·507 Å [3]		
1·588	112·2	2·537	106·6	2·499		
1·563	111·7	2·520	107·1	2·482		
1·601	112·9	2·519	105·8	2·482		
1·602	112·4	2·526	106·3	2·499		
1·594 Å	112·7°	2·530 Å	106·3°	2·494 Å		
1·579 Å [2]	116·3° [1]	2·544 Å [1]	108·1° [4]	2·491 Å [4]	108·1° [1]	2·556 Å [1]
1·564	115·5	2·554	108·6	2·496	106·5	2·506
1·562	112·9	2·510	109·8	2·511	104·3	2·466
1·590	115·0	2·533	108·9	2·515	106·0	2·544
1·574 Å	114·9°	2·535 Å	108·9°	2·503 Å	106·2°	2·518 Å
1·546 Å [3]			112·7° [3]	2·534 Å [3]	105·9° [3]	2·469 Å [3]
1·553			112·7	2·544	106·1	2·483
1·551			110·9	2·495	108·0	2·509
1·550 Å			112·1°	2·524 Å	106·7°	2·487 Å
1·728 Å [1]	112·9° [3]	2·769 Å [3]	105·8° [3]	2·704 Å [3]		
1·768	111·3	2·761	107·7	2·727		
1·748 Å	112·1°	2·765 Å	106·8°	2·716 Å		
1·670 Å [3]			114·4° [3]	2·744 Å [3]	104·1° [3]	2·633 Å [3]
1·693			111·1	2·733	107·8	2·736
1·682 Å			112·8°	2·739 Å	106·0°	2·685 Å

pound. The two determinations agree in all essential features of the structures, including the proposed hydrogen bonding schemes. They disagree, however, by more than twice the pooled standard deviations in the values of three of the cell parameters and of 15 of the 42 atomic positional parameters. It is unlikely that the specimens used by the two groups of investigators really had slightly different crystal structures. Therefore, it is to be assumed that the accuracy of one of the two determinations, or of both, is not as high as the stated precisions would make us believe. We have to conclude that systematic errors in the measurement of one or both data sets played a larger role than we might have wished. We thank Drs Ferraris and Chiari for a copy of their manuscript.

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