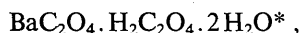


l'acide oxalique à température plus élevée. L'étude de la décomposition du sel  $\text{BaC}_2\text{O}_4\cdot\text{H}_2\text{C}_2\text{O}_4$  nous a en effet permis d'observer le dépôt, sur les parois froides de la thermobalance, de petits cristaux d'acide oxalique identifiés par analyse aux rayons X, cet acide s'étant bien entendu hydraté au contact de la vapeur d'eau contenue dans le tube.

L'ensemble de ces résultats conduit donc à écrire la formule du sel



ce qui traduit une représentation plus complète de ses propriétés. Nous indiquons par un astérisque que l'eau est liée faiblement par forces résiduelles.

### Références

- AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.  
 COX, E. G., DOUGILL, M. W. & JEFFREY, G. A. (1952). *J. Chem. Soc.* p. 4854.  
 HAAS, D. J. (1964). *Acta Cryst.* **17**, 1511.  
 HAHN, T. (1957). *Z. Kristallogr.* **109**, 438.  
 HODGSON, D. J. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 469.  
*International Tables for X-ray Crystallography* (1952). Vol. I. Birmingham: Kynoch Press.  
 MUTIN, J. C., WATELLE, G., PROTAS, J. & DUSAUSOY, Y. (1970). *Bull. Soc. Chim. Fr.* Sous presse.

*Acta Cryst.* (1970). **B26**, 1574

## The Crystal Structure of $\text{Na}_2\text{HASO}_4\cdot 7\text{H}_2\text{O}$

BY G. FERRARIS AND G. CHIARI

*Istituto di Mineralogia dell'Università and III Sezione del Centro Nazionale di Cristallografia del C.N.R., via S. Massimo 24, 10123 Torino, Italy*

(Received 21 July 1969)

$\text{Na}_2\text{HASO}_4\cdot 7\text{H}_2\text{O}$  crystallizes in the monoclinic system, space group  $P2_1/n$  ( $C_{2h}^2$ ). Unit-cell parameters are:  $a_0 = 10.6586$  (17),  $b_0 = 11.0107$  (22),  $c_0 = 9.3940$  (14) Å,  $\beta = 95^\circ 26'$  (1').  $Z = 4$ ,  $D_m = 1.874$ ,  $D_c = 1.843$  g.cm<sup>-3</sup>. The crystal structure was solved and refined using 2384 reflexions (95% of those accessible to Cu  $K\alpha$  radiation) to a final  $R$  value of 0.05; hydrogen atoms were located and included in the refinement. The structure contains layers normal to [101] in which the two crystallographically independent Na atoms coordinate six oxygen atoms of the water molecules. The Na-polyhedra form chains along [010], which are joined by hydrogen bonds. The  $\text{AsO}_4$  tetrahedra lie between these layers and link them by hydrogen bonds involving their own oxygen atoms and those of the water molecules.

The crystal structure of  $\text{Na}_2\text{HASO}_4\cdot 7\text{H}_2\text{O}$ , described in this paper, was studied as part of a programme of structural research on acid and hydrated arsenates. After studying some Ca arsenates (Calleri & Ferraris, 1967; Ferraris, 1969; Ferraris & Chiari, 1970) we selected this Na arsenate because the ratio of cations to water molecules suggested that the oxygen atoms of the  $\text{AsO}_4$  groups were not Na coordinated; this should permit a determination of distances and bond angles in an 'isolated'  $\text{AsO}_4$  tetrahedron.

### Experimental

#### Preparation and crystal data

$\text{Na}_2\text{HASO}_4\cdot 7\text{H}_2\text{O}$  crystals suitable for an X-ray study were obtained by recrystallization of the commercial product. It is possible to obtain single crystals with dimensions even larger than 1 cm by growing from a seed crystal in saturated aqueous solution at 60–80°C. The crystals always show a well-developed pinacoidal form and are thus usually tabular.

Several morphological studies have led to the classification of  $\text{Na}_2\text{HASO}_4\cdot 7\text{H}_2\text{O}$  as monoclinic prismatic and these are reported in the literature (e.g. Porter & Spiller, 1956).

X-ray analysis (based both on Weissenberg and precession photographs and single-crystal diffraction) confirmed the monoclinic prismatic symmetry. The absent reflexions  $h0l$  with  $h+l$  odd and  $0k0$  with  $k$  odd assigned the compound to the space group  $P2_1/n$  ( $C_{2h}^2$ ). The reciprocal unit-cell parameters were refined by a least-squares procedure using high  $\theta$  angles, measured at room temperature on a single-crystal diffractometer ( $\lambda\alpha_1 = 1.54050$ ,  $\lambda\alpha_2 = 1.54434$  Å); the following values (standard deviations in parentheses) were obtained for the direct unit-cell parameters:  $a_0 = 10.6586$  (17),  $b_0 = 11.0107$  (22),  $c_0 = 9.3940$  (14) Å,  $\beta = 95^\circ 26'$  (1').

On the basis of our X-ray measurements, we can say that the axial ratio quoted in the literature ( $a:b:c = 1.2294:1:1.3526$ ,  $\beta = 97^\circ 14'$ ) agrees with that of a non-primitive unit-cell with parameters:  $a_0 = 13.528$ ,  $b_0 =$

11-011,  $c_0 = 14.861 \text{ \AA}$ ,  $\beta = 97^\circ 15'$  ( $a_0 : b_0 : c_0 = 1.2286 : 1 : 1.3497$ ). The transformation matrix for the conversion of the indices of the non-primitive cell to those of our primitive cell is  $\frac{1}{2}0 - \frac{1}{2}/010/\frac{1}{2}0\frac{1}{2}$ ; thus the best-developed form and cleavage reported in literature are, in our system,  $\{101\}$  and  $\{10\bar{1}\}$  respectively.

During the present study we found that the powder spectrum of ASTM card No. 3-118 (*ASTM X-ray Powder Data file*) is incorrect. The results obtained by us from a powder spectrum of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  ( $\lambda\alpha_1 = 1.93597$ ,  $\lambda\alpha_2 = 1.93991 \text{ \AA}$ ; camera radius =  $143.2 \text{ mm}$ ) are reported in Table 1; the indices were also assigned on the basis of the intensity values measured on the single crystal. The powder spectrum of the arsenate studied is analogous to that (ASTM card No. 10-191) of the corresponding phosphate  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ ; this is in accordance with the results of the morphological study reported in Porter & Spiller (1956) ( $a : b : c = 1.2047 : 1 : 1.3272$ ,  $\beta = 96^\circ 57'$  for the phosphate). However, the values of the unit-cell parameters quoted for the phosphate ( $Z = 2$ ) (ASTM card No. 10-191) are not comparable, except for  $b_0$  and  $\beta$ , with those of the arsenate; on the basis of the powder spectra and of the morphological data the correctness of the phosphate unit-cell parameters seems questionable.

Table 1. Observed and calculated  $d$  spacings, indices and intensities (on an arbitrary scale) of the reflexions of the powder spectrum of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$

(Fe  $K\alpha$  radiation; camera radius =  $143.2 \text{ mm}$ .)

$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{obs}}$
7.64 Å	7.641 Å	110	wv
7.14	7.128	011	wv
6.71	6.708	101	s
6.14	6.125	$\bar{1}11$	vs
5.71	5.729	111	vs
5.52	5.505	020	vs
5.30	5.306	200	s
4.79	4.780	210	vs
4.403	4.4108	$\bar{1}21$	wv
4.297	4.3039	012	vs
4.118	4.1162/4.1151	211/ $\bar{1}12$	wv
3.864	3.8726	112	wv
3.691	3.6852	$\bar{2}02$	wv
3.626	3.6241	$\bar{2}21$	wv
3.568	3.5640	022	wv
3.495	3.4947	$\bar{2}12$	m
3.417	3.4171	301	m
3.358	3.3541	202	wv
3.289	3.2855	$\bar{1}31$	vs
3.210	3.2094/3.2085	301/212	w
3.072	3.0812/3.0705/3.0624	311/ $\bar{1}03/\bar{2}22$	vs
2.958	2.9577	$\bar{1}13$	s
2.903	2.9033	$\bar{3}21$	s
2.866	2.8644	222	vs
2.823	2.8284/2.8280/2.8199	321/ $\bar{1}32/113$	wv
2.757	2.7527	040	s
2.717	2.7193	$\bar{2}13$	wv
2.652	2.6528	400	m
2.602	2.6005	$\bar{2}32$	w
2.581	2.5790/2.5787/2.5777	410/ $\bar{1}41/123$	w
2.549	2.5470/2.5469/2.5466	$\bar{4}11/330/141$	w
2.502	2.5009	$\bar{3}31$	s

Table 1 (cont.)

2.415	2.4160	331	wv
2.357	2.3551	$\bar{1}33$	w
2.341	2.3380	004	wv
2.287	2.2917/2.2870/2.2837	142/014/133	w
2.242	2.2436	$\bar{3}23$	wv
2.219	2.2183	204	w
2.189	2.1913	313	wv
2.174	2.1753/2.1752/2.1746	412/332/ $\bar{2}14$	wv
2.153	2.1500	430	wv
2.130	2.1278	242	wv
2.113	2.1132	501	wv
2.090	2.0894	341	w
2.074	2.0753	511	w
2.052	2.0496	$\bar{1}43$	s
2.032	2.0339/2.0329/2.0288	250/214/501	m
1.9942	1.9950/1.9922	511/052	wv
1.9721	1.9729/1.9726/1.9711	521/251/034	w
1.9101	1.9101/1.9096	409/333	s
1.9023	1.9035/1.8989	521/432	s
1.8748	1.8725	105	wv
1.8379	1.8370/1.8351	503/060	s
1.8187	1.8173/1.8158	414/351	m
1.8018	1.8020/1.8003	234/061	wv
1.7901	1.7895/1.7888	$\bar{1}53/155$	wv
1.7748	1.7728	$\bar{1}25$	w
$d_{\text{obs}}$	$I_{\text{obs}}$	$d_{\text{obs}}$	$I_{\text{obs}}$
1.7589 Å	wv	1.5082 Å	wv
1.7334	wv	1.4922	w
1.7237	w	1.4755	wv
1.6851	wv	1.4621	wv
1.6662	w	1.468	wv
1.6463	w	1.4520	wv
1.6347	wv	1.4255	wv
1.6126	w	1.4149	wv
1.5943	wv	1.4020	wv
1.5771	wv	1.3870	wv
1.5612	wv	1.3768	wv
1.5497	wv	1.3602	wv
1.5410	w	1.3514	wv
1.5299	wv	1.3397	wv
1.5221	wv	1.3318	wv

Other physical data for  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  are: M. W.  $312.01$ ;  $V = 1097.50 \text{ \AA}^3$ ,  $D_m = 1.874 \text{ g.cm}^{-3}$  (flotation),  $Z = 4$ ,  $D_c = 1.843 \text{ g.cm}^{-3}$ ,  $F(000) = 632e$ ; linear absorption coefficient for Cu  $K\alpha$  radiation,  $\mu = 58 \text{ cm}^{-1}$ .

#### Intensity measurement

Intensities, all on the same relative scale, were collected on an automatic three-circle General Electric diffractometer, equipped with a Na(Tl)I scintillation counter, with nickel-filtered Cu  $K\alpha$  radiation. A crystal was mounted with its [001] direction coincident with the  $\varphi$  axis of the goniostat; the crystal dimensions were  $0.10$  (along the  $z$  axis)  $\times 0.10 \times 0.06 \text{ mm}$ . The  $\theta$ - $2\theta$  scanning technique was employed ( $1^\circ$  per minute), varying the interval of integration from  $2$  to  $3.50^\circ$  as a function of  $2\theta$ ; the background was measured for an interval of  $0.5^\circ$  on both sides of each peak. We measured 2,384 independent reflexions corresponding to about 95% of those accessible to Cu  $K\alpha$  radiation. 244 of the reflexions measured were considered 'unobserved' and excluded from the refinement after checking that the corresponding  $F_c$  values were less

Table 2. Moduli of observed and calculated structure amplitudes with corresponding phase angles on an absolute scale

H	K	L	F <sub>o</sub>	F <sub>c</sub>	ALPHA	H	K	L	F <sub>o</sub>	F <sub>c</sub>	ALPHA	H	K	L	F <sub>o</sub>	F <sub>c</sub>	ALPHA	H	K	L	F <sub>o</sub>	F <sub>c</sub>	ALPHA	H	K	L	F <sub>o</sub>	F <sub>c</sub>	ALPHA							
2	0	0	80.3	80.1	1.7	-3	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
10	0	0	180.2	180.0	-176.3	-4	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
0	0	0	47.4	46.9	2.8	-4	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
17	0	0	122.7	122.0	-176.3	-5	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
1	0	0	19.1	19.4	3.5	-5	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	1	0	175.4	174.3	2.1	-6	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
4	1	0	50.3	51.3	-176.2	-7	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
5	1	0	58.0	56.8	-177.1	-8	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
7	1	0	19.3	19.1	1.6	-8	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
8	1	0	22.8	22.7	-176.6	-10	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
10	1	0	25.0	25.1	2.9	-10	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
11	1	0	8.4	8.4	-176.0	-11	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
12	1	0	58.8	52.7	3.8	-11	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
13	1	0	3.6	4.6	2.6	-11	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	121.1	120.2	-177.0	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	9.3	8.5	4.2	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	37.9	37.7	-176.3	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	19.4	19.4	1.6	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	33.2	35.1	5.2	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	5.8	6.5	-176.4	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	21.9	21.7	-177.4	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	32.7	32.7	1.4	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	8.1	8.1	2.4	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	10.2	10.2	-177.2	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	15.4	15.4	-176.9	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	21.1	21.4	-176.0	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	3.6	3.6	2.6	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	45.4	47.4	-10.2	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	47.6	47.6	2.4	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	77.6	77.6	2.4	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	7.8	7.8	2.4	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	20.9	23.2	-177.0	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
2	0	2	13.1	13.1	7.0	-13	2	1	140.1	140.5	-176.2	3	10	1	46.7	46.8	2.4	1	8	2	36.4	35.2	-177.6	-6	2	9	6.6	6.6	-177.3	-1	1	1	23.9	26.1	-176.5	
11	3	0	4.5	7.1	-176.8	-13	3	1	32.8	32.0	-176.2	4	12	1	28.4	28.4	4.2	1	10	1	22.8	22.8	-177.2	-10	3	1	11.1	11.1	-176.2	-13	3	1	32.8	32.0	-176.2	
11	3	0	5.9	5.9	4.4	-13	3	1	32.8	32.0	-176.2	4	12	1	28.4	28.4	4.2	1	10	1	22.8	22.8	-177.2	-10	3	1	11.1	11.1	-176.2	-13	3	1	32.8	32.0	-176.2	
2	4	0	10.2	10.2	17.6	-13	3	1	32.8	32.0	-176.2	4	12	1	28.4	28.4	4.2	1	10	1	22.8	22.8	-177.2	-10	3	1	11.1	11.1	-176.2	-13	3	1	32.8	32.0	-176.2	
2	4	0	18.9	18.9	10.2	-176.0	-13	3	1	32.8	32.0	-176.2	4	12	1	28.4	28.4	4.2	1	10	1	22.8	22.8	-177.2	-10	3	1	11.1	11.1	-176.2	-13	3	1	32.8	32.0	-176.2
8	4	0	65.2	70.8	-176.3	-13	3	1	32.8	32.0	-176.2	4	12	1	28.4	28.4	4.2	1	10	1	22.8	22.8	-177.2	-10	3	1	11.1	11.1	-176.2	-13	3	1	32.8	32.0	-176.2	
8	4	0	30.6	30.7	-1.1	-13	3	1	32.8	32.0	-176.2	4	12	1	28.4	28.4	4.2	1	10	1	22.8	22.8	-177.2	-10	3	1	11.1	11.1	-176.2	-13	3	1	32.8	32.0	-176.2	
8	4	0	11.8	11.1	-4.8	-13	3	1	32.8	32.0	-176.2	4	12	1	28.4	28.4	4.2	1	10	1	22.8	22.8	-177.2	-10	3	1	11.1	11.1	-176.2	-13	3	1	32.8	32.0	-176.2	
8	4	0	19.7	20.9	-10.8	-13	3	1	32.8	32.0	-176.2	4	12	1	28.4	28.4	4.2	1	10	1	22.8	22.8	-177.2	-10	3	1	11.1	11.1	-176.2	-13	3	1	32.8	32.0	-176.2	
11	4	0	12.5	11.2	-13.9	-13	3	1	32.8	32.0	-176.2	4	12	1	28.4	28.4	4.2	1	10	1	22.8	22.8	-177.2	-10	3	1	11.1	11.1	-176.2	-13	3	1	32.8	32.0	-176.2	
11	4	0	7.8	8.0	-17.2	-13	3	1	32.8	32.0	-176.2	4	12	1	28.4	28.4	4.2	1	10	1	22.8	22.8														

Table 2 (cont.)

Table with multiple columns containing numerical data, organized in a grid-like structure with various headers and sub-headers.

than about 2.5e; they are not listed in the amplitudes Table (Table 2).

The calculation of atomic scattering factors, including the real and imaginary parts of the correction for anomalous scattering by the Na and As atoms, was done by linear interpolation of the values reported, for neutral atoms, in *International Tables for X-ray Crystallography* (1962). Owing to the dimensions of the crystal used and to the value of  $\mu$  no absorption correction was made.

### Solution and refinement of the structure

The structure was solved by the heavy atom method. A three-dimensional Patterson and subsequent electron density syntheses ( $R$ , from the contribution of As alone, was 0.51) located all the atoms except hydrogen. A least-squares refinement was then started, varying, in the first three cycles, the positional and isotropic thermal parameters and the overall scaling factor ( $R=0.08$ ). After three successive cycles with anisotropic thermal parameters ( $R=0.053$ ), a three-dimensional difference map was computed from which it was possible to deduce the coordinates of all 15 hydrogen atoms. The heights of the positive maxima corresponding to the positions of the hydrogen atoms varied approximately from 0.5 to 1 e.Å<sup>-3</sup>. Since the total number of such maxima was greater than the number of independent hydrogen atoms a selection was made after calculation of the bond distances and angles for all of them. Two further least-square cycles were

computed in which, owing to storage limitations, only the positional parameters of the oxygen and hydrogen atoms and the isotropic thermal parameters of the latter were varied ( $R=0.047$ ; weighted  $R=0.059$ ; standard error of an observation of unit weight = 0.95).

A final three-dimensional difference map confirmed the correctness of the refinement; randomly distributed ripples of height  $\pm 0.6$  e.Å<sup>-3</sup> appeared and only one trough, situated near the arsenic atom, of  $-1$  e.Å<sup>-3</sup> in depth.

The refinement, based on  $|F|$  values, was carried out using the full-matrix least-squares program of Busing, Martin & Levy (1962) modified to take into account the imaginary part of the atomic scattering factors. The weighting scheme used throughout the refinement was:

$$w_{hkl} = A/(B|F_o|^2 + |F_o| + C)$$

for  $|F_o| \geq C$ .

$$w_{hkl} = D|F_o|^2 + E$$

for  $|F_o| < C$ .

The constants  $A$ ,  $D$  and  $E$  were given values such that  $0 < w_{hkl} < 1$  and the two weighting schemes coincide when  $|F_o| = C$ ; the other constants were varied during the refinement in order to maintain  $\sum wA^2$  at a satisfactorily constant value for the amplitudes batched in various groups.

Table 2 presents the final values of  $|F_o|$  and  $|F_c|$  and the corresponding phase angles  $\alpha$ ; the 38 reflexions marked with an asterisk were given zero weight during the refinement because either their intensity was low or they were thought to be affected by extinction or

Table 3. Fractional atomic coordinates and vibrational parameters (Å<sup>2</sup>) with the significant figures of the estimated standard deviations in parentheses

	$x/a_0$	$y/b_0$	$z/c_0$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
As(1)	0.39609 (5)	0.26557 (5)	0.10272 (6)	1.13 (2)	1.36 (2)	1.33 (2)	0.07 (2)	0.02 (2)	0.02 (2)
Na(1)	0.9796 (2)	0.3957 (2)	0.1356 (3)	2.66 (10)	2.26 (9)	2.55 (10)	-0.06 (7)	0.40 (8)	-0.07 (7)
Na(2)	0.9789 (2)	0.1018 (2)	0.1460 (3)	2.81 (11)	2.41 (9)	2.78 (11)	-0.18 (7)	0.64 (9)	-0.09 (7)
O(1)	0.3124 (4)	0.1778 (4)	-0.0159 (4)	1.66 (15)	2.68 (18)	2.05 (17)	0.01 (13)	-0.00 (13)	-0.68 (14)
O(2)	0.5521 (3)	0.2477 (3)	0.0986 (4)	1.06 (13)	1.97 (17)	2.67 (17)	0.14 (11)	0.22 (12)	0.09 (13)
O(3)	0.3520 (4)	0.2541 (3)	0.2670 (4)	1.84 (17)	1.98 (17)	2.13 (15)	-0.10 (15)	0.31 (14)	0.14 (19)
O(4)	0.3619 (4)	0.4168 (4)	0.0608 (5)	2.72 (20)	1.64 (16)	2.53 (19)	0.72 (13)	0.66 (15)	0.43 (13)
W(1)	0.3643 (4)	0.0376 (4)	0.4121 (5)	2.07 (18)	2.22 (17)	3.02 (21)	-0.20 (14)	0.15 (15)	0.33 (15)
W(2)	0.0950 (4)	0.2511 (4)	0.3032 (5)	1.76 (16)	3.65 (22)	2.21 (17)	-0.01 (14)	0.09 (13)	0.01 (15)
W(3)	0.1460 (4)	-0.0229 (4)	0.0710 (5)	2.54 (20)	2.72 (19)	2.77 (21)	-0.03 (15)	0.15 (16)	-0.01 (15)
W(4)	0.5553 (4)	0.2539 (4)	0.4816 (4)	2.09 (16)	2.65 (19)	2.15 (17)	-0.17 (14)	0.08 (13)	0.16 (14)
W(5)	0.6113 (4)	0.0076 (4)	0.1845 (5)	2.61 (20)	2.24 (17)	2.68 (20)	0.19 (14)	0.52 (16)	0.21 (14)
W(6)	0.6329 (4)	0.4846 (4)	0.1991 (5)	2.08 (17)	2.06 (16)	2.35 (19)	0.09 (13)	0.05 (14)	0.06 (14)
W(7)	0.8175 (4)	0.2498 (3)	0.1931 (5)	2.00 (15)	2.19 (17)	2.63 (17)	0.14 (13)	0.39 (13)	-0.02 (14)
H(1)	0.862 (7)	0.075 (7)	0.476 (8)	2.0 (2)					
H(2)	0.341 (10)	0.091 (9)	0.348 (10)	4.0 (2)					
H(3)	0.204 (10)	0.517 (9)	0.102 (10)	4.0 (2)					
H(4)	0.176 (8)	0.253 (7)	0.312 (9)	2.0 (1)					
H(5)	0.089 (8)	0.249 (7)	0.385 (9)	2.0 (2)					
H(6)	0.216 (10)	0.010 (10)	0.081 (10)	5.0 (2)					
H(7)	0.338 (6)	0.418 (7)	0.372 (7)	2.0 (1)					
H(8)	0.497 (7)	0.256 (6)	0.405 (7)	1.0 (1)					
H(9)	0.114 (12)	0.228 (11)	-0.049 (13)	8.0 (4)					
H(10)	0.596 (10)	0.096 (10)	0.172 (11)	6.0 (3)					
H(11)	0.883 (13)	0.467 (12)	0.380 (14)	9.0 (4)					
H(12)	0.694 (9)	0.473 (9)	0.235 (10)	4.0 (2)					
H(13)	0.608 (10)	0.402 (11)	0.176 (11)	4.0 (3)					
H(14)	0.802 (7)	0.253 (6)	0.280 (9)	3.0 (2)					
H(15)	0.729 (8)	0.238 (7)	0.148 (9)	3.0 (2)					

some measurement error ( $R=0.050$  for all reflexions of Table 2).

Table 3 shows the final values, with their standard deviations in parentheses, of the fractional coordinates and of the  $B_{ij}$  coefficients of the expression:

$$\exp \left( - \frac{1}{4} \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} h_i h_j a_i^* a_j^* \right).$$

Column *A* of Table 4 shows the root-mean-square displacements of the atoms (except the hydrogen atoms) along the three principal directions of thermal vibration and, in the last three columns, the angles which these directions make with the crystallographic axes are given. The anisotropy is not very marked: all the vibrational ellipsoids are practically solids of revolution, except those of the oxygen atoms of the  $\text{AsO}_4$  group which have three axes of different length. The orientation of the ellipsoids is random, as is to be expected in an essentially ionic structure. The thermal parameters of the hydrogen atoms are discussed below.

Table 4. *Parameters characterizing the principal directions 1, 2, 3 of thermal vibration for all the atoms except hydrogen*

Root-mean-square displacements (*A*) and angles which the principal directions make with the *x* (*B*), *y* (*C*) and *z* (*D*) axes.

		<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
As(1)	1	0.131 Å	94°	47°	43°
	2	0.133	67	46	124
	3	0.117	156	76	113
Na(1)	1	0.176	129	97	34
	2	0.187	39	99	58
	3	0.169	87	11	79
Na(2)	1	0.176	115	49	48
	2	0.201	47	103	51
	3	0.171	53	44	114
O(1)	1	0.150	39	115	123
	2	0.199	83	34	123
	3	0.139	52	68	51
O(2)	1	0.158	82	11	98
	2	0.184	91	83	9
	3	0.114	8	98	94
O(3)	1	0.503	127	42	104
	2	0.555	83	63	30
	3	0.424	38	60	116
O(4)	1	0.166	126	96	31
	2	0.207	45	65	60
	3	0.126	113	26	98
<i>W</i> (1)	1	0.168	50	131	71
	2	0.201	101	69	22
	3	0.155	42	49	100
<i>W</i> (2)	1	0.168	105	91	9
	2	0.215	90	1	89

Table 4 (cont.)

		<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
<i>W</i> (3)	3	0.149	15	90	81
	1	0.186	98	9	94
	2	0.189	114	89	18
<i>W</i> (4)	3	0.178	25	81	72
	1	0.165	120	115	37
	2	0.187	108	26	71
<i>W</i> (5)	3	0.159	36	85	59
	1	0.172	39	90	134
	2	0.195	54	70	47
<i>W</i> (6)	3	0.165	103	20	104
	1	0.162	60	45	64
	2	0.177	119	104	28
<i>W</i> (7)	3	0.158	44	131	81
	1	0.169	66	25	98
	2	0.183	78	89	17
	3	0.154	27	115	105

### Description and discussion of the structure

The structure of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  does not seem to pose any of the problems regarding the cation coordination number or the location of the hydrogen bonding systems, which were encountered in the arsenate structures previously studied in this Institute (Calleri & Ferraris, 1967; Ferraris, 1969; Ferraris & Chiari, 1970). This is due to the facts that the coordination polyhedra of the two crystallographically independent Na atoms appear quite regular, that it was possible to locate all the hydrogen atoms in this structure, and finally that the number of short O—O contacts ( $< 3 \text{ \AA}$ ) is equal to the presumed number of hydrogen bonds.

For this compound we are therefore in a position to confirm certain theories instead of using them to support hypotheses of the structural features. This is particularly true for the  $\text{HAsO}_4$  group (see Table 5 for bond distances and angles) in which the oxygen atom O(4),\* bonded to the acid hydrogen atom H(1), is characterized by an As—O distance (1.742 Å) clearly longer than the other three (average value = 1.670 Å), thus confirming, at least qualitatively, the ideas of Cruickshank (1961) and Cruickshank & Robinson (1966) on  $\text{XO}_4^-$  ions. It must be remarked that, while

\* The notation is as in Figs. 1, 2 and 3; As(1), Na(1), Na(2), O(1), O(2), O(3), O(4), *W*(1), ..., *W*(7), H(1), ..., H(15) are crystallographically independent. Wherever two numbers separated by a comma are included in brackets, the first (1, 2 or 3) denotes the equivalent atom positions generated by  $\bar{x}, \bar{y}, \bar{z}$ :  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ;  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ . A prime indicates an atom position generated by lattice vectors.

Table 5. *Interatomic distances and angles in the  $\text{AsO}_4$  group*

E.s.d.'s are given in parentheses.			
As(1)—O(1)	1.669 (4) Å	O(2)—O(4)	2.751 (6) Å
As(1)—O(2)	1.679 (4)	O(3)—O(4)	2.648 (6)
As(1)—O(3)	1.661 (4)	∠ O(1)—As(1)—O(2)	112.6 (2)°
As(1)—O(4)	1.742 (4)	O(1)—As(1)—O(3)	113.3 (2)
O(1)—O(2)	2.785 (5)	O(1)—As(1)—O(4)	108.4 (2)
O(1)—O(3)	2.782 (5)	O(2)—As(1)—O(3)	112.4 (2)
O(1)—O(4)	2.766 (5)	O(2)—As(1)—O(4)	107.1 (2)
O(2)—O(3)	2.775 (5)	O(3)—As(1)—O(4)	102.2 (2)

the other three As-O distances do not differ significantly from their average value, the difference between the shortest [As-O(3) = 1.661 Å] and longest [As-O(2) = 1.679 Å] is significant according to the *t* test (Cruickshank & Robertson, 1953). The differences in the bonds between As and O(1), O(2), O(3) are related to the lengths of the four hydrogen bonds formed by each of these oxygen atoms with water molecules. Passing

from the shortest to the longest of the above bonds the following situation results: for O(3) two of the hydrogen bonds are shorter than 2.80 Å, for O(1) only one, while for O(2) all the hydrogen bonds are longer than 2.81 Å (Table 8). The average values of the four hydrogen bonds formed by O(3), O(1) and O(2) are respectively 2.810, 2.860 and 2.859 Å; the average for O(2) is, however, strongly influenced by the hydrogen

Table 6. *Interatomic distances and angles in the Na(1) coordination polyhedron*

E.s.d.'s are given in parentheses.			
Na(1)—W(3,1')	2.444 (5) Å	< W(7)—Na(1)—W(2')	76.0 (2)°
Na(1)—W(2,1')	2.357 (5)	W(7)—Na(1)—W(2,5')	80.8 (2)
Na(1)—W(2')	2.482 (5)	W(7)—Na(1)—W(3,1')	94.5 (2)
Na(1)—W(3,4')	2.383 (5)	W(7)—Na(1)—W(3,4')	88.1 (2)
Na(1)—W(2,5')	2.372 (5)	W(2,1)—Na(1)—W(2)	103.3 (2)
Na(1)—W(7)	2.457 (5)	W(2,1)—Na(1)—W(2,5)	97.7 (2)
W(7)—W(2')	3.04	W(2,1')—Na(1)—W(3,1)	86.8 (2)
W(7)—W(2,5')	3.13	W(2,1')—Na(1)—W(3,4')	93.3 (2)
W(7)—W(3,1')	3.61	W(3,1)—Na(1)—W(3,4)	81.8 (2)
W(7)—W(3,4')	3.37	W(3,4')—Na(1)—W(2')	76.5 (2)
W(2,1)—W(2)	3.80	W(2)—Na(1)—W(2,5)	95.3 (2)
W(2,1)—W(2,5)	3.56	W(2,5')—Na(1)—W(3,1')	104.5 (2)
W(2,1')—W(3,1)	3.30	W(2,5')—Na(1)—W(3,4')	167.6 (2)
W(2,1')—W(3,4')	3.45	W(2')—Na(1)—W(3,1')	156.5 (2)
W(3,1)—W(3,4)	3.16	W(7)—Na(1)—W(2,1')	178.2 (2)
W(3,4')—W(2')	3.04		
W(2)—W(2,5)	3.59		
W(2,5')—W(3,1)	3.56		

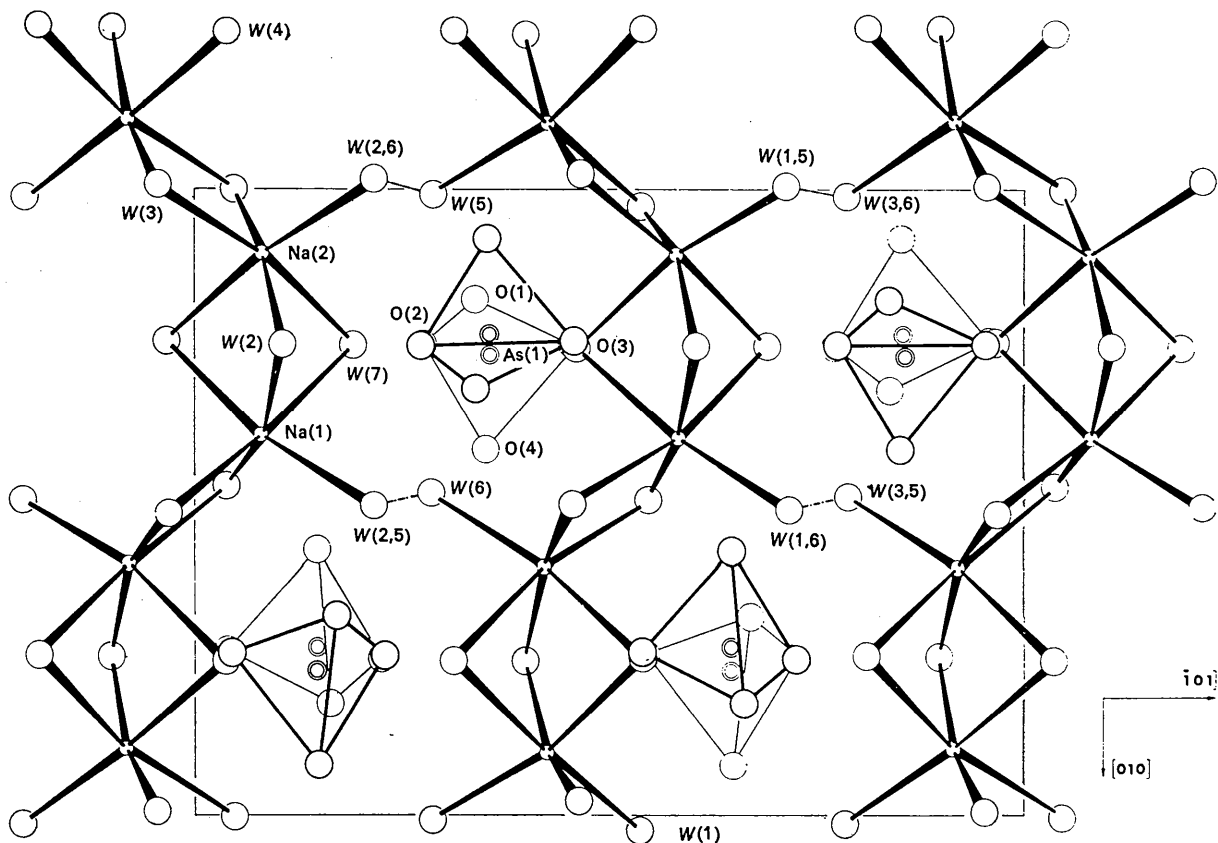


Fig. 1. View along [101] of one Na-polyhedra layer with the adjacent  $\text{AsO}_4$  tetrahedra; the hydrogen bridges, type W-W, are drawn. The two-dimensional unit-cell is the (100) face of the non-primitive unit cell (see text).

bridge 2.995 Å long. The value of the sum of the As—O bond lengths (6.75 Å) is in good agreement with that found in others arsenates (e.g. Ferraris & Chiari, 1970).

The coordination number is 6 for both the crystallographically independent Na atoms which coordinate only the oxygen atoms of the water molecules at the

Table 7. *Interatomic distances and angles in the Na(2) coordination polyhedron*

E.s.d.'s are given in parentheses.			
Na(2)—W(2')	2.464 (5) Å	< W(3)—Na(2)—W(2)	102.3 (2)°
Na(2)—W(3')	2.407 (5)	W(3)—Na(2)—W(1,3)	85.1 (2)
Na(2)—W(7)	2.441 (5)	W(3')—Na(2)—W(2,6')	107.5 (2)
Na(2)—W(1,3')	2.484 (5)	W(3')—Na(2)—W(3,4')	83.4 (2)
Na(2)—W(2,6')	2.352 (5)	W(7)—Na(2)—W(2')	76.6 (2)
Na(2)—W(3,4')	2.411 (5)	W(7)—Na(2)—W(1,3')	92.9 (2)
W(3)—W(2)	3.80	W(7)—Na(2)—W(2,6')	81.2 (2)
W(3)—W(1,3)	3.31	W(7)—Na(2)—W(3,4')	87.9 (2)
W(3')—W(2,6')	3.84	W(1,3')—Na(2)—W(3,4')	83.8 (2)
W(3')—W(3,4')	3.20	W(3,4')—Na(2)—W(2')	76.3 (2)
W(7)—W(2')	3.04	W(2')—Na(2)—W(2,6')	104.5 (2)
W(7)—W(1,3')	3.58	W(2,6')—Na(2)—W(1,3')	93.0 (2)
W(7)—W(2,6')	3.12	W(3,4')—Na(2)—W(2,6)	168.5 (2)
W(7)—W(3,4')	3.37	W(2)—Na(2)—W(1,3)	157.7 (2)
W(1,3')—W(3,4')	3.27	W(3')—Na(2)—W(7)	171.1 (2)
W(3,4')—W(2')	3.04		
W(2')—W(2,6')	3.82		
W(2,6')—W(1,3')	3.50		

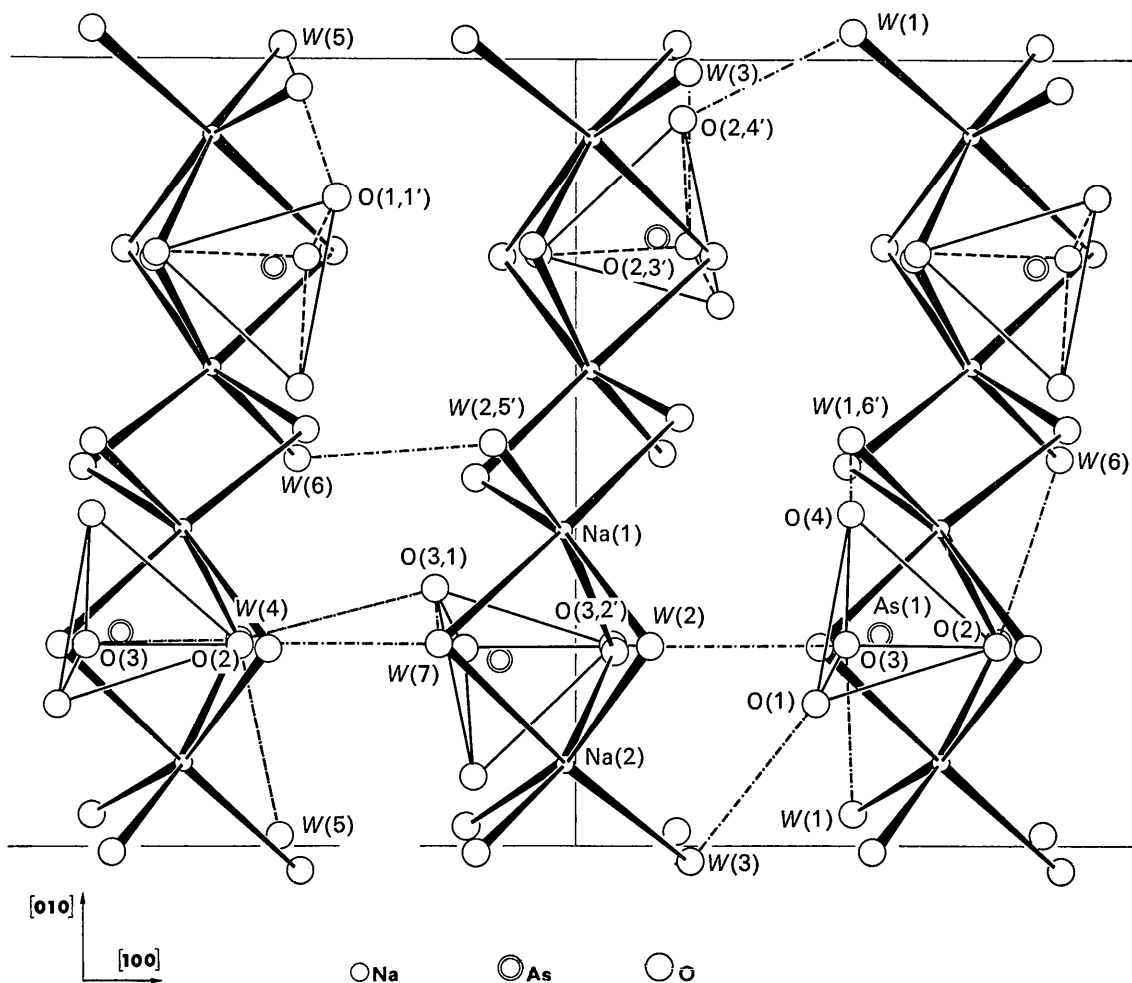


Fig. 2. View of the structure along [001]; about two unit cells are drawn.



corners of two nearly regular octahedra, as can be seen from the values reported in Tables 6 and 7. Each water molecule is so oriented as to make two hydrogen bonds with two oxygen atoms belonging to different  $\text{AsO}_4$  tetrahedra, with the exception of  $W(6)$  whose hydrogen atom  $\text{H}(12)$  is involved in a bond with  $W(2,5')$ . The oxygen atoms of the water molecules are coordinated by two Na atoms, excluding  $W(5)$  and  $W(6)$  which make contact with one hydrogen atom in place of a sodium atom: in fact  $W(6)$  makes contact with the acid hydrogen atom  $\text{H}(2,1')$ , and  $W(5)$  with hydrogen  $\text{H}(2,12')$ . In this way, when the values of bond angles are also considered (those with the Na atoms are not reported), it is seen that each water molecule assumes the classical tetrahedral configuration.

The parameters of the hydrogen atoms, deduced from a three-dimensional difference map and subsequently refined by a least-squares procedure, are not, of course, very accurate: the high temperature factors assumed by some of them might denote that the accuracy of these coordinates is even lower than that suggested by their standard deviations. However, the e.s.d.'s are perhaps optimistic because all the parameters were not varied simultaneously. Nevertheless it is thought that almost all these hydrogen bonds are of the non-linear type (see bond distances and angles in Tables 8 and 9), as already suggested in several structures and confirmed in a few based on neutron-diffraction data (see *e.g.* Bacon, 1963). This type of bonding is, on the other hand, in agreement with several  $\text{O} \cdots \text{W} \cdots \text{O}$  angles (whose values are fairly

Table 8. *Interatomic distances involving hydrogen atoms and hydrogen bridges*

E.s.d.'s are given in parentheses.

A	B	C	A-B	B-C	A-C
$W(1)-\text{H}(2)$	$\cdots \cdots \text{O}(3)$		0.86 (9) Å	1.96 (10) Å	2.743 (6) Å
$W(1)-\text{H}(2,3')$	$\cdots \cdots \text{O}(2,4')$		0.76 (10)	2.08 (10)	2.787 (6)
$W(2)-\text{H}(4)$	$\cdots \cdots \text{O}(3)$		0.86 (9)	1.96 (9)	2.793 (6)
$W(2)-\text{H}(5)$	$\cdots \cdots \text{O}(3,2')$		0.78 (8)	2.08 (8)	2.855 (6)
$W(3)-\text{H}(6)$	$\cdots \cdots \text{O}(1)$		0.83 (10)	2.34 (10)	2.995 (6)
$W(3)-\text{H}(2,7')$	$\cdots \cdots \text{O}(2,3')$		0.85 (7)	2.07 (7)	2.888 (6)
$W(4)-\text{H}(8)$	$\cdots \cdots \text{O}(3)$		0.91 (7)	1.92 (7)	2.817 (6)
$W(4)-\text{H}(3,9)$	$\cdots \cdots \text{O}(3,1)$		0.74 (13)	2.18 (13)	2.840 (6)
$W(5)-\text{H}(10)$	$\cdots \cdots \text{O}(2)$		0.99 (11)	1.86 (11)	2.819 (6)
$W(5)-\text{H}(2,11')$	$\cdots \cdots \text{O}(1,1')$		0.76 (13)	2.05 (13)	2.754 (6)
$W(6)-\text{H}(12)$	$\cdots \cdots W(2,5')$		0.72 (10)	2.17 (10)	2.852 (6)
$W(6)-\text{H}(13)$	$\cdots \cdots \text{O}(2)$		0.96 (12)	1.92 (12)	2.878 (6)
$W(7)-\text{H}(14)$	$\cdots \cdots \text{O}(3,1)$		0.85 (8)	2.06 (8)	2.853 (6)
$W(7)-\text{H}(15)$	$\cdots \cdots \text{O}(2)$		1.00 (9)	1.91 (9)	2.884 (6)
$\text{O}(4)-\text{H}(3,1')$	$\cdots \cdots W(1,6')$		0.80 (8)	1.93 (7)	2.678 (6)

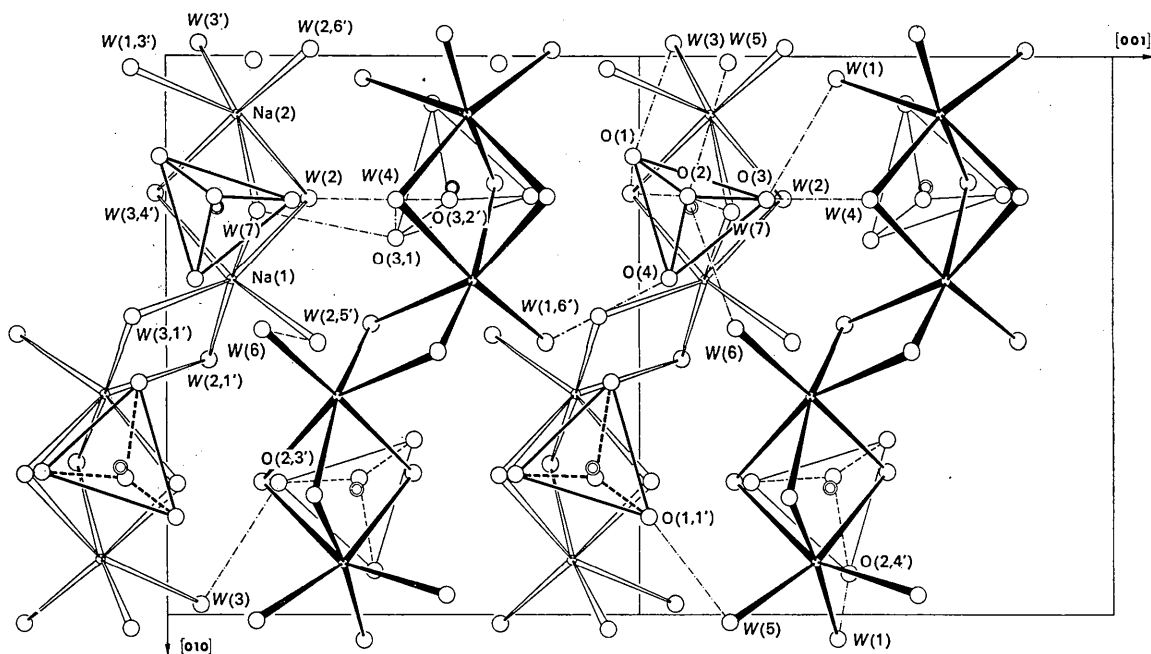


Fig. 3. View of the structure along  $[100]$ ; two unit cells are drawn.

Table 9. *Interatomic angles involving hydrogen atoms and hydrogen bridges*

E.s.d.'s are given in parentheses.

A	B	C	D	E	$\angle ABC$	$\angle CDE$	$\angle BCD$	$\angle ACE$
O(3)···H(2)—W(1)—H(2,3')···O(2,4')					151 (9)°	154 (10)°	83 (10)°	117.3 (2)°
O(3)···H(4)—W(2)—H(5)···O(3,2')					162 (8)	173 (7)	95 (8)	111.6 (2)
O(1)···H(6)—W(3)—H(2,7')···O(2,3')					130 (10)	161 (7)	97 (8)	142.8 (2)
O(3)···H(8)—W(4)—H(3,9')···O(3,1)					170 (7)	149 (13)	103 (11)	133.0 (2)
O(2)···H(10)—W(5)—H(2,11')···O(1,1')					165 (9)	154 (13)	120 (12)	127.0 (2)
O(2)···H(13)—W(6)—H(12)···W(2,5')					171 (9)	158 (10)	99 (10)	116.9 (2)
O(2)···H(15)—W(7)—H(14)···O(3,1)					165 (7)	156 (7)	98 (7)	101.0 (2)
O(4)···H(3,1')—W(1,6')					155 (8)			

accurate) which are appreciably different from about  $105^\circ$  (Table 9), a value to be expected for linear hydrogen bonds. In particular we note that the  $W-H \cdots O$  angle farthest from  $180^\circ$  [ $W(3)-H(6) \cdots O(1) = 130^\circ$ ], corresponds to the weakest hydrogen bond [ $W(3) \cdots O(1) = 2.995 \text{ \AA}$ ] and to the largest  $O \cdots W \cdots O$  angle [ $O(1) \cdots W(3) \cdots O(2,3') = 142.8^\circ$ ].

Figs. 1, 2 and 3 illustrate the projection of the structure on to planes (101), (001) and (100) respectively. The two crystallographically independent Na-octahedra share a face; the pairs of octahedra are joined by shared edges and thus form a zigzag chain in the direction of the  $y$  axis. These chains are connected, in the  $[\bar{1}01]$  direction (Fig. 1) by the only hydrogen bond involving pairs of water molecule oxygen atoms [ $W(5) \cdots W(2,6') = 2.852 \text{ \AA}$ ]. There is thus a layer of Na-polyhedra parallel to (101) as shown in Fig. 1. The  $AsO_4$  tetrahedra are located between these layers and they connect both the layers along [101] and two contiguous chains of one layer by hydrogen bonding of the  $W \cdots O$  type. Two neighbouring layers are related by a pseudo-periodicity along [101] and are almost superimposed in the projection on (101).

This superposition is not shown in Fig. 1, which has been drawn to illustrate the fact that the  $AsO_4$  tetrahedra are not superimposed on the Na-octahedra.

The projection along [001] (Fig. 2), unlike that along [101] (Fig. 1), shows overcrowded and empty regions alternating along [100]. It is possible to single out layers parallel to (100) in which the  $As$ -tetrahedra occupy the 'inlets' of the zigzag chains of Na-octahedra which connect two adjacent chains by hydrogen bridges (Fig. 3). A succession of hydrogen bonds,

nearly parallel to the  $x$  axis, links these layers (Fig. 2).

Finally we point out that, along [010], the water molecules lie practically on four families of planes,  $b_0/4$  apart, which alternate with four planes of sodium atoms. The arsenic atoms are at the same height as the first and the third water molecule plane; the faces shared by the Na-coordinated polyhedra also lie on these planes.

The reason for the easy cleavage {101} is quite clear from consideration of the structural features.

We are indebted to Dr D. W. Jones and to Professor M. Calleri for critical reading of the manuscript.

#### References

- BACON, G. E. (1963). *Applications of Neutron Diffraction in Chemistry*. Oxford: Pergamon Press.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS A Fortran Crystallographic Least-Squares Program*. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CALLERI, M. & FERRARIS, G. (1967). *Period. Miner.* **36**, 1.
- CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* p. 5486.
- CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 968.
- CRUICKSHANK, D. W. J. & ROBINSON, E. A. (1966). *Spectrochim. Acta*, **22**, 555.
- FERRARIS, G. (1969). *Acta Cryst.* **B25**, 1544.
- FERRARIS, G. & CHIARI, G. (1970). *Acta Cryst.* **B26**, 403.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- PORTER, M. W. & SPILLER, R. C. (1956). *The Barker Index of Crystals*, Vol. II. Cambridge: Heffer.