

## Determination of Hydrogen Atom Positions in the Crystal Structure of Pharmacolite, $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$ , by Neutron Diffraction

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(Received 11 March 1970)

The mineral pharmacolite,  $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$ , crystallizes in the monoclinic space group  $Ia$  ( $C_2^4$ ),  $a = 5.975$ ,  $b = 15.434$ ,  $c = 6.280$  Å,  $\beta = 114^\circ 50'$ , with four formula units per cell. All five crystallographically independent hydrogen atoms were located by a neutron Fourier difference synthesis. Three-dimensional least-squares refinement with 318 independent neutron reflexions (46% of those accessible with  $\lambda = 1.04$  Å and  $2\theta < 90^\circ$ ) led to a final  $R$  value of 0.053 over 318 reflexions. These were recorded from a natural crystal on a manually operated diffractometer. Although the estimated standard deviations of the hydrogen positional coordinates of about 0.03 Å are slightly higher than might have been expected, the final Fourier difference synthesis displays no spurious peaks. The anionic hydrogen atom, H(1), has been explicitly located at a single site 1.1 Å from O(1), which has a long As–O bond of 1.73 Å; H(1) has a relatively short (2.70 Å) bent hydrogen bond to O(4) of another anion [designated O(12)]. Within experimental error, the two water molecules have the same H–O–H angle as in an isolated molecule. While both water molecules are coplanar with the two oxygen atoms to which each is hydrogen-bonded, they differ in other respects.  $W(1)$  (type  $H$ ) is a donor in two closely linear, moderately strong, hydrogen bonds (2.74, 2.80 Å) to arsenate oxygen atoms, but  $W(2)$  (type  $D$ ) has two bent hydrogen bonds; one of 2.79 Å goes to an arsenate oxygen atom but an unusually weak one (3.07 Å) is linked to the other water molecule,  $W(1)$ .

### Introduction

A recent accurate X-ray analysis (Ferraris, 1969), carried out as part of a series of studies of acidic, and generally hydrated, arsenates (Calleri & Ferraris, 1967; Ferraris & Chiari, 1970) and phosphates (Jones & Smith, 1960; Jones & Cruickshank, 1961; Curry, Denne & Jones, 1968), has shown that the positions of the heavy atoms in the crystal structure of the mineral pharmacolite,  $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$ , are closely related to the positions of the corresponding atoms in the structures of the analogous salts brushite,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  (Jones & Smith, 1962), and gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (Atoji & Rundle, 1958; Denne & Jones, 1969). All three structures involve layers normal to [010] in which Ca atoms are coordinated by six O atoms of the approximately tetrahedral anions and by two O atoms of water molecules. Piezoelectric measurements indicated that absent reflexions in pharmacolite and brushite should be interpreted in terms of space group  $Ia$  ( $C_2^4$ ) rather than  $I2/a$  ( $C_{2h}^6$ ), but there is no evidence that the gypsum structure departs from centrosymmetry. In view of the interest in the small differences in atomic sites and hydrogen bonding between these structures, and of small deviations from centrosymmetry, a single-crystal neutron-diffraction study of pharmacolite has been undertaken so that the positions of water and anionic hydrogen atoms could be located explicitly and the stereochemistry of the  $[\text{AsO}_4\text{H}]^{2-}$  group established.

For neutrons, the hydrogen atoms in  $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$  represent 29% of the scattering power, calculated as

$$\frac{\sum_{\text{H atoms}} |b|}{\sum_{\text{all atoms}} |b|}.$$

### Experimental

Preliminary crystallographic and other physical data were taken to be as reported by Ferraris (1969): monoclinic, space group  $Ia$  (No. 6,  $C_2^4$ );  $a = 5.975$ ,  $b = 15.434$ ,  $c = 6.280$  Å,  $\beta = 114^\circ 50'$ ; M.W. 216.0;  $Z = 4$ ,  $D_m = 2.725$  g.cm $^{-3}$ .

A natural roughly prismatic Andreasberg (Harz) single crystal, of dimensions  $1.3 \times 1.5 \times 5.0$  mm and weight about 0.027 g, elongated about the  $c$  axis, was borrowed from the mineralogical collection of the Mineralogical Institute, University of Turin. With the  $c$  axis mounted along the instrumental  $\varphi$ -rotation axis, neutron intensity data for a wavelength monochromatized to 1.04 Å were collected for the  $hkl$  and  $\bar{h}kl$  octants on a manually operated four-circle single-crystal 'Badger' diffractometer at the DIDO reactor, Atomic Energy Research Establishment, Harwell. Setting angles were computed by a program written by M.J.D. Powell (private communication) for the Chilton Atlas computer. Slight adjustments were made to  $\theta$  (and  $\varphi$ ) to obtain maximum peak intensity.

Counts were recorded at  $2\theta$  increments of  $0.1^\circ$  with the  $\theta$ - $2\theta$  step-scan. A beam approximately 1.3 cm square was incident on the sample, and the counter was preceded by a 13 cm collimator tube with  $1.3 \times 2.5$  cm (vertical) entrance slit; Soller slits were not employed. At each point, the counting time was controlled by a

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fission chamber which monitored the intensity of the incident beam. For a monitor count of  $5 \times 10^4$ , the counting time was 15 seconds per step. Intensities were measured over  $2\theta$  angular ranges of at least  $3^\circ$  and backgrounds over ranges of  $0.5^\circ$  on each side of the peaks; typically, counting took a total of about 15 minutes per reflexion.

Of the 691 reflexions with  $2\theta < 90^\circ$  accessible in the  $hkl$  and  $\bar{h}k\bar{l}$  octants, a search was made for those 461 (67%) for which the calculated intensity (without hydrogen) was  $> 2 \times 10^{-24} \text{ cm}^2$ . Integrated intensity measurements, ranging from counts of 200 to 25,000, were made on those 318 reflexions (46% of those accessible) which gave ratemeter readings above the background level. For several sample reflexions, the background counts (from 30 to 60 per step) were plotted against  $2\theta$ , and these graphs were used to deduce backgrounds for other reflexions. After integrated counts had been calculated by hand, the computer program by Denne (1968) was used to subtract background from peak,

apply the Lorentz correction, and yield structure amplitudes and their e.s.d.'s. No correction was made for absorption; extinction is discussed later.

Structure analysis and refinement

Location of the hydrogen atoms

A three-dimensional Fourier difference synthesis with the X-ray data (Ferraris, 1969), without any anomalous scattering correction, and with calculated structure factors based on the heavy atoms only, led to apparently satisfactory sites for the water hydrogen atoms but to an acidic hydrogen site badly masked by diffraction ripples from the As atoms. Refinement, from  $R$  value 0.19 to 0.15 in five cycles, was unsatisfactory in that the acidic hydrogen atom oscillated. From a difference Fourier synthesis with the neutron data, computed on the ATLAS version of the *X-ray 63 System*, and the X-ray determined sites of the non-hydrogenic atoms only ( $R=0.20$ ), however, all hydrogen atom po-

Table 1. Final list of moduli of observed and calculated structure factors and cosines of phase angles

L	h	k	l	FO	CSAL	L	h	k	l	FO	CSAL	L	h	k	l	FO	CSAL	L	h	k	l	FO	CSAL
1	1	0	0	3.1773	0.00000	1	0	0	1	3.1773	0.00000	1	0	0	1	3.1773	0.00000	1	0	0	1	3.1773	0.00000
1	1	1	0	4.02	0.08711	1	1	0	0	4.02	0.08711	1	1	0	0	4.02	0.08711	1	1	0	0	4.02	0.08711
1	1	1	1	1.76	0.00094	1	1	1	0	1.76	0.00094	1	1	1	1	1.76	0.00094	1	1	1	1	1.76	0.00094
1	1	1	1	2.46	0.08918	1	1	1	1	2.46	0.08918	1	1	1	1	2.46	0.08918	1	1	1	1	2.46	0.08918
1	1	1	1	7.25	0.10000	1	1	1	1	7.25	0.10000	1	1	1	1	7.25	0.10000	1	1	1	1	7.25	0.10000
1	1	1	1	4.37	0.07140	1	1	1	1	4.37	0.07140	1	1	1	1	4.37	0.07140	1	1	1	1	4.37	0.07140
1	1	1	1	2.31	0.00875	1	1	1	1	2.31	0.00875	1	1	1	1	2.31	0.00875	1	1	1	1	2.31	0.00875
1	1	1	1	2.78	0.07497	1	1	1	1	2.78	0.07497	1	1	1	1	2.78	0.07497	1	1	1	1	2.78	0.07497
1	1	1	1	2.47	0.05805	1	1	1	1	2.47	0.05805	1	1	1	1	2.47	0.05805	1	1	1	1	2.47	0.05805
1	1	1	1	3.15	0.10000	1	1	1	1	3.15	0.10000	1	1	1	1	3.15	0.10000	1	1	1	1	3.15	0.10000
1	1	1	1	4.87	0.09074	1	1	1	1	4.87	0.09074	1	1	1	1	4.87	0.09074	1	1	1	1	4.87	0.09074
1	1	1	1	8.21	0.07849	1	1	1	1	8.21	0.07849	1	1	1	1	8.21	0.07849	1	1	1	1	8.21	0.07849
1	1	1	1	2.75	0.01211	1	1	1	1	2.75	0.01211	1	1	1	1	2.75	0.01211	1	1	1	1	2.75	0.01211
1	1	1	1	2.41	0.06644	1	1	1	1	2.41	0.06644	1	1	1	1	2.41	0.06644	1	1	1	1	2.41	0.06644
1	1	1	1	3.28	0.07400	1	1	1	1	3.28	0.07400	1	1	1	1	3.28	0.07400	1	1	1	1	3.28	0.07400
1	1	1	1	10.73	0.03800	1	1	1	1	10.73	0.03800	1	1	1	1	10.73	0.03800	1	1	1	1	10.73	0.03800
1	1	1	1	3.33	0.03915	1	1	1	1	3.33	0.03915	1	1	1	1	3.33	0.03915	1	1	1	1	3.33	0.03915
1	1	1	1	3.05	0.09968	1	1	1	1	3.05	0.09968	1	1	1	1	3.05	0.09968	1	1	1	1	3.05	0.09968
1	1	1	1	3.20	0.07042	1	1	1	1	3.20	0.07042	1	1	1	1	3.20	0.07042	1	1	1	1	3.20	0.07042
1	1	1	1	2.98	0.09202	1	1	1	1	2.98	0.09202	1	1	1	1	2.98	0.09202	1	1	1	1	2.98	0.09202
1	1	1	1	1.75	0.10380	1	1	1	1	1.75	0.10380	1	1	1	1	1.75	0.10380	1	1	1	1	1.75	0.10380
1	1	1	1	2.63	0.09938	1	1	1	1	2.63	0.09938	1	1	1	1	2.63	0.09938	1	1	1	1	2.63	0.09938
1	1	1	1	7.05	0.09135	1	1	1	1	7.05	0.09135	1	1	1	1	7.05	0.09135	1	1	1	1	7.05	0.09135
1	1	1	1	2.94	0.08185	1	1	1	1	2.94	0.08185	1	1	1	1	2.94	0.08185	1	1	1	1	2.94	0.08185
1	1	1	1	4.65	0.09825	1	1	1	1	4.65	0.09825	1	1	1	1	4.65	0.09825	1	1	1	1	4.65	0.09825
1	1	1	1	3.32	0.10000	1	1	1	1	3.32	0.10000	1	1	1	1	3.32	0.10000	1	1	1	1	3.32	0.10000
1	1	1	1	5.95	0.05943	1	1	1	1	5.95	0.05943	1	1	1	1	5.95	0.05943	1	1	1	1	5.95	0.05943
1	1	1	1	3.34	0.05938	1	1	1	1	3.34	0.05938	1	1	1	1	3.34	0.05938	1	1	1	1	3.34	0.05938
1	1	1	1	5.56	0.10000	1	1	1	1	5.56	0.10000	1	1	1	1	5.56	0.10000	1	1	1	1	5.56	0.10000
1	1	1	1	1.78	0.10000	1	1	1	1	1.78	0.10000	1	1	1	1	1.78	0.10000	1	1	1	1	1.78	0.10000
1	1	1	1	7.49	0.08271	1	1	1	1	7.49	0.08271	1	1	1	1	7.49	0.08271	1	1	1	1	7.49	0.08271
1	1	1	1	2.76	0.02904	1	1	1	1	2.76	0.02904	1	1	1	1	2.76	0.02904	1	1	1	1	2.76	0.02904
1	1	1	1	5.20	0.08000	1	1	1	1	5.20	0.08000	1	1	1	1	5.20	0.08000	1	1	1	1	5.20	0.08000
1	1	1	1	4.18	0.04000	1	1	1	1	4.18	0.04000	1	1	1	1	4.18	0.04000	1	1	1	1	4.18	0.04000
1	1	1	1	2.08	0.10000	1	1	1	1	2.08	0.10000	1	1	1	1	2.08	0.10000	1	1	1	1	2.08	0.10000
1	1	1	1	3.11	0.05000	1	1	1	1	3.11	0.05000	1	1	1	1	3.11	0.05000	1	1	1	1	3.11	0.05000
1	1	1	1	2.61	0.05000	1	1	1	1	2.61	0.05000	1	1	1	1	2.61	0.05000	1	1	1	1	2.61	0.05000
1	1	1	1	1.01	0.08843	1	1	1	1	1.01	0.08843	1	1	1	1	1.01	0.08843	1	1	1	1	1.01	0.08843
1	1	1	1	3.78	0.09091	1	1	1	1	3.78	0.09091	1	1	1	1	3.78	0.09091	1	1	1	1	3.78	0.09091
1	1	1	1	1.2	0.09838	1	1	1	1	1.2	0.09838	1	1	1	1	1.2	0.09838	1	1	1	1	1.2	0.09838
1	1	1	1	3.33	0.09181	1	1	1	1	3.33	0.09181	1	1	1	1	3.33	0.09181	1	1	1	1	3.33	0.09181
1	1	1	1	1.55	0.09946	1	1	1	1	1.55	0.09946	1	1	1	1	1.55	0.09946	1	1	1	1	1.55	0.09946
1	1	1	1	7.35	0.09251	1	1	1	1	7.35	0.09251	1	1	1	1	7.35	0.09251	1	1	1	1	7.35	0.09251
1	1	1	1	5.81	0.09550	1	1	1	1	5.81	0.09550	1	1	1	1	5.81	0.09550	1	1	1	1	5.81	0.09550
1	1	1	1	7.13	0.09091	1	1	1	1	7.13	0.09091	1	1	1	1	7.13	0.09091	1	1	1	1	7.13	0.09091
1	1	1	1	2.02	0.08724	1	1	1	1	2.02	0.08724	1	1	1	1	2.02	0.08724	1	1	1	1	2.02	0.08724
1	1	1	1	3.75	0.02083	1	1	1	1	3.75	0.02083	1	1	1	1	3.75	0.02083	1	1	1	1	3.75	0.02083
1	1	1	1	3.81	0.05943	1	1	1	1	3.81	0.05943	1	1	1	1	3.81	0.05943	1	1	1	1	3.81	0.05943
1	1	1	1	3.03	0.09548	1	1	1	1	3.03	0.09548	1	1	1	1	3.03	0.09548	1	1	1	1	3.03	0.09548
1	1	1	1	1.83	0.07697	1	1	1	1	1.83	0.07697	1	1	1	1	1.83	0.07697	1	1	1	1	1.83	0.07697
1	1	1	1	4.29	0.09548	1	1	1	1	4.29	0.09548	1	1	1	1	4.29	0.09548	1	1	1	1	4.29	0.09548
1	1	1	1	4.96	0.09500	1	1	1	1	4.96	0.09500	1	1	1	1	4.96	0.09500	1	1	1	1	4.96	0.09500
1	1	1	1	7.51	0.07021	1	1	1	1	7.51	0.07021	1	1	1	1	7.51	0.07021	1	1	1	1	7.51	0.07021
1	1	1	1	3.81	0.05106	1	1	1	1	3.81	0.05106	1	1	1	1	3.81	0.05106	1	1	1	1	3.81	0.05106
1	1	1	1	3.52	0.05116	1	1	1	1	3.52	0.05116	1	1	1	1	3.52	0.05116	1	1	1	1	3.52	0.05116
1	1	1	1	7.06	0.09984	1	1	1	1	7.06	0.09984	1	1	1	1	7.06	0.09984	1	1	1	1	7.06	0.09984
1	1	1	1	4.99	0.09984	1	1	1	1	4.99	0.09984	1	1	1	1	4.99	0.09984	1	1	1	1	4.99	0.09984
1	1	1	1	4.76	0.09904	1	1	1	1	4.76	0.09904	1	1	1	1	4.76	0.09904	1	1	1	1	4.76	0.09904
1	1	1	1	6.29	0.09981	1	1	1	1	6.29	0.09981	1	1	1	1	6.29	0.09981	1	1	1	1	6.29	0.09981
1	1	1	1	4.79	0.04452	1	1	1	1	4.79	0.04452	1	1	1	1	4.79	0.04452	1	1	1	1	4.79	0.04452
1	1	1	1	5.11	0.07432	1	1	1	1	5.11	0.07432	1	1	1	1	5.11	0.07432	1	1	1	1		

sitions were readily located. The nuclear scattering lengths used here and subsequently were: As, 0.63; Ca, 0.49; O, 0.577; and H,  $-0.378 \times 10^{-12}$  cm.

### Structure refinement

In view of the high accuracy of the As, Ca and O atom positions established in the X-ray determination (Ferraris, 1969), and the relative paucity of the neutron data available, no attempt was made to use the latter for refinement of the heavy atom parameters. The designation of atoms is the same as adopted by Ferraris (1969). Structure factors calculated with the As, Ca, and O parameters from the X-ray analysis, and H coordinates from the neutron difference synthesis, with a  $B$  value of  $3 \text{ \AA}^2$ , gave an initial  $R$  value of 0.11. Three cycles of isotropic least-squares refinement of the hydrogen parameters only, minimizing structure factor differences (rather than their squares), and with weighting  $1/\sigma$ , where  $\sigma$  was derived from the data reduction program, gave some oscillation of parameters. This was reduced by applying only one half of the predicted shifts; two cycles led to a structure with reasonable bond lengths and angles and an  $R$  value of 0.077. In three cycles of full-matrix least-squares anisotropic refinement, by the *ORFLS* program of *X-ray 63* on *ATLAS* with all parameters for the hydrogen atoms allowed to vary, principal temperature coefficients of several H atoms, especially H(1), were not all positive definite. For these, half the predicted shifts were applied and two further cycles, in which only the temperature coefficients were free to vary, led to  $R=0.075$ ; only H(1) remained with temperature factor not positive definite.

As some test of the incidence of extinction,  $F_o/F_c$  was plotted against the measured intensity to give a line from which an extinction correction, ranging from a minimum of  $F_{\text{corr}} = F_{\text{obs}}/0.97$  for  $I_{\text{meas}} = 3000$  to  $F_{\text{corr}} = F_{\text{obs}}/0.87$  at a maximum  $I_{\text{meas}}$  of 25,000, was derived. As a result of these corrections,  $R$  fell to 0.70. Opportunity was taken to check on suspiciously discordant values and individual backgrounds were deduced for some of these reflexions; these changes reduced  $R$  to 0.061. From here, four further cycles of least-squares refinement, in which all hydrogen parameters were varied, showed some small oscillations and slightly negative temperature coefficients for H(1) and H(4). Application of half shifts led to complete convergence, with final shifts less than standard deviations, and a final  $R$  value 0.053 over all reflexions listed in Table 1 giving final  $|F_o|$  and  $|F_c|$  values. A final Fourier

difference synthesis provided no suggestion that the acidic hydrogen atom occupies more than a single site; Table 2 gives the final positional coordinates (and their e.s.d.'s) of the hydrogen atoms, together with  $B_{ij}$  coefficients in the expression

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

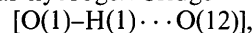
Coordinates for the As, O, and Ca atoms are not listed since they are unchanged from those reported by Ferraris (1969).

### Discussion and description of the structure

Fig. 1 shows the clinographic projection, along the  $x$  axis, of the contents of one unit cell, including the hydrogen atoms. Apart from  $W(2)-H(5) \cdots W(1)$ ,\* all the hydrogen bonds in pharmacolite (Table 3) are as described by Ferraris (1969) on the basis of the positions of the heavy atoms; thus the description of the structure is substantially unchanged. It should be emphasized that, while the  $H_2W(1)$  molecules form an infinite chain along the  $x$  axis, through their two hydrogen bridges with oxygen atoms of type O(3), the  $H_2W(2)$  molecules are not linked together. The latter form both an inter-strata hydrogen bond [ $W(2)-H(4) \cdots O(9)$ ] and also a (very weak) linkage with  $W(1)$ , connecting two non-contiguous Ca-polyhedra of the same chain (Fig. 1).

Together with the phosphorus analogue brushite,  $CaHPO_4 \cdot 2H_2O$  (Curry & Jones, 1970), this is the first structure containing  $(XO_4H)^{-}$  ions for which the acidic hydrogen atom has been located by the neutron diffraction technique; we now have experimental confirmation of the hypothesis (Cruickshank, 1961) that the acidic hydrogen atom is bound to the oxygen atom forming the longest X-O bond. Thus, an X-ray determination of the X-O lengths, together with the O  $\cdots$  O contacts, is indeed likely to provide a useful indication of the positions of the hydrogen atoms.

The non-linear hydrogen bridge



in which the acidic hydrogen atom in pharmacolite is engaged, has the shortest O  $\cdots$  O distance and the longest O-H length of all the hydrogen bonds in this structure (Table 3). This is in accord with the empiric-

\* Ferraris (1969) inferred that H(5) lay along  $W(2) \cdots O(13)$  because the  $W(2) \cdots W(1)$  contact had not been noticed at the time.

Table 2. Fractional atomic coordinates and vibrational parameters ( $\text{\AA}^2$ ) with significant figures of estimated standard deviations in parentheses

	$x/a_0$	$y/b_0$	$z/c_0$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
H(1)	0.1512 (51)	0.3328 (15)	0.3009 (41)	4.5 (1.1)	2.0 (1.0)	2.5 (1.0)	-0.4 (0.9)	2.3 (0.9)	0.4 (0.8)
H(2)	0.1567 (51)	0.9880 (14)	0.2466 (52)	2.3 (0.8)	1.4 (0.9)	4.2 (1.2)	0.1 (0.8)	2.3 (0.9)	-0.6 (0.8)
H(3)	-0.0196 (50)	0.9137 (15)	0.2459 (48)	3.4 (1.1)	2.8 (1.0)	3.2 (1.0)	0.1 (0.9)	2.6 (0.8)	0.0 (0.9)
H(4)	0.2643 (68)	1.0075 (17)	0.7800 (53)	5.3 (1.5)	2.1 (1.0)	2.7 (1.3)	0.4 (1.1)	1.6 (1.2)	0.3 (1.0)
H(5)	0.2536 (58)	0.9348 (20)	0.6202 (51)	4.4 (1.2)	4.1 (1.3)	3.1 (1.0)	-0.3 (1.1)	1.1 (1.0)	0.6 (1.0)

ally established correlation between O–H and O...O lengths (see *e.g.* Hamilton & Ibers, 1968), which is also followed qualitatively for all the hydrogen bonds in pharmacolite except  $W(1)\text{--}H(3)\cdots O(15')$ .

#### The conformation of the water molecules

In the pharmacolite structure, the two groups consisting of a donor water oxygen atom, its two hydrogen atoms, and the two acceptor oxygen atoms are each planar; their best mean planes,  $\alpha$  (Schomaker, Waser, Marsh & Bergman, 1959), are reported in Table 3, in fractional coordinates and referred to the cell axes.

Comparison of the two H–O–H angles with the value in an isolated water molecule ( $104.5^\circ$ ) indicates that the water molecules in pharmacolite are at most slightly

distorted. In spite of this, only the two hydrogen bridges associated with  $W(1)$  are nearly linear; the other two, associated with  $W(2)$ , are certainly non-linear. The degree of linearity of the hydrogen bridges is clearly correlated with the size of the O...W...O angle: while  $O(11')\cdots W(1)\cdots O(15')$  is only slightly smaller than the  $H(2)\text{--}W(1)\text{--}H(3)$  angle,

$$O(9)\cdots W(2)\cdots W(1)$$

is as much as  $14^\circ$  smaller than  $H(4)\text{--}W(2)\text{--}H(5)$ . In both the water molecules the acceptor oxygen atoms are nearer to the  $\angle$ H–O–H bisectors than are the hydrogen atoms. It is important to note, however, that all the hydrogen bonds in pharmacolite are bent only towards the bisector, *i.e.* they still lie within the planes reported in Table 3.

Table 3. Interatomic distances (above) ( $\text{\AA}$ ) and (for columns  $\overline{A\alpha}$  to  $\overline{E\alpha}$ ) angles (deg) (below) involving hydrogen atoms and hydrogen bonds; least-squares planes  $\alpha$ , for atoms in columns A, B, C, D, E, and distances of atoms from the planes

Thus  $\overline{A\alpha}$  denotes displacement of atom A from plane  $\alpha$ , and  $\overline{AB}$  denotes the separation of atoms A and B. Significant figures of the e.s.d.'s are given below.

A	B	C	D	E	$\overline{A\alpha}$	$\overline{B\alpha}$	$\overline{C\alpha}$	$\overline{D\alpha}$	$\overline{E\alpha}$	$\overline{AB}$	$\overline{AC}$	$\overline{BC}$
$O(11')\cdots H(2)\text{--}W(1)\text{--}H(3)\cdots O(15')$					0.004	$\angle ABC$ –0.036	$\angle ACE$ 0.016	$\angle BCD$ –0.037	$\angle CDE$ 0.004	1.78 2	2.741 11	0.97 2
$\alpha$	$0.502X - 1.227Y + 5.437Z = 0.243$					176 3	103.3 4	106 3	174 2	1.82 3	2.799 13	0.99 3
$O(9)\cdots H(4)\text{--}W(2)\text{--}H(5)\cdots W(1)$					0.002	–0.012	–0.012	–0.106	–0.009	1.85 3	2.787 12	0.96 3
$\alpha$	$5.849X + 0.705Y - 1.452Z = 1.135$					166 3	91.1 4	105 3	167 3	2.18 3	3.074 16	0.92 4
$O(12)\cdots H(1)\text{--}O(1)$										1.67 3	2.707 13	1.06 3

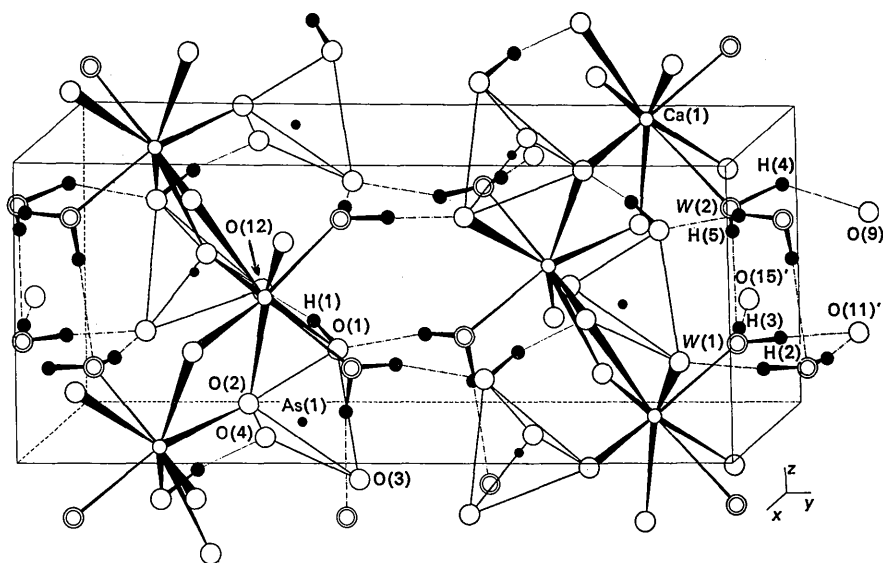


Fig. 1. Unit cell of pharmacolite in clinographic projection down the  $a$  axis; hydrogen atoms are shown as black circles and water oxygen atoms as double circles.

If the hydrogen-bonded water molecules in the pharmacolite structure are classified in terms of their lone-pair electrons (Chidambaran, Sequeira & Sikka, 1964),  $H_2W(2)$  is of type *D* [ $W(2)$  is in contact with a Ca atom], while  $H_2W(1)$  is of type *H* [ $W(1)$  is Ca-coordinated and an acceptor of the  $W(2)-H(5)\cdots W(1)$  hydrogen bond]. However the group Ca(1), O(9), H(4),  $W(2)$ , H(5) and  $W(1)$  is not truly planar, as would be the case if Ca(1) were exactly on the 'twofold axis' of the water molecule. These atoms are, respectively,  $-0.04$ ,  $-0.08$ ,  $0.09$ ,  $0.15$ ,  $0.22$  and  $0.06$  Å distant from their best least-squares plane, which has equation:

$$0.960X - 0.039Y - 0.150Z = 0.086.$$

The angles which the line Ca(1)- $W(2)$  makes with H(5), H(4),  $W(1)$ , and O(9) are 119, 136, 122.6 and 144.2°\* respectively. The second water molecule (type *H*), on the other hand, has a roughly tetrahedral configuration; in fact the  $\beta$  plane through Ca(1),  $W(1)$  and H(5) makes an angle of 63° with the plane containing  $W(1)$ , H(2), H(3), O(11) and O(15) (Table 3). The line of intersection between the  $\alpha$  and  $\beta$  planes makes angles of 39 and 67° with  $W(1)-H(2)$  and  $W(1)-H(3)$  respectively; angle Ca(1) $\cdots W(1)-H(5)$  is 131°.

At first sight, it seems that the electrostatic charges balances for  $W(1)$  and  $W(2)$  are completely different, recalling that  $W(1)$  is an acceptor in a hydrogen bond; however this hydrogen bond is unusually weak (3.07 Å) and, moreover,  $W(1)$  is a donor in two hydrogen bridges (2.74, 2.80 Å) appreciably stronger in total than the two (2.79, 3.07 Å) donated by  $W(2)$ . Therefore, if, following Baur (1962), we distribute the electrostatic charges roughly inversely with atomic distances, the charges balance appears more satisfactory, especially if one bears in mind that the true nature of the chemical bonds involved is not known.

Some evidence suggests that the stability of the water molecule configurations in pharmacolite may be low, and that  $W(2)$ , especially, plays little part in the stability of the structure. The  $W(2)-H(5)\cdots W(1)$  hydrogen bond is certainly very weak and Abbona & Ferraris (1970) have shown that, in the dehydration of pharmacolite by heating, at least two endothermic reactions precede the breakdown of the pharmacolite structure (before this, there are merely a few small shifts in the lines of the X-ray powder spectrum). This may be associated with either a change in orientation of water molecules prior to their complete loss, or with insensitivity of the structure to water loss, or with both. A plausible hypothesis seems to be that, under heating,  $H_2W(2)$  rotates around  $W(2)-H(5)$ , and takes up the configuration found in the analogous structure of gypsum,  $CaSO_4 \cdot 2H_2O$  (Atoji & Rundle, 1958); this would lead to a hydrogen bridge  $W(2)-H(5)\cdots O(13)$ . We note that  $\angle O(9)\cdots W(2)\cdots O(13) = 111.1(4)^\circ$ ,

$W(2)\cdots O(13) = 3.140(15)$  Å, and  $H(5)\cdots O(13) = 2.85(4)$  Å.

#### Accuracy of the structure and thermal motion

Despite the low *R* value of 0.053 and the satisfactory ratio between the number of reflexions (318) and the number of variables (46), the apparent e.s.d.'s are generally higher than those reported for some comparable structures refined from neutron-diffraction data. This may be associated with our minimization of  $||F_o| - |F_c||$ , rather than the more commonly minimized  $|F_o|^2 - |F_c|^2$ . Admittedly, small errors in the heavy-atom positions could influence the location of hydrogen atoms, but there are other indications that the accuracy of the  $CaHAsO_4 \cdot 2H_2O$  structure is not inferior to those of some others with lower apparent e.s.d.'s. Thus the final difference Fourier synthesis shows only random ripples and an absence of anomalous peaks on, or near, the positions of the atoms; and the spread of O-H lengths is substantially in accord with the variation in O $\cdots$ O lengths. For the root-mean-square deviation (Table 5), the  $B_{ij}$   $\sigma$ -values (Table 2) imply  $\sigma$ 's of about one-half of the values of the r.m.s.d.'s. In spite of this, the three principal r.m.s.d.'s (Table 5) all differ from their mean values (0.18, 0.24 and 0.14 Å respectively) by substantially less than their  $\sigma$ 's. On the assumption that the thermal parameters are meaningful, we have corrected the O-H bond lengths for thermal motion according to Busing & Levy (1964). Table 4 presents the lower and upper limits for the corrected length, together with the uncorrected length and the length on the assumption of the O-H 'riding' model.

Table 4. O-H bonds lengths: uncorrected (*A*) and corrected for thermal motion (*B*, *C*, *D*); lower (*B*) and upper (*C*) limits and 'riding' model (*D*)

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
O(1)-H(1)	1.059 Å	1.063 Å	1.172 Å	1.081 Å
$W(1)-H(2)$	0.965	0.966	1.088	0.974
$W(1)-H(3)$	0.986	0.988	1.109	1.000
$W(2)-H(4)$	0.959	0.961	1.129	0.978
$W(2)-H(5)$	0.916	0.921	1.084	0.944

Table 5. Parameters characterizing the principal directions 1, 2, 3 of thermal vibration for the hydrogen atoms: root-mean-square displacement (*A*) and angles which the principal directions make with the *a* (*B*), *b* (*C*) and *c* (*D*) axes

		<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
H(1)	1	0.18 Å	104°	40°	50°
	2	0.24	33	98	83
	3	0.12	119	129	40
H(2)	1	0.15	49	41	104
	2	0.24	81	101	36
	3	0.10	137	51	58
H(3)	1	0.19	90	4	93
	2	0.23	56	87	59
	3	0.12	146	68	31

\* In Ferraris (1969) the value of this angle is erroneously reported as 114.2°.

Table 5 (cont.)

		A	B	C	D
H(4)	1	0.18	103	69	24
	2	0.26	13	84	103
	3	0.16	91	22	109
H(5)	1	0.22	55	43	84
	2	0.26	35	121	124
	3	0.19	91	117	35

The authors thank Mr D. H. C. Harris and the University Support Group, A.E.R.E., for assistance. We are grateful to the S.R.C. for making available neutron-beam and computational facilities, the Italian C.N.R. for the award of a NATO Fellowship to G.F. and to Bradford University for the award of a scholarship to J.Y.

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## A Neutron Diffraction Study of the Crystal Structure of Sodium Arsenate Heptahydrate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$

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(Received 11 March 1970)

The positions of all 15 independent hydrogen atoms in the crystal structure of disodium hydrogen orthoarsenate heptahydrate,  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ , approximately located in a previous single-crystal X-ray analysis, have been confirmed by neutron diffraction. Anisotropic least-squares refinement of the hydrogen atoms led to a final  $R$  value of 0.068 over 476 independent neutron intensities measured on a manually operated diffractometer. No correction was made for absorption but an empirical extinction correction was applied. The neutron analysis, in which hydrogen atom positions were located with coordinate estimated standard deviations of about 0.04 Å, confirms the hydrogen-bonding system deduced from the X-ray analysis. The anionic hydrogen atom, H(1), is carried by the oxygen atom O(4), with the longest As–O bond (1.74 Å compared with an average length of 1.67 Å); while the markedly non-linear hydrogen bond of O(4)–H(1) to the water oxygen atom O(6) is relatively short at 2.68 Å, O(4)–H(1) is not quite the longest O–H distance in the structure. Each of the seven water molecules is closely coplanar with the two oxygen atoms to which it is hydrogen-bonded, although nearly all the hydrogen bonds are significantly bent. In terms of the classification by lone pair orientation, five of the water molecules are of type  $A$  and two of type  $G$ . Water H–O–H angles range from 104 to 110°, with an e.s.d. of about 3°.

### Introduction

The crystal structure of disodium hydrogen orthoarsenate heptahydrate, or sodium arsenate heptahydrate,  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ , has been determined by single-crystal

X-ray analysis by Ferraris & Chiari (1970*a*) and, together with its phosphorus isomorph,  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  independently by Baur & Khan (1970). Each of the two crystallographically independent sodium ions (in layers perpendicular to [010]) is approximately octahe-