

## The Crystal Structure of Pharmacolite, $\text{CaH}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$

BY G. FERRARIS

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

(Received 18 September 1968)

Pharmacolite,  $\text{CaH}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$ , crystallizes in the monoclinic system, space group  $Ia$  ( $C_2^2$ ). Unit-cell parameters are:  $a_0 = 5.9745$ ,  $b_0 = 15.4340$ ,  $c_0 = 6.2797$  Å,  $\beta = 114^\circ 50'$ .  $Z = 4$ ,  $D_m = 2.725$ ,  $D_c = 2.731$  g.cm<sup>-3</sup>. The crystal structure was refined with 618 diffractometer-measured reflexions (97% of those accessible to Cu  $K\alpha$  radiation), correcting for the anomalous scattering of As and Ca, to a final  $R$  value of 0.04. The structure is analogous to those of gypsum and brushite, containing layers normal to [010] in which Ca atoms are coordinated by six oxygen atoms in  $\text{AsO}_4$  tetrahedra (one of which is an OH group rather weakly bonded to Ca) and two water molecules at the surface of the layers. The layers are joined by hydrogen bonds, which are also formed by both water molecules and OH groups within the layers.

### Introduction

The crystal structure of pharmacolite,



described in this paper, was studied as part of a programme of structural research on some phases of the system  $\text{CaHAsO}_2\text{-H}_2\text{O}$ , with particular interest in those occurring in nature (Calleri & Ferraris, 1965, 1967).

On the basis of unit-cell parameters and rather doubtful morphological data,\* pharmacolite has generally been considered to be isostructural with gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and brushite,  $\text{CaH}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ . As regards the latter, however, Jones & Smith (1962) refined its structure assuming space group  $Ia$  (after piezoelectric effect measurement) and not space group  $I2/a$  which was chosen by Beevers (1958), so that the hypothesis of strict isostructuralism between gypsum and brushite is not valid. The problem of the symmetry and structure of pharmacolite remained, therefore, to be settled.

### Experimental

#### Crystal data

X-ray diffraction analysis (based both on Weissenberg photographs and single-crystal diffractometry) confirmed that the unit cell of pharmacolite is similar to that of gypsum and brushite, with parameters near to those quoted in Dana's *System of Mineralogy* (Dana & Dana, 1951) and by Fischer (1960).

The unit-cell parameters were refined by a least-squares procedure, using high  $\theta$  angles measured, at room temperature, on a single-crystal diffractometer

(Cu  $K\alpha_1 = 1.54050$ ; Cu  $K\alpha_2 = 1.54434$  Å); the following values (standard deviations in parentheses) were obtained:  $a_0 = 5.9745(5)$ ,  $b_0 = 15.4340(15)$ ,  $c_0 = 6.2797(6)$  Å,  $\beta = 114^\circ 50'(1')$ .

The absent reflexions  $hkl$  with  $h+k+l$  odd and  $h0l$  with  $h$  (and  $l$ ) odd, do not allow the ambiguity between space groups  $I2/a$  ( $C_{2h}^2$ ) and  $Ia$  ( $C_2^2$ ) to be resolved; the latter space group was chosen because a piezoelectric test, on a large number of synthetic crystals prepared according to Guerin's (1941) method, was positive. In a preliminary work (Calleri & Ferraris, 1965) pharmacolite was assigned to space group  $C_{2h}^2$  because the piezoelectric test on a few fragments of natural crystals had proved negative. The identity of the natural and synthetic crystals was checked, both by X-ray and infrared spectra. The intensities were collected from a natural crystal and the refinement confirmed the space group  $Ia$ .

Other physical data are: M.W. = 216.03,  $V = 525.50$  Å<sup>3</sup>,  $D_m = 2.725$  g.cm<sup>-3</sup> (flotation, natural crystals),  $Z = 4$ ,  $D_c = 2.731$  g.cm<sup>-3</sup>,  $F(000) = 424$  e, linear absorption coefficient for Cu  $K\alpha$  radiation  $\mu = 172$  cm<sup>-1</sup>.

#### Intensity measurement

Intensities 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. For these measurements a natural prismatic crystal from Andreasberg (Harz) was mounted with its elongation direction, coincident with the  $z$  axis, parallel to the  $\phi$  axis of the goniostat; this crystal was 0.40 mm long and had a cross-section of  $0.07 \times 0.07$  mm<sup>2</sup>. The  $\theta$ - $2\theta$  scanning technique was employed ( $1^\circ$  per minute), varying the interval of integration from  $2$  to  $4^\circ$  as a function of  $2\theta$ ; the background was measured for an interval of  $0.5^\circ$  on both sides of each peak. In the quadrant of the reciprocal lattice with positive  $k$  it was possible to measure the intensities of 568 reflexions, corresponding to about 97% of the total

\* In Dana's *System of Mineralogy* (Dana & Dana, 1951) this mineral is simply classified as monoclinic; Strunz (1957) assigns it to space group  $A2$ , probably in analogy with brushite, investigated by Terpstra (1937); Fischer (1960) proposes space groups  $C2/c$  or  $Cc$ .

independent reflexions of the Laue group  $2/m$  and accessible to Cu  $K\alpha$  radiation. The reflexions of the equatorial layer were measured in two of the octants of the limiting sphere which have positive  $k$ , which are independent according to the point group  $m$ , in order to have data for testing for the anomalous scattering effect (in all 618 reflexions).

The intensities were converted to amplitudes by standard formulae; for the computation of atomic scattering factors the values reported, for neutral atoms, in *International Tables for X-ray Crystallography* (1962) were linearly interpolated after application, for As and Ca, of the real part of the correction for the anomalous scattering [ $f'_{As} = -1.2$  (*International Tables*, 1962),  $f'_{Ca} = 0.4$  (Saravia & Caticha-Ellis, 1966)].

Owing to the small dimensions of the crystal used and to the fact that the percentage error in their measurement is consequently large, it was decided not to make an absorption correction. Considering the agreement between  $F_o$  and  $F_c$  no correction for the extinction effect was made.

### Solution and refinement of the structure

Assuming that pharmacolite and brushite were isomorphous, the Ca, P (for As) and O coordinates of the latter (Jones & Smith, 1962) were used, yielding an index  $R=0.30$  with an overall isotropic vibrational factor  $B=1.5 \text{ \AA}^2$ . Since this encouraging value of  $R$  seemed to confirm the correctness of the hypothesis, the positional parameters and the overall scaling factor were refined by the full-matrix least-squares program of Busing, Martin & Levy (1962), with minor modifications to take into account the imaginary part of the atomic scattering factors. The refinement was based on  $|F|$  values and the  $R$  index has the usual meaning, as quoted in the program description.

The position of the atoms, especially the  $x$  coordinates of the oxygens, changed considerably during the first cycle and  $R$  dropped to 0.18; the origin was fixed by keeping the  $x$  and  $z$  coordinates of the As atom constant. Three successive cycles, with individual isotropic thermal parameters, reduced  $R$  to 0.075.

Throughout the refinement, the following weighting scheme was used:

$$\begin{aligned} w_{hkl} &= A/(BF_o^2 + |F_o| + C) \text{ for } |F_o| \geq C, \\ w_{hkl} &= DF_o^2 \text{ for } |F_o| < C; \end{aligned} \quad (2)$$

the constants  $A$  and  $D$  were given values such that  $0 < w_{hkl} < 1$  and the two weighting systems coincided when  $|F_o| = C$ ;  $C$  and  $B$  were varied slightly during the refinement in order to maintain  $\sum w\Delta^2$  at a satisfactorily constant value for the amplitudes in various groups. The values of  $C$  were around  $2|F_{\min}|$ , and those of  $B$  around  $2|F_{\max}|$ .

Subsequent cycles, with anisotropic vibrational parameters, reduced  $R$  to 0.040. At this stage the correction for the imaginary part of the anomalous scattering of As and Ca was introduced according to the values

for Cu  $K\alpha$  radiation in the literature (*International Tables*, 1962). Assigning indices of type  $hk\bar{l}$  and  $\bar{h}k\bar{l}$  to the independent reflexions,  $R$  reached a minimum value of 0.039 (weighted  $R = 0.043$ , the standard error of an observation of unit weight was 0.387), while with the orientation  $hkl$ ,  $\bar{h}kl$ ,  $R$  was greater (0.043, weighted  $R = 0.048$ , the standard error of an observation of unit weight was 0.431). According to the test proposed by Hamilton (1965), the ratio of the two weighted  $R$  values indicates that the former orientation is the correct one. This is confirmed by the inspection of the 50 couples of reflexions  $hk0$  and  $\bar{h}k0$ , which have been included separately in the refinement; the ratio of the observed intensities is, in fact, nearly always in agreement with the ratio of the squares of the corresponding structure factors.

As regards the absolute values of the parameters, the correction for the imaginary part of the anomalous scattering caused a negative variation not greater than the corresponding  $\sigma$  values for all the  $z$  coordinates, except for that of the Ca atom, whose shift was positive and of the order of  $3\sigma$ . The symmetry of space group  $Ia$  cancels out the effect on the  $y$  coordinates; the variations of the  $x$  coordinates are not significant because the reflexions were measured with positive and negative  $h$  (Cruickshank & McDonald, 1967). The above-mentioned variations increased the regularity of the coordination polyhedra of the Ca and of the  $AsO_4$  groups (Tables 3 and 4).

With reference to the possibility of correlating the polarity of the structure with the morphology, one can only say that the crystal, well formed at one end only, was mounted with this end upwards.

Table 1 presents the final values of  $|F_c|$ 's,  $|F_o|$ 's and of the corresponding phase angles  $\alpha$ ; the reflexions marked with an asterisk were given zero weight during the refinement because either the intensity was small or they were thought to be probably affected by extinction ( $R=0.050$  for all reflexions of Table 1). Table 2 shows the final values, with their standard deviations in parentheses, of the fractional coordinates and of the  $B_{ij}$  coefficients of the expression:

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

### Description and discussion of the structure

The essential features of the crystal structure of pharmacolite are practically the same as those described for haidingerite (Calleri & Ferraris, 1967; Binas, 1966; Cassini, Herpin & Permingeat, 1966): there are layers of  $AsO_4$  tetrahedra normal to  $[010]$  joined by hydrogen bonds and through the coordination of Ca atoms (Fig. 1). An analysis of the distribution of valence, coordination and hydrogen bonds is worth while, before giving a more detailed description of the structure.

The Ca atom is undoubtedly coordinated by five oxygen atoms of the  $AsO_4$  groups [two of type O(2),

two of type O(4) and one of type O(3)]\* plus two oxygen atoms belonging to water molecules; these seven atoms, whose distances from Ca range between 2.326 and 2.664 Å (Table 3), produce around the coordinating centre an electronegative screen which is geometrically irregular. At this point some consideration of the oxygen atom O(1), which is at a distance of 2.962 Å from the Ca atom is necessary. As already stated in the work on haidingerite (Calleri & Ferraris, 1967), it is fairly common to find Ca-coordinated polyhedra in which

\* The notation is as in Fig. 1. As(1), Ca(1), O(1), O(2), O(3), O(4), W(1) and W(2) are crystallographically independent. Other numbers indicate the equivalent atom positions generated by  $\frac{1}{2}+x, \bar{y}, z$ ;  $x, \frac{1}{2}-y, \frac{1}{2}+z$ ;  $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$ . A prime indicates an atom position generated by lattice vectors.

one of the contacts with oxygen atoms is significantly longer than the others; the several authors disagree as to whether such atoms are really coordinated by calcium. Structures in which Ca-O distances of about 2.9 Å have been considered to correspond to real coordinative bonding are:  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (Webb, 1966) and bustamite, CaMnSi<sub>2</sub>O<sub>6</sub> (Peacor & Prewitt, 1963). In the case of pharmacolite there are good reasons for considering that the oxygen atom O(1) is simultaneously bound to a hydrogen atom and interacting weakly with the cation.

As is clear from an inspection of Table 4, three of the As-O bonds are equal, to within the accuracy of the results (mean value=1.672 Å), and shorter than the fourth (1.729 Å); according to the considerations of

Table 1. *Moduli of observed and calculated structure amplitudes with the corresponding phase angles (absolute scale)*

H	K	L	FO	FC	ALPHA	H	K	L	FO	FC	ALPHA	H	K	L	FO	FC	ALPHA	H	K	L	FO	FC	ALPHA
0	0	0	145.2	187.7	-164.4	3	17	0	20.9	18.4	82.7	2	16	2	20.2	20.1	159.2	-3	1	0	37.0	36.9	-142.1
0	0	0	139.0	181.5	170.4	0	18	0	24.5	23.2	-12.1	4	16	7	11.6	10.5	56.5	5	1	0	29.4	28.4	42.4
0	0	0	127.0	137.2	-3.9	-2	18	0	38.4	36.9	176.2	-1	18	0	11.8	10.8	122.4	7	1	0	36.4	35.2	-139.0
0	0	0	125.1	136.4	11.5	7	18	0	45.1	43.6	-108.0	1	18	0	11.8	10.8	122.4	0	7	0	15.3	14.0	20.0
0	0	0	68.3	68.3	-175.2	-1	19	0	14.9	16.8	-44.1	3	18	1	41.2	42.6	-170.0	2	19	0	31.3	29.0	-150.4
0	0	0	65.4	65.4	-171.6	1	19	0	14.9	16.8	-44.1	0	18	2	18.0	16.5	156.0	0	2	0	37.7	36.7	14.0
-1	1	0	58.0	57.8	7.3	0	1	0	30.2	27.0	-17.0	2	18	2	24.8	22.7	-37.2	2	2	0	22.2	21.1	161.5
-1	1	0	56.6	56.4	176.4	0	1	0	13.7	9.4	-105.4	0	2	0	78.9	83.7	16.0	1	19	2	12.6	13.6	-152.4
-1	1	0	52.2	50.9	-171.6	0	2	0	22.2	21.1	161.5	0	2	0	32.0	30.7	-131.5	0	2	0	24.6	23.6	138.5
3	1	0	54.1	52.3	-9.4	-4	1	1	12.8	12.6	110.9	-2	1	0	106.4	103.2	142.4	-2	1	0	34.0	34.0	6.0
3	1	0	33.8	34.2	21.2	-4	1	1	45.1	42.4	145.3	-4	0	2	81.8	79.5	-5.6	-2	1	0	37.7	36.6	118.5
3	1	0	35.1	35.1	159.0	0	1	1	18.2	17.6	-114.4	0	2	0	76.3	79.0	155.0	-1	3	0	24.6	24.6	138.5
0	2	0	74.4	124.7	-177.2	6	1	1	18.4	17.6	-66.8	0	0	7	74.3	73.6	-181.4	4	1	0	37.5	37.6	-85.7
-2	2	0	26.1	29.1	5.2	* 1	2	1	122.4	152.5	6.5	-1	1	2	103.5	103.0	16.3	3	1	0	26.5	26.6	-157.4
-2	2	0	28.5	29.2	-159.0	* 2	2	1	159.3	163.6	-178.4	* 2	2	1	84.4	84.2	-1.7	0	2	0	69.3	68.4	-170.1
-4	2	0	80.3	82.2	104.3	* 3	2	1	105.5	105.9	5.1	* 3	2	1	12.7	12.7	173.7	3	2	0	24.6	24.6	138.5
-4	2	0	81.5	83.9	-157.2	* 4	2	1	107.5	110.7	-186.2	* 4	2	1	84.4	84.2	-1.7	0	2	0	69.3	68.4	-170.1
-6	2	0	38.2	38.7	15.1	-5	2	1	99.2	97.2	179.0	-5	2	1	15.9	18.7	94.4	-2	3	0	94.3	88.0	-161.6
-6	2	0	35.1	35.2	-2.9	5	2	1	102.7	82.0	13.6	-5	2	1	45.4	45.4	-135.1	2	3	0	49.4	48.6	-177.1
-6	2	0	18.7	13.4	-141.0	7	1	1	53.9	53.7	-186.3	7	1	1	18.3	19.4	-37.7	5	2	1	73.1	76.7	26.7
-6	2	0	18.4	13.3	-38.3	0	3	1	27.0	31.7	-183.7	0	2	2	132.8	134.4	-175.9	0	2	1	52.6	47.0	-145.5
-3	3	0	10.8	9.7	-117.1	-2	3	1	46.9	44.1	-150.2	-2	2	2	83.2	79.6	7.8	0	3	0	29.6	28.3	48.5
-3	3	0	9.8	8.8	-68.4	0	3	1	47.9	45.9	-150.2	0	2	2	121.9	120.9	27.8	0	3	0	38.1	36.1	-170.8
-5	3	0	10.1	10.1	94.8	-4	3	1	34.7	34.6	7.3	-4	2	2	54.8	52.1	-175.4	-2	3	0	43.1	41.8	-170.8
-5	3	0	9.8	10.3	83.9	-4	3	1	43.7	42.7	-57.8	-4	2	2	40.7	44.6	-165.8	-4	3	0	23.7	24.8	41.8
-2	4	0	52.9	59.3	-176.9	0	3	1	21.8	25.6	159.1	0	2	2	46.7	46.6	-159.1	0	2	1	37.2	38.0	-147.8
-2	4	0	101.3	107.1	31.1	6	3	1	24.2	24.9	-173.6	-1	3	2	25.3	22.4	-11.7	6	3	0	24.3	24.3	-134.9
-2	4	0	95.8	106.4	0.3	* 1	4	1	110.7	120.7	-7.9	* 1	3	2	48.6	46.4	25.2	-1	4	0	20.2	22.6	-122.1
-4	4	0	33.3	33.6	-134.9	* 1	4	1	130.9	171.3	-175.7	* 1	3	2	127.5	137.6	-85.9	0	4	0	90.6	81.1	-175.5
-4	4	0	30.4	29.0	141.1	-3	4	1	108.6	108.7	172.4	-3	4	0	20.3	17.9	63.2	-3	4	0	90.1	88.4	-167.0
-6	4	0	29.1	27.8	-18.5	-5	4	1	122.2	130.5	-3.0	-5	4	0	19.5	21.7	-44.2	-2	4	0	105.6	106.1	26.2
-6	4	0	29.9	28.6	-18.5	-5	4	1	122.2	130.5	-3.0	-5	4	0	19.5	21.7	-44.2	-2	4	0	105.6	106.1	26.2
-1	5	0	76.5	77.4	-178.7	5	4	1	80.4	79.9	-165.5	7	3	2	16.8	16.8	87.2	5	4	0	100.9	101.0	-151.0
-1	5	0	74.1	77.8	-2.4	4	4	1	55.5	57.6	20.6	* 0	4	2	2.8	2.2	130.3	7	4	0	64.4	63.5	23.5
-3	5	0	46.8	45.8	-105.4	0	4	1	40.8	40.8	151.5	0	4	2	18.2	18.2	168.9	0	4	0	37.4	37.4	-168.9
-3	5	0	46.8	45.3	159.3	-2	5	1	40.7	41.1	23.1	-2	4	2	42.3	40.6	54.8	-2	5	0	36.2	36.1	48.4
-5	5	0	20.8	19.9	171.6	-2	5	1	16.5	14.6	144.7	-2	4	2	20.9	19.8	149.3	-2	5	0	43.0	44.8	26.3
-5	5	0	22.2	21.6	-134.9	-2	5	1	22.2	21.6	-134.9	-2	4	2	11.1	10.9	137.7	-2	5	0	40.6	40.6	137.7
0	6	0	63.3	70.1	7.9	4	5	1	24.2	24.7	-138.6	6	4	2	49.1	47.3	37.8	4	5	0	43.5	42.4	165.3
0	6	0	121.3	136.3	166.9	-6	5	1	21.8	25.1	31.3	-1	5	1	15.1	17.3	-166.2	6	5	0	14.4	13.2	-52.3
-6	6	0	118.0	126.1	166.9	-6	5	1	21.8	25.1	31.3	-1	5	1	15.1	17.3	-166.2	6	5	0	14.4	13.2	-52.3
-6	6	0	82.8	80.0	-2.5	-1	6	1	39.1	39.1	-105.6	-3	5	2	14.4	15.6	97.1	-1	6	0	61.5	59.9	-6.5
-6	6	0	82.8	80.0	-2.5	-1	6	1	39.1	39.1	-105.6	-3	5	2	14.4	15.6	97.1	-1	6	0	61.5	59.9	-6.5
-6	6	0	85.3	85.3	188.6	-6	6	1	59.2	60.0	46.3	3	5	2	39.3	38.6	-122.8	3	5	0	28.0	26.7	17.6
-6	6	0	70.7	70.8	188.6	-6	6	1	59.2	60.0	46.3	3	5	2	39.3	38.6	-122.8	3	5	0	28.0	26.7	17.6
6	6	0	72.7	73.6	-157.6	-3	6	1	30.8	28.6	-142.0	5	5	2	10.1	9.7	-51.6	5	6	0	36.7	36.2	-7.2
6	6	0	18.4	18.4	-188.6	-3	6	1	30.8	28.6	-142.0	5	5	2	10.1	9.7	-51.6	5	6	0	36.7	36.2	-7.2
1	7	0	15.7	15.1	-86.0	5	6	1	34.6	33.9	-131.2	0	6	2	138.0	157.7	-14.0	0	6	0	17.3	17.1	160.7
1	7	0	19.3	20.0	-174.2	0	7	1	19.1	15.4	42.6	-2	6	2	120.1	123.4	-166.6	-2	7	0	16.3	16.6	178.4
-5	7	0	20.2	22.8	-105.4	0	7	1	129.9	141.1	-167.9	0	7	1	129.9	141.1	-167.9	0	7	1	129.9	141.1	-167.9
-5	7	0	18.5	19.0	-22.5	2	7	1	10.3	9.2	-10.5	-4	6	2	11.2	11.2	175.7	-4	6	2	11.2	11.2	175.7
-5	7	0	19.4	20.8	-180.8	4	7	1	17.5	17.4	-15.1	4	7	1	9.2	9.2	147.0	4	7	1	9.2	9.2	147.0
6	8	0	99.7	110.9	-11.1	6	7	1	10.1	8.9	42.4	1	7	2	81.5	80.9	11.1	6	8	0	11.0	10.6	-86.1
2	8	0	97.6	110.9	8.9	-1	8	1	79.2	84.1	-170.9	1	7	2	48.9	47.7	-170.8	1	8	0	57.3	55.1	14.0
2	8	0	97.6	110.9	8.9	-1	8	1	79.2	84.1	-170.9	1	7	2	48.9	47.7	-170.8	1	8	0	57.3	55.1	14.0
-8	8	0	58.0	58.8	-165.3	-3	8	1	53.4	52.0	-8.6	-3	8	1	68.0	67.9	10.3	-3	8	0	73.4	73.0	-163.1
-8	8	0	55.2	56.9	-18.1	3	8	1	63.0	64.0	-157.4	-5	7	2	32.1	33.2	29.8	-5	8	0	46.0	45.3	14.9
-8	8	0	58.9	58.7	29.0	-5	8	1	52.1	53.8	174.8	5	7	2	28.5	28.8	168.8	5	8	0	51.1	50.2	43.5
-1	9	0	23.9	22.4	108.1	5	8	1	42.8	41.3	12.7	7	7	2	24.0	24.5	29.0	-2	9	0	29.5	29.4	-138.3
-1	9	0	23.5	22.4	71.7	0	9	1	11.5	13.4	33.0	0	8	2	90.5	92.1	-175.6	0	9	0	34.3	33.4	-157.4
-3	9	0	25.8	26.4	12.5	-2	9	1	32.7														

Cruickshank (1961) on  $XO_4^-$  ions, the latter oxygen atom should belong to an OH group. Moreover the oxygen atom O(1) is at a distance of 2.707 Å from O(12), which is a reasonable value for a hydrogen bond. We notice, incidentally, that the distance O(4')-O(10) is only 2.766 Å long, but the presence of a hydrogen bond in this case must be excluded since O(4')-O(10) is one of the edges of the coordination polyhedron of calcium.

This situation is nearly the same as in haidingerite except that in that case the oxygen atom with the greater As-O length is certainly not coordinated by Ca. In the pharmacolite structure, on the other hand, the oxygen atom O(1) is, in the author's opinion, interacting with the Ca atom.

The exclusion of O(1) from the coordination polyhedron of Ca would leave a very large 'mesh' between

O(1) and Ca while one of the edges [O(2)-W(7)] of the resulting polyhedron would be 4.45 Å long. The inclusion of O(1) generates a polyhedron (Fig. 2) similar to that found in grossularite (Abrahams & Geller, 1958), with twelve triangular faces, eight vertices and eighteen edges, whose lengths are reported in Table 3.

The difference between the Ca-O(1) distance (2.962 Å) in pharmacolite, and also in brushite (2.82 Å) and that found for the corresponding atoms in the similar structure of gypsum (2.575 Å), is appreciable but not such as to exclude the possibility of interaction between the Ca and O(1) atoms. The greater distance must, in the author's opinion, be related to the fact that in the first two acid salts O(1) is involved in a bond with the acidic hydrogen atom.

The hypothesis of an occupation of alternative sites by the acidic hydrogen atoms, perhaps valid for brush-

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

	$x/a_0$	$y/b_0$	$z/c_0$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Ca	0.2605 (8)	0.8262 (1)	0.0093 (8)	0.998 (66)	0.772 (60)	1.08 (12)	0.06 (13)	0.44 (7)	0.06 (12)
As	0.25320	0.32425 (6)	-0.01400	0.426 (33)	0.495 (36)	1.020 (43)	0.052 (78)	0.237 (27)	-0.059 (86)
O(1)	0.2391 (17)	0.3746 (6)	0.2260 (15)	2.24 (35)	0.81 (33)	1.54 (33)	-0.17 (26)	1.08 (28)	-0.27 (24)
O(2)	0.5340 (15)	0.2786 (5)	0.0991 (16)	0.60 (28)	1.05 (31)	1.56 (31)	-0.03 (26)	-0.05 (25)	-0.38 (30)
O(3)	0.1941 (14)	0.3978 (5)	-0.2238 (14)	1.28 (29)	1.61 (36)	1.46 (35)	0.47 (27)	0.60 (24)	0.59 (29)
O(4)	0.0273 (14)	0.2503 (6)	-0.1177 (16)	0.57 (29)	0.93 (29)	1.38 (32)	0.05 (22)	0.19 (25)	0.23 (24)
W(1)	0.1414 (17)	0.9257 (5)	0.2435 (17)	1.96 (36)	1.11 (32)	2.67 (40)	-0.11 (26)	1.58 (32)	-0.66 (27)
W(2)	0.2671 (20)	0.9456 (5)	0.7685 (18)	3.08 (40)	1.31 (30)	2.61 (40)	-0.12 (30)	1.74 (35)	0.25 (31)

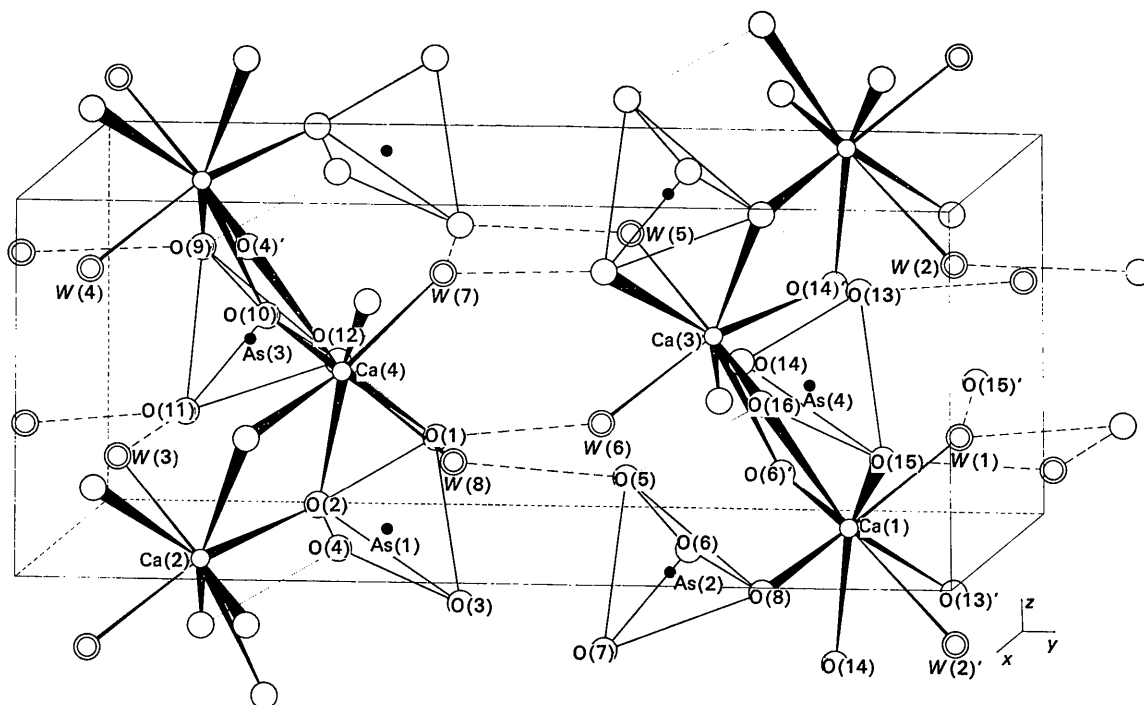


Fig. 1. Clinographic projection, along the  $x$  axis, of the contents of one unit-cell.

ite, seems to be excluded\* by some of the considerations discussed above.

Let us now consider the orientation and environment of the water molecules. The water molecule whose oxygen atom is labelled  $W(1)$  seems, without doubt, to be involved in two hydrogen bonds:  $W(1)-\text{O}(11)=2.741 \text{ \AA}$  and  $W(1)-\text{O}(15')=2.799 \text{ \AA}$  [ $\angle \text{O}(11)-W(1)-\text{O}(15')=103^\circ$ ] (Table 5). The molecule in question attains therefore, through these bonds and the contact with Ca, the typical configuration described in the literature. Such hydrogen bonds are present also in gypsum and brushite; one links two adjacent layers, while the other is on the surface of a layer.

The configuration of the water molecule whose oxygen atom is labelled  $W(2)$  and which has three neighbouring oxygen atoms [ $\text{O}(9)$  at  $2.787$ ,  $\text{O}(14')$  at  $2.911$  and  $\text{O}(13)$  at  $3.140 \text{ \AA}$ ], is not so apparent. Since  $W(2)-\text{O}(14')$  is one of the edges of the calcium-coordinated polyhedron (' $\text{CaO}_8$  polyhedron') it cannot be considered as a possible hydrogen bridge; on the other hand there is no reason why  $W(2)$  and  $\text{O}(9)$  should not form a hydrogen bond which links two adjacent layers. The second hydrogen atom of  $W(2)$  probably lies in

\* In the brushite structure three Ca-O distances are long and the tetrahedron  $\text{AsO}_4$  appears rather irregular, which could be cited in support of an occupation of alternative sites by the acidic hydrogen atom; however, the accuracy of the determination of the brushite structure does not seem to be very high.

the direction  $W(2)-\text{O}(13)$  ( $3.140 \text{ \AA}$ ) without forming a real hydrogen bond as it does in gypsum [ $W(2)-\text{O}(13)=2.801 \text{ \AA}$ ]. In pharmacolite the possibility of a second hydrogen bond of  $W(2)$  is no doubt hindered by the fact that atom  $\text{O}(1)$  [crystallographically equivalent to  $\text{O}(13)$  and  $\text{O}(9)$ ] is already bound to the acidic hydrogen atom, participates in the first hydrogen bond of  $W(2)$  and is inside the coordination sphere of calcium.

In conclusion, the distribution of the hydrogen atoms of the water molecules seems to be, at least qualitatively, the same as that found in gypsum by neutron diffraction (Atoji & Rundle, 1958); there are, however, only three hydrogen bonds involving water molecules instead of four, two of them involving oxygen atoms of type  $\text{O}(3)$  (coordinated by only one Ca,  $\text{Ca}-\text{O}(3)=2.664 \text{ \AA}$ ) and one oxygen atom of type  $\text{O}(1)$ . Oxygen atoms of type  $W(1)$  form an infinite chain, along the  $x$  axis, of hydrogen bonds; this chain, which is similar to a 'square-wave', is in a plane almost parallel to (001) (Fig. 1). Oxygen atoms of type  $W(2)$  behave similarly even if  $W(2)-\text{O}(13)$  cannot be considered as a true hydrogen bond.

The layers of tetrahedra, normal to [010], in pharmacolite have different features from those of haidingerite (Figs. 1 and 2). In the former compound As and Ca atoms are at the same level; the layers are thinner than in haidingerite thus leaving a larger space for accommodating an extra water molecule. The water molecules are situated on the surface of the layers, facing

Table 3. *Interatomic distances in the Ca-coordination polyhedron before (B) and after (A) the correction for anomalous scattering*

	A	B	A	B
Ca(1)-O(13')	2.962 (11) Å	2.965 (11) Å	$W(2')-\text{O}(15)$	3.22 Å
Ca(1)-O(14')	2.466 (11)	2.445 (11)	$W(2')-\text{O}(8)$	3.34
Ca(1)-O(6')	2.326 (9)	2.344 (9)	$W(2')-\text{O}(13')$	3.25
Ca(1)-O(15)	2.664 (9)	2.665 (10)	$\text{O}(14')-\text{O}(13')$	2.67
Ca(1)-O(8)	2.376 (9)	2.351 (10)	$W(2')-\text{O}(14')$	2.91
Ca(1)-O(16)	2.504 (10)	2.518 (10)	$\text{O}(14')-\text{O}(6')$	3.26
Ca(1)- $W(1)$	2.430 (9)	2.454 (10)	$\text{O}(14')-\text{O}(8)$	2.77
Ca(1)- $W(2')$	2.395 (10)	2.381 (10)	$\text{O}(8)-\text{O}(16)$	3.14
$W(1)-\text{O}(15)$	3.25		$\text{O}(8)-\text{O}(15)$	3.20
$W(1)-\text{O}(13')$	3.23		$\text{O}(8)-\text{O}(6')$	3.76
$W(1)-\text{O}(16)$	3.42		$\text{O}(13)-\text{O}(6')$	3.27
$W(1)-\text{O}(6')$	3.43		$\text{O}(16)-\text{O}(6')$	2.77
$W(1)-W(2')$	3.39		$\text{O}(16)-\text{O}(15)$	2.68

Table 4. *Interatomic distances and angles in the  $\text{AsO}_4$  group before (B) and after (A) the correction for anomalous scattering*

	A	B	A
As(1)-O(1)	1.729 (9) Å	1.740 (9) Å	$\text{O}(2)-\text{O}(4)$
As(1)-O(2)	1.678 (9)	1.674 (9)	$\text{O}(3)-\text{O}(4)$
As(1)-O(3)	1.661 (9)	1.655 (9)	$\angle \text{O}(1)-\text{As}(1)-\text{O}(2)$
As(1)-O(4)	1.677 (9)	1.681 (9)	$\text{O}(1)-\text{As}(1)-\text{O}(3)$
$\text{O}(1)-\text{O}(2)$	2.668 (13)		$\text{O}(1)-\text{As}(1)-\text{O}(4)$
$\text{O}(1)-\text{O}(3)$	2.747 (13)		$\text{O}(2)-\text{As}(1)-\text{O}(3)$
$\text{O}(1)-\text{O}(4)$	2.766 (13)		$\text{O}(2)-\text{As}(1)-\text{O}(4)$
$\text{O}(2)-\text{O}(3)$	2.857 (12)		$\text{O}(3)-\text{As}(1)-\text{O}(4)$
			2.784 (13) Å
			2.680 (12)
			103.1 (5)°
			108.2 (4)
			108.6 (4)
			117.7 (4)
			112.2 (4)
			106.8 (5)

each other and forming the hydrogen bonds discussed above. Inside the layers it is possible to recognize chains of  $\text{AsO}_4$  tetrahedra parallel to the  $z$  axis and twinning around the  $y$  axis; similar chains of  $\text{CaO}_8$  polyhedra alternate with the former ones (Fig. 2). The tetrahedra are linked to each other by hydrogen bonds of type  $\text{O}(1)\text{--O}(12)$ , while  $\text{CaO}_8$  polyhedra share an edge [ $\text{O}(16)\text{--O}(6')=2.766 \text{ \AA}$ ] in the direction of the chain\*. It is to be remarked that there is no linkage between chains of the same type within a layer, in contrast with the haidingerite structure where  $\text{CaO}$  polyhedra form a net. Two adjacent layers, related by a glide-plane of type  $a$ , are so shifted as to superimpose  $\text{AsO}_4$  and  $\text{CaO}_8$  chains; the  $\text{CaO}_8$  polyhedra, so shifted, are linked by the hydrogen bonding of the water molecules. This type of structure explains the easy  $\{010\}$  cleavage.

Pierrot (1964) noticed that some samples of haidingerite were a pseudomorph of pharmacolite and that, in a dry atmosphere, a transition occurs between the two phases. This transformation is clear when one

\* This edge with the two edges,  $\text{O}(1)\text{--O}(2)$  and  $\text{O}(3)\text{--O}(4)$ , shared by  $\text{CaO}_8$  polyhedra with  $\text{AsO}_4$  tetrahedra are the shortest  $\text{O--O}$  contacts (excluding, of course, the hydrogen bridges), in accordance with their function of opposing the repulsion between positive atoms.

remembers that the two water molecules in pharmacolite are crystallographically independent, and that one of them takes part in only one hydrogen bond; it can therefore escape easily through the interlayer cavities. The loss of half the water molecules is accompanied by a rearrangement of the  $\text{CaO}_8$  polyhedra chains which bend themselves, taking a zigzag configuration around their elongation direction ( $x$  axis for haidingerite). Consequently the Ca cation loses coordination with both the expelled water molecule and the oxygen atom  $\text{O}(1)$ , and coordinates with  $\text{O}(4)$ , which in haidingerite is in contact with three Ca atoms (the numbering of atoms is the same in both papers).

The column A of Table 6 shows the root mean square displacements of the atoms along the three principal directions of thermal vibration; in the last three columns are reported the angles which these directions make with the crystallographic axes. The vibration is not very marked, with the exception of the water oxygen atom  $W(2)$  which is loosely bound in the structure. All the atoms have a remarkable anisotropy; but, while the ellipsoid of the Ca atom is practically one of revolution, those of the other atoms are three-axis ellipsoids. The orientation of the ellipsoids is random, as is to be expected in an essentially ionic structure.

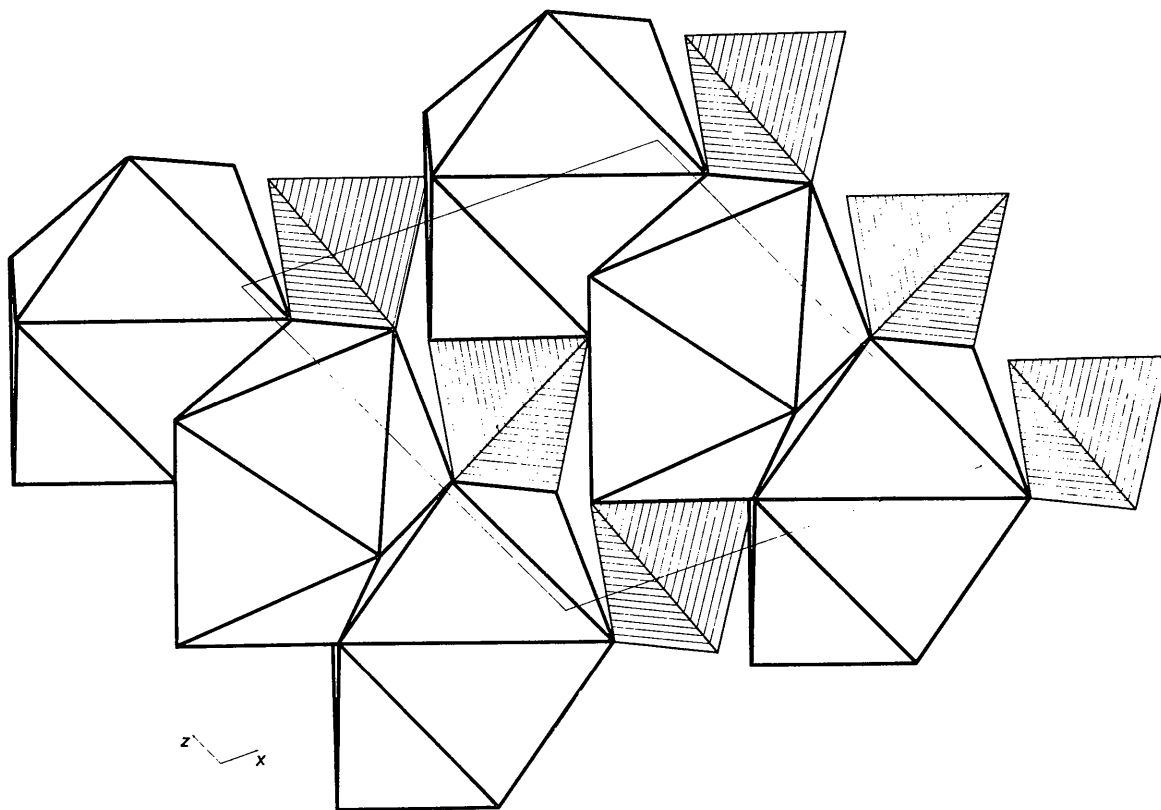


Fig. 2. Packing of the Ca-coordination polyhedra and the  $\text{AsO}_4$  tetrahedra in one layer projected along the  $y$  axis.

Table 5. *Interatomic distances and angles involving water molecules and the oxygen atoms participating in hydrogen bonds*

O(1)—O(12)	2.707 (13) Å	$\angle$ O(1)—O(12)—As(3)	101.7 (4)°
W(1)—O(11)	2.741 (11)	O(11)—W(1)—O(15')	103.3 (4)
W(1)—O(15')	2.799 (13)	O(11)—W(1)—Ca(1)	128.3 (4)
W(2)—O(9)	2.787 (12)	O(15')—W(1)—Ca(1)	118.6 (4)
W(2)—O(13)	3.140 (15)	O(9)—W(2)—O(13)	111.1 (4)
$\angle$ O(12)—O(1)—As(1)	101.4 (4)	O(9)—W(2)—Ca(1')	114.2 (4)
		O(13)—W(2)—Ca(1')	92.2 (3)

Table 6. *Parameters characterizing the principal directions 1, 2, 3 of thermal vibration for all the atoms: root-mean-square displacements (A) and angles which the principal directions make with the x (B), y (C) and z (D) axes*

		A	B	C	D
Ca	1	0.112	10°	80°	111°
	2	0.118	95	80	22
	3	0.098	99	13	95
As	1	0.083	52	46	86
	2	0.119	112	98	8
	3	0.074	133	45	82
O(1)	1	0.13	125	109	23
	2	0.17	36	98	80
	3	0.09	95	21	69
O(2)	1	0.11	112	23	76
	2	0.17	124	108	21
	3	0.08	42	76	75
O(3)	1	0.13	152	98	39
	2	0.17	78	41	61
	3	0.10	65	130	66
O(4)	1	0.10	72	21	107
	2	0.14	115	73	17
	3	0.08	32	101	85
W(1)	1	0.14	33	57	113
	2	0.19	76	107	43
	3	0.09	120	38	56
W(2)	1	0.16	131	64	34
	2	0.20	47	89	68
	3	0.12	72	26	114

I am indebted to Dr G. Chiari for preparing the synthetic pharmacolite and to Professor G. Rigault, to Dr M. Calleri and to Dr D. W. Jones for critical reading of the manuscript.

## References

- ABRAHAMS, S. C. & GELLER, S. (1958). *Acta Cryst.* **11**, 437.  
 ATOJI, M. & RUNDLE, R. E. (1958). *J. Chem. Phys.* **29**, 1306.  
 BEEVERS, C. A. (1958). *Acta Cryst.* **11**, 273.  
 BINAS, H. (1966). *Z. anorg. Chem.* **347**, 133.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *A Fortran Crystallographic Least-Squares Program*. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.  
 CALLERI, M. & FERRARIS, G. (1965). *Atti Accad. Sci. Torino*, **100**, 171.  
 CALLERI, M. & FERRARIS, G. (1967). *Period. Miner.* **36**, 1.  
 CASSIEN, M., HERPIN, P. & PERMINGEAT, F. (1966). *Bull. Soc. franç. Minér. Crist.* **89**, 18.  
 CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* p. 5486.  
 CRUICKSHANK, D. W. J. & McDONALD, W. S. (1967). *Acta Cryst.* **23**, 9.  
 DANA, J. W. & DANA, E. S. (1951). *The System of Mineralogy*, rewritten by PALACHE, C., BERMAN, H. & FRONDEL, C. (1963). Vol. II. New York: John Wiley.  
 FISCHER, E. (1960). *Chem. d. Erde* **20**, 162.  
 GUERIN, H. (1941). *Ann. Chim.* **16**, 101.  
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 JONES, D. W. & SMITH, J. A. S. (1962). *J. Chem. Soc.* p. 1414.  
 PEACOR, D. R. & PREWITT, C. T. (1963). *Amer. Min.* **48**, 588.  
 PIERROT, R. (1964). *Bull. Soc. franç. Minér. Crist.* **87**, 169.  
 SARAVIA, L. S. & CATICHA-ELLIS, S. (1966). *Acta Cryst.* **20**, 927.  
 STRUNZ, H. (1957). *Mineralogische Tabellen*. Leipzig: Akademische Verlagsg.  
 TERPSTRA, P. (1937). *Z. Kristallogr.* **97**, 229.  
 WEBB, N. C. (1966). *Acta Cryst.* **21**, 942.