

## The Crystal Structure of CaHAsO<sub>4</sub> (Weilite)

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*

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CaHAsO<sub>4</sub> (weilite) crystallizes in the triclinic system, space group *P* $\bar{1}$ . Unit-cell parameters are:  $a_0 = 7.0591$  (8),  $b_0 = 6.8906$  (9),  $c_0 = 7.2006$  (16) Å,  $\alpha = 97^\circ 26'$  (1'),  $\beta = 103^\circ 33'$  (1'),  $\gamma = 87^\circ 45'$  (1');  $Z = 4$ . Weilite is isostructural with monetite (CaHPO<sub>4</sub>); the present X-ray study was based on the structure of the latter as a starting model. 96% (1475) of the reflexions accessible to Cu *K* $\alpha$  radiation were measured on a single-crystal diffractometer; corrections for absorption and anomalous scattering (As and Ca atoms) were applied. The structure presents layers, parallel to the (001) plane, in which the two Ca atoms are crystallographically independent and coordinate respectively seven and eight oxygen atoms; the As-tetrahedra are on the layer surface. A plausible system of hydrogen bonds is proposed on the basis of the oxygen atom positions and contacts.

### Introduction

The crystal structure of CaHAsO<sub>4</sub> (weilite) illustrated in this paper, was studied as a part of a programme of structural research on some phases of the system CaHAsO<sub>4</sub>-H<sub>2</sub>O, with particular interest in those occurring in nature (Calleri & Ferraris, 1965, 1967; Ferraris, 1969).

The compound CaHAsO<sub>4</sub> has been found in nature, associated with pharmacolite, by Herpin & Pierrot (1963) and named weilite. From measurements on X-ray powder and rotation spectra, these authors deduced that weilite is triclinic with unit-cell parameters:  $a_0 = 7.11$ ,  $b_0 = 6.94$ ,  $c_0 = 7.15$  Å,  $\alpha = 94^\circ 19'$ ,  $\beta = 101^\circ 35'$ ,  $\gamma = 87^\circ 22'$ .

From the chemical formulae, unit-cell parameters and powder spectra, they argued that CaHAsO<sub>4</sub> and CaHPO<sub>4</sub> were isostructural. The crystal structure of the latter compound has been the object of study both by X-ray diffraction (MacLennan & Beever, 1955; Jones & Cruickshank, 1961) and neutron diffraction (Curry, Denne & Jones, 1968); such an interest is justified by the difficulties met in locating the hydrogen atoms and in deciding between the *P*1 and *P* $\bar{1}$  space groups.

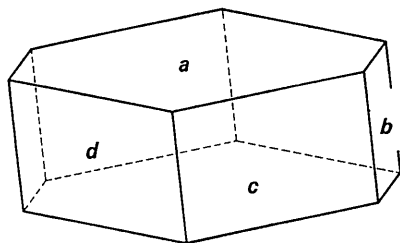


Fig. 1. Clinographic projection of a typical weilite crystal: *a*, *b*, *c* and *d* are (100), (010), (001) and (011) faces respectively.

We have therefore examined the crystal structure of CaHAsO<sub>4</sub> with the aim of explaining the stereochemistry of Ca atoms and (AsO<sub>4</sub>H)<sup>2-</sup> groups and, possibly, of settling the problems raised by studies of the monetite structure.

### Experimental

#### Preparation and crystal data

CaHAsO<sub>4</sub> crystals, suitable for an X-ray study, were grown by the Pierrot (1964) method. The crystals so obtained are limpid and colourless; they exhibit a vitreous luster and are stout and tabular, sometimes lozenge shaped.

Cu *K* $\alpha$  X-ray diffraction analysis (based both on Weissenberg photographs and single-crystal diffractometry) and morphological studies confirmed that the compound CaHAsO<sub>4</sub> is triclinic and identifiable with the natural weilite. The forms found are (Fig. 1);  $a = \{100\}$  (predominant),  $b = \{010\}$  (the least developed),  $c = \{001\}$  and  $d = \{011\}$ ; imperfect cleavage  $\{001\}$ .

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:

$$a_0 = 7.0591 (8), \quad b_0 = 6.8906 (9), \quad c_0 = 7.2006 (16) \text{ \AA}, \\ \alpha = 97^\circ 26' (1'), \quad \beta = 103^\circ 33' (1'), \quad \gamma = 87^\circ 45' (1').$$

These values are comparable to, but not in good agreement with, those given by Herpin & Pierrot (1963); the crystallographic orientation chosen seems to have been the same, but nevertheless the above authors found  $\{001\}$  as the predominant form and not  $\{100\}$ . We think, however, that they mistook the *x* for the *z* axis when indexing; in fact on the (100) face we measured, by the Becke-line method, refractive indices (1.688,



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

	$x/a_0$	$y/a_0$	$z/a_0$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
As(1)	0.2048 2	0.3776 2	0.7243 2	0.251 38	0.336 37	0.237 40	-0.094 26	-0.229 29	0.123 28
As(2)	0.2978 2	0.9414 2	0.2087 2	0.580 41	0.769 41	0.328 46	0.079 30	-0.324 32	0.228 32
Ca(1)	0.3024 3	0.4323 3	0.2796 3	0.774 70	1.305 73	0.511 79	0.184 56	-0.419 57	0.288 59
Ca(2)	0.1724 3	0.8339 3	0.6606 3	0.925 72	0.670 67	0.702 79	-0.187 54	-0.526 59	0.349 57
O(1)	0.3219 11	0.3363 10	0.9531 11	1.58 31	0.88 27	0.76 30	0.11 23	0.20 25	0.49 22
O(2)	0.3565 12	0.4976 11	0.6274 10	1.56 29	0.98 26	0.37 27	-0.79 22	-0.32 23	0.53 22
O(3)	0.1361 11	0.1656 10	0.5893 11	1.37 29	0.85 26	0.69 28	-0.64 22	-0.40 22	-0.02 22
O(4)	0.0235 11	0.5384 10	0.7410 11	0.73 27	1.04 27	1.16 30	0.35 21	-0.20 23	0.01 22
O(5)	0.3366 10	0.8260 11	0.0003 11	0.46 26	1.29 28	1.06 31	0.00 22	-0.57 22	-0.19 24
O(6)	0.4650 12	0.1132 12	0.3036 11	1.45 31	1.83 31	0.44 29	-0.71 26	-0.27 24	-0.17 24
O(7)	0.0819 11	0.0651 11	0.1601 12	0.78 27	1.79 31	1.37 34	0.46 24	-0.25 24	0.80 25
O(8)	0.2878 13	0.7757 1	0.3537 12	2.38 35	0.86 27	0.91 31	0.65 25	0.00 26	0.76 23

Table 3. Parameters characterizing the principal directions of thermal vibration for all atoms: root-mean-square displacements (r.m.s.d.) and angles which the principal directions make with the  $x$  ( $A$ ),  $y$  ( $B$ ) and  $z$  ( $C$ ) axes

	r.m.s.d.	$A$	$B$	$C$		r.m.s.d.	$A$	$B$	$C$
As(1)	0.062 $\text{\AA}$ 0.091 0.012	70° 136 53	20° 71 94	110° 46 50	O(3)	0.11 $\text{\AA}$ 0.16 0.05	85° 30 61	39° 109 58	136° 119 60
As(2)	0.100 0.114 0.019	81 30 62	16 88 106	85 133 44	O(4)	0.11 0.15 0.07	87 129 39	44 122 116	56 39 73
Ca(1)	0.128 0.136 0.034	112 40 59	40 53 104	62 122 46	O(5)	0.12 0.16 0.03	111 124 42	32 122 86	72 34 62
Ca(2)	0.086 0.151 0.049	68 143 61	22 78 108	93 46 44	O(6)	0.13 0.17 0.05	46 129 70	52 42 75	130 85 40
O(1)	0.12 0.14 0.07	96 6 89	45 84 46	53 99 141	O(7)	0.14 0.16 0.06	139 92 49	118 41 116	46 57 61
O(2)	0.08 0.18 0.03	54 36 97	51 119 127	72 113 30	O(8)	0.13 0.19 0.02	99 15 102	54 73 41	44 105 130

Table 4. Interatomic distances and angles concerning the two crystallographically independent  $\text{AsO}_4$  groups

As(1)-O(1)	1.722 (8) $\text{\AA}$	As(2)-O(5)	1.676 (8) $\text{\AA}$
As(1)-O(2)	1.701 (8)	As(2)-O(6')	1.667 (8)
As(1)-O(3)	1.661 (7)	As(2)-O(7')	1.704 (8)
As(1)-O(4)	1.677 (7)	As(2)-O(8)	1.668 (8)
O(1)-O(2)	2.796 (11)	O(5)-O(6')	2.746 (11)
O(1)-O(3)	2.761 (11)	O(5)-O(7')	2.740 (11)
O(1)-O(4)	2.754 (11)	O(5)-O(8)	2.720 (12)
O(2)-O(3)	2.763 (10)	O(6')-O(7')	2.678 (11)
O(2)-O(4)	2.662 (11)	O(6')-O(8)	2.792 (11)
O(3)-O(4)	2.812 (10)	O(7')-O(8)	2.765 (11)
O(1)-As-O(2)	109.5 (4)°	O(5)-As-O(6')	110.5 (4)°
O(1)-As-O(3)	109.4 (4)	O(5)-As-O(7')	108.3 (4)
O(1)-As-O(4)	108.3 (4)	O(5)-As-O(8)	108.9 (4)
O(2)-As-O(3)	110.6 (4)	O(6')-As-O(7')	105.2 (4)
O(2)-As-O(4)	104.0 (4)	O(6')-As-O(8)	113.7 (4)
O(3)-As-O(4)	114.9 (4)	O(7')-As-O(8)	110.2 (4)

CaHAsO<sub>4</sub> was mounted with its *z* axis parallel to the  $\phi$  axis of the goniostat; for the crystal used the distances between the faces *a*, *b*, *c*, *d* (Fig. 1) and their centrosymmetric equivalents are 0.15, 0.48, 0.28 and 0.30 mm respectively.

The  $\theta$ - $2\theta$  scanning technique was employed (1° per minute), varying the integration interval from 2 to 3.5° as a function of  $2\theta$ ; the background was measured for an interval of 0.5° on both sides of each peak. It was possible to measure the intensities of 1475 reflexions, corresponding to about 96% of the independent reflexions according to the Laue group  $\bar{1}$  and accessible to Cu *K* $\alpha$  radiation. For 136 reflexions the intensities were zero or only slightly greater than the background ( $I_{\text{meas}}$  was about 20 counts against a value of about 83,000 counts for the strongest reflexion). After checking that the corresponding  $F_c$ 's had values not greater than about  $2e$ , these reflexions were considered 'unobserved' and excluded from the final refinement; they are not listed in Table 1.

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 both the real and imaginary correction for anomalous scattering. Absorption correction was applied, using the program *GONO9* by Hamilton (1966). No correction was made for the extinction effect.

### Solution and refinement of the structure

Initially we had measured visually on films only the intensities of *hk0*, *h0l* and *0kl* reflexions; assuming that weillite and monetite were isomorphous, the Ca, P (for As) and O coordinates of the latter (Jones & Cruickshank, 1961) were used in the phase calculations. Projections of electron density onto the planes (100), (010) and (001) showed the two compounds to be substantially isostructural. We then collected three-dimensional data, and refined the positional and vibrational parameters 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 was as given in the program. The position of the atoms, with respect to those of monetite did not change appreciably during the refinement. After some cycles with individual isotropic thermal parameters, the refinement was continued with anisotropic thermal parameters. At this stage difficulties in obtaining convergence were encountered because the temperature factors of some atoms varied from definite-positive. In particular, the temperature factors of the atoms As (1), As (2) and O (8) were only brought back to definite-positive after the application of a 'fudge-factor' of 0.4.

The final *R* value for the 1293 reflexions used throughout the refinement is 0.069 (weighted  $R=0.085$ ); the

standard error of an observation of unit weight is 0.902. The following weighting scheme was used:

$$w_{hkl} = \frac{A}{BF_o^2 + |F_o| + C} \quad \text{for } |F_o| \geq C, \quad (1)$$

$$w_{hkl} = DF_o^2 \quad \text{for } |F_o| < C; \quad (2)$$

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* values, around  $2|F_{\text{min}}|$  and  $5/|F_{\text{max}}|$  respectively, were such as to give an approximate constancy to  $\sum w\Delta^2$  for amplitudes arranged in various groups.

At the end of the least-squares refinement a three-dimensional difference Fourier synthesis was calculated in order to check the refinement and in the hope (not realized) of locating hydrogen atoms. In fact, particularly in the neighbourhood of the heavy atoms, there were broad ripples sometimes reaching the maximum value of  $\pm 1.5e$ . These ripples and the relatively high *R* value are, in our opinion, connected with the poor approximation of the absorption correction owing to the bad habit of our crystal.

Table 1 presents the final values of the  $|F_o|$ 's and  $|F_c|$ 's and of the corresponding phase angles  $\alpha$ . The 46 reflexions marked with an asterisk were given zero weight during the refinement because either the intensity was small or they were probably affected by extinc-

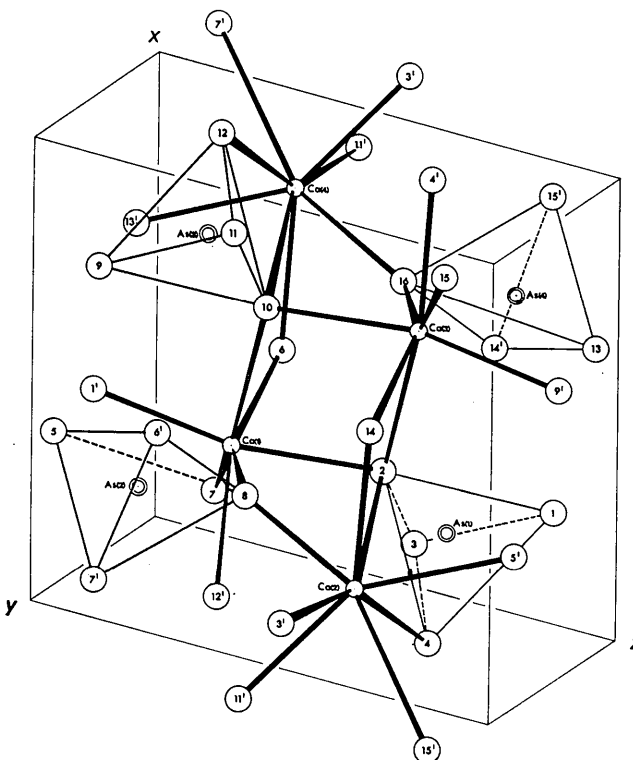


Fig. 2. Clinographic projection, along the *y* axis, of the content of one unit cell.

tion or some measurement error; the  $R$  value for all the reflexions of Table 1 (1339) is 0.077.

Table 2 shows the final values of the fractional coordinates and of the  $B_{ij}$  coefficients of the expression

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

Table 3 shows the root-mean-square displacements of the atoms along the three principal directions of thermal vibration and the angles which these directions make with the crystallographic axes  $x$ ,  $y$  and  $z$  (columns  $A$ ,  $B$  and  $C$  respectively). The orientation of the ellipsoids is random, as it is to be expected in an essentially ionic structure.

### Description and discussion of the structure

In the weilite unit-cell there are four discrete  $\text{AsO}_4$  tetrahedral groups, two of which are crystallographically independent.\* The interatomic distances and bond angles in the  $\text{AsO}_4$  tetrahedra are reported in Table 4 with their standard deviations in parentheses. The two crystallographically independent tetrahedra do not exhibit the same trend in interatomic distances and this will be discussed in the following.

Atom Ca(1) has seven neighbouring oxygen atoms at distances reported in Table 5; we included among them O(7), whose distance from Ca(1) is 2.940 (8) Å,

\* The atom notation is shown in Figs. 2, 3 and 5. The crystallographically independent atoms are: As(1), As(2), Ca(1), Ca(2) and O(1) to O(8); other numbers mark atoms generated by inversion centres, while an apex indicates atoms generated by lattice vectors.

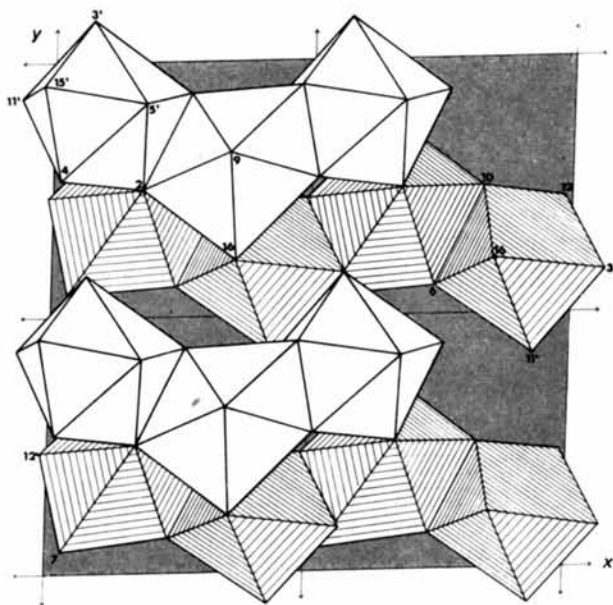


Fig. 3. Packing of Ca-polyhedra in one layer; four unit cells projected onto the  $xy$  plane.

on the basis of considerations similar to those for pharmacolite (Ferraris, 1969). The Ca(1)-coordinated atoms are at the vertices of a very distorted pentagonal bipyramid (Figs. 2 and 3); O(1') and O(2) are the vertices opposite the pentagonal section. The best mean-plane for the five atoms of this section, referred to the crystallographic axes (Schomaker, Waser, Marsh & Bergman, 1959), has the following equation, in fractional coordinates:

$$1.294X - 1.270Y + 7.179Z = -1.192. \quad (4)$$

The deviations from plane (4) of O(6), O(7), O(8), O(10) and O(12'), forming the pentagonal section, are about 0.24, -0.22, -0.01, -0.12 and 0.11 Å respectively. This Ca polyhedron ('CaO<sub>7</sub>-polyhedron') has two very large 'meshes' as can be deduced by inspection of the interatomic distances concerning its edges [O(1')-O(8) = 3.945 Å and O(2)-O(7) = 4.330 Å]; facing these meshes are atoms O(3) and O(5) whose distances from Ca(1) are 3.505 and 3.638 Å respectively.

Atom Ca(2) has eight neighbouring oxygen atoms at the distances reported in Table 5. The resulting, very distorted, polyhedron (Figs. 2 and 3) ('CaO<sub>8</sub>-polyhedron') has a pentagonal section on opposite sides of which there are respectively a vertex formed by O(3') and an other two vertices formed by O(2) and O(4). The five atoms forming the pentagonal section 'lie' in the best mean plane:

$$0.519X + 6.832Y - 0.916Z = -5.310, \quad (5)$$

but their deviations from the mean plane are more marked than those of the corresponding atoms of the CaO<sub>7</sub>-polyhedron. In fact the distances from plane (5) of O(5'), O(8), O(11'), O(14) and O(15') are -0.41, -0.19, -0.05, 0.39 and 0.26 Å respectively. Owing to its length (4.217 Å), edge O(4)-O(8) was not outlined in Fig. 3 and so the CaO<sub>8</sub>-polyhedron presents a 'square' face; corresponding to this face and to the edge O(3')-O(5'), it has two large 'meshes'. In front of these the atoms O(12') and O(1') are respectively 3.634 and 3.841 Å from atom Ca(2).

In the weilite structure all oxygen atoms are coordinated by two calcium atoms with the exception of O(1), which is coordinated by only one, and O(5), which is coordinated by three calcium atoms.

In the zone between 3500 and 1300  $\text{cm}^{-1}$  the weilite infrared spectrum has maxima at 3420, 2920, 2825, 2350 and 1550  $\text{cm}^{-1}$ ; all these maxima have corresponding maxima in the monetite spectrum (see e.g. Petrov, Šoptrajanov, Fuson & Lawson, 1967) except for the very weak maximum at 2920  $\text{cm}^{-1}$ . From the similarity between the infrared spectra of weilite (Fig. 4) and monetite, the hypothesis that these two compounds have a similar hydrogen atom arrangement seems plausible. For monetite, Curry, Denne & Jones (1968) found, by a trial method based on neutron diffraction data, that, while the hydrogen atom H(1) is definitely bound to the oxygen atom O(1), the other crystallographically independent hydrogen atom is probably distributed be-

tween O(7) and O(6), *i.e.* there are at least three distinct hydrogen atom sites. Since, in monetite, H(3) lies on a Ca-polyhedron edge, the prediction of hydrogen sites in weilite merits some discussion.

While the attachment of H(1) to O(1) and its contact with O(13) are not in doubt [O(1)–O(13)=2.582 (11) Å],\* the position of the hydrogen atom associated with the As(2) tetrahedron is less clear. In particular, the

\* The As(1)–O(1) bond length (1.722 Å) is appropriate for an As–OH bond (see Cruickshank, 1961); also As(1)–O(2) is indeed anomalously long (1.701 Å), but such a situation was found in the haidingerite structure also (Calleri & Ferraris, 1967) and it can be explained by considering that in both cases the oxygen atom involved is that coordinated by three Ca atoms.

longest As(2)–O bond [As(2)–O(7')=1.704 Å] is still comparatively short for an As–OH (Cruickshank, 1961; Cruickshank & Robinson, 1966). Comparison of O–O contacts for the oxygen atoms in the As(2) tetrahedron [O(5)–O(14'), O(6)–O(10), O(6)–O(16), all Ca-polyhedra edges (Table 5), and O(7)–O(15), 2.397 (12) Å] suggests that H(2) forms a symmetrical hydrogen bridge (or possibly a tunnel) between O(7) and O(15). Further, H(3) appears either to lie on the centre of symmetry ( $\frac{1}{2}, 0, \frac{1}{2}$ ), relating O(6) and O(14), and O(8) and O(16), or to be statistically linked to O(6) and O(14); in the latter case, it may form either a bifurcated hydrogen bond with O(10) and O(16) or a bent hydrogen bond with O(16) only.

Table 5. *Interatomic distances and angles concerning the two crystallographically independent Ca-polyhedra*

Ca(1)–O(1')	2.384 (8) Å	Ca(2)–O(2)	2.626 (8) Å
Ca(1)–O(2)	2.427 (8)	Ca(2)–O(3')	2.399 (7)
Ca(1)–O(6)	2.449 (8)	Ca(2)–O(4)	2.525 (7)
Ca(1)–O(7)	2.940 (8)	Ca(2)–O(5')	2.459 (8)
Ca(1)–O(8)	2.356 (8)	Ca(2)–O(8)	2.504 (9)
Ca(1)–O(10)	2.392 (8)	Ca(2)–O(11')	2.438 (8)
Ca(1)–O(12')	2.271 (8)	Ca(2)–O(14)	2.546 (8)
		Ca(2)–O(15')	2.470 (8)
O(1')–O(10)	3.414 (11)	O(3')–O(8)	3.256 (11)
O(1')–O(8)	3.945 (11)	O(3')–O(11)	2.989 (11)
O(1')–O(12')	3.657 (11)	O(3')–O(15)	3.227 (11)
O(1')–O(7)	3.283 (11)	O(3')–O(5')	3.974 (12)
O(1')–O(6)	3.081 (11)	O(3')–O(14)	3.340 (11)
O(2)–O(10)	3.039 (11)	O(2)–O(8)	2.884 (11)
O(2)–O(8)	3.061 (11)	O(2)–O(14)	2.938 (11)
O(2)–O(12')	3.293 (11)	O(2)–O(5')	3.290 (11)
O(2)–O(7)	4.330 (12)	O(2)–O(4)	2.662 (11)
O(2)–O(6)	3.463 (11)	O(4)–O(5')	3.115 (11)
O(10)–O(8)	3.061 (11)	O(4)–O(15')	2.841 (11)
O(8)–O(12')	3.039 (11)	O(4)–O(11')	3.321 (11)
O(12')–O(7)	2.841 (11)	O(4)–O(8)	4.217 (12)
O(7)–O(6)	2.678 (11)	O(5')–O(14)	2.943 (11)
O(6)–O(10)	2.938 (11)	O(14)–O(8)	2.693 (11)
		O(8)–O(11')	3.122 (11)
		O(11')–O(15')	3.008 (11)
		O(15')–O(5')	3.019 (11)

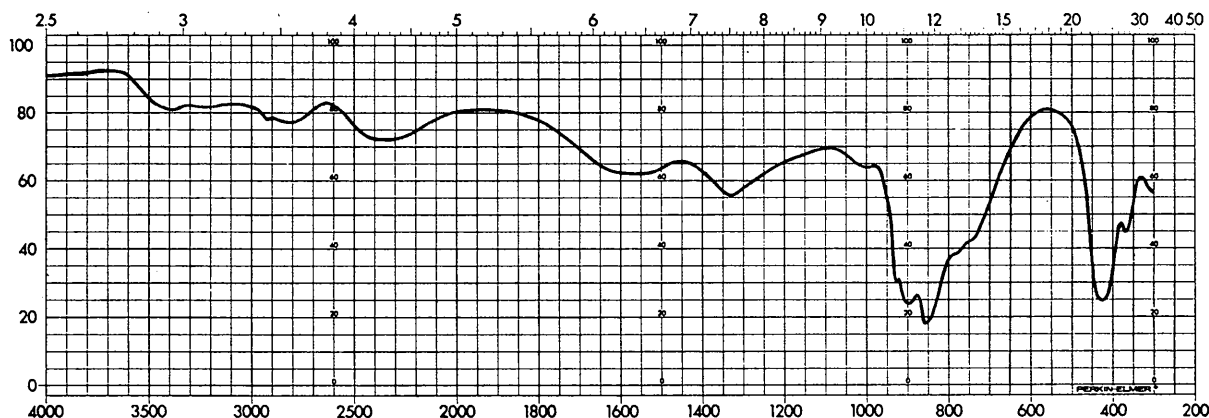


Fig. 4. Infrared spectrum of weilite. Perkin–Elmer 621 spectrophotometer; 1 mg of  $\text{CaHAsO}_4$  in 150 mg KBr disk.

The occurrence of H(3) at an inversion centre 'coordinating' O(6) and O(14), 1.67 Å, and O(8) and O(16), 2.18 Å, would explain both

(a) the relative similarity of bonds from As(2) to O(5), O(6) and O(8) [H(3) does not form OH groups], and

(b) the shortness of the O(8)–O(14) and O(6)–O(16) Ca-polyhedra edges.

The proposed hydrogen bonding system O(1)–O(13), O(7)–O(15), O(9)–O(5) (Fig. 5) links four As-tetrahedra astride two contiguous unit cells: As(1), As(4), As(2) and As(3) tetrahedra, in that sequence. These groups, in turn, are connected along the *z* axis by H(3) atoms; every As-tetrahedron shares an edge with a Ca-polyhedron.

Fig. 2 is a clinographic projection along the *y* axis of the content of one unit cell of the weilite structure. The common feature of this compound with haidingerite,  $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ , (Binas, 1966; Calleri & Ferraris, 1967; Cassien, Herpin & Permingeat, 1966) and with pharmacolite,  $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$ , (Ferraris, 1969) is the assembly of As-tetrahedra and Ca-polyhedra in parallel double layers (Figs. 2 and 3).<sup>\*</sup> One of these layers, parallel to the *xy* plane, is sketched in Fig. 3 which is a drawing, in false perspective, of  $\text{CaO}_7$  and  $\text{CaO}_8$ -polyhedra projected onto the (001) plane; the As tetrahedra, not shown in Fig. 3, are on the surface of the layer

<sup>\*</sup> Our layers are doubled with respect to those used in the description of the structure of monetite (Jones & Cruickshank, 1961).

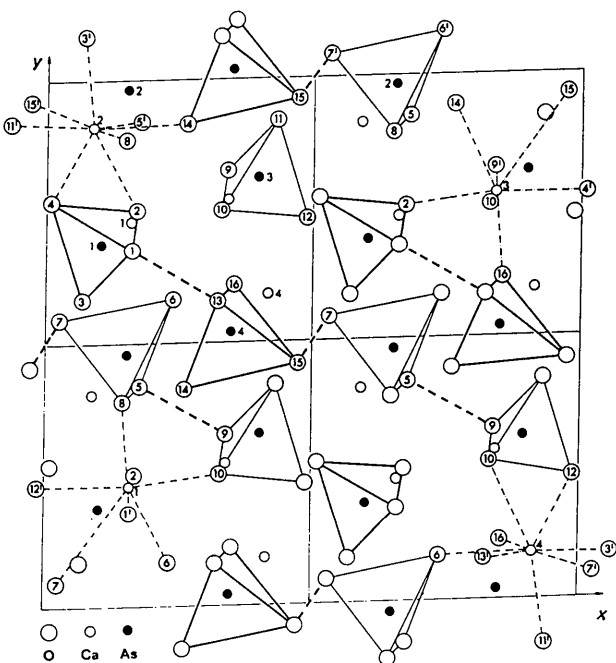


Fig. 5. Packing of  $\text{AsO}_4$  groups, hydrogen bonds and Ca coordination; four unit cells projected onto the *xy* plane.

(Fig. 5). The Ca-polyhedra, which are inside the layers, are linked together along the *x* axis in the sequence Ca(2)–Ca(3)–Ca(2) and make two centrosymmetric chains twining around the *y* axis and at different heights on the *z* axis; these Ca-polyhedra share, along the *x* axis, edges O(2)–O(14) and O(15)–O(4') in that order, and along the *z* and *y* axes they share respectively edges O(2)–O(8), O(2)–O(10) and O(3')–O(11'). Two contiguous layers are linked by the hydrogen bond O(7)–O(15); in addition O(5'), or O(1'), of one layer is coordinated by Ca(2), or Ca(1), of another. The lack of space between layers and their framework linkage by coordination bonds are peculiarities of the weilite structure with respect to those of haidingerite and pharmacolite. We may note also that, passing from the dihydrated to the anhydrous compound, the chains of Ca-polyhedra are isolated in pharmacolite, linked only inside the layers in haidingerite and finally that they form a framework in weilite, *i.e.* the structure becomes progressively more crowded: the calculated density is in fact equal to 2.731, 2.971 and 3.541  $\text{g.cm}^{-3}$  for the three compounds respectively. It is also clear why the cleavage, parallel to the layers, is, in weilite, less perfect than in the other two salts.

With regard to a possible ambiguity between space groups  $P1$  and  $P\bar{1}$  for weilite, as well as for monetite, for which a minute piezoelectric effect has been noted (D. W. Jones, private communication), we may conclude that the lack of centrosymmetry could apply only to the hydrogen atoms. In fact the position of all other atoms is 'regular' and we think we have explained all the peculiarities of the weilite structure in the above discussion. In particular we found the sum of the As–O distances, 6.76 and 6.72 Å for our two independent tetrahedra, to be in good agreement with those found in the few crystals studied so far, containing discrete arsenate ions: 6.73 Å for haidingerite, 6.74 Å for pharmacolite, 6.74 Å for 1-methyl-2-quinolinium dihydrogen arsenate (Currie & Speakman, 1969) and 6.61 and 6.70 Å for  $2\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$  (Worzala, 1968). This last consideration is an extension of the results by Cruickshank (1961) on some  $\text{XO}_4$  groups.

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## References

- BINAS, H. (1966). *Z. anorg. allg. 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 Acad. 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. & ROBINSON, E. A. (1966). *Spectrochim. Acta*, **22**, 555.  
 CURRIE, M. & SPEAKMAN, J. C. (1969). *J. Chem. Soc. (A)*, p. 1648.  
 CURRY, N. A., DENNE, W. A. & JONES, D. W. (1968). *Bull. Soc. chim. Fr.* p. 1748.  
 FERRARIS, G. (1969). *Acta Cryst.* **B25**, 1544.  
 HERPIN, P. & PIERROT, R. (1963). *Bull. Soc. franç. Minér. Crist.* **86**, 368.  
 HAMILTON, W. C. (1966). *World List of Crystallographic Computer Programs*, program No. 225.  
*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 JONES, D. W. & CRUICKSHANK, D. W. J. (1961). *Z. Kristallogr.* **116**, 101.  
 MACLENNAN, G. & BEEVERS, C. A. (1955). *Acta Cryst.* **8**, 583.  
 PETROV, I., ŠOPTRAJANOV, B., FUSON, N. & LAWSON, J.R. (1967). *Spectrochim. Acta*, **23A**, 2637.  
 PIERROT, R. (1964). *Bull. Soc. franç. Minér. Crist.* **87**, 169.  
 SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.  
 WORZALA, H. (1968). *Acta Cryst.* **B24**, 987.

*Acta Cryst.* (1970). **B26**, 410

## Structure Cristalline de Dérivés d'Acides Aminés I. L-Alanyl-glycine

PAR MICHEL H. J. KOCH ET GABRIEL GERMAIN

*Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, Belgique*

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The crystal structure of L-alanyl-glycine has been determined by X-ray diffraction. L-Alanyl-glycine crystallizes in the space group  $P2_1$  with cell dimensions  $a = 5.283$ ,  $b = 11.810$ ,  $c = 5.510$  Å and  $\beta = 101.58^\circ$  with  $Z = 2$ . This non-centrosymmetric structure was solved by the 'quadrant permutation' method. The structure is simple but interesting in that one proceeded from the collection of data to the correct solution with scarcely any human intervention. It was refined by three-dimensional anisotropic matrix least-squares analysis (block-diagonal approximation). A final  $R$  index of 0.047 for 586 observed reflexions was obtained. The molecules are held together by hydrogen bonds forming a three-dimensional network. The planes of the carboxyl and the amide groups are nearly perpendicular. The bond lengths and angles are in close agreement with the mean values proposed by Marsh & Donohue.

### Introduction

Cet article entre dans le cadre d'une étude comparative de la conformation d'acides aminés et d'oligopeptides et de certains de leurs complexes. Ainsi dans une prochaine publication la structure de la L-alanyl-glycine sera comparée avec celle de LiBr-L-alanyl-glycine.  $2\text{H}_2\text{O}$ .

### Données cristallographiques

L-Alanyl-glycine,  $\text{NH}_3^+\text{-CH}(\text{CH}_3)\text{-CO-NH-CH}_2\text{-COO}^-$   
 $M = 146,15$ .

Les cristaux proviennent de la firme Sigma, St Louis, Mo., U.S.A. Système monoclinique;  $a = 5,283$ ,  $b = 11,810$   $c = 5,510$  Å;  $\beta = 101,58^\circ$ .

Les écarts-types sont de l'ordre de 0,005 Å  
 $V = 336,8$  Å<sup>3</sup>;  $D_m = 1,435$  g.cm<sup>-3</sup> - Kratky & Kuriyama (1931);  $D_c = 1,442$  g.cm<sup>-3</sup>;  $Z = 2$ ;  $F(000) : 156$ ; groupe spatial  $P2_1$ .

Les paramètres de la maille et le groupe spatial avaient été déterminés par Lenel (1932):

$$a = 5,29, \quad b = 11,67, \quad c = 5,47 \text{ Å}, \quad \beta = 101,5^\circ.$$

Nous les avons remesurés au diffractomètre à quatre cercles Picker en prenant quelques réflexions intenses

sur les rangées réciproques  $h00, 0k0$  et  $00l$  en faisant la moyenne de  $+2\theta$  et de  $-2\theta$ .

Nous avons employé suivant le cas les fentes symétriques avec le rayonnement  $\text{Cu } K\alpha_1$  ( $\lambda = 1,54051$  Å) ou les asymétriques ( $L/R$ ) avec  $\text{Cu } K\beta$  ( $\lambda = 1,39217$  Å). Le cristal utilisé pour la mesure des paramètres avait les dimensions suivantes:  $0,1 \times 0,2 \times 0,1$  mm. L'axe unique coïncidait avec l'axe  $\varphi$  du diffractomètre.

### Partie expérimentale

Les intensités de 601 réflexions uniques ( $2\theta \leq 130^\circ$ ) ont été mesurées au diffractomètre automatique (radiation  $\text{Cu } K$ , filtre et atténuateurs Ni) en faisant un balayage continu  $\omega - 2\theta$  ( $\Delta 2\theta \pm 0,80$ ) et deux mesures de fond continu. Les valeurs de  $2\theta$  correspondaient à  $\lambda = 1,54242$  Å (moyenne arithmétique de  $\lambda\alpha_1$  et  $\lambda\alpha_2$ ). L'axe unique se trouvait dans le prolongement de l'axe  $\varphi$ . La réflexion 002 a servi de référence et a été mesurée toutes les 35 réflexions. Son intensité n'a subi aucune variation significative au cours du temps. Nous avons appliqué les facteurs de Lorentz et de polarisation pour les valeurs de  $2\theta$  correspondant au centre du balayage. Compte tenu des dimensions du cristal ( $0,3 \times 0,2 \times 0,1$  mm) nous avons négligé l'absorption.