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Crystal Structure of $Ca_5(HAsO_4)_2(AsO_4)_2.9H_2O$ (Guérinite)

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Guérinite is monoclinic, space group $P2_1/n$, with $a=17{\cdot}63$ (1), $b=6{\cdot}734$ (3), $c=23{\cdot}47$ (2) Å, $\beta=90{\cdot}6$ (1)°; crystals are nearly always $\{\bar{1}01\}$ twins and/or aggregates around [010]. 1251 non-zero reflexions were collected from a very poor single crystal on a diffractometer (Cu $K\alpha$ radiation) and were used to solve the structure by direct methods and refine it isotropically by least-squares calculations to $R=0{\cdot}13$; the unit cell contains five formula units with one Ca out of 25 and five H_2O out of 45 disordered in large cavities. The number of acidic hydrogen atoms and the overall hydrogen-bonding scheme were determined on the basis of bond-length/bond-strength correlations and of bond lengths and angles. $\{\bar{1}01\}$ layers, linked by hydrogen bonds, are built up by distorted Ca polyhedra (C.N. 7 or 8) and As tetrahedra which share many geometrical elements with one another.

Introduction

Guérinite was discovered by Nefedov (1961) and described by Pierrot (1964), who confirmed its identity with synthetic $5CaO.2As_2O_5.10H_2O$ prepared by Guérin (1941). It is the most hydrated member of the group to which vladimirite $[Ca_5H_2(AsO_4)_4.5H_2O]$ and sainfeldite $[Ca_5(HAsO_4)_2(AsO_4)_2.4H_2O]$ belong. The crystal structure of sainfeldite (Ferraris & Abbona, 1972) and that of the isostructural hureaulite $[Mn_5(HPO_4)_2(PO_4)_2.4H_2O]$ (Moore & Araki, 1973; Menchetti & Sabelli, 1973) have been described and, by analogy, the chemical formula of guérinite can be written $Ca_5H_2(AsO_4)_4.9H_2O$.

A structure determination of guérinite has been carried out as part of a research programme on acidic and hydrated compounds [the last paper in the series is Ferraris & Franchini-Angela (1974)].

Experimental

Crystal data

We used colourless crystals from a sample of synthetic guérinite kindly supplied by Professor H. Guérin (*a*), and a sample prepared by us (*b*), according to Pierrot's (1964) method. The crystals are thin-lamellar $\{10\bar{1}\}$, strongly elongated [010] and grouped in rosette-like aggregates; they are striated [010], show straight extinction and a very easy $\{10\bar{1}\}$ cleavage.

Weissenberg photographs showed that the apparent single crystals were of three types: (i) fascicular aggregates around [010]; (ii) $\{10\bar{1}\}$ twins with orthorhombic symmetry; (iii) very thin single crystals ($P2_1/n$ symmetry), with hardly detectable diffraction intensities, which seemed to be generated by cleavage of (i). By least-squares refinement of 29 θ values measured on a single-crystal diffractometer ($\lambda\alpha=1{\cdot}54051$, $\lambda\alpha_1=1{\cdot}54178$ Å), the following unit-cell parameters were obtained: $a=17{\cdot}63$ (1), $b=6{\cdot}734$ (3), $c=23{\cdot}47$ (2) Å, $\beta=90{\cdot}6$ (1)°; they imply that the content of the unit cell is

$$5[Ca_5H_2(AsO_4)_4.9H_2O]. \qquad (1)$$

Other physical data are: M.W. 920·231, $V=2786{\cdot}5$ Å^3, $D_m=2{\cdot}68$ g cm^{-3} (Pierrot, 1964), space group $P2_1/n$, $D_c=2{\cdot}74$ g cm^{-3}, $F(000)=2260$, μ(Cu $K\alpha$ radiation) = 180 cm^{-1}.

Intensity measurements

The intensities, all on the same relative scale, were measured by a General Electric three-circle diffractometer on a single crystal from sample (*a*); it had its *y* axis along the instrumental φ axis and the following slightly idealized dimensions: 0·045, 0·009 and 0·813 mm across the opposite faces of $\{101\}$, $\{10\bar{1}\}$ and $\{010\}$ respectively. Because of the small (010) cross-section of the crystal its scattering power was low; therefore, a scanning speed of 0·5° min^{-1} was used (θ–2θ scanning, 0·5° background on both sides of each peak) and the data collection had to be restricted to $2\theta\le 100°$ (Cu $K\alpha$ radiation). On average the integrated intensities were about 100 times smaller than those of other similar compounds measured with the same instrument. A standard reflexion (444) was periodically checked; 394 of the 1645 measured reflexions* were considered unobserved ($|F_c|$ consistently less than $|F_o|$).

An absorption correction (0·68–0·93 for $|F_o|$) was applied (Hamilton, 1966). The atomic scattering factors, including $\Delta f'$ and $\Delta f''$, were linear interpolations of the values reported in *International Tables for X-ray Crystallography* (1962).

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* A list of $|F_o|$ and $|F_c|$ has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30426 (7 pp.). Copies may be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Solution of the structure and unit-cell content

According to (1) the numbers of Ca atoms (25) and of H_2O molecules (45) in the cell are odd; since in $P2_1/n$ positions with odd multiplicity are not possible, there are several possibilities: (i) the structure is disordered; (ii) the chemical formula is different from (1); (iii) the space group is apparently but not exactly true; (iv) the observed symmetry is the result of further twinning.

The structure solution could be carried out in $P2_1/n$ by the program *MULTAN* (Germain, Main & Woolfson, 1971) in spite of the above difficulties. The statistics of the intensities showed centrosymmetry and the solution with the highest 'combined' figure of merit revealed the positions of 5 As atoms, 6 Ca atoms and some oxygen atoms in the asymmetric unit. Eventually, several difference syntheses showed 20 AsO_4 tetrahedra, 24 Ca atoms and 40 oxygens non-bonded to As in the cell, *i.e.* a content in agreement with a formula like

$$4[Ca_6H_3(AsO_4)_5.10H_2O] \qquad (2)$$

but not with (1).

The main difference between (1) and (2) is the As/Ca ratio which is $\frac{4}{5}$ in (1) and $\frac{5}{6}$ in (2), *i.e.* 21·78 % of Ca and 32·57 % of As instead of 21·50 % and 33·50 %, respectively [total water 19·58 and 18·53 % for (1) and (2), respectively]. The difference in calcium content is very small, but even the difference in arsenic (and, worse, in total water) may be within the range of experimental error for chemical analyses on this kind of compound.[*]

Some clarifying results can be obtained by comparing the thermal evolution of guérinite to that of sainfeldite, the chemical formula of which is well known (Ferraris & Abbona, 1972; Pierrot, 1964). Pierrot's (1964) thermal study showed that guérinite loses its water and transforms into $5CaO.2As_2O_5$ at 500 °C; our TGA curves agreed with those of Pierrot (1964) and, moreover, an X-ray study with a Guinier camera confirmed that both guérinite and sainfeldite transform into the same compound, $5CaO.2As_2O_5$, at about 500 °C.[†] Therefore, the fact that a final product with As/Ca $= \frac{4}{5}$ is obtained for both compounds and the value of loss of water for guérinite from TGA data prove that Pierrot's (1964) chemical formula (1) is correct.

Now hypothesis (i) of a disordered structure seems to be the only one possible. In fact, in the crystal structure several 'empty' cavities can be observed; in two of these a difference map showed two residual peaks (Table 1) which, on the basis of their heights and of least-squares refinements, were assigned to two independent positions of a disordered Ca atom with occupation factors 0·17 (3) and 0·08 (3), respectively. These values account for the missing 25th calcium atom in the unit cell, since their total multiplicity is $4 \times 0{\cdot}17 + 4 \times 0{\cdot}08 = 1{\cdot}00$.

Table 1. *Fractional atomic coordinates* ($\times 10^4$ *for* As *and* Ca, $\times 10^3$ *for others) and thermal parameters B* ($Å^2 \times 10$; $Å^2$ *for* St) *with significant figures of e.s.d.'s in parentheses*

	x	*y*	*z*	*B*
As(1)	5981 (3)	9483 (9)	3379 (2)	11 (1)
As(2)	4020 (3)	2581 (9)	3188 (2)	12 (1)
As(3)	3328 (3)	5099 (9)	1686 (2)	11 (1)
As(4)	4032 (3)	3719 (9)	4830 (2)	13 (1)
As(5)	5473 (3)	7671 (10)	1521 (2)	20 (2)
Ca(1)	5497 (6)	4225 (17)	3794 (4)	17 (3)
Ca(2)	4516 (6)	8850 (17)	4333 (4)	15 (2)
Ca(3)	4521 (6)	7754 (17)	2712 (4)	19 (3)
Ca(4)	5155 (6)	2668 (17)	2140 (4)	18 (2)
Ca(5)	2248 (6)	5102 (18)	2820 (4)	18 (2)
Ca(6)	2194 (6)	573 (16)	4876 (4)	17 (3)
O(1)	561 (1)	1008 (4)	275 (1)	3 (6)
O(2)	687 (2)	868 (7)	325 (2)	44 (9)
O(3)	537 (2)	754 (6)	357 (2)	29 (8)
O(4)	614 (2)	1124 (6)	387 (2)	32 (8)
O(5)	388 (2)	95 (5)	268 (1)	5 (7)
O(6)	447 (1)	172 (4)	374 (1)	00 (6)
O(7)	460 (2)	438 (6)	299 (2)	33 (9)
O(8)	327 (2)	344 (5)	336 (1)	23 (8)
O(9)	306 (2)	604 (5)	105 (1)	19 (7)
O(10)	339 (1)	679 (4)	219 (1)	8 (6)
O(11)	414 (2)	417 (5)	162 (1)	12 (7)
O(12)	271 (2)	355 (7)	190 (2)	46 (11)
O(13)	456 (2)	166 (4)	497 (1)	00 (6)
O(14)	321 (1)	287 (4)	449 (1)	3 (6)
O(15)	372 (2)	507 (5)	542 (1)	18 (8)
O(16)	442 (2)	520 (6)	440 (2)	48 (10)
O(17)	487 (2)	953 (5)	164 (1)	11 (7)
O(18)	505 (2)	616 (5)	98 (1)	8 (7)
O(19)	634 (2)	835 (6)	132 (2)	40 (9)
O(20)	557 (2)	630 (5)	210 (1)	14 (7)
W(1)	361 (2)	773 (5)	354 (1)	14 (7)
W(2)	346 (2)	874 (5)	499 (1)	12 (7)
W(3)	636 (2)	442 (7)	298 (2)	49 (11)
W(4)	624 (2)	242 (7)	156 (2)	48 (11)
W(5)	158 (2)	491 (5)	377 (1)	12 (7)
W(6)	210 (2)	−61 (7)	584 (2)	52 (11)
W(7)	179 (2)	726 (6)	472 (2)	38 (9)
W(8)	84 (2)	115 (7)	505 (2)	55 (11)
W(9)	225 (2)	382 (7)	546 (2)	56 (12)
W(10)	736 (2)	732 (6)	216 (2)	40 (9)
St(1)	476 (7)	142 (20)	31 (5)	9 (3)
St(2)	545 (11)	71 (30)	51 (8)	7 (4)

The two sites are both surrounded by six atoms which are between 2·6 and 3·5 Å, 2·5 and 3·3 Å from St(1)[*] and St(2) respectively (Table 2); such cavities

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[*] An analysis by means of atomic absorption spectrophotometry on samples (*a*) and (*b*) gave 21·90 % Ca and 33·73 % As, 21·65 % Ca and 32·80 % As, respectively.

[†] For guérinite, three intermediate unknown phases (*A*, *B*, *C*) can be observed; for sainfeldite, only one intermediate phase is observed, which corresponds to *C* and has a powder diagram similar to that of $5CaO.2As_2O_5$. TGA results for guérinite show a loss of water at 500 °C of 19·03 and 20·15 % (two measurements).

[*] Figures in parentheses denote atoms in the asymmetric unit; a second figure, ranging from 2 to 4, is included for atoms in the positions: $\bar{x},\bar{y},\bar{z}$ and $\pm(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$. Roman numerals represent the translations: I, $-\mathbf{b}$; II, $+\mathbf{b}$; III, $+\mathbf{a}+\mathbf{b}+\mathbf{c}$; IV, $+\mathbf{a}-\mathbf{b}$; V, $+\mathbf{a}+2\mathbf{b}+\mathbf{c}$; VI, $-\mathbf{c}$; VII, $-\mathbf{a}$; VIII, $+\mathbf{a}$; IX, $+\mathbf{a}+\mathbf{b}$.

obviously cannot accommodate Ca^{2+} ions with a great stability. It seems therefore reasonable to suppose that around each of the two sites there are also five independent positions for the five missing water molecules, so that the disordered cation always carries five water molecules with it; these would therefore be disordered over eight possible positions, like the calcium, and would show a height of only one electron on the difference map. Such a hypothesis is also supported by an occupation factor larger for St(1) than for St(2); a calcium surrounded by five water molecules will be accommodated more easily on St(1) since the cavity around this site is, on average, larger than that around St(2) (Table 2). Because of this fact and in order to avoid steric interference (*cf.* St···St distances in Table 2), the positions occupied by the disordered atoms will not be completely random.

Table 2. *Interatomic distances* (Å) *and oxygen*–Ca–*oxygen angles* (°) *for the* Ca *coordination polyhedra*

E.s.d.'s are, on the average, 0·04, 0·05, 0·1 and 0·2 Å for Ca–O, O–O, St–O and St–St distances respectively; they are 1·5° for angles.

Ca(1)–O(3)	2·31
Ca(1)–O(4)^{I}	2·32
Ca(1)–O(6)	2·48
Ca(1)–O(7)	2·45
Ca(1)–O(15,2)^{III}	2·34
Ca(1)–O(16)	2·47
Ca(1)–*W*(3)	2·46
Average	2·40
O(3)——*W*(3)	3·07 (80)°
O(3)——O(7)	2·86 (74)
O(3)——O(16)	3·02 (79)
O(3)——O(15,2)^{III}	3·35 (92)
O(4)^{I}——*W*(3)	3·03 (79)
O(4)^{I}——O(7)	4·00 (114)
O(4)^{I}——O(16)	4·23 (124)
O(4)^{I}——O(6)	2·98 (77)
O(4)^{I}——O(15,2)^{III}	3·01 (80)
O(6)——O(7)	2·52 (62)
O(6)——O(16)	2·81 (69)
O(16)——O(7)	3·37 (87)
O(7)——*W*(3)	3·09 (78)
W(3)——O(15,2)^{III}	3·79 (104)
O(15,2)^{III}–O(16)	3·30 (87)
Ca(2)–O(3)	2·51
Ca(2)–O(6)^{II}	2·38
Ca(2)–O(13)^{II}	2·42
Ca(2)–O(13,2)^{III}	2·32
Ca(2)–O(16)	2·47
Ca(2)–*W*(1)	2·55
Ca(2)–*W*(2)	2·43
Average	2·44
O(16)——O(13,2)^{III}	3·13 (82)
O(16)——*W*(2)	3·25 (83)
O(16)——*W*(1)	2·99 (73)
O(16)——O(3)	3·02 (75)
O(6)^{II}——O(13,2)^{III}	4·14 (124)
O(6)^{II}——*W*(2)	3·99 (112)
O(6)^{II}——*W*(1)	3·12 (78)
O(6)^{II}——O(3)	3·26 (84)
O(6)^{II}——O(13)^{II}	2·89 (74)
O(13)^{II}——*W*(2)	2·76 (69)
O(13)^{II}——O(13,2)^{III}	2·73 (70)
O(13,2)^{III}–*W*(2)	3·50 (95)
W(2)——*W*(1)	3·45 (89)
W(1)——O(3)	3·10 (76)
O(3)——O(13,2)^{III}	3·47 (92)
Ca(3)–O(1)	2·48
Ca(3)–O(3)	2·51
Ca(3)–O(5)^{II}	2·43
Ca(3)–O(7)	2·37
Ca(3)–O(10)	2·41
Ca(3)–O(17)	2·87
Ca(3)–O(20)	2·54
Ca(3)–*W*(1)	2·53
Average	2·52
O(5)^{II}–O(1)	3·11 (79)
O(5)^{II}–O(3)	4·06 (111)
Ca(4)–O(1)^{I}	2·40
Ca(4)–O(5)	2·83
Ca(4)–O(7)	2·51
Ca(4)–O(11)	2·38
Ca(4)–O(17)^{I}	2·47
Ca(4)–O(20)	2·56
Ca(4)–*W*(4)	2·37
Average	2·50
Ca(4)–*W*(3)	3·11
Average	2·58
W(4)—O(11)	3·90 (110)°
W(4)—O(20)	3·15 (79)
W(4)—O(1)^{I}	3·41 (91)
W(4)—O(17)^{I}	3·11 (80)
O(5)—O(7)	2·74 (61)
O(5)—O(1)^{I}	3·11 (73)
O(5)—O(17)^{I}	3·16 (73)
O(5)—O(11)	3·33 (79)
O(7)—O(1)^{I}	3·45 (89)
O(7)—O(20)	3·00 (73)
O(7)—O(11)	3·31 (85)
O(1)^{I}—O(17)^{I}	2·94 (74)
O(17)^{I}–O(11)	3·38 (88)
O(11)–O(20)	3·11 (78)
O(20)–O(1)^{I}	2·96 (129)
W(3)—O(1)^{I}	3·25 (71)
W(3)—O(7)	3·09 (66)
W(3)—O(20)	2·77 (58)
Ca(5)–O(5,3)	2·37
Ca(5)–O(8)	2·46
Ca(5)–O(10)	2·75
Ca(5)–O(10,3)^{I}	2·50
Ca(5)–O(12)	2·54
Ca(5)–O(12,3)	2·42
Ca(5)–*W*(5)	2·54
Average	2·51
O(12,3)—O(10)	3·13 (74)
O(12,3)—O(5,3)	3·26 (86)
O(12,3)—*W*(5)	3·18 (80)
O(12,3)—O(8)	3·89 (106)
O(10,3)^{I}–O(8)	3·38 (86)
O(10,3)^{I}–O(12)	3·13 (77)
O(10,3)^{I}–O(5,3)	3·14 (80)
O(10,3)^{I}–*W*(5)	3·09 (76)
O(5,3)——*W*(5)	3·54 (93)
O(5,3)——O(12)	3·40 (88)
O(5,3)——O(10)	4·06 (105)
W(5)——O(8)	3·30 (83)
O(8)——O(10)	3·55 (86)
O(10)——O(12)	2·58 (58)
O(12)——O(8)	3·56 (91)
Ca(6)–O(93)^{I}	2·24
Ca(6)–O(14)	2·53
Ca(6)–*W*(2)^{I}	2·56
Ca(6)–*W*(6)	2·40
Ca(6)–*W*(7)^{I}	2·37

Table 2 (*cont.*)

O(5)^{II}–*W*(1)	3·01 (75)
O(5)^{II}–O(10)	3·14 (81)
O(5)^{II}–O(17)	3·16 (73)
O(7)—O(3)	2·86 (72)
O(7)—O(20)	3·00 (75)
O(7)—O(10)	3·26 (86)
O(7)—*W*(1)	3·14 (80)
O(10)–*W*(1)	3·25 (82)
W(1)–O(3)	3·10 (76)
O(3)—O(1)	2·61 (63)
O(3)—O(20)	3·57 (90)
O(1)—O(20)	2·96 (72)
O(1)—O(17)	2·94 (66)
O(20)–O(17)	2·72 (60)
O(17)–O(10)	3·47 (82)
O(20)–O(10)	3·86 (102)
St(1)–O(17)^{I}	3·4
St(1)–O(18,2)^{IX}	3·5
St(1)–*W*(5,3)^{I}	3·4
St(1)–*W*(7,3)^{I}	2·8
St(1)–*W*(8,4)^{VI}	2·6
St(1)–*W*(8,3)	3·5
St(1)···St(2)	1·4
St(1)···St(1,2)^{VIII}	2·6
St(1)···St(2,2)^{VIII}	2·4
Ca(6)–*W*(8)	2·46
Ca(6)–*W*(9)	2·58
Average	2·45
W(9)—*W*(6)	3·12 (78)
W(9)—*W*(8)	3·20 (79)
W(9)—O(9,3)^{I}	4·03 (113)
W(9)—O(14)	2·90 (69)
W(9)—*W*(2)^{I}	4·19 (109)
W(7)^{I}—*W*(6)	3·04 (79)
W(7)^{I}—*W*(8)	3·21 (83)
W(7)^{I}—O(9,3)^{I}	3·14 (86)
W(7)^{I}—*W*(2)^{I}	3·18 (80)
W(8)—*W*(6)	3·12 (80)
W(6)—*W*(2)^{I}	3·15 (79)
W(2)^{I}—O(14)	3·05 (74)
O(14)—O(9,3)^{I}	2·84 (73)
O(9,3)^{I}–*W*(8)	3·25 (87)
O(9,3)^{I}–*W*(2)^{I}	3·93 (110)
St(2)–O(17)^{I}	3·0
St(2)–O(18)^{I}	3·3
St(2)–O(19)^{I}	2·9
St(2)–*W*(4)	3·1
St(2)–*W*(8,4)^{VI}	2·5
St(2)–*W*(9,4)^{VI}	3·2
St(2)···St(1)	1·4
St(2)···St(1,2)^{VIII}	2·4
St(2)···St(2,2)^{VIII}	3·0

Hypotheses (iii) and (iv) cannot be completely rejected, but we note that even a unit cell with $P1$ symmetry should contain disorder since in $P2_1/n$ a single disordered atom appears distributed among eight positions, *i.e.* on two independent sets with a fourfold multiplicity.

Refinement of the structure

The crystal structure has been refined isotropically (Table 1) by the full-matrix least-squares program of Busing, Martin & Levy (1962), with minor modifications, and in the later cycles the following weighting scheme ($|F_o|$ on 1·17 times the absolute scale) was used

$$w = 1692/(0{\cdot}025|F_o|^2 + 9|F_o| + 400) \quad \text{if} \quad |F_o| \ge 110$$
$$w = 1 \quad \text{if} \quad |F_o| < 110.$$

The final values of R and R_w were 0·13 and 0·15, respectively. Attempts to refine anisotropically the heavy atoms led to non-positive definite values for their temperature factors; in particular, the values of B_{22} for these atoms were negative. A final difference synthesis showed scattered peaks with some concentration near the heavy-atom positions and with a maximum height of ±2·5 e $Å^{-3}$.

Discussion

Owing to the experimental conditions of measurements and to the disorder in the structure, the e.s.d.'s of the atomic parameters are large. However, it can be assumed that the structure determined is correct, except perhaps for details.

Electrostatic balance

The number of acidic hydrogen atoms per formula unit, and whether the 'water molecules' are really H_2O molecules or rather OH^- ions, are still open questions. An answer based on the lengths of the As–O bonds and of the O···O contacts only might be ambiguous in this structure with low accuracy; the bond-length criterion, therefore, has been used with recent correlations between bond distances and bond strengths (Baur, 1970; Brown & Shannon, 1973; Donnay & Allmann, 1970; Ferraris & Catti, 1973). The bond strengths s which the oxygen atoms receive from the cations were calculated from the relation (Brown & Shannon, 1973)

$$s=s_0(R/R_0)^{-N}; \tag{3}$$

the oxygens were interpreted as O^{2-}, OH^-, or H_2O if s was close to 2, 1 or 0 v.u., respectively (Donnay & Allmann, 1970). After taking into account the possible hydrogen bonds and calculating their bond strengths according to Donnay & Allmann (1970), it was checked that s was about 2 v.u. for all the oxygens.

The values of s_0 and R_0 given for (3) by Brown & Shannon (1973) correspond closely to the cationic charge (p) divided by the coordination number (CN) and to the average cation–oxygen distances for the most frequent CN of each cation, respectively. When, as in this case, the crystal structure shows coordination polyhedra with an average cation–oxygen distance markedly different from R_0, the sum of the s values donated by a cation can be very different from p. This causes difficulties in evaluating the bond strength on the oxygens. In order to avoid this difficulty, following in part Donnay & Allmann (1970), one could compute special curves (3) for each polyhedron (Allmann, 1973), or normalize the $\sum s$ for each cation to p (*cf.* Giuseppetti & Tadini, 1973) or use other similar artifices. We observed that the different ways all led to the same conclusions for the purpose of detecting O^{2-}, OH^- and H_2O, since the problem is mainly a matter of scale for s. The clearest results were obtained with values of N from Brown & Shannon (1973), R_0 replaced by the average cation–oxygen distance of the polyhedron, and $s_0=p/\mathrm{CN}$.

Hydrogen bonding

Table 3 shows the hydrogen-bonding scheme which gives the best agreement with the requirement of s values close to 2 v.u. for all the oxygens. All O···O contacts which are less than 3·15 Å and are not edges of coordination polyhedra (Baur, 1972; 1973) are involved in the hydrogen-bonding scheme proposed and the oxygen atoms not bonded to As atoms always belong to H_2O molecules. Further, the As(5) group always has the configuration $(AsO_3OH)^{2-}$ [H is bonded to O(18)]; the As(4) group has the same configuration, but the hydrogen is equally likely to be bonded to O(14) or to O(15); only 50% of the As(1) groups have a hydrogen which is bonded to O(2). As a result, on average, half the AsO_4 groups have the configuration $(AsO_3OH)^{2-}$, and the unit cell contains five $Ca_5(HAsO_4)_2(AsO_4)_2.9H_2O$ units.

Table 3. *Interatomic distances* (Å) *and angles* (°) *involving the hydrogen bonds*

E.s.d.'s are 0·05 Å for O···O distances and 2° for angles.

A	*B*	*C*	*AB*	*BC*	∠*ABC*
O(12,3)	$W(1)$	O(8)	2·60	2·98	88
$\mathrm{O(4,2)^{V}}$	$W(2)$	O(15)	2·76	2·71	67
$W(10,3)^{\mathrm{IV}}$	$W(3)$	O(2)	2·70	3·08	106
$\mathrm{O(19)^{I}}$	$W(4)$	$W(6,4)^{\mathrm{VI}}$	2·80	3·14	122
$\mathrm{O(9,3)^{I}}$	$W(5)$	$\mathrm{O(17,3)^{I}}$	2·72	2·72	101
$\mathrm{O(19,4)^{VII}}$	$W(6)$	$\mathrm{O(4,2)^{III}}$	2·56	3·20	109
		$\mathrm{O(2,2)^{III}}$		3·08	108
$W(9)$ · · * · ·	$W(7)$	$W(5)$	2·99	2·76	93
$\mathrm{O(18,4)^{VII}}$	$W(8)$	$\mathrm{O(18,3)^{I}}$	3·04	2·86	111
$W(7)$	$W(9)$ · * ·	O(15)	2·99	2·74	90
$\mathrm{O(2,3)^{IV}}$	$W(10)$	O(19)	2·97	2·75	106
As(1)	*O(2)	$W(10)$	1·69	2·86	123
As(4)	*O(14)	O(8)	1·75	2·70	111
		O(6)		2·96	74
As(4)	*O(15)	$W(9)$	1·75	2·74	100
As(5)	O(18)	O(11)	1·79	2·58	98

* See text.

A doubtful point of the proposed hydrogen-bonding scheme involves $W(7)$, O(15) and $W(9)$. In all the possible assignments of the donor and acceptor functions, $W(7)$ or $W(9)$, which are close to St(1) and St(2) respectively, have a hydrogen atom free from hydrogen bonds; however, hydrogen bonds are very likely to exist between them and the nearby disordered water molecules. It has been suggested that O(15) should be donor to $W(9)$ [and this to $W(7)$] rather than to $W(2)$, by considering the high s value which $W(2)$ receives from two Ca ions; the small angle O(15)···$W(2)$···$\mathrm{O(4,2)^{V}}$ might be explained by a possible bifurcated hydrogen bond of $W(2)$ with O(4,2) and O(13), where $W(2)\cdots\mathrm{O}(13)$ (2·76 Å) would also be an edge of a Ca polyhedron [$\mathrm{O}(15)\cdots W(2)\cdots\mathrm{O}(13) = 123°$, $\mathrm{O}(4,2)^{\mathrm{V}}\cdots W(2)\cdots\mathrm{O}(13) = 81°$]. However, different donor–acceptor schemes are possible, within the system O(15), *W*(7) and *W*(9), according to the occupation of St(1) or St(2), and according to whether O(15) or O(14) is actually bonded to the acidic hydrogen atom which belongs to the As(4) group. With the exception of O(2), the assignment of the acidic hydrogen atoms is in agreement with the As–OH distances and with the angles As–OH$\cdots$O (Tables 3 and 4), which should be close to the tetrahedral value, like the angles As–O–H (Ferraris, 1970; Ferraris, Jones & Yerkess, 1972). Oxygens involved in hydrogen bonds and coordinated Ca atoms, including St, form a satisfactory tetrahedral environment around the water molecules (Ferraris & Franchini-Angela, 1972).

Table 4. *Interatomic distances and* O–As–O *angles in the* $\mathrm{AsO_4}$ *groups*

E.s.d.'s are, on average, 0·035 and 0·045 Å for As–O and O–O distances respectively and 2° for the angles

As(1)–O(1)	1·65 Å	O(1)—O(2)	2·67 Å	106°
As(1)–O(2)	1·69	O(1)—O(3)	2·61	100
As(1)–O(3)	1·75	O(1)—O(4)	2·88	120
As(1)–O(4)	1·67	O(2)—O(3)	2·86	112
Average	1·69	O(2)—O(4)	2·60	102
		O(3)—O(4)	2·91	117
As(2)–O(5)	1·65	O(5)—O(6)	2·75	115
As(2)–O(6)	1·62	O(5)—O(7)	2·74	112
As(2)–O(7)	1·66	O(5)—O(8)	2·57	109
As(2)–O(8)	1·51	O(6)—O(7)	2·52	101
Average	1·61	O(6)—O(8)	2·57	110
		O(7)—O(8)	2·59	110
As(3)–O(9)	1·69	O(9)—O(10)	2·79	113
As(3)–O(10)	1·65	O(9)—O(11)	2·64	108
As(3)–O(11)	1·57	O(9)—O(12)	2·68	110
As(3)–O(12)	1·59	O(10)–O(11)	2·59	107
Average	1·63	O(10)–O(12)	2·58	105
		O(11)–O(12)	2·64	114
As(4)–O(13)	1·70	O(13)–O(14)	2·75	106
As(4)–O(14)	1·75	O(13)–O(15)	2·93	116
As(4)–O(15)	1·75	O(13)–O(16)	2·75	113
As(4)–O(16)	1·58	O(14)–O(15)	2·77	105
Average	1·69	O(14)–O(16)	2·67	107
		O(15)–O(16)	2·71	109
As(5)–O(17)	1·67	O(17)–O(18)	2·76	106
As(5)–O(18)	1·79	O(17)–O(19)	2·82	115
As(5)–O(19)	1·67	O(17)–O(20)	2·72	110
As(5)–O(20)	1·66	O(18)–O(19)	2·82	110
Average	1·69	O(18)–O(20)	2·79	108
		O(19)–O(20)	2·68	107

Description of the structure

The crystal structure is characterized by $(\bar{1}01)$ layers built up by Ca polyhedra (Fig. 1) which are linked to each other and to the As tetrahedra by sharing vertices, edges and faces. The three oxygens O(2), O(18) and O(19) and the water molecule, *W*(10), which are not Ca-coordinated, are situated between the layers, which are held together by most of the hydrogen bonds in the structure. However, since both St(1) and St(2) are found between the layers, the disordered Ca atom is likely to coordinate oxygens belonging to contiguous layers, for instance *W*(7) and *W*(8) (Table 2), forming an additional link besides that of the hydrogen bonds. The $\{10\bar{1}\}$ cleavage is satisfactorily explained by this scheme. About the $\{10\bar{1}\}$ twinning, it can be observed that two contiguous layers show facing surfaces which are related, to a first approximation, by a $(10\bar{1})$ glide plane with a rough $(a+c)/4$ translation.

Ca(1), Ca(2), Ca(5) and Ca(6) have a coordination number of 7, Ca(3) coordinates 8 and Ca(4) 7 oxygens, but the latter has an eighth oxygen which is 3·11 Å distant. All the coordination polyhedra are irregular. The Ca–O distances are generally fairly close to their average values; however, Ca(3), Ca(4) and Ca(5) each show a Ca–O distance which is markedly longer than the average, and Ca(6) shows a much shorter distance. The irregularities of the Ca polyhedra may be related to the fact that they share many geometrical elements. Each of the Ca(1), Ca(4) and Ca(5) polyhedra shares an edge with an As tetrahedron, and the Ca(3) polyhedron shares two edges with two As tetrahedra. The As(2) tetrahedron shares two edges with the Ca(1) and Ca(4) polyhedra. The following shared edges belong to Ca polyhedra related by a symmetry operation: $\mathrm{O}(13)^{\mathrm{II}}\cdots\mathrm{O}(13,2)^{\mathrm{III}}$ between Ca(2) and $\mathrm{Ca}(2,2)^{\mathrm{III}}$; $\mathrm{O}(12)\cdots\mathrm{O}(10,3)^{\mathrm{I}}$ and $\mathrm{O}(10)\cdots\mathrm{O}(12,3)$ shared by Ca(5) with Ca(5,3) and $\mathrm{Ca}(5,3)^{\mathrm{II}}$ respectively. The face $\mathrm{O}(1)\cdots\mathrm{O}(5)^{\mathrm{II}}\cdots\mathrm{O}(17)$ is shared by the Ca(3) with the $\mathrm{Ca}(4)^{\mathrm{II}}$ polyhedron.

Although a greater crowding of polyhedra, developing along [010], can be observed around Ca(3) and Ca(4), it cannot be compared with the characteristic groups of five octahedra sharing edges which are present in sainfeldite (Ferraris & Abbona, 1972) and are linked together in a three-dimensional network by sharing vertices.

Crystals of guérinite develop $\{\bar{1}01\}$ form, which has faces parallel to the layers, and grow along the direction [010] of the piles where Ca(3) and Ca(4) share faces; growth along the direction perpendicular to the layers is greatly restricted.

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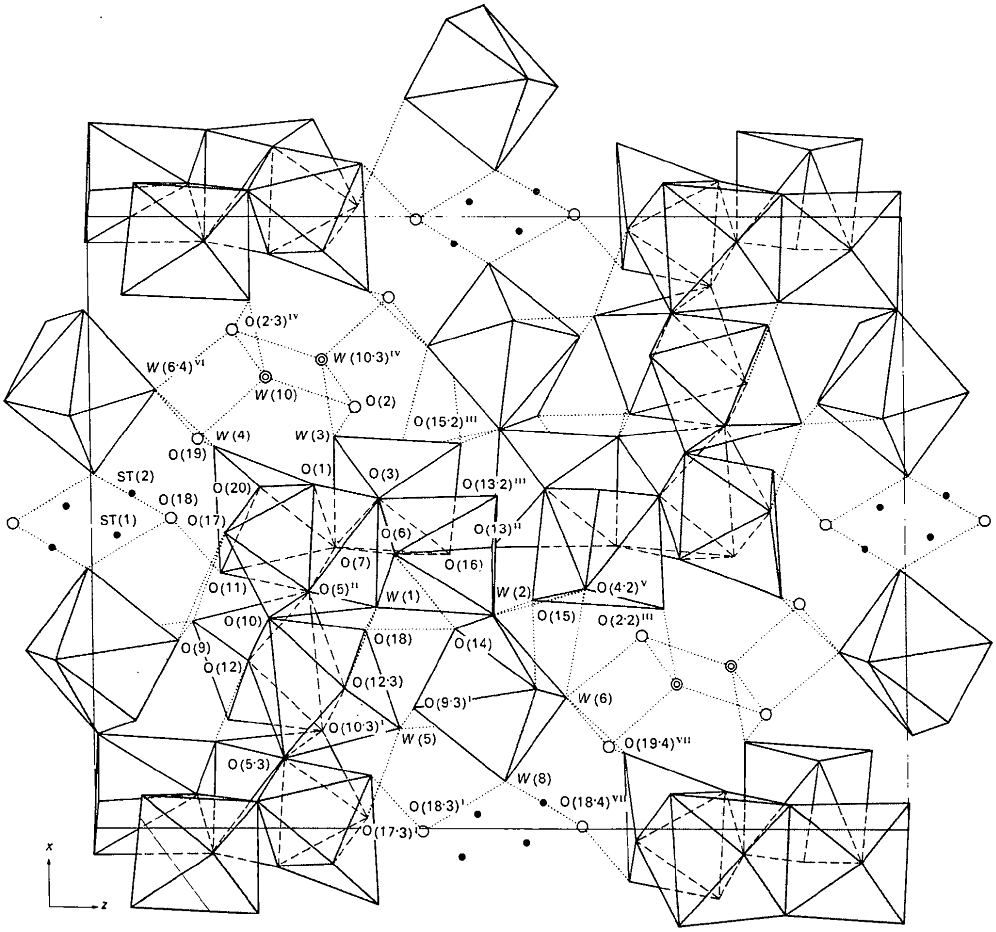

Fig. 1. Unit cell of guérinite in projection on to the (010) plane. Calcium coordination polyhedra are shown but not arsenic and calcium atoms. Circles and double circles represent oxygen and water oxygen atoms, respectively, which are not calcium coordinated. O(1) and O(5)$^{\mathrm{ii}}$ belong to the upper (grey) polyhedron only. Hydrogen bonds are shown as dotted lines.

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