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Hydrogen Bonding in the Crystalline State. Crystal Structure of MgHAsO₄.7H₂O, Roesslerite*

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Roesslerite, magnesium hydrogen arsenate heptahydrate ($MgHAsO_4.7H_2O$), crystallizes in the monoclinic system, space group $C2/c$. Unit-cell parameters are: $a_0 = 6.6918$ (5), $b_0 = 25.744$ (2), $c_0 = 11.538$ (1) Å, $\beta = 95.15$ (1)°; $Z = 8$. The crystal structure was refined anisotropically to $R = 0.030$, using 2157 non-zero reflexions measured on an automatic three-circle diffractometer (Cu $K\alpha$ radiation). Corrections for absorption, secondary extinction (including an increase of the mosaicity during the measurements) and anomalous scattering were applied. The hydrogen atoms were located from difference maps and the acidic hydrogen atom appears to be involved in two symmetrical hydrogen bonds. The two crystallographically independent magnesium atoms are coordinated by six water molecules; the seventh water molecule is linked by hydrogen bonds only. No oxygen atoms are shared by coordination polyhedra and the crystal structure can be described in terms of layers parallel to (010) or to (001).

Introduction

Roesslerite, magnesium hydrogen arsenate heptahydrate ($MgHAsO_4.7H_2O$), is a secondary mineral usually associated with other arsenates (Palache, Berman & Frondel, 1963) and, according to its known properties, is isostructural with $MgHPO_4.7H_2O$, phospho-roesslerite.

An X-ray crystal-structure determination of roesslerite has been carried out as a part of a programme of structural research on hydrogen bonding and on the role of the water molecule in the crystalline state [*cf.* Ferraris & Franchini-Angela (1972), Chiari & Ferraris (1971) and references therein]; in particular, acidic arsenates (or phosphates) are often likely to have symmetrical hydrogen bonds [*cf.* Ferraris, Jones & Yerkess (1972) and references therein].

Preparation and crystal data

Transparent, colourless crystals of $MgHAsO_4.7H_2O$, suitable for X-ray study, were grown by the method of Mattrat & Guérin (1960). Cu $K\alpha$ X-ray diffraction analyses (Weissenberg and single-crystal diffractometry) confirmed the monoclinic symmetry (Palache *et al.*, 1963) and, to a first approximation, the unit-cell parameters reported by Fischer (1964); the crystals are tabular {010} and elongated along [100]. The space group $C2/c$ (C_{2h}^6, No. 15) has been chosen on the basis of systematic absences (Cc or $C2/c$), the absence of a piezoelectric effect,* and the examination of the Harker sections; the successful refinement of the structure confirmed the validity of this choice.

The reciprocal unit-cell parameters were refined by a least-squares procedure using 36 θ values greater than 65°, which were measured at room temperature on a single-crystal diffractometer ($\lambda\alpha_1 = 1.54050$, $\lambda\alpha_2 =$

1·54434 Å); the following direct unit-cell parameters (standard deviations in parentheses) were obtained:

$a_0 = 6·6918$ (5) Å $b_0 = 25·744$ (2) Å $c_0 = 11·538$ (1) Å
$\beta = 95·15$ (1)°.

Table 1 shows data for the X-ray powder spectrum of $MgHAsO_4.7H_2O$; the indexing was on the basis of both computed interplanar distances (d_{calc}) and the single-crystal intensities.

Our optical observations are in agreement with those reported by Keller (1971) and confirm that previous optical data (cf. Palache et al., 1963) are erroneous; in particular, roesslerite is biaxial negative. Other physical data are: M.W. 290·23, $V = 1979·6$ Å^3, $D_m = 1·943$ (Palache et al., 1963), $D_c = 1·948$ gcm^{-3}, $Z = 8$, $F(000) = 1184$, linear absorption coefficient for Cu $K\alpha$ radiation $\mu = 62$ cm^{-1}.

Intensity measurements

Intensities were measured on a General Electric automatic three-circle diffractometer (θ–2θ scanning, 2° min^{-1}, 0·5° background on both sides of each peak) from a crystal mounted with its x axis along the instrumental φ axis and coated with a thin plasticizing film to prevent dehydration. Of the 2157 independent reflexions measured, 114 were rejected because they were very weak ($|F_c| < |F_o|$). A standard reflexion (222) was checked every 50 reflexions; its value, on a relative scale, increased from 35400 to 39000 during 94 hours of measurements. This surprising variation, which could be ascribed to an increase in the mosaicity

of the crystal under X-ray exposure, was fitted to an approximately exponential curve; all the reflexions were put on the same relative scale on the basis of this graph. During the final stage of the refinement, a secondary extinction correction was introduced; with a least-squares procedure, we deduced, for the function

$$I_c/I_o = k(1 + gI_c) ,$$

$k = 0·931$ and $g = 3·10^{-6}$ e^{-2}. An absorption correction (transmission factor 0·53–0·81) was applied using the program GONO9 (Hamilton, 1966). Dimensions of the slightly idealised crystal are: 0·07, 0·21 and 0·61 mm across the opposite faces of $\{010\}$, $\{001\}$ and $\{100\}$ respectively; $\{100\}$ is a rough approximation for an uneven fracture. Atomic scattering factors, with both real and imaginary corrections for anomalous scattering, were a linear interpolation of the values reported for neutral atoms in International Tables for X-ray Crystallography (1962).

Solution and refinement of the structure

The independent As atom was readily located in a three-dimensional Patterson function; a difference synthesis ($R = 0·45$) showed all the non-hydrogen atoms except for one oxygen atom which emerged from a subsequent synthesis ($R = 0·16$). There are eight formula units in the unit cell and, except for magnesium and acidic hydrogen (see below), all the atoms are in general positions.

After a preliminary isotropic refinement ($R = 0·08$), anisotropic vibrational parameters were included and

Table 1. *Intensities (on arbitrary scale), observed and calculated interplanar spacings and indices for the reflexions of the X-ray powder spectrum of roesslerite (Fe $K\alpha$, $\lambda = 1·93728$ Å)*

I_{obs}	d_{obs}(Å)	d_{calc} (Å)	hkl	I_{obs}	d_{obs} (Å)	d_{calc}(Å)	hkl
m	12·98	12·87	020	vw	2·457	2·4639/2·4597/2·4497	083/$\bar{2}$62/134
w	8·55	8·57	021	vw	2·412	2·4138/2·4110	173/$\bar{1}$54
vs	6·44	6·436	040	vw	2·244	2·2447/2·2445/2·2424	$\bar{2}$63/$\bar{2}$24/281
vw	5·74	5·745	002	vw	2·206	2·2082/2·2040	1.11.0/$\bar{1}$93
m	5·24	5·247	022	w	2·157	2·1566	1.11.1
w	4·908	4·9194	$\bar{1}$31	vw	2·125	2·1303	$\bar{3}$12
s	4·659	4·6620	131	vw	2·099	2·0990	174
s	4·476	4·4890	$\bar{1}$12	w	2·076	2·0743	$\bar{3}$32
ms	4·275	4·2907/4·2861	060/042	vw	2·046	2·0505	$\bar{1}$55
vs	4·075	4·0745	150	vw	2·006	2·0061	312
vw	3·751	3·7510	132	vw	1·9472	1·9490	$\bar{3}$33
mw	3·661	3·6713	023	vw	1·8925	1·8943/1·8896	026/$\bar{2}$45
w	3·419	3·4270/3·4132	$\bar{1}$13/$\bar{1}$52	vw	1·8654	1·8653/1·8652	$\bar{3}$53/1.13.1
w	3·325	3·3324	200	vw	1·8422	1·8422/1·8411	$\bar{1}$36/$\bar{2}$.10.3
w	3·281	3·2915	043	vw	1·8108	1·8094	333
vw	3·133	3·1361	$\bar{1}$71	vw	1·7693	1·7711/1·7689	$\bar{1}$56/2.12.1
vw	3·026	3·0380	221	vw	1·7453	1·7454	$\bar{2}$.12.2
w	2·993	2·9977	133	vw	1·7107	1·7123	$\bar{3}$92
m	2·857	2·8574	063	vw	1·6795	1·6821/1·6783	314/$\bar{1}$76
mw	2·795	2·8076/2·0838	082/024	vw	1·6503	1·6502	$\bar{1}$.15.1
mw	2·706	2·7141/2·7145	222/$\bar{1}$14	vw	1·6232	1·6250/1·6204	$\bar{1}$17/2.10.4
mw	2·621	2·6233	044	vw	1·5793	1·5816/1·5786	3.11.1/441
vw	2·571	2·5744	0.10.0	vw	1·5490	1·5494	0.16.2
w	2·522	2·5267	261				

Plus 27 very weak reflexions with the following d_{obs} (Å):

1·4808, 1·4507, 1·4320, 1·4128, 1·3995, 1·3865, 1·3559, 1·3405, 1·3129, 1·3002, 1·2902, 1·2770, 1·2541, 1·2286, 1·2187, 1·2017, 1·1927, 1·1679, 1·1568, 1·1457, 1·1388, 1·0957, 1·0894, 1·0280, 1·0207, 1·0118, 1·0063.

the R value fell to 0·05. At this stage, a three-dimensional difference synthesis showed several maxima of 0·4–1·0 eÅ^{-3}; from these, most of the hydrogen atoms were located with the aid of a calculation of bond distances and angles. After the extinction correction had been applied a new difference synthesis revealed the remaining hydrogen atoms. The eight acidic hydrogen atoms required in a unit cell by the chemical formula appear on two special positions: inversion centre $(0, 0, 0)$ and twofold axis $(0, y, \frac{1}{4})$; thus they imply two 'symmetrical' hydrogen bonds. While the peak at $(0, 0, 0)$ does not show any anomalies, that at $(0, y, \frac{1}{4})$ has the appearance of a broad single-peak with two lobes.

The least-squares refinement, including isotropic hydrogen atoms, was ended when all the shifts were less than the corresponding estimated standard deviations (e.s.d.)* and the R value was 0·030.

The full-matrix least-squares program of Busing, Martin & Levy (1962), with minor modifications, was used with the following weighting scheme ($|F_c|$ on absolute scale) in the final cycles:

$$w = \frac{55}{0·01\ F_o^2 + 0·25\ |F_o| + 35} \quad \text{for} \quad |F_o| \geq 18$$

$$w = 0·0114\ |F_o| + 0·6 \quad \text{for} \quad |F_o| < 18.$$

The final weighted R value and the standard error of one observation were 0·036 and 1·61 respectively. Table

2 shows the fractional coordinates and the B_{ij} coefficients in the expression:

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

together with the e.s.d.'s (in parentheses).

Discussion

The symmetrical hydrogen bonds

Since the two short oxygen–oxygen contacts $[O(2)\cdots O(2^v) = 2·491$ Å and $O(3)\cdots O(3^{ii}) = 2·539$ Å]† are across symmetry elements, some type of sharing of the acidic hydrogen atom is necessary; we must therefore be sure about the space group before the chemical sense of the contacts can be discussed. In addition to previous considerations, the consistency of bond lengths and angles (Tables 3, 4 and 5) with those found in similar structures would be surprising if the short O$\cdots$O contacts were merely a spurious consequence of an arbitrary centrosymmetric refinement.

Of course, the centrosymmetry could apply (within experimental error) to the heavy atoms (As, Mg and O) only and the acidic atom could be attached to only one oxygen atom. Such a situation, which could be expected to yield a piezoelectric effect, is however in conflict with correlations between bond lengths and

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* A list of $|F_o|$ and F_c values has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30027. Copies may be obtained either through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England, or from the authors.

† The labelling of the atoms is as follow: a single figure in parentheses (or no figure) denotes an atom of the asymmetric unit; a superscript, ranging from ii to viii, is included for atoms in the positions: $\bar{x}, \bar{y}, \bar{z}$; $\pm(\frac{1}{2}+x, \frac{1}{2}+y, z)$; $\pm(\bar{x}, y, \frac{1}{2}-z)$ and $\pm(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$. Capital Roman numerals represent the following translations: I, $+$a; II, $+$c; III, $-$a.

Table 2. *Fractional atomic coordinates and vibrational parameters* (Å^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}
As	0·05256 (4)	0·09415 (1)	0·04532 (2)	1·07 (1)	0·98 (1)	0·83 (1)	0·09 (1)	0·10 (1)	0·06 (1)
Mg(1)	0	0·44902 (4)	$\frac{1}{4}$	1·33 (4)	1·07 (4)	0·98 (4)	0	0·17 (3)	0
Mg(2)	$\frac{1}{4}$	0·22076 (4)	$\frac{1}{4}$	1·36 (4)	0·90 (4)	1·63 (4)	0	0·09 (3)	0
O(1)	0·2915 (3)	0·0818 (1)	0·0908 (2)	1·25 (6)	1·61 (7)	1·72 (7)	0·10 (5)	0·02 (5)	0·04 (5)
O(2)	−0·0490 (3)	0·1337 (1)	0·1433 (2)	1·71 (7)	1·51 (7)	1·25 (6)	0·33 (5)	1·15 (5)	−0·40 (5)
O(3)	−0·0842 (3)	0·0383 (1)	0·0451 (2)	1·47 (7)	1·18 (6)	1·96 (7)	−0·25 (5)	0·12 (5)	−0·14 (5)
O(4)	0·0231 (3)	0·1230 (1)	−0·0839 (1)	2·13 (7)	1·64 (7)	0·99 (6)	0·17 (6)	0·17 (5)	0·32 (5)
W(1)	0·0451 (3)	0·4445 (1)	0·4277 (2)	1·72 (7)	3·36 (9)	1·06 (7)	−0·42 (7)	0·08 (6)	0·02 (6)
W(2)	0·2174 (3)	0·3911 (1)	0·2423 (2)	1·58 (7)	1·99 (7)	1·47 (7)	0·47 (6)	0·23 (6)	0·10 (6)
W(3)	−0·2125 (4)	0·5062 (1)	0·2573 (2)	3·43 (10)	2·34 (9)	2·35 (9)	1·48 (7)	1·03 (7)	1·08 (7)
W(4)	0·2102 (3)	0·2206 (1)	0·1755 (2)	1·71 (8)	1·68 (8)	3·62 (10)	0·08 (6)	−0·59 (7)	0·13 (7)
W(5)	0·4141 (3)	0·2759 (1)	0·3666 (2)	2·48 (9)	1·78 (8)	3·48 (10)	−0·04 (7)	0·67 (9)	−1·09 (7)
W(6)	0·4402 (3)	0·1615 (1)	0·3682 (2)	1·68 (7)	1·39 (7)	2·23 (8)	−0·10 (7)	0·21 (6)	0·42 (6)
W(7)	0·0097 (4)	0·3047 (1)	0·3949 (2)	3·41 (10)	1·97 (8)	2·41 (9)	−0·20 (7)	0·22 (7)	−0·28 (7)

	x/a_0	y/b_0	z/c_0	B		x/a_0	y/b_0	z/c_0	B
H(1)	0·148 (9)	0·452 (2)	0·460 (5)	3·0 (1·1)	H(9)	0·276 (8)	0·282 (2)	0·371 (5)	4·4 (1·1)
H(2)	−0·047 (8)	0·443 (2)	0·479 (5)	3·3 (1·1)	H(10)	0·475 (8)	0·306 (2)	0·387 (5)	3·7 (1·1)
H(3)	0·290 (9)	0·386 (2)	0·294 (5)	2·6 (1·1)	H(11)	0·532 (8)	0·139 (2)	0·367 (5)	2·0 (1·1)
H(4)	0·291 (8)	0·391 (2)	0·190 (5)	2·0 (1·2)	H(12)	0·332 (8)	0·147 (2)	0·365 (5)	2·7 (1·1)
H(5)	−0·280 (10)	0·519 (3)	0·315 (6)	3·0 (1·2)	H(13)	0·015 (8)	0·305 (2)	0·466 (5)	4·0 (1·2)
H(6)	−0·230 (11)	0·523 (3)	0·208 (6)	4·0 (1·1)	H(14)	−0·037 (8)	0·332 (2)	0·362 (5)	4·5 (1·2)
H(7)	0·136 (8)	0·198 (2)	0·165 (5)	5·0 (1·1)	H(15)	0	0·134	$\frac{1}{4}$	6·0 (1·6)
H(8)	0·140 (8)	0·250 (2)	0·150 (5)	2·3 (1·1)	H(16)	0	0	0	5·2 (1·6)

electrostatic bond strengths p (Baur, 1970).* If H(15) and H(16) are shared between symmetry-related oxygen atoms, O(2) and O(3) (acceptors also of two hydrogen bonds from water molecules) receive 2·10 v.u. compared with 1·76 v.u. of O(1) and O(4) (acceptors of three hydrogen bonds from water molecules); such a difference is in agreement with the corresponding As–O lengths which are, respectively, longer [O(2) and O(3)] and shorter [O(1) and O(4)] than the average As–O value (*cf.* Ferraris, 1970; Chiari & Ferraris, 1971; Ferraris & Abbona, 1972; Kálmán, 1971).

Furthermore, equal (within e.s.d.'s) As–O(2) and As–O(3) lengths involve similar environments for O(2) and O(3) which are acceptors of two hydrogen bonds from water molecules. We note also that the present hydrogen-bond system of the water molecules is comparable, especially for the anionic oxygens, with that found in similar compounds, *i.e.* FeSO$_4$.7H$_2$O (melanterite) (Baur, 1964) and MgSO$_4$.7H$_2$O (epsomite) (Fer-

raris, Jones & Yerkess, 1973). The latter, in particular, shows two underbonded anionic oxygens, corresponding to O(2) and O(3) in roesslerite, which accept only two hydrogen bonds (compared with the three bonds received by the other two oxygens).

While the above discussion indicates an equal degree of involvement of H(15) with O(2), O(2^v) and H(16) with O(3), O(3^{ii}), it does not prove that the acidic hydrogen atom lies midway between the oxygen atoms. Other models might require the acidic hydrogen to be (i) distributed statically between O(2) and O(3), (ii) dynamically oscillating in a double-minimum potential, or (iii) on a 'quasi-symmetrical' position (*cf.* Schlemper, Hamilton & La Placa, 1971). The length of the two O···O contacts, comparable, however, with those found in other compounds (*cf.* Bacon & Curry, 1956, 1960) with supposed symmetrical hydrogen bonds, would favour hydrogen atoms not in equilibrium midway along the O···O separations, as apparently supported, at least for O(2)···O(2^v), by the broad single-peak with two lobes seen in the difference synthesis. The assumption of these lobes as hydrogen sites leads to an O(2)–H distance of 0·92 Å (H···O =

* The bond strength of a hydrogen bond is divided in the ratio 0·83/0·17 v.u. between the donor and the acceptor atom (*cf.* Baur, 1970).

Table 3. *Interatomic distances [corrected (B) and uncorrected (A) for the thermal motion] and angles (O–As–O) in the* AsO$_4$ *group*

Estimated standard deviations are 0·002 and 0·003 Å for As–O and O–O distances respectively, and 0·1° for the angles•

	A	B			
As–O(1)	1·668 Å	1·674 Å	O(1)–O(2)	2·756 Å	109·4°
As–O(2)	1·708	1·714	O(1)–O(3)	2·760	109·8
As–O(3)	1·706	1·713	O(1)–O(4)	2·787	113·6
As–O(4)	1·663	1·670	O(2)–O(3)	2·709	105·0
			O(2)–O(4)	2·723	107·7
Average	1·686	1·693	O(3)–O(4)	2·774	110·9
			Average	2·752	

Table 4. *Interatomic distances [corrected (B) and uncorrected (A) for the thermal motion] and angles (W–Mg–W) concerning the two independent* Mg *polyhedra*

Estimated standard deviations are 0·002 and 0·003 Å for Mg–W and W–W distances respectively; 0·1° for the angles.

	A	B		A	B
Mg(1)–W(1) Mg(1)–W(1^v)	2·049 Å	2·057 Å	Mg(2)–W(4) Mg(2)–W(4^v)$_1$	2·050 Å	2·060 Å
Mg(1)–W(2) Mg(1)–W(2^v)	2·092	2·097	Mg(2)–W(5) Mg(2)–W(5^v)$_1$	2·074	2·085
Mg(1)–W(3) Mg(1)–W(3^v)	2·053	2·066	Mg(2)–W(6) Mg(2)–W(6^v)$_1$	2·108	2·112
Average	2·066	2·073	Average	2·077	2·086
W(1) –W(2) W(1)^v–W(2^v)	2·872 Å	87·8°	W(4) –W(5) W(4^v)–W(5^v)$_1$	2·867 Å	88·1°
W(1) –W(2^v) W(1^v)–W(2)	2·866	87·6	W(4) –W(5^v)$_1$ W(4^v)–W(5)	2·968	92·1
W(1) –W(3) W(1^v)–W(3^v)	2·958	92·3	W(4) –W(6) W(4^v)–W(6^v)$_1$	3·002	92·4
W(1) –W(3^v) W(1^v)–W(3)	2·960	92·3	W(4) –W(6^v)$_1$ W(4^v)–W(6)	2·873	87·4
W(2) –W(3^v) W(3) –W(2^v)	2·964	91·3	W(5) –W(6) W(5^v)–W(6^v)$_1$	2·951	89·8
W(2) –W(2^v)	2·931	89	W(5) –W(5^v)$_1$	3·020	93·5
W(3) –W(3^v)	2·864	88·5	W(6) –W(6^v)$_1$	2·911	87·3
W(1) –Mg(1)–W(1^v)		173·6°	W(4)–Mg(2)–W(4^v)$_1$		179·8°
W(2) –Mg(1)–W(3) W(2^v)–Mg(1)–W(3^v)		179·7	W(5)–Mg(2)–W(6^v)$_1$		
			W(6)–Mg(2)–W(5^v)$_1$		174·5

1·58 Å, O–H···O = 171°, As–O–H = 122°) and, on hypothesis (ii), to a separation of 0·69 Å between the two wells of a symmetrical potential function, in good agreement with theoretical computations (cf. Hamilton & Ibers, 1968). While the near linearity of the two hydrogen bonds is in agreement with the correlation between the angle O–H···O and the distance O–H reported by Ferraris et al. (1972), one of the two As–O–H angles (Table 3) is even larger than that (116·8°) found in Ca(H₂AsO₄)₂ (Ferraris et al., 1972) for a symmetrical hydrogen bond. In view of all these problems a neutron-diffraction study of roesslerite is in hand.

Description of the structure

The O–As–O angles (Table 3) increase with decrease of the average value of the two corresponding As–O distances as noted in general by Baur (1970).

The two crystallographically independent Mg atoms show a fairly regular octahedral coordination (Table 4) involving oxygen atoms of the water molecules only. The longest coordination bonds belong to $W(2)$ and $W(6)$ which receive the largest (2·17 v.u.) bond strength; while $W(1)$, $W(3)$, $W(4)$ and $W(5)$ (bond strength 2·00 v.u.) are in contact with only one Mg and are of type D (Chidambaram, Sequeira & Sikka,

1964; Ferraris & Franchini-Angela, 1972), $W(2)$ and $W(6)$ also accept a hydrogen bond and are of type H. Within the rough approximation of the hydrogen-atom positions, the Mg–W direction of $W(1)$, $W(3)$, $W(4)$ and $W(5)$ makes angles of 6, 1, 17 and 31°, respectively, with the plane of the corresponding water molecule. Therefore $W(5)$ appears as a limiting case of type D [M^{2+} along a direction making an angle not larger than 30° with the bisector of the lone-pair orbitals (Ferraris & Franchini-Angela, 1972)]. $W(7)$ is unique among the water molecules in that it is not coordinated by Mg and that it donates two weak (2·860 and 3·055 Å) hydrogen bonds; this may be responsible for the easy dehydration of roesslerite.

Fig. 1 is a clinographic projection, along the x axis, of the crystal structure which, with its isolated As tetrahedra and Mg octahedra, does not show strongly individualized layers or chains. Along [010] (Fig. 2) there are layers, around $y = 0$ and $y = 0.5$, with the sequence As–Mg(1)–Mg(1)–As and Mg(2) octahedra clustered around $y = 0.25$; these are connected, through the hydrogen bonds donated by $W(7)$, to the contiguous Mg(1) layer. The same water molecule, through its accepted hydrogen bonds, links the Mg(2) octahedra to form chains along [100]. The water molecules $W(4)$, $W(5)$ and $W(6)$ supply other hydrogen bonds between
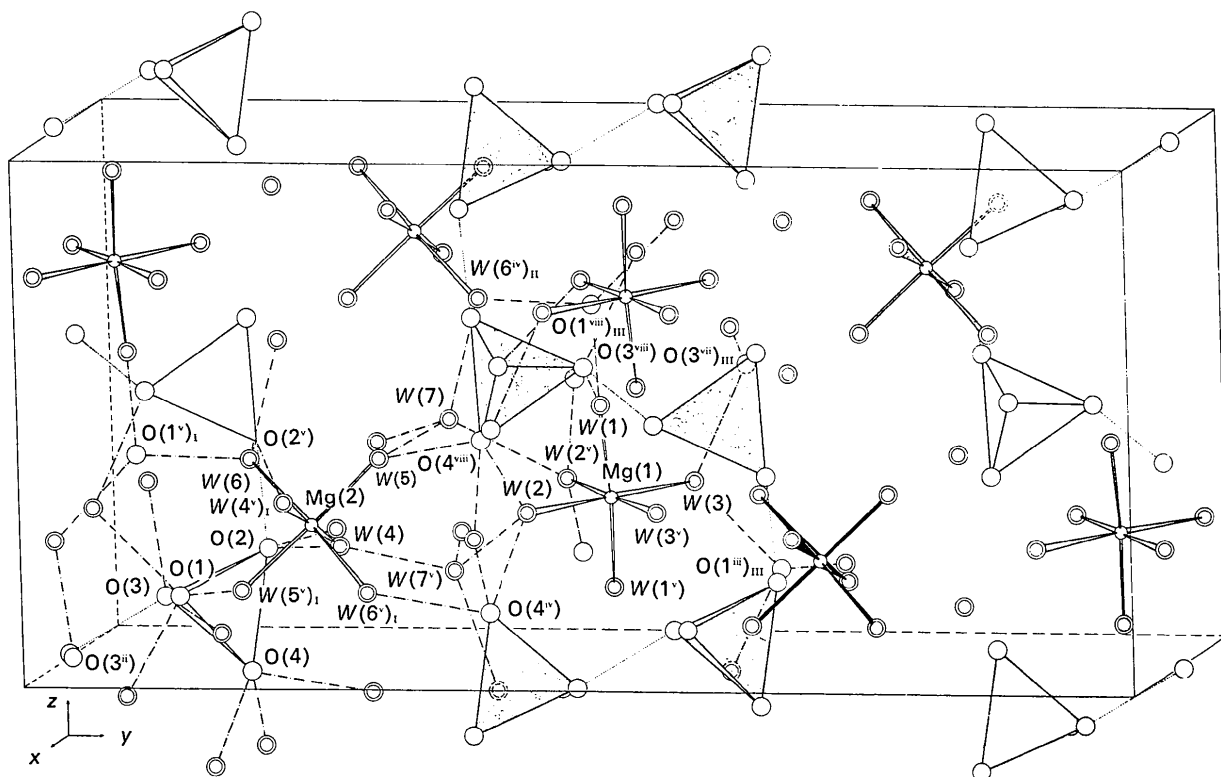

Fig. 1. Unit cell of MgHAsO₄.7H₂O (roesslerite) in clinographic projection down the x axis; water oxygen atoms are shown as double circles and magnesium atoms as small circles. In the figure are reported the hydrogen bonds donated by the water molecules (dashed-dotted lines) and by the acidic hydrogen (dotted lines) of the asymmetric unit. The circle representing O(2') is not shown.

contiguous layers. The linkage between different units within the complex layer containing Mg(1) octahedra is effected by the hydrogen bonds of $W(1)$ and $W(2)$, arranged as a rhombus, and of $W(3)$; in addition, while O(2)–H(15)–O(2^v) is on the surface of the layer, O(3)–H(16)–O(3^{ii}) lies across it connecting the two surfaces of As tetrahedra. The two O$\cdots$O hydrogen bonds

Table 5. Interatomic distances (Å) and angles (°) involving hydrogen bonds

Estimated standard deviations are 0·06 Å and 5° for distances and angles involving hydrogen atoms, 0·003 Å and 0·1° for distances and angles involving oxygen atoms only.

A	B	C	D	E	AB	BC	AC	CE	CD	DE	BD	∠BCD	∠ACE	∠ABC	∠CDE
O(3^{viii})···H(1)—W(1)—H(2)···O(1^{viii})					1·98	0·78	2·754	2·731	0·90	1·86	1·36	109	106·8	174	162
O(4^{viii})···H(3)—W(2)—H(4)···O(4^{iv})					2·02	0·75	2·757	2·657	0·82	1·85	1·21	102	89·6	170	168
O(3^{viii})$_{III}$···H(5)—W(3)—H(6)···O(1^{iii})$_{III}$					1·99	0·90	2·879	2·738	0·72	2·04	1·32	101	112·7	172	163
O(2)···H(7)—W(4)—H(8)···O(4^{viii})					2·07	0·77	2·834	2·701	0·92	1·78	1·34	106	106·4	175	176
W(7)···H(9)—W(5)—H(10)···O(2^v)					1·92	0·94	2·853	2·747	0·91	1·87	1·47	105	88·2	170	162
O(1^v)···H(11)—W(6)—H(12)···O(2^v)					1·92	0·85	2·741	2·706	0·81	1·92	1·36	109	115·3	162	163
W(6^{iv})$_{II}$···H(13)—W(7)—H(14)···O(2^v)					2·10	0·82	2·860	3·055	0·84	2·23	1·40	116	106·5	155	167
As —O(2)—H(15)···O(2^v)								2·491	1·246	1·246		124·9			180
As —O(3)—H(16)···O(3^{ii})								2·539	1·270	1·270		113·4			180

Table 6. Parameters characterizing the principal directions 1, 2, 3 of the thermal vibration for As, Mg and O atoms

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

|		A (Å)	B (°)	C (°)	D (°)
As	1	0·109	125	39	72
	2	0·119	35	57	83
	3	0·101	90	109	19
Mg(1)	1	0·117	90	0	90
	2	0·130	13	90	82
	3	0·110	103	90	8
Mg(2)	1	0·131	12	90	83
	2	0·144	102	90	7
	3	0·107	90	0	90
O(1)	1	0·144	74	16	92
	2	0·149	104	85	10
	3	0·124	21	105	80
O(2)	1	0·139	48	113	55
	2	0·161	47	48	111
	3	0·106	108	51	43
O(3)	1	0·143	29	118	97
	2	0·158	92	99	10
	3	0·114	62	30	84
O(4)	1	0·147	111	30	68
	2	0·166	21	71	86
	3	0·104	91	112	23
W(1)	1	0·143	14	76	96
	2	0·209	104	14	88
	3	0·116	90	90	6
W(2)	1	0·136	88	103	15
	2	0·171	58	34	83
	3	0·127	32	121	103
W(3)	1	0·156	130	79	37
	2	0·250	46	56	67
	3	0·119	110	36	117
W(4)	1	0·148	67	24	85
	2	0·226	113	88	18
	3	0·134	34	114	73
W(5)	1	0·174	14	76	100
	2	0·227	80	115	29
	3	0·124	100	29	63
W(6)	1	0·147	16	103	86
	2	0·174	93	67	23
	3	0·123	75	27	112
W(7)	1	0·179	95	114	25
	2	0·209	8	97	93
	3	0·152	84	26	66
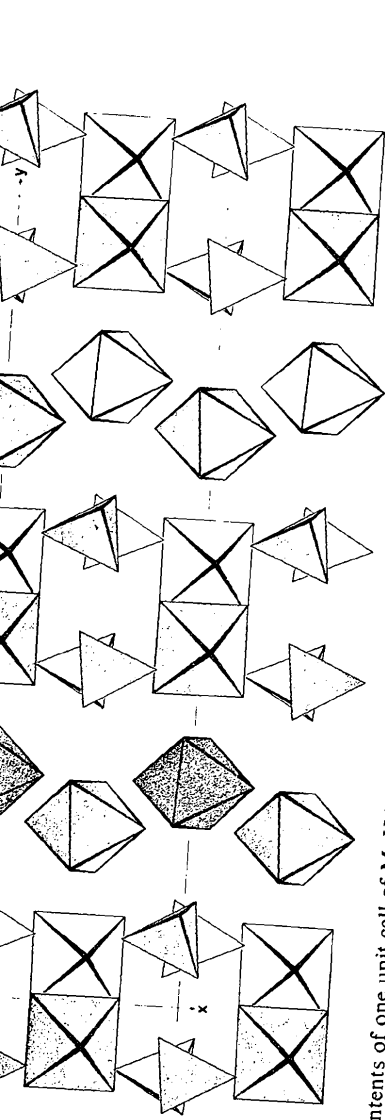
Fig. 2. The contents of one unit cell of $MgHAsO_4.7H_2O$ in projection onto the (001) plane. Mg octahedra are at $z = -\frac{1}{4}$ (white) $z = \frac{1}{4}$ (grey) and $z = \frac{3}{4}$ (dark grey); As tetrahedra are at $z = 0$ (pale grey) and $z = \frac{1}{2}$ (grey). $W(7)$ is not shown.

link together all the As tetrahedra in a zigzag chain along [001]; this chain crosses the Mg(1) layer.

From another aspect (Figs. 1 and 2), one can see alternating layers of As tetrahedra and Mg octahedra parallel to (001) plane; while all the magnesium atoms lie exactly in the same planes ($z = 0.25$ and 0.75), the arsenic atoms are around planes $z = 0$ and $z = 0.50$. Within such layers, both the octahedra and the tetrahedra are arranged in rows parallel to [100]; the two types of layers are to some extent interpenetrated but connected by hydrogen bonds only. The above-mentioned chains of As tetrahedra are across the layers with $O(3)\cdots O(3^{ii})$ completely in the As layer and $O(2)\cdots O(2^v)$ crossing the Mg plane.

From this description of the structure, cleavage, involving only hydrogen bonds, would be expected for several planes; Palache *et al.* (1963) report an imperfect {111} cleavage.

The thermal motion

Table 6 lists parameters characterizing the magnitude and orientation of the thermal motion, which appears randomly distributed with respect to the crystallographic directions. For all the oxygen atoms, there is an approximate alignment of the shortest principal axis of the ellipsoids along the corresponding As–O or Mg–W directions. The difference in magnitude of the thermal vibration seemed to justify an application of the riding model (Busing & Levy, 1964) for motional correction of the As–O and Mg–W bond lengths (Tables 3 and 4). The constancy (within 0·006 Å) of the corrected average As–O length in different structures refined both with X-ray data [present work, Ferraris & Abbona (1972) and Catti & Ferraris (1973)] and with neutron data (Ferraris *et al.*, 1972) provides support for the contention that the experimental data give a fair estimate of the thermal parameters.

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