

Hydrogen Bonding in the Crystalline State. Refinement of the Crystal Structure of $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$, Arsenstruvite*

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Magnesium ammonium arsenate hexahydrate, $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ (arsenstruvite), is isostructural with the phosphate struvite and crystallizes in the orthorhombic system, space group $Pmn2_1$. Unit-cell parameters are: $a_0 = 7.054$ (4), $b_0 = 6.205$ (3), $c_0 = 11.368$ (6) Å; $Z = 2$. The crystal structure was refined anisotropically to $R = 0.030$, using 1110 non-zero hkl and $h\bar{k}l$ (equivalent by Laue symmetry) reflexions measured on an automatic three-circle diffractometer (Cu $K\alpha$ radiation). Corrections for absorption, secondary extinction and anomalous scattering, which allowed the determination of the correct polarity, were applied. The hydrogen atoms were located from a difference map; one of the four independent water molecules (all coordinated by Mg) is very weakly hydrogen bonded and the ammonium group shows disorder around a fixed N-H direction. The Mg and As polyhedra are fairly regular and connected by hydrogen bonds only; the crystal structure, built up from Mg octahedra and ammonium groups sandwiched between As tetrahedra, is discussed in the light of bond-length and bond-strength correlations.

Introduction

Magnesium ammonium arsenate hexahydrate, $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$, is isostructural with struvite, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ [Whitaker & Jeffery, 1970*a, b* (WJa, WJb)], and possibly with a family of compounds (Magnano, 1965) where K, Tl or Rb substitute for NH_4 ; analogous compounds with Cs have, instead, higher symmetry (Ferrari, Cavalca & Nardelli, 1955*a, b*; Cavalca, Nardelli & Cesari, 1955). The ammonium arsenate, even if not known as a mineral, is often called arsenstruvite (Hey, 1962).

Approximate ($R = 0.20$) bidimensional X-ray studies of arsenstruvite appeared in 1955 (González & Lerma, 1955; González & Garcia-Blanco, 1955). Because of our interest in hydrogen-bonded arsenates [*cf.* Ferraris, Franchini-Angela & Catti (1972) and the previous paper in the series (Ferraris & Franchini-Angela, 1973)] and the controversy about the behaviour of NH_4^+ in struvite (WJa, b), a new X-ray study of the crystal structure of $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ has been carried out.

Experimental

Preparation and crystal data

Single crystals of $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ suitable for X-ray study were prepared by De Schulten's (1903) method; they are transparent and colourless, tabular {010} and elongated [100] with a trapezoidal habit.

Other forms, indexed according to the polarity indicated by the present X-ray analysis, are {001}, {012}, {011}, {031}, {10 $\bar{1}$ } and {110}.

Preliminary Weissenberg photographs and single-crystal diffractometry confirmed the crystallographic data given by Whitaker (1970). Systematic absences are in accordance with either $Pmn2_1$ (C_{2v}^7 , No. 31) or $Pmnm$ (D_{2h}^3 , No. 59); the centrosymmetric space group has been rejected both by analogy with struvite and on the basis of a definite anomalous-scattering effect (see below).

$M. W. 289.366$; $a_0 = 7.054(4)$, $b_0 = 6.205(3)$, $c_0 = 11.368(6)$ Å (Whitaker, 1970); $V = 497.6$ Å³; $D_m = 1.935(3)$ g cm⁻³ (Whitaker, 1970), $D_c = 1.930$ g cm⁻³, $Z = 2$; $F(000) = 296$; linear absorption coefficient for Cu $K\alpha$ radiation, $\mu = 61$ cm⁻¹.

Intensity measurements

Integrated intensities were measured by a General Electric automatic three-circle diffractometer (θ - 2θ scanning, 2° min⁻¹, 0.5 background on both sides of each peak); the crystal, mounted with its x axis along the instrumental ϕ axis and coated with a thin plasticizing film, had the following slightly idealized dimensions: 0.21 mm (across {001}), 0.07 mm (across {010}) and 0.24 mm from the centre of the crystal to both (10 $\bar{1}$) and ($\bar{1}0\bar{1}$). Two octants of reflexions (hkl and $h\bar{k}l$, according to the polarity of the structure), equivalent according to Laue symmetry only, were measured; of the 1152 measured reflexions, 42 (all satisfying the condition $|F_c| < |F_o|$) were rejected because they were very weak. The intensity of a standard reflexion, 222, checked every 60 reflexions, showed a constant value.

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A secondary extinction correction, performed by a least-squares fit of the function

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

will be discussed below. An absorption correction (transmission factor 0.60–0.81) was applied by the program GONO9 (Hamilton, 1966). Atomic scattering factors, including $\Delta f'$ and $\Delta f''$ corrections, were linear interpolations of values for neutral atoms (*International Tables for X-ray Crystallography*, 1962).

Structure analysis

Assuming that arsenstruvite and struvite were isostructural, the final set of coordinates (excluding the hydrogen atoms) of the latter (WJa) were used, yielding, after one least-squares cycle with individual isotropic thermal parameters, $R=0.18$ for the two measured octants. The origin was fixed by keeping the z coordinate of the As atom constant. The isotropic refinement was stopped when $R=0.08$ and the shifts were smaller than the corresponding e.s.d.'s.

Location of the hydrogen atoms

After an anisotropic least-squares cycle, a three-dimensional Fourier difference synthesis showed positive peaks in the positions expected, according to the struvite structure, for the hydrogen atoms of the water molecules; the height of these peaks was, however, no larger (0.4–1 e) than that of spurious peaks. The situation around the nitrogen atom was roughly the same as that found in struvite: a peak on a special position, indicating a hydrogen atom H(1)* pointing towards O(1), and elsewhere a positive electron density with two low maxima. Whitaker & Jeffery (1970*a,b*), after several trials, disregarded the low maxima and refined a freely rotating NH_4^+ even if they were inclined to consider this group rotating, possibly unevenly, around the N–O(1) direction. A different interpretation, at least for arsenstruvite, is here proposed: the two low

maxima on general positions are assigned to hydrogen atoms H(9) and H(10) with an occupancy factor of $\frac{2}{3}$, in order to distribute, on the whole, four hydrogen atoms including H(1) around the special position occupied by the nitrogen atom. Such a model turned out to be refinable and will be discussed below.

Polarity of the structure and completion of the refinement

A least-squares cycle, anisotropic for the heavy atoms and including the hydrogen atoms, reduced R to 0.05; an extinction correction, according to (1), gave $g=79 \times 10^{-7} \text{ e}^{-2}$ and $k=1.004$. The polarity of the structure was then tested both on the basis of the R value and of Bijvoet pairs; for the correct indexing R dropped to 0.037. Because of the introduction of $\Delta f''$ and the linear approximation of (1), a second extinction correction proved necessary: $g=0.91 \times 10^{-7} \text{ e}^{-2}$ and $k=0.983$ were obtained. Two cycles completed the refinement ($R=0.030$)*.

The parameters of the hydrogen atoms, isotropically refined, were always incremented by only a fraction of the computed shift. The full-matrix least-squares program by Busing, Martin & Levy (1962), with minor modifications, was used with the following weighting scheme (constants are for the last cycle):

$$w = \frac{77}{0.03F_o^2 + 2|F_o| + 25} \quad \text{for } |F_o| \geq 12.5 \quad (2)$$

$$w = 0.036|F_o| + 0.10 \quad \text{for } |F_o| < 12.5. \quad (3)$$

The final weighted R value and the standard error of one observation were 0.033 and 0.64 respectively. Table 1 shows the fractional coordinates and the B_{ij} coefficients in the expression:

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

The e.s.d.'s are in parentheses.

* A single figure in parentheses (or no figure) denotes an atom of the asymmetric unit; a second figure (2, 3, 4) is included for atoms in the positions: \bar{x}, y, z ; $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$ and $\frac{1}{2} + x, \bar{y}, \frac{1}{2} + z$. Roman numbers represent the following translations: I, +b; II, -a and III, +c.

* A list of structure factors is available either from the authors or as Supplementary Publication No. 30048. Copies may be obtained from the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.

Table 1. Fractional atomic coordinates and vibrational parameters (\AA^2) with the significant figures of the estimated standard deviations in parentheses

The fractional coordinates are $\times 10^5$ for As, $\times 10^4$ for Mg to N and $\times 10^3$ for H(1) to H(10); the anisotropic temperature factors are $\times 10^2$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As	0	-588 (11)	-50	120 (2)	101 (2)	113 (2)	0	0	-3 (3)
Mg	0	3733 (3)	3717 (2)	128 (7)	125 (7)	134 (7)	0	0	-3 (6)
O(1)	0	-236 (8)	-1490 (3)	253 (19)	234 (19)	128 (12)	0	0	-9 (15)
O(2)	0	-2563 (7)	574 (4)	182 (16)	112 (15)	184 (16)	0	0	24 (13)
O(3)	1972 (4)	1234 (5)	444 (3)	158 (11)	185 (11)	184 (9)	-17 (10)	-4 (9)	-39 (9)
W(1)	0	6762 (10)	2889 (6)	491 (37)	182 (25)	177 (23)	0	0	43 (18)
W(2)	0	757 (8)	4597 (5)	132 (17)	286 (19)	476 (26)	0	0	222 (17)
W(3)	2165 (5)	2663 (6)	2625 (3)	230 (16)	280 (13)	153 (12)	54 (12)	-8 (12)	-40 (12)
W(4)	2062 (4)	4789 (5)	4863 (5)	250 (11)	186 (11)	224 (82)	5 (11)	-184 (16)	-56 (16)
N	0	3694 (18)	7312 (8)	371 (38)	275 (35)	211 (32)	0	0	59 (27)

Table 1 (cont.)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
H(1)	0	270 (19)	771 (9)	1.0 (2.1)
H(2)	0	684 (23)	204 (13)	1.3 (3.0)
H(3)	0	799 (18)	318 (9)	2.8 (2.2)
H(4)	115 (8)	23 (10)	485 (11)	2.1 (1.2)
H(5)	178 (12)	187 (13)	213 (7)	4.8 (1.9)
H(6)	294 (10)	200 (11)	302 (6)	0.5 (1.5)
H(7)	236 (11)	637 (13)	506 (9)	6.8 (1.9)
H(8)	315 (12)	380 (13)	529 (9)	2.2 (2.0)
H(9)	80 (19)	350 (20)	681 (10)	5.0 (3.0)
H(10)	85 (19)	450 (18)	740 (10)	5.4 (3.1)

Discussion

Symmetry

Because of difficulties associated with the arrangement of NH_4^+ , which has its nitrogen atom on a mirror plane, some doubt could arise about the space group. The correctness within experimental errors of the refined structure is supported by (i) plausibility of bond lengths and angles including those involving symmetry elements; (ii) low value of *R* (0.030) and consequent satisfactory refinement, which includes the hydrogen atoms and extends to two octants of reflexions equivalent according to Laue symmetry only; (iii) reasonable agreement between observed and calculated values of Bijvoet pairs.

Ammonium group

Even if the successfully refined model of NH_4^+ is only an approximation, one can nevertheless conclude that this group has some amount of disorder around the N–H(1) direction which, in its turn, is locked approximately along N–O(1).

While the values of the tetrahedral angles between H(10) and H(9) or H(1) (116 and 108° respectively) are satisfactory, other H–N–H angles range from 70 [H(10)–N–H(9)] to 135° [H(9)–N–H(10,2)], with values of 88 and 99° for those involving H(9), H(9,2) and H(10), H(10,2) respectively. This means that the three positions effectively occupied by the disordered hydro-

gens, at a given time or within a given unit cell, correspond only approximately to those attributed to H(10) and H(9) (and symmetry-related atoms); one must, however, remember that the e.s.d. for H–N–H angles is about 10°.

NH_4^+ is surrounded by O(1), *W*(4), *W*(3) and symmetry related *W*(4,2) and *W*(3,2); the four oxygens of these water molecules lie on a plane perpendicular to the mirror plane. At somewhat larger distances, several other oxygen atoms directly face the ammonium group. According to preliminary data reported by Magnano (1965), arsenstruvite is isostructural with $\text{MgTlAsO}_4 \cdot 6\text{H}_2\text{O}$, where the required coordination polyhedron around Tl could be attained by the approach of some oxygen atom facing NH_4^+ in the NH_4 arsenate. The refined model of NH_4^+ , implying some degree of hydrogen bonding of H(9) and H(10) with *W*(3), *W*(4), *W*(3,2) and *W*(4,2) (instead of directional hydrogen bonds) fits the reported isostructurality well.

Electrostatic balance and hydrogen bonding

Several correlations between bond length and electrostatic bond strength, which are particularly useful for testing the reliability of crystal structures, have recently been proposed* (*cf.* Baur, 1970; Brown & Shannon, 1972; Donnay & Allmann, 1970; Ferraris & Catti, 1972).

In the case of arsenstruvite, the under-bonding of O(1), O(2) and O(3) requires a remarkable shortness (*cf.* Ferraris & Franchini-Angela, 1972) of the hydrogen bonds involved (three for each oxygen, Table 2);

* At the moment we prefer to do semi-quantitative comparisons only: for this purpose the linear approach proposed by Baur (1970) [Khan & Baur (1972) for the ammonium group] appears satisfactory. In particular, Ferraris & Catti (1972) find that Baur's correlations are all contained in the following rule: the percentage variation of a coordination bond length, with respect to its average value, is proportional to the difference between the bond strength received by the oxygen atom and the value of 2 v.u. which the oxygen should receive according to Pauling's second rule.

Table 2. *Interatomic distances (Å) and angles (°) involving hydrogen atoms and hydrogen bonds: estimated standard deviations are given below the values*

For the NH_4 group and <i>W</i> (1), see the text.															
<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>AB</i>	<i>BC</i>	<i>AC</i>	<i>CE</i>	<i>CD</i>	<i>DE</i>	<i>BD</i>	<i>BCD</i>	<i>ACE</i>	<i>ABC</i>	<i>CDE</i>
O(2) ^I ··· H(2)– <i>W</i> (1)–H(3) ··· W(2) ^I					1.71	0.97	2.665	3.149	0.83	2.36	1.48	110	119.1	170	162
					15	15	8	8	11	11	18	11	1	14	6
O(3,3) ··· H(4)– <i>W</i> (2)–H(4,2) ··· O(3,4) ^{II}					1.74	0.92	2.649	2.650	0.92	1.74	1.63	123	107.5	168	168
					6	6	3	3	6	6	8	6	1	5	5
O(3) ··· H(5)– <i>W</i> (3)–H(6) ··· O(1,3)					1.96	0.79	2.636	2.698	0.82	1.90	1.30	108	101.6	143	163
					8	8	5	3	7	7	11	8	1	8	7
O(3,3) ^I ··· H(7)– <i>W</i> (4)–H(8) ··· O(2,3)					1.62	1.03	2.644	2.619	1.10	1.55	1.71	107	102.2	174	164
					8	8	4	3	8	8	11	6	1	7	8
<i>W</i> (4) ··· H(9)					2.52	0.81	3.215				1.28	108	127.9	145	
					12	12	4				12	9	1	11	
				N–H(1) ··· O(1) ^{III}				2.794	0.77	2.03					170
								12	11	12					11
					2.26	0.79	3.039				1.32	116	126.1	168	
<i>W</i> (3,3) ^I ··· H(10)					12	12	3				12	9	1	11	

their comparable strength justifies equality, within e.s.d.'s, of the As-O lengths (Table 3). $W(3)$ and $W(4)$, which are Mg-coordinated and donors of pairs of hydrogen bonds, appear regularly bonded and accordingly establish with the neighbouring ammonium group only a weak hydrogen bond [$N \cdots W(3) = 3.039 \text{ \AA}$], or possibly no bond at all [$N \cdots W(4) = 3.215 \text{ \AA}$]; it is to be noted, also, that $Mg-W(4)$ is shorter than $Mg-W(3)$ (Table 4).

Table 3. *Interatomic distances, corrected (B) (riding model) and uncorrected (A) for the thermal motion, and angles (O-As-O) in the AsO_4 group*

Estimated standard deviations are given in parentheses; multiplicity of the bond is given on the left.

	A	B
1As-O(1)	1.692 (4) Å	1.702 Å
1As-O(2)	1.688 (4)	1.693
2As-O(3)	1.685 (3)	1.691
Average	1.688	1.694
1O(1)-O(2)	2.755 (6) Å	109.2 (2)°
2O(1)-O(3)	2.757 (3)	109.5 (1)
2O(2)-O(3)	2.741 (3)	108.7 (1)
1O(3)-O(3,2)	2.782 (4)	111.3 (1)
Average	2.756	

Table 4. *Interatomic distances, corrected (B) (riding model) and uncorrected (A) for the thermal motion, and angles (W-Mg-W) in the Mg octahedron*

Estimated standard deviations are given in parentheses; multiplicity of the bond is given on the left.

	A	B
1Mg-W(1)	2.103 (7) Å	2.116 Å
1Mg-W(2)	2.101 (5)	2.116
2Mg-W(3)	2.078 (4)	2.085
2Mg-W(4)	2.060 (4)	2.076
Average	2.080	2.092
2W(1)-W(3)	2.983 (3) Å	91.1 (1)°
2W(1)-W(4)	2.941 (4)	89.9 (1)
2W(2)-W(3)	2.960 (4)	90.2 (1)
2W(2)-W(4)	2.911 (3)	88.8 (1)
1W(3)-W(3,2)	3.055 (5)	94.7 (1)
2W(3)-W(4)	2.867 (6)	87.7 (1)
1W(4)-W(4,2)	2.910 (4)	89.9 (1)
Average	2.941	

The long contact $W(1) \cdots W(2)'$ (3.15 Å) is considered a very weak hydrogen bond in the light both of geometric peculiarities (Ferraris & Franchini-Angela, 1972) and of bond-length bond-strength correlations. The consequent overbonding of $W(1)$ and $W(2)$, with respect to $W(3)$ and $W(4)$, is in accordance with differences among Mg-W contacts (Table 4). $W(2) \cdots H(3)$ and $W(2) \cdots Mg$ form angles of -20 and 48° , respectively, with the plane of the $W(2)$ water molecule; $W(2)$ is, therefore, of type G (Chidambaram, Sequeira & Sikka, 1964; Ferraris & Franchini-Angela, 1972). The same environment of type G [Mg and H(10) are 55 and -52° , respectively, out of the water molecule plane]

supports some interaction of $W(3)$ with NH_4^+ . $W(1)$, which has Mg along the bisector of its lone-pair orbitals, is of type C, as well as $W(4)$, if any interaction of the ammonium group with this water molecule is excluded [Mg and H(9) are 5° and -66° , respectively, out of the water molecule plane].

Description of the structure

Fig. 1 shows, in clinographic projection down the x axis, one unit cell of $MgNH_4AsO_4 \cdot 6H_2O$. Differences with respect to struvite are in the crystallochemical interpretation of details only, like the configuration of the ammonium group and the weak $W(1) \cdots W(2)$ hydrogen bond.

Since the fairly regular Mg-octahedra do not include tetrahedral oxygen atoms and the polyhedra are linked by hydrogen bonds only, it should be possible to describe the structure in terms of several types of layers; those corresponding to the observed cleavages $\{010\}$ and $\{001\}$ are, however, outstanding. Along $[001]$ the Mg octahedra and the As tetrahedra lie on two slightly different planes and form single layers where $[010]$ rows of the two types of polyhedra alternate in the x direction; the ammonium group is on the side of the Mg plane. With periodicity b , instead, there is a complex layer (Fig. 2) which is built up from Mg octahedra and

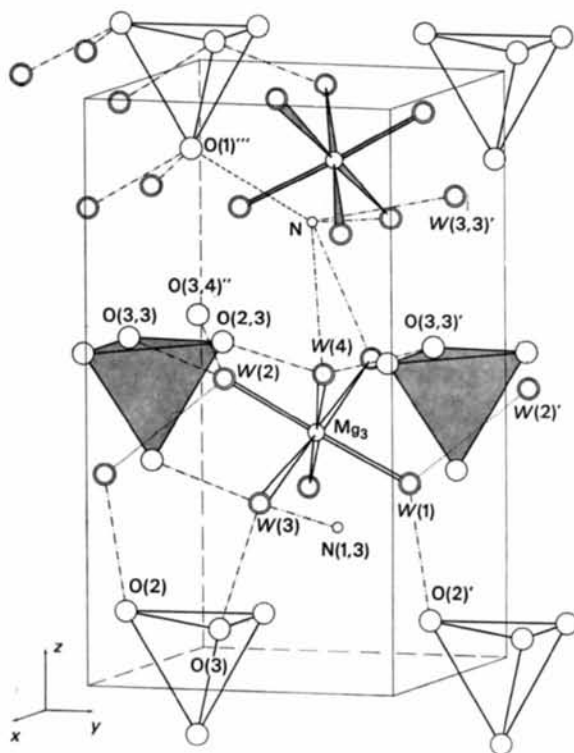


Fig. 1. Unit cell of $MgNH_4AsO_4 \cdot 6H_2O$ in clinographic projection down the x axis: polyhedra in grey are nearer (in the x direction) than those in white. The hydrogen bonds, reported for the asymmetric set only, are shown as variously dotted and dashed lines; for some contacts involving N (double points and dash) and $W(1)$ (dotted lines) see the text.

Table 5. Parameters characterizing the principal directions 1, 2, 3 of the thermal vibration for the atoms refined anisotropically: root-mean-square displacements (*A*) and angles which the principal directions make with the *x*(*B*), *y*(*C*) and *z*(*D*) axes.

		<i>A</i> (Å)	<i>B</i> (°)	<i>C</i> (°)	<i>D</i> (°)
As	1	0.120	90	105	15
	2	0.123	0	90	90
	3	0.112	90	15	75
Mg	1	0.13	0	89	90
	2	0.13	90	107	17
	3	0.13	90	18	72
O(1)	1	0.17	90	5	95
	2	0.18	0	90	90
	3	0.13	90	85	5
O(2)	1	0.15	0	90	90
	2	0.16	90	73	17
	3	0.12	90	17	107
O(3)	1	0.15	36	108	120
	2	0.17	98	44	133
	3	0.13	56	52	57
W(1)	1	0.17	90	43	47
	2	0.25	0	90	90
	3	0.13	90	133	43
W(2)	1	0.13	90	33	123
	2	0.28	90	57	33
	3	0.13	0	90	90
W(3)	1	0.16	31	117	76
	2	0.20	60	33	103
	3	0.13	96	72	19
W(4)	1	0.16	115	25	96
	2	0.26	122	98	33
	3	0.13	42	66	58
N	1	0.20	90	31	59
	2	0.22	0	90	90
	3	0.15	90	121	31

ammonium groups sandwiched between As tetrahedra. While all the As groups are practically on the same plane, the Mg octahedra lie on two different planes; both types of polyhedra are arranged along [100] rows. The absence of bonds between polyhedra of the same type, with the exception of the very weak $W(1) \cdots W(2)^{\dagger}$ hydrogen bond, does not allow the formation of chains in correspondence with the reported rows of polyhedra.

Since the thermal motions of light and heavy atoms differ appreciably in magnitude (Table 5), the As–O and Mg–W distances (Tables 3 and 4) have been corrected according to the riding model of Busing & Levy (1964); the largest thermal displacement of these atoms tends to be normal to the bond direction.

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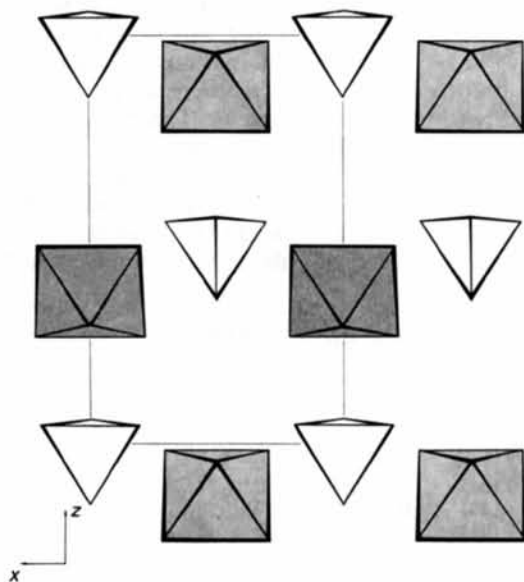


Fig. 2. The contents of the unit cell of $MgNH_4AsO_4 \cdot 6H_2O$ in projection onto the (010) plane; proximity of the polyhedra is in decreasing sequence: dark grey, light grey, white. Hydrogen bonds and ammonium groups are not shown.