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# The crystal structure of rösslerite $MgHAsO_4 \cdot 7H_2O$

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**Auszug**

Rößlerit, $MgHAsO_4 \cdot 7H_2O$ kristallisiert in der Raumgruppe $C2/c$ mit $a = 6{,}687 \pm 0{,}003$, $b = 25{,}73 \pm 0{,}01$, $c = 11{,}531 \pm 0{,}005$ Å, $\beta = 95°7' \pm 5'$ und $Z = 8$. Die Struktur wurde mittels Patterson- und Fourier-Synthesen bestimmt und nach der Methode der kleinsten Quadrate bis $R = 11{,}2\%$ verfeinert. Die Struktur setzt sich zusammen aus $AsO_2(OH_{1/2})_2$-Tetraedern, $Mg(H_2O)_6$-Oktaedern in zwei unabhängigen Lagen und isolierten Wassermolekülen, die sämtlich durch Wasserstoffbindungen zusammenhängen. Die Lagen der H-Atome wurden aus stereochemischen und kristallographischen Überlegungen gefolgert. Das $AsO_2(OH_{1/2})_2$-Tetraeder und die Oktaeder sind deformiert; die mittleren (unkorrigierten) Abstände betragen: As—O = 1,691 ± 0,003 Å, Mg—O = 2,077 ± 0,003 Å. Der (Mg—O)-Abstand ist jedoch länger, wenn das O-Atom des Wassers Rezeptoratom der Wasserstoffbindung ist. Die Wärmebewegung wurde analysiert; unter der Annahme, daß die leichteren Atome zusammen mit ihren schwereren Nachbaratomen schwingen, folgen als korrigierte Bindungslängen: As—O = 1,695 Å, Mg—$OH_2$ = 2,086 Å.

**Abstract**

Rösslerite $MgHAsO_4 \cdot 7H_2O$ crystallizes in the monoclinic system with cell dimensions $a = 6.687 \pm 0.003$, $b = 25.73 \pm 0.01$, $c = 11.531 \pm 0.005$ Å, $\beta = 95° 7' \pm 5'$. The space group is $C2/c$ and there are eight molecules per unit cell. The structure has been solved from a Patterson synthesis and partially phased Fourier syntheses and least-squares refinement has been completed on three-dimensional data (2065 structure factors within the CuK$\alpha$ sphere). The final residual is 11.2%. The structure consists of $AsO_2(OH_{1/2})_2$ tetrahedra, $Mg \cdot 6H_2O$ octahedra in two independent positions and isolated water molecules held together by hydrogen bonds. The position of the hydrogen bonds have been inferred from stereochemical and crystallographic evidence. The $AsO_2(OH_{1/2})_2$ tetrahedron is distorted, with a mean (uncorrected) arsenic—oxygen bond length of 1.691 ± 0.003 Å and the $Mg \cdot 6H_2O$ octahedra are also distorted, with a mean

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(uncorrected) magnesium—water oxygen of 2.077 ± 0.003 Å. However in this case if the water oxygen is a receptor atom for a hydrogen bond the magnesium—water oxygen bond is lengthened. The thermal vibrations have been analyzed and the mean corrected bond lengths are arsenic—oxygen 1.695, magnesium—water oxygen 2.086 (assuming riding motion in each case).

## Introduction

The crystal structure of rösslerite $MgHAsO_4 \cdot 7H_2O$ has been determined.

## Experimental

Rösslerite crystals were prepared by an analogous method to that given by MELLOR (1929) for the preparation of phosphorrösslerite; a disodium hydrogen arsenate solution replacing the disodium hydrogen phosphate solution. The crystals had acicular habit, their length being parallel to $a$ and breadth to $c$.

The crystal optics, morphology and Laue symmetry confirmed PALACHE, BERMAN and FRONDEL (1951) and FISCHER (1960) in that the crystals belong to the monoclinic system.

The cell dimensions were determined by FARQUHAR and LIPSON's (1946) method from oscillation photographs taken with copper radiation ($CuK\alpha_1 = 1.54050$ Å, $CuK\alpha_2 = 1.54434$ Å, $CuK\alpha_m = 1.54178$ Å, $CuK\beta = 1.39217$ Å) and are

$$a = 6.687 \pm 0.003 \text{ Å}$$
$$b = 25.73 \pm 0.01 \text{ Å}$$
$$c = 11.531 \pm 0.005 \text{ Å}$$
$$\beta = 95°7' \pm 5'.$$

The measured density (by flotation) is $1.954 \pm 2$ g/cm³. Previous determinations are reported as 1.943 g/cm³. (PALACHE, BERMAN and FRONDEL, 1951) and 1.930 g/cm³ (FISCHER, 1960), while that calculated for $Z = 8$ is $1.951 \pm 2$ g/cm³.

Systematic absences ($hkl$ absent when $h + k = 2n + 1$, $h0l$ when $h = 2n + 1$ and $l = 2n + 1$, $0k0$ when $k = 2n + 1$) were determined from Weissenberg photographs and indicate the space group to be either $Cc$ or $C2/c$. Application of the WILSON (1949a, 1949b) ratio test and the $N(z)$ test (HOWELLS, PHILLIPS and ROGERS, 1949, 1950) to the $hkl$, $hk0$ and $0kl$ data indicated that the probable space group was $C2/c$.

Crystals of approximately equidimensional cross-section parallel to $a$ and $c$ were obtained by cleaving the original crystals, the average thicknesses being $0.198 \pm 0.022$ mm and $0.243 \pm 0.050$ mm, respectively.

The intensity data were collected on multiple-film equi-inclination Weissenberg photographs taken about the $a$ (zero to fifth layers) and $c$ (zero to fourth layers) axes with filtered copper radiation. The peak heights of the diffraction spots were photometered. In this way the intensities of 1849 independent reflections were estimated. Those reflections too weak to measure (another 216) were given half the intensity of the weakest measurable, these reflections were then processed with the others.

The observed intensities were corrected for PHILLIPS effect (1954) absorption (assuming cylindrical specimens, linear absorption coefficient 59.8 $cm^{-1}$) and Lorentz and polarization factors. The two sets of photographs were correlated by the method of HAMILTON, ROLLETT and SPARKS (1965) and the scale factor and average temperature factor were obtained by Wilson's (1942) method.

## Structure determination and refinement

Although the $a$ and $c$ axes Patterson projections clearly show the positions of the arsenic-arsenic vectors (see subsequent paper, STREET and WHITAKER, 1973), no attempt was made to solve these.

The three-dimensional Patterson synthesis gave two possible sets of position parameters for the arsenic, namely 0.05, 0.09, 0.05 or 0.05, 0.09, 0.45 (the later position corresponds to the arsenic atom being in the acute angle of the unit cell).

Three-dimensional Fourier syntheses were calculated with structure factors phased for each of these positions. The first position of the arsenic atom gave a synthesis from which it was possible to obtain the positions of the oxygen atoms in the arsenate group, two independent magnesium atoms in special positions, six water molecules (three independent positions) octahedrally arranged about one of the magnesium atoms, and two water molecules (one independent position) about the other, i.e. $MgAsO_4 \cdot 4\,H_2O$. Unfortunately four other water molecules about the second magnesium atom could not be uniquely placed, there being two possible positions for them and the seventh water molecule also could not be positioned uniquely.

The second position of the arsenic atom gave a Fourier synthesis which was stereochemically unacceptable due to many interatomic

distances less than 2 Å and impossible to interpret in terms of an $AsO_4$ tetrahedron and $Mg(H_2O)_6$ octahedron. Hence work assuming this position of the arsenic atom was discontinued.

A further Fourier synthesis was calculated with structure factors phased for the configuration $MgAsO_4 \cdot 4H_2O$ with the arsenic atom in the obtuse angle; from this synthesis the positions of the remaining water molecules were found.

The atomic scattering factors used for arsenic, magnesium and oxygen were those from the *International tables for x-ray crystallography* 1962). The factor used for magnesium was that for the neutral atom.

The structure was then refined by diagonal matrix least-squares [DIAMOND (1964), based on CRUICKSHANK's method (PEPINSKY, ROBERSTON and SPEAKMAN, 1961)] using the S.R.C. Atlas at Chilton. A weighting scheme was included in the refinement such that the weight $\omega$ of each reflection was proportional to $\frac{1}{\sigma^2}$ where $\sigma$ is the estimated standard deviation of intensity (the minimized function being $\Sigma\omega\Delta F^2$, $\Delta F = F_{obs} - F_{calc}$). The refinement was continued for both isotropic and anisotropic temperature factors until the recommended shifts were less than one tenth of the appropriate standard deviation (MASON, 1964).

In the isotropic refinement, 53 parameters were simultaneously refined and except for the scale factor the final parameters are given in Table 1. In the case of the anisotropic refinement, the total number of parameters refined was 119 and again with the exception of the

Table 1. *Parameters and standard deviations after isotropic refinement*

| | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| As | 0.0525(2) | 0.09417(3) | 0.0454(1) | 0.84(1) Å$^2$ |
| O(1) | 0.2925(11) | 0.0817(2) | 0.0902(5) | 1.00(9) |
| O(2) | −0.0871(11) | 0.0382(2) | 0.0451(6) | 1.27(10) |
| O(3) | −0.0486(11) | 0.1344(2) | 0.1433(5) | 0.96(9) |
| O(4) | 0.0225(12) | 0.1227(2) | −0.0848(5) | 1.21(9) |
| Mg(1) | 0.5 | 0.2207(2) | 0.25 | 0.94(6) |
| $H_2O(1)$ | 0.5612(11) | 0.1616(2) | 0.1309(6) | 1.20(9) |
| $H_2O(2)$ | 0.2081(13) | 0.2214(3) | 0.1767(7) | 2.03(12) |
| $H_2O(3)$ | 0.5835(14) | 0.2759(3) | 0.1344(7) | 2.30(13) |
| Mg(2) | 0 | 0.4490(1) | 0.25 | 0.63(5) |
| $H_2O(4)$ | −0.0492(14) | 0.4434(3) | 0.0713(7) | 2.12(12) |
| $H_2O(5)$ | 0.2176(12) | 0.3910(2) | 0.2417(6) | 1.36(9) |
| $H_2O(6)$ | 0.2133(13) | 0.5062(3) | 0.2435(7) | 2.01(11) |
| $H_2O(7)$ | −0.0080(13) | 0.3044(3) | 0.1035(7) | 1.86(11) |

Table 2. *Parameters and standard deviations after anisotropic refinement*

Positions

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| As | 0.0527(1) | 0.09417(3) | 0.0454(1) |
| O(1) | 0.2915(10) | 0.0819(2) | 0.0891(5) |
| O(2) | −0.0863(10) | 0.0380(2) | 0.0451(5) |
| O(3) | −0.0488(10) | 0.1343(2) | 0.1432(5) |
| O(4) | 0.0235(10) | 0.1229(2) | −0.0843(5) |
| Mg(1) | 0.5 | 0.2206(1) | 0.25 |
| $H_2O(1)$ | 0.5603(10) | 0.1612(2) | 0.1307(5) |
| $H_2O(2)$ | 0.2089(11) | 0.2204(2) | 0.1767(7) |
| $H_2O(3)$ | 0.5838(12) | 0.2762(3) | 0.1343(7) |
| Mg(2) | 0 | 0.4489(1) | 0.25 |
| $H_2O(4)$ | −0.0475(11) | 0.4442(3) | 0.0718(6) |
| $H_2O(5)$ | 0.2184(11) | 0.3911(2) | 0.2418(6) |
| $H_2O(6)$ | 0.2120(12) | 0.5064(2) | 0.2428(7) |
| $H_2O(7)$ | −0.0085(12) | 0.3040(2) | 0.1037(7) |

Vibrations ($\times 10^4$)

| | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{23}$ | $B_{31}$ | $B_{12}$ |
|---|---|---|---|---|---|---|
| As | 38(3) | 3(0.1) | 14(1) | 1(0.3) | 8(2) | 3(1) |
| O(1) | 22(14) | 4(1) | 26(4) | 4(3) | 7(13) | 6(5) |
| O(2) | 92(17) | 1(1) | 34(4) | − 1(2) | 28(14) | 4(5) |
| O(3) | 51(15) | 4(1) | 20(3) | 2(2) | 12(12) | 13(5) |
| O(4) | 56(16) | 5(1) | 19(4) | 3(3) | 32(12) | −6(5) |
| Mg(1) | 31(9) | 1(0.4) | 30(2) | 0 | 17(8) | 0 |
| $H_2O(1)$ | 38(14) | 4(1) | 30(4) | −11(3) | 14(13) | 2(5) |
| $H_2O(2)$ | 67(17) | 5(1) | 65(6) | −13(4) | −29(18) | −2(6) |
| $H_2O(3)$ | 115(19) | 6(1) | 61(6) | 16(4) | 100(19) | 11(6) |
| Mg(2) | 38(9) | 2(0.4) | 11(2) | 0 | 16(7) | 0 |
| $H_2O(4)$ | 65(17) | 12(1) | 22(3) | 0(3) | 31(14) | 11(6) |
| $H_2O(5)$ | 63(16) | 3(1) | 32(4) | 1(3) | 2(14) | 15(5) |
| $H_2O(6)$ | 136(20) | 8(1) | 42(4) | −14(4) | 79(17) | −54(7) |
| $H_2O(7)$ | 119(18) | 3(1) | 56(5) | − 1(3) | 31(18) | 10(6) |

The anisotropic temperature factor is defined by exp $-[h^2B_{11} + k^2B_{22} + l^2B_{33} + klB_{23} + lhB_{31} + hkB_{12})]$.

scale fator these are listed in Table 2. The residuals for the isotropic and anisotropic temperature refinements were 12.0% and 11.2%, respectively.

Comparison of the observed and calculated structure factors (Table 3) indicates that for some intense reflections, e.g. 040, 060,

Table 3. *Observed and calculated structure factors*

| l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 0 1 | | | 0 12 1 | | | 0 26 1 | | | 1 5 1 | | | 1 11 1 | | | 1 17 1 | | | 1 27 1 | | | 2 4 1 | |
| 2 2257 | 2770 | 7 -2772 | -2796 | 4 -1232 | -1113 | -10 2556 | 2508 | -3 2094 | 2040 | 11 -1216 | -765 | -7 -464 | -626 | -9 2060 | 1829 | | | | | | | |
| 4 575 | 568 | 8 -1237 | -1247 | 5 -168 | - 78 | -9 -533 | - 18 | -2 2773 | 2783 | 12 1395 | 1394 | -6 -884 | -748 | -8 620 | 598 | | | | | | | |
| 6 -4806 | -5158 | 9 -918 | -946 | 6 -268 | -194 | -8 1410 | 1108 | -1 285 | 238 | 1 19 1 | | -5 177 | 414 | -7 3833 | 4011 | | | | | | | |
| 8 -716 | -427 | 10 -808 | -976 | 7 -687 | -617 | -7 464 | 310 | 0 2099 | 2208 | | | -4 -2654 | -2307 | -6 -3660 | -3524 | | | | | | | |
| 10 -4316 | -5004 | 11 185 | 19 | 8 1313 | 1337 | -6 503 | 516 | 1 -661 | -606 | -12 -379 | -806 | -3 -1338 | -1049 | -5 958 | 769 | | | | | | | |
| 12 -1204 | -1197 | 12 -2000 | -1997 | 9 -687 | -711 | -5 3539 | 3222 | 2 1531 | 1365 | -11 -800 | -630 | -2 -1663 | -1456 | -4 -1769 | -1957 | | | | | | | |
| 14 -1836 | -1801 | 13 1221 | 1197 | | | -4 -3466 | -4444 | 3 -1423 | -1324 | -10 177 | 268 | -1 -244 | -185 | -3 1008 | 1013 | | | | | | | |
| 0 2 1 | | | 0 14 1 | | | 0 28 1 | | -3 3748 | 3627 | 4 1991 | 1867 | -9 -2387 | -2212 | 0 -2126 | -1771 | | | | | | | |
| 2 3038 | 3203 | 0 -349 | -105 | 0 -2360 | -2034 | -2 -3579 | -4587 | 5 148 | 53 | -8 -158 | -632 | 1 422 | 333 | -1 -1539 | -1604 | | | | | | | |
| 3 -4161 | -5031 | 1 -4080 | -4414 | 2 -1831 | -1715 | 0 -4511 | -7521 | 7 -1035 | -900 | -6 1043 | 1112 | 3 1267 | 1079 | 1 -1001 | -1065 | | | | | | | |
| 4 4578 | 4533 | 2 -2841 | -2939 | 3 1868 | 1696 | 1 -1746 | -1523 | 8 -2418 | -2318 | -5 -3693 | -3838 | 4 -177 | -134 | 2 -2748 | -2666 | | | | | | | |
| 5 -1333 | -1613 | 3 -3491 | -3662 | 4 202 | 474 | 2 -3241 | -3260 | 9 -533 | -516 | -4 202 | 251 | 5 177 | 371 | 3 -3683 | -3582 | | | | | | | |
| 6 -3018 | -2806 | 4 -1916 | -1776 | 5 853 | 857 | 3 -1538 | -1317 | 10 -3634 | -3071 | -3 -2681 | -2510 | 6 1387 | 1365 | 4 3330 | 3288 | | | | | | | |
| 7 -4497 | -4901 | 5 -4746 | -5457 | 6 714 | 613 | 4 1950 | 1804 | 11 -426 | -448 | -2 1355 | 1300 | 7 664 | 587 | 5 -1261 | -1177 | | | | | | | |
| 8 -1920 | -1676 | 6 451 | 584 | 7 1265 | 1294 | 5 -3382 | -2839 | 12 -1287 | -1217 | -1 -1893 | -1888 | 8 1294 | 1311 | 6 1042 | 1522 | | | | | | | |
| 9 -2523 | -2517 | 7 -827 | -806 | | | 6 3463 | 3199 | 13 752 | 763 | 0 -1641 | -1596 | | | 7 -2587 | -2599 | | | | | | | |
| 10 -1706 | -1808 | 8 1402 | 1339 | 0 30 1 | | 7 -1363 | -1052 | | | 1 3576 | 3657 | 1 29 1 | | 8 3086 | 3025 | | | | | | | |
| 11 -418 | -573 | 9 -947 | -1078 | 0 666 | 602 | 8 1975 | 1757 | 1 13 1 | | 2 1499 | 1421 | -7 -177 | -1503 | 9 451 | 623 | | | | | | | |
| 12 -383 | -470 | 10 823 | 962 | 1 625 | 557 | 9 224 | 202 | -13 -306 | -491 | 3 3690 | 3862 | -6 -682 | -627 | 10 2160 | 1869 | | | | | | | |
| 13 1909 | 1874 | 11 698 | 786 | 2 1458 | 1566 | 10 2638 | 2891 | -12 -177 | -289 | 4 296 | 306 | -5 -1780 | -1717 | 11 202 | 204 | | | | | | | |
| 14 -635 | -638 | 12 1356 | 1368 | 3 358 | 343 | 11 224 | 213 | -11 1403 | 1166 | 5 1554 | 3117 | -4 224 | 379 | 12 1378 | 1196 | | | | | | | |
| 0 4 1 | | 13 168 | 55 | 4 -148 | -360 | 12 1959 | 1765 | -10 -209 | -273 | 6 340 | 270 | -3 -575 | -632 | 13 1433 | 1383 | | | | | | | |
| 0 -2861 | -4234 | | | 5 1462 | 1469 | 13 158 | 177 | -9 1939 | 1923 | 7 1088 | 1171 | -2 -1420 | -1299 | 2 6 1 | | | | | | | | |
| 1 960 | 810 | 0 16 1 | | | | 14 735 | 919 | -8 177 | 80 | 8 -1924 | -1888 | -1 -202 | -434 | | | | | | | | | |
| 2 -3798 | -4988 | 0 -4129 | -4766 | 0 32 1 | | 1 7 1 | | -7 3540 | 3631 | 9 1978 | 1660 | 0 744 | 799 | -14 2001 | 2160 | | | | | | | |
| 3 -4455 | -6240 | 1 -2285 | -2008 | 0 2305 | 2393 | | | -6 868 | 791 | 10 597 | 512 | 1 1452 | 1327 | -13 -487 | -419 | | | | | | | |
| 4 1326 | 946 | 2 -2730 | -2858 | 1 -857 | -794 | -14 696 | 629 | -5 4367 | 4437 | 11 -920 | -848 | 2 -158 | -127 | -12 2034 | 1841 | | | | | | | |
| 5 -2681 | -2734 | 3 1182 | 1147 | 2 1555 | 1641 | -13 1271 | 1194 | -4 512 | 374 | 1 21 1 | | 3 2319 | 2244 | -11 -454 | -541 | | | | | | | |
| 6 718 | 635 | 4 -1567 | -1518 | 3 237 | 183 | -12 2837 | 2663 | -3 1395 | 1168 | | | 4 589 | 556 | -10 2250 | 2228 | | | | | | | |
| 7 -3075 | -3192 | 5 -842 | -866 | 4 454 | 547 | -11 -1405 | -1471 | -2 913 | 1458 | -10 -1946 | -1911 | 5 2217 | 2195 | -9 -2177 | -2140 | | | | | | | |
| 8 1932 | 1851 | 6 -770 | -796 | | | -10 1317 | 1212 | -1 -1903 | -1763 | -9 -379 | -616 | 6 -362 | -391 | -8 -729 | -599 | | | | | | | |
| 9 -244 | -338 | 7 1426 | 1415 | 1 1 1 | | -9 -2610 | -2578 | 0 -216 | - 69 | -8 -924 | -875 | | | -7 -705 | -639 | | | | | | | |
| 10 1513 | 1570 | 8 1622 | 1749 | -14 -1207 | -1190 | -8 1352 | 1193 | 1 -1873 | -1651 | -7 -2193 | -1897 | 1 31 1 | | -6 -1517 | -1327 | | | | | | | |
| 11 -1356 | -1254 | 9 -301 | -421 | -13 -185 | -463 | -7 -4622 | -4780 | 2 -1750 | -1662 | -6 950 | 1042 | -4 1032 | 1051 | -5 -729 | -625 | | | | | | | |
| 12 1853 | 1776 | 10 2947 | 2899 | -12 -2714 | -2510 | -6 -2711 | -2549 | 3 -3479 | -3435 | -5 418 | 243 | -3 -230 | -201 | -4 -4728 | -5419 | | | | | | | |
| 13 1108 | 1087 | 11 935 | 927 | -11 177 | 4 | -5 -998 | -989 | 4 -800 | -746 | -4 2456 | 2465 | -2 1609 | 1504 | -3 903 | 644 | | | | | | | |
| 14 112 | 244 | 12 2457 | 2657 | -10 -2712 | -2760 | -4 -792 | -1033 | 5 -3434 | -3403 | -3 -640 | -716 | -1 882 | 883 | -2 -2855 | -3131 | | | | | | | |
| 0 18 1 | | | | -9 1620 | 1248 | -3 -112 | -249 | 6 -158 | -176 | -2 2785 | 2808 | 0 2040 | 1985 | -1 -2298 | -1784 | | | | | | | |
| 0 6 1 | | | | -8 -2918 | -2602 | -2 -4827 | -6006 | 7 -2595 | -2647 | -1 1041 | 953 | 1 349 | 335 | 0 -2101 | -2537 | | | | | | | |
| 0 -3933 | -6519 | 0 1401 | 1231 | -7 4359 | 4109 | -1 3376 | 3425 | 8 177 | 49 | 0 2485 | 2601 | 2 1213 | 1197 | 1 4671 | 5453 | | | | | | | |
| 1 335 | 355 | 1 875 | 865 | -6 2304 | 1984 | 0 209 | 78 | 9 -530 | -396 | 1 -158 | -182 | 3 553 | 363 | 2 -1231 | -1131 | | | | | | | |
| 2 -3475 | -3812 | 2 -3475 | -3812 | -5 1844 | 1726 | 1 2620 | 2669 | 10 209 | 127 | 2 2098 | 2103 | 4 689 | 771 | 3 2514 | 2424 | | | | | | | |
| 3 -3603 | -4598 | 3 3874 | 4085 | -4 1668 | 2739 | 2 2379 | 1545 | 11 575 | 636 | 3 158 | 291 | | | 4 -2272 | -1860 | | | | | | | |
| 4 3853 | 3898 | 4 1369 | 1305 | -3 1791 | 2084 | 3 1736 | 1922 | 12 -484 | -328 | 4 168 | 105 | 1 33 1 | | 5 125 | 296 | | | | | | | |
| 5 -2429 | -2359 | 5 2834 | 3186 | -2 4497 | 7043 | 4 - 97 | -154 | 13 1088 | 1182 | 5 -610 | -710 | 0 1160 | 1769 | 6 3556 | 3351 | | | | | | | |
| 6 -1213 | -962 | 6 -952 | -929 | -1 -729 | -777 | 5 1167 | 1172 | | | 6 -474 | -405 | | | 7 680 | 138 | | | | | | | |
| 7 1910 | 1725 | 7 2626 | 3174 | 0 2576 | 3854 | 6 -2073 | -1606 | 1 15 1 | | 7 1155 | 1164 | 2 0 1 | | 8 3156 | 3380 | | | | | | | |
| 8 536 | 605 | 8 1536 | 1771 | 1 -1338 | -1422 | 7 2549 | 2257 | -13 -345 | -288 | 8 -1928 | -1728 | -14 -1947 | -2012 | 9 451 | 492 | | | | | | | |
| 9 2967 | 2922 | 9 1015 | 882 | 2 3840 | 4391 | 8 1676 | 1602 | -12 1995 | 2015 | 9 494 | 523 | -12 -2802 | -2407 | 10 3493 | 3067 | | | | | | | |
| 10 1326 | 1240 | 10 -415 | -486 | 3 -2503 | -2662 | 9 1152 | 1020 | -11 533 | 520 | 10 -2423 | -2551 | -10 -1981 | -1912 | 11 -1312 | -1262 | | | | | | | |
| 11 2375 | 2616 | 11 279 | 280 | 4 -1459 | -1260 | 10 1104 | 1044 | -10 1678 | 1667 | 11 746 | 832 | -8 1184 | 1010 | 12 1125 | 1062 | | | | | | | |
| 12 158 | 113 | 12 1358 | 1392 | 5 -3710 | -3320 | 11 -209 | -358 | -9 224 | 292 | 1 23 1 | | -6 -584 | -242 | 13 -1208 | -1063 | | | | | | | |
| 13 1476 | 1428 | | | 6 986 | 599 | 12 2378 | 2039 | -8 1451 | 1474 | | | -4 -1440 | -931 | | | | | | | | | |
| 14 -1143 | -1113 | 0 20 1 | | 7 -1789 | -1610 | 13 -1851 | -1838 | -7 3274 | 3366 | -10 -868 | -852 | -2 5176 | 7178 | 2 8 1 | | | | | | | | |
| 14 1355 | 1427 | 0 2116 | 2156 | 8 -3258 | -3181 | 14 387 | 600 | -6 158 | 290 | -9 1636 | 1562 | 0 5319 | 8406 | -14 668 | 721 | | | | | | | |
| 0 8 1 | | 1 853 | 770 | 9 177 | 19 | 1 9 1 | | -5 835 | 668 | -8 -1060 | -963 | 2 3892 | 4042 | -13 -1130 | -1076 | | | | | | | |
| | | 2 1952 | 1810 | 10 -1516 | -1612 | | | -4 -2209 | -1997 | -7 1687 | 1360 | 4 -837 | -860 | -12 -177 | -430 | | | | | | | |
| 0 754 | 526 | 3 2523 | 2636 | 11 -224 | -153 | -14 -804 | -847 | -3 1773 | 1686 | -6 784 | 775 | 6 -3358 | -3255 | -11 -447 | -673 | | | | | | | |
| 1 244 | 564 | 4 2249 | 2149 | 12 -2946 | -2808 | -13 274 | 271 | -2 -4261 | -4409 | -5 1724 | 1737 | 8 -2759 | -2705 | -10 673 | 627 | | | | | | | |
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| 3 1981 | 1917 | 6 -1025 | -1030 | 14 -367 | -448 | -11 -1298 | -1195 | 0 -3336 | -3578 | -3 1803 | 1691 | 12 -1702 | -1474 | -8 -1521 | -1520 | | | | | | | |
| 4 915 | 685 | 7 1883 | 2099 | | | -10 -1440 | -1539 | 1 367 | 306 | -2 2657 | 2823 | | | -7 -2874 | -2917 | | | | | | | |
| 5 5037 | 5639 | 8 -983 | -878 | 1 3 1 | | -9 -1242 | -1162 | 2 -3118 | -3078 | -1 823 | 630 | 2 2 1 | | -6 2437 | 2253 | | | | | | | |
| 6 661 | 621 | 9 844 | 877 | -14 -148 | - 78 | -8 158 | 251 | 3 -2599 | -2491 | 0 2241 | 2478 | -14 -125 | -405 | -5 -4338 | -4693 | | | | | | | |
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| 0 10 1 | | 4 1518 | 1519 | -5 6220 | 6906 | 1 3745 | 3991 | 12 1775 | 1597 | 9 -148 | - 19 | -5 2199 | 2040 | 4 -2979 | -2729 | | | | | | | |
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| 3 3272 | 3472 | 9 -237 | -144 | 0 -1490 | -1486 | 6 -804 | -881 | -10 2677 | 2495 | -8 -429 | -399 | 0 -185 | - 54 | 9 -168 | -141 | | | | | | | |
| 4 2605 | 2553 | 10 -2399 | -2579 | 1 -4356 | -6053 | 7 1287 | 1034 | -9 -209 | -349 | -7 1763 | 1612 | 1 -3307 | -3825 | 10 766 | 765 | | | | | | | |
| 5 1023 | 907 | 11 -224 | -270 | 2 429 | 132 | 8 -2555 | -2453 | -8 1251 | 1427 | -6 -1503 | -1387 | 2 4484 | 4391 | 11 -2781 | -2280 | | | | | | | |
| 6 -1549 | -1463 | | | 3 -3539 | -3912 | 9 -177 | -135 | -7 -2610 | -2684 | -5 2346 | 1950 | 3 -1715 | -2008 | 12 -168 | -244 | | | | | | | |
| 7 148 | 6 | 0 24 1 | | 4 -589 | -364 | 10 -1868 | -1570 | -6 -177 | -308 | -4 403 | 663 | 4 846 | 684 | 13 -1793 | -1703 | | | | | | | |
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| 9 -256 | -220 | 1 -1598 | -1715 | 6 1434 | 1227 | 12 -1472 | -1232 | -4 -3276 | -3219 | -2 -2114 | -1928 | 6 137 | 111 | 2 10 1 | | | | | | | | |
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| 11 194 | 531 | 3 -1360 | -1429 | 8 1455 | 1197 | 14 279 | 428 | -2 -3014 | -2776 | 0 -1697 | -1508 | 8 -2599 | -2436 | -12 -3088 | -3014 | | | | | | | |
| 12 -1753 | -1762 | 4 -250 | -357 | 9 -3486 | -3369 | | | -1 694 | 595 | 1 -1802 | -1740 | 9 -1621 | -1598 | -11 -2111 | -2012 | | | | | | | |
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| 14 -1468 | -1673 | 6 -256 | -309 | 11 2000 | 1731 | -13 -550 | -563 | 1 -454 | -252 | 3 -1799 | -1647 | 11 1433 | 1201 | -9 -209 | -504 | | | | | | | |
| 0 12 1 | | 7 -1900 | -1768 | 12 -202 | -137 | -12 -1485 | -1426 | 2 -1531 | -1272 | 4 910 | 1005 | 12 -464 | -648 | -8 -963 | -660 | | | | | | | |
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| 0 -605 | -132 | 9 -1180 | -1135 | 14 -306 | -260 | -10 -2556 | -2829 | 4 -1589 | -1496 | 6 -185 | - 62 | | | -6 3853 | 3930 | | | | | | | |
| 1 857 | 610 | 0 26 1 | | | | 1 5 1 | | -9 1271 | 915 | 5 4336 | 4617 | 2 4 1 | | -5 705 | 119 | | | | | | | |
| 2 2516 | 2651 | | | | | | | -8 -1307 | -1129 | 6 1301 | 1308 | 8 1230 | 1162 | -14 1087 | 1174 | | | | | | | |
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| 4 984 | 852 | 1 158 | 66 | -13 177 | 31 | -6 -735 | -585 | 8 1352 | 1352 | | | -12 2057 | 1758 | -2 5410 | 6514 | | | | | | | |
| 5 -3515 | -3640 | 2 -1892 | -1616 | -12 2198 | 2078 | -5 -1178 | -953 | 9 -451 | -503 | 1 27 1 | | -11 2282 | 2263 | -1 2285 | 2084 | | | | | | | |
| 6 285 | 203 | 3 -1139 | -1004 | -11 -202 | -641 | -4 6078 | 7363 | 10 2979 | 2711 | -8 673 | 671 | -10 1221 | 911 | 0 -395 | - 68 | | | | | | | |

Table 3. *(Continued)*

| l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2 10 | l | | 2 18 | l | | 2 26 | l | | 3 3 | l | | 3 11 | l | | 3 17 | l | | 3 27 | l | | 4 6 | l |
| 1 | 1936 | 1845 | -12 | 844 | 841 | -5 | -1023 | -972 | 4 | 1182 | 990 | -13 | -500 | -492 | 5 | 1278 | 1122 | -1 | 1392 | 1223 | -12 | 464 | 540 |
| 2 | 2881 | 2701 | -11 | -1316 | -1117 | -4 | -3133 | -2894 | 5 | -3609 | -3676 | -12 | -1006 | -992 | 6 | 1795 | 1798 | 0 | -1459 | -1314 | -11 | -1484 | -1323 |
| 3 | 1631 | 1763 | -10 | 873 | 719 | -3 | 1233 | 1076 | 6 | 1988 | 1634 | -11 | 1087 | 950 | 7 | 570 | 635 | 1 | 268 | 242 | -10 | 194 | 52 |
| 4 | -2675 | -2501 | -9 | -2189 | -1934 | -2 | -1969 | -1673 | 7 | -1195 | -874 | -10 | -1860 | -1477 | 8 | 2422 | 2048 | 2 | -148 | - 28 | -9 | -1261 | -1251 |
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| 7 | 2359 | 2166 | -6 | -2225 | -2202 | 1 | 185 | 244 | 10 | 687 | 684 | -7 | 1428 | 1084 | 11 | -594 | -592 | 5 | -575 | -655 | -6 | -2389 | -2388 |
| 8 | -3417 | -3873 | -5 | -2815 | -2899 | 2 | -358 | -283 | 11 | 2908 | 2496 | -6 | 2069 | 2048 | | 3 19 | l | 6 | 1806 | 2042 | -5 | 279 | 265 |
| 9 | -796 | -759 | -4 | -1214 | -1147 | 3 | -1408 | -1288 | 12 | 158 | 107 | -5 | 301 | 64 | | | | | | | -4 | -4207 | -4428 |
| 10 | -1112 | -1079 | -3 | -2058 | -1875 | 4 | 316 | 506 | 13 | 2013 | 1918 | -4 | 4621 | 5289 | -11 | -1438 | -1473 | | 3 29 | l | -3 | -168 | -201 |
| 11 | -1154 | -869 | -2 | 542 | 421 | 5 | 1448 | 1169 | | 3 5 | l | -3 | 399 | 407 | -10 | -274 | -160 | -5 | -703 | -594 | -2 | -2405 | -2458 |
| 12 | -1603 | -1453 | -1 | 602 | 538 | 6 | 2330 | 2323 | | | | -2 | 2111 | 1928 | -9 | -2474 | -2168 | -4 | 137 | 90 | -1 | 2375 | 2406 |
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| -11 | 1136 | 901 | 5 | 2877 | 2926 | -6 | 125 | 127 | -9 | -168 | -354 | 4 | 592 | 391 | -3 | -868 | -738 | 2 | -862 | -822 | 5 | 707 | 977 |
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| -8 | -168 | -238 | 8 | 1101 | 856 | -3 | -862 | -699 | -6 | -2877 | -2714 | 7 | -216 | -226 | 0 | -1184 | -1182 | | 3 31 | l | 8 | 2494 | 2065 |
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| -2 | 3654 | 3737 | -11 | -316 | -399 | 3 | 2425 | 2381 | 0 | -4799 | -5978 | | | | 6 | -209 | -282 | | | | | | |
| -1 | -913 | -713 | -10 | -698 | -741 | 4 | 490 | 496 | 1 | - 97 | - 74 | | 3 13 | l | 7 | 194 | 137 | -12 | 1079 | 886 | -13 | -1416 | -1536 |
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| 1 | -2852 | -2871 | -8 | -873 | -744 | 6 | 1570 | 1658 | 3 | -748 | -454 | -12 | -437 | -405 | 9 | -880 | -715 | -8 | 2883 | 3020 | -11 | -2082 | -1785 |
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| | 2 14 | l | 5 | 2215 | 1816 | 5 | 1102 | 1381 | -13 | -256 | -340 | 1 | -3668 | -4149 | -1 | 250 | 229 | -13 | 733 | 697 | 2 | 481 | 414 |
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| 2 | -1912 | -1754 | -2 | 1758 | 1768 | -6 | 2711 | 2744 | 4 | 2503 | 2187 | -9 | 846 | 718 | -5 | 1414 | 1266 | 4 | -209 | -111 | -7 | -158 | -284 |
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| 12 | 539 | 451 | 8 | -1394 | -1358 | 4 | -1863 | -1789 | | 3 9 | l | 1 | -474 | -408 | 5 | -2017 | -1749 | | | | 3 | 844 | 883 |
| | 2 16 | l | 9 | 1123 | 1175 | 5 | -1730 | -1391 | | | | 2 | -744 | -515 | 6 | -675 | -640 | -13 | 316 | 282 | 4 | -3214 | -3382 |
| | | | 10 | -1967 | -2171 | 6 | -3216 | -3283 | -13 | -1337 | -1244 | 3 | -3644 | -3767 | 7 | 148 | 257 | -12 | 615 | 782 | 5 | 440 | 550 |
| -12 | 2381 | 2692 | | | | 7 | 584 | 462 | -12 | -671 | -890 | 4 | 1062 | 952 | 8 | -1439 | -1351 | -11 | 2520 | 2108 | 6 | -3023 | -3528 |
| -11 | -296 | -113 | | 2 24 | l | 8 | -2236 | -2356 | -11 | -3343 | -2958 | 5 | -1336 | -1269 | | 3 25 | l | -10 | -158 | -263 | 7 | 418 | 421 |
| -10 | 2575 | 2293 | -10 | - 79 | -131 | 9 | 1058 | 900 | -10 | 331 | 395 | 6 | 2024 | 2124 | | | | -9 | 1017 | 1053 | 8 | -2509 | -2380 |
| -9 | 316 | 91 | -9 | 1831 | 1789 | 10 | -1511 | -1298 | -9 | -1947 | -1929 | 7 | 158 | 17 | -8 | -527 | -432 | -8 | -829 | -786 | 9 | -1644 | -1375 |
| -8 | -1104 | -1037 | -8 | -158 | - 61 | 11 | 185 | 429 | -8 | 1394 | 1291 | 8 | 2610 | 2259 | -7 | 1400 | 1132 | -7 | 2455 | 2332 | 10 | -395 | -411 |
| -7 | 468 | 552 | -7 | 2917 | 2766 | 12 | -158 | -369 | -7 | -1332 | -1046 | 9 | 1391 | 1180 | -6 | -1961 | -1719 | -6 | -3135 | -3215 | 11 | -893 | -825 |
| -6 | -804 | -874 | -6 | -177 | - 62 | 13 | 1549 | 1427 | -6 | -750 | -505 | 10 | 1386 | 1105 | -5 | 1495 | 1232 | -5 | -592 | -502 | | | |
| -5 | -1263 | -1223 | -5 | 1283 | 1040 | | 3 3 | l | -5 | -1208 | -1096 | 11 | 917 | 834 | -4 | -2021 | -1619 | -4 | -1980 | -1796 | | 4 12 | l |
| -4 | -3782 | -3925 | -4 | -285 | -404 | | | | -4 | 2599 | 2261 | | | | -3 | -1551 | -1186 | -3 | 1017 | 764 | -12 | -1490 | -1481 |
| -3 | -589 | -584 | -3 | 685 | 691 | -14 | 112 | 150 | -3 | -1795 | -1663 | | 3 17 | l | -2 | -2859 | -2572 | -2 | -3035 | -3256 | -11 | 1764 | 1719 |
| -2 | -3916 | -4099 | -2 | -731 | -626 | -13 | 1717 | 1554 | -2 | 2910 | 2800 | -12 | 840 | 833 | -1 | -474 | -443 | -1 | -3702 | -4625 | -10 | 168 | 11 |
| -1 | -279 | -176 | -1 | -1396 | -1445 | -12 | -185 | -160 | -1 | 2744 | 2571 | -11 | -764 | -595 | 0 | -230 | - 55 | 0 | -1214 | -1151 | -9 | 1566 | 1405 |
| 0 | -2175 | -2383 | 0 | 158 | 50 | -11 | 1391 | 1267 | 0 | 2901 | 2988 | -10 | 818 | 849 | 1 | -3049 | -2717 | 1 | -2033 | -2096 | -8 | 788 | 631 |
| 1 | 840 | 783 | 1 | -1996 | -1737 | -10 | 345 | 311 | 1 | 3382 | 3886 | -9 | -474 | -953 | 2 | 379 | 332 | 2 | -383 | -182 | -7 | 1239 | 1116 |
| 2 | 1008 | 824 | 2 | 358 | 475 | -9 | 3276 | 3605 | 2 | -403 | -469 | -8 | -451 | -615 | 3 | -1383 | -1151 | 3 | -3053 | -3232 | -6 | 2587 | 2628 |
| 3 | -168 | - 33 | 3 | -4084 | -3768 | -8 | 158 | 171 | 3 | 4589 | 4887 | -7 | -2011 | -2053 | 4 | 2239 | 2132 | 4 | 3285 | 3191 | -5 | 158 | 180 |
| 4 | -1129 | -959 | 4 | 345 | 463 | -7 | 2142 | 1784 | 4 | -1005 | -910 | -6 | -1706 | -1567 | 5 | -2011 | -1928 | 5 | 750 | 387 | -4 | 2922 | 2978 |
| 5 | 379 | 244 | 5 | -2339 | -2142 | -6 | -1451 | -1328 | 5 | 2884 | 2514 | -5 | -1301 | -1118 | 6 | 559 | 507 | 6 | 2758 | 2880 | -3 | -411 | -417 |
| 6 | 1454 | 1436 | 6 | 177 | 497 | -5 | 2099 | 2033 | 6 | -2884 | -2605 | -4 | -2306 | -2326 | 7 | 311 | 311 | 7 | 654 | 746 | -2 | 4201 | 4679 |
| 7 | -316 | -572 | 7 | -158 | -237 | -4 | -1854 | -1562 | 7 | 1329 | 743 | -3 | 530 | 579 | | 3 27 | l | 8 | 1983 | 2103 | -1 | -3415 | -3557 |
| 8 | 2311 | 1892 | 8 | 137 | 175 | -3 | -564 | -435 | 8 | -1626 | -1452 | -2 | -1897 | -1790 | | | | 9 | 2601 | 2385 | 0 | -399 | -411 |
| 9 | -194 | -364 | 9 | 112 | 579 | -2 | -331 | -273 | 9 | -2241 | -2143 | -1 | 1864 | 2037 | -7 | -869 | -898 | 10 | 407 | 517 | 1 | -1561 | -1551 |
| 10 | 3025 | 2895 | | 2 26 | l | -1 | -316 | -373 | 10 | -2768 | -2397 | 0 | -1689 | -1500 | -6 | -2530 | -2574 | 11 | 158 | 253 | 2 | -1990 | -2020 |
| 11 | 429 | 481 | | | | 0 | -168 | - 99 | 11 | -2283 | -2031 | 1 | -290 | -421 | -5 | 148 | 94 | 12 | 202 | 329 | 3 | -1112 | -1075 |
| 12 | 1275 | 1394 | -8 | -125 | -160 | 1 | -4454 | -5134 | 12 | 274 | 190 | 2 | -804 | -719 | -4 | -2636 | -2506 | | 4 6 | l | 4 | -2468 | -2584 |
| | | | -7 | 1872 | 1843 | 2 | -1963 | -1922 | | | | 3 | 2394 | 2366 | -3 | -256 | -329 | | | | 5 | -1355 | -1112 |
| | | | -6 | -1396 | -1210 | 3 | -2625 | -2479 | | | | 4 | 932 | 853 | -2 | -1982 | -1791 | -13 | -673 | -652 | 6 | -1159 | -1152 |

Table 3. *(Continued)*

| l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ | l | 25 $F_o$ | 25 $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 4 12 | 1 | | 4 20 | 1 | | 5 3 | 1 | | 5 9 | 1 | | 5 17 | 1 | | 6 4 | 1 | | 6 20 | 1 | | 7 13 | 1 |
| 7 | -407 | -444 | 6 | -2170 | -2014 | -12 | -500 | -515 | 3 | 1541 | 1342 | 4 | 1204 | 1077 | -2 | -316 | -402 | 2 | -1686 | -1399 | 4 | -718 | -731 |
| 8 | -2116 | -1913 | 7 | -635 | -750 | -11 | 1530 | 1455 | 4 | -1518 | -1499 | 5 | 185 | 178 | -1 | -2267 | -2444 | 3 | 1119 | 1068 | | 7 15 | 1 |
| 9 | 1464 | 1414 | 8 | -1075 | -1144 | -10 | 185 | 211 | 5 | 415 | 348 | 6 | 1880 | 1800 | 0 | 1025 | 1104 | 4 | -2142 | -2117 | | | |
| 10 | -716 | -533 | | | | -9 | 2529 | 2768 | 6 | -711 | -708 | 7 | -788 | -739 | 1 | -794 | -880 | | 6 22 | 1 | -4 | -290 | -251 |
| 11 | 1385 | 1400 | | 4 22 | 1 | -8 | -158 | -195 | 7 | -158 | -382 | 8 | 399 | 325 | 2 | 148 | 196 | | | | -3 | -148 | - 98 |
| | | | -9 | 878 | 914 | -7 | 185 | 343 | 8 | -2696 | -2278 | | | | 3 | -1668 | -1926 | -4 | 1860 | 1715 | -2 | 137 | 363 |
| | 4 14 | 1 | -8 | 1052 | 879 | -6 | -1137 | -1080 | 9 | -1759 | -1636 | | 5 19 | 1 | 4 | 2107 | 2468 | -3 | -387 | -404 | -1 | -1251 | -1192 |
| -11 | 1759 | 1689 | -7 | 1249 | 1260 | -5 | 838 | 584 | 10 | -316 | -293 | -9 | -1268 | -1398 | | 6 6 | 1 | -2 | -468 | -500 | 0 | 1462 | 1422 |
| -10 | -168 | -212 | -6 | 1802 | 1737 | -4 | -1308 | -1009 | | 5 11 | 1 | -8 | -177 | -140 | | | | -1 | -1379 | -1319 | 1 | -367 | -531 |
| -9 | 2407 | 2197 | -5 | -474 | -626 | -3 | -4811 | -5193 | | | | -7 | 349 | 429 | -4 | -1648 | -1548 | 0 | -678 | -621 | 2 | 2088 | 2032 |
| -8 | -827 | -826 | -4 | 3239 | 3068 | -2 | 742 | 765 | -11 | 820 | 805 | -6 | 1632 | 1404 | -3 | 1860 | 1823 | 1 | -671 | -516 | 3 | -989 | -931 |
| -7 | -395 | -382 | -3 | 194 | 140 | -1 | -2971 | -3272 | -10 | -158 | -159 | -5 | -185 | -139 | -2 | 375 | 551 | 2 | -1667 | -1628 | 4 | 1643 | 1976 |
| -6 | -1330 | -1165 | -2 | 798 | 591 | 0 | -487 | -695 | -9 | -185 | - 40 | -4 | -415 | -424 | -1 | 691 | 889 | 3 | - 79 | -837 | | | |
| -5 | 1401 | 1467 | -1 | -2504 | -2324 | 1 | -2760 | -3071 | -8 | 3288 | 3065 | -3 | 2487 | 2277 | 0 | 733 | 852 | | | | | 7 17 | 1 |
| -4 | -279 | -217 | 0 | 1203 | 1045 | 2 | -696 | -539 | -7 | 158 | 403 | -2 | 1423 | 1434 | 1 | 290 | 296 | | 6 24 | 1 | -4 | -724 | -660 |
| -3 | -814 | -826 | 1 | -296 | -314 | 3 | 490 | 355 | -6 | 2448 | 2624 | -1 | 2150 | 2086 | 2 | 1860 | 2049 | -1 | -886 | -1459 | -3 | 930 | 665 |
| -2 | -1182 | -1097 | 2 | -1090 | -982 | 4 | 418 | 277 | -5 | -340 | -372 | 0 | -474 | -580 | 3 | 838 | 808 | | | | -2 | 112 | 158 |
| -1 | -901 | -902 | 3 | -1510 | -1341 | 5 | -1375 | -1031 | -4 | 3513 | 3655 | 1 | 2493 | 2401 | 4 | 1433 | 1651 | | 7 1 | 1 | -1 | 1632 | 1617 |
| 0 | 487 | 551 | 4 | -1464 | -1393 | 6 | 1284 | 1158 | -3 | 177 | 48 | 2 | 185 | 326 | | | | -4 | 1276 | 946 | 0 | 1270 | 1322 |
| 1 | -4051 | -4816 | 5 | -411 | -354 | 7 | 2051 | 2205 | -2 | 1529 | 1323 | 3 | 1044 | 948 | | 6 8 | 1 | -3 | -746 | -738 | 1 | 216 | 261 |
| 2 | 375 | 341 | 6 | -2334 | -2366 | 8 | 454 | 581 | -1 | -1313 | -1254 | 4 | -1995 | -1738 | -4 | 177 | 96 | -2 | -358 | -351 | 2 | 1852 | 1725 |
| 3 | -2350 | -2479 | 7 | -429 | -625 | 9 | 451 | 609 | 0 | -148 | -191 | 5 | 716 | 608 | -3 | 2630 | 2750 | -1 | -1413 | -1697 | | 7 19 | 1 |
| 4 | 437 | 526 | 8 | -578 | -701 | 10 | 185 | 198 | 1 | -1058 | -1174 | 6 | 148 | 16 | -2 | 437 | 684 | 0 | -1139 | -1243 | | | |
| 5 | -1784 | -1772 | | 4 24 | 1 | 11 | 1962 | 2232 | 2 | -2276 | -2466 | 7 | -1628 | -1631 | -1 | 1374 | 1423 | 1 | -311 | -367 | -3 | 1703 | 2487 |
| 6 | 820 | 823 | | | | | | | 3 | -224 | -305 | | | | 0 | 733 | 852 | | 6 24 | 1 | -2 | 79 | 52 |
| 7 | 851 | 786 | -8 | -383 | -412 | | 5 5 | 1 | 4 | -1851 | -1830 | | 5 21 | 1 | 1 | 2710 | 3132 | 3 | -990 | -927 | -1 | 1059 | 1149 |
| 8 | 1085 | 1014 | -7 | 1628 | 1653 | -12 | 137 | 305 | 5 | 735 | 668 | -8 | 1257 | 1352 | 2 | 599 | 603 | 4 | -2544 | -2553 | | 8 0 | 1 |
| 9 | 1385 | 1167 | -6 | -615 | -539 | -11 | 349 | 607 | 6 | -2946 | -2546 | -7 | -1032 | -1115 | 3 | 285 | 260 | | | | | | |
| 10 | 125 | 81 | -5 | 158 | 114 | -10 | -399 | -521 | 7 | 490 | 403 | -6 | 2425 | 2374 | 4 | -584 | -568 | | 7 3 | 1 | -4 | 1612 | 1596 |
| | 4 16 | 1 | -4 | -550 | -540 | -9 | 158 | 27 | 8 | -1383 | -1202 | -5 | 918 | 814 | | | | -4 | 202 | 23 | -2 | -2102 | -2333 |
| | | | -3 | -2096 | -1929 | -8 | -2632 | -3001 | 9 | 827 | 751 | -4 | 2679 | 2456 | | 6 10 | 1 | -3 | -3704 | -3686 | 0 | -2081 | -2307 |
| -11 | -1034 | -1084 | -2 | 177 | 135 | -7 | -1068 | -1104 | 10 | -1335 | -1276 | -3 | 418 | 522 | -4 | 746 | 732 | -2 | 290 | 531 | 2 | -1976 | -2212 |
| -10 | -274 | -265 | -1 | -1255 | -996 | -6 | -2869 | -2724 | | 5 13 | 1 | -2 | 1641 | 1368 | -3 | 331 | 150 | -1 | -1976 | -1968 | 4 | -850 | -1014 |
| -9 | 168 | 408 | 0 | 274 | 79 | -5 | -971 | -806 | | | | -1 | 1088 | 1110 | -2 | 1561 | 1268 | 0 | 230 | 534 | | 8 2 | 1 |
| -8 | -1341 | -1240 | 1 | -2740 | -2625 | -4 | -3215 | -3313 | -11 | 2035 | 2368 | 0 | -1100 | -901 | -1 | 1329 | 1453 | 1 | -1715 | -1730 | | | |
| -7 | -158 | -286 | 2 | 168 | 92 | -3 | 158 | 189 | -10 | -461 | -370 | 1 | -168 | -143 | 0 | -764 | -809 | 2 | -447 | -378 | -4 | -137 | -165 |
| -6 | -2082 | -2134 | 3 | -2895 | -2943 | -2 | -1294 | -1122 | -9 | 1993 | 1968 | 2 | -1750 | -1676 | 1 | -148 | -169 | 3 | 335 | 389 | -3 | -2689 | -2605 |
| -5 | 1213 | 1171 | 4 | -158 | - 42 | -1 | -395 | -280 | -8 | 148 | 28 | 3 | 216 | 128 | 2 | -1307 | -1426 | 4 | 158 | 147 | -2 | -137 | -117 |
| -4 | -3388 | -3961 | 5 | -594 | -755 | 0 | -415 | -372 | -7 | 875 | 880 | 4 | -2257 | -2258 | 3 | 862 | 954 | | | | -1 | -2302 | -2692 |
| -3 | -671 | -818 | 6 | 112 | 141 | 1 | -570 | -581 | -6 | 1155 | 1239 | 5 | -1235 | -1130 | 4 | -3057 | -3015 | | 7 5 | 1 | 0 | -913 | -923 |
| -2 | -2602 | -2879 | | | | 2 | 1756 | 1666 | -5 | -230 | -341 | 6 | -1694 | -1564 | | | | -4 | -1081 | -737 | 1 | -250 | -367 |
| -1 | 949 | 829 | | 4 26 | 1 | 3 | 912 | 863 | -4 | 1071 | 972 | | | | | 6 12 | 1 | -3 | -340 | -353 | 2 | -1473 | -1471 |
| 0 | -148 | - 49 | -6 | -2333 | -2557 | 4 | 2957 | 3065 | -3 | -2095 | -2027 | | 5 23 | 1 | -4 | 1008 | 1107 | -2 | 597 | 817 | 3 | 855 | 908 |
| 1 | -905 | -817 | -5 | 262 | 336 | 5 | 185 | 240 | -2 | 494 | 496 | -7 | 250 | 314 | -3 | -2345 | -2494 | -1 | -399 | -417 | 4 | -542 | -726 |
| 2 | 2474 | 2701 | -4 | -2390 | -2405 | 6 | 3208 | 3428 | -1 | -3569 | -3999 | -6 | 1369 | 1421 | -2 | 1548 | 1527 | 0 | 230 | 445 | | 8 4 | 1 |
| 3 | 335 | 128 | -3 | 311 | 352 | 7 | -605 | -717 | 0 | 158 | 222 | -5 | -709 | -577 | -1 | -1764 | -2050 | 1 | -403 | -533 | | | |
| 4 | 1968 | 2189 | -2 | -1187 | -1055 | 8 | 1656 | 1323 | 1 | -2420 | -2733 | -4 | 399 | 349 | 0 | -1403 | -1455 | 2 | 2488 | 2443 | -4 | 137 | 159 |
| 5 | -707 | -685 | -1 | -2214 | -2109 | 9 | 407 | 261 | 2 | -383 | -416 | -3 | -875 | -737 | 1 | -906 | -1227 | 3 | 645 | 608 | -3 | -1121 | -776 |
| 6 | 1629 | 1442 | 0 | -418 | -447 | 10 | 724 | 654 | 3 | -1490 | -1560 | -2 | 444 | 459 | 2 | -1023 | -1218 | 4 | 2191 | 2117 | -2 | 137 | 448 |
| 7 | 471 | 452 | 1 | -645 | -633 | 11 | 764 | 873 | 4 | -285 | -469 | -1 | -1612 | -1402 | 3 | -168 | -156 | | | | -1 | -1909 | -1867 |
| 8 | 1777 | 1755 | 2 | 137 | 172 | | | | 5 | -158 | -179 | 0 | -340 | -389 | 4 | -2122 | -2006 | | 7 7 | 1 | 0 | 1683 | 1886 |
| 9 | -137 | -340 | 3 | -202 | -242 | | 5 7 | 1 | 6 | -379 | -283 | 1 | -2084 | -1896 | | | | -4 | -194 | -258 | 1 | -617 | -589 |
| 10 | 1162 | 1254 | 4 | 1411 | 1486 | -12 | 997 | 1073 | 7 | 1391 | 1246 | 2 | -362 | -337 | | 6 14 | 1 | -3 | 1363 | 1242 | 2 | 1152 | 1189 |
| | 4 18 | 1 | 5 | 353 | 357 | -11 | -1951 | -1995 | 8 | -125 | -213 | 3 | -1645 | -1623 | -4 | -256 | -339 | -2 | -1654 | -1673 | 3 | - 97 | -228 |
| | | | | | | -10 | -451 | -597 | 9 | 1980 | 1941 | 4 | -1156 | -1144 | -3 | -2040 | -1837 | -1 | 3032 | 3271 | | | |
| -10 | -125 | -186 | | 4 28 | 1 | -9 | -2411 | -2225 | | | | 5 | -331 | -353 | -2 | -383 | -479 | 0 | 2064 | 2139 | | 8 6 | 1 |
| -9 | -1273 | -1165 | -4 | -920 | -741 | -8 | -415 | -470 | | 5 15 | 1 | | | | -1 | -1098 | -1027 | 1 | 345 | 454 | -4 | -484 | -543 |
| -8 | 687 | 848 | -3 | 518 | 495 | -7 | -2202 | -2361 | -10 | -889 | -962 | | 5 25 | 1 | 0 | 873 | 810 | 2 | 983 | 967 | -3 | 1133 | 1088 |
| -7 | -1275 | -957 | -2 | -1675 | -1852 | -6 | -2364 | -2356 | -9 | 426 | 628 | -4 | -1053 | -984 | 1 | -2474 | -2468 | 3 | 437 | 462 | -2 | 1298 | 1397 |
| -6 | -2936 | -2723 | -1 | 1593 | 1711 | -5 | 177 | 119 | -8 | -2047 | -2041 | -3 | -1623 | -1537 | 2 | 1320 | 1149 | 4 | 2059 | 1925 | -1 | 559 | 435 |
| -5 | 158 | 18 | 0 | -790 | -768 | -4 | -2417 | -2369 | -7 | 2464 | 2383 | -2 | -1500 | -1488 | 3 | 158 | 87 | | | | 0 | 1418 | 1556 |
| -4 | 657 | 621 | 1 | 1213 | 1188 | -3 | 2658 | 2630 | -6 | -2074 | -2165 | -1 | -1836 | -1787 | 4 | 1873 | 1860 | | 7 9 | 1 | 1 | -202 | -199 |
| -3 | 168 | 342 | 2 | 194 | 137 | -2 | -2498 | -2547 | -5 | -1839 | -2005 | 0 | -125 | - 41 | | | | -4 | 1355 | 1137 | 2 | 2114 | 2432 |
| -2 | -1876 | -2034 | 3 | 1126 | 1351 | -1 | 3779 | 4111 | -4 | -1508 | -1356 | 1 | -1337 | -1148 | | 6 16 | 1 | -3 | 768 | 696 | 3 | -678 | -722 |
| -1 | 2427 | 2559 | | | | 0 | 1779 | 1736 | -3 | -375 | -143 | 2 | 835 | 674 | -4 | -2570 | -2401 | -2 | -932 | -882 | | | |
| 0 | 766 | 713 | | 5 1 | 1 | 1 | 3116 | 3321 | -2 | -978 | -930 | 3 | -944 | -937 | -3 | -185 | -400 | -1 | 1694 | 1630 | | 8 8 | 1 |
| 1 | 2073 | 2429 | -12 | -850 | -726 | 2 | 2783 | 2920 | -1 | -2430 | -2556 | | | | -2 | -804 | -721 | 0 | -1251 | -1321 | -4 | -112 | -246 |
| 2 | -1244 | -1312 | -11 | 1137 | 984 | 3 | 1414 | 1237 | 0 | 285 | 426 | | 5 27 | 1 | -1 | 1017 | 876 | 1 | 1204 | 1219 | -3 | 2323 | 2317 |
| 3 | 1792 | 1875 | -10 | 1494 | 1127 | 4 | 1639 | 1450 | 1 | -599 | -552 | -2 | -509 | -595 | 0 | 1623 | 1572 | 2 | -1082 | -1224 | -2 | 112 | 22 |
| 4 | 2321 | 2686 | -9 | 1450 | 1639 | 5 | -290 | -269 | 2 | 1533 | 1680 | 0 | -367 | -520 | 1 | 512 | 545 | 3 | 720 | 528 | -1 | 837 | 935 |
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| 6 | 790 | 756 | -7 | 1553 | 1579 | 7 | -821 | -776 | 4 | 2375 | 2226 | | | | 3 | -148 | - 47 | | 7 11 | 1 | 1 | 957 | 1118 |
| 7 | 209 | 160 | -6 | 4108 | 4650 | 8 | 1837 | 1636 | 5 | 1227 | 1163 | -4 | 1730 | 1658 | 4 | 1734 | 1656 | | | | 2 | 804 | 838 |
| 8 | 464 | 545 | -5 | -2098 | -2108 | 9 | -1584 | -1408 | 6 | 1758 | 1689 | -2 | -1102 | -1196 | | | | | | | | | |
| | | | -4 | 1705 | 1665 | 10 | 274 | 123 | 7 | -584 | -523 | 0 | -1014 | -1162 | | 6 18 | 1 | -4 | 1447 | 1272 | | 8 10 | 1 |
| | 4 20 | 1 | -3 | -2194 | -2016 | | | | 8 | 1407 | 1339 | 2 | -2268 | -2636 | -3 | 2233 | 1776 | -3 | -536 | -325 | | | |
| -10 | -335 | -421 | -2 | 1899 | 1910 | | 5 9 | 1 | 9 | 1490 | 1606 | 4 | -853 | -858 | -2 | 158 | 162 | -4 | 675 | 90 | -2 | -1063 | -1098 |
| -9 | -990 | -1026 | -1 | -671 | -631 | -12 | 97 | 110 | | 5 17 | 1 | | 6 2 | 1 | -1 | 2611 | 2531 | 0 | 168 | 91 | -4 | -289 | -393 |
| -8 | 1948 | 1889 | 0 | -1651 | -2440 | -11 | -2295 | -2416 | | | | | | | | 194 | 270 | 1 | 148 | 231 | -2 | -573 | -590 |
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| -6 | 1756 | 1578 | 2 | -642 | -617 | -9 | -2219 | -1892 | -8 | -2033 | -1896 | -3 | -3672 | -3513 | 1 | 2691 | 2601 | 3 | -137 | - 82 | 0 | -1284 | -1385 |
| -5 | 754 | 214 | 3 | -1941 | -1809 | -8 | 407 | 661 | -7 | 177 | 12 | -2 | -758 | -825 | 2 | 349 | 329 | 4 | -1375 | -1411 | 1 | - 97 | - 11 |
| -4 | 2122 | 1751 | 4 | -3713 | -4080 | -7 | -542 | -494 | -6 | -2057 | -1962 | -1 | -2982 | -3640 | 3 | | | | | | | | |
| -3 | 1266 | 915 | 5 | 437 | 462 | -6 | 1721 | 1549 | -5 | 1210 | 1035 | 0 | -742 | -818 | 4 | 2180 | 2004 | | 7 13 | 1 | | 8 12 | 1 |
| -2 | 1000 | 979 | 6 | -1383 | -1425 | -5 | 335 | 320 | -4 | -2528 | -2741 | 1 | -1746 | -2031 | | | | -3 | -910 | -1370 | | | |
| -1 | 1187 | 1031 | 7 | 1360 | 1202 | -4 | 896 | 688 | -3 | 1245 | 1212 | 2 | -148 | -510 | | 6 20 | 1 | -4 | -168 | - 94 | -2 | 335 | 382 |
| 0 | 746 | 813 | 8 | -2031 | -1846 | -3 | 1505 | 1267 | -2 | 158 | 164 | 3 | -148 | -281 | -4 | 1085 | 744 | -3 | -2070 | -1864 | -1 | -855 | -1172 |
| 1 | 1078 | 1126 | 9 | 1145 | 1033 | -2 | 2018 | 1914 | -1 | 437 | 405 | 4 | -1270 | -1356 | -2 | 581 | 440 | -2 | 194 | 341 | 0 | -1102 | -1782 |
| 2 | -958 | -972 | 10 | 657 | 642 | -1 | 3050 | 3016 | 0 | 168 | 197 | | 6 4 | 1 | -1 | 1216 | 1134 | 0 | 137 | 163 | | | |
| 3 | 1821 | 1622 | 11 | 542 | 498 | 0 | -137 | -518 | 1 | 1888 | 1984 | | | | | | | 1 | -1723 | -1746 | | | |
| 4 | -887 | -842 | | | | 1 | 2806 | 3167 | 2 | 2424 | 2290 | -4 | -1008 | -840 | 0 | -536 | -635 | 2 | 137 | 268 | | | |
| 5 | 901 | 847 | | | | 2 | -321 | -448 | 3 | 711 | 531 | -3 | -1749 | -1701 | 1 | 125 | 136 | 3 | -209 | -319 | | | |

$11\bar{2}$, 150, 200 and 400, the observed structure factors are considerably smaller than the calculated ones. This is probably due to extinction. No corrections were applied to these reflections and they were included

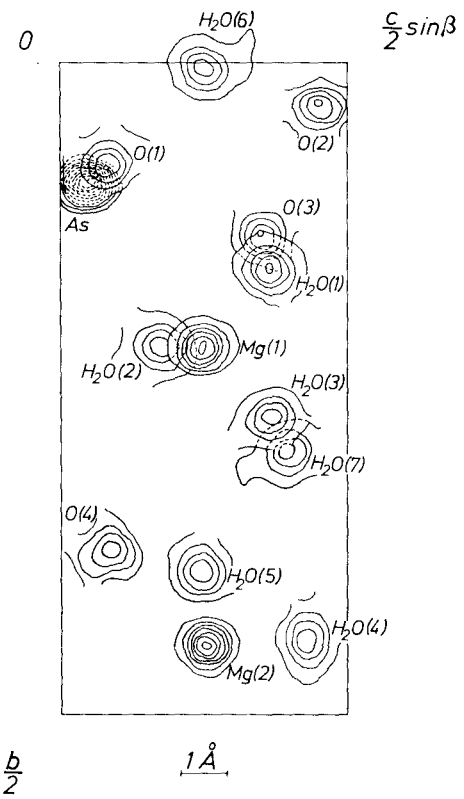


Fig. 1. A composite electron-density map of the asymmetric unit calculated on sections through the atomic peaks. The contouring is at intervals of 10 e Å$^{-3}$ around the arsenic atom, 6 e Å$^{-3}$ around the magnesium atoms and 4 e Å$^{-3}$ around the other atoms. The first contour is at zero, but this contour is not always completely indicated to avoid confusion with spurious peaks

in the refinement. The structure factors in Table 3 are the absolute values multiplied by 25. A composite electron-density map of an asymmetric unit is given in Fig. 1. In this map the largest spurious peaks are of height 6.3 e/Å$^3$ in the ripple around the arsenic atom and 3.4 e/Å$^3$ in the remainder of the synthesis.

## Discussion of the structure

### General

The structure consists of $HAsO_4$ distorted tetrahedra, two crystallographically independent $Mg \cdot (H_2O)_6$ octahedra and isolated water molecules, held together by hydrogen bonds. These bonds are predo-

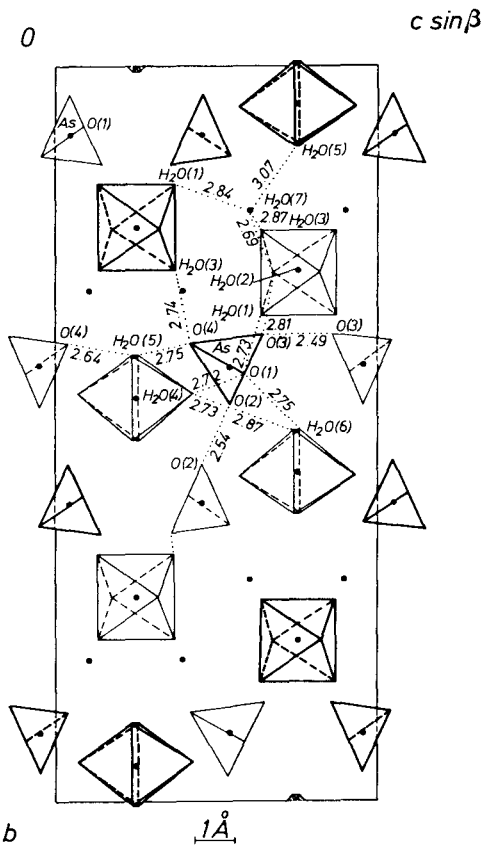


Fig. 2. The $a$-axis projection of the complete cell. Those groupings associated with arsenic or magnesium atoms or isolated water molecules with $x$ coordinate equal to or greater than 0.5 are drawn with bold lines. One independent set of proposed hydrogen bonds is indicated by broken lines

minantly electrostatic in character (MOELLER, 1952; SMITH, 1955; PAULING, 1960) and so the bonding may also be thought of as ionic. Figure 2 shows the relationship between the units of which the structure is composed.

## Bond lengths and angles uncorrected for thermal vibration

### $HAsO_4$ tetrahedron

The individual values of the arsenic-oxygen and oxygen-oxygen distances are given in Table 4. The weighted mean values are:

| | |
|---|---|
| arsenic—oxygen | $1.691 \pm 0.003$ Å |
| oxygen—oxygen | $2.754 \pm 0.003$ Å. |

In this and subsequent tables, atoms in equivalent positions are represented by superscripts

for general positions

| | | | |
|---|---|---|---|
| I | $\bar{x}$, | $\bar{y}$, | $\bar{z}$ |
| II | $\bar{x}$, | $y$, | $\frac{1}{2} - z$ |
| III | $x$, | $\bar{y}$, | $\frac{1}{2} + z$ |
| IV | $\frac{1}{2} + x$, | $\frac{1}{2} + y$, | $\frac{1}{2} + z$ |
| V | $\frac{1}{2} - x$, | $\frac{1}{2} - y$, | $\frac{1}{2} - z$ |
| VI | $\frac{1}{2} - x$, | $\frac{1}{2} + y$, | $\bar{z}$ |
| VII | $\frac{1}{2} + x$, | $\frac{1}{2} - y$, | $z$ |

while for special positions

| | | | |
|---|---|---|---|
| I | 0, | $\bar{y}$, | $\frac{3}{4}$ |
| II | $\frac{1}{2}$, | $\frac{1}{2} + y$, | $\frac{1}{4}$ |
| III | $\frac{1}{2}$, | $\frac{1}{2} - y$, | $\frac{3}{4}$ |

The mean value for the arsenic-oxygen bond is in reasonable agreement (within three times the larger standard deviation) with the average result of most other investigations (Table 5). There are, however, two exceptions, the results of BAUR and KHAN (1970) and TILLMANNS and BAUR (1971), both of which are considerably smaller than the present one. In the case of the first of these (BAUR and KHAN, 1970), the structure determined, $Na_2HAsO_4 \cdot 7H_2O$, had been solved by FERRARIS and CHIARI (1970b) who obtained a significantly longer mean As—O bond, so much so that BAUR and KHAN (1970) concluded "that systematic errors in the measurement of one or both data sets played a larger role than we might have wished". In view of the general agreement of FERRARIS and CHIARI's (1970b) result with those found from other structures it would appear more probable that BAUR and KHAN's (1970) data contains the systematic error. In the case of the result of TILLMANNS and BAUR (1971), it would appear from the published work that the experimental procedure was the same as for BAUR and KHAN (1970), in which case the same unknown systematic error may have re-occurred. Whatever the reason these are the two results which are significantly low. Incidentally, in Table 5 not all authors gave the errors in the mean, some have been calculated from the errors in the individual distances.

The $HAsO_4$ tetrahedron is very distorted, two bonds are significantly (greater than three lines the standard deviation) larger than the mean while the other two are significantly shorter, the long ones are equal within experimental error and so are the two short ones.

Table 4. *Bond length and angle*

| | Distance | | Distance | | Angle |
|---|---|---|---|---|---|
| | | $HAsO_4$ tetrahedron | | | |
| As—O(1) | 1.661(7) Å | O(1)—O(2) | 2.773(9) Å | O(1)—As—O(2) | 110.3(3)° |
| As—O(2) | 1.718(6) | O(1)—O(3) | 2.764(9) | O(1)—As—O(3) | 110.0(3) |
| As—O(3) | 1.713(6) | O(1)—O(4) | 2.772(9) | O(1)—As—O(4) | 112.9(3) |
| As—O(4) | 1.665(5) | O(2)—O(3) | 2.724(7) | O(2)—As—O(3) | 105.2(3) |
| Mean | 1.691(3) | O(2)—O(4) | 2.781(7) | O(2)—As—O(4) | 110.6(3) |
| | | O(3)—O(4) | 2.726(8) | O(3)—As—O(4) | 107.6(3) |
| | | Mean | 2.754(3) | | |
| | | $Mg \cdot 6H_2O$ octahedra | | | |
| Mg(1)—$H_2O$(1) | 2.120(6) Å | $H_2O$(1)—HO($1^{II}$) | 2.935(8) Å | $H_2O$(1)—Mg(1)—$H_2O(1^{II})$ | 87.6(2)° |
| Mg(1)—$H_2O$(2) | 2.052(8) | $H_2O$(1)—$H_2O$(2) | 2.889(9) | $H_2O$(1)—Mg(1)—$H_2O$(2) | 87.6(2) |
| Mg(1)—$H_2O$(3) | 2.067(8) | $H_2O(1)—H_2O(2^{II})$ | 3.004(10) | $H_2O(1)—Mg(1)—H_2O(2^{II})$ | 92.1(3) |
| Mg(2)—$H_2O$(4) | 2.055(6) | $H_2O$(1)—$H_2O$(3) | 2.964(8) | $H_2O$(1)—Mg(1)—$H_2O$(3) | 90.1(3) |
| Mg(2)—$H_2O$(5) | 2.093(7) | $H_2O$(2)—$H_2O$(3) | 2.967(10) | $H_2O$(2)—Mg(1)—$H_2O$(3) | 92.2(3) |
| Mg(2)—$H_2O$(6) | 2.057(7) | $H_2O(2)—H_2O(3^{II})$ | 2.863(11) | $H_2O(2)—Mg(1)—H_2O(3^{II})$ | 88.1(3) |
| Mean | 2.077(3) | $H_2O(3)—H_2O(3^{II})$ | 2.984(12) | $H_2O(3)—Mg(1)—H_2O(3^{II})$ | 92.4(3) |
| | | $H_2O$(4)—$H_2O$(5) | 2.873(10) | $H_2O$(4)—Mg(2)—$H_2O$(5) | 87.7(3) |
| | | $H_2O(4)—H_2O(5^{II})$ | 2.869(9) | $H_2O(4)—Mg(2)—H_2O(5^{II})$ | 87.5(3) |
| | | $H_2O$(4)—$H_2O$(6) | 2.976(10) | $H_2O$(4)—Mg(2)—$H_2O$(6) | 92.7(3) |
| | | $H_2O(4)—H_2O(6^{II})$ | 2.960(10) | $H_2O(4)—Mg(2)—H_2O(6^{II})$ | 92.1(3) |
| | | $H_2O(5)—H_2O(5^{II})$ | 2.944(10) | $H_2O(5)—Mg(2)—H_2O(5^{II})$ | 89.4(3) |
| | | $H_2O$(5)—$H_2O$(6) | 2.969(8) | $H_2O$(5)—Mg(2)—$H_2O$(6) | 91.4(3) |
| | | $H_2O(6)—H_2O(6^{II})$ | 2.855(11) | $H_2O(6)—Mg(2)—H_2O(6^{II})$ | 87.9(3) |
| | | Mean | 2.935(3) | | |

However, distortion of arsenate and $HAsO_4$ tetrahedra is very common, it occurs in all except two of the compounds listed in Table 5, the exceptions being pharmacosiderite (BUERGER, DOLLASE and GARAYCOCHEA-WITTKE, 1967) and $Na_3AsO_4(NaOH)_{0-0.25} \cdot H_2O$ (TILLMANNS and BAUR, 1971).

In all cases of distorted arsenate tetrahedra reported, oxygen atoms of the tetrahedron are involved in coordination to the cation and it has beeen pointed out (CALVO and LEUNG, 1969) that the shortest arsenic-oxygen bond distance involves the oxygen with the lowest coordination number. The effect of this can be appreciable, FINNEY (1966) found individual arsenic-oxygen bonds in the range 1.615 Å to 1.773 Å. However in rösslerite none of the $HAsO_4$ oxygen atoms is coordinated to the magnesium atom and this effect must be absent.

CRUICKSHANK (1961) pointed out that for $HSO_4$ and $HPO_4$ the

Table 5. *Comparison of observed bond lengths*

Arsenic—oxygen

| Reference | Compound | As—O |
|---|---|---|
| GHOSE, FEHLMANN and SUNDARALINGAM (1965) | $Cu_3AsO_4(OH)_3$ | 1.704(14) Å |
| FINNEY (1966) | $Cu_2(AsO_4)OH \cdot 3H_2O$ | 1.683(6) |
| JOST, WORZALA and THILO (1966) | $As_2O_5 \cdot \frac{5}{3} H_2O$ | 1.693(12) |
| CALLERI and FERRARIS (1967) | $CaH(AsO_4) \cdot H_2O$ | 1.682(3) |
| BUERGER, DOLLASE and GARAYCOCHEA-WITTKE (1967) | Pharmacosiderite | 1.69(1) |
| * POULSEN and CALVO (1968) | $Cu_3(AsO_4)_2$ | 1.684(7) |
| CALVO and LEUNG (1969) | $Zn_2Cu(AsO_4)_2$ | 1.678(7) |
| FERRARIS (1969) | $CaH(AsO_4) \cdot 2H_2O$ | 1.686(4) |
| * FERRARIS and CHIARI (1970a) | $CaHAsO_4$ | 1.685(3) |
| FERRARIS and CHIARI (1970b) | $Na_2HAsO_4 \cdot 7H_2O$ | 1.688(2) |
| BAUR and KHAN (1970) | $Na_2HAsO_4 \cdot 7H_2O$ | 1.678(2) |
| KHAN, STRAUMANIS and JAMES (1970) | $(NH_4)_2HAsO_4$ | 1.695(4) |
| CHIARI and FERRARIS (1971) | $Ca(H_2AsO_4)_2$ | 1.686(3) |
| TILLMANNS and BAUR (1971) | $Na_3AsO_4 \cdot (NaOH)_{0-0.25} \cdot 12H_2O$ | 1.669(4) |
| This work | $MgHAsO_4 \cdot 7H_2O$ | 1.691(3) |

* Two independent tetrahedra investigated.

Table 5. *(Continued)*

Magnesium—oxygen

| Reference | Compound | Mg—O |
|---|---|---|
| Margulis and Templeton (1962) | $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ | 2.064(3) Å |
| Nardelli, Fava and Giraldi (1962) | $MgS_2O_3 \cdot 6H_2O$ | 2.083(6) |
| Zalkin, Ruben and Templeton (1964) | $MgSO_4 \cdot 6H_2O$ | 2.066(1) |
| ** Baur (1964a) | $MgSO_4 \cdot 4H_2O$ | 2.077(2) |
| Baur (1964b) | $MgSO_4 \cdot 7H_2O$ | 2.065(2) |
| Johnson (1965) | $[Mg(H_2O)_6][MgC_6H_5O_7 \cdot H_2O]_2 \cdot 2H_2O$ | 2.074(1) |
| Sasvari and Jeffrey (1966) | $MgCl_2 \cdot 12H_2O$ | 2.062(4) |
| Sutor (1967) | $MgHPO_4 \cdot 3H_2O$ | 2.083(3) |
| Baggio, Amzel and Becka (1969) | $MgS_2O_3 \cdot 6H_2O$ | 2.068(2) |
| Whitaker and Jeffery (1970) | $MgNH_4PO_4 \cdot 6H_2O$ | 2.071(1) |
| Stephan, MacGillavry and Koch (1972) | $KHCO_3 \cdot MgCO_3 \cdot 4H_2O$ | 2.072(2) |
| Stephan and MacGillavry (1972) | $MgCO_3 \cdot 3H_2O$ | 2.082(3) |
| Baur and Rolin (1972) | $MgSO_4 \cdot 5H_2O$ | 2.063(2) |
| This work | $MgHASO_4 \cdot 7H_2O$ | 2.077(3) |

** Neutron diffraction study.

bond S—O(H) or P—O(H) is longer than those of the type S—O or P—O. A similar effect has been found in $HAsO_4$ groups by Calleri and Ferraris (1967), Ferraris (1969), Ferraris and Chiari (1970a, b), Baur and Khan (1970) and Khan, Straumanis and James (1970), all of whom found the phenomena of one long bond (in the range 1.721 Å to 1.767 Å) and three shorter ones.

Thus in the present case one expects one long and three short bonds of approximately equal length. However, instead, two long bonds of equal length are obtained together with two short ones of equal length. This can only be explained by the hydrogen being connected to two oxygen atoms, O(2) and O(3), the true configuration being $AsO_2(OH_{1/2})_2$. Further evidence for this configuration is obtained when considering the distances of the neighbouring oxygen atoms to this tetrahedron.

As already mentioned, with the exception of two results (Baur and Khan, 1970; Tillmanns and Baur, 1971), the mean arsenic-oxygen distances are in good agreement with each other regardless of whether

Table 6. *Comparison of observed angles in hydrogen arsenate ions*

| Reference | | Mean angles | | |
|---|---|---|---|---|
| | | O—As—O | O—As—O(H) | O(H)—As—O(H) |
| CALLERI and FERRARIS (1967) | $CaH(AsO_4) \cdot H_2O$ | 111.3° | 107.7° | |
| FERRARIS (1969) | $CaH(AsO_4) \cdot 2H_2O$ | 112.2 | 106.6 | |
| FERRARIS and CHIARI (1970a)* | $CaHAsO_4$ | 109.8 | 109.1 | |
| FERRARIS and CHIARI (1970b) | $Na_2HAsO_4 \cdot 7H_2O$ | 112.8 | 105.9 | |
| BAUR and KHAN (1970) | $Na_2HAsO_4 \cdot 7H_2O$ | 112.9 | 105.8 | |
| KHAN, STRAUMANIS and JAMES (1970) | $(NH_4)_2HAsO_4$ | 111.9 | 106.9 | |
| CHIARI and FERRARIS (1971)** | $Ca(H_2AsO_4)_2$ | 118.4 | 108.7 | 102.2° |
| | | | 113.6 | 105.6 |
| This work | | 112.9 | 109.6 | 105.2 |

* Two independent tetrahedra investigated, but only one included because the hydrogen bonding about the other could not be determined.

** Two independent tetrahedra investigated, results given for both.

the group is an arsenate or $HAsO_4$ group. This suggests that individual bond lengths alter to achieve electrostatic balance irrespective of the individual bonding.

In addition to distortion of the $HAsO_4$ tetrahedron due to different bond lengths, there is also angular distortion. The smallest O—As—O is that involving O(2) and O(3), i.e. between the $(OH_{1/2})$ groups, while the largest is that involving O(1) and O(4). This is to be expected; there will be mutual repulsion between the oxygen atoms and this will be dependent on the distance between them. For the same O—As—O, the repulsion between oxygen atoms further away from the arsenic will be less than for oxygen atoms closer to the arsenic and in the absence of outside forces the angles subtended at the arsenic would alter so that the repulsions would become equal. Thus one would expect O—As—O to be greater than O—As—O(H), which in turn would be greater than O(H)—As—O(H) and this is obtained in the present case. Examination of the mean angles for other $HAsO_4$ and $H_2AsO_4$ ions shows the same effect (Table 6). However, in general the effect is less obvious, detailed examination of individual angles indicates, with the exception of one compound $Na_2HAsO_4 \cdot 7H_2O$ (FERRARIS and CHIARI, 1970b; BAUR and KHAN, 1970) that the

ranges of angles about the mean are so large that there are considerable overlaps of individual groups. This is probably due to many of the oxygen atoms being simultaneously coordinated to the cation and being subjected to further distortion due to this. In the present case and that of $Na_2HAsO_4 \cdot 7H_2O$ (FERRARIS and CHIARI, 1970b; BAUR and KHAN, 1970), none of the arsenate oxygen atoms is coordinated to the cation and thus there can be no distortion from this cause.

## $Mg \cdot (H_2O)_6$ octahedron

The individual values of the magnesium-oxygen and oxygen-oxygen distances are given in Table 4. The weighted mean values are:

| | |
|---|---|
| magnesium—oxygen | $2.077 \pm 0.003$ Å |
| oxygen—oxygen | $2.935 \pm 0.003$ Å |

There are two independent octahedra in the structure, but neither of the means of each of these is significantly different from the mean of both.

Detailed examination of the individual values indicates that the octahedron is very distorted, the range of magnesium-oxygen distances being $11\sigma$, where $\sigma$ is the individual standard deviation. In addition the "right angles" vary between $87.5 \pm 0.3°$ and $92.7 \pm 0.3°$, i.e. differences of $8\sigma$ and $9\sigma$ from the regular value. Some of this distortion may be due to thermal vibration. The average value for the magnesium-oxygen distance is compared with those obtained by other investigators (Table 5); the agreement is reasonable. It is interesting to note that some distortion of the $Mg \cdot (H_2O)_6$ octahedron occurs in every compound in this table.

A detailed examination of the hydrogen bonding of this compound, see below, indicates that, very probably, the water molecules $H_2O(2)$, $H_2O(3)$, $H_2O(4)$ and $H_2O(6)$ are each bonded to three atoms; electrostatically to a magnesium and hydrogen-bonded to two oxygen atoms, which may be either an arsenate oxygen or an isolated water molecule. However, water molecules $H_2O(1)$ and $H_2O(5)$ are associated with four bonds; three of these are the same as for the other water molecules but in addition they are both acceptor atoms for hydrogen bonds from the isolated water molecule $H_2O(7)$. It is interesting to note that both these water molecules are considerably further away from the

magnesium atom than the others, the mean distance for these two is 2.109 ± 0.005 Å compared with the mean for the other four of 2.057 ± 0.004 Å. This phenomena has been noticed previously. In the case of magnesium sulfate heptahydrate BAUR (1964b) found that the average magnesium-oxygen (water) bond length was 2.096 Å when the oxygen atom was an acceptor atom for a hydrogen bond. On the other hand, in the cases of the oxygen atom not being an acceptor for a hydrogen bond, the mean magnesium-oxygen (water) bond length was 2.050 Å. He suggests that for acceptor atoms the sum of the electrostatic bonds is increased and the magnesium-oxygen (water) distance lengths to achieve electrostatic balance. The present structure is in excellent agreement with this idea, but the distortion may be due to other factors in addition. Considerable variation, 2.046 to 2.108 Å, of the magnesium-water distance occurs in magnesium ammonium phosphate hexahydrate (WHITAKER and JEFFERY, 1970) in which there are no inter-water hydrogen bonds.

Consider now the sum of the angles Mg—$H_2O$—$O_a$, Mg—$H_2O$—$O_b$ and $O_a$—$H_2O$—$O_b$ about each of the six water molecules (Table 7). These sums are 348.4 ± 0.5°, 360.0 ± 0.6°, 348.2 ± 0.6°, 360.1 ± 0.6°, 341.1 ± 0.5° and 356.5 ± 0.5° for the water molecules designated one to six, respectively, i.e. each group of magnesium, water and two bound oxygen atoms and/or water molecules is approximately coplanar This has already been noted before by WHITAKER and JEFFERY (1970) who found an average value of 356° in struvite compared with an average of 352° in the present substance. However, in the present case, two water molecules, $H_2O(1)$ and $H_2O(5)$, are acceptor atoms for hydrogen bonds and this would presumably distort the atomic configuration. This is borne out by the results, the deviation from planar is larger for these two atoms. Moreover the directions of the deviations are such that they could be due to mutual repulsion by the charge in the acceptor bond. If these two are excluded from

Table 7. *Angles around each water molecule in the* $Mg \cdot (H_2O)_6$ *octahedra*

| $O_a$ | $H_2O$ | $O_b$ | Mg—$H_2O$—$O_a$ | Mg—$H_2O$—$O_b$ | $O_a$—$H_2O$—$O_b$ | Sum |
|---|---|---|---|---|---|---|
| O(1) | $H_2O(1)$ | O(3) | 119.5(3)° | 113.0(3)° | 115.9(3)° | 348.4(5)° |
| O(3) | $H_2O(2)$ | $H_2O(7)$ | 127.3(4) | 126.4(4) | 106.3(3) | 360.0(6) |
| $O(4^{V})$ | $H_2O(3)$ | $H_2O(7)$ | 135.3(4) | 124.5(3) | 88.4(3) | 348.2(6) |
| $O(1^{V})$ | $H_2O(4)$ | O(2) | 130.3(4) | 122.5(3) | 107.3(3) | 360.1(6) |
| $O(4^{V})$ | $H_2O(5)$ | $O(4^{VII})$ | 129.0(3) | 122.3(3) | 89.8(3) | 341.1(5) |
| $O(1^{VI})$ | $H_2O(6)$ | $O(2^{IV})$ | 115.6(3) | 127.6(3) | 113.3(3) | 356.5(5) |

consideration the average sum about the other four water molecules becomes 356° in even better agreement with coplanarity and the case of struvite (WHITAKER and JEFFERY, 1970).

## Hydrogen bonding

No attempt was made to determine the positions of the hydrogen atoms due to insufficient accuracy of the data. However, the position of the hydrogen bonds could be inferred.

## $HAsO_4$ tetrahedron

As already mentioned, the arsenic-oxygen bond lengths suggest a configuration of $AsO_2(OH_{1/2})_2$ and this configuration is confirmed by finding two very short inter-tetrahedra bonds. These bonds are

$$O(2)—O(2^{I}) = 2.541 \pm 0.008 \text{ Å}$$

$$O(3)—O(3^{II}) = 2.490 \pm 0.008 \text{ Å}$$

and if the space group is correct, the position of the symmetry elements demand that these hydrogen bonds must either be symmetrical or, in each bond, the hydrogen atom must be at random in one of two positions, in either case the atomic configuration becomes $AsO_2(OH_{1/2})_2$ in agreement with the bonding inferred from the arsenic-oxygen-bonds. The fact that the inter-oxygen distance in both these hydrogen bonded pairs is so short suggests the possibility that both these bonds are symmetrical (PIMENTEL and MCCLELLAN, 1960a).

## Water molecules

As already mentioned the position of the hydrogen bonds could be obtained by making certain assumptions:

a) there is no hydrogen bonding between water molecules within the same $Mg \cdot (H_2O)_6$ octahedron. On those occassions where the hydrogen atoms in this octahedron have been determined directly from difference Fourier syntheses, no hydrogen bonding has been observed between water molecules in the same octahedron (ZALKIN, RUBEN and TEMPLETON, 1964; WHITAKER and JEFFERY, 1970)

b) hydrogen bonds will be, in general, shorter than contacts not involving hydrogen bonding

Table 8. *Oxygen-oxygen distances involved in hydrogen bonding*
See Table 4 for oxygen-oxygen distances within the $Mg \cdot (H_2O)_6$ octahedra

| $O_a$ | $H_2O$ | $O_b$ | $O_a$—$H_2O$ | $H_2O$—$O_b$ | $O_a$—$H_2O$—$O_b$ |
|---|---|---|---|---|---|
| O(1) | $H_2O(1)$ | O(3) | 2.733(8) Å | 2.696(9) Å | 115.9(3)° |
| O(3) | $H_2O(2)$ | $H_2O(7)$ | 2.813(9) | 2.689(9) | 106.3(3) |
| $O(4^V)$ | $H_2O(3)$ | $H_2O(7)$ | 2.740(9) | 2.871(11) | 88.4(3) |
| $O(1^V)$ | $H_2O(4)$ | $O(2^V)$ | 2.717(9) | 2.727(10) | 107.3(3) |
| $O(4^V)$ | $H_2O(5)$ | $O(4^{VII})$ | 2.639(9) | 2.754(9) | 89.8(3) |
| $O(1^{VI})$ | $H_2O(6)$ | $O(2^{IV})$ | 2.746(9) | 2.868(10) | 113.3(3) |
| $H_2O(1^V)$ | $H_2O(7)$ | $H_2O(5)$ | 2.839(10) | 3.070(9) | 106.1(3) |

c) water molecules cannot donate more than two hydrogen atoms to the bonding scheme and the two receptor atoms subtend an angle of about 109° at the donator.

Based upon these three assumptions it was possible to infer a system of hydrogen bonds which involved the fourteen shortest oxygen-oxygen distances [excluding those in the same $Mg \cdot (H_2O)_6$ octahedron]. A list of these hydrogen-bonded distances and the angle $O_a$—$H_2O$—$O_b$ is given in Table 8 and the proposed bonding scheme given diagrammatically in Fig. 3. The bond lengths involved in hydrogen bonding vary from 2.639 ± 0.009 Å to 3.070 ± 0.009 Å; these lengths are reasonable when compared with hydrogen bonding in other inorganic crystals (PIMENTAL and MCCLELLAN, 1960b). The

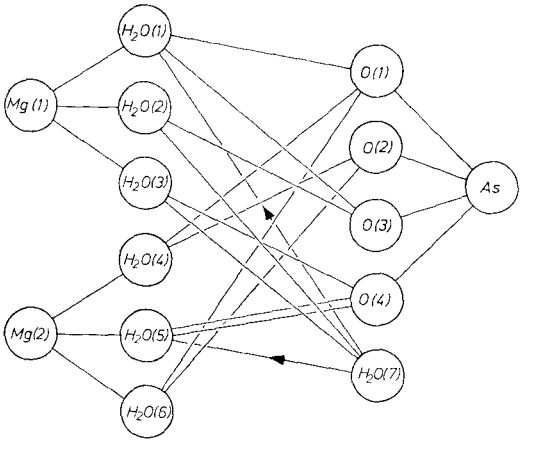


Fig. 3. Schematic diagram of proposed bonding

shortest distance not involved in this bonding scheme is considerably longer, $3.256 \pm 0.009$ Å between $H_2O(5)$ and $H_2O(7^{II})$. The angles subtended by the receptor atoms at the donator vary considerably (Table 8) from the tetrahedral angle. This is not unusual. In oxalic acid dihydrate GARRETT (1954) found a value of this angle as low as 84°, while in copper sulfate pentahydrate BACON and CURRY (1962) found values in the range 105° to 130°. In both cases neutron-diffraction techniques were used and it was found that the hydrogen bond was non-collinear so that the hydrogen atoms subtended an angle of 109° at the water oxygen although the acceptor atoms did not. The same effect has also been found in cupric chloride dihydrate (PETERSON and LEVY, 1957) and chromium potassium alum (BACON and GARDNER, 1958). Thus it can be seen that the distances and angles in the present scheme are not unreasonable.

## Analyses of thermal vibrations

The root-mean-square displacements and the direction cosines of the axes of the thermal-vibration ellipsoids with respect to orthogonal axes are given in Table 9. The errors in the displacements were obtained by calculating the vibration ellipsoids for the values in Table 2 plus the standard deviation, and minus the standard deviation and averaging over similar atoms.

In the case of the arsenic atom, the vibration ellipsoid is a prolate sphere with its unique axis 27° from the direction of O(2); however, the distortion from isotropic is small. For the arsenate oxygen atoms the vibration ellipsoids approximate to oblate spheres, the shortest axes of which make angles of 14°, 39°, 44° and 48° with the respective arsenic-oxygen bond, while the longest axes make angles of 77°, 71°, 67° and 64°, respectively.

The magnesium atoms have very dissimilar vibration ellipsoids, the first is very eccentric, the longest axis is inclined at almost equal angles to directions of $H_2O(1)$, $H_2O(2)$ and $H_2O(3)$; 52°, 59° and 53° respectively while the shortest axis is almost equally inclined to $H_2O(1)$ and $H_2O(3)$, 44° and 46° respectively and almost perpendicular to $H_2O(2)$, 88°. For the second magnesium atom, the vibration ellipsoid is a prolate sphere within experimental error. Again the longest axis is almost equally inclined to the directions of the three water molecules, the angles between this axis and the three directions being 47°, 59° and 59° respectively for $H_2O(4)$, $H_2O(5)$ and $H_2O(6)$.

Of the six water molecules coordinated to a magnesium atom, the vibration ellipsoids of five approximate to prolate spheres while that of the sixth, $H_2O(5)$, approximates to an oblate sphere. It is noticeable that the longest axes of vibration are approximately perpendicular to relevant magnesium-water bond, the angles being 80°, 83°, 81°, 84°, 84° and 90° for the water molecules numbered one to six, respectively. The shortest axes of vibration are in general approximately parallel to the magnesium-water bond, the angles being 22°, 46°, 13°, 54°, 11° and 0°, respectively; however, due to most of the vibration ellipsoids approximating to prolate spheres, the latter angles probably contain large errors.

Table 9. *Root-mean-square displacements and orientation with respect to orthogonal axes.* (*I* parallel to *a*, *J* parallel to *b*, *K* perpendicular to *a* and *b*)

| | Root-mean-square displacement | Direction cosines with respect to | | |
|---|---|---|---|---|
| | | *I* | *J* | *K* |
| As | 0.109 ± 2 | −0.332 | −0.847 | −0.414 |
| | 0.095 ± 2 | 0.129 | −0.476 | 0.870 |
| | 0.084 ± 2 | 0.935 | −0.235 | −0.267 |
| O(1) | 0.139 ± 11 | 0.075 | 0.559 | 0.826 |
| | 0.113 ± 11 | −0.221 | −0.798 | 0.560 |
| | 0.066 ± 11 | 0.972 | −0.224 | 0.064 |
| O(2) | 0.159 ± 11 | −0.561 | −0.026 | −0.827 |
| | 0.134 ± 11 | 0.820 | 0.123 | −0.560 |
| | 0.059 ± 11 | 0.116 | −0.992 | −0.047 |
| O(3) | 0.135 ± 11 | −0.607 | −0.704 | −0.368 |
| | 0.112 ± 11 | −0.264 | −0.256 | 0.929 |
| | 0.081 ± 11 | 0.749 | −0.662 | 0.032 |
| O(4) | 0.137 ± 11 | −0.373 | 0.928 | −0.013 |
| | 0.131 ± 11 | 0.595 | 0.250 | 0.764 |
| | 0.078 ± 11 | 0.712 | 0.277 | −0.645 |
| Mg(1) | 0.142 ± 10 | 0.117 | 0.000 | 0.993 |
| | 0.079 ± 10 | 0.993 | 0.000 | −0.117 |
| | 0.041 ± 10 | 0.000 | 1.000 | 0.000 |
| $H_2O(1)$ | 0.157 ± 11 | −0.003 | −0.522 | 0.853 |
| | 0.099 ± 11 | 0.819 | 0.488 | 0.302 |
| | 0.074 ± 11 | 0.574 | −0.699 | −0.426 |

Table 9. *(Continued)*

| | Root-mean-square displacement | Direction cosines with respect to | | |
|---|---|---|---|---|
| | | *I* | *J* | *K* |
| $H_2O(2)$ | 0.221 ± 11 | −0.271 | −0.275 | 0.923 |
| | 0.126 ± 11 | 0.778 | −0.627 | 0.041 |
| | 0.102 ± 11 | 0.567 | 0.729 | 0.384 |
| $H_2O(3)$ | 0.233 ± 11 | −0.457 | −0.328 | −0.827 |
| | 0.129 ± 11 | 0.713 | −0.691 | −0.119 |
| | 0.105 ± 11 | −0.532 | −0.644 | 0.550 |
| Mg(2) | 0.101 ± 10 | 0.773 | 0.000 | 0.634 |
| | 0.078 ± 10 | 0.000 | 1.000 | 0.000 |
| | 0.072 ± 10 | −0.634 | 0.000 | 0.773 |
| $H_2O(4)$ | 0.199 ± 11 | −0.180 | −0.983 | −0.035 |
| | 0.137 ± 11 | 0.620 | −0.141 | 0.772 |
| | 0.096 ± 11 | 0.763 | −0.118 | −0.635 |
| $H_2O(5)$ | 0.148 ± 11 | −0.256 | −0.058 | 0.965 |
| | 0.139 ± 11 | 0.741 | 0.630 | 0.234 |
| | 0.078 ± 11 | 0.621 | −0.775 | 0.118 |
| $H_2O(6)$ | 0.242 ± 11 | 0.647 | −0.592 | 0.480 |
| | 0.138 ± 11 | −0.317 | 0.364 | 0.876 |
| | 0.064 ± 11 | 0.694 | 0.719 | −0.048 |
| $H_2O(7)$ | 0.195 ± 11 | 0.220 | 0.015 | 0.975 |
| | 0.164 ± 11 | 0.940 | 0.265 | −0.216 |
| | 0.094 ± 11 | 0.262 | −0.964 | −0.044 |

## Bond lengths corrected for thermal vibration

Busing and Levy (1964) have pointed out that one of the effects of thermal vibration is to alter the apparent bond lengths and showed how to correct for these effects. Corrected bond lengths have been calculated for arsenic-oxygen and magnesium-oxygen for three cases; (A) atoms are vibrating in phase, (B) the lighter atoms are riding on the inner ones, and (C) the atoms are moving independently of each other. The values are given in Table 10.

In the case of arsenic-oxygen bond lengths one would expect that the oxygen atoms would ride on the arsenic, in which case the vibrations parallel to the bond would be the same for both arsenic and oxygen, while the largest vibrations of the oxygen atoms would be

Table 10. *Bond lengths corrected for thermal vibrations*

| | Uncorrected bond length | Standard deviation | Corrected bond lengths | | |
|---|---|---|---|---|---|
| | | | *A* (in phase) | *B* (riding) | *C* (independent) |
| As—O(1) | 1.661 Å | 0.007 Å | 1.662 Å | 1.665 Å | 1.677 Å |
| As—O(2) | 1.718 | 0.006 | 1.719 | 1.723 | 1.734 |
| As—O(3) | 1.713 | 0.006 | 1.713 | 1.715 | 1.726 |
| As—O(4) | 1.665 | 0.005 | 1.665 | 1.668 | 1.680 |
| Mean | 1.691 | 0.003 | 1.691 | 1.695 | 1.706 |
| Mg(1)—$H_2O$(1) | 2.120 | 0.006 | 2.120 | 2.123 | 2.132 |
| Mg(1)—$H_2O$(2) | 2.052 | 0.008 | 2.055 | 2.063 | 2.072 |
| Mg(1)—$H_2O$(3) | 2.067 | 0.008 | 2.070 | 2.079 | 2.088 |
| Mg(2)—$H_2O$(4) | 2.055 | 0.006 | 2.058 | 2.064 | 2.071 |
| Mg(2)—$H_2O$(5) | 2.093 | 0.007 | 2.094 | 2.099 | 2.106 |
| Mg(2)—$H_2O$(6) | 2.057 | 0.007 | 2.063 | 2.072 | 2.079 |
| Mean | 2.077 | 0.003 | 2.080 | 2.086 | 2.094 |

perpendicular to the relevant bond. Examination of the vibration ellipsoids indicates that this is only approximately correct, this suggests that some other factors are influencing the vibration ellipsoids and thus some evidence for the independent model. However, for this model, the axes of the vibration ellipsoids would be randomly oriented with respect to the bonds. This is not so and because of this the riding corrected value would appear to be the best; thus

$$\text{arsenic—oxygen} = 1.695 \pm 0.003 \text{ Å}.$$

In the case of the $Mg \cdot (H_2O)_6$ octahedra the shortest r.m.s. displacements of the oxygen atoms are along the bonds, except for $H_2O(2)$ and $H_2O(4)$. However, as most of the vibration ellipsoids approximate to prolate spheres this is probably not very significant, probably more important is that the longest axes are approximately perpendicular to the appropriate Mg—O bond. The value of the smallest displacement is approximately the same as that for the magnesium atom; thus again the riding model would appear to be the best; thus

$$\text{magnesium—oxygen} = 2.086 \pm 0.003 \text{ Å}.$$

MARGULIS and TEMPLETON (1962), BAUR (1964a) and WHITAKER and JEFFERY (1970) have all taken the riding model to be the best for the $Mg \cdot (H_2O)_6$ octahedron. The values obtained are 2.075

$\pm$ 0.003 Å, 2.081 $\pm$ 0.002 Å and 2.081 $\pm$ 0.001 Å, respectively; the present value is in good agreement with these. On the other hand ZALKIN, RUBEN and TEMPLETON (1964) have taken the thermal motion in this octahedron to be "in-phase". Values for both types of motion are given in the present case.

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