Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

$Mg_7(AsO_4)_2(HAsO_4)_4$: a new magnesium arsenate with a very strong hydrogen bond

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Received 1 July 2004
Accepted 23 July 2004
Online 21 August 2004

A new compound, heptamagnesium bis(arsenate) tetrakis(hydrogenarsenate), $Mg_7(AsO_4)_2(HAsO_4)_4$, was synthesized by a hydrothermal method. The structure is based on a three-dimensional framework of edge- and corner-sharing MgO_6, $MgO_4(OH)_2$, MgO_5, $AsO_3(OH)$ and AsO_4 polyhedra. Average Mg—O and As—O bond lengths are in the ranges 2.056–2.154 and 1.680–1.688 Å, respectively. Each of the two non-equivalent OH groups is bonded to both an Mg and an As atom. One OH group is involved in a very short hydrogen bond [O···O = 2.468 (3) Å]. The formula unit is centrosymmetric, with all atoms in general positions except for one Mg atom, which has site symmetry $\overline{1}$. The compound is isotypic with $Mn_7(AsO_4)_2(HAsO_4)_4$ and $M_7(PO_4)_2(HPO_4)_4$, where M is Fe, Co or Mn.

Comment

$Mg_7(AsO_4)_2(HAsO_4)_4$ is a new magnesium arsenate hydrogenarsenate and was synthesized by a hydrothermal method. It is the sixth simple magnesium arsenate containing protonated AsO_4 tetrahedra. The other compounds known are the two minerals brassite ($MgHAsO_4 \cdot 4H_2O$; Brasse & Remy, 1970; Fontan *et al.*, 1973; Protas & Gindt, 1976) and rösslerite ($MgHAsO_4 \cdot 7H_2O$; Ferraris & Franchini-Angela, 1973; Street & Whitaker, 1973; Whitaker, 1973), and the synthetic compounds $MgHAsO_4 \cdot H_2O$ (Guerin & Mattrat, 1958; Mattrat & Guerin, 1960; Stahl-Brasse, 1972), $MgHAsO_4 \cdot 2.5H_2O$ (Guerin & Mattrat, 1958; Brasse *et al.*, 1971; Stahl-Brasse, 1972), $Mg(H_2AsO_4)_2$ (Grunze & Thilo, 1964) and $Mg(H_2AsO_4)_2 \cdot H_2O$ (Grunze & Thilo, 1964). The crystal structures of the last four compounds have not been determined.

The crystal structure of $Mg_7(AsO_4)_2(HAsO_4)_4$ is based on a three-dimensional framework of edge- and corner-sharing MgO_6, $MgO_4(OH)_2$, MgO_5, $AsO_3(OH)$ and AsO_4 polyhedra (Figs. 1 and 2). The asymmetric unit contains four crystallographically distinct Mg sites, three As sites, twelve O sites and two H sites. The formula unit is centrosymmetric, with all atoms in general positions except for atom Mg1, which has site symmetry $\overline{1}$. Each of the two non-equivalent OH groups is bonded to both an Mg and an As atom.

Atom Mg1 lies at the centre of an $Mg1O_6$ octahedron with considerable bond-length distortion (Table 1). In contrast, $Mg2O_6$ and $Mg4O_4(OH)_2$ represent less distorted octahedra, and atom Mg3 is surrounded by five O ligands, forming a distorted $Mg3O_5$ trigonal bipyramid. Five-coordinate Mg is relatively rare but has also been observed in the arsenate $BaMgAs_2O_7$ (Mihajlović *et al.*, 2004), in other oxysalts, such as $BiMg_2VO_6$ (Huang & Sleight, 1992), $LiMgBO_3$ (Norrestam, 1989), $SrMgP_2O_7$ (Tahiri *et al.*, 2002), $Mg_5Na_2(PO_4)_4$ (Yamakawa *et al.*, 1994) and $Mg_3Ti_4P_6O_{24}$ (Benmoussa *et al.*, 1990), and in the minerals farringtonite [$Mg_3(PO_4)_2$; Nord & Kierkegaard, 1968] and grandidierite [$(Mg,Fe)Al_3SiBO_9$; Stephenson & Moore, 1968]. The Mg2-, Mg3- and Mg4-centred polyhedra share common edges to form zigzag chains nearly parallel to [$\overline{1}$01]. In contrast, the $Mg1O_6$ octahedron only shares corners with adjacent polyhedra. Average Mg—O bond lengths are 2.154 Å for Mg1, 2.086 Å for Mg2, 2.056 Å for Mg3 and 2.073 Å for Mg4. These values are reasonably close to the average in oxidic Mg compounds (2.085 Å; Baur, 1981). As expected from the distortion theorem (Brown & Shannon, 1973; Brown, 1981), the largest average bond length is shown by the most distorted octahedron, *viz*. $Mg1O_6$.

The three non-equivalent As atoms all show tetrahedral coordination. The AsO_4 groups are relatively regular, although the two protonated groups, centred by As1 and As3, show a stronger angular and bond-length distortion in comparison with the unprotonated $As2O_4$ tetrahedron. The two As—OH bonds, As1—O4^{iv} and As3—O11^{viii} [symmetry codes: (iv) $-x, -y, -1-z$; (viii) $x-1, y, z$], are distinctly longer than the As—O bonds (Table 1), which is in good agreement with earlier observations that protonated XO_4 (X is P or As) oxyanion groups generally show an elongated X—OH distance (Ferraris, 1970; Ferraris & Ivaldi, 1984). Average

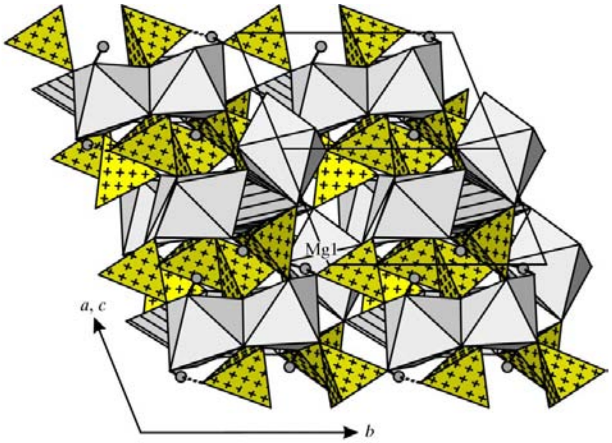

Figure 1
A polyhedral representation of the crystal structure of $Mg_7(AsO_4)_2(HAsO_4)_4$ in a view along [10$\overline{1}$], *i.e.* nearly parallel to the zigzag chains built from the edge-sharing Mg2-, Mg3- and Mg4-centred polyhedra (the $Mg1O_6$ octahedron, centered by Mg1 on the origin, is not involved in this chain). MgO_6 octahedra are unmarked, the distorted $Mg3O_5$ trigonal bipyramids are striped and AsO_4 tetrahedra are marked with crosses. The very short hydrogen bond is also shown (dotted line).

DOI: 10.1107/S010827010401813X

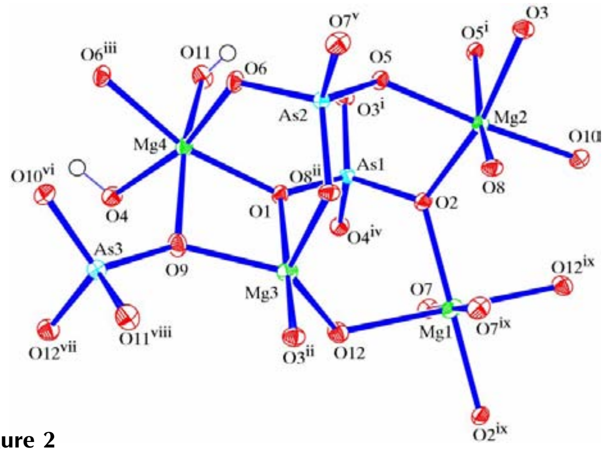

Figure 2
A view of the connectivity in the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $-x, 1 - y, -z$; (iii) $-x, 1 - y, -1 - z$; (iv) $-x, -y, -1 - z$; (v) $x, 1 + y, z$; (vi) $x - 1, y, z - 1$; (vii) $-1 - x, -y, -1 - z$; (viii) $x - 1, y, z$; (ix) $-x, -y, -z$.]

As—O bond lengths are within a close range, with values of 1.688 Å for As1, 1.680 Å for As2 and 1.685 Å for As3. A very short hydrogen bond [2.468 (3) Å] occurs *via* O4—H1···O7^{iv} (Table 2), in contrast with a second, longer, hydrogen bond *via* O11—H2···O10^{i} [2.666 (4) Å; symmetry code: (i) $1 - x, 1 - y, -z$].

A bond-valence analysis of the structure was performed using parameters from Brese & O'Keeffe (1991). This confirms the divalent character of all four Mg atoms, with bond-valence sums of 1.78 (Mg1), 2.10 (Mg2), 1.88 (Mg3) and 2.15 (Mg4) v.u. (valence units). Bond-valence sums for the three As atoms amount to 4.97 (As1), 5.07 (As2) and 5.01 (As3) v.u., and the O ligands have sums of 1.96 (O1), 1.85 (O2), 1.96 (O3), 1.52 (O4 = OH), 2.03 (O5), 2.02 (O6), 1.60 (O7), 2.07 (O8), 1.97 (O9), 1.77 (O10), 1.46 (O11 = OH) and 1.85 (O12) v.u. Thus, the most underbonded O ligand (O7) represents the acceptor of the very strong hydrogen bond (see above), whereas the second most underbonded O ligand (O10) accepts the less strong second hydrogen bond.

The title compound is isotypic with $Mn_7(AsO_4)_2(HAsO_4)_4$ (Rojo *et al.*, 2002) and $M_7(PO_4)_2(HPO_4)_4$, where M is Fe^{II} (Zhou *et al.*, 2002), a mixture of Fe^{II} and Fe^{III} (Vencato *et al.*, 1994), Co^{II} (Lightfoot & Cheetham, 1988; Rojo *et al.*, 2001), and Mn^{II} (Cudennec *et al.*, 1986; Riou *et al.*, 1987; Rojo *et al.*, 2002). The Zn–P, Co–As and Zn–As analogues are apparently not known. The unit-cell volume of the title compound is distinctly smaller than that of its Mn^{II} analogue [491.0 (3) Å^3; Rojo *et al.*, 2002], as would be expected from the effective ionic radii of Mg^{II} and (high-spin) Mn^{II} (0.720 and 0.830 Å, respectively; Shannon, 1976).

Experimental

The title compound was prepared by a hydrothermal method. A mixture of magnesium hydroxide (0.215 g), scandium(III) oxide (0.167 g) and arsenic(V) acid (0.390 g) was added to distilled water (1.5 ml) and the resulting mixture (pH 4.5) sealed in a Teflon-lined stainless steel autoclave. The bomb was placed in an air oven at 493 K, held for 7 d, and then allowed to cool slowly to room temperature in the oven. The reaction products were washed with distilled water and dried slowly at room temperature in air. The large majority of the well crystallized reaction products consisted of previously unknown $Mg_3(AsO_4)_2\cdot H_2O$, forming sprays of very small colourless acicular crystals. Although the crystal size of this phase was insufficient for X-ray data collection, an X-ray powder diffraction pattern clearly indicates that it is isostructural with its Co and Ni analogues (Palazzi *et al.*, 1978), the crystal structures of which are not known. The minor component, $Mg_2(As_2O_7)\cdot 2H_2O$ (Wu *et al.*, 1996), formed similar but larger sprays of acicular crystals. The title compound formed minor quantities of small colourless lenticular to tabular crystals. Their crystal habit is dominated by the pinacoids {102}, {10$\overline{2}$} (uncertain) and {010}; the first two are somewhat curved and show a weak striation parallel to [010]. A fourth reaction product, small colourless rounded prisms of adamite-type $Mg_2(AsO_4)(OH)$ (Rojo *et al.*, 1997), was only present in trace amounts.

Crystal data

$Mg_7(AsO_4)_2(HAsO_4)_4$
$M_r = 1007.72$
Triclinic, $P\overline{1}$
$a = 6.6440$ (10) Å
$b = 8.042$ (2) Å
$c = 9.750$ (2) Å
$\alpha = 104.70$ (3)°
$\beta = 107.89$ (3)°
$\gamma = 101.16$ (3)°
$V = 458.2$ (2) Å^3

$Z = 1$
$D_x = 3.652$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2620 reflections
$\theta = 2.0$–30.0°
$\mu = 11.19$ mm^{-1}
$T = 293$ (2) K
Plate, colourless
0.12 × 0.07 × 0.04 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ψ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.347$, $T_{max} = 0.663$
5192 measured reflections

2649 independent reflections
2411 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 29.9°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.061$
$S = 1.09$
2649 reflections
178 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 1.44P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.09$ e Å^{-3}
$\Delta\rho_{min} = -0.99$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0034 (6)

Table 1
Selected interatomic distances (Å).

Mg1—O7	2.049 (2)	Mg4—O1	2.061 (2)
Mg1—O2	2.132 (2)	Mg4—O6^{iii}	2.074 (2)
Mg1—O12	2.281 (2)	Mg4—O11	2.074 (3)
Mg2—O10	2.024 (2)	Mg4—O9	2.113 (3)
Mg2—O5	2.050 (2)	As1—O3^{i}	1.667 (2)
Mg2—O8	2.063 (2)	As1—O1	1.677 (2)
Mg2—O5^{i}	2.070 (2)	As1—O2	1.689 (2)
Mg2—O2	2.125 (3)	As1—O4^{iv}	1.717 (2)
Mg2—O3	2.185 (3)	As2—O6	1.673 (2)
Mg3—O8^{ii}	2.002 (3)	As2—O5	1.673 (2)
Mg3—O3^{ii}	2.051 (2)	As2—O8^{ii}	1.679 (2)
Mg3—O9	2.054 (2)	As2—O7^{v}	1.693 (2)
Mg3—O12	2.056 (3)	As3—O10^{vi}	1.652 (2)
Mg3—O1	2.119 (2)	As3—O12^{vii}	1.677 (2)
Mg4—O4	2.055 (3)	As3—O9	1.678 (2)
Mg4—O6	2.058 (3)	As3—O11^{viii}	1.731 (2)

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $-x, 1 - y, -z$; (iii) $-x, 1 - y, -1 - z$; (iv) $-x, -y, -1 - z$; (v) $x, 1 + y, z$; (vi) $x - 1, y, z - 1$; (vii) $-1 - x, -y, -1 - z$; (viii) $x - 1, y, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O11—H2⋯O10^{i}	0.71 (5)	1.97 (5)	2.666 (4)	166 (6)
O4—H1⋯O7^{iv}	0.88 (7)	1.59 (7)	2.468 (3)	174 (7)

Symmetry codes: (i) $1 - x, 1 - y, -z$; (iv) $-x, -y, -1 - z$.

The atomic coordinates of isotypic $Fe_7(PO_4)_2(HPO_4)_4$ (Zhou *et al.*, 2002) were used as starting values in the final step of the refinement. H atoms were freely refined and the resulting distances and angles are listed in Table 2. The highest peak is 1.59 Å from the O2 site and the deepest hole is 0.54 Å from the As3 site.

Data collection: *COLLECT* (Nonius, 2003); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999) and *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Financial support from the Austrian Science Foundation (FWF, grant No. P15220-N06) and the International Centre for Diffraction Data (grant No. 90-03 ET) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1465). Services for accessing these data are described at the back of the journal.

References

Baur, W. H. (1981). *Structure and Bonding in Crystals*, Vol. II, edited by M. O'Keeffe & A. Navrotsky, pp. 31–52. New York: Academic Press.

Benmoussa, A., Borel, M. M., Grandin, A., Leclaire, A. & Raveau, B. (1990). *J. Solid State Chem.* **84**, 299–307.

Brasse, R., Mattrat, P. & Guerin, H. (1971). *Bull. Soc. Chim. Fr.* pp. 821–822. (In French.)

Brasse, R. & Remy, F. (1970). *Bull. Soc. Chim. Fr.* pp. 2449–2450. (In French.)

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.

Brown, I. D. (1981). *Structure and Bonding in Crystals*, Vol. II, edited by M. O'Keeffe & A. Navrotsky, pp. 1–30. New York: Academic Press.

Brown, I. D. & Shannon, R. D. (1973). *Acta Cryst.* A**29**, 266–282.

Cudennec, Y., Riou, A. & Gerault, Y. (1986). *C. R. Acad. Sci. Sér. 2*, **302**, 1149–1154. (In French.)

Dowty, E. (1999). *ATOMS*. Version 5.0.4 for Windows and Macintosh. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Ferraris, G. (1970). *Rend. Soc. Ital. Mineral. Petrol.* **26**, 589–598. (In Italian.)

Ferraris, G. & Franchini-Angela, M. (1973). *Acta Cryst.* B**29**, 286–292.

Ferraris, G. & Ivaldi, G. (1984). *Acta Cryst.* B**40**, 1–6.

Fontan, F., Orliac, M., Permingeat, F., Pierrot, R. & Stahl, R. (1973). *Bull. Fr. Minéral. Cristallogr.* **96**, 365–370. (In French.)

Grunze, I. & Thilo, E. (1964). *Z. Anorg. Allg. Chem.* **331**, 102–111. (In German.)

Guerin, H. & Mattrat, P. (1958). *C. R. Acad. Sci.* **247**, 1125–1128. (In French.)

Huang, J. & Sleight, A. W. (1992). *J. Solid State Chem.* **100**, 170–178.

Lightfoot, P. & Cheetham, A. K. (1988). *Acta Cryst.* C**44**, 1331–1334.

Mattrat, P. & Guerin, H. (1960). *Bull. Soc. Chim. Fr.* pp. 601–609. (In French.)

Mihajlović, T., Kolitsch, U. & Effenberger, H. (2004). *J. Alloys Compd.* In the press.

Nonius (2003). *COLLECT*. Nonius BV, Delft, The Netherlands.

Nord, A. G. & Kierkegaard, P. (1968). *Acta Chem. Scand.* **22**, 1466–1474.

Norrestam, R. (1989). *Z. Kristallogr.* **187**, 103–110.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Palazzi, M., Guerin, H. & Lamic, C. (1978). *Bull. Soc. Chim. Fr.* pp. 119–120. (In French.)

Protas, J. & Gindt, R. (1976). *Acta Cryst.* B**32**, 1460–1466. (In French.)

Riou, A., Cudennec, Y. & Gerault, Y. (1987). *Acta Cryst.* C**43**, 821–823. (In French.)

Rojo, J. M., Larranaga, A., Mesa, J. L., Urtiaga, M. K., Pizarro, J. L., Arriortua, M. I. & Rojo, T. (2002). *J. Solid State Chem.* **165**, 171–177.

Rojo, J. M., Mesa, J. L., Lezama, L., Fernandez, J. R., Pizarro, J. L., Arriortua, M. I. & Rojo, T. (2001). *Int. J. Inorg. Mater.* **3**, 67–74.

Rojo, J. M., Mesa, J. L., Pizarro, J. L., Lezama, L., Arriortua, M. I. & Rojo, T. (1997). *J. Solid State Chem.* **132**, 107–112.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Stahl-Brasse, R. (1972). *Bull. Soc. Chim. Fr.* pp. 1761–1767. (In French.)

Stephenson, D. A. & Moore, P. B. (1968). *Acta Cryst.* B**24**, 1518–1522.

Street, R. L. T. & Whitaker, A. (1973). *Z. Kristallogr.* **137**, 246–255.

Tahiri, A. A., El-Bali, B., Lachkar, M., Ouarsal, R. & Zavalij, P. Y. (2002). *Acta Cryst.* E**58**, i9–i11.

Vencato, I., Moreira, L. F., Mattievich, E. & Mascarenhas, Y. P. (1994). *J. Brazil. Chem. Soc.* **5**, 43–51.

Whitaker, A. (1973). *Z. Kristallogr.* **137**, 194–219.

Wu, C.-H., Chen, T.-C. & Wang, S.-L. (1996). *Acta Cryst.* C**52**, 1326–1329.

Yamakawa, J., Yamada, T. & Kawahara, A. (1994). *Acta Cryst.* C**50**, 986–988.

Zhou, B. C., Yao, Y. W. & Wang, R. J. (2002). *Acta Cryst.* C**58**, i109–i110.