Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

$NaMg_4(AsO_4)_3$

Haj Abdallah Anissa,* Ayed Brahim and Haddad Amor

Département de Chimie, Faculté des Sciences de Monastir, 5000 Monastir, Tunisia

Correspondence e-mail: haj_anissa@yahoo.fr

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mg–O) = 0.003 Å
R factor = 0.018
wR factor = 0.045
Data-to-parameter ratio = 10.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 13 May 2004
Accepted 25 May 2004
Online 5 June 2004

The title compound, sodium tetramagnesium tris(arsenate), was prepared by solid-state reaction at 1243 K. The structure is built up from edge-sharing MgO_6 octahedra associated with the AsO_4 arsenate groups. The three-dimensional network encloses cavities in which Na^+ cations are located. This compound exhibits the $NaMg_4(VO_4)_3$ structure. The Na and one of the As atoms are on positions of $\overline{4}$ symmetry and the remaining cations all lie on twofold axes.

Comment

The compound $NaMg_4(AsO_4)_3$ crystallizes in the tetragonal system, space group $I\overline{4}2d$, with a closed three-dimensional framework. It is isostructural with the compounds $NaMg_4(VO_4)_3$ (Murashova *et al.*, 1988) and $NaNi_4(AsO_4)_3$ (Ben Smail *et al.*, 2002). However, it is completely different in structure from $NaMg_4(PO_4)_3$, which is analogous in composition but crystallizes in the orthorhombic system (Ben Amara *et al.*, 1983).

The asymmetric unit consists of two independent AsO_4 tetrahedra, one Na atom and an Mg_2O_{10} dimer formed by two edge-sharing MgO_6 octahedra. Each O atom of this unit connects two MgO_6 octahedra and one AsO_4 tetrahedron (Fig. 1). This arrangement is similar to those observed in $KNi_3(AsO_4)(As_2O_7)$ (Ben Smail & Jouini, 2000) and

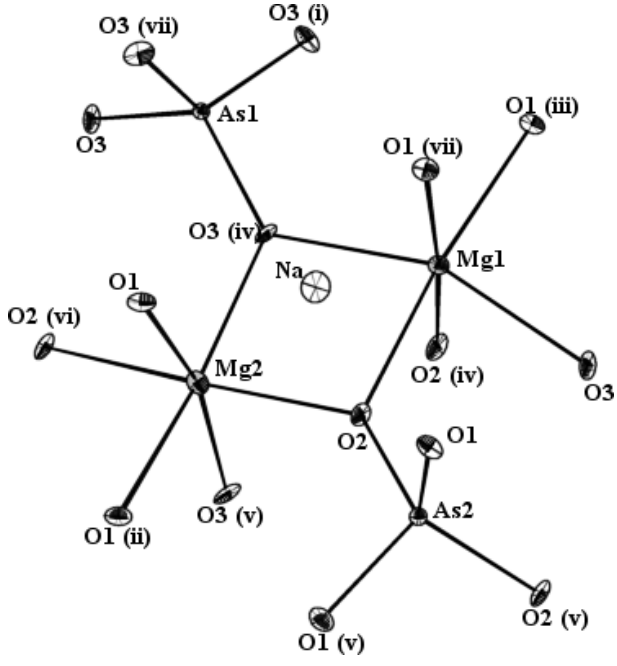

Figure 1
A fragment of the structure of Na $Mg_4(AsO_4)_3$, shown with 50% probability displacement ellipsoids.

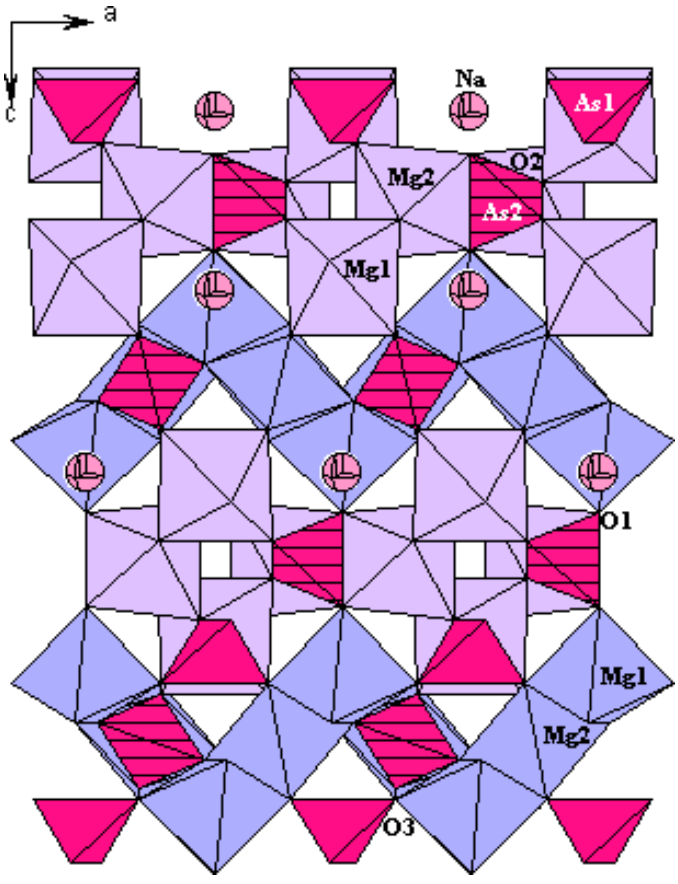

Figure 2
A view showing the association mode of the Mg_2O_{10} dimers as helical chains with AsO_4 tetrahedra.

$K_4Ni_7(AsO_4)_6$ (Ben Smail *et al.*, 1999).

The Mg_2O_{10} units form, by edge-sharing, infinite helical $(Mg_2O_8)_n$ chains running along the two directions [010] and [100]. Perpendicular chains are joined by O corners. The connection between chains in the same direction is assured by $As2O_4$ tetrahedra sharing two corners with two Mg_2O_{10} of the same chain and an edge with MgO_6 of the nearest parallel chain.

The $As1O_4$ tetrahedron shares its four vertices with two Mg_2O_{10} dimers of two perpendicular chains (Fig. 2). The Mg atom lies on a twofold axis and is surrounded by six O atoms, with mean Mg1—O and Mg2—O distances of 2.112 and 2.084 Å, respectively. The O—Mg1—O angles range from 80.93 (11) to 105.55 (11)°, whereas the O—Mg2—O angles vary between 74.00 (15) and 103.55 (17)°.

The As atoms are tetrahedrally coordinated by four O atoms. Atom As1 lies on a site with $\bar{4}$ symmetry, with an As1—O bond length of 1.692 (3) Å, and atom As2 lies on a twofold axis, with a mean As2—O distance of 1.697 Å. The AsO_4 bond angles range from about 99 to 121°. These are in the same range as in analogous arsenate compounds.

The resulting three-dimensional network encloses cavities in which the Na^+ cations are located. The Na^+ cation lies on a site with $\bar{4}$ symmetry and exhibits eightfold coordination, with Na—O2 2.321 (3) and Na—O3 2.710 (3) Å.

The bond-valence sums of the Na, Mg and As atoms (1.33, 2.02, 4.84 respectively) are compatible with their oxidation states (Brown & Altermatt, 1985).

Experimental

Single crystals of $NaMg_4(AsO_4)_3$ were prepared from a mixture of $NaNO_3$, $Mg(NO_3)_2{\cdot}6H_2O$ and $NH_4(H_2AsO_4)$ in a molar ratio of 1:2:2. The mixture was ground to a powder and then heated gradually in a porcelain crucible up to 1243 K. This temperature was held for 3 d and the mixture was then cooled slowly to room temperature at 10 K h^{-1}. The product was washed with hot water and colourless prismatic crystals of the title compound were extracted. Qualitative analysis by electron microscopy probe revealed that the compound contains Na, O, As and Mg.

Crystal data

$NaMg_4(AsO_4)_3$
M_r = 536.96
Tetragonal, $I\bar{4}2d$
a = 6.817 (1) Å
c = 19.242 (3) Å
V = 894.2 (2) Å^3
Z = 4
D_x = 3.989 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 2–27°
μ = 11.55 mm^{-1}
T = 293 (2) K
Prism, colourless
0.10 × 0.07 × 0.04 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.394, T_{max} = 0.630
1111 measured reflections
525 independent reflections
500 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 27.9°
$h = -8 \rightarrow 4$
$k = -1 \rightarrow 8$
$l = -1 \rightarrow 25$
2 standard reflections
frequency: 120 min
intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.045
S = 1.10
525 reflections
48 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0194P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0016 (3)
Absolute structure: Flack (1983), with 203 Friedel pairs
Flack parameter = −0.003 (17)

Table 1
Selected geometric parameters (Å, °).

As1—O3^{i}	1.692 (3)	Mg2—O3^{v}	2.017 (3)
As2—O2^{ii}	1.693 (2)	Mg2—O2^{vi}	2.080 (3)
As2—O1^{ii}	1.702 (3)	Mg2—O1	2.154 (3)
Mg1—O1^{iii}	2.078 (3)	Na—O1^{vii}	2.321 (3)
Mg1—O3^{iv}	2.088 (3)	Na—O2^{vi}	2.710 (3)
Mg1—O2	2.171 (3)		

Symmetry codes: (i) $-y, x, -z$; (ii) $x, -\frac{3}{2}-y, \frac{1}{4}-z$; (iii) $-1-y, x-1, -z$; (iv) $-x, -y, z$; (v) $1+x, -\frac{1}{2}-y, \frac{1}{4}-z$; (vi) $1-x, -1-y, z$; (vii) $1+y, -x, -z$.

Data collection: *CAD*-4 *EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97.

References

Ben Amara, M., Valsse, M., Olzcuaga, R., Le Flem, G. & Hagenmuller, P. (1983). *Acta Cryst.* C**39**, 936–939.
Ben Smail, R., Driss, A. & Jouini, T. (1999). *Acta Cryst.* C**55**, 284–286.
Ben Smail, R. & Jouini, T. (2000). *Acta Cryst.* C**56**, 513–514.
Ben Smail, R., Zid, M. F. & Jouini, T. (2002). *J. Soc. Chim. Tunisie*, **4**, 1665–1673.
Brandenburg, K. (1998). *DIAMOND*. Version 2.0. University of Bonn, Germany.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Macíček, J. & Yordanov, A. (1992). *J. Appl. Cryst.* **25**, 73–80.
Murashova, E. V., Velikodnyi, Yu. A. & Trunov, V. K. (1988). *Zh. Strukt. Khim.* **29**, 182–184.
North, A. C., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.