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$Ag_{1.49}Mn^{II}_{1.49}Mn^{III}_{1.51}(AsO_4)_3$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mn–O) = 0.009 Å
Disorder in main residue
R factor = 0.052
wR factor = 0.156
Data-to-parameter ratio = 11.0

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

The compound $Ag_{1.49}Mn^{II}_{1.49}Mn^{III}_{1.51}(AsO_4)_3$ (silver manganese arsenate) was prepared by a solid-state reaction. It crystallizes in the monoclinic system in space group *C*2/*c*. The three-dimensional network is built up from MnO_6 octahedra, sharing edges which are linked together by the arsenate groups (AsO_4). This arrangement delimits two types of hexagonal tunnels which accommodate Ag^+ cations. The compound is isostructural with the compounds $X(1)X(2)M(1)M(2)_2(PO_4)_3$ of the alluaudite structure.

Comment

$Ag_{1.49}Mn^{II}_{1.49}Mn^{III}_{1.51}(AsO_4)_3$ crystallizes in the monoclinic space group *C*2/*c* and is isostructural with the compounds $X(1)X(2)M(1)M(2)_2(PO_4)_3$ (Moore, 1971; Yakubovitch *et al.*, 1977) of the alluaudite structure type. The framework of $Ag_{1.49}Mn^{II}_{1.49}Mn^{III}_{1.51}(AsO_4)_3$ consists of infinite chains of MnO_6 octahedra, sharing two skew edges, running parallel to the [010] direction and having an Mn1–Mn2–Mn2 sequence. A projection of the structure, showing the displacement ellipsoids, is presented in Fig. 1.

In each chain, repetition of the $Mn1O_6$ and $Mn2O_6$ octahedra is ensured by *c*-glides and inversion centers, respectively. Atoms As2, Mn1 and Ag1 have twofold symmetry, Ag2 are on inversion centers and all other atoms are in general positions. The infinite chains are linked by $As1O_4$ and $As2O_4$ tetrahedra to form sheets parallel to (010). The $As2O_4$ tetrahedra share all four of their vertices with the MnO_6 octahedra, two with one chain and two with an adjacent chain. The $As1O_4$ tetrahedron shares its four oxygen vertices with four different MnO_6 octahedra belonging to three chains, two from the same

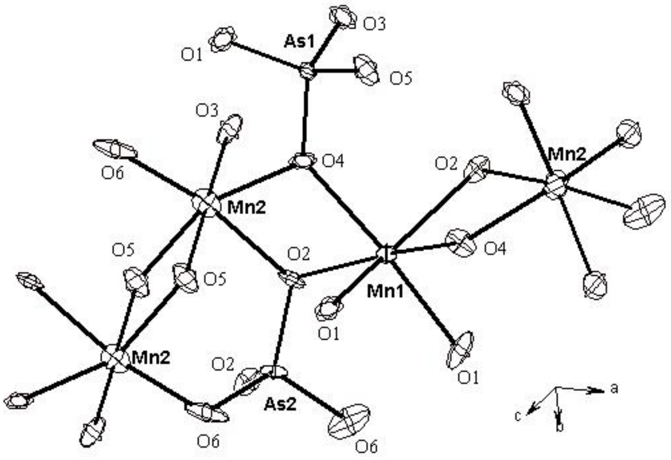

Figure 1
A projection of the structure, showing displacement ellipsoids at the 50% probability level.

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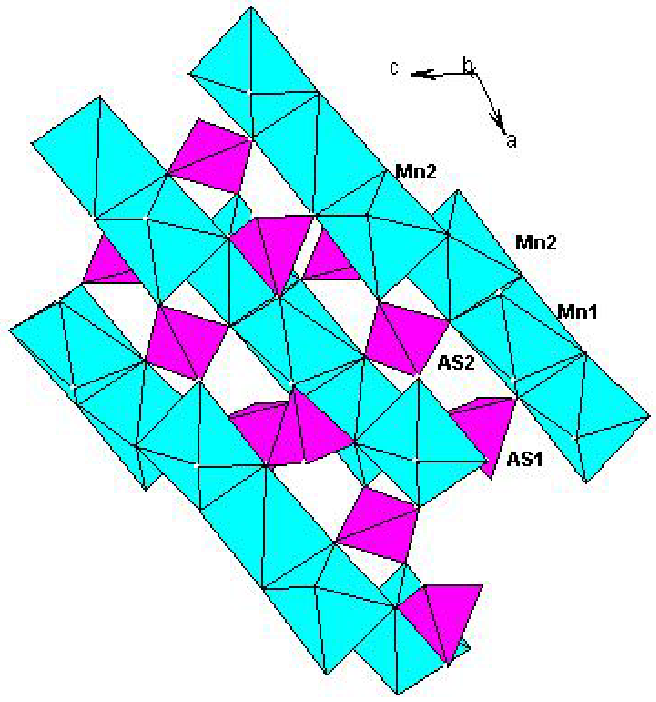

Figure 2
View showing the association between AsO_4 tetrahedra (purple) and MnO_6 octahedra (cyan).

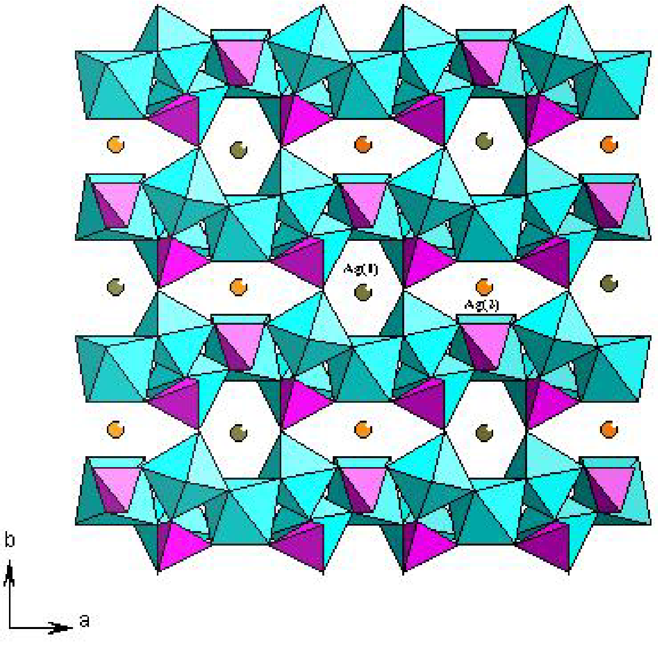

Figure 3
Projection of the structure of $Ag_{1.49}Mn^{II}_{1.49}Mn^{III}_{1.51}(AsO_4)_3$ along the [001] direction. In this presentation, the corners of the octahedra and tetrahedra are O atoms and the Mn and As atoms are at the center of each octahedron and tetrahedron, respectively. Small solid circles are Ag atoms.

chain and two from two different chains (Fig. 2). The MnO_6 octahedra appear to be highly distorted, especially around Mn1, for which the angle subtended by two of the *trans* O atoms is 143.9 (2)°. This distortion probably occurs as a result of the need to accommodate the connectivity of the AsO_4 tetrahedra, which are rather rigid entities and are responsible for holding adjacent chains together. This framework defines large tunnels running along the *c* direction. one tunnel along $(0,0,z)$ and the other along $(0,0.5,z)$ (Fig. 3). The silver cations $Ag1^+$ and $Ag2^+$ partially occupy sites in these tunnels. They exhibit two modes of coordination: $Ag1^+$ [site-occupation factor = 0.870 (7)], located in the second type of tunnel, has a square-planar environment, similar to the situation observed in $AgCo_3PO_4(HPO_4)_2$ (Guesmi & Driss, 2002) and $Ag2^+$ [site-occupation factor = 0.620 (7)], located in the first type, is linked to six O atoms. For electroneutrality, it is supposed that Mn2 has the average oxidation state 2.69, as indicated by the bond-valence sum (Brown & Altermatt, 1985) and based on parameters for $Mn^{2+}—O$; then the total charge contributed by Mn1 and Mn2 is $1 \times 2 + 2 \times 2.69 = 7.38$, which leaves a charge of 1.62 to be provided by the two tunnel sites, quite close to the value of 1.49 provided by the X-ray refinement.

Experimental

Single crystals of $Ag_{1.49}Mn^{II}_{1.49}Mn^{III}_{1.51}(AsO_4)_3$ were prepared by a conventional solid-state reaction. $NH_4H_2AsO_4$, MnO and $AgNO_3$ in a 1:2:3 ratio were ground together under acetone in an agate mortar. The mixture was heated in a porcelain crucible at 673 K for 4 h, cooled to room temperature, reground, and heated at 1073 K for 24 h, then cooled slowly to room temperature at a rate of 5 K h^{-1}. The product was washed with hot water. Brown parallelepiped-shaped crystals of the title compound were extracted. Their qualitative analysis by an electron microscope probe revealed them to contain Ag, As and Mn atoms.

Crystal data

$Ag_{1.49}Mn_3(AsO_4)_3$
$M_r = 742.29$
Monoclinic, $C2/c$
$a = 12.262$ (2) Å
$b = 12.934$ (3) Å
$c = 6.7070$ (9) Å
$\beta = 113.690$ (2)°
$V = 974.1$ (3) Å^3
$Z = 4$

$D_x = 5.062$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.8$–13.8°
$\mu = 16.92$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, brown
0.44 × 0.20 × 0.03 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.178$, $T_{max} = 0.309$
1112 measured reflections
1067 independent reflections
829 reflections with $I > 2\sigma(I)$

$R_{int} = 0.071$
$\theta_{max} = 27.0°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 16$
$l = -8 \rightarrow 7$
2 standard reflections
frequency: 120 min
intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.156$
$S = 1.07$
1067 reflections
97 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0825P)^2 + 48.2737P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2.61$ e Å^{-3}
$\Delta\rho_{min} = -2.08$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0015 (3)

Table 1
Selected geometric parameters (Å, °).

As1—O1	1.680 (9)	Mn2—O3^{iv}	2.038 (9)
As1—O5	1.688 (9)	Mn2—O4^{v}	2.076 (8)
As1—O4	1.693 (8)	Mn2—O5^{iii}	2.098 (9)
As1—O3	1.703 (9)	Mn2—O2^{iii}	2.121 (9)
As2—O6	1.682 (10)	Mn2—O5	2.198 (10)
As2—O2^{i}	1.688 (7)	Ag1—O3^{vi}	2.451 (9)
Mn1—O2^{ii}	2.226 (9)	Ag1—O3^{vii}	2.569 (9)
Mn1—O4^{i}	2.227 (8)	Ag2—O6^{i}	2.311 (10)
Mn1—O1^{iii}	2.242 (9)	Ag2—O1^{viii}	2.342 (9)
Mn2—O6	2.016 (12)	Ag2—O1^{ix}	2.595 (10)
O2^{ii}—Mn1—O2	143.9 (4)	O4^{x}—Mn1—O1^{iii}	87.7 (3)
O2—Mn1—O4^{i}	88.2 (3)	O2—Mn1—O1^{ix}	117.2 (4)
O2—Mn1—O4^{x}	71.9 (3)	O4^{x}—Mn1—O1^{ix}	158.5 (3)
O4^{i}—Mn1—O4^{x}	112.8 (5)	O1^{iii}—Mn1—O1^{ix}	72.9 (5)
O2—Mn1—O1^{iii}	92.4 (3)		

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

The occupation factors of the Ag1 and Ag2 sites are 0.870 (7) and 0.620 (7), respectively.

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.

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