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$Na_{1.72}Mn_{3.28}(AsO_4)_3$

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The single crystal of sodium manganese arsenate (1.72/3.28/12), $Na_{1.72}Mn_{3.28}(AsO_4)_3$, used for analysis was prepared by solid-state reaction at 1073 K. The compound crystallizes in the monoclinic system in space group $C2/c$. The structure consists of a complex network of edge-sharing MnO_6 octahedral chains, linked together by AsO_4 tetrahedra, forming two distinct channels, one containing Na^+ cations and the other occupied statistically by Mn^+ and Na^+ cations.

Comment

The crystal structure of $Na_{1.72}Mn_{3.28}(AsO_4)_3$ is isostructural with the compounds $X1X2M1M2_2(PO_4)_3$ (Moore, 1971; Yakubovitch *et al.*, 1977) of the alluaudite structure type. It can be described by an $Mn_3(AsO_4)_3$ framework built up by a complex arrangement of distorted MnO_6 octahedra and AsO_4 tetrahedra. A projection of the structure, showing the displacement ellipsoids, is presented in Fig. 1. The $Mn1O_6$ and $Mn3O_6$ octahedra are grouped through shared edges into chains with the sequence $(Mn1–Mn3–Mn3)_n$ running along the [010] direction. In each chain, repetition of the $Mn1O_6$ and $Mn3O_6$ octahedra are ensured by *c*-glide and inversion centers, respectively. The infinite chains of $Mn1O_6$ and $Mn3O_6$ polyhedra are linked together by $As1O_4$ and $As2O_4$ tetrahedra. $As2O_4$ tetrahedra always connect two chains and thus two of the $As2O_4$ O atoms belong of the same chain (Fig. 2*a*). The $As1O_4$ tetrahedron shares its four oxygen corners with four different MnO_6 octahedra belonging to three chains, two from the same chain and two from two different chains (Fig. 2*b*). The As2, Mn1 and Na1 atoms have twofold symmetry, Mn2 and Na2 are on inversion centres and all other atoms are in general positions.

In the present structure, the $Mn1O_6$ and $Mn3O_6$ octahedra which form the chains are distorted, with $d_{av}(Mn1—O) = 2.236\,(5)$ Å and $d_{av}(Mn3—O) = 2.092\,(2)$ Å. The *cis*-O—Mn1—O angles range from 71.4 (3) to 117.9 (3)°, whereas the O—Mn3—O angles range from 77.5 (3) to 109.6 (4)°. The As atoms are surrounded by four O atoms, with mean As1—O and As2—O distances of 1.692 and 1.691 Å, respectively. Mn1 and Mn3 have different oxidation states since they have different bond lengths. A bond-valence calculation (Brown & Altermatt, 1985), based on parameters for $Mn^{2+}—O$, gives a bond-valence sum of 1.80 for Mn1 and 2.69 for Mn3, which can be attributed to mixed-valence $Mn^{II/III}$. This gives an average

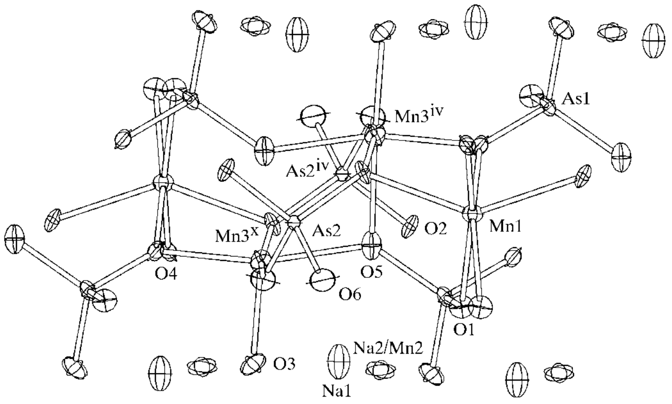

Figure 1
A view of a sheet of the anionic framework of $Na_{1.72}Mn_{3.28}(AsO_4)_3$, shown with 50% probability displacement ellipsoids. The symmetry codes are as in Table 1.

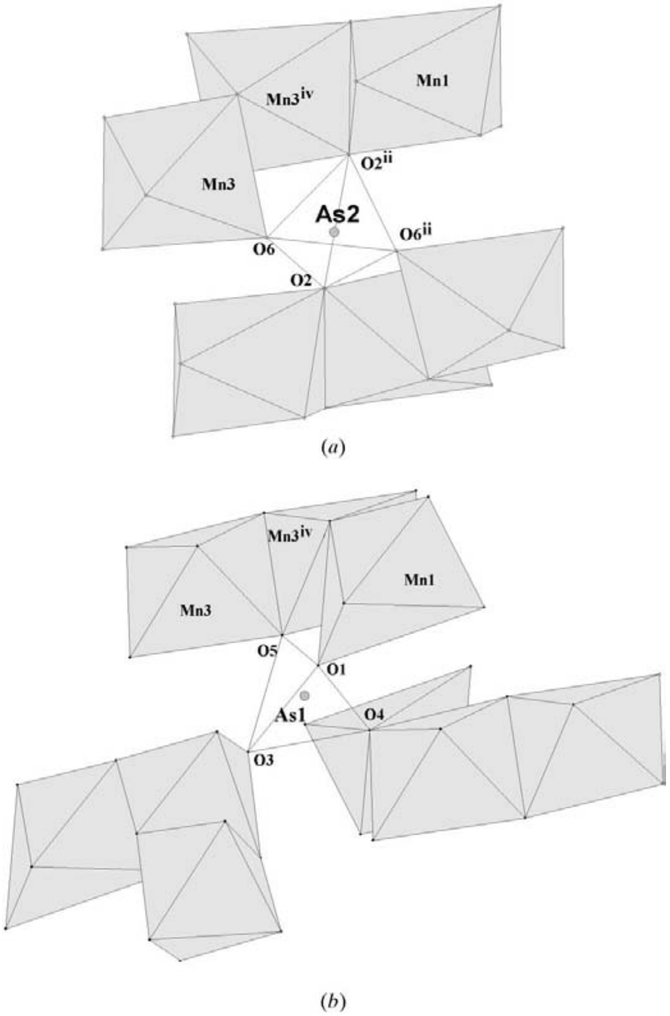

Figure 2
(*a*) A view showing the association between $As2O_4$ tetrahedra and MnO_6 octahedra, and (*b*) a view showing the association between $As1O_4$ tetrahedra and MnO_6 octahedra. The symmetry codes are as in Table 1.

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of 2.40. For electroneutrality, the Mn2 oxidation state should be 0.89 and the bond-valence calculation for this tetra-coordinated atom gives a value of 0.88. Since the difference between the shortest and longest Mn3—O bonds is 0.203 Å, the environment around this atom is distorted. A UV–visible spectoscopic study of this compound will probably reveal a Jahn–Teller effect for the Mn3 atom.

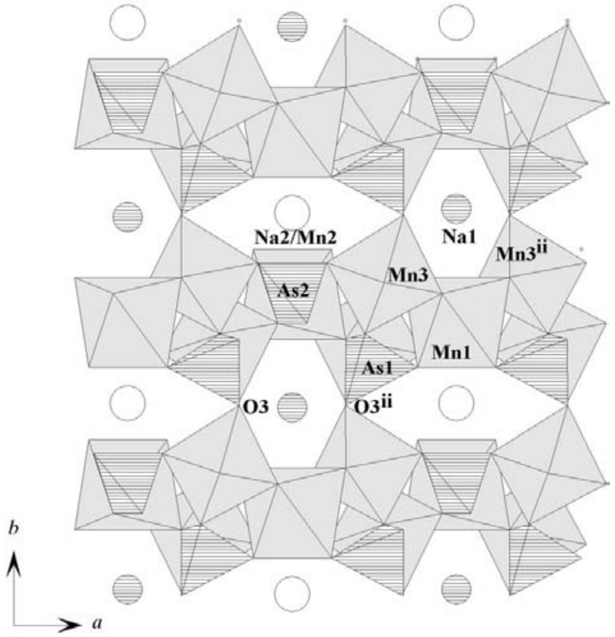

Figure 3
A projection of the structure of $Na_{1.72}Mn_{3.28}(AsO_4)_3$ along the [001] direction. The symmetry codes are as in Table 1.

This arrangement of polyhedra generates two sets of channels parallel to the c axis, located at $(\frac{1}{2},0,z)$ and $(0,0,z)$, respectively. Na^+ and Mn2^{2+} cations are located in these channels (Fig. 3).

The title structure is closely related to the alluaudite structure type. In $Na_{1.72}$ $Mn_{3.28}(AsO_4)_3$, the $X2$ site at (0,0,0) is empty, instead a site in the tunnel at $(0,0,z)$, shifted from the $X2$ site by ±0.25 along z, is occupied by Na1, which is similar to the situation observed in $NaCo_3(PO_4)(HPO_4)_2$ (Lii & Shih, 1994), $NaCo_3(AsO_4)(HAsO_4)_2$ (Lii & Shih, 1994), $NaMn_3(PO_4)(HPO_4)_2$ (Leroux *et al.*, 1995), $NaFe_{3.67}(PO_4)_3$ (Korzenski *et al.*, 1998), $Cu_2Mg_3(PO_4)_3$ (Wraner *et al.*, 1993) and $Cu_{1.35}Fe(PO_4)_3$ (Wraner *et al.*, 1993), whereas the $X1$ site at $(\frac{1}{2},0,0)$ contains the Mn2^{2+} and Na2$^+$ ions. Mn2 (site-occupation factor = 0.28) is located in a rectangular, slightly distorted, environment of two O atoms at distances of 2.340 (11) Å, with two others at distances of 2.360 (8) Å. The four corners of Mn2O$_4$ share vertexes with the Mn1O$_6$ and Mn3O$_6$ octahedra, which is similar to the situation found for FeO_4 in the structure of $NaFe_{3.67}(PO_4)_3$ (Korzenski *et al.*, 1998). The Na2 atoms (site-occupation factor = 0.72) are coordinated by four O atoms at distances of 2.340 (11) (×2) and 2.360 (8) Å (×2), and by two O atoms at longer distances of 2.600 (8) Å.

Experimental

Single crystals of $Na_{1.72}$ $Mn_{3.28}(AsO_4)_3$ were prepared by a conventional solid-state reaction. $NH_4H_2AsO_4$, MnO and Na_2CO_3 in a 3:2:1 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, heated at 1073 K for 24 h, and then cooled slowly to room temperature at a rate of 5 K h^{-1}. The product was washed with hot water. Brown parallelepipedic crystals of the title compound were extracted. Qualitative analysis by electron microscope probe revealed the crystals to contain Na, As and Mn atoms.

Crystal data

$Na_{1.72}Mn_{3.28}(AsO_4)_3$
$M_r = 636.49$
Monoclinic, $C2/c$
$a = 12.1975$ (10) Å
$b = 12.9531$ (10) Å
$c = 6.754$ (2) Å
$\beta = 113.85$ (4)°
$V = 976.1$ (3) Å^3
$Z = 4$

$D_x = 4.331$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.2$–13.8°
$\mu = 14.41$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, brown
0.04 × 0.02 × 0.01 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North *et al.*, 1968)
$T_{\min} = 0.805$, $T_{\max} = 0.863$
1159 measured reflections
1069 independent reflections
657 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.048$
$\theta_{\max} = 27.0°$
$h = -15 \rightarrow 14$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 8$
2 standard reflections
frequency: 120 min
intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.141$
$S = 1.01$
1069 reflections
97 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.43$ e Å^{-3}
$\Delta\rho_{\min} = -1.53$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0009 (2)

Table 1
Selected interatomic distances (Å).

As1—O1	1.671 (8)	Mn3—O4^{iv}	2.094 (9)
As1—O4	1.692 (9)	Mn3—O5^{i}	2.115 (9)
As1—O3	1.703 (9)	Mn3—O5	2.193 (11)
As1—O5	1.704 (9)	Na1—O3	2.429 (9)
As2—O6	1.684 (11)	Na1—O3^{v}	2.524 (9)
As2—O2	1.699 (8)	Na1—O2^{vi}	2.939 (12)
Mn1—O1^{i}	2.218 (9)	Na1—O4	2.953 (12)
Mn1—O4^{ii}	2.230 (9)	Mn2—O6^{vii}	2.340 (11)
Mn1—O2	2.262 (9)	Mn2—O1^{i}	2.360 (8)
Mn3—O6	1.990 (12)	Na2—O6^{ii}	2.340 (11)
Mn3—O3^{iii}	2.065 (9)	Na2—O1^{i}	2.360 (8)
Mn3—O2^{i}	2.093 (9)	Na2—O1^{iii}	2.600 (8)

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

Direct methods were used to locate the metal atoms, and the remaining atoms were found from successive Fourier difference maps.

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.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1372). Services for accessing these data are described at the back of the journal.

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