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$RbMn_6(As_2O_7)_2(As_3O_{10})$: a new manganese(II) arsenate

Brahim Ayed,* Anissa Haj Abdallah and Amor Hadded

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

Correspondence e-mail: brahimayed@yahoo.fr

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Mn–O) = 0.006 Å
R factor = 0.037
wR factor = 0.111
Data-to-parameter ratio = 12.5

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

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Single crystals of rubidium manganese arsenate, $RbMn_6(As_2O_7)_2(As_3O_{10})$, have been prepared by a solid-state reaction at 1173 K. The compound crystallizes in the monoclinic system, space group $P2_1/m$. The structure consists of a complex network of edge-sharing MnO_6 octahedra, forming folded layers that are linked together by As_2O_7 and As_3O_{10} groups, which is highly unusual. This arrangement delimits a tunnel parallel to the a-axis direction which accommodates Rb^+.

Comment

Transition metal oxide chemistry involving silicate, phosphate and arsenate oxyanions has attracted much attention because of their varied framework structures, which have interesting properties in terms of basic science as well as applied research. For example, the Nasicon tunnel structure, $NaZr_2(PO_4)_3$, discovered by Hagman & Kierkegaard (1968), shows interesting ionic conduction properties, whereas the non-linear optical phosphate, $KTiOPO_4$, is known for its second harmonic generation properties (Tordjman *et al.*, 1974). In an attempt to find similar materials with both octahedra and tetrahedra, we have extended our investigations to the system $Rb_2O—MnO—As_2O_5$. The choice of manganese is of particular interest because of its various oxidation states, ranging from II to VII. To our knowledge, rubidium manganese arsenates are rare and up to now only $RbMn_4(AsO_4)_3$ (Richard *et al.*, 1996) has been reported.

A new manganese(II) arsenate, $RbMn_6(As_2O_7)_2(As_3O_{10})$, has been prepared by a conventional solid-state reaction and characterized by single-crystal X-ray diffraction. The structure is composed of chains of edge-sharing MnO_6 octahedra running along the b axis, generated by mirror planes containing the shared edge between two $Mn3O_6$ octahedra

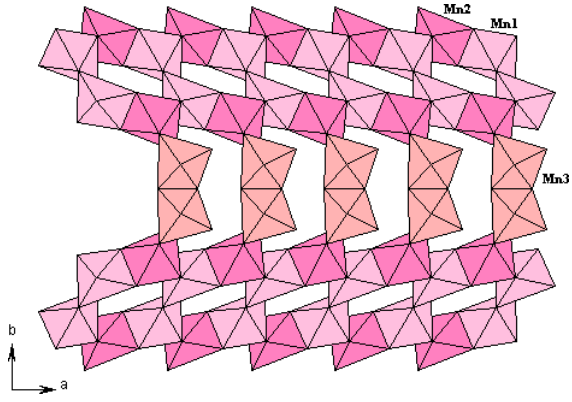

Figure 1
A projection of the structure down c, showing how Mn3 atoms link the Mn1–Mn2 chains into sheets.

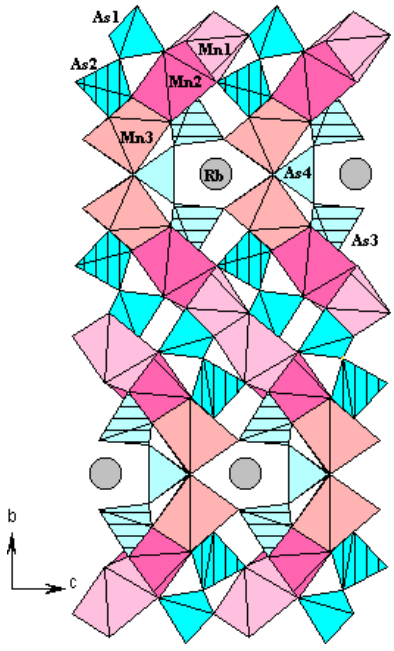

Figure 2
A projection of the $RbMn_6(As_2O_7)_2(As_3O_{10})$ structure, showing the single type of tunnel containing Rb^+ cations.

and centres of symmetry on the shared edges between two $Mn1O_6$ octahedra (Figs. 1 and 2). These chains are linked by an edge shared between $Mn1O_6$ and $Mn2O_6$ to form puckered layers perpendicular to the *c* axis. The layers are linked into a network by As_2O_7 and As_3O_{10} groups, leaving channels that contain the Rb atoms. A projection of the structure along the [100] direction is shown in Fig. 2. Each diarsenate group is formed by two tetrahedra, $As1O_4$ and $As2O_4$, interconnected through the corner (atom O13). The As1 tetrahedron shares three of its four remaining O-atom corners with three different Mn_2O_{10} dimers belonging to two layers, and the As2 tetrahedron shares two of the remaining O atoms with two Mn_2O_{10} groups and the third with the $Mn3O_6$ group; the O6—As1···As2—O3 pseudo-torsion angle is 60.06 (2)°, the As1—O13—As2 angle is 150.23 (2)° and the As—O13 bridge distance is, as expected, longer than the terminal distances; the mean values in the tetrahedra agree with the literature. Each As_3O_{10} group connects three pairs of $Mn3_2O_{10}$ belonging to two layers (Fig. 3). The terminal AsO_4 groups of As_3O_{10} are eclipsed by the central arsenate group; the As4···As3···As4^{ix} angle is 95.26 (2)° and the O10—As4···As3—O7 pseudo-torsion angle is 5.92 (4)°. The mean As4—$O_{terminal}$ distance is 1.663 (2) Å and the mean As—$O_{bridging}$ distance is 1.761 (1) Å. The Mn atoms are surrounded by six O atoms, with mean Mn1—O, Mn2—O and Mn3—O distances of 2.226 (3), 2.205 (5) and 2.206 (5) Å, respectively, whereas the O—Mn—O angles range from 70.9 (3) to 119.8 (2)°. The Rb^+ ions are located on centres of symmetry and exhibit tenfold coordination, with eight Rb—O distances lying between 2.846 (6) and 3.090 (7) Å and two other neighbours at distances of 3.456 (7) Å. Bond-valence calculations (Brown & Altermatt, 1985) based on these ten O-atom distances give an effective bond valence of 1.27, consistent with the cation charge of +1.

Experimental

The starting materials for synthesizing $RbMn_6(As_2O_7)_2(As_3O_{10})$ were $RbNO_3$, $NH_4H_2AsO_4$ and $Mn(SO_4)\cdot H_2O$. A mixture with an Rb/Mn/As ratio of 1:4:4 was heated slowly in a platinum crucible, first at 573 K for 4 h to eliminate NH_3, NO_2, H_2O and SO_2, and then at 1173 K for 20 h, and then cooled down to room temperature at a rate of 10 K h^{-1}. The prismatic crystals obtained after washing with hot water were colourless. Qualitative analysis of these crystals, by electron microscope probe, revealed that they contain Ru, Mn and As.

Crystal data

$As_7Mn_6O_{24}Rb$
M_r = 1323.53
Monoclinic, $P2_1/m$
a = 5.555 (1) Å
b = 27.830 (9) Å
c = 6.842 (2) Å
β = 107.56 (2)°
V = 1008.5 (5) Å^3
Z = 2
D_x = 4.358 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 1.5–27.0°
μ = 17.56 mm^{-1}
T = 293 (2) K
Prism, colourless
0.10 × 0.05 × 0.04 mm

Data collection

Enarf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.363, T_{max} = 0.495
2461 measured reflections
2240 independent reflections
1726 reflections with $I > 2\sigma(I)$
R_{int} = 0.079
θ_{max} = 27.0°
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 35$
$l = -8 \rightarrow 8$
2 standard reflections
frequency: 120 min
intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.111
S = 1.09
2240 reflections
179 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 3.8056P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.58 e Å^{-3}
$\Delta\rho_{min}$ = −1.47 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0007 (2)

Table 1
Selected geometric parameters (Å).

As1—O2	1.674 (6)	Rb—O8^{iii}	3.456 (6)
As1—O9	1.679 (6)	Mn1—O9^{vi}	2.143 (6)
As1—O3	1.681 (5)	Mn1—O3^{vii}	2.175 (6)
As1—O13	1.733 (6)	Mn1—O2^{viii}	2.189 (6)
As2—O12	1.661 (6)	Mn1—O1^{ix}	2.235 (6)
As2—O1^{i}	1.680 (5)	Mn1—O5^{viii}	2.255 (6)
As2—O6	1.683 (5)	Mn1—O9	2.366 (6)
As2—O13	1.734 (6)	Mn2—O6^{vii}	2.145 (6)
As3—O11	1.650 (8)	Mn2—O5^{vii}	2.156 (6)
As3—O4	1.658 (8)	Mn2—O1^{vii}	2.213 (5)
As3—O7^{ii}	1.721 (6)	Mn2—O2	2.217 (6)
As4—O10	1.656 (6)	Mn2—O3^{viii}	2.217 (6)
As4—O5	1.668 (5)	Mn2—O8	2.289 (6)
As4—O8	1.681 (5)	Mn3—O10^{i}	2.129 (6)
As4—O7	1.803 (6)	Mn3—O12	2.134 (6)
Rb—O10^{iii}	2.846 (6)	Mn3—O8	2.185 (5)
Rb—O7	2.971 (6)	Mn3—O6^{vii}	2.186 (6)
Rb—O11^{iv}	2.980 (8)	Mn3—O11	2.251 (5)
Rb—O4^{iv}	3.026 (8)	Mn3—O4^{vii}	2.351 (5)
Rb—O12^{v}	3.090 (6)		

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

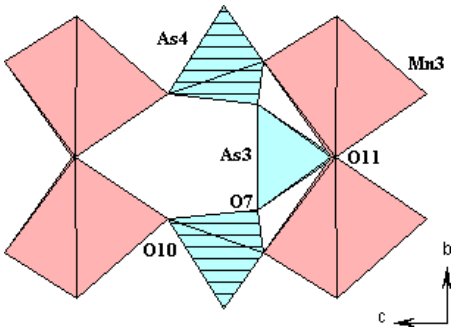

Figure 3
A view showing the association between As_3O_{10} and Mn_2O_{10} moieties along the [100] direction.

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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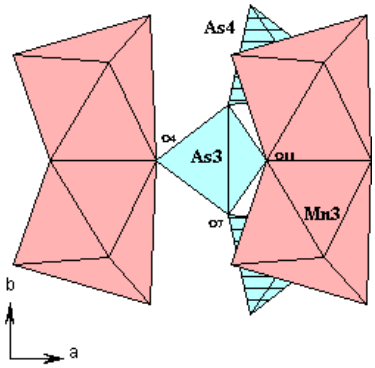

Figure 4
A view showing the association between As_3O_{10} and Mn_2O_{10} moieties along the [001] direction.

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