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Dipotassium trimanganese(II) tetrakis(hydrogenphosphite), $K_2[Mn_3(HPO_3)_4]$

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The title compound is a new mixed alkali/3*d* metal phosphite. It exhibits a layered structure formed by linear Mn_3O_{12} trimer units which contain face-sharing MnO_6 octahedra interconnected by $(HPO_3)^{2-}$ phosphite oxoanions. The K^+ cations located between the anionic $[Mn_3(HPO_3)_4]^{2-}$ sheets are ninefold coordinated. The presence of the alkaline ion leads to the highest symmetry and shortest interlayer distance compared with two previous compounds showing the same anionic framework and having ammonium salts as cations. The compound crystallizes in the space group $R\overline{3}m$, with two crystallographically independent Mn atoms occupying sites of $\overline{3}m$ and $3m$ symmetry. All the other atoms, except for the phosphite O atoms, are located on special positions with $3m$ symmetry.

Comment

After the discovery of microporous aluminophosphates, considerable efforts have been directed towards the synthesis of new open-framework transition metal phosphates because of their potential applications in catalysis, adsorption, ionic conduction, ion exchange, magnetism and electronics (Cheetham *et al.*, 1999). The phosphate group, $(PO_4)^{3-}$, has historically been one of the most productive oxoanions for obtaining new structures. The replacement of phosphate by phosphite in transition metal phosphates has attracted more and more research effort, notably since the synthesis of the first organically templated vanadium phosphite with an open framework (Bonavia *et al.*, 1995). In the hydrogenphosphite group, $(HPO_3)^{2-}$, the P atom remains in a low oxidation state of +3 and the group has trigonal pyramidal geometry, which provides versatility in allowing it to build either open or condensed frameworks.

In recent years, the family of transition metal phosphites has grown rapidly and numerous compounds with interesting structure diversity, such as V (Fu *et al.*, 2006), Fe (Chung *et al.*, 2006), Co (Li *et al.*, 2008) and Zn (Johnstone & Harrison, 2004) phosphites, have been reported. However, few phosphite compounds with the Mn^{II} cation are known (Attfield *et al.*, 1994; Fernandez *et al.*, 2000, 2001; Chung *et al.*, 2005). In order to extend the knowledge of phosphite materials incorporating metallic magnetic cations belonging to the first series of the transition elements, particularly in the presence of a second metal atom, this work focuses on the alkali metal–manganese–phosphite acid system. In this context, we obtained the title compound using hydrothermal treatment and autogenous pressure.

The structure of $K_2[Mn_3(HPO_3)_4]$ consists of a two-dimensional framework formed by MnO_6 octahedra and $(HPO_3)^{2-}$ pseudo-tetrahedra. As shown in Fig. 1, there are two crystallographically independent Mn and P atoms in the asymmetric unit, leading to two different octahedra and trigonal pyramids, respectively. The connection of the Mn octahedra by face-sharing forms an Mn_3O_{12} linear trimer unit, where atom Mn1 is located at the centre and atom Mn2 in the extremes. The M—O distances for the $Mn1O_6$ octahedron have identical values and the *trans* O—Mn1—O angles are 180°, due to the special position occupied by the Mn1 ions. In the $Mn2O_6$ octahedron, the mean Mn2—O bond distance is 2.1976 (11) Å and the *trans* O—Mn2—O angles deviate from the ideal value by approximately 6°. Finally, the *cis* and *trans* O—Mn—O angles in the MnO_6 unit indicate a topology near

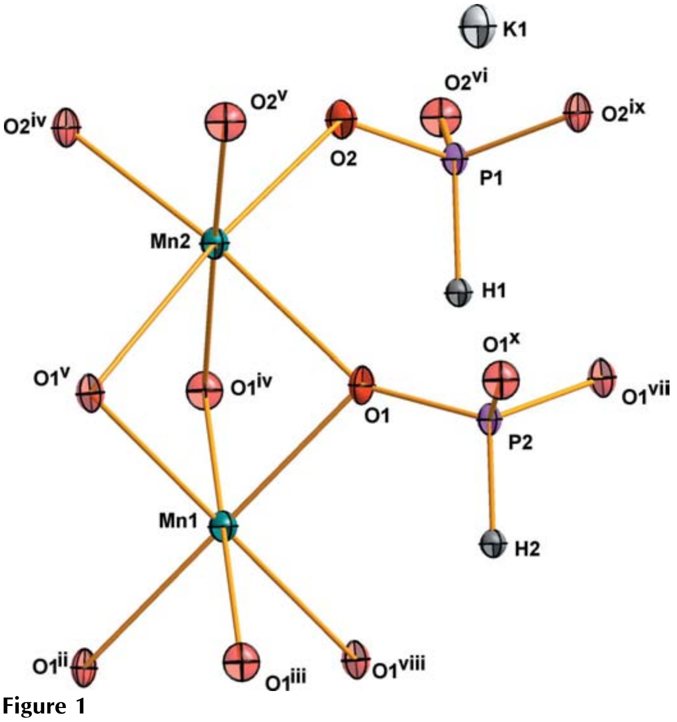

Figure 1
The asymmetric unit and symmetry-related atoms of $K_2[Mn_3(HPO_3)_4]$, shown with 50% probability displacement ellipsoids. [Symmetry codes: (ii) $-x, -y, -z$; (iii) $y, -x + y, -z$; (iv) $-y, x - y, z$; (v) $-x + y, -x, z$; (vi) $-x + y, -x + 1, z$; (vii) $-x + y + 1, -x + 1, z$; (viii) $x - y, x, -z$; (ix) $1 - y, 1 + x - y, z$; (x) $1 - y, x - y, z$.]

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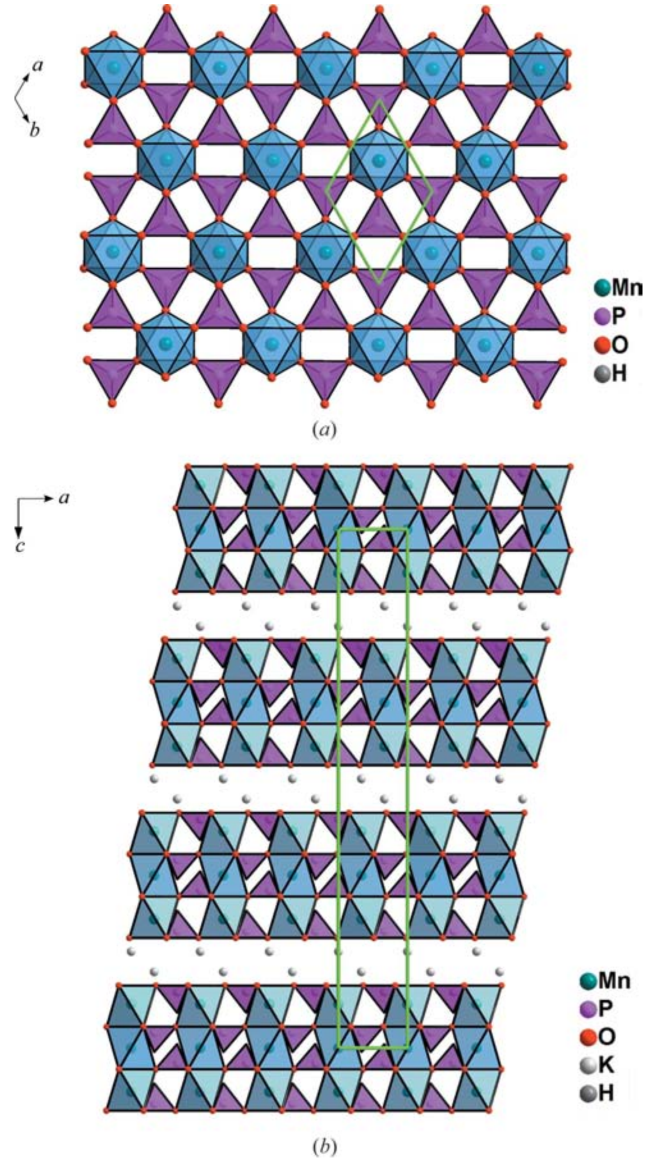

(a)

(b)

Figure 2
Projections along (*a*) the [001] direction, showing the $[Mn_3(HPO_3)_4]$ layer in $K_2[Mn_3(HPO_3)_4]$, and (*b*) the [010] direction, showing the two-dimensional framework in $K_2[Mn_3(HPO_3)_4]$.

octahedral. In the $(HPO_3)^{2-}$ trigonal pyramids, the P—O and H—P bonds present mean values of 1.5274 (10) and 1.37 (5) Å, respectively. The two independent phosphite groups link the trimeric entities through the O atoms, leading to layers which propagate in the *ab* plane (Fig. 2*a*).

This association of polyhedra leads to a layered structure formed by anionic sheets of formula $[Mn_3(HPO_3)_4]^{2-}$ stacked along the *c* axis, with an interlamellar distance estimated at 3.3 Å (Fig. 2*b*). While this anionic framework is known (Fernandez *et al.*, 2000, 2001), the title compound is the first example with an alkaline metal as the cation. The K^+ cations are located between the layers, compensating their negative charge, and are in ninefold coordination sites with interactions to three nearest-neighbour O atoms from one layer and six others further from another layer (Fig. 3). The coordination environment adopted by the K^+ cation is supported by bond-valence-sum (BVS) calculations (Brown & Altermatt, 1985), which give a value of 1.19 v.u. for K. The mean K—O bond distance of 2.880 (1) Å is near the values reported for $K_2Co(HPO_3)_2 \cdot 2H_2O$ [2.789 (2) Å; Ouarsal *et al.*, 2004] and $K_2Zn_3(HPO_3)_4$ [2.861 (7) Å; Ortiz-Avila *et al.*, 1989].

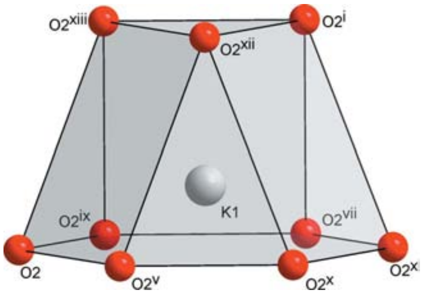

Figure 3
The ninefold coordination of the K^+ cation in $K_2[Mn_3(HPO_3)_4]$. [Symmetry codes: (i) $y + \frac{2}{3}, -x + y + \frac{1}{3}, -z + \frac{1}{3}$; (v) $-x + y, -x, z$; (vii) $-x + y + 1, -x + 1, z$; (ix) $1 - y, 1 + x - y, z$; (*x*) $1 - y, x - y, z$; (xi) $1 + x, y, z$; (xii) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$; (xiii) $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{1}{3} - z$.]

The formation of the manganese(II) phosphite indicates the reduction of this metal during the reaction. The oxidation state of manganese in the title compound was verified using BVS calculations, which give oxidation states of 1.91 and 2.04 v.u. for Mn1 and Mn2, respectively. These results are in a good agreement with the expected values for this element considering the $K_2[Mn_3(HPO_3)_4]$ chemical formula, and confirm the results obtained from the X-ray single-crystal structure determination.

The two phosphites, $(C_2H_{10}N_2)[Mn_3(HPO_3)_4]$ (Fernandez *et al.*, 2000) and $(C_3H_{12}N_2)[Mn_3(HPO_3)_4]$ (Fernandez *et al.*, 2001), showing the same layered architecture exhibited by the title compound, crystallize in the triclinic $P\overline{1}$ and monoclinic $C2/m$ space groups, respectively. It is noteworthy that in both compounds the absence of the threefold axis, due to the geometry of the intercalated cations located in the interlayer space, leads to lower symmetries compared with the trigonal symmetry obtained with the presence of K^+ cations in the structure. The Mn—O and P—O bond lengths and angles observed in $K_2[Mn_3(HPO_3)_4]$ are similar to those recorded for the two previously reported manganese(II) phosphites. Finally, the effect of the nature of the intercalated entities on the interlayer distance is obvious and was expected. In fact, the interlayer distance is *ca* 3.3 Å for the potassium compound, while it is *ca* 5.5 and *ca* 6 Å for the ethylenediammonium and propanediammonium phases, respectively.

Experimental

$K_2[Mn_3(HPO_3)_4]$ was prepared in a 23 ml Teflon-lined steel autoclave from a reaction mixture containing $(C_2H_3O_2)_3Mn \cdot 2H_2O$ (Acros Organics, 98%), H_3PO_3 (Aldrich, 99%), K_2CO_3 (Merck, 99%) and deionized water in a 0.2:1.5:0.8:28 molar ratio. After 72 h at 443 K, the vessel was cooled slowly to room temperature. Large light-pink crystals were recovered by vacuum filtration, washed with deionized water and dried in a desiccator.

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Crystal data

$K_2[Mn_3(HPO_3)_4]$
$M_r = 562.93$
Trigonal, $R\overline{3}m$
$a = 5.4489$ (1) Å
$c = 35.4321$ (9) Å
$V = 911.05$ (3) Å^3
$Z = 3$
Mo $K\alpha$ radiation
$\mu = 4.34$ mm^{-1}
$T = 293$ K
$0.14 \times 0.11 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{\min} = 0.544$, $T_{\max} = 0.647$
5846 measured reflections
864 independent reflections
761 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.063$
$S = 1.17$
864 reflections
30 parameters
Only H-atom coordinates refined
$\Delta\rho_{\max} = 1.76$ e Å^{-3}
$\Delta\rho_{\min} = -1.06$ e Å^{-3}

Both H atoms were located in a difference Fourier map and their $U_{\rm iso}$ values were constrained to be $1.2U_{\rm eq}$ of the corresponding P atom.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX*/*LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg, 1998); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3017). Services for accessing these data are described at the back of the journal.

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	2.2129 (10)	P1—H1	1.42 (5)
Mn1—Mn2	2.9994 (4)	P2—O1	1.5311 (10)
Mn2—O2	2.1186 (11)	P2—H2	1.32 (5)
Mn2—O1	2.2766 (10)	O2—K1	2.8829 (9)
P1—O2	1.5237 (10)	K1—O2$^{\rm i}$	2.8740 (12)
O1—Mn1—O1$^{\rm ii}$	180.00 (5)	O2—Mn2—O1$^{\rm iv}$	96.71 (3)
O1—Mn1—O1$^{\rm iii}$	98.38 (4)	O1—Mn2—O1$^{\rm iv}$	78.87 (4)
O1$^{\rm ii}$—Mn1—O1$^{\rm iii}$	81.62 (4)	O2$^{\rm vi}$—P1—O2	111.57 (4)
Mn2$^{\rm ii}$—Mn1—Mn2	180	O2—P1—H1	107.28 (5)
O2—Mn2—O2$^{\rm iv}$	87.45 (4)	O1$^{\rm vii}$—P2—O1	113.21 (4)
O2—Mn2—O1$^{\rm v}$	174.23 (4)	O1—P2—H2	105.41 (4)

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

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