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Dipotassium manganese(II) bis(dihydrogendiphosphate) dihydrate, $K_2Mn(H_2P_2O_7)_2\cdot 2H_2O$

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(P–O) = 0.002 Å
R factor = 0.037
wR factor = 0.063
Data-to-parameter ratio = 14.8

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

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The framework of $K_2Mn(H_2P_2O_7)_2\cdot 2H_2O$ consists of metallate layers linked by O—P—O bridges and weak hydrogen bridging bonds. Mn sites have an octahedral coordination by two bidentate $[H_2P_2O_7]^{2-}$ anions and two water molecules.

Comment

Bibliographic data on acidic metal pyrophosphates and their applications have been widely discussed in previous papers published by our research group (Alaoui *et al.*, 2002, 2003). The present work is a continuation of our investigations of the series $(A,T)_x(H_2P_2O_7)_y\cdot zH_2O$ (A = alkali metal and T = transition metal). We report here the synthesis and crystal structure of $K_2Mn(H_2P_2O_7)_2\cdot 2H_2O$.

In the structure of the title compound, potassium polyhedra share an edge to form dimers $[K_2O_{13}]$. These latter are linked by Mn···O interactions as they share a face with $[MnO_6]$. This results in a metallate layer, parallel to (010). Two such layers are linked by O—P—O bridges from $[H_2P_2O_7]$ moieties stacked in a parallel phosphate layer by weak bridging hydrogen bonds. Fig. 1 represents a perspective view of the structure.

Potassium occupies two kind of sites in the structure, one with seven- and the other with eightfold coordination. Average K···O distances in $[K1O_8]$ and $[K2O_7]$ are 2.953 (2) and 2.859 (2) Å, respectively. These values can be compared to 2.959 Å in $K_2Zn(H_2P_2O_7)_2\cdot 2H_2O$ (Alaoui *et al.*, 2003) or 2.908 Å in $K_2H_2P_2O_7$ (Larbot *et al.*, 1983).

Two bidentate $[H_2P_2O_7]^{2-}$ anions and two water molecules form the sixfold coordination of the Mn^{2+} cation in the

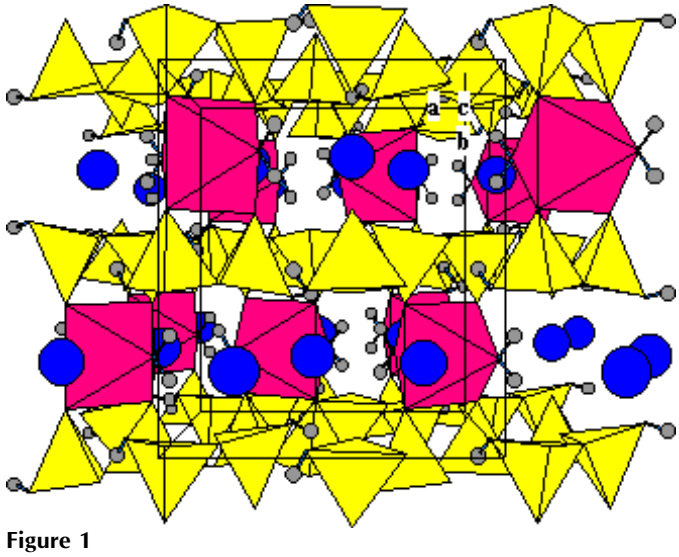

Figure 1
Projection along the c axis of $K_2Mn(H_2P_2O_7)_2\cdot 2H_2O$. Polyhedra: yellow $[H_2P_2O_7]$, rose $[MnO_6]$; circles: large blue K, small grey H.

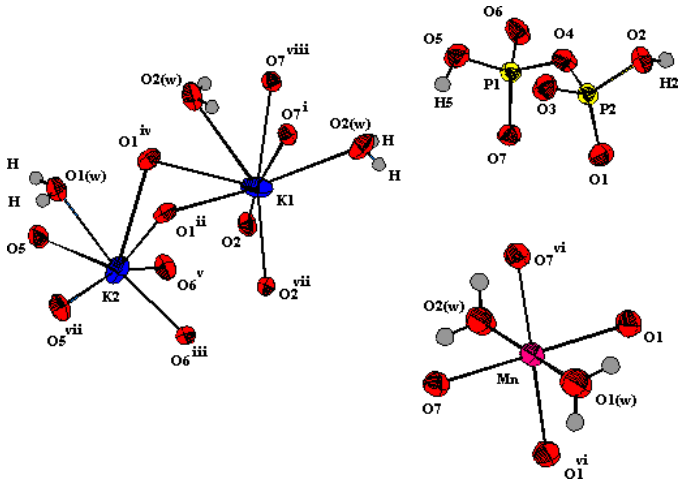

Figure 2
Coordination polyhedra with numbering of atoms of K^+, Mn^{2+} and P^{5+} in the title compound. Displacement ellipsoids are at the 50% probability level. [Symmetry codes: (i) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (ii) $-x, \frac{1}{2}+y, 1-z$; (iii) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}-z$; (iv) $-x, 1-y, 1-z$; (v) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (vi) $x, \frac{1}{2}-y, z$; (vii) $x, \frac{3}{2}-y, z$; (viii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$.]

structure. The average Mn—O distance in the distorted octahedron is 2.173 (2) Å, a value close to that found in $MnHP_2O_7$ (2.027 Å; Durif & Averbuch-Pouchot, 1982). [MnO_6] polyhedra are isolated, the shortest d_{Mn-Mn} being 5.716 Å. The irregularity in the manganese environments in $K_2Mn(H_2P_2O_7)_2{\cdot}2H_2O$ may be attributed in part to the Jahn–Teller effect. In fact, in the case of an octahedral crystal field, this phenomenon has an influence on the energy levels $3d^4$.

The phosphorus(V) atoms are coordinated by four O atoms in a slightly distorted tetrahedron. Of the four oxygen apices, one is a hydroxyl group. Two tetrahedra share a corner (O4) to form the $[H_2P_2O_7]^{2-}$ anion in a roughly eclipsed conformation. Average d_{P-O} of 1.534 (2) Å is similar to that found in $K_2Zn(H_2P_2O_7)_2{\cdot}2H_2O$ [1.537 (2) Å; Alaoui *et al.*, 2003] or 1.543 Å in $K_3H(H_2P_2O_7)_2$ (Dumas, 1978). The bridging angle P—O—P of 130.86 (13)° is close to that in $Ca_2P_2O_7$ (130.0°; Calvo, 1968) or 130.8 (2)° in $K_2Zn(H_2P_2O_7)_2{\cdot}2H_2O$. We display in Fig. 2 the coordination polyhedra of K, Mn and P in the current structure.

Experimental

Stoichiometric amounts of $Mn(CH_3COO)_2$ and $K_4P_2O_7$ were dissolved in distilled water. After a day of stirring at room temperature, the solution was allowed to stand for two weeks. Large prismatic, light pink crystals deposited; these were filtered off and washed with a water–ethanol solution (20:80).

Crystal data

$H_8K_2MnO_{16}P_4$
M_r = 521.08
Orthorhombic, *Pnma*
a = 9.7613 (8) Å
b = 11.1627 (9) Å
c = 13.3949 (11) Å
V = 1459.5 (2) Å^3
Z = 4
D_x = 2.371 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3757 reflections
θ = 2.4–30.8°
μ = 2.00 mm^{-1}
T = 294 (2) K
Needle, light pink
0.23 × 0.11 × 0.08 mm

Data collection

Bruker SmartApex CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*XPREP*; Sheldrick, 1997)
T_{min} = 0.670, T_{max} = 0.893
14 628 measured reflections
1890 independent reflections
1332 reflections with $I > 2\sigma(I)$
R_{int} = 0.079
θ_{max} = 28.3°
$h = -13 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.063
S = 1.00
1890 reflections
128 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0136P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.84 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

Table 1
Selected geometric parameters (Å).

Mn1—O1	2.141 (2)	P2—O4	1.610 (2)
Mn1—O7	2.158 (2)	K1—O2	2.702 (2)
Mn1—O1*W*	2.192 (4)	K1—O7^{i}	2.845 (2)
Mn1—O2*W*	2.247 (4)	K1—O2*W*^{i}	2.984 (4)
P1—O6	1.485 (2)	K1—O1^{ii}	3.093 (2)
P1—O7	1.502 (2)	K1—O2*W*^{iv}	3.358 (4)
P1—O5	1.545 (2)	K2—O6^{iii}	2.712 (2)
P1—O4	1.596 (2)	K2—O5	2.714 (2)
P2—O3	1.491 (2)	K2—O1*W*^{ix}	3.027 (4)
P2—O1	1.503 (2)	K2—O1^{x}	3.068 (2)
P2—O2	1.539 (2)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O3^{xi}	0.79 (3)	2.00 (3)	2.776 (3)	169 (4)
O2*W*—H2*W*···O7^{xii}	0.79 (3)	2.16 (3)	2.833 (4)	144 (3)
O2—H2···O6^{xiii}	0.76 (3)	1.75 (3)	2.505 (3)	172 (4)
O5—H5···O3^{v}	0.89 (3)	1.64 (3)	2.528 (3)	176 (3)

Symmetry codes: (v) $1-x, 1-y, 1-z$; (xi) $1-x, y-\frac{1}{2}, 1-z$; (xii) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z$; (xiii) $x-\frac{1}{2}, y, \frac{1}{2}-z$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL*97.

References

Alaoui, A. T., Ouarsal, R., Lachkar, M., El Bali, B. & Bolte, M. (2002). *Acta Cryst.* E**58**, i91–i92.
Alaoui, A. T., Ouarsal, R., Lachkar, M., Zavalij, P. Y. & El Bali, B. (2003). *Acta Cryst.* E**59**, i50–i52.
Bruker (1999). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Calvo, C. (1968). *Inorg. Chem.* **7**, 1345–1351.
Dowty, E. (1999). *ATOMS for Windows and Macintosh*. Version 5. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
Dumas, Y. (1978). *Acta Cryst.* B**34**, 3514–3519.
Durif, A. & Averbuch-Pouchot, M. T. (1982). *Acta Cryst.* B**38**, 2883–2885.
Larbot, A., Durant, J., Norbert, A. & Le Cot, L. (1983). *Acta Cryst.* C**39**, 6–8.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97 and *XPREP*. University of Göttingen, Germany.