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Synthesis and Crystal Structure of $KMn_2O(PO_4)(HPO_4)$

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$KMn_2O(PO_4)(HPO_4)$ crystallizes in the monoclinic space group $P2_1/m$, with $a = 6.226(1)$, $b = 6.890(2)$, $c = 8.809(1)$ Å, and $\beta = 107.67(1)°$. For $Z = 2$ the calculated density is 3.282 g cm^{-3}. Crystals were obtained hydrothermally, from a mixture of Mn_3O_4, KH_2PO_4, and H_2O, by slow cooling from 673 K under an external nitrogen pressure of 3 kbar. The structure was solved by Patterson and Fourier methods and refined to final agreement factors $R = 0.024$, $R_w = 0.027$. The structure is composed of zigzag chains of edge sharing MnO_6 octahedra linked together by PO_4 tetrahedra to form sheets parallel to the *bc* plane. These sheets are linked to adjacent ones via additional PO_4 tetrahedra and hydrogen bonds. The resulting framework encloses channels running parallel to the [011] direction in which the potassium resides. © 1988 Academic Press, Inc.

Introduction

Very little synthetic or structural work has been reported on the orthophosphates of Mn^{3+}. $MnPO_4$ is reported to have the low pressure $FePO_4$ structure (*1*), and the structure of $MnPO_4 \cdot H_2O$ (previously reported as $MnPO_4 \cdot 1.5H_2O$) has recently been determined (*2*). The only other crystal structure reported in this system is that of the mixed valence mineral bermanite, $Mn_3(PO_4)_2(OH)_2 \cdot 4H_2O$ (*3*).

In the system K–Mn–PO_4–H_2O only one phase has been reported—$KMnPO_4 \cdot H_2O$ (*4*)—but this has not been structurally characterized. The present paper reports the synthesis and structure of a new potassium manganese (III) phosphate, $KMn_2O(PO_4)(HPO_4)$.

Experimental

Crystals of the title compound were prepared hydrothermally from a mixture of 0.76 g Mn_3O_4 and 1.36 g KH_2PO_4 (an approximate molar ratio K : Mn : P = 1 : 1 : 1) in 6 g H_2O. The starting mixture was sealed in a gold tube, 6 in. long by $\frac{1}{4}$ in. diameter, and heated to 673 K under an external nitrogen pressure of 3 kbar. Slow cooling at 10 K hr^{-1} to room temperature produced red-brown needle-like crystals up to 2 mm in length together with a poorly crystalline dark-brown phase. Qualitative X-ray microanalysis in a JEOL 2000FX electron microscope on several of the crystals revealed K, Mn, and P as the only heavy elements present.

A crystal of dimensions 0.75 × 0.10 ×

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0.03 mm was mounted on an Enraf–Nonius CAD4 automated diffractometer and the unit cell was determined on the basis of 25 accurately centered reflections in the range $2\theta = 50$–$60°$. At 25°C crystal data are $a = 6.226(1)$ Å, $b = 6.890(2)$ Å, $c = 8.809(1)$ Å, $\beta = 107.67(1)°$, giving $V = 360.0$ Å^3 and $\rho_{calc} = 3.282$ g cm^{-3} for $Z = 2$.

Diffraction intensities were measured using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.70930$ Å) using the ω-2θ scan method, in the angular range $2\theta < 75°$. A total of 3090 data were collected, of which 2725 remained after merging equivalent reflections. Of these, 2551 were regarded as observed according to the criterion $I > 3\sigma(I)$. Three standard reflections were systematically monitored, the variation in intensity never being greater than 3% over the data collection period.

Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied ($\mu = 44.2$ cm^{-1}). Systematic absences ($0k0$; $k = 2n + 1$) indicated the space group $P2_1$ or $P2_1/m$, with the latter being assumed for subsequent structure solution and refinement.

A Patterson map revealed the positions of Mn(1), Mn(2), K(1), and P(2), and the remaining atoms were located by a series of difference Fourier maps. Structure refinement was carried out using the Oxford CRYSTALS system (*5*). A full matrix least-squares refinement, using zero-valent scattering factors (*6*) and isotropic thermal parameters for all atoms, yielded a residual of $R = 0.058$. At this stage the position of H(1) was determined. Bond strength–bond length calculations (*7*) provide a simple way of predicting to which atom a hydrogen may be bonded, and in this case the valence sums around all the O atoms except O(1) ($s = 1.80$ vu) and O(5) ($s = 1.30$ vu) were close to the expected value of 2.0 vu. This suggested that H(1) should be attached to O(5), with a hydrogen bond contributing to the valence sum around O(1). A close look at the difference Fourier map at this stage revealed a peak of about 0.6 e Å^{-3} among the stop 10 peaks, which could account for the missing H atom. This atom was included in the refinement and led to a chemically sensible result without the use of constraints. During the final stages of refinement, H(1) was refined isotropically and all other atoms were refined anisotropically. Corrections were made for anomalous dispersion and secondary extinction effects, and a three term Chebyschev weighting scheme (*8*) with parameters 5.04, 0.52, and 3.84 was employed. A total of 83 parameters was refined during the final cycles and the final agreement factors were $R = 0.024$, $R_w = 0.027$.

Results and Discussion

Final atomic coordinates and thermal parameters are given in Tables Ia and b and selected distances and angles in Table II. The structure is composed of an infinite framework of edge and face sharing MnO_6 and PO_4 polyhedra, enclosing cavities occupied by the K^+ ions. Dominating the structure are zigzag chains of edge-sharing MnO_6 octahedra running parallel to the *b* axis, which are interconnected to neighboring chains, within, above, and below the *bc* plane, by PO_4 tetrahedra (Fig. 1). The "Mn chains" are composed of Mn(2) octahedra sharing *cis* edges (i.e., the O(2)–O(7) edges) with two Mn(1) octahedra, which in turn share *trans* edges with two Mn(2) octahedra. The *cis*-edge sharing of the Mn(2) octahedron leads to a considerable distortion of this octahedron—the O(7)–Mn(2)–O(7) angle being only 157.76°. Since both Mn sites are occupied by Mn(III) there is obviously a requirement for a Jahn–Teller distortion. The observed elongation of the Mn(1)–O(7) and Mn(2)–O(7) bond lengths to 2.234 Å and 2.250 Å, respectively, is typical of Mn(III) in oxide systems (*2, 9*).

Interconnection of adjacent Mn chains

TABLE Ia

FINAL ATOMIC COORDINATES AND ISOTROPIC/EQUIVALENT ISOTROPIC THERMAL PARAMETERS

Atom	x/a	y/b	z/c	U(iso)/ U(equiv)[a]
Mn(1)	0.5000	0.0000	0.0000	0.0046
Mn(2)	0.46427(3)	0.2500	0.28702(2)	0.0051
K(1)	0.94812(5)	0.2500	0.82656(4)	0.0139
P(1)	0.89085(5)	0.2500	0.18995(3)	0.0055
P(2)	0.43163(5)	0.2500	0.65307(3)	0.0059
O(1)	0.7895(2)	0.2500	0.3291(1)	0.0085
O(2)	0.4192(1)	0.2500	0.0623(1)	0.0055
O(3)	0.5208(2)	0.2500	0.5109(1)	0.0102
O(4)	0.1457(2)	0.2500	0.2613(1)	0.0115
O(5)	0.1665(2)	0.2500	0.6030(1)	0.0152
O(6)	0.8153(1)	0.06801(9)	0.08467(8)	0.0082
O(7)	0.5153(1)	0.07046(9)	0.75590(8)	0.0084
H(1)	0.090(8)	0.2500	0.514(6)	0.08(2)

[a] U(equiv) is defined as $\frac{1}{3} \Sigma_i \Sigma_j \; U_{ij} a_i^* a_j^* a_i \cdot a_j$.

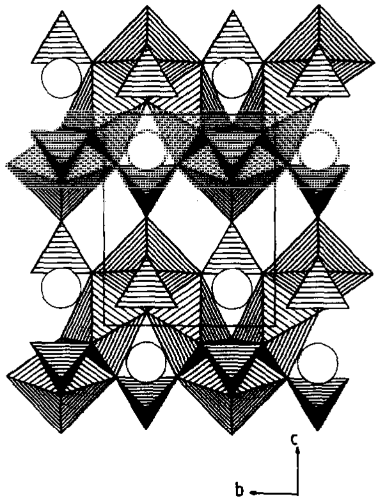

FIG. 1. Polyhedral representation of the framework, viewed along [100]. The zigzag "Mn chains" can be clearly seen. K atoms are shown as open circles. H atoms are not shown.

within the *bc* plane is provided by the P(2) tetrahedron. The relatively short O(7)–O(7) edge of this tetrahedron bridges one of the chains and connects it, via O(3), to an adjacent chain. The remaining vertex of this tetrahedron, O(5), is involved in hydrogen bonding to the P(1) tetrahedron above or below via O(5)–H(1)---O(1) (Fig. 2); the relevant geometry involved with this linkage is given in Table II. In addition to this weak link, a stronger link between neighboring Mn(1)–Mn(2)–P(2) sheets is provided by the P(1) tetrahedron. This tetrahedron bridges the three vertices (2 × O(6) and one O(1)) of one chain and connects it, via O(4), to the Mn(2) octahedron of the neighboring layer. The linking of the three

TABLE Ib

ANISOTROPIC THERMAL PARAMETERS[a]

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Mn(1)	0.00729(8)	0.00226(8)	0.00632(8)	−0.00112(4)	0.00172(5)	−0.00020(4)
Mn(2)	0.00611(8)	0.00486(8)	0.00450(8)	0.0000	0.00175(5)	0.0000
K(1)	0.0128(1)	0.0110(1)	0.0207(1)	0.0000	0.00658(9)	0.0000
P(1)	0.0060(1)	0.0045(1)	0.0058(1)	0.0000	0.00149(8)	0.0000
P(2)	0.0095(1)	0.0046(1)	0.0047(1)	0.0000	0.00235(9)	0.0000
O(1)	0.0086(3)	0.0108(3)	0.0072(3)	0.0000	0.0034(2)	0.0000
O(2)	0.0101(3)	0.0027(3)	0.0061(3)	0.0000	0.0022(2)	0.0000
O(3)	0.0132(3)	0.0159(4)	0.0058(3)	0.0000	0.0040(3)	0.0000
O(4)	0.0060(3)	0.0187(4)	0.0129(4)	0.0000	0.0016(3)	0.0000
O(5)	0.0097(4)	0.0342(6)	0.0098(4)	0.0000	0.0014(3)	0.0000
O(6)	0.0093(2)	0.0060(2)	0.0109(2)	−0.0028(2)	0.0023(2)	−0.0002(2)
O(7)	0.0168(3)	0.0046(2)	0.0082(2)	0.0018(2)	0.0034(2)	0.0002(2)

[a] The U's are defined by $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{23}klb^*c^*)]$.

TABLE II

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (DEG) AND POLYHEDRAL EDGE LENGTHS (Å)

	Distance	*Angle*	*Edge*
Mn(1) octahedron			
Mn(1)–O(2) × 2	1.921(1)		
Mn(1)–O(6) × 2	1.934(1)		
Mn(1)–O(7) × 2	2.234(1)		
O(2)–Mn(1)–O(6)	× 2	89.76(3)	2.720(1)
O(2)–Mn(1)–O(6)	× 2	90.24(3)	2.732(1)
O(2)–Mn(1)–O(7)	× 2	99.88(3)	3.187(1)
O(2)–Mn(1)–O(7)	× 2	80.12(3)	2.685(1)
O(6)–Mn(1)–O(7)	× 2	89.08(3)	2.932(1)
O(6)–Mn(1)–O(7)	× 2	90.92(3)	2.979(1)
Mn(2) octahedron			
Mn(2)–O(1)	1.945(1)		
Mn(2)–O(2)	1.913(1)		
Mn(2)–O(3)	1.896(1)		
Mn(2)–O(4)	1.927(1)		
Mn(2)–O(7) × 2	2.250(1)		
O(1)–Mn(2)–O(2)		90.85(4)	2.748(1)
O(1)–Mn(2)–O(3)		86.99(4)	2.644(1)
O(1)–Mn(2)–O(4)		175.96(4)	
O(1)–Mn(2)–O(7)	× 2	85.60(2)	2.859(1)
O(2)–Mn(2)–O(3)		177.84(4)	
O(2)–Mn(2)–O(4)		93.20(4)	2.790(1)
O(2)–Mn(2)–O(7)	× 2	79.87(2)	2.685(1)
O(3)–Mn(2)–O(4)		88.96(4)	2.678(1)
O(3)–Mn(2)–O(7)	× 2	99.95(2)	3.183(1)
O(4)–Mn(2)–O(7)	× 2	95.11(2)	3.090(1)
O(7)–Mn(2)–O(7)		157.76(4)	
P(1) tetrahedron			
P(1)–O(1)	1.540(1)		
P(1)–O(4)	1.519(1)		
P(1)–O(6) × 2	1.546(1)		
O(1)–P(1)–O(4)		107.41(6)	2.465(1)
O(1)–P(1)–O(6)	× 2	110.75(3)	2.539(1)
O(4)–P(1)–O(6)	× 2	109.74(3)	2.507(1)
O(6)–P(1)–O(6)		108.44(5)	2.508(1)
P(2) tetrahedron			
P(2)–O(3)	1.516(1)		
P(2)–O(5)	1.574(1)		
P(2)–O(7) × 2	1.528(1)		
O(3)–P(2)–O(5)		112.60(6)	2.571(1)
O(3)–P(2)–O(7)	× 2	110.19(3)	2.497(1)
O(5)–P(2)–O(7)	× 2	107.81(4)	2.507(1)
O(7)–P(2)–O(7)		108.08(5)	2.474(1)
K(1) polyhedron			
K(1)–O(2)	3.036(1)		
K(1)–O(3)	3.212(1)		
K(1)–O(4)	3.540(1)		
K(1)–O(5)	2.712(1)		
K(1)–O(6) × 2	2.623(1)		
K(1)–O(6) × 2	2.927(1)		
K(1)–O(7) × 2	2.857(1)		
Geometry around H(1)			
O(5)–H(1)	0.78(5)		
O(1)–H(1)	2.08(5)		
O(1)–O(5)	2.809(1)		
O(1)–H(1)–O(5)	156(5)		

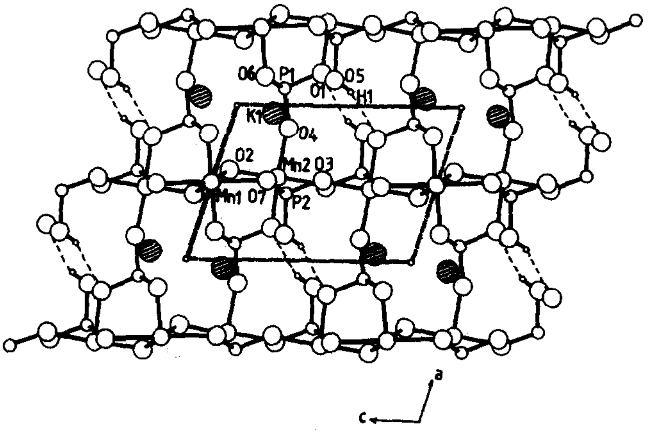

FIG. 2. Projection along [010], showing the interlayer linkages via P(1) and H(1).

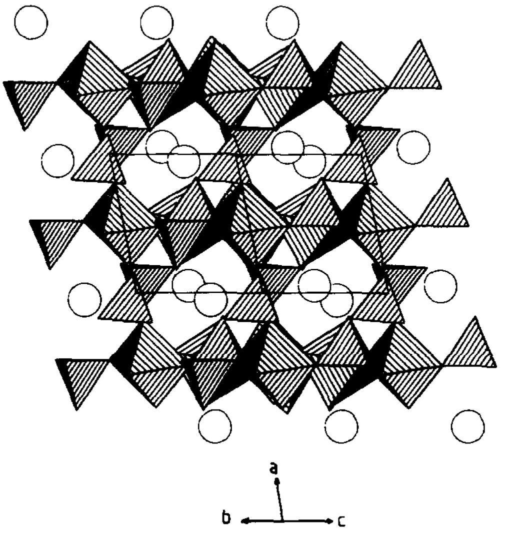

FIG. 3. Polyhedral model of the framework viewed along [011], showing the channels running parallel to this direction. K atoms are shown as open circles.

Mn octahedra of one chain by the P(1) tetrahedron leads to some degree of "puckering" of the Mn chain perpendicular to the *bc* plane. When viewed parallel to the *bc* plane the lamellar nature of the framework becomes apparent. Figure 2 shows the projection along [010]—the layers involving the Mn chains and P(2) can be seen "edge-on," and the interlayer links via H(1) and $P(1)O_4$ can be clearly seen. The void spaces between the layers are occupied by the large K^+ ions, a feature which can be seen along [011] (Fig. 3). The coordination around K(1) is probably best described as eightfold, though the 10 nearest neighbor distances have been included in Table II. Using valence–sum calculations it can be deduced that the valence requirements of K(1) are satisfied by the nearest eight of these, with K–O distances ranging from 2.623 to 3.036 Å ($s = 1.06$ vu for the contributions from O(2), O(5) O(6) (×4), and O(7) (×2)).

This phase represents a new structure type with potentially interesting properties. The zirconium phosphates, for example $Zr(HPO_4)_2 \cdot H_2O$ (*10*), possess layered structures in which the only interlayer interaction is of the Van der Waals type and are well known for their ion-exchange properties (*11*). The present compound has a more rigid structure, with interlayer connections being made by the bridging phosphate groups. A similar type of structure is found in the phosphate $Na_4Ni_7(PO_4)_6$ (*12*). However, we have so far been unable to prepare the phase in bulk quantities suitable for chemical study. In the high-pressure synthesis described above, the phase appears as a minor component of a two-phase mixture. The major product is a poorly crystalline dark-brown phase, the composition of which has been partially determined by analytical electron microscopy, giving a K:Mn:P ratio of approximately 4:5:4. This phase appears as the sole product of the reaction under less extreme conditions (250°C and 30 bar).

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