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Synthesis and Structure of a Novel Layered Phosphate $NH_4Mn_2O(PO_4)(HPO_4) \cdot H_2O$

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A novel layered phosphate, $NH_4Mn_2O(PO_4)(HPO_4) \cdot H_2O$, has been synthesized hydrothermally at 220°C under autogeneous water vapor pressure. The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 6.879(2)$, $b = 7.741(2)$, and $c = 16.244(3)$ Å. The structure was solved by Patterson and Fourier methods and refined to final agreement factors $R = 0.026$, $R_w = 0.028$. Dominating the structure are zigzag chains of edge-sharing MnO_6 octahedra running parallel to a, which are interconnected via bridging PO_4 groups to form continuous sheets lying in the ab plane. Adjacent sheets in the c direction are separated by NH_4^+ ions, and held together via H-bonding. The relationship of the structure to that of the more compact $KMn_2O(PO_4)(HPO_4)$ is discussed.

Introduction

We are currently undertaking a detailed synthetic and structural study on the phosphates of the first-row transition metals: manganese, iron, and cobalt. As part of this study, we recently characterized the hydrate $MnPO_4 \cdot H_2O$ (*1*) (previously and erroneously reported as $MnPO_4 \cdot 1.5H_2O$ (*2*)) by synchrotron X-ray powder diffraction, and also described the synthesis and structure of the new Mn(III) oxyphosphate, $KMn_2O(PO_4)(HPO_4)$ (*3*). Prior to that work, the only well-characterized phosphate containing Mn^{3+} was the mineral bermanite, $Mn_3(PO_4)_2(OH)_2 \cdot 4H_2O$ (*4*), although the orthophosphate $MnPO_4$ was reported to have the low-pressure $FePO_4$ structure (*5*). The present paper expands on our earlier work and describes the synthesis and structure of $NH_4Mn_2O(PO_4)(HPO_4) \cdot H_2O$, a compound whose composition is close to that of $KMn_2O(PO_4)(HPO_4)$ but whose structure, though related, has a more open, layer-like nature. The differences in structure may be correlated with the differences under reaction conditions.

Experimental

A mixture of 0.76 g Mn_3O_4 and 1.15 g $NH_4H_2PO_4$ (molar ratio $NH_4:Mn:P = 1:1:1$) was added to 15 ml distilled water and sealed in a Teflon-lined stainless-steel autoclave. The reaction mixture was held at 220°C for 48 hr before cooling to room temperature. The product was filtered, washed with water, and dried in air. On visual inspection, the product showed a remarkable similarity to that described in the prepara-

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tion of $KMn_2O(PO_4)(HPO_4)$ (*3*), being composed of a poorly crystalline dark brown phase, together with less than 5% of a second, crystalline phase. The latter exhibited the same characteristics as $KMn_2O(PO_4)(HPO_4)$, being red-brown in color and needle-like in morphology, suggesting that the new phase might merely represent the ammonium analog of the above compound. Qualitative analysis in the electron microscope confirmed that the crystals contained both manganese and phosphorus, though it was not possible to confirm or deny the presence of nitrogen using this method. In order to investigate the new phase further, a single-crystal study was carried out. A suitable crystal was mounted and aligned on an Enraf–Nonius CAD4 diffractometer. The unit cell was determined on the basis of 25 well-centered reflections in the angular range 15° < θ < 20°. Details of subsequent data collection and refinement are given in Table I. A semiempirical absorption correction, based on the ψ-scans of three reflections, was applied, together with corrections for Lorentz and polarization effects. Systematic absences uniquely defined the space group as the acentric $P2_12_12_1$, and all subsequent data analysis was carried out on this basis.

TABLE I

DATA COLLECTION AND REFINEMENT PARAMETERS

Formula weight	352.9
Space group	$P2_12_12_1$
a (Å)	6.879(2)
b (Å)	7.741(2)
c (Å)	16.244(3)
V (Å^3)	865.0
D_{calc} (g cm^{-3}) (Z = 4)	2.707
F(000)	688
μ(Mo $K\alpha$) (cm^{-1})	32.1
Crystal size (mm)	0.30 × 0.05 × 0.015
θ min, max (deg)	0.0–30.0
Scan mode	$\omega - 2\theta$
ω scan width	$1.35 + 0.35 \tan \theta$
Min/max scan speed	0.8/5.5° min^{-1}
Min/max h,k,l	$h(-1/9)$, $k(-1/10)$, $l(-1/22)$
Total data	2009
Total unique data	1456
Observed data ($I > 3\sigma(I)$)	1117
Absorption correction: min, max	1.00, 1.31
No. of parameters	165
Weights	$w = 1$
Extinction parameter	9.0(9)
Max residual electron density (eÅ^{-3})	0.5
Final R, R_w	0.026, 0.028

A Patterson map was used to elucidate the positions of two heavy atoms, Mn(1) and Mn(2), with the remaining nonhydrogen atoms being found from two successive difference Fourier maps. The contents of the asymmetric unit at this stage consisted of 2 manganese, 2 phosphorus, 10 oxygen, and 1 ambiguous nitrogen/oxygen atom. The local environment of the ambiguous atom suggested either an ammonium ion or a water molecule in some sort of channel or cavity—the nearest-neighbor distances were about 2.8 Å. Bond-strength calculations (*6*) were carried out at this stage in order to determine the presence of any hydrogen atoms and to help determine the nature of the mystery atom. These showed that both manganese sites were occupied by Mn(III); valence sums being 3.11 v.u. and 3.26 v.u. for Mn(1) and Mn(2), respectively. Three of the oxygens were found to be considerably undersaturated; valence sums of 1.31, 1.19, and 0.47 v.u. being calculated for O(2), O(4), and O(9). These values clearly suggest O(9) to be part of a water molecule, while O(2) and O(4) must share a common hydrogen atom (the O(2)–O(4) distance being very short at 2.47 Å). In order to maintain electroneutrality, the ambiguous atom mentioned previously must be assigned as a nitrogen atom, representing an ammonium ion, thus giving the final stoichiometry $NH_4Mn_2O(PO_4)(HPO_4) \cdot H_2O$. The necessary seven hydrogen atoms were located by careful scrutiny of the penultimate difference Fourier map. Subsequent refinement, with all nonhydrogen atoms given anisotropic temperature factors and all hydrogen atoms refined isotropically, together with corrections for anomalous dispersion and secondary extinction effects, converged to final agreement factors $R = 0.026$, $R_w = 0.028$, for the refinement of 165 least-squares parameters. The weighting $w = 1$ was used throughout the refinement. All crystallographic data analysis was carried out using the Oxford CRYSTALS system (*7*). Scattering factors were taken from "International Tables for X-Ray Crystallography" (*8*).

Results and Discussion

Final atomic coordinates and anisotropic temperature factors are given in Tables II and III, respectively. Selected interatomic bond distances and angles are given in Table IV. A STRUPLO (*9*) view of the structure along [001] is shown in Fig. 1. The relationship of the structure to that of $KMn_2O(PO_4)(HPO_4)$ (Fig. 2) is best seen from this aspect. Zigzag *cis–trans–cis* chains of edge-sharing, Jahn–Teller distorted MnO_6 octahedra are again present and run parallel to the *a*-axis. These chains are held together by bridging PO_4 groups to form continuous sheets within the *ab* plane. The exact nature of the interchain linkage differs from that found in $KMn_2O(PO_4)(HPO_4)$, a fact brought about by the need to accommodate the extra water molecule in the present case. In this case, the

TABLE II

FINAL ATOMIC COORDINATES AND ISOTROPIC/EQUIVALENT ISOTROPIC THERMAL PARAMETERS FOR $NH_4Mn_2O(PO_4)(HPO_4) \cdot H_2O$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U* (iso)/*U* (equiv)
Mn(1)	0.1332(1)	0.42798(8)	0.04325(4)	0.0079
Mn(2)	0.3837(1)	0.7521(1)	0.00091(4)	0.0065
P(1)	0.1327(2)	0.1018(1)	0.92622(7)	0.0071
P(2)	0.3662(2)	0.2629(1)	0.65574(6)	0.0081
N(1)	0.3548(8)	0.4548(6)	0.3064(2)	0.0180
O(1)	0.1339(6)	0.2997(4)	0.9414(2)	0.0107
O(2)	0.3736(6)	0.2137(4)	0.7458(2)	0.0125
O(3)	0.0474(5)	0.5213(5)	0.5361(2)	0.0111
O(4)	0.1198(6)	0.0754(5)	0.8312(2)	0.0165
O(5)	0.0490(5)	0.3074(5)	0.3885(2)	0.0108
O(6)	0.3163(4)	0.0219(5)	0.9616(2)	0.0093
O(7)	0.1826(5)	0.1856(5)	0.6139(2)	0.0123
O(8)	0.3593(6)	0.4623(4)	0.6481(2)	0.0113
O(9)[a]	0.1193(8)	0.2051(5)	0.1111(3)	0.0267
O(10)	0.3655(5)	0.3534(3)	0.4868(2)	0.0076
H(1)	0.21(1)	0.13(1)	0.798(5)	0.04(2)
H(2)	0.25(2)	0.38(2)	0.305(8)	0.10(4)
H(3)	0.16(2)	0.44(1)	0.830(6)	0.07(3)
H(4)	0.35(1)	0.48(1)	0.255(5)	0.05(2)
H(5)	0.45(1)	0.39(1)	0.332(5)	0.05(3)
H(6)	0.070(9)	0.238(8)	0.168(4)	0.02(2)
H(7)	0.232(9)	0.106(9)	0.105(4)	0.02(2)

[a] 0(9) belongs to the water molecule.

TABLE III

ANISOTROPIC THERMAL PARAMETERS FOR $NH_4Mn_2O(PO_4)(HPO_4) \cdot H_2O$

Atom	*U*(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
Mn(1)	0.0093(3)	0.0062(2)	0.0085(2)	0.0004(2)	0.0003(3)	0.0000(3)
Mn(2)	0.0057(2)	0.0073(2)	0.0071(2)	−0.0013(2)	0.0004(2)	−0.0012(2)
P(1)	0.0067(4)	0.0064(4)	0.0084(1)	−0.0002(3)	0.0005(5)	−0.0005(5)
P(2)	0.0085(4)	0.0102(4)	0.0065(4)	0.0011(4)	0.0011(4)	−0.0004(5)
N(1)	0.020(2)	0.022(2)	0.014(2)	−0.000(2)	0.003(2)	0.002(2)
O(1)	0.017(1)	0.008(1)	0.010(1)	0.002(1)	−0.001(1)	0.003(2)
O(2)	0.020(1)	0.023(2)	0.006(1)	0.005(1)	−0.004(2)	−0.000(2)
O(3)	0.009(1)	0.013(2)	0.012(2)	−0.002(1)	0.000(1)	0.002(1)
O(4)	0.019(2)	0.023(2)	0.011(1)	−0.001(1)	−0.001(1)	0.002(2)
O(5)	0.010(2)	0.013(2)	0.011(2)	0.001(1)	−0.001(1)	−0.001(1)
O(6)	0.006(1)	0.010(1)	0.017(2)	0.002(1)	−0.000(1)	0.003(1)
O(7)	0.011(2)	0.016(2)	0.013(2)	0.005(1)	−0.002(1)	−0.003(1)
O(8)	0.018(1)	0.009(1)	0.009(1)	−0.000(1)	0.001(2)	−0.001(2)
O(9)[a]	0.042(2)	0.018(2)	0.026(2)	0.002(2)	0.006(2)	0.002(2)
O(10)	0.007(1)	0.007(1)	0.009(1)	−0.0009(9)	0.001(1)	0.001(1)

[a] 0(9) belongs to the water molecule.

TABLE IV

SELECTED INTERATOMIC DISTANCES (Å), ANGLES (DEG), AND POLYHEDRAL EDGE LENGTHS (Å) FOR $NH_4Mn_2O(PO_4)(HPO_4) \cdot H_2O$

	Distance	Angle	Edge
Mn(1) octahedron			
Mn(1)–O(1)	1.930(3)		
Mn(1)–O(3)	2.236(3)		
Mn(1)–O(6)	2.216(3)		
Mn(1)–O(8)	1.905(3)		
Mn(1)–O(9)	2.050(4)		
Mn(1)–O(10)	1.925(3)		
O(1)–Mn(1)–O(3)		92.5(2)	3.017(5)
O(1)–Mn(1)–O(6)		93.6(2)	3.028(5)
O(1)–Mn(1)–O(8)		175.2(1)	
O(1)–Mn(1)–O(9)		91.6(2)	2.856(5)
O(1)–Mn(1)–O(10)		92.5(1)	2.786(4)
O(3)–Mn(1)–O(6)		159.2(1)	
O(3)–Mn(1)–O(8)		86.6(2)	2.851(5)
O(3)–Mn(1)–O(9)		102.8(2)	3.011(6)
O(3)–Mn(1)–O(10)		79.4(1)	2.669(4)
O(6)–Mn(1)–O(8)		88.9(1)	2.893(5)
O(6)–Mn(1)–O(9)		86.9(2)	3.124(5)
O(6)–Mn(1)–O(10)		80.5(1)	2.683(4)
O(8)–Mn(1)–O(9)		84.0(2)	2.649(5)
O(8)–Mn(1)–O(10)		91.9(1)	2.754(4)
O(9)–Mn(1)–O(10)		175.2(2)	
Mn(2) octahedron			
Mn(2)–O(3)	2.243(4)		
Mn(2)–O(5)	1.940(4)		
Mn(2)–O(6)	2.234(3)		
Mn(2)–O(7)	1.953(4)		
Mn(2)–O(10)	1.906(3)		
Mn(2)–O(10)	1.914(3)		
O(3)–Mn(2)–O(5)		88.0(2)	2.915(5)
O(3)–Mn(2)–O(6)		178.1(2)	
O(3)–Mn(2)–O(7)		92.5(2)	3.036(5)
O(3)–Mn(2)–O(10)		99.8(1)	3.181(4)
O(3)–Mn(2)–O(10)		79.5(1)	2.669(4)
O(5)–Mn(2)–O(6)		90.1(1)	2.962(5)
O(5)–Mn(2)–O(7)		179.4(2)	
O(5)–Mn(2)–O(10)		88.9(1)	2.693(5)
O(5)–Mn(2)–O(10)		90.0(1)	2.724(5)
O(6)–Mn(2)–O(7)		89.4(2)	2.952(6)
O(6)–Mn(2)–O(10)		80.4(1)	2.683(4)
O(6)–Mn(2)–O(10)		100.3(1)	3.191(4)
O(7)–Mn(2)–O(10)		90.6(1)	2.746(5)
O(7)–Mn(20–O(10)		90.5(1)	2.744(5)
O(10)–Mn(2)–O(10)		178.7(1)	
P(1) tetrahedron			
P(1)–O(1)	1.552(3)		
P(1)–O(3)	1.516(3)		
P(1)–O(4)	1.559(3)		
P(1)–O(6)	1.520(3)		
O(1)–P(1)–O(3)		110.3(2)	2.517(5)
O(1)–P(1)–O(4)		106.7(2)	2.496(4)
O(1)–P(1)–O(6)		109.7(2)	2.511(5)
O(3)–P(1)–O(4)		107.4(2)	2.479(5)
O(3)–P(1)–O(6)		111.1(2)	2.503(4)
O(4)–P(1)–O(6)		111.6(2)	2.546(5)
P(2) tetrahedron			
P(2)–O(2)	1.513(3)		
P(2)–O(5)	1.547(4)		
P(2)–O(7)	1.555(4)		
P(2)–O(8)	1.549(3)		
O(2)–P(2)–O(5)		109.5(2)	2.499(5)
O(2)–P(2)–O(7)		110.7(2)	2.524(5)
O(2)–P(2)–O(8)		109.2(2)	2.497(4)
O(5)–P(2)–O(7)		108.8(2)	2.522(4)
O(5)–P(2)–O(8)		109.8(2)	2.533(5)
O(7)–P(2)–O(8)		108.9(2)	2.525(5)
Coordination around N(1)			
N(1)–H(2)	0.94(12)		
N(1)–H(3)	0.90(11)		
N(1)–H(4)	0.86(8)		
N(1)–H(5)	0.94(9)		
H(2)–N(1)–H(3)		120(9)	
H(2)–N(1)–H(4)		95(9)	
H(2)–N(1)–H(5)		102(7)	
H(3)–N(1)–H(4)		101(8)	
H(3)–N(1)–H(5)		113(8)	
H(4)–N(1)–H(5)		126(8)	
Other distances			
Ow(9)–H(6)	1.01(6)		
Ow(9)–H(7)	1.09(7)		
H(6)–O(9)–H(7)		119(7)	
O(4)–H(1)	0.92(8)		
Hydrogen bonds			
Donor–H–Acceptor	D–A	H–A	D–H–A
O(4)–H(1)–O(2)	2.474(5)	1.56(7)	175(8)
O(9)–H(6)–O(2)	2.942(5)	1.98(6)	156(5)
N(1)–H(2)–O(5)	2.740(6)	2.02(12)	132(10)
N(1)–H(5)–O(7)	2.819(6)	1.90(9)	165(8)

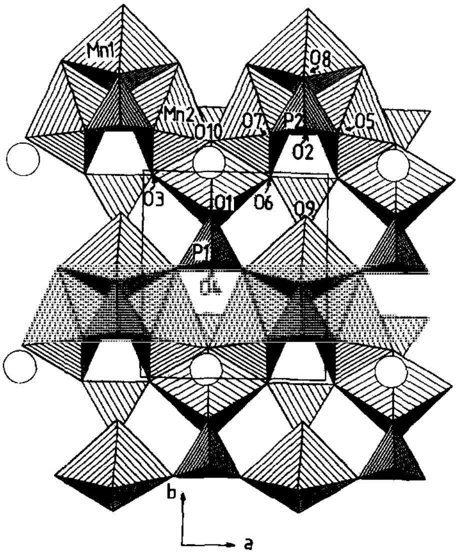

FIG. 1. View of the $NH_4Mn_2O(PO_4)(HPO_4) \cdot H_2O$ structure along [001]. NH_4^+ ions are represented by open circles.

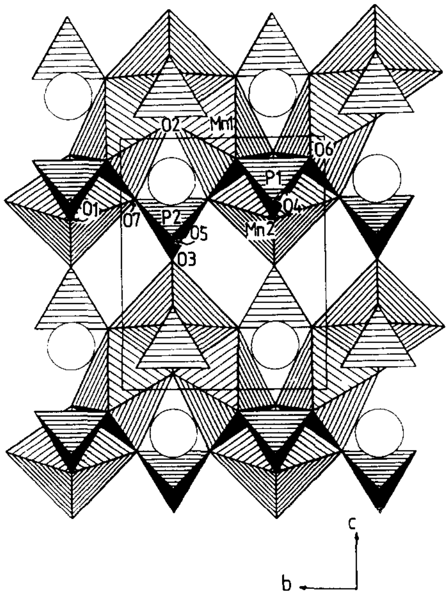

FIG. 2. View of the $KMn_2O(PO_4)(HPO_4)$ structure along [100], for comparison with Fig. 1. Note the relative dispositions of the NH_4^+ and K^+ ions (large circles) and the mode of intralayer linkage via the PO_4 groups.

Mn octahedron sharing *cis* edges, Mn(1), is linked to neighboring chains within the plane not by the "in-plane" vertex, as is the case in the potassium compound, but by the "out-of-plane" vertex, O(1). The "in-plane" vertex in the present case is, in fact, the oxygen atom of the water molecule, O(9). This requirement forces a larger degree of buckling of the *ab* layers in the present compound than occurs in $KMn_2O(PO_4)(HPO_4)$, a fact which can be clearly seen with reference to the [100] view of the structure shown in Fig. 3. From this, the layer-like nature of the structure also becomes more apparent, together with the disposition of the NH_4^+ ions relative to the layers. In contrast to the case of $KMn_2O(PO_4)(HPO_4)$, there are no rigid interlayer bridges via PO_4 groups; linkages between adjacent layers are made merely by hydrogen bonding, either directly, via O(4)–H(1)–O(2) and O(9)–H(6)–O(2), or indirectly, via the hydrogen bonds associated with the NH_4^+ group (see Table IV). The O(4)–O(2) distance of 2.47 Å represents a very strong hydrogen bond; the average distance for such contacts involving HPO_4^{2-} groups is 2.597 Å (*10*) with a corresponding average P–O distance of 1.581 Å (cf. 1.559 Å in the present case). However, a donor–acceptor distance of 2.448 Å was recently reported in the phosphate $Co_7(PO_4)_2(HPO_4)_4$ (*11*), and even shorter contacts are associated with symmetrical hydrogen bonds in, for example, $Na_5Cu_3H(PO_4)_4$ (*12*) (O–O = 2.388 Å).

Careful comparison of the structures of $KMn_2O(PO_4)(HPO_4)$ and $NH_4Mn_2O(PO_4)(HPO_4) \cdot H_2O$ clearly shows that the latter compound adopts a more open, less rigid structure. A simple demonstration of this is found by comparing their respective densities (3.28 and 2.71 g cm^{-3}, respectively). This difference may be correlated with the differences in conditions of synthesis.

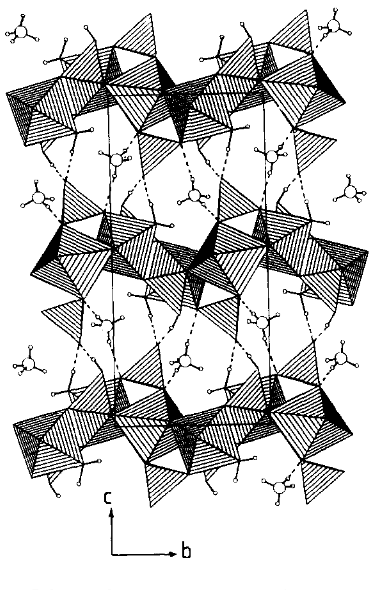

FIG. 3. View of the $NH_4Mn_2O(PO_4)(HPO_4) \cdot H_2O$ structure along [100]. Large circles, nitrogen; small circles, hydrogen. Hydrogen bonds shown as dashed lines.

Whereas $KMn_2O(PO_4)(HPO_4)$ was prepared under relatively severe conditions, at 400°C and 3 kbar pressure, $NH_4Mn_2O(PO_4)(HPO_4) \cdot H_2O$ was prepared under much milder conditions, at 220°C and 30 bar pressure. These conditions allow the water molecule to be retained within the structure and lead to the more loosely bound, hydrogen-bonded layer structure. This is potentially the more interesting structure from the chemical point of view since it provides a possible system for ion exchange and intercalation of guest species, as is well known in the zirconium (*13*) and vanadium (*14, 15*) phosphates. A reliable method of obtaining these compounds in a pure state would be desirable before such possibilities can be tested; in both of the reported syntheses a poorly crystalline dark brown phase predominates. This is presumably related to both of the characterized phases, but we have been unable to define its composition with any certainty.

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