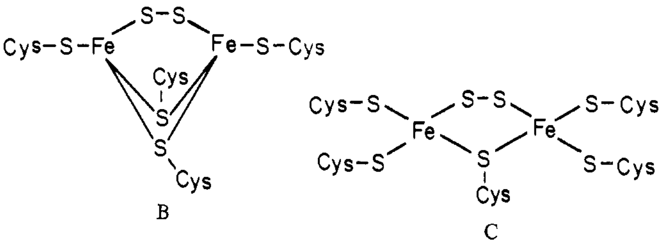

B

C

Structure C requires a fifth cysteine which is in fact present in all plant ferredoxins except in *Equisetum* ferredoxin.[31]

Registry No. $[(C_5H_5)Fe(SC_2H_5)S]_2$, 39796-99-1.

(31) S. J. Aggarwal, K. K. Rao, and H. Matsubara, *J. Biochem. (Tokyo)*, 69, 609 (1971).

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Crystal Structure of Manganese Pyrophosphate Dihydrate, $Mn_2P_2O_7 \cdot 2H_2O$

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Manganese pyrophosphate dihydrate, $Mn_2P_2O_7 \cdot 2H_2O$, crystallizes in the monoclinic space group $P2_1/n$. A unit cell with dimensions $a = 6.461$ (2), $b = 14.325$ (4), and $c = 7.570$ (4) Å, and $\beta = 95.20$ (4)° contains four formula units. The manganese ions are each coordinated to five oxygen atoms and a water molecule in a distorted octahedral arrangement with a mean manganese–oxygen distance of 2.192 (1) Å. Chains of octahedra with shared edges run through the structure. The two ends of the pyrophosphate anion are 20° from the completely eclipsed conformation and the P–O–P bridge angle is 127.5 (2)°. The mean P–O distance for the terminal P–O bonds is 1.520 (2) Å while for the bridge oxygen the mean P–O bond distance is 1.613 (3) Å. The structure was solved by the symbolic addition method, based on diffractometer data collected with Mo Kα radiation, and it was refined by block-diagonal least squares to a conventional R value of 0.038 for 1506 reflections.

Introduction

In the solid state, the pyrophosphate ion is found to assume a rather wide range of conformations. The anhydrous pyrophosphate salts of the divalent metal ions, magnesium, zinc, and copper, exist in two phases. In the high-temperature (β) phase and in $Mn_2P_2O_7$, the pyrophosphate ion has a linear P–O–P bridge with considerable disorder in the bridge oxygen atoms.[1-4] The terminal PO_3 groups are oriented so as to present a staggered conformation when the ion is viewed along the P–P direction. In the low-temperature (α) phases of magnesium[5] and copper[6] pyrophosphate, the pyrophosphate ion is in a staggered conformation but with a bent P–O–P bridge. The high-temperature (α) phases of $Ca_2P_2O_7$[7] and $Sr_2P_2O_7$[8] contain pyrophosphate ions with bent bridge bonds but with an exactly eclipsed conformation in $Sr_2P_2O_7$ and an almost eclipsed conformation in $Ca_2P_2O_7$. The low-temperature form (β) of $Ca_2P_2O_7$ (and presumably the isostructural β-$Sr_2P_2O_7$) has bent P–O–P bonds and is almost eclipsed.[9] The crystal structure of only one hydrated pyrophosphate has been determined, $Na_4P_2O_7 \cdot 10H_2O$.[10,11] In that structure the bridge bonds are bent and the conformation is staggered. The crystal structure determination of $Mn_2P_2O_7 \cdot 2H_2O$ was undertaken to study the conformation of the $P_2O_7^{4-}$ ion in another type of crystal environment and to assess more fully the conformational range available to the pyrophosphate anion.

Experimental Section

Amorphous manganese pyrophosphate was prepared by mixing together solutions of manganese chloride and sodium pyrophosphate.[12] The precipitate was dissolved with sulfur dioxide and the sulfur dioxide was then removed slowly by bubbling carbon dioxide through the solution. A pink precipitate formed that was a mixture of microcrystals under 2 μ and larger prismatic crystals measuring up to 0.1 mm in length.

One of the larger crystals with dimensions 0.09 × 0.07 × 0.03 mm was chosen for X-ray analysis and mounted on a goniometer head. Preliminary examination of the reciprocal lattice and a determination of approximate lattice constants were made with a Buerger precession camera and Mo K radiation. The reciprocal lattice symmetry indicated that the crystal was monoclinic and the systematic extinction of $h0l$ reflections for $h + l$ odd and $0k0$ reflections for k odd established the space group uniquely as $P2_1/n$. This space group has the equivalent positions $x, y, z; \bar{x}, \bar{y}, \bar{z}; \bar{x} + {}^1/_2, y + {}^1/_2, \bar{z} + {}^1/_2; x + {}^1/_2, \bar{y} + {}^1/_2, z + {}^1/_2$ and is merely a nonstandard orientation of $P2_1/c$. The lattice constants were refined by centering 12 high-angle reflections on the detector of an automated Picker four-circle diffractometer and using the 2θ angles measured with Mo Kα_1 radiation ($\lambda = 0.70926$ Å) as input to a least-squares adjustment. The final lattice constants obtained in this way were $a = 6.461$ (2), $b = 14.325$ (4), and $c = 7.570$ (4) Å and $\beta = 95.20$ (4)° at 25.5°. The density measured by flotation in a mixture of benzene and *s*-tetrabromoethane was 2.95 g/cm^3. The density calculated for four molecules of $Mn_2P_2O_7 \cdot 2H_2O$ per unit cell is 3.06 g/cm^3.

The intensity data were collected by the 2θ scan method with Zr-filtered Mo Kα radiation on an automated Picker four-circle diffractometer. A 3° target take-off angle was used and the scan range was increased from a minimum value of 1.0° to allow for dispersion as 2θ increased. The scans were made at 1°/min and the total number of counts recorded. Net intensities were calculated by sub-

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(1) C. Calvo, *Can. J. Chem.*, 43, 1139 (1965).

(2) C. Calvo, *Can. J. Chem.*, 43, 1147 (1965).

(3) B. E. Robertson and C. Calvo, *Can. J. Chem.*, 46, 605 (1968).

(4) K. Lukaszewicz and R. Smajkiewicz, *Rocz. Chem.*, 35, 741 (1961).

(5) C. Calvo, *Acta Crystallogr.*, 23, 289 (1967).

(6) B. E. Robertson and C. Calvo, *Acta Crystallogr.*, 22, 665 (1967).

(7) C. Calvo, *Inorg. Chem.*, 7, 1345 (1968).

(8) L. Hagman, T. Jansson, and C. Magneli, *Acta Chem. Scand.*, 22, 1419 (1968).

(9) N. C. Webb, *Acta Crystallogr.*, 21, 942 (1966).

(10) D. M. Mac Arthur and C. A. Beevers, *Acta Crystallogr.*, 10, 428 (1957).

(11) W. S. McDonald and D. W. J. Cruickshank, *Acta Crystallogr.*, 22, 43 (1967).

(12) H. Bassett, W. L. Bechwell, and J. B. Hutchinson, *J. Chem. Soc.*, 1412 (1936).

Table I. Atomic Fractional Parameters (x, y, z) and Thermal Parameters Both $\times 10^4$ [a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Mn(1)	4472 (1)	2458 (1)	1490 (1)	45 (2)	12 (1)	32 (1)	−5 (1)	8 (2)	1 (1)
Mn(2)	7408 (1)	1081 (1)	9182 (1)	44 (2)	12 (1)	35 (1)	4 (1)	9 (2)	−2 (1)
P(3)	2436 (2)	860 (1)	8466 (2)	32 (2)	9 (1)	28 (2)	5 (2)	5 (3)	−2 (2)
P(4)	4334 (2)	1874 (1)	5729 (2)	36 (2)	9 (1)	23 (2)	5 (2)	2 (3)	−1 (2)
O(5)	3327 (6)	961 (2)	6550 (5)	47 (8)	10 (1)	34 (5)	3 (4)	16 (10)	7 (5)
O(6)	2033 (6)	−163 (3)	8678 (5)	92 (9)	10 (2)	40 (6)	10 (5)	1 (12)	−6 (6)
O(7)	4150 (6)	1258 (3)	9774 (5)	45 (8)	15 (2)	38 (5)	−12 (5)	6 (10)	−1 (6)
O(8)	463 (6)	1440 (2)	8395 (5)	41 (7)	10 (2)	49 (6)	12 (5)	18 (11)	6 (6)
O(9)	4632 (6)	1598 (2)	3839 (5)	84 (9)	10 (2)	26 (5)	1 (4)	−1 (11)	−12 (6)
O(10)	6351 (6)	2061 (3)	6879 (5)	40 (8)	17 (2)	28 (5)	6 (5)	−10 (10)	3 (6)
O(11)	2777 (6)	2672 (2)	5908 (5)	7 (8)	10 (2)	54 (6)	6 (5)	25 (11)	2 (6)
O(12)	9319 (7)	1488 (3)	4304 (6)	91 (10)	32 (2)	68 (7)	−15 (6)	9 (14)	−28 (8)
O(13)	7560 (7)	−4 (3)	7166 (6)	101 (10)	19 (2)	92 (8)	−30 (6)	−1 (14)	−24 (7)

[a] The B_{ij} values are coefficients in $T = \exp[-2\pi^2(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk]$. Standard deviations are given in parentheses.

tracting the background determined by counting with the instrument stationary at each end of the scan range. Below $2\theta = 30°$ the total background count time was set to be half the scan time while above $2\theta = 30°$ it was set equal to the scan time. Three standard reflections were measured after every 80 reflections to monitor stability. Of the 2204 reflections in the sphere of diffraction up to $2\theta = 60°$, 1506 had net intensities greater than 2.5 times their standard error and, hence, were considered to be observed. The net intensities were corrected for Lorentz and polarization effects and for the small variation (under 6%) of the standard intensities. No extinction or absorption corrections were made. The transmission factor through the longest direction in the crystal was 0.61 and through the shortest, 0.89.

Structure Determination. The structure was solved by use of the symbolic addition method.[13] The computer program of Hall[14] was used to determine the signs of 301 reflections. These signs and the observed structure amplitudes gave an approximate electron density map which revealed the positions of the two independent manganese and two independent phosphorus atoms. The coordinates of these four atoms were used to calculate signs of the observed reflections. An electron density map calculated with the complete observed data set revealed the positions of all the remaining nonhydrogen atoms. The structure was refined to a value of $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.041$ by the block-diagonal least-squares method using anisotropic thermal parameters.

A Fourier map of the difference electron density revealed a number of peaks with density between 0.5 and 1.0 e/Å^3. Three were in positions that were physically reasonable for a hydrogen atom on a water molecule. These atoms were included with isotropic temperature factors and refined by further least-squares cycles. The final R value was 0.038.

During the refinement a weighting scheme with $\sqrt{w} = 1$ when $|F_o| \leq 40$ and $\sqrt{w} = |F_o|/40$ when $|F_o| > 40$ was used. For the final few refinement cycles the weighting scheme was $\sqrt{w} = 1/\{1 + [(|F_o| - P_1)/P_2]^4\}^{1/2}$ where P_1 and P_2 were determined to be both equal to 40 by the criterion that the mean value of $w(|F_o| - |F_c|)$ should be reasonably independent of $|F_o|$. Atomic scattering factors for Mn^{2+}, P, O$^-$, and O were taken from the compilation of Cromer and Mann[15] and anomalous dispersion corrections[16] were applied to the manganese and phosphorus scattering factors. The final atomic parameters for the heavy atoms are listed in Table I and for the hydrogen atoms in Table II. A comparison of observed and calculated structure factors is available.[17]

Description and Discussion of the Structure. A zig-zag chain made up of manganese coordination octahedra which share edges runs through the structure in the a–c plane (see Figure 1). The two types of manganese, Mn(1) and Mn(2), alternate along the chain and each chain is related to another one by the 2_1 axis. Both the pyrophosphate ions and the water molecules are coordinated to the manganese.

Table II. Hydrogen Atom Fractional Parameters (x, y, z) $\times 10^3$ and Isotropic Thermal Parameters (Å^{-2})

	x	y	z	B
H(14)	145 (13)	16 (6)	271 (11)	2.0 (1.9)
H(15)	662 (15)	−32 (7)	694 (13)	3.5 (2.1)
H(16)	866 (11)	124 (5)	425 (10)	1.6 (1.3)

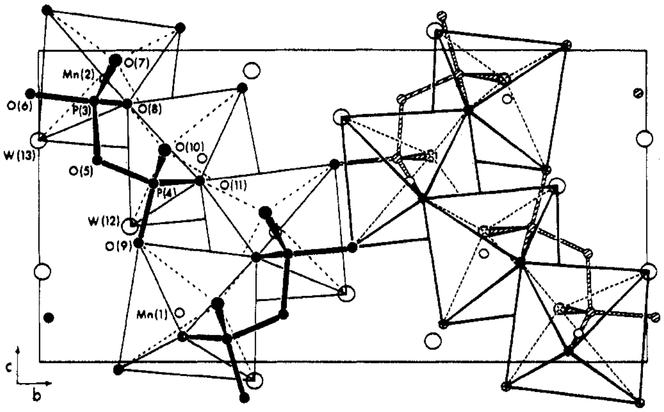

Figure 1. A projection of the $Mn_2P_2O_7 \cdot 2H_2O$ structure onto the *bc* plane. The manganese ions are shown as small, open circles and their coordination octahedra are outlined. The atoms of the pyrophosphate ion are shown as solid circles. The large circles indicate the positions of the oxygen atoms in the water molecules and are labeled w(12) and w(13).

Manganese Coordination. The distances and angles within each of the two types of coordination octahedra about manganese are given in Table III. The coordination is considerably distorted from that of a perfect octahedron, but this is not unusual in structures of this type where the ligands are not identical. The mean manganese–oxygen distances are Mn(1)–O, 2.191 (2) Å and Mn(2)–O, 2.194 (2) Å. These are in agreement with the previously determined average value of 2.181 (3) Å in manganeseammonium sulfate hexahydrate.[18]

The geometry of the manganese coordination can be seen in the stereoscopic drawing of Figure 2. Each manganese is chelated across the P–O–P bridge of one pyrophosphate anion and each is also coordinated to one water molecule.

Pyrophosphate Anion. A drawing of the pyrophosphate anion is shown in Figure 3 and bond distances and angles are given in Table IV. The bridge angle is 127.5 (2)° and the conformation is about 20° from eclipsed when viewed down the P–P axis (see Figure 4). This places the geometry of the anion in between that of the staggered conformation found in the α phases of Mg and Cu pyrophosphate[5,6] and the eclipsed conformation found in the high- and low-temperature forms of $Ca_2P_2O_7$ and $Sr_2P_2O_7$.[7-9] The mean bond distances of 1.520 (2) Å for the terminal P–O bonds and 1.613 (3) Å for the P–O bridge bonds are within the range found for other

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(13) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

(14) S. R. Hall, "NRC Crystallographic Programs for the IBM/360 System," National Research Council, Ottawa, Canada, 1968.

(15) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(16) D. T. Cromer and D. J. Liberman, *J. Chem. Phys.*, **53**, 189 (1970).

(17) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2136.

(18) H. Montgomery, R. V. Chastain, and E. C. Lingafelter, *Acta Crystallogr.*, **20**, 731 (1966).

Table III. Distances (Å) and Angles (deg) in the Coordination Sphere of Manganese[a,b]

	Distances		
Mn(1)-O(7^{i})	2.153 (4)	Mn(2)-O(6^{iv})	2.092 (4)
Mn(1)-O(8^{iii})	2.194 (4)	Mn(2)-O(7)	2.206 (4)
Mn(1)-O(9)	2.158 (4)	Mn(2)-O(8^{v})	2.175 (4)
Mn(1)-O(10^{ii})	2.176 (4)	Mn(2)-O(10)	2.293 (4)
Mn(1)-O(11^{iii})	2.227 (4)	Mn(2)-O(11^{vi})	2.213 (4)
Mn(1)-O(12^{ii})	2.236 (5)	Mn(2)-O(13)	2.187 (4)
	Angles		
O(7^{i})-Mn(1)-O(8^{iii})	167.79 (14)	O(6^{iv})-Mn(2)-O(7)	90.93 (14)
O(7^{i})-Mn(1)-O(9)	92.09 (14)	O(6^{iv})-Mn(2)-O(8^{v})	105.27 (14)
O(7^{i})-Mn(1)-O(10^{ii})	107.13 (14)	O(6^{iv})-Mn(2)-O(10)	172.66 (14)
O(7^{i})-Mn(1)-O(11^{iii})	81.73 (14)	O(6^{iv})-Mn(2)-O(11^{vi})	92.79 (14)
O(7^{i})-Mn(1)-O(12^{ii})	95.59 (15)	O(6^{iv})-Mn(2)-O(13)	94.47 (16)
O(8^{iii})-Mn(1)-O(11^{iii})	87.83 (13)	O(7)-Mn(2)-O(10)	81.97 (13)
O(8^{iii})-Mn(1)-O(12^{ii})	89.49 (15)	O(7)-Mn(2)-O(11^{vi})	80.85 (13)
O(9)-Mn(1)-O(8^{iii})	83.08 (14)	O(8^{v})-Mn(2)-O(7)	159.22 (14)
O(9)-Mn(1)-O(10^{ii})	95.58 (14)	O(8^{v})-Mn(2)-O(10)	82.07 (13)
O(9)-Mn(1)-O(11^{iii})	98.05 (14)	O(8^{v})-Mn(2)-O(11^{vi})	85.37 (13)
O(9)-Mn(1)-O(12^{ii})	172.30 (15)	O(8^{v})-Mn(2)-O(13)	82.96 (15)
O(10^{ii})-Mn(1)-O(8^{iii})	84.35 (13)	O(11^{vi})-Mn(2)-O(10)	87.93 (13)
O(10^{ii})-Mn(1)-O(11^{iii})	165.96 (14)	O(13)-Mn(2)-O(7)	109.11 (15)
O(10^{ii})-Mn(1)-O(12^{ii})	84.66 (15)	O(13)-Mn(2)-O(10)	86.17 (15)
O(11^{iii})-Mn(1)-O(12^{ii})	83.63 (15)	O(13)-Mn(2)-O(11^{vi})	167.54 (15)

[a] Standard deviations are reported in parentheses. [b] The superscripts in this table and in Table V indicate that the atom is related to an atom of the same number reported in Table I in the following manner: (i) $x, y, -1 + z$; (ii) $-^1/_2 + x, ^1/_2 - y, -^1/_2 + z$; (iii) $^1/_2 + x, ^1/_2 - y, -^1/_2 + z$; (iv) $1 - x, -y, 2 - z$; (v) $1 + x, y, z$; (vi) $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; (vii) $1 - x, -y, 1 - z$.

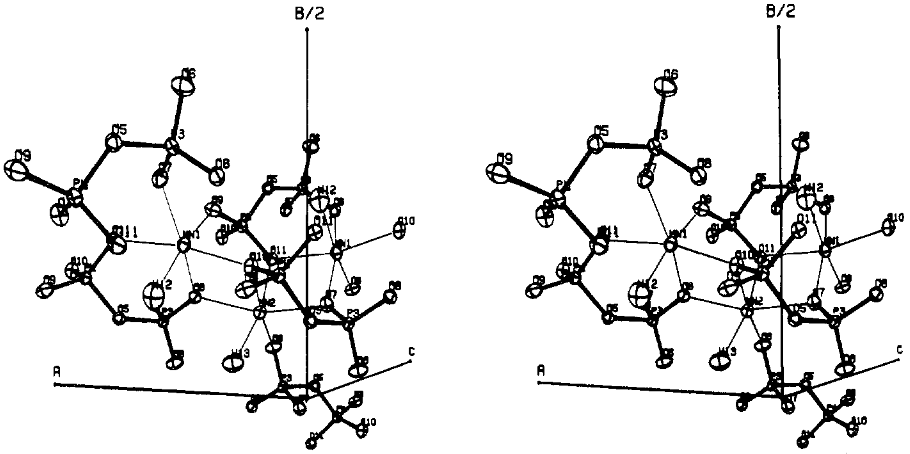

Figure 2. A stereoscopic view of the $Mn_2P_2O_7 \cdot 2H_2O$ structure that illustrates the environment of the two manganese atoms. The manganese coordination is indicated by solid lines.

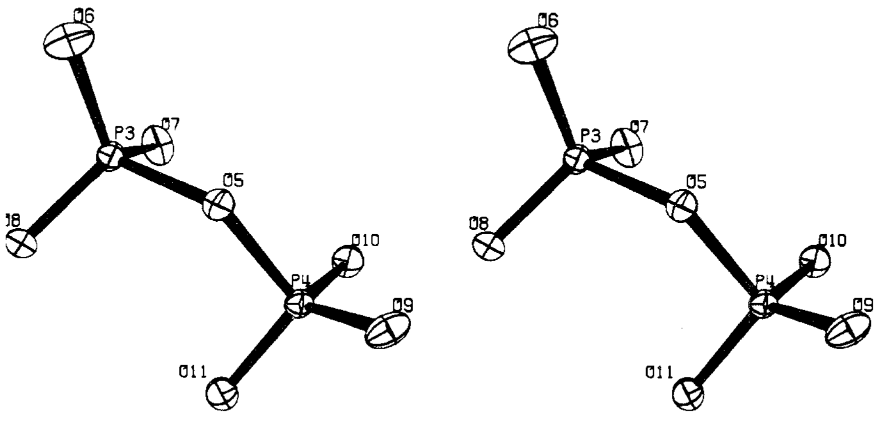

Figure 3. A stereoscopic view of the pyrophosphate anion in $Mn_2P_2O_7 \cdot 2H_2O$.

pyrophosphate anions with bent bridge bonds.[5-11] In particular, they are quite close to the values in $Na_4P_2O_7 \cdot 10H_2O$[11] which has a mean terminal P-O bond length of 1.523 (4) Å, a mean bridge P-O bond length of 1.612 (5) Å, and a P-O-P bridge angle of 130.2 (6)°.[6]

The bridge oxygen has no really close intermolecular contacts and this is a feature commonly found in pyrophosphate structures with the exception of β-$Ca_2P_2O_7$[9] where the bridge oxygen may form weak bonds to calcium and in the room temperature form of $Na_4P_2O_7$[19] where there is a close approach of 2.426 Å between the bridge oxygen atom and a sodium ion. In the manganese compound, the two shortest manganese-bridge oxygen approaches are at 3.16 (1) and 3.36 (1) Å. These are considerably longer than the mean Mn-O coordination distance of 2.192 (1) Å.

There are no intermolecular oxygen approaches to the bridge

(19) K. Y. Leung and C. Calvo, *Can. J. Chem.*, **50**, 2519 (1972).

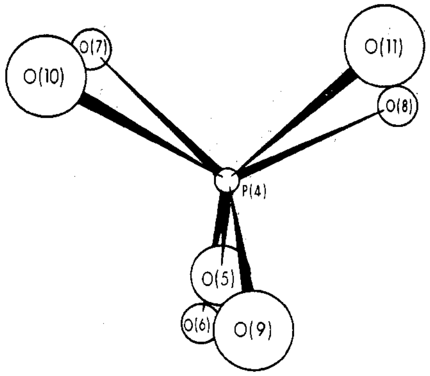

Figure 4. A projection of the pyrophosphate anion onto a plane perpendicular to the P-P direction.

Table IV. Distances (Å) and Angles (deg) in the Pyrophosphate Anion[a]

	Distances		
P(3)-O(5)	1.615 (4)	P(4)-O(5)	1.611 (4)
P(3)-O(6)	1.499 (4)	P(4)-O(9)	1.513 (4)
P(3)-O(7)	1.527 (4)	P(4)-O(10)	1.524 (4)
P(3)-O(8)	1.518 (4)	P(4)-O(11)	1.537 (4)
	Angles		
P(3)-O(5)-P(4)	127.5 (2)	O(5)-P(4)-O(9)	104.1 (2)
O(5)-P(3)-O(6)	105.2 (2)	O(5)-P(4)-O(10)	106.0 (2)
O(5)-P(3)-O(7)	104.6 (2)	O(5)-P(4)-O(11)	106.2 (2)
O(5)-P(3)-O(8)	106.4 (2)	O(9)-P(4)-O(10)	114.3 (2)
O(6)-P(3)-O(7)	114.8 (2)	O(9)-P(4)-O(11)	114.7 (2)
O(6)-P(3)-O(8)	112.6 (2)	O(10)-P(4)-O(11)	110.7 (2)
O(7)-P(3)-O(8)	112.2 (2)		

[a] Standard deviations are given in parentheses.

Table V. Possible Hydrogen-Bond Distances and Angles[a]

		O-H, Å	H···O, Å	O···O, Å	O-H···O angle, deg
O(12)-H(16)···	O(9)	0.55 (7)	2.64 (7)	3.02 (1)	130 (8)
O(12)	$O(6^{vii})$			3.02 (1)	
O(12)	$O(11^{iii})$			2.93 (1)	
O(12)	$O(11^{v})$			2.98 (1)	
O(12)	O(10)			2.97 (1)	
O(12)	$O(5^{v})$			3.06 (1)	
O(13)-H(14)···	$O(6^{v})$	0.67 (9)	2.40 (9)	3.02 (1)	155 (9)
O(13)-H(15)···	$O(9^{vii})$	0.77 (10)	2.06	2.76 (1)	150 (10)
O(13)	$O(8^{v})$			2.89 (1)	
O(13)	O(5)			3.06 (1)	
O(13)	O(10)			3.06 (1)	

[a] All oxygen atoms within 3.10 Å of O(12) and O(13) are included. Standard deviations are given in parentheses. See Table IV for explanation of superscripts.

oxygen of less than 3.0 Å, and, hence, if hydrogen bonding does occur at the bridge oxygen, it is weak. The closest oxygen approaches are from a water molecule O(12), at 3.06 Å, and two water molecules, O(13), at 3.06 and 3.13 Å.

Water Molecules. Each water molecule is coordinated to a manganese atom and surrounded by a number of oxygen atoms at the varying distances shown in Table V. Some of the oxygen-oxygen distances are comparable to those in which hydrogen bonding has been invoked in other structures, but in spite of the knowledge of the approximate positions of three of the four hydrogen atoms, a complete hydrogen bonding assignment of two bonds per water molecule cannot be made.

In the water molecule containing O(13), two hydrogen atoms, H(14) and H(15), have been located. The angle H(14)-O(13)-H(15) is 124 (10)°, considerably larger than would be expected (105°), and suggests that the hydrogen atom positions have been poorly located. It should be noted that the estimated standard deviation for this angle is high, around 10°. The short approach between O(13) and $O(9^{vii})$ of 2.76 Å almost certainly involves H(15) in a hydrogen bond. However, H(14) is pointing in the general direction of $O(6^{v})$ which is 2.40 Å away from H(14) and 3.02 Å from O(13). If a hydrogen bond is involved between O(13) and $O(6^{v})$, it is weak. The second shortest approach to O(13) is the atom $O(8^{v})$ at 2.89 Å, but this approach probably does not involve a hydrogen bond because the angle $Mn(2)-O(13)-O(9^{v})$ of 48° would mean that a hydrogen atom would need to be pointing close to the direction of a positively charged manganese and this is unlikely.

Similar problems arise with the water molecule containing O(12). The shortest oxygen approach to O(12) is by $O(11^{iii})$ at 2.93 Å. This offers a possibility for weak hydrogen bonding because the angle Mn(1)-O(12)-O(11) is 111°, and this would place the hydrogen atom well away from the manganese ion. However, the next two short distances of 2.97 and 2.98 Å would involve hydrogen atoms pointing to within 48° of the manganese ion. The angle Mn(1)-O(12)-H(16) is 118° and this means that the hydrogen atom is pointing well away from the manganese ion, but if this hydrogen atom is involved in a hydrogen bond, the bond must be weak since the nearest atom to it is O(9) at 2.64 Å.

We are thus left with the conclusion that the only certain hydrogen bond in this structure is that between O(13) and $O(9^{vii})$. Other hydrogen bond type interactions are either weak or nonexistent.

Computer Programs Used. Data reduction, Fourier, least-squares, and structure-factor calculations were carried out with the NRC programs of Ahmed, Hall, Pippy, and Saunderson.[20] The stereoscopic drawings were made with ORTEP.[21]

Registry No. $Mn_2P_2O_7 \cdot 2H_2O$, 40548-17-2.

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(20) F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Saunderson, "NRC Crystallographic Programs for the IBM/360 System," National Research Council of Canada, Ottawa, Canada, 1966.

(21) C. K. Johnson, "ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.