

## Structure of Manganese(II) Trisodium Tripolyphosphate Dodecahydrate

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**Abstract.**  $\text{MnNa}_3\text{P}_3\text{O}_{10}\cdot 12\text{H}_2\text{O}$ ,  $M_r = 593.01$ , monoclinic,  $P2_1/n$ ,  $a = 14.763$  (2),  $b = 9.325$  (4),  $c = 15.140$  (4) Å,  $\beta = 89.87$  (2)°,  $V = 2084.2$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.89$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 9.87$  cm<sup>-1</sup>,  $F(000) = 1212$ , room temperature,  $R = 0.035$ ,  $wR = 0.037$  for 2279 unique reflections with  $I > 3\sigma(I)$ . The structure is composed of discrete  $[\text{MnP}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}]^{3-}$  units, held together by intervening  $\text{Na}^+$  ions and  $\text{H}_2\text{O}$  molecules *via* a complex system of Na–O and hydrogen bonds. The  $\text{Mn}^{2+}$  ion is in a distorted octahedral environment, three vertices being occupied by O atoms of water molecules, and three by the chelating  $\alpha,\beta,\gamma$ -triphosphate ligand. A notable feature of the structure is a five-coordinate O atom, the coordination sphere of which consists of a P atom and four hydrogen-bonded H atoms.

**Introduction.** Considerable attention has recently focused on the coordination geometries of complexes of polyphosphate chains with kinetically inert metal ions. These structures serve as models for the metal-phosphate moieties of biologically important complexes. For example, in recent studies of the possible chelation modes of the enzymatically active Mg adenosine diphosphate and Mg adenosine triphosphate, the structures of the following cobaltamine triphosphates have been determined:  $\beta,\gamma$ -bidentate  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{P}_3\text{O}_{10}]\cdot\text{H}_2\text{O}$  (Merritt & Sundaralingam, 1980),  $\alpha,\gamma$ -bidentate  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{P}_3\text{O}_{10}]\cdot\text{H}_2\text{O}$  (Merritt, Sundaralingam & Cornelius, 1981),  $\alpha,\beta,\gamma$ -tridentate  $[\text{Co}(\text{NH}_3)_3\text{H}_2\text{P}_3\text{O}_{10}]$  (Merritt & Sundaralingam, 1981) and  $\beta$ - and  $\gamma$ -unidentate  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{P}_3\text{O}_{10}]\cdot\text{H}_2\text{O}$  (Haromy, Gilletti, Cornelius & Sundaralingam, 1984).

The first crystallographic study of the isomorphous series of compounds  $M^{II}\text{Na}_3\text{P}_3\text{O}_{10}\cdot 12\text{H}_2\text{O}$  ( $M^{II} = \text{Ni}, \text{Co}, \text{Mg}, \text{Mn}, \text{Ni}$  or  $\text{Zn}$ ) reported unit-cell parameters and space group for each phase (Rakotomahanina, Averbuch-Pouchot & Durif, 1972). A model for the structure of the  $\text{Mn}^{II}$  phase has been reported (Herceg, 1974) but was not published in full. Recently, the crystal structures of the  $\text{Cu}^{II}$  (Jouini, Dabbabi, Averbuch-Pouchot, Durif & Guitel, 1984) and the  $\text{Cd}^{II}$  (Lutsko & Johansson, 1984) isomorphs have been determined. H atoms were located for the  $\text{Cd}^{II}$

compound, but not for the  $\text{Cu}^{II}$  compound. The present paper reports the crystal structure of  $\text{Na}_3\text{MnP}_3\text{O}_{10}\cdot 12\text{H}_2\text{O}$ , with an emphasis on some interesting features of the hydrogen bonding present in the phase.

**Experimental.** Crystals of  $\text{Na}_3\text{MnP}_3\text{O}_{10}\cdot 12\text{H}_2\text{O}$  were prepared as described by Rakotomahanina, Averbuch-Pouchot & Durif (1972). A needle-like crystal, dimensions approximately  $0.25 \times 0.02 \times 0.01$  mm, was mounted on an Enraf–Nonius CAD-4 diffractometer. The unit-cell constants were determined from the positions of 25 carefully centred reflections. Data were collected using the  $\omega$ - $2\theta$  scan mode with  $\omega$  scan width  $(0.9 + 0.35 \tan\theta)^\circ$ , scan speed  $0.8$ – $6.71^\circ$  min<sup>-1</sup>, using graphite-monochromated Mo  $K\alpha$  radiation over the range  $0 < \theta < 25^\circ$  and  $+h, +k, \pm l$ . 3 standard reflections intensity variation  $< 5\%$ . 4925 reflections were measured, of which 2279 were used for refinement, after merging equivalent reflections (merging  $R = 0.032$ ); those with  $I < 3\sigma(I)$  were regarded as unobserved. Direct methods, using the program MITHRIL (Gilmore, 1984), were used to locate the Mn, Na, P and some of the O atoms. The remaining O and all of the H atoms were located by a series of difference Fourier maps, after refinement of the heavy-atom positions. During the final stages of refinement soft constraints were applied to the water-molecule geometries by giving the O–H bond lengths a value of  $0.96$  Å, and the O–H–O bond angles a value of  $106^\circ$ , with e.s.d.'s of  $0.03$  Å and  $3^\circ$  respectively. These values are in accordance with the average values given for water-molecule geometry in crystalline hydrates studied by neutron diffraction (Chiari & Ferraris, 1982). A full-matrix least-squares refinement on  $F$ , with all non-H atoms anisotropic and all H atoms refined with an equal isotropic temperature factor, converged at  $R = 0.035$ ,  $wR = 0.037$ . A Chebyshev weighting scheme (Carruthers & Watkin, 1979) with parameters 12.0, 16.4 and 66.6 was applied. At convergence r.m.s. shift/e.s.d. =  $0.1$ , and the highest peak in the difference Fourier map =  $0.5 e \text{ \AA}^{-3}$ . Structure analysis and refinement was carried out using the Oxford CRYSTALS system (Carruthers & Watkin, 1981) on a VAX 11/750 computer. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). No corrections for absorption or extinction.

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**Discussion.** The structure is essentially isomorphous with those of the Cd<sup>II</sup> (Lutsko & Johansson, 1984) and Cu<sup>II</sup> (Jouini, Dabbabi, Averbuch-Pouchot, Durif & Guitel, 1984) phases. Fractional atomic coordinates and isotropic thermal parameters are given in Table 1, and selected distances and angles in Table 2.\* The coordination geometry around Mn(1) is shown in Fig. 1. It has a distorted octahedral environment, being chelated by the  $\alpha,\beta,\gamma$ -tridentate triphosphate ligand on one side, with the other three positions being occupied

by water molecules. In order to accommodate the tridentate chelation, the triphosphate chain is fairly sharply bent, with a P—P—P angle of 95.5 (2)°.

Crystal packing is shown in Fig. 2. The structure is held together by a complex system of hydrogen bonds (Table 3) and Na—O bonds. All three crystallographically different Na atoms are coordinated by

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43300 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates with *e.s.d.*'s and isotropic/ equivalent isotropic temperature factors

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub>/U<sub>iso</sub></i>
Mn(1)	0.25136 (5)	0.04405 (8)	0.81774 (5)	0.0150
P(1)	0.39221 (8)	0.2766 (1)	0.91092 (8)	0.0153
P(2)	0.09508 (9)	0.2697 (1)	0.90466 (8)	0.0152
P(3)	0.24157 (9)	0.1550 (1)	1.01758 (8)	0.0155
Na(1)	-0.1438 (1)	0.4642 (2)	0.7092 (1)	0.0282
Na(2)	0.1134 (2)	0.1944 (3)	0.1999 (2)	0.0372
Na(3)	-0.7534 (1)	0.2642 (2)	0.5628 (1)	0.0265
O(1)	0.3578 (2)	0.1968 (4)	0.8300 (2)	0.0196
O(2)	0.2509 (2)	0.0220 (4)	0.9632 (2)	0.0192
O(3)	0.1429 (3)	-0.3666 (4)	0.0165 (3)	0.0286
O(4)	0.0953 (2)	0.4308 (4)	0.8962 (2)	0.0212
O(5)	0.1477 (2)	0.3635 (4)	0.6787 (2)	0.0215
O(6)	0.4023 (2)	0.4355 (4)	0.8938 (2)	0.0206
O(7)	-0.0130 (3)	0.6050 (5)	0.7854 (3)	0.0340
O(8)	0.2491 (2)	0.5497 (4)	0.8262 (2)	0.0206
O(9)	0.0059 (3)	0.0829 (4)	0.1048 (3)	0.0298
O(10)	0.1456 (2)	0.1970 (4)	0.8300 (2)	0.0204
O(11)	0.6291 (3)	0.3501 (5)	0.9839 (3)	0.0282
O(12)	-0.1566 (2)	0.1394 (4)	0.1790 (2)	0.0208
O(13)	0.4739 (2)	0.2056 (4)	0.9503 (2)	0.0267
O(14)	0.3126 (3)	0.2710 (4)	0.9847 (2)	0.0262
O(15)	0.2457 (2)	0.1457 (4)	1.1148 (2)	0.0228
O(16)	0.0021 (2)	0.2072 (4)	0.9219 (2)	0.0222
O(17)	0.1493 (2)	0.2335 (4)	0.9960 (2)	0.0228
O(18)	-0.0182 (3)	0.4371 (5)	0.6092 (2)	0.0292
O(19)	0.0681 (3)	0.0143 (5)	0.3109 (3)	0.0382
O(20)	0.2235 (4)	-0.5287 (6)	0.1571 (3)	0.0434
O(21)	0.1962 (3)	0.2955 (5)	0.3235 (3)	0.0331
O(22)	0.1194 (3)	-0.2350 (4)	0.2216 (3)	0.0315
H(1)	0.020 (4)	0.538 (6)	0.821 (4)	0.070 (5)
H(2)	0.262 (2)	0.296 (7)	0.324 (5)	0.070 (5)
H(3)	0.083 (4)	-0.213 (7)	0.173 (3)	0.070 (5)
H(4)	0.576 (3)	0.296 (6)	0.967 (5)	0.070 (5)
H(5)	-0.102 (3)	0.132 (8)	0.148 (4)	0.070 (5)
H(6)	0.176 (4)	0.227 (6)	0.367 (4)	0.070 (5)
H(7)	0.194 (4)	-0.487 (8)	0.108 (3)	0.070 (5)
H(8)	0.118 (4)	-0.435 (6)	-0.024 (4)	0.070 (5)
H(9)	0.133 (4)	0.320 (8)	0.732 (3)	0.070 (5)
H(10)	0.608 (4)	0.423 (6)	1.020 (4)	0.070 (5)
H(11)	0.103 (5)	-0.170 (6)	0.265 (3)	0.070 (5)
H(12)	0.407 (3)	0.179 (7)	0.461 (4)	0.070 (5)
H(13)	0.855 (4)	0.185 (8)	0.232 (3)	0.070 (5)
H(14)	0.296 (3)	0.497 (7)	0.852 (4)	0.070 (5)
H(15)	0.093 (3)	0.392 (8)	0.653 (4)	0.070 (5)
H(16)	0.194 (3)	0.515 (7)	0.848 (4)	0.070 (5)
H(17)	0.004 (2)	0.007 (8)	0.325 (4)	0.070 (5)
H(18)	0.010 (5)	0.114 (6)	0.045 (2)	0.070 (5)
H(19)	0.781 (2)	0.08 (1)	0.637 (4)	0.070 (5)
H(20)	0.022 (4)	0.620 (7)	0.733 (3)	0.070 (5)
H(21)	0.977 (5)	0.014 (4)	0.892 (4)	0.070 (5)
H(22)	-0.026 (5)	0.383 (6)	0.558 (3)	0.070 (5)
H(23)	-0.006 (5)	0.532 (4)	0.591 (4)	0.070 (5)
H(24)	0.095 (4)	0.032 (9)	0.367 (3)	0.070 (5)

Table 2. Selected bond lengths (Å) and bond angles (°) with *e.s.d.*'s in parentheses

Mn(1)	O(1)	2.129 (3)	O(1)	O(2)	3.034 (5)		
Mn(1)	O(2)	2.212 (3)	O(1)	O(7)	3.003 (5)		
Mn(1)	O(5)	2.249 (4)	O(1)	O(12)	2.758 (5)		
Mn(1)	O(8)	2.181 (3)	O(2)	O(5)	3.004 (5)		
Mn(1)	O(10)	2.123 (4)	O(2)	O(10)	3.027 (5)		
Mn(1)	O(12)	2.210 (4)	O(2)	O(12)	2.974 (5)		
P(1)	O(1)	1.522 (4)	O(3)	O(4)	2.717 (5)		
P(1)	O(6)	1.512 (4)	O(3)	O(16)	2.766 (5)		
P(1)	O(13)	1.501 (4)	O(3)	O(20)	2.871 (6)		
P(1)	O(14)	1.621 (4)	O(4)	O(7)	2.832 (5)		
P(2)	O(4)	1.508 (4)	O(4)	O(8)	2.737 (5)		
P(2)	O(10)	1.513 (4)	O(5)	O(10)	2.767 (5)		
P(2)	O(16)	1.513 (4)	O(5)	O(12)	2.888 (5)		
P(2)	O(17)	1.635 (4)	O(5)	O(18)	2.755 (5)		
P(3)	O(2)	1.495 (4)	O(6)	O(8)	2.704 (5)		
P(3)	O(14)	1.586 (4)	O(6)	O(11)	2.764 (5)		
P(3)	O(15)	1.476 (4)	O(6)	O(19)	2.787 (5)		
P(3)	O(17)	1.581 (4)	O(7)	O(18)	3.095 (6)		
Na(1)	O(15)	2.401 (4)	O(9)	O(12)	2.699 (5)		
Na(1)	O(18)	2.404 (4)	O(9)	O(16)	3.002 (6)		
Na(1)	O(20)	2.416 (5)	O(9)	O(16)	2.738 (5)		
Na(1)	O(21)	2.421 (5)	O(9)	O(17)	3.025 (5)		
Na(1)	O(22)	2.408 (5)	O(11)	O(13)	2.707 (5)		
Na(2)	O(7)	2.397 (5)	O(11)	O(19)	3.046 (6)		
Na(2)	O(9)	2.384 (5)	O(11)	O(21)	2.951 (5)		
Na(2)	O(15)	2.381 (4)	O(13)	O(18)	2.740 (6)		
Na(2)	O(19)	2.467 (5)	O(13)	O(18)	2.752 (5)		
Na(2)	O(21)	2.427 (5)	O(16)	O(22)	2.833 (5)		
Na(3)	O(2)	2.436 (4)	O(19)	O(22)	2.794 (6)		
Na(3)	O(3)	2.362 (4)	O(20)	O(21)	3.032 (6)		
Na(3)	O(5)	2.461 (4)	O(21)	O(22)	2.819 (6)		
Na(3)	O(11)	2.362 (4)					
Na(3)	O(12)	2.440 (4)					
O(2)	Mn(1)	O(1)	88.6 (1)	O(21)	Na(1)	O(20)	77.6 (2)
O(5)	Mn(1)	O(1)	90.5 (1)	O(22)	Na(1)	O(15)	89.0 (1)
O(5)	Mn(1)	O(2)	84.7 (1)	O(22)	Na(1)	O(18)	93.7 (2)
O(8)	Mn(1)	O(1)	94.3 (1)	O(22)	Na(1)	O(20)	85.9 (2)
O(8)	Mn(1)	O(2)	176.0 (1)	O(22)	Na(1)	O(21)	163.4 (2)
O(8)	Mn(1)	O(5)	92.6 (1)	O(9)	Na(2)	O(7)	89.0 (2)
O(10)	Mn(1)	O(1)	94.9 (1)	O(15)	Na(2)	O(7)	134.8 (2)
O(10)	Mn(1)	O(2)	88.6 (1)	O(15)	Na(2)	O(9)	97.8 (2)
O(10)	Mn(1)	O(5)	171.2 (1)	O(19)	Na(2)	O(7)	107.5 (2)
O(10)	Mn(1)	O(8)	93.8 (1)	O(19)	Na(2)	O(9)	86.3 (2)
O(12)	Mn(1)	O(1)	169.4 (1)	O(19)	Na(2)	O(15)	117.4 (2)
O(12)	Mn(1)	O(2)	84.5 (1)	O(21)	Na(2)	O(7)	86.4 (2)
O(12)	Mn(1)	O(5)	80.7 (1)	O(21)	Na(2)	O(9)	166.4 (2)
O(12)	Mn(1)	O(8)	92.2 (1)	O(21)	Na(2)	O(15)	94.5 (2)
O(12)	Mn(1)	O(10)	93.0 (1)	O(21)	Na(2)	O(19)	82.9 (2)
O(6)	P(1)	O(1)	112.0 (2)	O(3)	Na(3)	O(2)	114.6 (2)
O(13)	P(1)	O(1)	112.0 (2)	O(5)	Na(3)	O(2)	75.7 (1)
O(13)	P(1)	O(6)	114.9 (2)	O(5)	Na(3)	O(3)	164.7 (2)
O(14)	P(1)	O(1)	107.3 (2)	O(11)	Na(3)	O(2)	112.0 (2)
O(14)	P(1)	O(6)	102.7 (2)	O(11)	Na(3)	O(3)	91.0 (2)
O(14)	P(1)	O(13)	107.1 (2)	O(11)	Na(3)	O(5)	95.5 (1)
O(10)	P(2)	O(4)	112.4 (2)	O(12)	Na(3)	O(2)	75.2 (1)
O(16)	P(2)	O(4)	113.6 (2)	O(12)	Na(3)	O(3)	98.7 (1)
O(16)	P(2)	O(10)	113.7 (2)	O(12)	Na(3)	O(5)	72.2 (1)
O(17)	P(2)	O(4)	106.0 (2)	O(12)	Na(3)	O(11)	164.2 (2)
O(17)	P(2)	O(10)	107.4 (2)	P(1)	O(1)	Mn(1)	130.2 (2)
O(17)	P(2)	O(16)	102.7 (2)	P(3)	O(2)	Mn(1)	118.1 (2)
O(14)	P(3)	O(2)	109.5 (2)	Na(3)	O(2)	Mn(1)	86.0 (1)
O(15)	P(3)	O(2)	119.8 (2)	Na(3)	O(2)	P(3)	155.4 (2)
O(15)	P(3)	O(14)	108.9 (2)	Na(3)	O(5)	Mn(1)	84.6 (1)
O(17)	P(3)	O(2)	110.4 (2)	P(2)	O(10)	Mn(1)	136.6 (2)
O(17)	P(3)	O(14)	100.9 (2)	Na(3)	O(12)	Mn(1)	86.0 (1)
O(17)	P(3)	O(15)	105.7 (2)	P(3)	O(14)	P(1)	135.7 (3)
O(18)	Na(1)	O(15)	96.0 (1)	Na(1)	O(15)	P(3)	130.4 (2)
O(20)	Na(1)	O(15)	105.9 (2)	Na(2)	O(15)	P(3)	119.5 (2)
O(20)	Na(1)	O(18)	158.0 (2)	Na(2)	O(15)	Na(1)	108.5 (2)
O(21)	Na(1)	O(15)	93.2 (2)	P(3)	O(17)	P(2)	133.9 (2)
O(21)	Na(1)	O(18)	102.4 (2)	Na(2)	O(21)	Na(1)	92.3 (2)

five O atoms; both Na(1) and Na(2) are coordinated to the terminal O(15) atom on P(3), to O(21) belonging to a water molecule, and to three further independent water molecules each. The Na(3) polyhedron, however, shares a face with the  $MnO_6$  octahedron, namely O(2), O(5) and O(12), and is completed by two water molecules. All the H atoms [except H(19)] take part in hydrogen bonding.

The three water molecules to Mn(1) act solely as hydrogen-bond donors, forming direct links between adjacent complexes *via* O(5)—H(9)···O(10), O(8)—H(14)···O(6), O(8)—H(16)···O(4) and O(12)—H(13)···O(1). There are no intracomplex hydrogen bonds. The remaining water molecules participate in a

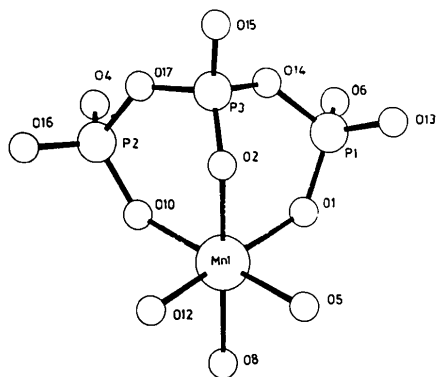


Fig. 1. Coordination geometry around Mn(1), showing the tridentate chelation of the  $\alpha, \beta, \gamma$ -triphosphate group.

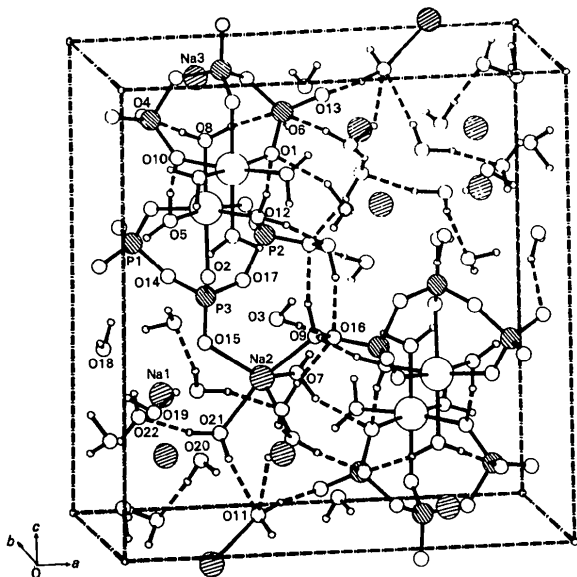


Fig. 2. Crystal packing within the unit cell, with hydrogen bonds shown as dashed lines. All the Na atoms are five-coordinate but, for clarity, only the coordination around Na(2) is shown.

three-dimensional network of intercomplex hydrogen bonds. All the water molecules act as hydrogen-bond donors, whilst O(3), O(9), O(11), O(18), O(19) and O(22) also act as acceptors; twice in the case of O(11), leading to this atom being five-coordinated. The terminal O atoms on P(1) and P(3) accept three hydrogen bonds each [O(4), O(6) and O(13)] whilst O(16) is within hydrogen-bonding distance of four H atoms, leading to a distorted trigonal bipyramidal coordination (Fig. 3). All the H atoms are believed to be correctly located.

Table 3. *Hydrogen bonding*

Hydrogen bond $D-H \cdots A$	Symmetry code	$D-A$ (Å)	$H-A$ (Å)	$D-H-A$ (°)
O(3)—H(8)···O(4)	[1: 0, -1, -1]	2.717	1.77	169.0
O(3)—H(12)···O(16)	[3: 0, 0, 1]	2.766	1.85	172.2
O(5)—H(9)···O(10)	[1: 0, 0, 0]	2.767	1.88	157.8
O(5)—H(15)···O(18)	[1: 0, 0, 0]	2.755	1.82	175.2
O(7)—H(1)···O(4)	[1: 0, 0, 0]	2.832	1.88	171.8
O(7)—H(20)···O(1)	[2: 0, 0, 1]	3.003	2.14	150.0
O(8)—H(14)···O(6)	[1: 0, 0, 0]	2.704	1.79	165.2
O(8)—H(16)···O(4)	[1: 0, 0, 0]	2.737	1.81	172.7
O(9)—H(18)···O(16)	[3: 0, 0, 1]	2.738	2.06	170.3
O(9)—H(21)···O(16)	[1: 0, 0, -1]	3.002	1.89	148.4
O(11)—H(4)···O(13)	[1: 0, 0, 0]	2.707	1.75	172.3
O(11)—H(10)···O(6)	[3: 1, 1, 2]	2.764	1.86	164.2
O(12)—H(5)···O(9)	[1: 0, 0, 0]	2.699	1.78	166.9
O(12)—H(13)···O(1)	[4: -1, 0, -1]	2.758	1.85	167.2
O(18)—H(22)···O(13)	[4: -1, 0, -1]	2.740	1.83	170.7
O(18)—H(23)···O(13)	[2: 0, 0, 1]	2.752	1.80	174.4
O(19)—H(17)···O(6)	[4: -1, 0, -1]	2.787	1.90	150.0
O(19)—H(24)···O(11)	[2: 0, 0, 0]	3.046	2.15	157.8
O(20)—H(7)···O(3)	[1: 0, 0, 0]	2.871	1.94	168.5
O(21)—H(2)···O(22)	[2: 0, 0, 0]	2.819	1.91	156.0
O(21)—H(6)···O(11)	[4: -1, 0, -1]	2.951	2.04	159.0
O(22)—H(3)···O(16)	[3: 0, 0, 1]	2.833	1.90	167.9
O(22)—H(11)···O(19)	[1: 0, 0, 0]	2.794	1.93	155.5
Mean value		2.806	1.89	164.3
Mean e.s.d.		0.005	0.03	0.6

Acceptor atom symmetry code is given as  $x, y$  and  $z$  translation, preceded by the symmetry operation as follows: (1)  $x, y, z$ ; (2)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (3)  $-x, -y, -z$ ; (4)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ .

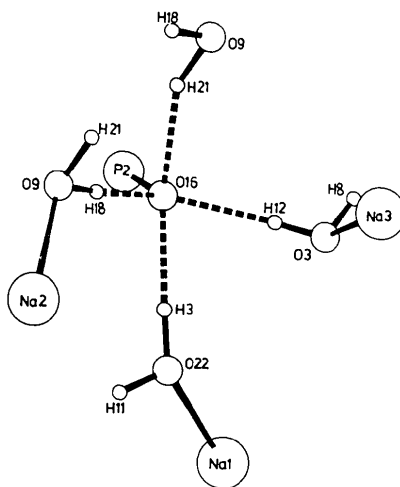


Fig. 3. The O(16) environment, showing distorted trigonal bipyramidal coordination of P(2) and four hydrogen-bonded H's (see Table 3).

The proposed hydrogen-bonding scheme is supported (a) by the O—O distances in Table 2, and (b) by the observation of peaks in the difference Fourier map attributable to H atoms. Table 2 includes all O—O distances (not including O atoms in the same phosphate group) out to a distance of 3.10 Å. Nearly all of these short contacts may be attributed to O—H...O interactions. As can be seen, O(16) has four oxygen near neighbours in the range 2.738 to 3.003 Å, all of which suggest some degree of interaction between the atoms concerned. It appears that H(19) does not take part in hydrogen bonding; this seems reasonable as the nearest possible acceptor, O(21), is at a distance 3.032 Å from O(20).

We also conducted a  $^{31}\text{P}$  solid-state magic-angle-spinning NMR study of the isomorphous compound  $\text{Na}_3\text{ZnP}_3\text{O}_{10}\cdot 12\text{H}_2\text{O}$ ; spectra of the title compound cannot be obtained owing to the paramagnetism of the  $\text{Mn}^{2+}$  ion. Broad resonances were observed at  $-6.0$  and  $-19.3$  p.p.m. (upfield relative to 85% phosphoric acid solution). The relative intensities of the two peaks show that the terminal P nuclei resonate at lower field than the bridging P, in agreement with previous work (Grimmer & Haubenreisser, 1983). However, the presence of the quadrupolar Na nuclei causes sufficient broadening to make the terminal P nuclei indistinguishable.

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## Structure of $\zeta_1\text{-Mn}_{5.11}\text{Ge}_2$

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**Abstract.**  $M_r = 425.97$ , trigonal,  $P3c1$ ,  $a = 7.198$  (1),  $c = 39.227$  (4) Å,  $V = 1760.1$  Å<sup>3</sup>,  $D_x = 7.233$  Mg m<sup>-3</sup>,  $Z = 18$  (92 Mn and 36 Ge per unit cell),  $\text{Mo } K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 31.0$  mm<sup>-1</sup>,  $F(000) = 3452$ ,  $T = 295$  K, final  $R(F) = 0.0557$ ,  $wR(F) = 0.0400$  for 923

independent reflections. The structure is characterized by two kinds of fundamental layers having three atoms stacked alternately by  $c/30$ . Additional atoms are placed on three threefold axes. Ge atoms are located every 2.5 layers and Mn atoms are placed at the