sented in the figures are reported. These plots suggest that: (1) In AnWS, as a straightforward consequence of the Al/Si ratio = 1 and of the perfect alternation Al–Si, the charge-balance trend cannot be influenced by the Al occupancy. The charge balance is merely achieved through the tetrahedral distortion. (2) In AnQ, as already pointed out (Chiari, Facchinelli & Bruno, 1978), the Al occupancy plays a significant role in balancing the different $\sum s(\text{Ca–O})$. The representation adopted here allows an evaluation to be made of the significant contribution of the tetrahedral distortion to the charge balance. (3) In BytL again, the two factors cooperate in a way similar to that in BytQ and AnQ.

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The Crystal Structures of Manganese(II) Phosphinate Monohydrate, Zinc Phosphinate Monohydrate, and Anhydrous Zinc Phosphinate

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Abstract

The structures of $Mn(H_2PO_2)_2.H_2O$ [$P2_1/n$, a = 12·013 (16), b = 8·100 (7), c = 13·450 (17) Å, β = 106·28 (3)°, Z = 8; R = 0·080 for 1553 reflections], $Zn(H_2PO_2)_2.H_2O$ [$P2_1/c$, a = 7·692 (6), b = 7·391 (9), c = 10·490 (11) Å, β = 104·15 (4)°, Z = 4; R = 0·051 for 960 reflections], and $Zn(H_2PO_2)_2$ [$Pmma$, a = 6·482 (7), b = 5·363 (4), c = 7·436 (9) Å, Z = 2; R = 0·083 for 302 reflections] have been determined from photographic data. In the monohydrates, which have extended three-dimensional structures, the water molecule is coordinated as well as all anion O atoms, and the MO_6 octahedra are edge-linked in pairs. In $Zn(H_2PO_2)_2$ a layer structure is present, containing chains of edge-linked ZnO_6 octahedra.

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Introduction

The structures of crystalline phosphinic acid, $H_2PO(OH)$ (Williams, 1966), and $Ca(H_2PO_2)_2$ (Loopstra, 1958) have been determined by neutron diffraction, and those of a number of phosphinates by X-ray diffraction: $Mg(H_2PO_2)_2.6H_2O$ (Galigné & Dumas, 1973), $CaNa(H_2PO_2)_3$ (Matsuzaki & Iitaka, 1969), $Mn(bpy)(H_2PO_2)_2$ (Weakley, 1978), and $Ln(H_2PO_2)_3.H_2O$ (Ln = La, Eu) (Ionov, Aslanov, Rybakov & Porai-Koshits, 1973*a*,*b*). In the lanthanide salts, the coordination number of eight for Ln^{3+} is achieved by coordination of the water as well as by participation of the anion in both Ln—O—Ln and Ln—O—P—O—Ln bridges. The present work was carried out to determine whether similar structural features are present in $M^{II}(H_2PO_2)_2.H_2O$ (M^{II} = Mn, Zn) in which the coordination number of the cation is expected to be six or less, and whether the dehydration of $Zn(H_2PO_2)_2.H_2O$ is accompanied by a decrease in coordination number. The compounds will be designated MPM [$Mn(H_2PO_2)_2.H_2O$], ZPM [$Zn(H_2PO_2)_2.H_2O$], and ZP [$Zn(H_2PO_2)_2$].

Experimental

ZPM and ZP were prepared as described by Brun, Dumail & Maurin (1971). The form of MPM usually obtained by a similar procedure was evidently isostructural with ZPM, which it resembled in space group and cell parameters [$P2_1/c$, a = 7·87 (1), b = 7·42 (1), c = 10·77 (1) Å, β = 103·0 (1)°, Z = 4] and in the distribution of intensities in corresponding zero- and upper-level Weissenberg photographs. The variant here designated MPM was obtained by chance and the exact conditions for its formation could not be established.

Crystal data

MPM, $Mn(H_2PO_2)_2.H_2O$, monoclinic, $P2_1/n$, a = 12·013 (16), b = 8·100 (7), c = 13·450 (17) Å, β = 106·28 (3)°, Z = 8, D_m = 2·13, D_x = 2·146 Mg m^{-3}, $F(000)$ = 792, μ(Cu $K\alpha$) = 21·2 mm^{-1}.

ZPM, $Zn(H_2PO_2)_2.H_2O$, monoclinic, $P2_1/c$, a = 7·692 (6), b = 7·391 (9), c = 10·490 (11) Å, β = 104·15 (4)°, Z = 4, D_m = 2·46, D_x = 2·45 Mg m^{-3}, $F(000)$ = 424, μ(Cu $K\alpha$) = 10·7 mm^{-1}.

ZP, $Zn(H_2PO_2)_2$, orthorhombic, $Pmma$, a = 6·482 (7), b = 5·363 (4), c = 7·436 (9) Å, Z = 2, D_x = 2·52 Mg m^{-3}, $F(000)$ = 192, μ(Cu $K\alpha$) = 11·7 mm^{-1}.

Equi-inclination Weissenberg photographs (Cu radiation, λ = 1·5418 Å) of levels h0–7l and hk0–2 for MPM, 0–5kl and h0–5l for ZPM, and h0–3l and hk0–6 for ZP were scanned by the SRC Microdensitometer Service, Rutherford Laboratory. Each data set was corrected for absorption; however, for ZPM this made no significant difference to the final residual or to the atomic coordinates and e.s.d.'s, and all results quoted for ZPM derive from the data without absorption correction.

Structure determination and refinement

The structures were determined by the heavy-atom method, and refined by full-matrix least squares (anisotropic thermal parameters for all non-hydrogen atoms) with *SHELX*-76 (Sheldrick, 1976). In MPM and ZPM the stronger peaks in weighted difference maps towards the end of refinement included ones near the expected positions of the anion H atoms (P—H distances 1·23 to 1·53 Å for MPM and 1·18 to 1·68 Å for ZPM). The H atoms were included at calculated positions (d_{P-H} 1·40 Å, U_H 0·05 Å^2) in the last cycles for all three compounds. Refinement with unit weights converged at R = 0·080 for MPM (1553 data, 147 parameters), R = 0·051 for ZPM (960 data, 73 parameters), and R =

Table 1. *Atomic coordinates* (×10^4) *for* MPM, $Mn(H_2PO_2)_2.H_2O$

	x	y	z
Mn(1)	4778 (2)	1083 (3)	8262 (2)
Mn(2)	3950 (2)	2461 (3)	5736 (2)
P(1)	2814 (3)	4279 (5)	7440 (3)
P(2)	4182 (3)	2366 (5)	496 (3)
P(3)	5115 (3)	1384 (5)	3830 (3)
P(4)	1532 (3)	1659 (6)	2247 (4)
O(1)	1618 (7)	4424 (12)	6765 (8)
O(2)	3547 (7)	2926 (11)	7222 (7)
O(3)	4735 (8)	2349 (13)	−362 (8)
O(4)	3979 (7)	762 (12)	984 (7)
O(5)	4172 (7)	1512 (12)	4318 (8)
O(6)	5286 (7)	−256 (11)	3362 (7)
O(7)	637 (7)	1355 (13)	1241 (7)
O(8)	1167 (7)	2301 (14)	3137 (8)
Aq(1)	2156 (7)	1602 (12)	5178 (8)
Aq(2)	3295 (7)	4876 (11)	5097 (8)

Table 2. *Atomic coordinates* (×10^4) *for* ZPM, $Zn(H_2PO_2)_2.H_2O$, *and* ZP, $Zn(H_2PO_2)_2$

(i) ZPM	x	y	z
Zn	1925 (1)	413 (2)	1040 (1)
P(1)	400 (3)	1835 (3)	3491 (2)
P(2)	4686 (3)	3773 (3)	1936 (2)
O(1)	268 (7)	3531 (8)	4276 (5)
O(2)	624 (8)	2088 (9)	2119 (6)
O(3)	4053 (8)	2130 (9)	1081 (6)
O(4)	6683 (8)	3998 (10)	2345 (6)
Aq	2871 (9)	−1451 (11)	−182 (7)
(ii) ZP	x	y	z
Zn	0	0	0
P(1)	2500	5000	1444 (6)
P(2)	2500	0	6321 (6)
O(1)	2500	2622 (16)	375 (10)
O(2)	513 (11)	0	7333 (11)

0·083 for ZP (302 data, 27 parameters).* The final coordinates are given in Tables 1 and 2 and derived distances and angles in Tables 3 and 4.

Table 3. *Bond lengths* (Å) *and angles* (°) *for* MPM, $Mn(H_2PO_2)_2.H_2O$

Mn(1)—O(1^{i})	2·142 (10)	Mn(2)—Aq(1)	2·188 (9)
Mn(1)—O(2)	2·283 (8)	Mn(2)—Aq(2)	2·192 (9)
Mn(1)—O(3^{ii})	2·129 (11)	P(1)—O(1)	1·473 (9)
Mn(1)—O(4^{iii})	2·155 (10)	P(1)—O(2)	1·486 (8)
Mn(1)—O(6^{iii})	2·266 (10)	P(2)—O(3)	1·485 (10)
Mn(1)—O(8^{iv})	2·164 (10)	P(2)—O(4)	1·506 (10)
Mn(2)—O(2)	2·217 (9)	P(3)—O(5)	1·463 (10)
Mn(2)—O(5)	2·141 (10)	P(3)—O(6)	1·508 (9)
Mn(2)—O(6^{ii})	2·209 (10)	P(4)—O(7)	1·495 (10)
Mn(2)—O(7^{iii})	2·172 (10)	P(4)—O(8)	1·479 (10)
Aq(1)···O(3^{i})	2·92 (2)	Aq(2)···O(4^{vi})	2·80 (2)
Aq(1)···O(8)	2·73 (2)	Aq(2)···O(7^{iii})	2·76 (2)
Mn(1)···Mn(2)	3·448 (5)		
O(2)—Mn(1)—O(3)	92·8 (4)	O(6^{iii})—Mn(2)—O(7^{iv})	88·7 (4)
O(1^{i})—Mn(1)—O(6^{iii})	89·0 (4)	O(2)—Mn(2)—O(5)	167·8 (4)
O(4^{iii})—Mn(1)—O(8^{iv})	90·4 (4)	O(1)—P(1)—O(2)	117·8 (6)
O(3^{i})—Mn(1)—O(6^{iii})	167·8 (4)	O(3)—P(2)—O(4)	119·5 (6)
Aq(1)—Mn(2)—O(2)	85·4 (3)	O(5)—P(3)—O(6)	117·5 (6)
Aq(2)—Mn—O(5)	95·3 (4)	O(7)—P(4)—O(8)	119·3 (5)

Symmetry code: (i) $\frac{1}{2} - x, -\frac{1}{2} + y, 1\frac{1}{2} - z$; (ii) $x, y, 1 + z$; (iii) $1 - x, -y, 1 - z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Table 4. *Bond lengths* (Å) *and angles* (°) *for* ZPM, $Zn(H_2PO_2)_2.H_2O$, *and* ZP, $Zn(H_2PO_2)_2$

(i) ZPM

Zn—O(1^{i})	2·121 (6)	Zn—Aq	2·124 (6)
Zn—O(1^{ii})	2·145 (6)	P(1)—O(1)	1·512 (6)
Zn—O(2)	2·087 (6)	P(1)—O(2)	1·503 (6)
Zn—O(3)	2·060 (6)	P(2)—O(3)	1·514 (7)
Zn—O(4^{ii})	2·053 (6)	P(2)—O(4)	1·499 (6)
Aq···O(3^{iii})	2·80 (1)	Zn···Zn^{iv}	3·277 (2)
Aq···O(2^{iii})	2·98 (1)		
O(3)—Zn—O(2)	96·3 (3)	O(2)—Zn—Aq	171·6 (3)
O(1^{i})—Zn—Aq	86·4 (3)	O(1)—P(1)—O(2)	117·3 (4)
O(1^{ii})—Zn—O(4^{ii})	91·7 (3)	O(3)—P(2)—O(4)	114·6 (4)

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

(ii) ZP

Zn—O(1)	2·164 (6)	P(1)—O(1)	1·502 (8)
Zn—O(2)	2·011 (8)	P(2)—O(2)	1·492 (8)
Zn···Zn	3·241*		
O(1)—Zn—O(2)	90·2 (3)	O(1)—P(1)—O(1^{ii})	116·1 (7)
O(1)—Zn—O(1^{i})	81·1 (3)	O(2)—P(2)—O(2^{iii})	119·4 (7)

Symmetry code: (i) $x, -y, z$; (ii) $x, 1 - y, z$; (iii) $\frac{1}{2} - x, y, z$.

* Atoms at 0,0,0 and $\frac{1}{2}$,0,0.

Discussion

The structures are shown in Figs. 1, 2 and 3. The P—O lengths range from 1·463 to 1·514 Å, and the O—P—O angles from 114·6 to 119·5°. Values spanning similar ranges have been reported for $H_2PO_2^-$ in other determinations of similar accuracy (Williams, 1966; Matsuzaki & Iitaka, 1969; Galigné & Dumas, 1973; Weakley, 1978). The ability of the O—P—O angle to vary favours the bridging role of $H_2PO_2^-$. There is no apparent correlation between the mean P—O distance and either the O—P—O angle or the number of coordinate bonds formed by the O atoms. However, the cation–oxygen distance is, as expected, longer if the anion O atom links two cations.

The structures of MPM and ZPM (Figs. 1 and 2) show resemblances to those of $Ln(H_2PO_2)_3.H_2O$ (Ionov *et al.*, 1973*a*,*b*) in that all phosphinate O atoms, and the water molecules, are bonded to a cation, and

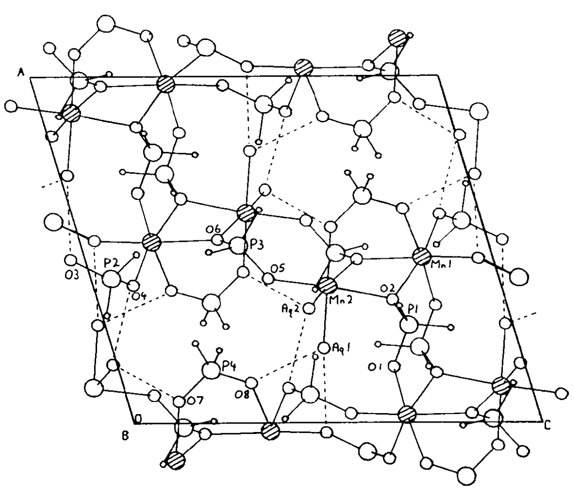

Fig. 1. $Mn(H_2PO_2)_2.H_2O$: projection down *b*.

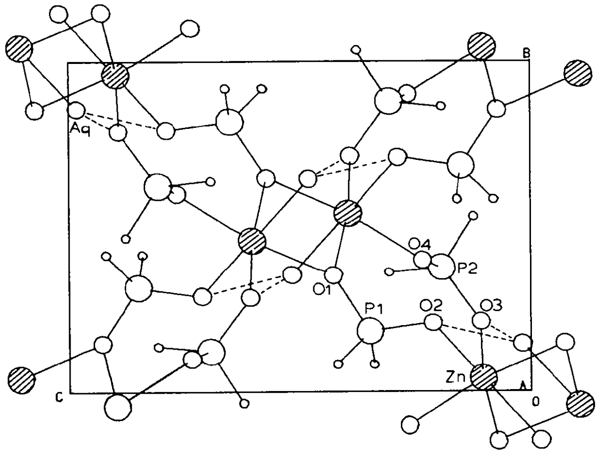

Fig. 2. $Zn(H_2PO_2)_2.H_2O$: projection down *a**.

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* Lists of structure factors and anisotropic thermal parameters for all three compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33971 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

some O atoms are bonded to two. They differ from $Ln(H_2PO_2)_3.H_2O$ and from one another in points of detail. In particular, the Zn and Mn atoms are in near-octahedral coordination, and the octahedra are linked by edge-sharing to give M_2O_{10} groups. The Zn—O and Mn—O lengths are within the normal ranges for octahedral coordination.

In MPM (Fig. 1) the asymmetric unit contains one Mn_2O_{10} group, in which the Mn atoms are structurally distinct since one is bonded to six anion O atoms and the other to four anion O atoms and two water molecules. Atoms of types O(2) and O(6) are involved in the edge-sharing between octahedra. The Mn atoms within a Mn_2O_{10} group are also linked *via* a Mn—O—P—O—Mn bridge [involving P(4)]. Similar bridges through P(2) and P(3) link the groups into chains along *c*. Other bridges involving P(1) cross-link the chains into a three-dimensional network, the cross-links forming spirals about the screw axis. Possible hydrogen bonds, involving the water molecules and O(3), O(4), O(7), and O(8), occur both within *c* axis chains (2·76 Å) and between chains (2·73, 2·80, 2·93 Å).

In ZPM (Fig. 2) the Zn_2O_{10} groups lie at crystallographic centres of symmetry. The O(1) atoms define the shared edges of octahedra. Each group is linked through Zn—O—P—O—Zn bridges to eight other groups so that a three-dimensional network results. The water molecule makes just two contacts with anion O atoms which appear compatible with hydrogen-bonding, if contacts within the same coordination sphere are excluded: one (2·93 Å) is with O(2) bonded to the other Zn atom in the same group, and the other (2·79 Å) is with O(3) in the next group along *a*.

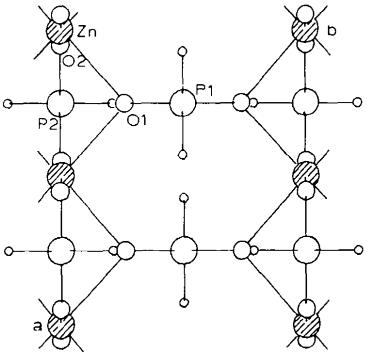

Fig. 3. $Zn(H_2PO_2)_2$: projection down *c*.

The product of dehydration, ZP, has a simple, open layer structure (Fig. 3) extending parallel to the *ab* plane. Chains of ZnO_6 octahedra linked by sharing opposite edges extend along *a*. The Zn atoms lie at sites of $2/m$ symmetry, and the anions have *mm* symmetry. The atoms O(1) of one anion are each bonded to two Zn atoms and those of the other anion, O(2), are each bonded to one. There are no close contacts between layers. This structure is to be contrasted with that of di(organo)phosphinates such as $Zn(BuPhPO_2)_2$ (Giordano, Randaccio & Ripamonti, 1969), which form linear polymers in which the bulky substituents force tetrahedral coordination on the Zn atom.

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