

KZn(HP₂O₇)·2H₂O and KMn(HP₂O₇)·2H₂O: acid pyrophosphate metallates(II) with layer structures

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The crystal structures of the isomorphous title compounds, namely potassium zinc hydrogen pyrophosphate dihydrate and potassium manganese hydrogen pyrophosphate dihydrate, consist of acidic pyrophosphate–metallate(II) layers joined by K⁺ ions and hydrogen-bridging bonds. The Zn²⁺/Mn²⁺ ions are octahedrally surrounded by four pyrophosphate O atoms and by two water molecules. The (HP₂O₇)³⁻ anions exhibit eclipsed conformations. The metal ions and water O atoms lie on mirror planes, as does the central O atom of the (HP₂O₇)³⁻ anion.

Comment

Compared to anhydrous diphosphates (El Bali *et al.*, 2001, and references therein), little information is available in the literature concerning the crystal structures of acidic metal diphosphates and hydrated metal diphosphates. Structural data have only been reported for the following compounds: CaNH₄HP₂O₇ (Mathew & Schroeder, 1977), Cr(NH₃)₄HP₂O₇·2H₂O (Haromy *et al.*, 1984), K₃Cu₂[(P₂O₇)(HP₂O₇)] (Effenberger, 1987), Ca₂KH₃(P₂O₇)₂·2H₂O (Mathew *et al.*, 1993) and Cr(HP₂O₇)(NH₃)₃ (Haromy *et al.*, 1999). The biological applications of acidic metal diphosphates are well known, *viz.* their role in some enzyme-catalyzed reaction processes (Haromy *et al.*, 1984) and their use as inhibitors in the formation and dissolution of apatite crystals *in vitro* (Mathew *et al.*, 1993). The title compounds, KZn(HP₂O₇)·2H₂O, (I), and KMn(HP₂O₇)·2H₂O, (II), are isotopic. The octahedral coordination around the Mn/Zn atoms and the pyrophosphate groups in (I) and (II) are shown in Fig. 1, together with the atom-numbering schemes. The three-

dimensional structure is built from acidic pyrophosphate–metallate(II) layers [*M* = Zn in (I) and Mn in (II)] stacked along the *c* axis (Fig. 2), alternating with layers of K⁺ cations. The Zn²⁺/Mn²⁺ ions are octahedrally surrounded by four O atoms from three different pyrophosphate anions, and by two water molecules (Tables 1 and 2). The angle between the plane through water molecule OW5 and the M²⁺–OW5 bond is about 141.8° (143.3°), while the corresponding angle involving OW6 is significantly smaller, *i.e.* $\varphi = 107.8^\circ$ (108.6°) [items in parentheses are for the manganese compound, (II)]. We attribute these quite different values to differences in the hydrogen-bridging bonds from H5W (H6W) to O2 (O4) of the

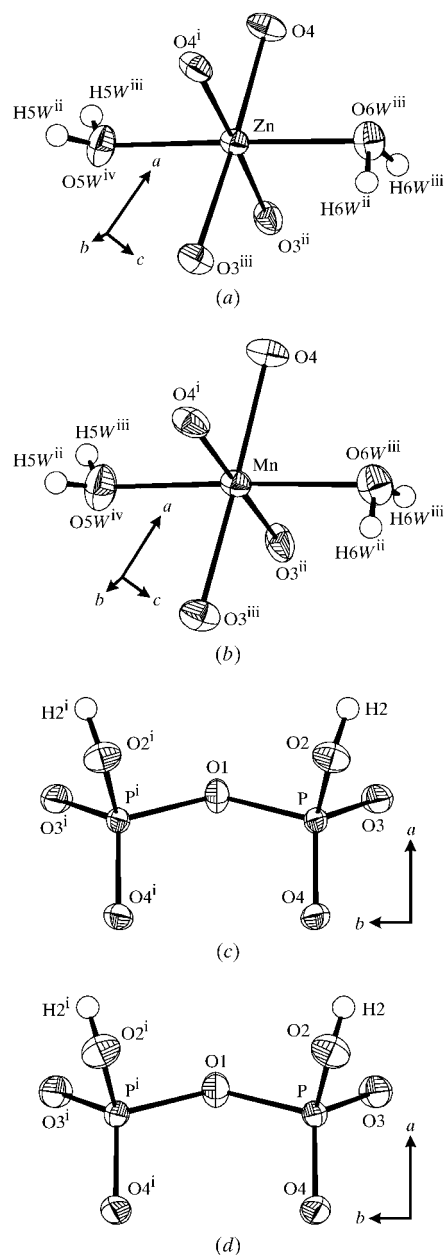


Figure 1

Views of the $[MO_4(H_2O)_2]^{2+}$ coordination polyhedra for (a) *M* = Zn and (b) *M* = Mn, and the pyrophosphate groups for (c) *M* = Zn and (d) *M* = Mn in $KM(HP_2O_7) \cdot 2H_2O$. Ellipsoids are shown at the 75% probability level. [Symmetry codes: (i) $x, -y + \frac{1}{2}, z$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $x - \frac{3}{2}, -y, \frac{1}{2} + z$; (iv) $x - \frac{3}{2}, -y, z - \frac{1}{2}$.]

diphosphate anions, which basically result from a slightly longer O5W–O2 distance of ~ 2.83 Å compared to an O6W–O4 distance of ~ 2.67 Å. Apparently, the coordination mode of water to a transition metal ion, expressed by the angle between the plane through the water molecule and the M^{2+} –OH₂ bond, is quite flexible.

The powder reflectance spectrum of KMn(HP₂O₇)·2H₂O, (II) (Fig. 3a), shows the spin-forbidden absorption bands typically found for Mn²⁺. The transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$, ${}^6A_{1g} \rightarrow ({}^4E_g, {}^4A_{1g})$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$ can be recognized. Thus, the spectrum provides, in addition to the X-ray study, clear evidence for a manganese(II) hydrogen pyrophosphate instead of a manganese(III) compound. The band positions are similar to those found for anhydrous manganese(II) phosphates, such as Mn₂P₂O₇, Mn₂P₄O₁₂ and Mn₂Si(P₂O₇)₂ (Glaum *et al.*, 2002), and for the hexaqua complex of Mn²⁺ (Figgis & Hitchman, 2000). The Raman spectrum of (II) (Fig. 3b) is in agreement with the different P–O bond distances found in the pyrophosphate anions (Table 2). We attribute the strong emission at $\nu = 1015$ cm⁻¹ to the symmetric stretching vibration of the external PO₃ groups, while the weaker signals at $\nu = 1123$ and 1183 cm⁻¹ most likely belong to asymmetric stretches of the external PO₃ groups (Rulmont *et al.*, 1991). The signal at 787 cm⁻¹ might be assigned to the symmetric stretch of the P–O–P bridge.

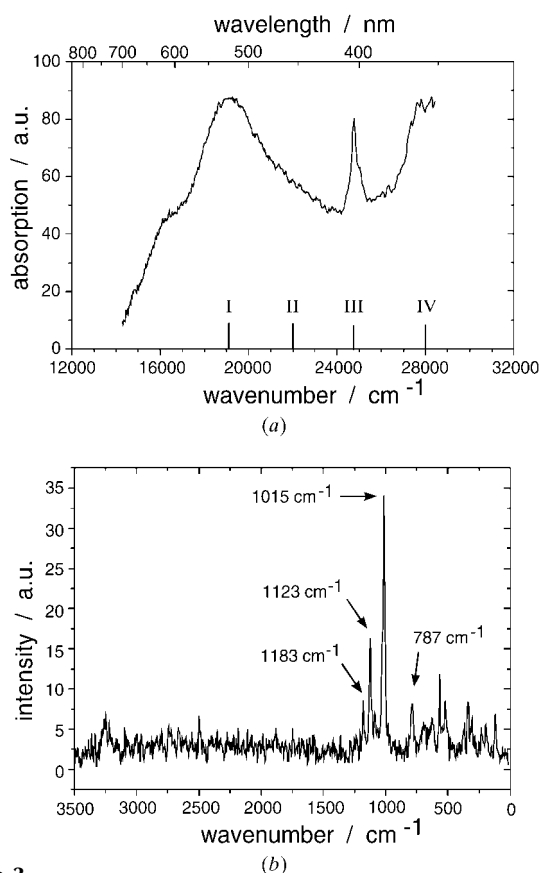


Figure 3
(a) Powder reflectance spectrum and (b) the Raman spectrum for KZn(HP₂O₇)·2H₂O, (II). Assignment of the electronic transitions in (a): I = ${}^6A_{1g} \rightarrow {}^4T_{1g}$, II = ${}^6A_{1g} \rightarrow {}^4T_{2g}$, III = ${}^6A_{1g} \rightarrow ({}^4E_g, {}^4A_{1g})$, IV = ${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$.

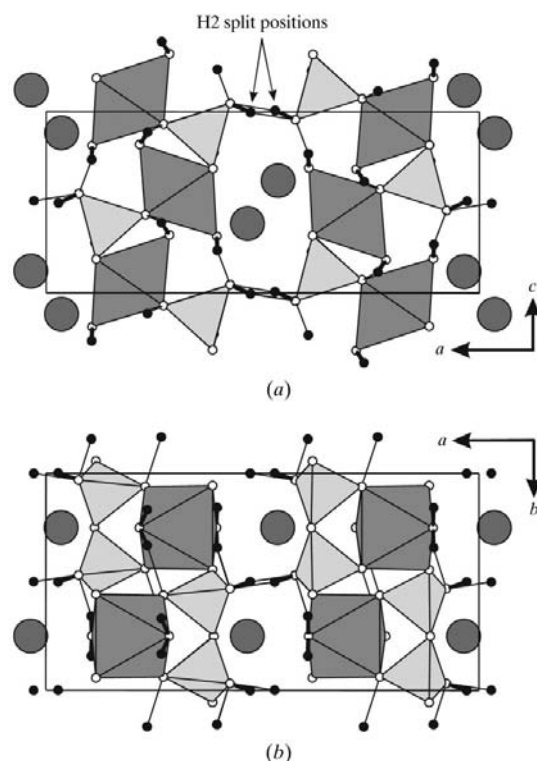


Figure 2
Projections of the crystal structure of KM(HP₂O₇)·2H₂O ($M = \text{Zn}$ and Mn) (a) along the b axis and (b) along the c axis, with schematic coordination polyhedra. Key: dark-grey polyhedra = $[\text{MO}_6]$, light-grey polyhedra = $[\text{P}_2\text{O}_7]$ groups, large grey circles = K^+ ions, small black circles = H^+ ions, O–H bonds are bold black bonds and hydrogen-bridging bonds are thin lines.

Experimental

The title compounds were obtained by mixing equimolar quantities of K₄P₂O₇ and ZnCl₂·4H₂O [or MnCl₂·4H₂O in the case of (II)] in a few ml of concentrated HCl. The former reactant was obtained by heating K₂HPO₄ at 873 K for 6 h. From the solution left at room temperature, well shaped colourless [or rose coloured in the case of (II)] crystals with edge-lengths up to 1 mm were deposited after 2–3 d.

Compound (I)

Crystal data

KZn(HP₂O₇)(H₂O)₂
 $M_r = 315.45$
 Orthorhombic, $Pnma$
 $a = 15.4727$ (12) Å
 $b = 7.7820$ (9) Å
 $c = 6.5009$ (7) Å
 $V = 782.76$ (14) Å³
 $Z = 4$
 $D_x = 2.677$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 40 reflections
 $\theta = 5.3$ – 17.5°
 $\mu = 4.10$ mm⁻¹
 $T = 293$ (2) K
 Prismatic, colourless
 $0.4 \times 0.4 \times 0.3$ mm

Data collection

Bruker P4 diffractometer
 $2\theta/\omega$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.175$, $T_{\max} = 0.292$
 1080 measured reflections
 738 independent reflections
 692 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -1 \rightarrow 18$
 $k = -9 \rightarrow 1$
 $l = -1 \rightarrow 7$
 3 standard reflections every 97 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.066$
 $S = 1.11$
 738 reflections
 77 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.9013P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.38 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXTL*
 Extinction coefficient: 0.0275 (18)

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.061$
 $S = 1.06$
 2633 reflections
 79 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2 + 0.2440P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.73 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

Zn1—O3 ⁱ	2.111 (2)	P1—O1	1.6160 (14)
Zn1—O4	2.059 (2)	P1—O2	1.543 (2)
Zn1—O5W ⁱⁱ	2.136 (3)	P1—O3	1.503 (2)
Zn1—O6W ⁱⁱ	2.160 (3)	P1—O4	1.505 (2)
O1—P1—O2	105.67 (14)	O2—P1—O4	110.65 (12)
O1—P1—O3	103.93 (13)	O3—P1—O4	115.53 (12)
O1—P1—O4	108.52 (13)	P1—O1—P1 ⁱⁱⁱ	130.91 (19)
O2—P1—O3	111.80 (12)		

Symmetry codes: (i) $\frac{3}{2} - x, -y, \frac{1}{2} + z$; (ii) $\frac{3}{2} - x, -y, z - \frac{1}{2}$; (iii) $x, \frac{1}{2} - y, z$.

Compound (II)

Crystal data

KMn(HP₂O₇)(H₂O)₂
 $M_r = 305.02$
 Orthorhombic, *Pnma*
 $a = 15.7186$ (5) \AA
 $b = 7.8706$ (5) \AA
 $c = 6.5297$ (5) \AA
 $V = 807.82$ (8) \AA^3
 $Z = 4$
 $D_x = 2.508 \text{ Mg m}^{-3}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 Non-profiled ω scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.409$, $T_{\max} = 0.463$
 17 404 measured reflections
 2633 independent reflections
 2278 reflections with $I > 2\sigma(I)$

Mo $K\alpha$ radiation
 Cell parameters from 21 reflections
 $\theta = 5.0\text{--}25.0^\circ$
 $\mu = 2.57 \text{ mm}^{-1}$
 $T = 293$ (2) K
 Prismatic, pink
 $0.30 \times 0.30 \times 0.30 \text{ mm}$

$R_{\text{int}} = 0.046$
 $\theta_{\max} = 40.0^\circ$
 $h = -22 \rightarrow 28$
 $k = -14 \rightarrow 14$
 $l = -11 \rightarrow 11$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Table 2

Selected geometric parameters (\AA , $^\circ$) for (II).

Mn—O3 ⁱ	2.1828 (7)	P—O1	1.6136 (4)
Mn—O4	2.1330 (7)	P—O2	1.5424 (7)
Mn—O5W ⁱⁱ	2.2183 (11)	P—O3	1.5052 (7)
Mn—O6W ⁱⁱ	2.2676 (11)	P—O4	1.4995 (7)
O1—P—O2	105.76 (5)	O2—P—O4	110.32 (4)
O1—P—O3	103.82 (4)	O3—P—O4	115.63 (4)
O1—P—O4	108.80 (4)	P ⁱⁱⁱ —O1—P	131.80 (6)
O2—P—O3	111.81 (4)		

Symmetry codes: (i) $\frac{3}{2} - x, -y, \frac{1}{2} + z$; (ii) $\frac{3}{2} - x, -y, z - \frac{1}{2}$; (iii) $x, \frac{1}{2} - y, z$.

All H atoms were located from difference Fourier maps. Within the limits of the method, the positions of the H atoms were refined allowing for isotropic displacement parameters. A split position with half-occupancy (around a centre of inversion) was introduced for the acid H2 atom. Attempts to resolve this splitting in non-centrosymmetric subgroups of *Pnma* did not lead to an improved refinement.

For compound (I), data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1991); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

For compound (II), data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1366). Services for accessing these data are described at the back of the journal.

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