

Synthesis and Characterization of $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$, a New Metal(II) Phosphate Hydrate

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The new manganese phosphate hydrate, $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$, has been obtained as a single phase product using hydrothermal methods and the structure has been determined by single crystal X-ray diffraction. The title compound crystallizes in the monoclinic space group Cc with $a = 934.18(10)$, $b = 1743.68(18)$, $c = 815.15(8)$ pm, $\beta = 92.616(2)^\circ$, $V = 1326.4(2) \cdot 10^6$ pm³, $Z = 4$, and the refinement led to $R1 = 0.0281$ and $Rw2 = 0.0728$ (all data). The structure is composed of $[\text{PO}_4]$ and $[\text{MnO}_x]$ polyhedra ($x = 6, 7$) and might be described as a distorted primitive hexagonal packing of $[\text{PO}_4]$ tetrahedra which are held together by Mn^{2+} ions partially located in distorted trigonal prismatic positions. This leads to a dense three-dimensional framework structure. Magnetic susceptibility measurements verified the presence of high-spin Mn^{2+} ions and thermogravimetric data confirm the chemical composition deduced from the single crystal structure determination.

1. Introduction

Transition metal phosphates and arsenates have been extensively investigated due to their structural variability. Many of these materials are studied for their use as catalysts, ion exchangers, ionic conductors, or for intercalation reactions [1]. In the course of a systematic investigation of manganese phosphates and arsenates we found a number of new compounds [2] as well as synthetic analogs of minerals [3, 4]. Manganese phosphates and manganese phosphate hydrates have been synthesized either by hydrothermal or by high-temperature methods and are also found in nature. Up to now the following compounds have been found and characterized by single-crystal structure determination or from microcrystalline powders: Mn(III)-compounds are MnP_3O_9 [5], $\text{MnPO}_4 \cdot \text{H}_2\text{O}$ [6], $\text{Mn}(\text{PO}_4) \cdot 0.962 \text{D}_2\text{O} \cdot 0.038 \text{H}_2\text{O}$ [7], MnHP_2O_7 [8]. Manganese in the oxidation state +2 is observed in $\text{MnP}_4\text{O}_{11}$ [9], $\text{Mn}_2\text{P}_2\text{O}_7$ [10], $\beta\text{-Mn}_3(\text{PO}_4)_2$ [11], $\text{Mn}_2\text{P}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$ [12], $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 2 \text{H}_2\text{O}$ [13], $\text{Mn}_7(\text{HPO}_4)_4(\text{PO}_4)_2$ [14], $\text{Mn}(\text{HPO}_4) \cdot 3 \text{H}_2\text{O}$ [15], and in the minerals hureaulite $\text{Mn}_5(\text{HPO}_4)_2(\text{PO}_4)_2 \cdot 4 \text{H}_2\text{O}$ [16], triploidite $\text{Mn}_2(\text{PO}_4)(\text{OH})$ [17], switzerite $\text{Mn}_3(\text{PO}_4)_2(\text{H}_2\text{O})_7$ [18], and gatehou-

seite $\text{Mn}_5(\text{OH})_4(\text{PO}_4)_2$ [19]. The only mixed-valence Mn(II/III) phosphate known up to now is the mineral bermanite $\text{Mn}(\text{II})\text{Mn}_2(\text{III})_2(\text{OH})_2(\text{PO}_4)_2 \cdot 4 \text{H}_2\text{O}$ [20]. In this paper, the synthesis, the crystal structure as well as the thermal and magnetic properties of $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ are presented.

2. Experimental Section

2.1. Hydrothermal synthesis

Single phase $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ was synthesized under hydrothermal conditions using Teflon-lined autoclaves (Parr, USA). Reagent grade chemicals were used as received from Aldrich. A typical synthesis was performed as follows: 7.5 ml of an aged 2 M solution of $\text{Mn}(\text{OOCCH}_3)_2$ (15 mmol) was combined with 2.5 ml of 4 M H_3PO_4 (10 mmol) and stirred for 10 min. Then 1.97 ml piperidine (20 mmol) was added and the resulting gel was stirred until homogeneous. The mixture was heated under autogeneous pressure for 48 h at 175 °C. The product was filtered and then rinsed with water and acetone. It contained pink needle-like crystals. The X-ray powder pattern obtained using a Scintag X2 powder diffractometer ($\text{Cu-K}\alpha$ radiation) compared well with the simulated powder pattern using the single crystal structure data.

Table 1. Summary of the crystallographic data.

Empirical formula	$\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$
Space group	<i>Cc</i>
<i>a</i> [pm]	934.18(10)
<i>b</i> [pm]	1743.68(18)
<i>c</i> [pm]	815.15(8)
β [°]	92.616(2)
Volume [10^6 pm^3]	1326.4(2)
<i>Z</i>	4
Formula mass	727.54
ρ [g/cm^3]	3.643
F(000)	1392
Crystal size (mm^3)	$0.507 \times 0.094 \times 0.072$
μ [mm^{-1}]	6.126
Absorption correction	empirical
$T_{\text{min.}} / T_{\text{max.}}$	0.62618 / 1.00
θ Range [°]	2.34 - 23.29
Range in <i>hkl</i>	$-8 \leq h \leq 10, -18 \leq k \leq 19,$ $-9 \leq l \leq 9$ <i>hkl, $\bar{h}kl, h\bar{k}l, hk\bar{l}$</i>
Total data collected	2929
Unique data	1509
Obs. data ($I > 2\sigma(I)$)	1472
Extinction coefficient	0.0180(7)
<i>R</i> (int)	0.041
<i>R</i> 1, <i>wR</i> 2 ($I > 2\sigma(I)$)	0.0265, 0.0674
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0281, 0.0728
Goodness of fit	1.148
BASF	0.16(3)
No. of variables	246
Δe min / max [$\text{e}\text{\AA}^{-3}$]	-0.538 / 0.610

2.2. Crystal structure determination

A suitable single crystal was carefully selected under a polarizing microscope. The single crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo- K_α radiation, $\lambda = 71.073 \text{ pm}$) operating at 45 kV and 40 mA. A hemisphere of intensity data was collected at room temperature with ω -scans (width of 0.30° and exposure time of 30 s per frame). For data reduction the program SAINT was used and the absorption correction was carried out using SADABS [21]. The single crystal structure was solved by direct methods and refined using the program package SHELXTL [22]. Whereas the structure solution and the refinement converged well in the acentric space group *Cc*, attempts to solve the structure in the centrosymmetric space group *C2/c* led to no satisfactory results. The space group *Cc* was also confirmed by detecting the NLO effect of second-harmonic generation. Second-harmonic generation is a powerful method of testing crystalline materials for the absence of a centre of inversion. The structure of the crystal was refined as a

Table 2. Atomic coordinates and equivalent isotropic displacement parameters [pm^2] for $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ (I). U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom*	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
Mn1	0.79924(14)	0.08221(7)	0.46039(15)	185(4)
Mn2	0.44189(14)	0.37259(8)	0.33718(17)	169(3)
Mn3	0.04152(14)	0.20312(8)	0.37429(15)	172(3)
Mn4	0.00677(14)	0.31184(8)	0.02754(15)	176(4)
Mn5	0.76873(15)	0.41511(7)	0.42468(16)	181(4)
Mn6	0.58987(15)	0.11989(7)	0.10064(15)	169(3)
P1	0.3265(2)	0.23956(13)	0.1730(3)	150(5)
P2	0.7205(2)	0.25519(13)	0.2250(3)	147(5)
P3	0.0471(3)	0.03192(12)	0.1906(3)	158(5)
P4	0.1213(2)	0.44964(12)	0.2902(3)	151(5)
O1	0.3745(7)	0.1617(3)	0.1083(7)	205(14)
O2	0.3832(7)	0.3079(3)	0.0712(8)	169(13)
O3	0.1632(7)	0.2409(3)	0.1723(8)	192(14)
O4	0.3928(7)	0.2527(3)	0.3472(8)	183(14)
O5	0.8840(7)	0.2610(3)	0.2229(7)	180(14)
O6	0.6608(7)	0.3310(3)	0.2867(8)	190(14)
O7	0.6746(7)	0.1855(3)	0.3295(7)	166(13)
O8	0.6573(7)	0.2359(3)	0.0525(7)	160(13)
O9	0.0646(6)	0.0748(3)	0.0263(7)	178(14)
O10	0.1952(7)	0.0034(3)	0.2485(8)	225(14)
O11	0.9436(7)	0.9646(3)	0.1632(7)	184(14)
O12	0.9844(7)	0.0882(3)	0.3153(8)	183(14)
O13	0.1244(7)	0.4108(3)	0.1228(7)	181(14)
O14	0.2404(6)	0.4188(3)	0.4128(7)	190(14)
O15	0.1452(6)	0.5346(3)	0.2723(7)	195(14)
O16	0.9822(7)	0.4328(3)	0.3743(8)	204(14)
O17	0.8174(9)	0.3949(4)	0.9830(9)	365(19)
H1	0.803(14)	0.411(6)	0.873(11)	440
H2	0.803(13)	0.422(6)	0.081(12)	440

* All atoms are in Wyckoff position 4a.

racemic twin with a fractional contribution of 0.16(3). The hydrogen atoms found in the difference electron density map were refined using a restraint to the O-H distances in the water molecule (SADI). Furthermore the temperature factors of the H atoms were fixed to be 1.2 times the value of the oxygen atom. Experimental data and results of the structure determination are given in Table 1. Atomic coordinates with isotropic displacement parameters are shown in Table 2, and the bond lengths as well as the valence sums are summarized in Table 3. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (*49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412152.

2.3. Physical measurements

Magnetic susceptibility data were collected on a SQUID magnetometer Quantum Design, Inc. using a

Table 3. Bond lengths [pm] and bond valence sums for $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$.

P1-O = 153.9(7)		P3-O = 153.8(6)	
$\Sigma_s(\text{P1-O}) = 4.945$		$\Sigma_s(\text{P3-O}) = 4.958$	
P1-O1	153.1(6)	P3-O9	154.9(6)
P1-O2	155.8(6)	P3-O10	152.4(7)
P1-O3	152.5(7)	P3-O11	153.0(6)
P1-O4	154.1(7)	P3-O12	154.8(6)
P2-O = 153.8(6)		P4-O = 152.8(6)	
$\Sigma_s(\text{P2-O}) = 4.953$		$\Sigma_s(\text{P4-O}) = 5.094$	
P2-O5	153.2(7)	P4-O13	152.4(6)
P2-O6	152.8(6)	P4-O14	155.7(6)
P2-O7	155.5(6)	P4-O15	150.6(6)
P2-O8	153.7(6)	P4-O16	152.5(7)
Mn1-O = 222.8(6)		Mn4-O = 221.3(6)	
$\Sigma_s(\text{Mn1-O}) = 1.874/1.921^*$		$\Sigma_s(\text{Mn4-O}) = 1.948$	
Mn1-O2	224.5(6)	Mn4-O3	221.4(6)
Mn1-O7	237.2(6)	Mn4-O4	210.2(6)
Mn1-O11	223.9(6)	Mn4-O5	219.1(6)
Mn1-O12	214.2(6)	Mn4-O7	230.1(6)
Mn1-O13	215.2(6)	Mn4-O13	217.1(6)
Mn1-O14	292.5(6)	Mn4-O17	229.7(6)
Mn1-O15	221.6(6)		
Mn2-O = 220.8(6)		Mn5-O = 213.6(7)	
$\Sigma_s(\text{Mn2-O}) = 2.041$		$\Sigma_s(\text{Mn5-O}) = 1.982/2.011^*$	
Mn2-O2	248.3(6)	Mn5-O1	220.8(6)
Mn2-O4	214.2(6)	Mn5-O6	208.1(7)
Mn2-O6	222.6(6)	Mn5-O9	212.1(6)
Mn2-O9	209.1(6)	Mn5-O10	219.4(6)
Mn2-O11	214.3(6)	Mn5-O16	207.8(7)
Mn2-O14	216.3(6)	Mn5-O10	310.2(7)
Mn3-O = 214.1(6)		Mn6-O = 219.6(7)	
$\Sigma_s(\text{Mn3-O}) = 1.956/1.979^*$		$\Sigma_s(\text{Mn6-O}) = 2.038$	
Mn3-O2	224.0(6)	Mn6-O1	214.3(7)
Mn3-O3	214.7(6)	Mn6-O7	229.8(6)
Mn3-O5	213.1(6)	Mn6-O8	215.9(6)
Mn3-O8	206.6(6)	Mn6-O14	223.0(6)
Mn3-O12	212.3(6)	Mn6-O15	209.1(6)
Mn3-O17	319.0(6)	Mn6-O16	225.6(7)

* Valence sums: Mn-O distances < 250 pm / all listed Mn-O distances.

polycrystalline sample, which was first cooled to 5 K at zero field and then warmed to 300 K under an applied field of 5000 G. Thermal properties were measured on a Mettler Toledo TGA/SDTA 851 thermogravimetric analyser which was coupled to a Balzer ThermoStar Mass Spectrometer GSD 300 T for the identification of volatile products.

3. Results and Discussion

Whereas metal(II) phosphate hydrates $\text{M}_3^{\text{II}}(\text{PO}_4)_2 \cdot x \text{H}_2\text{O}$ with $x \geq 1$ are well known and characterized

by X-ray crystallography, to our knowledge the title compound presents the first example of a metal(II) phosphate with the composition $\text{M}(\text{II})_3(\text{PO}_4)_2 \cdot 0.5 \text{H}_2\text{O}$ ($\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$).

3.1. Synthesis

The synthesis of $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ was attempted using different manganese compounds such as $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$, MnCO_3 and $\text{Mn}(\text{OOCCH}_3)_2$ as starting materials. Interestingly, only manganese acetate led to the formation of the title compound. In addition, the preparation of $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ was only possible when an aged solution (aged for 14 days) was used. Freshly prepared solutions under the same reaction conditions led to the formation of hureaulite $\text{Mn}_5(\text{PO}_4)_2(\text{HPO}_4)_2 \cdot 4 \text{H}_2\text{O}$ [16].

3.2 X-ray crystal structure

The crystal structure of $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ is composed of Mn^{2+} and PO_4^{3-} ions and one H_2O molecule is coordinated to two Mn^{2+} ions. The ions form a complex, dense, three-dimensional framework of $[\text{PO}_4]$ and $[\text{MnO}_x]$ polyhedra ($x = 6, 7$). The asymmetric unit of the title compound is shown in Fig. 1. In the crystal structure six independent Mn^{2+} ions (Fig. 2) which are six- or sevenfold coordinated are observed. The polyhedra $[\text{Mn}(1)\text{O}_7]$, $[\text{Mn}(3)\text{O}_6]$, and $[\text{Mn}(5)\text{O}_6]$ each

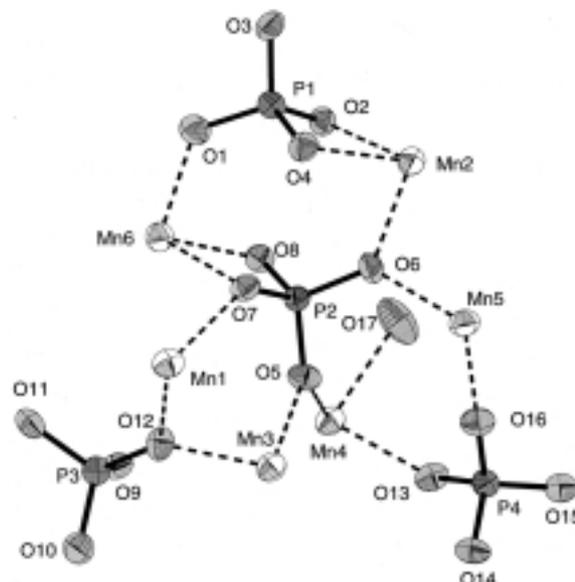


Fig. 1. Asymmetric unit of $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$. Thermal ellipsoids are shown at the 75 % probability level.

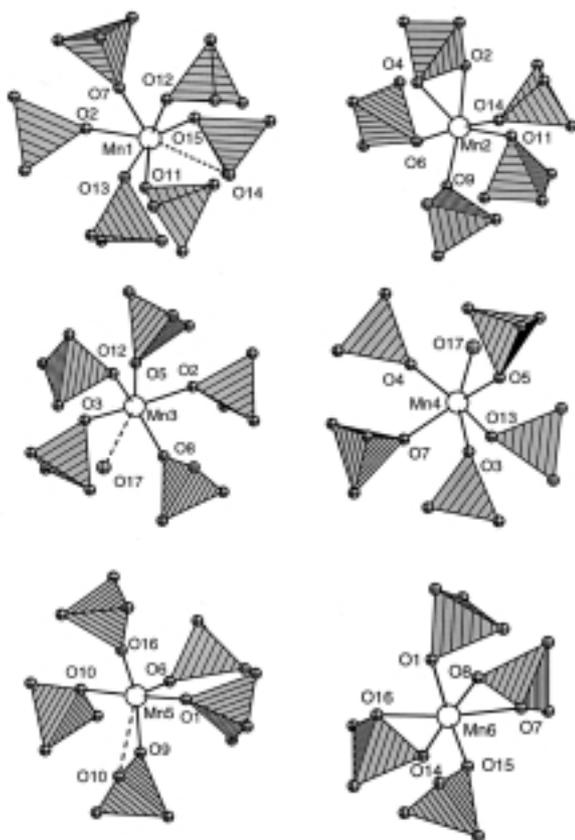


Fig. 2. Coordination of the Mn^{2+} ions by the phosphate groups in $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$. Dotted bonds describe Mn-O distances larger than 250 pm, O17 is the oxygen atom of the water molecule involved in the coordination of Mn3 and Mn4.

show one rather long distance $d(\text{Mn}-\text{O}) = 292.5, 319.0$ and 310.2 pm, respectively, and might be also described as 6+1 and 5+1 coordination polyhedra (Table 3). The mean distances of the remaining six and five oxygen atoms are 222.8, 214.1 and 213.6 pm for Mn1, Mn3 and Mn5, respectively, and compare well with the mean distances $d(\text{Mn}-\text{O})$ of 220.8, 221.3 and 219.6 pm of the other $[\text{MnO}_6]$ polyhedra. These Mn-O distances are similar to values observed in other manganese phosphates ($\text{Mn}_2(\text{PO}_4)(\text{OH})$: $d(\text{Mn}-\text{O}) = 210.9 - 223.5$ pm, β' - $\text{Mn}_3(\text{PO}_4)_2$: $d(\text{Mn}-\text{O}) = 212.6 - 224.2$ pm) and to the sum of the ionic radii of Mn^{2+} and O^{2-} ($97 + 122 = 2.19$ pm) [23].

The $[\text{PO}_4]$ polyhedra act as monodentate and bidentate ligands (Fig. 2). The mean $d(\text{P}-\text{O})$

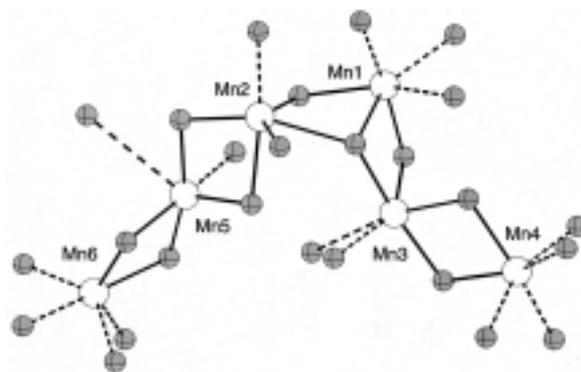


Fig. 3. Edge-sharing MnO_x chains in $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$. Solid lines describe the bonds involved in the connection of the $[\text{MnO}_x]$ polyhedra ($x = 6, 7$) forming the building unit.

distances of 153.9(7), 153.8(6), 153.8(6) and 152.8(6) pm for the four independent $[\text{PO}_4]$ tetrahedra agree well with the distances reported for other manganese phosphates such as $\text{Mn}_2(\text{PO}_4)(\text{OH})$ [17] or β' - $\text{Mn}_3(\text{PO}_4)_2$ [11] where mean $d(\text{P}-\text{O})$ distances of 153.6 - 154.2 pm and 153.3 - 153.6 pm, respectively, are observed. The oxygen atoms O(1) to O(16) are connected to the phosphorus atoms and bridge either three (O(2), O(7) and O(14)) or two Mn^{2+} ions. The oxygen atom of the water molecule (O(17)) is strongly coordinated to Mn(4) (Mn(4)-O(17): 229.7(6) pm) and has weak interactions to Mn(3) (Mn(3)-O(17): 319.0(6) pm). The hydrogen atoms of the water molecule have been located. The angle $\text{H}(1)-\text{O}(17)-\text{H}(2)$ is $129(10)^\circ$, considerably larger than would be expected (105°), and suggests that the hydrogen atom positions have been poorly defined. Nevertheless, the H atoms take part in hydrogen bonding $\text{O}-\text{H}(1) \cdots \text{O}(10)$: 204.6 pm and $\text{O}-\text{H}(2) \cdots \text{O}(10)$: 223.3 pm. This is also confirmed by the bond valence calculation where a value of 1.622 is observed, which deviates significantly from the expected value 2.0.

The three-dimensional structure of $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ might be described in two ways. Looking at the Mn^{2+} ions, a building unit of six edge-sharing $[\text{MnO}_x]$ polyhedra ($x = 6, 7$) can be constructed (Fig. 3). Since all oxygen atoms bridge either two or three Mn^{2+} ions, these building units are connected to a three-dimensional network which is further stabilized by the phosphorus atoms. Starting from the $[\text{PO}_4]$ polyhedra a distorted primitive hexagonal packing of the tetrahedra along the c -axis

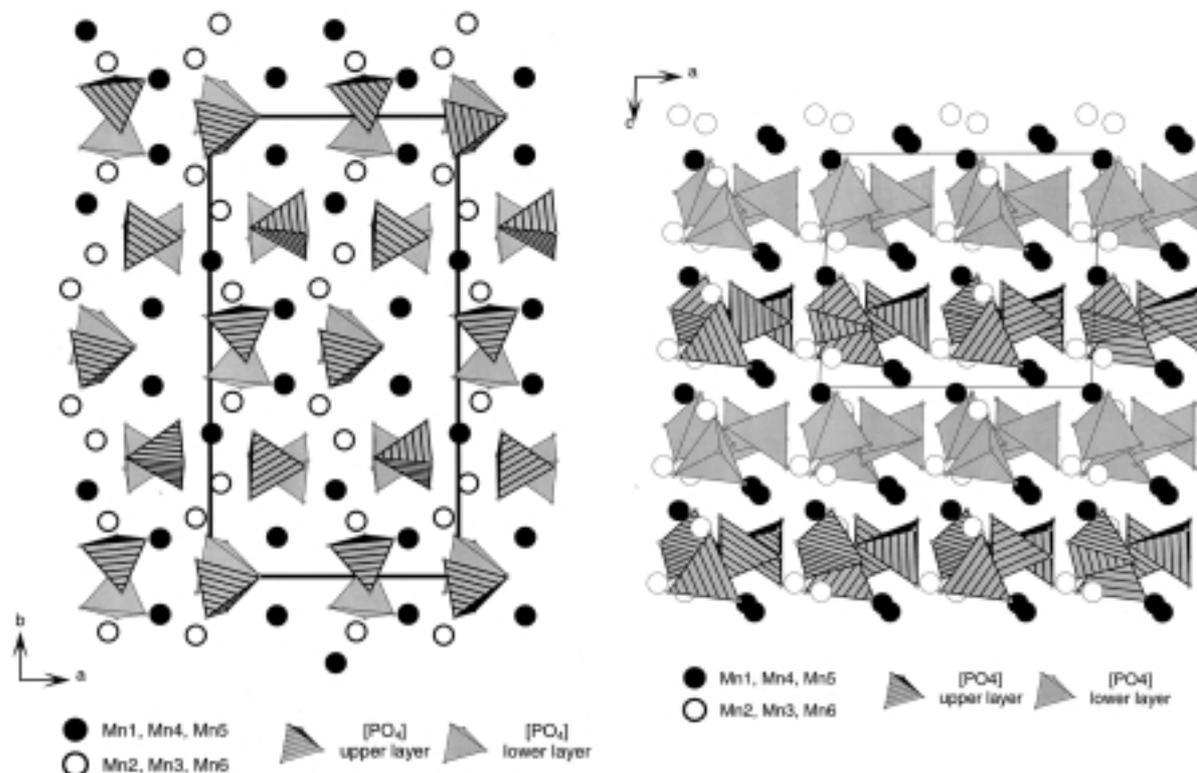


Fig. 4. Distorted primitive hexagonal packing of the $[\text{PO}_4]$ polyhedra in $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$. *Left*: view along $[001]$, *right*: view along $[010]$.

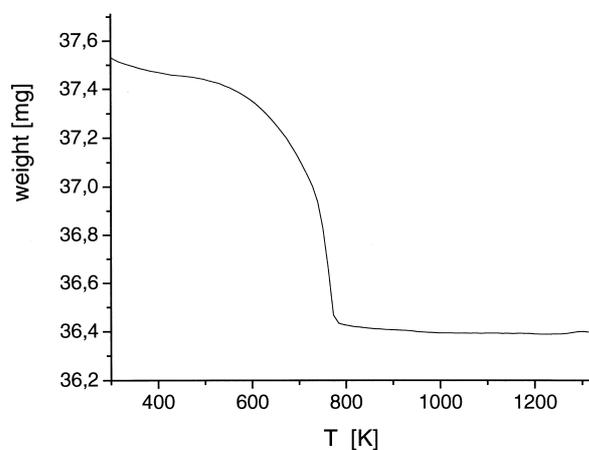


Fig. 5. TGA curve of $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$.

can be constructed (Fig. 4). The Mn^{2+} ions interconnect the PO_4^{3-} units. Whereas Mn1, Mn4 and Mn5 can be thought to occupy the distorted trigonal prismatic voids, the remaining manganese atoms are found in positions of low symmetry.

3.3. Thermal properties

TG/MS measurements showed that the crystal water was lost in one step between 570 and 770 K (Fig. 5). The observed weight loss of 2.84% compares well with the theoretical value of 2.46%. The larger loss could be due to surface water. No volatile products except water were observed in the investigated temperature range.

3.4. Magnetic properties

Magnetic studies were undertaken in order to confirm the +2 oxidation state of Mn and to determine if $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ has magnetic ordering. Fig. 6 shows the plot of the temperature dependence of the inverse molar magnetic susceptibility over the temperature range 5 - 300 K. The title compound displays Curie-Weiss behaviour over a wide range of temperatures with a Curie constant of $C = 4.34(1) \text{ emu K}^{-1}$ per mol Mn and a Weiss constant of $\Theta = -64.4(6) \text{ K}$. The Curie constant corresponds to an effective magnetic moment of $5.90 \mu_B$, which

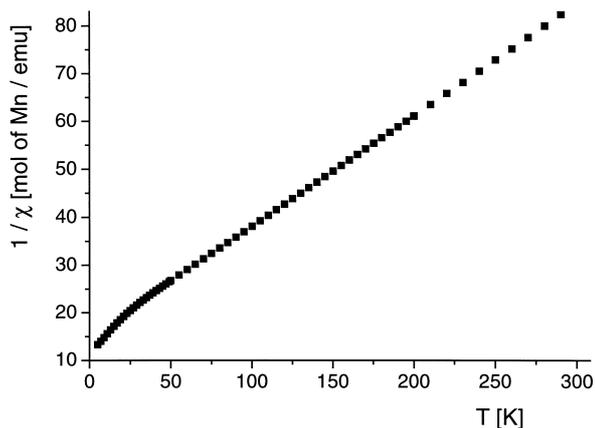


Fig. 6. The inverse molar magnetic susceptibility of polycrystalline $\text{Mn}_6(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$ plotted as a function of the temperature over the range 5 - 300 K.

is consistent with high-spin Mn^{2+} ions (d^5) in an octahedral environment (expected: $5.92 \mu_B$). At temperatures below 20 K, a small deviation from the ideal Curie-Weiss behaviour is detected.

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