



# Unique charge ordering of manganese in a new mixed valent phosphate $K_3Mn^{II}_3Mn^{III}(PO_4)(H_{0.5}PO_4)_2(HPO_4)_2$

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## ABSTRACT

A new mixed-valent manganese phosphate,  $K_3Mn^{II}_3Mn^{III}(PO_4)(H_{0.5}PO_4)_2(HPO_4)_2$ , has been synthesized using hydrothermal method. Its monoclinic  $C2/c$  structure ( $a = 12.5506(16) \text{ \AA}$ ,  $b = 10.4816(18) \text{ \AA}$ ,  $c = 13.6723(10) \text{ \AA}$ ,  $\beta = 103.758(11)^\circ$ ) forms a 3D framework of  $MnO_6$  octahedra,  $MnO_5$  trigonal bipyramids,  $PO_4$  and  $PO_3OH$  tetrahedra. The main structural feature of this phosphate deals with its  $[Mn_4O_{16}]_\infty$  chains running along  $\bar{c}$ , which are interconnected through  $PO_4$  and  $PO_3OH$  tetrahedra, forming intersecting tunnels running along  $[110]$ ,  $[1\bar{1}0]$  and  $[001]$ . The geometry of the  $[Mn_4O_{16}]_\infty$  chains and the charge ordering of manganese in the latter are unique: they consist of trimeric units of divalent manganese " $Mn_3^{II}O_{12}$ " alternating with single trivalent  $Mn^{III}O_6$  octahedra along  $\bar{c}$ . In each " $Mn_3^{II}O_{12}$ " unit one central  $Mn^{II}O_6$  octahedron shares two opposite edges with two  $Mn^{II}O_5$  trigonal bipyramids. Along  $\bar{c}$ , one Mn(II) octahedron alternates with one Mn(III) octahedron by sharing one corner. The relationships between the structure of this unique charge ordered phosphate and other manganese phosphates are discussed.

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## 1. Introduction

Manganese phosphates form an extremely large family that has been widely studied in view of applications as catalysts, ionic conductors and ion exchangers. From a fundamental viewpoint, these materials have been extensively explored for their magnetic properties [1–10]. Though manganese offers several oxidation states, mainly  $Mn^{2+}$ ,  $Mn^{3+}$  and  $Mn^{4+}$ , most of the manganese phosphates that have been synthesized and studied for their magnetic properties are Mn(II) phosphates. In contrast, the number of Mn(III) phosphates that have been synthesized to date is rather limited. In the systems Mn–P–O and Mn–P–O–H, only four phosphates of trivalent manganese are actually known— $Mn(PO_3)_3$  [11],  $MnH_3P_2O_6 \cdot 2H_2O$  [12],  $MnHP_2O_7$  [13,14] and  $MnPO_4 \cdot H_2O$  [15]—whereas, in the systems A–Mn–P–O and A–Mn–P–O–H with A being alkaline or alkaline earth element, only twelve Mn(III) compounds are mentioned in the literature, i.e.  $AMnHP_3O_{10}$  with  $A = Cs, K, Rb$  [16–20],  $LiMnPO_4OH$  [21],  $Na_2MnP_5O_{15}$  [22],  $KMn_2OPO_4HPO_4$  [23],  $NH_4Mn_2OPO_4(HPO_4) \cdot H_2O$  [24],  $LiMnP_2O_7$  [14],  $Ca_2(H_2O)_2Mn_3O_2(PO_4)_3 \cdot H_2O$  [25],  $CsMn(PO_4)_3$  [26],  $Sr_2Mn(PO_4)(P_2O_7)$  [27] and  $Na_3MnH(P_{0.9}O_4)_2$  [28]. Importantly, phosphates involving a Mn(II)/Mn(III) mixed valence of manganese are extremely rare. In the Mn–P–O and Mn–P–O–H systems, no mixed valence phosphate has been

synthesized excepts the natural mineral Bermanite  $Mn^{II}(H_2O)_4[Mn_2^{III}(OH)_2(PO_4)_2]$  [29] which was shown to exhibit an ordered distribution of the  $Mn^{2+}$  and  $Mn^{3+}$  species. In the A–Mn–P–O and A–Mn–P–O–H systems only one mixed valence manganese phosphate seems to be known,  $CsMn_2P_6O_{18}$  [30], whose isolated octahedra are statistically occupied by  $Mn^{2+}$  and  $Mn^{3+}$  species in its two allotropic forms. Thus, the discovery of new mixed valence manganese phosphates appears as a challenge, the more that such compounds should be of interest for their magnetic properties. For this purpose, we have revisited the system K–Mn–P–O–H, using hydrothermal synthesis. We report herein on a new mixed valent phosphate,  $K_3Mn^{II}_3Mn^{III}(PO_4)(H_{0.5}PO_4)_2(HPO_4)_2$ , whose intersecting tunnel structure consists of infinite chains of edge- and corner-sharing  $MnO_6$  and  $MnO_5$  polyhedra, interconnected through  $PO_4$  and  $PO_3OH$  tetrahedra. We emphasize the unique charge ordering of manganese in those chains, suggesting the possibility of attractive magnetic properties.

## 2. Experimental

### 2.1. Synthesis

The single crystal used for the structure determination of  $K_3Mn_4(PO_4)(H_{0.5}PO_4)_2(HPO_4)_2$  was extracted from a batch prepared under hydrothermal conditions in the following way. A mixture of MnO,  $Mn_2O_3$  and  $KH_2PO_4$  in the respective molar ratio

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2:1:20, was placed in a 21 ml Teflon-lined stainless steel autoclave with 2 ml of deionized water (pH of the so-prepared solution  $\approx 5$ ). It was heated at 200 °C during 15 h and then cooled to room temperature during 30 h. After cooling, the solid products were collected by filtration of the final solution (pH  $\approx 5$ ), washed with deionized water and dried in air. The examination of the resulting brown powder revealed the presence of dark brown crystals corresponding to the title compound, orange needle-like crystals of  $\text{KMn}_2\text{O}(\text{PO}_4)(\text{HPO}_4)$  [23] and colorless crystals of  $\text{K}_4\text{Mn}_3(\text{HPO}_4)_4(\text{H}_2\text{PO}_4)_2$  [31].

Many attempts have been performed in order to prepare  $\text{K}_3\text{Mn}_4(\text{PO}_4)(\text{H}_{0.5}\text{PO}_4)_2(\text{HPO}_4)_2$  in the form of a polycrystalline monophasic sample, but all of them failed. However, the synthesis of micro-crystals of  $\text{K}_3\text{Mn}_4(\text{PO}_4)(\text{H}_{0.5}\text{PO}_4)_2(\text{HPO}_4)_2$  (mixed with other compounds) can be reproduced by using the experimental procedure described above.

## 2.2. Crystal studies: EDX analysis and X-ray diffraction

Semi-quantitative analyses of some brown crystals extracted from the preparation were performed with an EDAX microprobe mounted on a ZEISS Supra 55 scanning electron microscope. They revealed the presence of K, Mn and P elements in the approximate ratio 3–4–5 in the crystals, in agreement with the composition deduced from the single crystal X-ray diffraction study. Several crystals were then optically selected to be tested. A single crystal, with dimensions  $0.103 \times 0.025 \times 0.026 \text{ mm}^3$ , was chosen for the structure determination and refinement. The data were collected with a Bruker–Nonius Kappa CCD four-circle diffractometer equipped with a bidimensional CCD detector and using the  $\text{MoK}\alpha$  radiation. Strategy using  $\varphi$  and  $\omega$  scans with  $0.8^\circ$  per frame,  $160 \text{ s}^\circ$ , two iterations, was determined. The crystal–detector distance was fixed at  $Dx = 34 \text{ mm}$ . Data were reduced and corrected for Lorentz and polarization effects with the EvalCCD [32] package. The observed reflection conditions  $hkl$ :  $h+k = 2n$ ,  $h0l$ :  $h,l = 2n$ ,  $(0kl)$ :  $k = 2n$ ,  $hk0$ :  $h+k = 2n$ ,  $0k0$ :  $k = 2n$ ,  $h00$ :  $h = 2n$ ,  $00l$ :  $l = 2n$  were compatible with the  $C2/c$  space group (no. 15). The structure was solved and refined in this centrosymmetric space group, using the JANA2006 program [33]. Table 1 gives the data collection, cell and refinement parameters for single crystal X-ray diffraction study. The structure of  $\text{K}_3\text{Mn}_4(\text{PO}_4)(\text{H}_{0.5}\text{PO}_4)_2(\text{HPO}_4)_2$  was determined using the heavy atom method and successive difference synthesis and Fourier synthesis. K, Mn, P and O atoms were located. The refinement of their atomic coordinates and anisotropic thermal parameters led to the reliability factors  $R = 0.0397$  and  $R_w = 0.0419$ . The maximum of residual electronic densities was  $4.66 \text{ e}^- \text{ \AA}^{-3}$ . Bond valence sum (BVS) calculations [34] were thus performed at this stage of the refinement for potassium, manganese and phosphorus cations and oxygen anions and lead to the values of about 1.2 for K, 3.2 for Mn1, 1.8 for Mn2 and Mn3, 4.7 for P and between 1.8 and 2.1 for O1 to O7, whereas O8, O9 and O10 had respective BVS values of 1.35, 1.54 and 1.52. The chemical formula for the cell content deduced from this refinement, “ $\text{K}_3\text{Mn}_4(\text{PO}_4)_5$ ”, suggested that three positive charges per cell unit were missing to ensure the charge balance. Assuming that these missing positive charges were corresponding to hydrogen atoms bonded to O8, O9 and O10, difference Fourier maps were calculated. From their examination, two hydrogen atoms H1 and H2 could be located, at about  $1 \text{ \AA}$  from O8 and O9, respectively, and at 1.6 and  $1.4 \text{ \AA}$  from O10 and O9, respectively. Note that the H2 atom was located close to the (0; 0; 0) position (i.e. close to the inversion center), leading to too short H2–H2 distances of  $0.54 \text{ \AA}$ ; the site occupancy for H2 was thus fixed to 0.5. The chemical formula for this compound was then  $\text{K}_3\text{Mn}_3^{\text{II}}\text{Mn}^{\text{III}}(\text{PO}_4)(\text{H}_{0.5}\text{PO}_4)_2(\text{HPO}_4)_2$  ( $Z = 4$ ), for which charge

**Table 1**

Data collection, cell and refinement parameters from single crystal X-ray diffraction study of  $\text{K}_3\text{Mn}_4(\text{PO}_4)(\text{H}_{0.5}\text{PO}_4)_2(\text{HPO}_4)_2$ .

Crystal data	
Chemical formula	$\text{K}_3\text{Mn}_4(\text{PO}_4)(\text{H}_{0.5}\text{PO}_4)_2(\text{HPO}_4)_2$
$M$ ( $\text{g mol}^{-1}$ )	814.92
Cell setting, space group	Monoclinic, $C2/c$
Atomic parameters	$a = 12.5506$ (16) $\text{\AA}$ $b = 10.4816$ (18) $\text{\AA}$ $c = 13.6723$ (10) $\text{\AA}$ $\beta = 103.758$ (11) $^\circ$ 1747.0 (4)
$V$ ( $\text{\AA}^3$ )	1747.0 (4)
$Z$	4
$\rho$ calc. ( $\text{g cm}^{-3}$ )	3.0974(7)
Crystal size ( $\text{mm}^3$ )	$0.103 \times 0.025 \times 0.026$
Data collection	
$\lambda$ ( $\text{MoK}\alpha$ )	0.71069 $\text{\AA}$
Scan strategy	$\varphi$ and $\omega$ scans $0.8^\circ/\text{frame}$ $160 \text{ s}^\circ$ Two iterations $Dx = 34 \text{ mm}$
$\theta$ range and limiting indices	$5.76^\circ \leq \theta \leq 35^\circ$ $0 \leq h \leq 20$ $0 \leq k \leq 16$ $-22 \leq l \leq 21$
Measured reflections	10722
Independent reflections	3830
$\mu$ ( $\text{mm}^{-1}$ )	4.106
Structure solution and refinement	
Parameters refined	148
Agreement factors	$R = 3.93\%$ ; $R_w = 4.16\%$
Weighting scheme	$w = 1/\sigma(F)^2$

**Table 2**

Atomic parameters for  $\text{K}_3\text{Mn}_4(\text{PO}_4)(\text{H}_{0.5}\text{PO}_4)_2(\text{HPO}_4)_2$ .

Atoms	Site occupancy	x	y	z	$U_{\text{eq}}^a$ ( $\text{\AA}^2$ )
Mn1	1	0	0.5	0	0.00908(19)
Mn2	1	0	0.35271(7)	−0.25	0.0107(2)
Mn3	1	0.24076(4)	0.28343(5)	0.16596(4)	0.01166(14)
K1	1	0.23658(7)	−0.07275(9)	0.08462(5)	0.0183(2)
K2	1	0.5	0.50553(13)	0.25	0.0234(4)
P1	1	0.22570(7)	0.56825(9)	0.15672(6)	0.0088(2)
P2	1	1.5	−0.12098(12)	0.25	0.0080(3)
P3	1	0.06135(7)	0.20584(8)	−0.03652(6)	0.0086(2)
O1	1	0.15433(18)	0.4988(2)	0.06440(16)	0.0125(7)
O2	1	0.0963(2)	0.2347(3)	−0.13597(16)	0.0143(7)
O3	1	0.4683(2)	−0.0300(2)	0.15811(15)	0.0114(7)
O4	1	1.1608(2)	0.1744(2)	0.04830(16)	0.0142(7)
O5	1	0.2863(2)	0.4661(2)	0.22710(16)	0.0134(7)
O6	1	0.1666(2)	0.6612(3)	0.21151(16)	0.0145(7)
O7	1	0.9974(2)	0.3211(2)	−0.01040(17)	0.0134(7)
O8	1	0.3108(2)	0.6475(3)	0.11260(17)	0.0154(7)
O9	1	0.9831(2)	0.0904(2)	−0.05812(17)	0.0143(7)
O10	1	1.5984(2)	−0.2074(2)	0.24408(17)	0.0137(7)
H1	1	0.3602	0.6851	0.1709	0.022
H2	0.5	0.9837	0.0163	−0.0083	0.019

<sup>a</sup> The atomic displacement parameters of all atoms were refined anisotropically and are given in the form of an equivalent isotropic displacement parameter defined by  $U_{\text{eq}} = \frac{1}{3} \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a^i a^j \bar{a}_i \bar{a}_j$ , except for hydrogen atoms for which atomic displacement was fixed to  $1.3U_{\text{eq}}(\text{O8})$  for H1 and  $1.3U_{\text{eq}}(\text{O9})$  for H2.

balance is respected. A refinement of atomic coordinates for all atoms, including hydrogen atoms, was performed, but it led to quite short O8–H1 and O9–H2 distances. The final refinement of the structure was thus performed on atomic coordinates of all

atoms except H1 and H2 (fixed at the coordinates found on the difference Fourier series), with anisotropic displacement parameters for K, Mn, P and O atoms. It led to the reliability factors  $R = 0.0393$  and  $R_w = 0.0416$ . The corresponding atomic coordinates, equivalent isotropic thermal parameters and their estimated standard deviations are listed in Table 2. Tables of the anisotropic displacement parameters for all atoms and detail of the bond valence calculations are available as supplementary material. Note that, after the introduction of H1 and H2, the bond valence calculation led to 2.0, 1.85 and 1.85 for O8, O9 and O10, respectively. The hydrogen bonds distances and angles are given in Table 3.

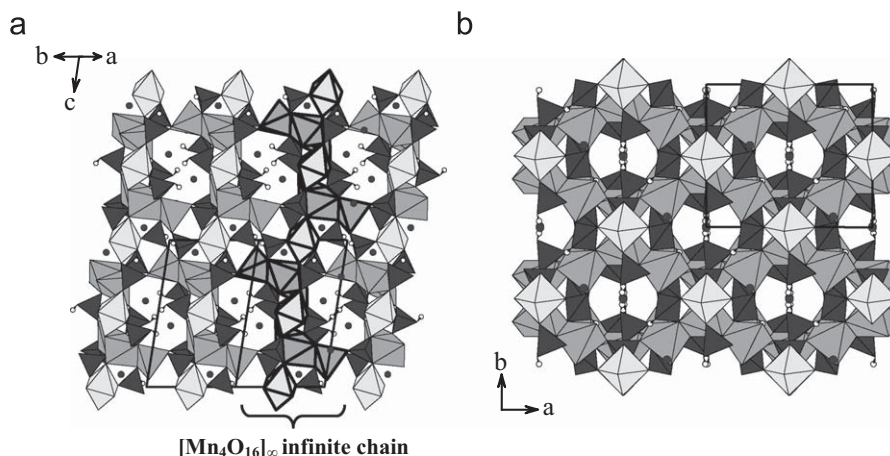
### 3. Description of the structure and discussion

The projections of the structure of  $K_3Mn_4(PO_4)(H_{0.5}PO_4)_2(HPO_4)_2$  along [110] (Fig. 1a) and along [001] (Fig. 1b) show that the three-dimensional framework  $[Mn_4P_5O_{17}(OH)_3]_{\infty}$  consists of  $MnO_6$  octahedra,  $MnO_5$  trigonal bipyramids,  $PO_4$  and  $PO_3OH$  tetrahedra forming S-shaped and butterfly-like tunnels running along [110] and [001], respectively. Note that the symmetry of the structure implies that similar S-shaped tunnels are running along  $[\bar{1}\bar{1}0]$ .

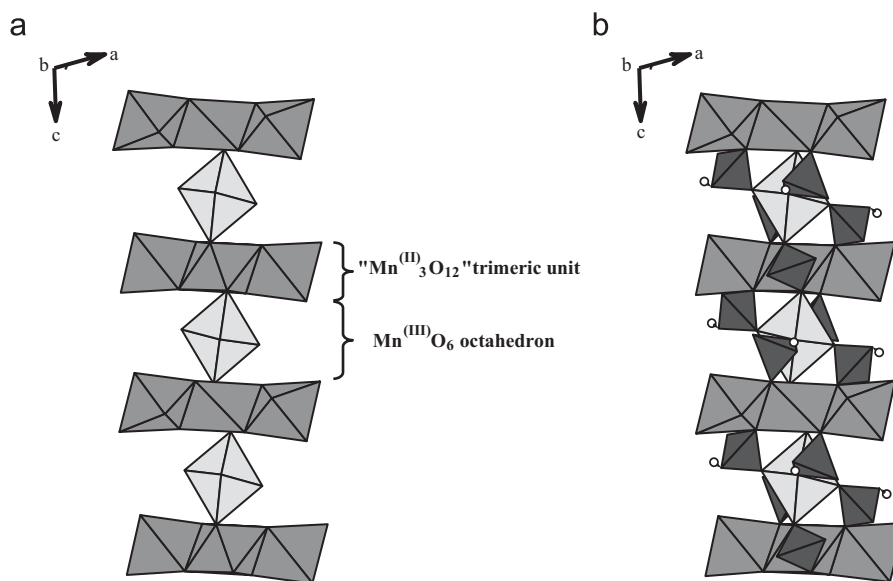
The main structural feature of  $K_3Mn_4(PO_4)(H_{0.5}PO_4)_2(HPO_4)_2$  resides in the presence of infinite  $[Mn_4O_{16}]_{\infty}$  chains running along

**Table 3**  
Distances and angles in the structure of  $K_3Mn_4(PO_4)(H_{0.5}PO_4)_2(HPO_4)_2$ .

Mn1	O1	O1	O3	O3	O7	O7
O1	<b>1.928(2)</b>	3.855(3)	2.934(4)	3.083(3)	2.727(3)	2.658(3)
O1	180	<b>1.928(2)</b>	3.083(3)	2.934(4)	2.658(3)	2.727(3)
O3	87.12(9)	92.88(9)	<b>2.311(2)</b>	4.622(3)	2.877(3)	3.078(4)
O3	92.88(9)	87.12(9)	180	<b>2.311(2)</b>	3.078(4)	2.877(3)
O7	91.46(11)	88.54(11)	86.06(10)	93.94(10)	<b>1.880(3)</b>	3.760(4)
O7	88.54(11)	91.46(11)	93.94(10)	86.06(10)	180	<b>1.880(3)</b>
Mn2	O2	O2	O3	O3	O6	O6
O2	<b>2.127(2)</b>	3.461(3)	3.196(4)	4.236(3)	3.395(4)	2.682(4)
O2	108.86(10)	<b>2.127(2)</b>	4.236(3)	3.196(4)	2.682(4)	3.395(4)
O3	94.47(9)	153.33(9)	<b>2.226(2)</b>	2.449(3)	3.144(4)	3.391(4)
O3	153.33(9)	94.47(9)	66.75(8)	<b>2.226(2)</b>	3.391(4)	3.144(4)
O6	100.71(9)	74.90(9)	88.51(9)	97.65(9)	<b>2.279(3)</b>	4.550(4)
O6	74.90(9)	100.71(9)	97.65(9)	88.51(9)	172.64(10)	<b>2.279(3)</b>
Mn3	O2	O4	O5	O6	O10	
O2	<b>2.188(3)</b>	3.147(4)	3.004(4)	2.682(4)	4.433(4)	
O4	96.36(10)	<b>2.033(2)</b>	3.997(3)	3.480(3)	3.211(4)	
O5	88.60(10)	149.17(9)	<b>2.113(3)</b>	3.321(4)	3.031(4)	
O6	75.23(9)	110.26(10)	100.45(9)	<b>2.207(2)</b>	3.180(4)	
O10	163.42(8)	95.71(10)	86.85(10)	89.93(9)	<b>2.292(3)</b>	
P1	O1	O5	O6	O8		
O1	<b>1.545(2)</b>	2.461(3)	2.612(3)	2.471(4)		
O5	106.94(14)	<b>1.518(2)</b>	2.517(4)	2.528(4)		
O6	116.57(13)	111.62(14)	<b>1.525(3)</b>	2.508(4)		
O8	104.40(13)	109.28(14)	107.65(15)	<b>1.581(3)</b>		
P2	O3	O3	O10	O10		
O3	<b>1.552(2)</b>	2.449(3)	2.567(3)	2.545(4)		
O3	104.18(14)	<b>1.552(2)</b>	2.545(4)	2.567(3)		
O10	111.79(13)	110.33(12)	<b>1.549(3)</b>	2.513(4)		
O10	110.33(12)	111.79(13)	108.43(16)	<b>1.549(3)</b>		
P3	O2	O4	O7	O9		
O2	<b>1.554(3)</b>	2.536(3)	2.514(4)	2.481(4)		
O4	110.96(14)	<b>1.524(2)</b>	2.536(3)	2.514(3)		
O7	108.75(15)	111.78(13)	<b>1.539(3)</b>	2.500(4)		
O9	106.50(14)	110.17(14)	108.50(15)	<b>1.542(3)</b>		
K1–O1 = 2.820(3)	K2–O2 = 3.055(3)					
K1–O3 = 2.877(3)	K2–O2 = 3.055(3)					
K1–O4 = 2.764(3)	K2–O5 = 2.658(3)					
K1–O5 = 2.688(3)	K2–O5 = 2.658(3)					
K1–O8 = 2.734(2)	K2–O8 = 3.043(3)					
K1–O8 = 3.073(3)	K2–O8 = 3.043(3)					
K1–O9 = 2.701(3)	K2–O9 = 2.864(3)					
K1–O10 = 3.076(2)	K2–O9 = 2.864(3)					
	K2–O10 = 3.261(3)					
	K2–O10 = 3.261(3)					
	Oa–H	Ob–H	Oa–H–Ob			
O8–H1–O10	0.969(2)	1.614(2)	155.46(18)			
O9–H2–O9	1.033(2)	1.438(2)	163.17(18)			



**Fig. 1.** Projection of the 3D-framework of  $K_3Mn^{II}_3Mn^{III}(PO_4)(H_{0.5}PO_4)_2(HPO_4)_2$  exhibiting intersecting tunnels along [110] (a) and [001] (b) where potassium cations, represented with dark balls, sit in.  $Mn^{(III)}$  stands in light-grey octahedron whereas  $Mn^{(II)}$  cations stand in medium-grey polyhedra.



**Fig. 2.** (a) One  $[Mn_4O_{16}]_{\infty}$  chain running along [001], built up of " $Mn^{(III)}_3O_{12}$ " trimeric units interconnected with  $Mn^{(III)}O_6$  octahedra. (b) Junction of the  $PO_4$  and  $PO_3(OH)$  tetrahedra on the  $[Mn_4O_{16}]_{\infty}$  chain.

$\vec{c}$ , and in their particular geometric configuration and the charge ordering of manganese in those chains (Fig. 2a). Each chain is indeed built up of trimeric units " $Mn^{III}_3O_{12}$ ", exclusively occupied by divalent manganese, alternating along  $\vec{c}$  with  $Mn^{III}O_6$  octahedra, only occupied by trivalent manganese. In the trimeric " $Mn^{III}_3O_{12}$ " units, the  $Mn^{II}O_6$  octahedron is central and shares two opposite edges with the two  $Mn^{II}O_5$  trigonal bipyramids. It is this central  $Mn^{II}O_6$  octahedron which shares its two remaining opposite apices with the  $Mn^{III}O_6$  octahedra, so that the  $[Mn_4O_{16}]_{\infty}$  chains can also be described as built up of infinite chains of corner-sharing octahedra running along  $\vec{c}$  according to the 1:1 sequence " $Mn^{3+}-Mn^{2+}-Mn^{3+} \dots$ ", whose  $Mn^{II}O_6$  octahedra share edges with  $Mn^{II}O_5$  bipyramids. Thus, the  $[Mn_4P_5O_{17}(OH)_3]_{\infty}$  3D-framework can be described as the assemblage of the  $[Mn_4O_{16}]_{\infty}$  chains through  $PO_4$  and  $PO_3OH$  tetrahedra.

The mode of connection between the octahedra and tetrahedra is also very original. Each  $Mn^{(III)}$  octahedron shares four of its apices with four  $PO_3OH$  tetrahedra, forming " $Mn^{III}P_4O_{14}(OH)_4$ " units (Fig. 3a), whereas each  $Mn^{(II)}$  octahedron shares one edge with one  $PO_4$  tetrahedron, so that tetrameric units " $Mn_3PO_{14}$ " of

edge-sharing polyhedra are formed (Fig. 3b). As a consequence, the whole  $[Mn_4P_5O_{17}(OH)_3]_{\infty}$  framework can also be described from the assemblage of these two sorts of units through the corners of their polyhedra, each  $MnO_5$  bipyramid belonging to a  $Mn_3PO_{14}$  unit sharing three apices with one  $PO_4$  tetrahedron and two  $PO_3(OH)$  tetrahedra of other units (Figs. 2b and 1).

The P–O distances observed in the  $PO_4$  and  $HPO_4$  tetrahedra are rather regular, ranging from 1.518 to 1.581(3) Å (Table 3). The  $PO_3OH$  tetrahedra (P1 and P3) are a little bit less regular than the  $PO_4$  tetrahedron (P2), due to the presence of the hydroxyl group. One can also notice that the P2 tetrahedron shares all of its apices, whereas P1 and P3 tetrahedra present one free apex corresponding to the hydroxyl groups, H2 atoms sitting in the tunnels (Fig. 1).

The  $Mn^{III}O_6$  octahedron (Mn1) exhibits a geometry characteristic of the Jahn–Teller effect, generally observed for trivalent manganese, with two groups of  $Mn^{III}-O$  distances: four equatorial ones comprised between 1.880(3) and 1.928(2) Å and two much longer apical ones of 2.311(2) Å (Table 3). The four shortest bonds correspond to the oxygen atoms (O1 and O7) shared with the four  $PO_3(OH)$  groups, whereas the two longer  $Mn1-O$  distances are

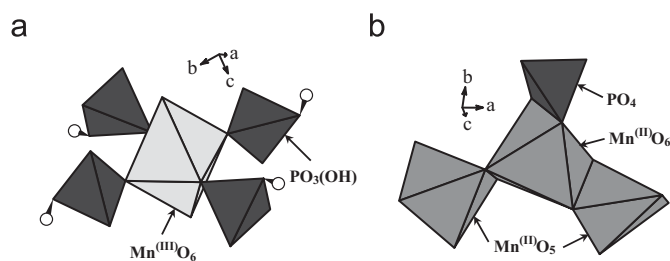


Fig. 3. “Mn<sup>III</sup>P<sub>4</sub>O<sub>14</sub>(OH)<sub>4</sub>” unit (a) and Mn<sub>3</sub><sup>III</sup>PO<sub>14</sub> unit (b).

observed for O3 which is shared with the Mn<sup>II</sup>O<sub>6</sub> octahedron (Mn2). The Mn–O distances of the Mn<sup>II</sup>O<sub>6</sub> octahedra are more homogeneous, since they are ranging from 2.127(2) to 2.279(3) Å (Table 3). However, the examination of the O–Mn2–O angles and O–O distances reveals that the Mn<sup>II</sup>O<sub>6</sub> octahedron is slightly distorted. Finally, the Mn<sup>II</sup>O<sub>5</sub> bipyramid (Mn3) is strongly distorted, as shown from the examination of the O–Mn3–O angles. The Mn3–O distances are comprised between 2.033(2) and 2.292(3) Å (Table 3). One can notice the presence in the structure of an oxygen atom located at 2.77 Å from Mn3, i.e. too far away from Mn3 to be considered in its coordination polyhedron. This phenomenon has already been observed in the frameworks of many manganese phosphates, such as in Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> [35], KMn<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub> [36], or SrMn<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub> [37] for instance.

The potassium cations are sitting in the tunnels with various coordinations. K1 is surrounded by eight oxygen atoms, with K1–O distances ranging from 2.688(3) to 3.076(2) Å, whereas K2 is 10-coordinated with K2–O distances comprised between 2.658(3) and 3.261(3) Å (Table 3).

Considering the various potassium manganese phosphates and hydroxyphosphates that are actually known, K<sub>3</sub>Mn<sub>4</sub>(PO<sub>4</sub>)(H<sub>0.5</sub>PO<sub>4</sub>)<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub> is from the viewpoint of manganese coordination rather exceptional since both MnO<sub>5</sub> and MnO<sub>6</sub> polyhedra are present in the same framework, whereas for most of the potassium phosphates, manganese exhibits an octahedral coordination as shown for K<sub>2</sub>Mn<sub>4</sub>(P<sub>10</sub>O<sub>30</sub>)(H<sub>2</sub>O)<sub>18</sub> [38], KMn(HP<sub>3</sub>O<sub>10</sub>) [18,19], KMn(HP<sub>2</sub>O<sub>7</sub>)(H<sub>2</sub>O)<sub>2</sub> [39] and K<sub>2</sub>Mn(H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> [40] whose frameworks contain only isolated MnO<sub>6</sub> octahedra, for KMnPO<sub>4</sub>·H<sub>2</sub>O [2] whose structure is built up of layers of corner-sharing MnO<sub>6</sub> octahedra and for KMn<sub>2</sub>O(PO<sub>4</sub>)(HPO<sub>4</sub>) [23] which forms chains of edge-sharing octahedra. To our knowledge, only one potassium phosphate, KMn<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub> [36], contains MnO<sub>5</sub> bipyramids and MnO<sub>6</sub> octahedra in the same framework, but they are isolated. Moreover, if we consider all the manganese phosphates reported in literature, there is only one other compound involving both MnO<sub>5</sub> bipyramids and MnO<sub>6</sub> octahedra: Li<sub>2</sub>Mn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> [41].

The second interesting structural feature of K<sub>3</sub>Mn<sub>4</sub>(PO<sub>4</sub>)(H<sub>0.5</sub>PO<sub>4</sub>)<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub> concerns the presence of trimeric units “Mn<sub>3</sub>O<sub>12</sub>”, never observed in the “pure” manganese phosphates. The only example of such a trimer “Mn<sub>3</sub>O<sub>12</sub>” has been observed in the phosphate Fe<sub>0.42</sub>Mn<sub>0.12</sub>Al<sub>0.13</sub>Ca<sub>2</sub>Mn<sub>4</sub>Be<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub> [42], but in that case the MnO<sub>5</sub> polyhedra are pseudo-pyramids. Note that the latter compound exhibits, as the present phosphate, the mixed valence Mn(II)/Mn(III) but without any charge ordering. It is worth pointing out that trimeric units of manganese polyhedra are rare in phosphates. Nevertheless two compounds exhibit some similarity with the present phosphate, the compound Mn<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>Ga<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub> [43] which exhibits trimeric Mn<sub>3</sub>O<sub>14</sub> units built up of edge-sharing octahedra, and the phosphate Fe<sub>4.32</sub>Mn<sub>0.62</sub>Zn<sub>0.06</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>5</sub> [44], which forms Mn<sub>2</sub>FeO<sub>12</sub> trimeric units built up of MnO<sub>6</sub> and FeO<sub>6</sub> face-sharing octahedra.

But the most important point deals with the mixed valence character, Mn(II)–Mn(III), of this phosphate and the unique charge ordering of manganese of K<sub>3</sub>Mn<sub>3</sub><sup>II</sup>Mn<sup>III</sup>(PO<sub>4</sub>)(H<sub>0.5</sub>PO<sub>4</sub>)<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub>, associated to the unidimensional arrangement of the MnO<sub>6</sub> and MnO<sub>5</sub> polyhedra in the structure. Only one compound, the mineral Bermanite Mn<sup>II</sup>(H<sub>2</sub>O)<sub>4</sub>[Mn<sup>III</sup>(OH)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>] [29] has been found to exhibit charge ordering in such Mn–P–O(–H) and A–Mn–P–O(–H) systems to date. The latter phase differs from K<sub>3</sub>Mn<sub>4</sub>(PO<sub>4</sub>)(H<sub>0.5</sub>PO<sub>4</sub>)<sub>2</sub>(HPO<sub>4</sub>)<sub>2</sub> by the fact that all manganese atoms are in octahedral coordinations, forming infinite chains of edge-sharing MnO<sub>6</sub> octahedra with a 1:1 Mn<sup>3+</sup>/Mn<sup>2+</sup> ordering.

#### 4. Conclusions

A mixed valent Mn(III)–Mn(II) phosphate involving charge ordering of manganese has been synthesized for the first time. The unique ordering of the Mn<sup>2+</sup> and Mn<sup>3+</sup> cations, in the infinite [Mn<sub>4</sub>O<sub>16</sub>]<sub>∞</sub> chains of this structure, and the Mn(II)–Mn(II) distances in the trimeric units (3.49 Å) as well as the Mn(II)–Mn(III) distances along the chains (3.75 Å) suggests the possibility of strong magnetic interactions. Unfortunately, it was not possible to prepare a monophasic powder sample for magnetic measurements. Attempts to grow larger crystals for magnetic studies of this attractive manganese phosphate are in progress.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.06.017.

#### References

- [1] S.G. Carling, P. Day, D. Visser, *Inorg. Chem.* 34 (1995) 3917–3927.
- [2] D. Visser, S.G. Carling, P. Day, J. Deportes, *J. Appl. Phys.* 69 (1991) 6016–6018.
- [3] F. Leroux, A. Marc, C. Payen, D. Guyomard, A. Verbaere, Y. Piffard, *J. Solid State Chem.* 115 (1995) 240–246.
- [4] G.E. Fanucci, J. Krzystek, M.W. Meisel, L.C. Brunel, D.R. Thalam, *J. Am. Chem. Soc.* 120 (22) (1998) 5469–5479.
- [5] M.A.G. Aranda, S. Bruque, J.P. Attfield, F. Palacio, R.B. Von Dreele, *J. Solid State Chem.* 132 (1997) 202–212.
- [6] J. Escobal, J.L. Mesa, J.L. Pizarro, L. Lezama, R. Olazenaga, T. Rojo, *J. Mater. Chem.* 9 (10) (1999) 2691–2696.
- [7] R.D. Adams, R. Layland, C. Payen, *Polyhedron* 14 (23–24) (1995) 3473–3480.
- [8] Y.N. Song, P.Y. Zavalij, N.A. Chernova, M.S. Whittingham, *Chem. Mater.* 15 (2003) 4968–4973.
- [9] K.O. Kongshaug, H. Fjellvasg, K.P. Lillerud, *J. Solid State Chem.* 156 (2001) 32–36.
- [10] D. Feng, C. Wang, W. Cheng, G. Li, S. Tian, F. Liao, M. Xiong, J. Lin, *Solid State Sci.* 11 (2009) 845–851.
- [11] M. Bagieu-Beucher, *Acta Crystallogr. B* 34 (1978) 1443–1446.
- [12] I. Cisarova, C. Novak, V. Petricek, B. Kratochvil, J. Loub, *Acta Crystallogr. B* 38 (1982) 1687–1689.
- [13] A. Durif, M.T. Averbuch-Pouchot, *Acta Crystallogr. B* 38 (1982) 2883–2885.
- [14] L.S. Ivashkevich, K.A. Selevich, A.I. Lesnikovich, A.F. Selevich, A.S. Lyakhov, *Z. Kristallogr.* 221 (2) (2006) 115–121.
- [15] P. Lightfoot, A.K. Cheetham, A.W. Sleight, *Inorg. Chem.* 26 (1987) 3544–3547.
- [16] E.V. Murashova, N.N. Chudinova, *Kristallografiya* 40 (1995) 476–484.
- [17] A.J. Wright, J.P. Attfield, *J. Solid State Chem.* 141 (1998) 160–163.
- [18] A.J. Wright, C. Ruiz-Valero, J.P. Attfield, *J. Solid State Chem.* 145 (1999) 479–483.
- [19] J. Mecherqui, W. Belam, A. Daoud, *Ann. Chim. (Paris)* 31 (1) (2006) 91–95.
- [20] A.J. Wright, J.P. Attfield, *Inorg. Chem.* 37 (1998) 3858–3861.
- [21] M.A.G. Aranda, J.P. Attfield, S. Bruque, *Angew. Chem. (German Edition)* 104 (8) (1992) 1056–1058.
- [22] E.V. Murashova, N.N. Chudinova, *Kristallografiya* 45 (4) (2000) 625–628.
- [23] P. Lightfoot, A.K. Cheetham, A.W. Sleight, *J. Solid State Chem.* 73 (1988) 325–329.
- [24] P. Lightfoot, A.K. Cheetham, *J. Solid State Chem.* 78 (1989) 17–22.
- [25] A.R. Kampf, *Am. Mineral.* 85 (2000) 1302–1306.
- [26] E.V. Murashova, N.N. Chudinova, *Neorg. Mater.* 36 (12) (2000) 1512–1515.
- [27] L. Dogan, M. Emiridag-Eanes, *Z. Kristallogr. New Cryst. Struct.* 222 (2) (2007) 89–90.

- [28] S. Ferdov, A.M.L. Lopes, Z. Lin, R.A. Sa Ferreira, *Chem. Mater.* 19 (2007) 6025–6029.
- [29] A.R. Kampf, P.B. Moore, *Am. Mineral.* 61 (1976) 1241–1248.
- [30] E.V. Murashova, N.N. Chudinova, *Kristallografiya* 41 (1996) 248–253.
- [31] D. Feng, C. Wang, W. Cheng, G. Li, S. Tian, F. Liao, M. Xiong, J. Lin, *Solid State Sci.* 11 (2009) 845–851.
- [32] A.J.M. Duisenberg, L.M.J. Kroon-Batenburg, A.M.M. Schreurs, *J. Appl. Crystallogr.* 36 (2003) 220–229.
- [33] V. Petricek, M. Dusek, L. Palatinus, *The Crystallographic Computing System*, Institute of Physics, Praha, Czech Republic, 2006.
- [34] N.E. Brese, M. O'Keeffe, *Acta Crystallogr. B* 47 (1991) 192–197.
- [35] P.B. Moore, *Am. Mineral.* 57 (1972) 24–35.
- [36] O.V. Yakubovich, O.A. Evdokimova, O.K. Mel'nikov, M.A. Simonov, *Kristallografiya* 31 (1986) 258–263.
- [37] B. El Bali, A. Boukhari, R. Glaum, M. Gerk, K. Maass, *Z. Anorg. Allg. Chem.* 626 (2000) 2557–2562.
- [38] U. Schuelke, M.T. Averbuch-Pouchot, *Z. Anorg. Allg. Chem.* 620 (1994) 545–550.
- [39] H. Assaoudi, A. Ennaciri, M. Harcharras, B. El Bali, F. Reinauer, R. Glaum, A. Rulmont, M.R. Spirlet, *Acta Crystallogr. C* 58 (2002) i79–i81.
- [40] A.A. Tahiri, R. Ouarsal, M. Lachkar, P.Yu. Zavalii, B. El Bali, *Acta Crystallogr. E* 59 (2003) i68–i69.
- [41] L. Adam, A. Guesdon, B. Raveau, *J. Solid State Chem.* 181 (2008) 3110–3115.
- [42] L. Fanfani, P.F. Zanazzi, A.R. Zanzari, *Tscher. Miner. Petrog.* 24 (1977) 169–178.
- [43] K.F. Hsu, S.L. Wang, *Inorg. Chem.* 39 (2000) 1773–1778.
- [44] G.J. Redhammer, G. Roth, G. Tippelt, M. Bernroeder, W. Lottermoser, G. Amthauer, R. Hochleitner, *Acta Crystallogr. C* 62 (2006) i24–i28.