

# A new aquamanganese(II) oxalate phosphate, $\text{Mn}(\text{C}_2\text{O}_4)\text{Mn}_3(\text{PO}_4)_2(\text{H}_2\text{O})_2$

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Key indicators: single-crystal X-ray study;  $T = 296\text{ K}$ ; mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$ ;  $R$  factor = 0.026;  $wR$  factor = 0.065; data-to-parameter ratio = 15.6.

The title salt, diaquatetramanganese(II) oxalate bis[orthophosphate(V)],  $\text{Mn}_4(\text{C}_2\text{O}_4)(\text{PO}_4)_2(\text{H}_2\text{O})_2$ , was synthesized hydrothermally and displays a three-dimensional framework structure. The asymmetric unit consists of two different  $\text{Mn}^{\text{II}}$  centers, half of an oxalate anion, a phosphate group and a coordinated water molecule. A crystallographic inversion center is located at the mid-point of the oxalate C—C bond. The distorted octahedral  $\text{MnO}_6$  and the tetragonal pyramidal  $\text{MnO}_5$  centers are linked through bridging oxalate and phosphate groups. The water molecule also has a weaker bonding contact to the five-coordinate Mn atom, which consequently exhibits a distorted octahedral geometry and also bridges the independent Mn atoms. The water molecule is a donor for intra- and intermolecular O—H...O hydrogen bonds.

## Related literature

For the structure of  $\text{HgC}_2\text{O}_4$  from synchrotron, X-ray and neutron powder diffraction data, see: Christensen *et al.* (1994). For a polymeric  $[\text{Ni}^{\text{II}}(\text{bpy})_3]_n^{2+} [\text{Mn}^{\text{II}}(\text{C}_2\text{O}_4)_3]_n^{2-}$  oxalate-bridged network structure, see: Decurtins *et al.* (1994). For the structures of indium selenite–oxalate and indium oxalate, see: Cao *et al.* (2009). For lanthanide–oxalate coordination polymers, see: Zhang *et al.* (2009).

## Experimental

### Crystal data

$\text{Mn}_4(\text{C}_2\text{O}_4)(\text{PO}_4)_2(\text{H}_2\text{O})_2$	$V = 601.73(2)\text{ \AA}^3$
$M_r = 266.88$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.2759(2)\text{ \AA}$	$\mu = 4.45\text{ mm}^{-1}$
$b = 6.5220(1)\text{ \AA}$	$T = 296\text{ K}$
$c = 10.0701(1)\text{ \AA}$	$0.21 \times 0.19 \times 0.17\text{ mm}$
$\beta = 116.926(1)^\circ$	

### Data collection

Bruker APEXII CCD area-detector diffractometer	5971 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2007)	1653 independent reflections
$T_{\text{min}} = 0.455$ , $T_{\text{max}} = 0.519$	1467 reflections with $I > 2\sigma(I)$
(expected range = 0.412–0.470)	$R_{\text{int}} = 0.031$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.065$	$\Delta\rho_{\text{max}} = 0.47\text{ e \AA}^{-3}$
$S = 1.05$	$\Delta\rho_{\text{min}} = -0.55\text{ e \AA}^{-3}$
1653 reflections	
106 parameters	
3 restraints	

Table 1

Selected bond lengths ( $\text{\AA}$ ).

Mn1—O2 <sup>i</sup>	2.1199 (15)	Mn2—O2 <sup>iv</sup>	2.1145 (15)
Mn1—O3 <sup>ii</sup>	2.1407 (15)	Mn2—O4 <sup>ii</sup>	2.1218 (15)
Mn1—O1	2.1584 (15)	Mn2—O1	2.1220 (16)
Mn1—O3 <sup>iii</sup>	2.2219 (15)	Mn2—O6 <sup>v</sup>	2.1809 (17)
Mn1—O5	2.2525 (15)	Mn2—O5	2.2190 (16)
Mn1—O7W	2.2637 (17)	Mn2—O7W <sup>vi</sup>	2.5641 (14)

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

Table 2

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O7W}-\text{H7A}\cdots\text{O6}$	0.85 (2)	2.00 (2)	2.828 (3)	167 (3)
$\text{O7W}-\text{H7B}\cdots\text{O4}^{\text{iii}}$	0.86 (2)	1.95 (2)	2.787 (2)	167 (3)

Symmetry code: (vii)  $-x + 1, -y, -z$ .

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2161).

## References

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**supplementary materials**

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## A new aquamanganese(II) oxalate phosphate, $\text{Mn}(\text{C}_2\text{O}_4)\text{Mn}_3(\text{PO}_4)_2(\text{H}_2\text{O})_2$

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### Comment

Over the past decades, the synthesis of new two and three dimensional inorganic materials has received great attention, due to their functional applications. Among the hybrid compounds are metal oxalates which exhibit vast diversity and unusual structural features. The oxalate anion displays various coordination modes when it is bound to metal cations. For example, the structures of  $\text{HgC}_2\text{O}_4$  (Christensen *et al.*, 1994),  $[\text{In}_2(\text{SeO}_3)_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$  (Cao *et al.*, 2009) and  $\text{Nd}(\text{C}_2\text{O}_4)(\text{CH}_3\text{COO})(\text{H}_2\text{O})$  (Zhang *et al.*, 2009) have been investigated in the past years. In this work, we designed and synthesized the title compound,  $\text{MnC}_2\text{O}_4\text{Mn}_3(\text{PO}_4)_2 \cdot 2(\text{H}_2\text{O})$ , which features a three-dimensional framework.

In the structure of the title compound, there are two  $\text{Mn}^{\text{II}}$  atoms, one phosphate, a half oxalate and one water per asymmetric unit (Fig. 1). Mn1 has a  $\text{MnO}_6$  octahedral coordination environment, but Mn2 is coordinated with five oxygen atoms (Fig. 2 and Fig. 3). The Mn—O oxalate distances (Table 1) are slightly longer than the Mn—O distances of 2.154 (2) Å and 2.166 (2) Å, observed in the polymeric anionic network structure  $[\text{Ni}^{\text{II}}(\text{bpy})_3]^{2+}_n [\text{Mn}^{\text{II}}(\text{C}_2\text{O}_4)_3]^{2-}_n$  (Decurtins *et al.*, 1994). The distorted octahedral  $\text{MnO}_6$  and tetragonal pyramidal  $\text{MnO}_5$  centers are linked through bridging oxalate and phosphate groups (Fig. 3). The water molecule has also a weaker bonding contact to the five coordinate atom Mn2, which consequently exhibits a distorted octahedral geometry and bridges the independent atoms Mn1 and Mn2 as well. The water molecule is a donor for intra- and intermolecular O—H $\cdots$ O hydrogen bonds (Table 2).

### Experimental

Colorless block crystals were synthesized hydrothermally from a mixture of,  $\text{H}_3\text{BO}_3$ ,  $\text{H}_2\text{C}_2\text{O}_4$ , ethylenediamine,  $\text{H}_3\text{PO}_4$  and water. In a typical synthesis, 0.98 g  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  was dissolved in a mixture of 5 mL water, with 0.92 g  $\text{H}_3\text{BO}_3$ , 2 ml (85%)  $\text{H}_3\text{PO}_4$  and 0.05 ml ethylenediamine at constant stirring. Finally, the mixture was kept in a 30 ml Teflon – lined steel autoclave at 443 K for 5 days. The autoclave was slowly cooled to room temperature. Colorless block crystals of the title compound were obtained.

### Refinement

The H atoms of the coordinated water molecule were refined with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$  and distance restraints  $d(\text{O}—\text{H})$  of 0.85 (1) Å and  $d(\text{H}\cdots\text{H})$  of 1.33 (1) Å, respectively. The highest peak in the difference map is 0.47  $e/\text{Å}^3$ , and 0.75 Å from O4, and the minimum peak is -0.55  $e/\text{Å}^3$ , and 0.60 Å from Mn1.

## Figures

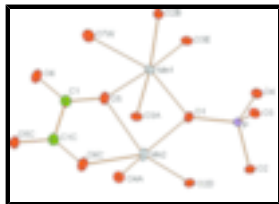


Fig. 1. A section of the coordination geometry in the title polymer structure. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (A) =  $-x + 1, y - 1/2, -z + 1/2$ ; (B) =  $-x + 1, y + 1/2, -z + 1/2$ ; (C) =  $-x, -y, -z$ ; (D) =  $-x + 1, -y, -z + 1$ ; (E) =  $x, -y + 1/2, z - 1/2$ ;

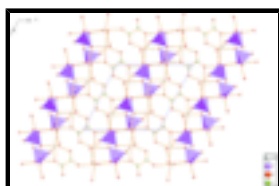


Fig. 2. Packing diagram for  $\text{Mn}(\text{C}_2\text{O}_4)\text{Mn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ , viewed along the  $b$  axis.

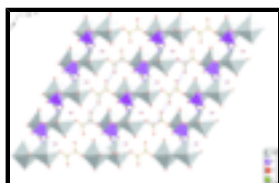
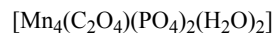


Fig. 3. Packing diagram for  $\text{Mn}(\text{C}_2\text{O}_4)\text{Mn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ , viewed along the  $b$  axis,  $\text{Mn}_2$  complex cations are omitted for clarity.

## poly[di aqua- $\mu$ -oxalato-di- $\mu$ -phosphato-tetramanganese(II)]

### Crystal data



$M_r = 266.88$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2ybc$

$a = 10.2759\ (2)\ \text{\AA}$

$b = 6.5220\ (1)\ \text{\AA}$

$c = 10.0701\ (1)\ \text{\AA}$

$\beta = 116.926\ (1)^\circ$

$V = 601.728\ (16)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 516$

$D_x = 2.946\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2504 reflections

$\theta = 2.2\text{--}29.9^\circ$

$\mu = 4.45\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Block, colourless

$0.21 \times 0.19 \times 0.17\ \text{mm}$

### Data collection

Bruker APEXII CCD area-detector diffractometer

1653 independent reflections

Radiation source: fine-focus sealed tube

1467 reflections with  $I > 2\sigma(I)$

Monochromator: graphite

$R_{\text{int}} = 0.031$

$T = 296\ \text{K}$

$\theta_{\text{max}} = 29.9^\circ$

$\phi$  and  $\omega$  scans

$\theta_{\text{min}} = 2.2^\circ$

Absorption correction: multi-scan (SADABS; Bruker, 2007)

$h = -14 \rightarrow 11$

$T_{\text{min}} = 0.455, T_{\text{max}} = 0.519$

$k = -9 \rightarrow 8$

5971 measured reflections

$l = -13 \rightarrow 13$

*Refinement*

Refinement on  $F^2$

Secondary atom site location: difference Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.026$

H atoms treated by a mixture of independent and constrained refinement

$wR(F^2) = 0.065$

$$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 0.1904P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$S = 1.05$

$(\Delta/\sigma)_{\max} < 0.001$

1653 reflections

$\Delta\rho_{\max} = 0.47 \text{ e } \text{\AA}^{-3}$

106 parameters

$\Delta\rho_{\min} = -0.55 \text{ e } \text{\AA}^{-3}$

3 restraints

Extinction correction: none

Primary atom site location: structure-invariant direct methods

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.38352 (4)	0.14623 (5)	0.02672 (4)	0.01004 (10)
Mn2	0.26622 (4)	-0.02679 (6)	0.26753 (4)	0.01198 (10)
P1	0.60110 (6)	0.15130 (8)	0.39476 (6)	0.00740 (13)
O1	0.45405 (17)	0.0984 (2)	0.26145 (16)	0.0123 (3)
O2	0.65691 (17)	-0.0342 (2)	0.50294 (16)	0.0110 (3)
O3	0.57805 (17)	0.3259 (2)	0.48610 (17)	0.0112 (3)
O4	0.71121 (17)	0.2029 (2)	0.33744 (17)	0.0124 (3)
O5	0.17132 (17)	0.0906 (3)	0.03574 (17)	0.0148 (3)
O6	-0.03134 (18)	0.0699 (3)	-0.18037 (17)	0.0174 (4)
O7W	0.22135 (19)	0.1426 (2)	-0.21781 (18)	0.0157 (4)
H7A	0.1384 (17)	0.118 (4)	-0.222 (3)	0.019*
H7B	0.231 (3)	0.043 (3)	-0.268 (3)	0.019*
C1	0.0400 (2)	0.0465 (3)	-0.0428 (2)	0.0122 (4)

## supplementary materials

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### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Mn1	0.01109 (18)	0.00852 (19)	0.01143 (17)	0.00060 (12)	0.00591 (14)	0.00116 (11)
Mn2	0.00891 (18)	0.0177 (2)	0.00885 (17)	-0.00151 (13)	0.00360 (14)	-0.00260 (12)
P1	0.0080 (3)	0.0070 (3)	0.0073 (2)	-0.00008 (19)	0.0035 (2)	-0.00015 (18)
O1	0.0098 (8)	0.0162 (8)	0.0092 (7)	-0.0004 (6)	0.0027 (6)	0.0008 (6)
O2	0.0140 (8)	0.0081 (8)	0.0102 (7)	0.0009 (6)	0.0050 (6)	0.0013 (5)
O3	0.0140 (8)	0.0099 (8)	0.0126 (7)	-0.0005 (6)	0.0084 (7)	-0.0016 (6)
O4	0.0129 (8)	0.0130 (8)	0.0133 (7)	-0.0006 (6)	0.0078 (6)	0.0011 (6)
O5	0.0088 (8)	0.0214 (9)	0.0121 (7)	-0.0022 (7)	0.0031 (6)	0.0005 (6)
O6	0.0105 (8)	0.0299 (10)	0.0111 (7)	-0.0017 (7)	0.0041 (7)	0.0022 (7)
O7W	0.0160 (9)	0.0179 (9)	0.0156 (8)	-0.0021 (7)	0.0091 (7)	-0.0014 (6)
C1	0.0106 (10)	0.0137 (11)	0.0134 (10)	0.0008 (8)	0.0064 (9)	-0.0014 (8)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Mn1—O2 <sup>i</sup>	2.1199 (15)	P1—O1	1.5386 (16)
Mn1—O3 <sup>ii</sup>	2.1407 (15)	P1—O3	1.5481 (15)
Mn1—O1	2.1584 (15)	P1—O2	1.5534 (15)
Mn1—O3 <sup>iii</sup>	2.2219 (15)	O2—Mn2 <sup>iv</sup>	2.1145 (15)
Mn1—O5	2.2525 (15)	O2—Mn1 <sup>ii</sup>	2.1199 (15)
Mn1—O7W	2.2637 (17)	O3—Mn1 <sup>i</sup>	2.1407 (15)
Mn2—O2 <sup>iv</sup>	2.1145 (15)	O3—Mn1 <sup>vi</sup>	2.2219 (15)
Mn2—O4 <sup>ii</sup>	2.1218 (15)	O4—Mn2 <sup>i</sup>	2.1218 (15)
Mn2—O1	2.1220 (16)	O5—C1	1.250 (3)
Mn2—O6 <sup>v</sup>	2.1809 (17)	O6—C1	1.249 (3)
Mn2—O5	2.2190 (16)	O7W—H7A	0.85 (2)
Mn2—O7W <sup>vi</sup>	2.5641 (14)	O7W—H7B	0.86 (2)
P1—O4	1.5225 (15)	C1—C1 <sup>v</sup>	1.558 (4)
O2 <sup>i</sup> —Mn1—O3 <sup>ii</sup>	168.73 (6)	O4—P1—O1	108.88 (8)
O2 <sup>i</sup> —Mn1—O1	104.10 (6)	O4—P1—O3	113.75 (9)
O3 <sup>ii</sup> —Mn1—O1	86.86 (6)	O1—P1—O3	109.23 (9)
O2 <sup>i</sup> —Mn1—O3 <sup>iii</sup>	91.66 (6)	O4—P1—O2	109.64 (9)
O3 <sup>ii</sup> —Mn1—O3 <sup>iii</sup>	82.11 (6)	O1—P1—O2	110.00 (9)
O1—Mn1—O3 <sup>iii</sup>	109.24 (6)	O3—P1—O2	105.28 (8)
O2 <sup>i</sup> —Mn1—O5	91.86 (6)	P1—O1—Mn2	127.44 (9)
O3 <sup>ii</sup> —Mn1—O5	93.07 (6)	P1—O1—Mn1	129.28 (9)
O1—Mn1—O5	77.51 (6)	Mn2—O1—Mn1	103.21 (7)
O3 <sup>iii</sup> —Mn1—O5	171.35 (6)	P1—O2—Mn2 <sup>iv</sup>	117.17 (8)
O2 <sup>i</sup> —Mn1—O7W	81.74 (6)	P1—O2—Mn1 <sup>ii</sup>	132.87 (9)
O3 <sup>ii</sup> —Mn1—O7W	89.39 (6)	Mn2 <sup>iv</sup> —O2—Mn1 <sup>ii</sup>	106.93 (6)
O1—Mn1—O7W	155.02 (6)	P1—O3—Mn1 <sup>i</sup>	126.88 (9)

O3 <sup>iii</sup> —Mn1—O7W	94.65 (6)	P1—O3—Mn1 <sup>vi</sup>	124.19 (9)
O5—Mn1—O7W	78.05 (6)	Mn1 <sup>i</sup> —O3—Mn1 <sup>vi</sup>	97.89 (6)
O4 <sup>ii</sup> —Mn2—O7W <sup>vi</sup>	154.66 (7)	P1—O4—Mn2 <sup>i</sup>	129.80 (9)
O2 <sup>iv</sup> —Mn2—O4 <sup>ii</sup>	129.04 (6)	C1—O5—Mn2	114.85 (14)
O2 <sup>iv</sup> —Mn2—O1	93.71 (6)	C1—O5—Mn1	143.03 (14)
O4 <sup>ii</sup> —Mn2—O1	89.96 (6)	Mn2—O5—Mn1	97.22 (6)
O2 <sup>iv</sup> —Mn2—O6 <sup>v</sup>	105.17 (6)	C1—O6—Mn2 <sup>v</sup>	114.67 (14)
O4 <sup>ii</sup> —Mn2—O6 <sup>v</sup>	92.47 (6)	Mn1—O7W—H7A	106.7 (18)
O1—Mn2—O6 <sup>v</sup>	153.30 (6)	Mn1—O7W—H7B	115.2 (18)
O2 <sup>iv</sup> —Mn2—O5	148.61 (6)	H7A—O7W—H7B	101.8 (13)
O4 <sup>ii</sup> —Mn2—O5	81.83 (6)	O6—C1—O5	126.6 (2)
O1—Mn2—O5	78.99 (6)	O6—C1—C1 <sup>v</sup>	118.0 (2)
O6 <sup>v</sup> —Mn2—O5	75.05 (6)	O5—C1—C1 <sup>v</sup>	115.4 (2)

Symmetry codes: (i)  $-x+1, y+1/2, -z+1/2$ ; (ii)  $-x+1, y-1/2, -z+1/2$ ; (iii)  $x, -y+1/2, z-1/2$ ; (iv)  $-x+1, -y, -z+1$ ; (v)  $-x, -y, -z$ ; (vi)  $x, -y+1/2, z+1/2$ .

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O7W—H7A $\cdots$ O6	0.85 (2)	2.00 (2)	2.828 (3)	167 (3)
O7W—H7B $\cdots$ O4 <sup>vii</sup>	0.86 (2)	1.95 (2)	2.787 (2)	167 (3)

Symmetry codes: (vii)  $-x+1, -y, -z$ .

Fig. 1

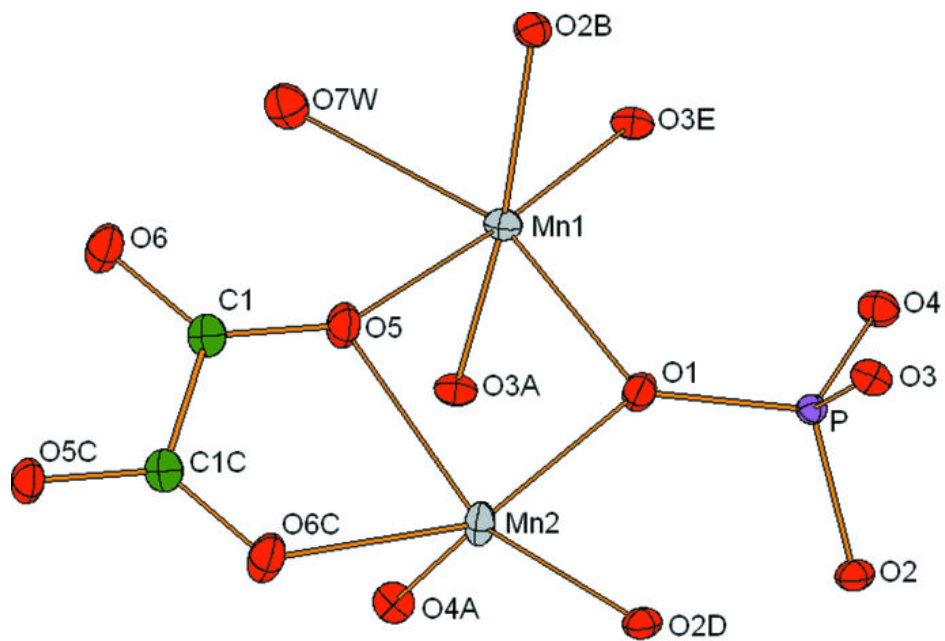




Fig. 2

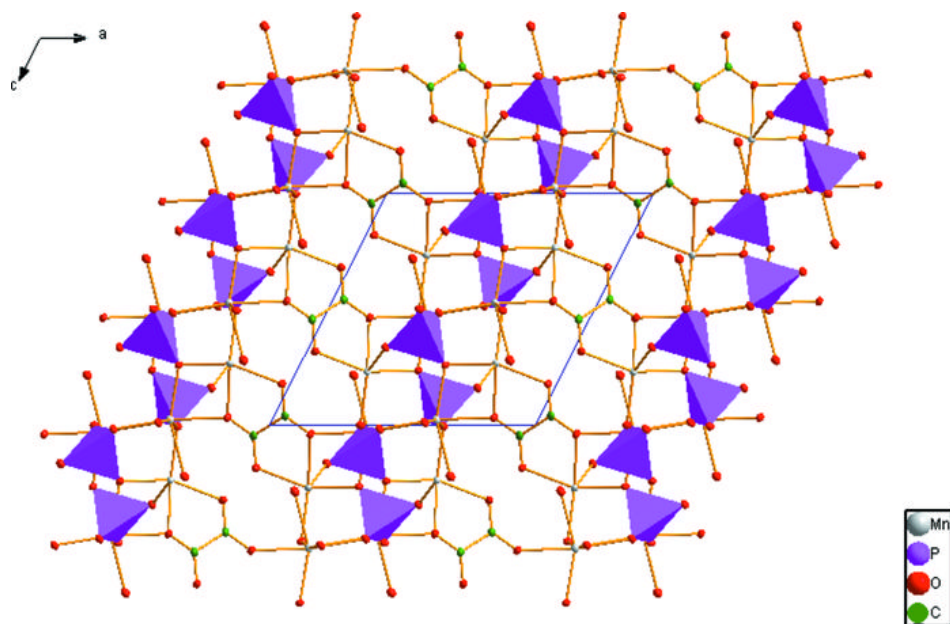


Fig. 3

