

# The monoclinic polymorph of catena-poly[[diaquamanganese(II)]- $\mu$ -oxalato- $\kappa^4 O^1, O^2:O^1', O^2'$ ]

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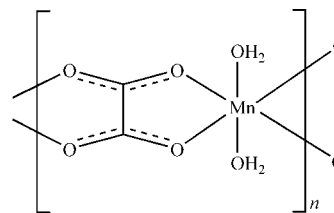
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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(C-C) = 0.002$  Å;  $R$  factor = 0.016;  $wR$  factor = 0.046; data-to-parameter ratio = 14.1.

The title polymer,  $[Mn(C_2O_4)(H_2O)_2]_n$ , was synthesized by the reaction of manganese(II) nitrate tetrahydrate with a proton-transfer compound, (pipzH<sub>2</sub>)(ox) (where oxH<sub>2</sub> is oxalic acid and pipz is piperazine), in aqueous solution. The structure features a six-coordinate Mn<sup>2+</sup> ion located on a twofold rotation axis, with a distorted octahedral geometry [Mn—O = 2.1728 (8)–2.1914 (9) Å]. The bond angles show that the two coordinated water molecules are arranged *trans*. One-dimensional linear chains are formed through bis-bidentate oxalate ligands bridging the Mn<sup>II</sup> ions. These structural units are held together by O—H...O hydrogen bonds. A neutron diffraction study of  $[Mn(\mu\text{-ox})(D_2O)_2]_n$ , using powdered samples, has been published recently in the same space group [Sledzinska, Murasik & Fischer (1987). *J. Phys. Solid State Phys.* **20**, 2247–2259]. However, it should be noted that an orthorhombic polymorph for the title polymer is also known [Huizing, van Hal, Kwestroo, Langereis & van Loosdregt (1977). *Mater. Res. Bull.* **12**, 605–611; Lethbridge, Congreve, Esslemont, Slawin & Lightfoot (2003). *J. Solid State Chem.* **172**, 212–218]. The present single-crystal X-ray study deals with the monoclinic polymorph. This phase is isostructural with the Co<sup>II</sup> analogue.

## Related literature

A preliminary report on the monoclinic polymorph of the title polymer was published by Deyrieux *et al.* (1973). For a neutron study of  $[Mn(\mu\text{-ox})(D_2O)_2]_n$ , see Sledzinska *et al.* (1987). The reported structure is isostructural with that based on Co<sup>II</sup> (Bacsá *et al.*, 2005). For further details of the related chemistry, see: Chiozzone *et al.* (2003); Aghabozorg *et al.* (2006); Verdagner (2001); Marinescu *et al.* (2002); Castillo *et al.* (2001); Fu *et al.* (2005); Wu *et al.* (2005).



## Experimental

### Crystal data

$[Mn(C_2O_4)(H_2O)_2]$   
 $M_r = 178.99$   
Monoclinic,  $C2/c$   
 $a = 11.7648$  (14) Å  
 $b = 5.6550$  (6) Å  
 $c = 9.6367$  (11) Å  
 $\beta = 125.843$  (6)°

$V = 519.71$  (10) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 2.49$  mm<sup>-1</sup>  
 $T = 296$  (2) K  
 $0.21 \times 0.21 \times 0.11$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Bruker, 1998)  
 $T_{\min} = 0.616$ ,  $T_{\max} = 0.763$

4187 measured reflections  
607 independent reflections  
604 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$   
 $wR(F^2) = 0.046$   
 $S = 1.10$   
607 reflections

43 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.46$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.40$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Mn1—O2 <sup>i</sup>	2.1728 (8)	Mn1—O3	2.1914 (9)
Mn1—O1	2.1849 (9)		
O2 <sup>ii</sup> —Mn1—O2 <sup>i</sup>	76.70 (4)	O2 <sup>i</sup> —Mn1—O3	90.19 (3)
O2 <sup>ii</sup> —Mn1—O1	179.57 (3)	O1—Mn1—O3	90.50 (3)
O2 <sup>i</sup> —Mn1—O1	103.35 (3)	O1 <sup>iii</sup> —Mn1—O3	90.24 (3)
O1—Mn1—O1 <sup>iii</sup>	76.61 (4)	O3—Mn1—O3 <sup>iii</sup>	179.05 (4)
O2 <sup>ii</sup> —Mn1—O3	89.07 (3)		

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

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3A...O1 <sup>v</sup>	0.95	1.85	2.7696 (12)	162
O3—H3B...O2 <sup>vi</sup>	0.95	1.86	2.7517 (12)	155

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

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2005); 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: BH2112).

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**supplementary materials**

*Acta Cryst.* (2007). E63, m2389-m2390 [ doi:10.1107/S1600536807040470 ]

## The monoclinic polymorph of *catena*-poly[[diaquamanganese(II)]- $\mu$ -oxalato- $\kappa^4 O^1, O^2: O^1', O^2'$ ]

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### Comment

Oxalato-bridged coordination compounds have played a key role in the theoretical and experimental development of areas such as molecular magnetism (Verdaguer, 2001) and crystal engineering (Marinescu *et al.*, 2002). It has been established that two crystal hydrates are formed in this system  $MnC_2O_4 \cdot 2H_2O$  and  $MnC_2O_4 \cdot 3H_2O$ . Both crystal hydrates differ in color and structure. The white  $\alpha$ - $MnC_2O_4 \cdot 2H_2O$  is monoclinic, space group  $C2/c$  (Deyrieux *et al.*, 1973), while the pink-colored  $MnC_2O_4 \cdot 3H_2O$  is orthorhombic, space group  $Pcca$  (Huizing *et al.*, 1977; Fu *et al.*, 2005; Wu *et al.*, 2005). However, the paper published by Deyrieux *et al.* does not include atomic coordinates. A neutron diffraction study for  $MnC_2O_4 \cdot two-dimensional_2O$ , using powdered samples, has been published recently (Sledzinska *et al.*, 1987). It is noticeable that an orthorhombic polymorphs for the title polymer is also known (Huizing *et al.*, 1977; Lethbridge *et al.*, 2003;). In this way, our X-ray study deals with the monoclinic polymorph. It is expected that the difference in the crystal lattice of the compounds and the different way of bonding of water molecules would affect some properties, such as a thermal stability, oxidation, and magnetic behavior. The wide variety of coordination modes of the oxalate anion with different metals allows the use of metal-oxalato units as excellent building blocks to construct a great diversity of homo- and heterometallic structural frameworks ranging from discrete polymeric entities (Chiozzone *et al.*, 2003) to one-, two- and three-dimensional networks (Castillo *et al.* 2001).

Figure 1 shows that the O3 and O3d atoms of the two coordinated water molecules occupy the axial positions, while O1, O1d, O2a and O2c atoms of bridging oxalate ligands form the equatorial plane. The O3—Mn—O3d angle is almost linear,  $179.05(4)^\circ$ . Therefore, coordination sphere around the  $Mn^{II}$  center, placed on a twofold symmetry axis, is almost octahedral. The torsion angles show that the oxalate ligand is planar. Also, the result shows that one-dimensional linear chains are formed in the crystal structure through bridging bis-bidentate oxalate ligands. The bond angles show that the two coordinated water molecules are arranged *trans*. A remarkable feature in the crystal structure of (I) is the presence of strong O—H $\cdots$ O hydrogen bonds, connecting one-dimensional chains in the crystal structure (Fig. 2). The title complex is isomorphous to the corresponding  $Co^{II}$ -based polymer (Bacsa *et al.*, 2005).

### Experimental

A solution of  $Mn(NO_3)_2 \cdot 4H_2O$  (125 mg, 0.5 mmol) in water (20 ml) was added to an aqueous solution of  $(pipzH_2)(ox)$  (253 mg, 1.0 mmol) in water (20 ml) in a 2:1 molar ratio (oxH<sub>2</sub> is oxalic acid and pipz is piperazine; see Aghabozorg *et al.*, 2006). Colorless crystals of (I) were obtained after a few days at room temperature.

## Refinement

H atoms for the water molecule O3 were found in a difference map but their positions regularized with O—H bond lengths constrained to 0.95 Å. H atoms were constrained to ride on O3 and were refined with an isotropic displacement parameter fixed to  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{O3})$ .

## Figures

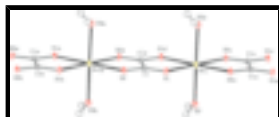


Fig. 1. Molecular structure of compound (I), displacement ellipsoids are drawn at the 50% probability level.

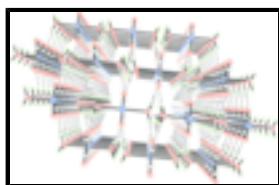


Fig. 2. Crystal packing of the title compound (I), hydrogen bonds are shown as dashed lines.

## *catena*-poly[[diaquamanganese(II)]- $\mu$ -oxalato- $\kappa^4\text{O}^1, \text{O}^2; \text{O}^1', \text{O}^2'$ ]

### Crystal data

$[\text{Mn}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]$

$M_r = 178.99$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 11.7648$  (14) Å

$b = 5.6550$  (6) Å

$c = 9.6367$  (11) Å

$\beta = 125.843$  (6)°

$V = 519.71$  (10) Å<sup>3</sup>

$Z = 4$

$F_{000} = 356$

$D_x = 2.288$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 3637 reflections

$\theta = 3.4\text{--}27.5^\circ$

$\mu = 2.49$  mm<sup>-1</sup>

$T = 296$  (2) K

Block, colourless

$0.21 \times 0.21 \times 0.11$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 100 pixels mm<sup>-1</sup>

$T = 296$ (2) K

$\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 1998)

$T_{\text{min}} = 0.616$ ,  $T_{\text{max}} = 0.763$

607 independent reflections

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

$R_{\text{int}} = 0.025$

$\theta_{\text{max}} = 27.7^\circ$

$\theta_{\text{min}} = 4.2^\circ$

$h = -15 \rightarrow 15$

$k = -7 \rightarrow 6$

$l = -12 \rightarrow 12$

4187 measured reflections

*Refinement*

Refinement on  $F^2$

Hydrogen site location: inferred from neighbouring sites

Least-squares matrix: full

H-atom parameters constrained

$R[F^2 > 2\sigma(F^2)] = 0.016$

$$w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 0.4357P]$$

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

$wR(F^2) = 0.046$

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

$S = 1.10$

$\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$

607 reflections

$\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$

43 parameters

Extinction correction: SHELXL97 (Sheldrick, 1997),

$$F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Primary atom site location: structure-invariant direct methods

Extinction coefficient: 0.0173 (15)

Secondary atom site location: difference Fourier map

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.5000	0.56903 (4)	0.7500	0.00841 (13)
C1	0.55073 (12)	1.07019 (17)	0.85025 (14)	0.0084 (2)
O1	0.58713 (8)	0.87221 (15)	0.92326 (10)	0.01030 (19)
O2	0.58807 (8)	1.26771 (14)	0.92238 (10)	0.00973 (19)
O3	0.31804 (9)	0.56581 (13)	0.75879 (11)	0.0116 (2)
H3A	0.2346	0.6137	0.6532	0.014*
H3B	0.3304	0.6569	0.8495	0.014*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Mn1	0.01051 (17)	0.00518 (17)	0.00806 (17)	0.000	0.00461 (13)	0.000
C1	0.0080 (5)	0.0101 (6)	0.0070 (6)	0.0001 (3)	0.0044 (5)	0.0001 (3)
O1	0.0124 (4)	0.0067 (4)	0.0085 (4)	0.0003 (3)	0.0043 (3)	0.0007 (3)
O2	0.0124 (4)	0.0065 (4)	0.0080 (4)	-0.0005 (3)	0.0047 (3)	-0.0006 (3)
O3	0.0121 (4)	0.0121 (4)	0.0086 (4)	0.0005 (3)	0.0049 (4)	-0.0009 (3)

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

Mn1—O2 <sup>i</sup>	2.1728 (8)	C1—O2	1.2515 (13)
Mn1—O2 <sup>ii</sup>	2.1728 (8)	C1—O1	1.2566 (13)
Mn1—O1	2.1849 (9)	C1—C1 <sup>iii</sup>	1.567 (2)
Mn1—O1 <sup>iii</sup>	2.1849 (9)	O2—Mn1 <sup>iv</sup>	2.1728 (8)
Mn1—O3	2.1914 (9)	O3—H3A	0.9501
Mn1—O3 <sup>iii</sup>	2.1914 (9)	O3—H3B	0.9500
O2 <sup>i</sup> —Mn1—O2 <sup>ii</sup>	76.70 (4)	O1—Mn1—O3 <sup>iii</sup>	90.24 (3)

## supplementary materials

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O2 <sup>i</sup> —Mn1—O1	179.57 (3)	O1 <sup>iii</sup> —Mn1—O3 <sup>iii</sup>	90.50 (3)
O2 <sup>ii</sup> —Mn1—O1	103.35 (3)	O3—Mn1—O3 <sup>iii</sup>	179.05 (4)
O2 <sup>i</sup> —Mn1—O1 <sup>iii</sup>	103.35 (3)	O2—C1—O1	126.19 (11)
O2 <sup>ii</sup> —Mn1—O1 <sup>iii</sup>	179.57 (3)	O2—C1—C1 <sup>iii</sup>	116.80 (6)
O1—Mn1—O1 <sup>iii</sup>	76.61 (4)	O1—C1—C1 <sup>iii</sup>	117.00 (6)
O2 <sup>i</sup> —Mn1—O3	89.07 (3)	C1—O1—Mn1	114.69 (7)
O2 <sup>ii</sup> —Mn1—O3	90.19 (3)	C1—O2—Mn1 <sup>iv</sup>	114.84 (7)
O1—Mn1—O3	90.50 (3)	Mn1—O3—H3A	112.1
O1 <sup>iii</sup> —Mn1—O3	90.24 (3)	Mn1—O3—H3B	113.9
O2 <sup>i</sup> —Mn1—O3 <sup>iii</sup>	90.19 (3)	H3A—O3—H3B	109.6
O2 <sup>ii</sup> —Mn1—O3 <sup>iii</sup>	89.07 (3)		
O2—C1—O1—Mn1	-179.34 (9)	O3—Mn1—O1—C1	-90.31 (8)
C1 <sup>iii</sup> —C1—O1—Mn1	0.46 (15)	O3 <sup>iii</sup> —Mn1—O1—C1	90.28 (8)
O2 <sup>ii</sup> —Mn1—O1—C1	179.38 (7)	O1—C1—O2—Mn1 <sup>iv</sup>	-179.48 (9)
O1 <sup>iii</sup> —Mn1—O1—C1	-0.18 (6)	C1 <sup>iii</sup> —C1—O2—Mn1 <sup>iv</sup>	0.72 (15)

Symmetry codes: (i)  $-x+1, y-1, -z+3/2$ ; (ii)  $x, y-1, z$ ; (iii)  $-x+1, y, -z+3/2$ ; (iv)  $x, y+1, z$ .

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3A $\cdots$ O1 <sup>v</sup>	0.95	1.85	2.7696 (12)	162
O3—H3B $\cdots$ O2 <sup>vi</sup>	0.95	1.86	2.7517 (12)	155

Symmetry codes: (v)  $x-1/2, -y+3/2, z-1/2$ ; (vi)  $-x+1, -y+2, -z+2$ .

Fig. 1

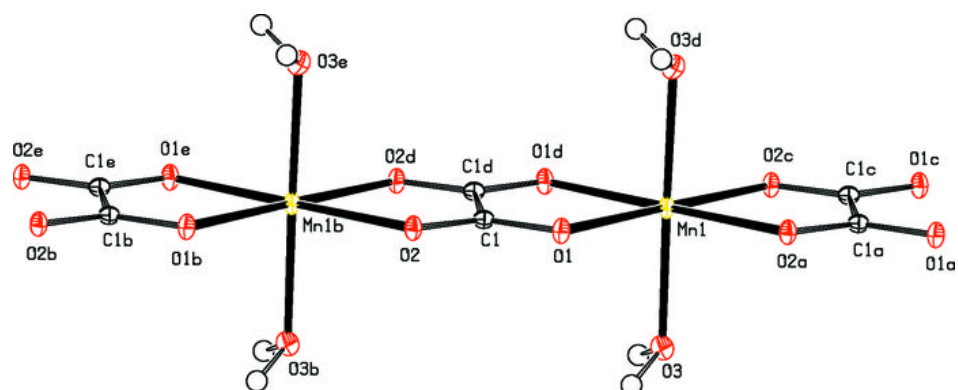




Fig. 2

