

## Poly[*diaqua-di- $\mu_3$ -malonato- $\mu$ -pyrazine-dimanganese(II)*]

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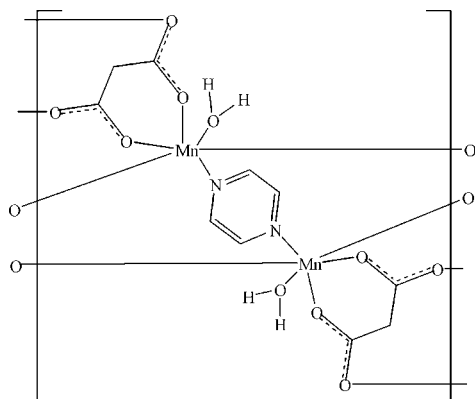
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.007$  Å;  $R$  factor = 0.045;  $wR$  factor = 0.117; data-to-parameter ratio = 10.9.

The title compound,  $[\text{Mn}_2(\text{C}_3\text{H}_2\text{O}_4)_2(\text{C}_4\text{H}_4\text{N}_2)(\text{H}_2\text{O})_2]_n$ , is isostructural with its  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  analogues, and the complex resides on a crystallographic centre of inversion (at the pyrazine ring centroid). The  $\text{Mn}^{\text{II}}$  atoms are linked *via* coordinated malonates, forming a two-dimensional network with cavities. These sheets are further connected into a three-dimensional network by bridging pyrazine ligands which have inversion symmetry. The coordination geometry around the  $\text{Mn}^{\text{II}}$  atom is a tetragonally elongated octahedron, with pyrazine N and aqua O atoms at the axial positions.

### Related literature

For studies and reviews of inorganic–organic hybrid materials, see: Chung *et al.* (1971); Okabe & Oya (2000); Serre *et al.* (2005); Pocker & Fong (1980); Scapin *et al.* (1997); Kim *et al.* (2001). For the isostructural analogues, see:  $\text{Co}^{\text{II}}$ : Delgado *et al.* (2003);  $\text{Ni}^{\text{II}}$ : Liu *et al.* (2005);  $\text{Zn}^{\text{II}}$ : Zhang *et al.* (2003); Delgado *et al.* (2003);  $\text{Cd}^{\text{II}}$ : Mao *et al.* (2004).



### Experimental

#### Crystal data

$[\text{Mn}_2(\text{C}_3\text{H}_2\text{O}_4)_2(\text{C}_4\text{H}_4\text{N}_2)(\text{H}_2\text{O})_2]$   
 $M_r = 430.10$   
 Monoclinic,  $P2_1/n$   
 $a = 7.0127$  (10) Å  
 $b = 14.490$  (2) Å  
 $c = 7.3711$  (10) Å  
 $\beta = 92.182$  (1)°  
 $V = 748.45$  (18) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.74$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 $0.36 \times 0.28 \times 0.24$  mm

#### Data collection

Bruker APEX II CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2001)  
 $T_{\text{min}} = 0.573$ ,  $T_{\text{max}} = 0.680$   
 2397 measured reflections  
 1314 independent reflections  
 1103 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.117$   
 $S = 1.00$   
 1314 reflections  
 116 parameters  
 3 restraints  
 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.72$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.40$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H2W}\cdots\text{O2}^i$	0.83 (4)	1.97 (4)	2.705 (5)	148 (7)
$\text{O1}-\text{H1W}\cdots\text{O3}^{ii}$	0.82 (4)	1.90 (4)	2.644 (5)	149 (7)

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2001); 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: GG2036).

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**supplementary materials**

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## Poly[*diaqua-di-μ*<sub>3</sub>-malonato-*μ*-pyrazine-dimanganese(II)]

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### Comment

In recent years, dicarboxylic acids have been widely used as polydentate ligands, which undergo various metal chelation reactions to form transition or rare earth metal complexes with interesting properties in materials science and in biological systems (Church *et al.*, 1971; Okabe & Oya, 2000; Serre *et al.*, 2005; Pocker & Fong, 1980; Scapin *et al.*, 1997). For example, Kim *et al.* (2001) focused on the syntheses of transition metal complexes containing benzene dicarboxylate and rigid aromatic pyridine ligands in order to study their electronic conductivity and magnetic properties. The importance of transition metal dicarboxylate complexes in materials science and biological systems prompted us to pursue synthetic strategies for these compounds, using malonate as a polydentate ligand and pyrazine as a rigid aromatic ligand. In this paper, we report the synthesis and X-ray crystal structure analysis of the title compound,  $[\text{Mn}_2(\text{C}_3\text{H}_2\text{O}_4)_2(\text{C}_4\text{H}_4\text{N}_2)(\text{H}_2\text{O})_2]_n$ .

The  $\text{Mn}^{\text{II}}$  atom has sixfold coordination, chelated by two O atoms from one malonate ligand to form a six-membered boat-type ring, and by two O atoms from two neighbouring malonates, one aqua molecule and one N atom from the bridging pyrazine ligand (Fig. 1). The Mn—O(carboxylate) and Mn—N bond lengths are in the range 2.060 (4) to 2.220 (4) and 2.269 (4) Å, respectively.

The packing diagram is shown in Fig. 2. If the pyrazine bridges are neglected, a two-dimensional network is formed by the  $[\text{Mn}(\text{malonate})(\text{H}_2\text{O})]$  moieties parallel to the (010) plane. There are hydrogen bonds (Table 2) between the aqua and malonate ligands in this network.

### Experimental

A mixture of manganese(II) sulfate (0.5 mmol), malonate acid (0.5 mmol), sodium hydroxide (1 mmol), pyrazine (1 mmol) and  $\text{H}_2\text{O}$  (8 ml) in a 25 ml Teflon-lined stainless steel autoclave was heated at 443 K for two days, and then cooled to room temperature. block crystals of complex (I) were obtained with a yield of 22%. Anal. Calc. for  $\text{C}_5\text{H}_6\text{NMnO}_5$ : C 27.91, H 2.79, N 6.51%; Found: C 27.88, H 2.75, N 6.47%.

### Refinement

All H atoms on C atoms were generated geometrically and treated as riding atoms with C—H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2$  times  $U_{\text{eq}}(\text{C})$ . The H atoms of the water molecule were located from difference density maps and were refined with distance restraints of  $d(\text{H—H}) = 1.38$  (2) Å,  $d(\text{O—H}) = 0.82$  (1) Å.

## Figures

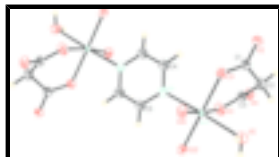


Fig. 1. Atom labeling scheme for the title complex (I), showing 30% probability displacement ellipsoids for non-H atoms. Atoms labeled with *i* are at the symmetry position  $(-x + 1, -y, -z + 1)$ .

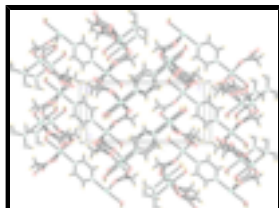


Fig. 2. Packing diagram for the title complex along the *c* axis.

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### Crystal data

$[\text{Mn}_2(\text{C}_3\text{H}_2\text{O}_4)_2(\text{C}_4\text{H}_4\text{N}_2)(\text{H}_2\text{O})_2]$

$M_r = 430.10$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P\ 2_1n$

$a = 7.0127\ (10)\ \text{\AA}$

$b = 14.490\ (2)\ \text{\AA}$

$c = 7.3711\ (10)\ \text{\AA}$

$\beta = 92.182\ (1)^\circ$

$V = 748.45\ (18)\ \text{\AA}^3$

$Z = 2$

$F_{000} = 432$

$D_x = 1.908\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

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

Cell parameters from 1314 reflections

$\theta = 2.8\text{--}25.1^\circ$

$\mu = 1.74\ \text{mm}^{-1}$

$T = 293\ (2)\ \text{K}$

Block, colorless

$0.36 \times 0.28 \times 0.24\ \text{mm}$

### Data collection

Bruker APEX II CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293\ (2)\ \text{K}$

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 2001)

$T_{\min} = 0.573$ ,  $T_{\max} = 0.680$

2397 measured reflections

1314 independent reflections

1103 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 25.1^\circ$

$\theta_{\min} = 2.8^\circ$

$h = -8 \rightarrow 3$

$k = -13 \rightarrow 16$

$l = -8 \rightarrow 8$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$$R[F^2 > 2\sigma(F^2)] = 0.045$$

$$wR(F^2) = 0.117$$

$$S = 1.00$$

1314 reflections

116 parameters

3 restraints

Primary atom site location: structure-invariant direct methods

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 2.2589P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.013$$

$$\Delta\rho_{\max} = 0.72 \text{ e } \text{Å}^{-3}$$

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

Extinction correction: SHELXL97 (Sheldrick, 1997),

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

Extinction coefficient: 0.051 (5)

### 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 ( $\text{Å}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C3	0.5846 (7)	0.3318 (3)	0.7561 (7)	0.0344 (11)
C4	0.6125 (8)	0.3910 (4)	0.5887 (7)	0.0432 (12)
H4A	0.7407	0.4162	0.5951	0.052*
H4B	0.5240	0.4424	0.5904	0.052*
C5	0.5834 (7)	0.3404 (3)	0.4123 (7)	0.0348 (11)
C2	0.4526 (8)	0.0744 (4)	0.5906 (8)	0.0507 (14)
H2	0.4135	0.1258	0.6549	0.061*
C1	0.6785 (7)	-0.0046 (4)	0.4448 (8)	0.0468 (13)
H1	0.8016	-0.0106	0.4036	0.056*
Mn1	0.83760 (8)	0.19134 (4)	0.58103 (7)	0.0172 (3)
N1	0.6323 (6)	0.0717 (3)	0.5372 (6)	0.0389 (10)
O2	0.6638 (5)	0.2528 (3)	0.7693 (5)	0.0433 (9)
O5	0.4862 (5)	0.3675 (2)	0.8747 (5)	0.0435 (9)
O3	0.6698 (5)	0.2644 (3)	0.3903 (5)	0.0464 (9)
O4	0.4753 (5)	0.3775 (2)	0.2943 (5)	0.0427 (9)
O1	1.0317 (6)	0.3107 (3)	0.5859 (5)	0.0473 (9)
H2W	1.087 (8)	0.313 (5)	0.489 (4)	0.080*
H1W	1.104 (7)	0.303 (5)	0.675 (5)	0.080*

## supplementary materials

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C3	0.038 (2)	0.031 (3)	0.034 (2)	0.000 (2)	0.0003 (19)	-0.005 (2)
C4	0.060 (3)	0.035 (3)	0.034 (3)	0.005 (2)	0.003 (2)	0.000 (2)
C5	0.039 (2)	0.029 (3)	0.036 (3)	0.003 (2)	0.005 (2)	0.004 (2)
C2	0.048 (3)	0.042 (3)	0.063 (4)	-0.006 (3)	0.018 (3)	-0.014 (3)
C1	0.041 (3)	0.037 (3)	0.063 (4)	-0.002 (2)	0.012 (2)	-0.009 (3)
Mn1	0.0218 (4)	0.0155 (4)	0.0144 (4)	0.0007 (2)	0.0018 (2)	-0.0006 (2)
N1	0.039 (2)	0.036 (2)	0.042 (2)	-0.0017 (18)	0.0021 (17)	-0.0012 (19)
O2	0.056 (2)	0.039 (2)	0.0350 (19)	0.0076 (17)	0.0117 (16)	0.0031 (15)
O5	0.049 (2)	0.040 (2)	0.043 (2)	0.0044 (16)	0.0172 (16)	-0.0004 (17)
O3	0.058 (2)	0.045 (2)	0.0355 (19)	0.0118 (18)	-0.0044 (16)	-0.0029 (16)
O4	0.053 (2)	0.0347 (19)	0.0399 (19)	0.0032 (17)	-0.0064 (16)	0.0032 (16)
O1	0.051 (2)	0.055 (2)	0.037 (2)	-0.0021 (18)	0.0019 (16)	0.0004 (18)

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

C3—O5	1.246 (6)	C1—C2 <sup>i</sup>	1.386 (8)
C3—O2	1.275 (6)	C1—H1	0.9300
C3—C4	1.521 (7)	Mn1—O5 <sup>ii</sup>	2.060 (3)
C4—C5	1.500 (7)	Mn1—O4 <sup>iii</sup>	2.070 (4)
C4—H4A	0.9700	Mn1—O3	2.087 (4)
C4—H4B	0.9700	Mn1—O2	2.082 (3)
C5—O4	1.254 (6)	Mn1—O1	2.200 (4)
C5—O3	1.270 (7)	Mn1—N1	2.269 (4)
C2—N1	1.335 (7)	O5—Mn1 <sup>iv</sup>	2.060 (3)
C2—C1 <sup>i</sup>	1.386 (8)	O4—Mn1 <sup>v</sup>	2.070 (4)
C2—H2	0.9300	O1—H2W	0.83 (4)
C1—N1	1.344 (7)	O1—H1W	0.82 (4)
O5—C3—O2	124.7 (5)	O4 <sup>iii</sup> —Mn1—O2	88.18 (14)
O5—C3—C4	115.3 (4)	O3—Mn1—O2	84.41 (14)
O2—C3—C4	119.9 (4)	O5 <sup>ii</sup> —Mn1—O1	90.42 (14)
C3—C4—C5	114.2 (4)	O4 <sup>iii</sup> —Mn1—O1	95.52 (14)
C3—C4—H4A	108.7	O3—Mn1—O1	86.84 (16)
C5—C4—H4A	108.7	O2—Mn1—O1	91.75 (15)
C3—C4—H4B	108.7	O5 <sup>ii</sup> —Mn1—N1	85.11 (15)
C5—C4—H4B	108.7	O4 <sup>iii</sup> —Mn1—N1	90.85 (15)
H4A—C4—H4B	107.6	O3—Mn1—N1	87.32 (16)
O4—C5—O3	124.2 (5)	O2—Mn1—N1	92.14 (15)
O4—C5—C4	116.8 (4)	O1—Mn1—N1	172.65 (15)
O3—C5—C4	119.0 (4)	C2—N1—C1	115.0 (4)
N1—C2—C1 <sup>i</sup>	123.3 (5)	C2—N1—Mn1	122.4 (4)
N1—C2—H2	118.3	C1—N1—Mn1	122.4 (3)
C1 <sup>i</sup> —C2—H2	118.3	C3—O2—Mn1	126.7 (3)

N1—C1—C2 <sup>i</sup>	121.7 (5)	C3—O5—Mn1 <sup>iv</sup>	131.0 (3)
N1—C1—H1	119.2	C5—O3—Mn1	127.8 (3)
C2 <sup>i</sup> —C1—H1	119.2	C5—O4—Mn1 <sup>v</sup>	124.9 (3)
O5 <sup>ii</sup> —Mn1—O4 <sup>iii</sup>	97.27 (15)	Mn1—O1—H2W	109 (5)
O5 <sup>ii</sup> —Mn1—O3	90.03 (15)	Mn1—O1—H1W	105 (5)
O4 <sup>iii</sup> —Mn1—O3	172.30 (14)	H2W—O1—H1W	114 (3)
O5 <sup>ii</sup> —Mn1—O2	173.92 (15)		

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

*Hydrogen-bond geometry (Å, °)*

<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>
O1—H2W $\cdots$ O2 <sup>ii</sup>	0.83 (4)	1.97 (4)	2.705 (5)	148 (7)
O1—H1W $\cdots$ O3 <sup>iii</sup>	0.82 (4)	1.90 (4)	2.644 (5)	149 (7)

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

Fig. 1

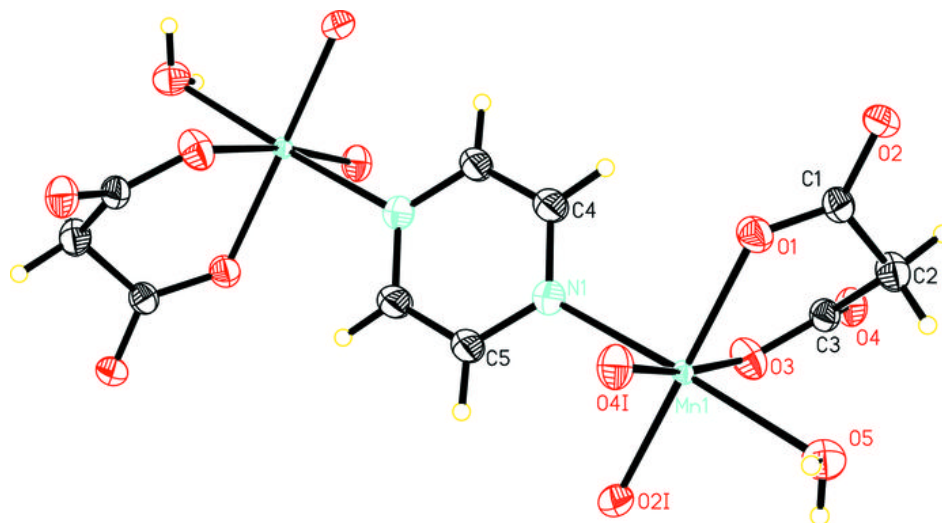




Fig. 2

