metal-organic compounds

catena-Poly[[[[3-(2-pyridyl)-1H-pyrazole]manganese(II)]-μ-oxalato] sesquihydrate]

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In the title compound, $\{[Mn(C_2O_4)(C_8H_7N_3)]\cdot 1.5H_2O\}_n$, the Mn^{II} ion is chelated by two O,O'-bidentate oxalate ions and an N,N'-bidentate 3-(2-pyridyl)pyrazole molecule, resulting in a distorted cis-MnN_2O_4 octahedral geometry for the metal ion. The bridging oxalate ions generate wave-like polymeric chains propagating in [001]. The packing is consolidated by N—H⋯O and O—H⋯O hydrogen bonds. One of the water O atoms lies on a crystallographic twofold axis.

Related literature

For coordination compounds with pyridyl-pyrazolide ligands, see: Ward et al. (1998, 2001).
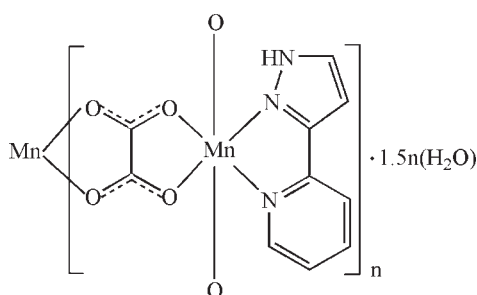
Experimental

Crystal data

[Mn(C₂O₄)(C₈H₇N₃)]·1.5H₂O
$M_r = 315.15$
Monoclinic, $C2/c$
$a = 29.460 (8)$ Å
$b = 9.236 (3)$ Å
$c = 9.875 (3)$ Å
$\beta = 102.706 (5)°$

$V = 2621.0 (13)$ Å³
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 1.03$ mm⁻¹
$T = 296$ K
$0.43 \times 0.28 \times 0.22$ mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2005)
$T_{min} = 0.665$, $T_{max} = 0.805$

6809 measured reflections
2438 independent reflections
2004 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.078$
$S = 1.00$
2438 reflections
186 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.22$ e Å⁻³
$\Delta\rho_{min} = -0.17$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Mn1—N1	2.280 (4)	Mn1—O2	2.168 (3)
Mn1—N2	2.223 (4)	Mn1—O1	2.191 (4)
Mn1—O4ⁱ	2.150 (3)	Mn1—O3ⁱ	2.208 (3)
N2—Mn1—N1	73.01 (16)		

Symmetry code: (i) $x, -y, z - \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H3A⋯O1W	0.86	1.89	2.748 (7)	175
O1W—H1W⋯O1ⁱⁱ	0.83 (5)	2.08 (4)	2.851 (6)	155 (6)
O1W—H2W⋯O2Wⁱⁱⁱ	0.82 (4)	2.10 (5)	2.819 (6)	148 (6)
O2W—H3W⋯O3ⁱᵛ	0.82 (5)	2.06 (4)	2.823 (4)	156 (6)

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

Data collection: SMART **or APEX2?** (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); 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: SHELXL97.

References

Bruker (2005). SMART, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). Acta Cryst. A**64**, 112–122.
Ward, M. D., Fleming, J. S., Psillakis, E., Jeffery, J. C. & McCleverty, J. A. (1998). Acta Cryst. C**54**, 609–612.
Ward, M. D., McCleverty, J. A. & Jeffery, J. C. (2001). Coord. Chem. Rev. **222**, 251–272.

supporting information

catena-Poly[[[[3-(2-pyridyl)-1*H*-pyrazole]manganese(II)]-*μ*-oxalato] sesquihydrate]

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S1. Comment

The tridentate ligand 3-(2-pyridyl)pyrazole and its derivatives have been used widely in the construction of supramolecular architectures by way of metal-organic coordination (Ward, Fleming *et al.* 1998; Ward, 2001).

As a continuation of these studies, we now report the crystal structure of the title complex, (I).

The Mn ion is hexcoordianted, chelated by two oxalate and one 3-(2-pyridyl)pyrazole ligand (Table 1). While each oxalate ligand acts as one bridge to chalate two Mn ions, forming one wave-like line with Mn···Mn distance being 5.652 /%A, shown in Figure 2. The structure is consolidated by N—H···O and O—H···O hydrogen bonds (Table 2, Figure 3).

S2. Experimental

A mixture of $Mn(CH_3COO)_2.4H_2O$ (1 mmol), 3-(2-pyridyl)pyrazole (1 mmol), oxalic acid (1 mmol), sodium hydroxide (1 mmol) and H_2O (10 ml) was stirred for 30 min in air. The mixture was then transferred to a 25 ml Teflon-lined hydrothermal bomb. The bomb was kept at 433 K for 72 h under autogenous pressure. Upon cooling, pink prisms of (I) were obtained from the reaction mixture.

S3. Refinement

The C-bound H atoms were geometrically planced (C—H = 0.93/%A) and refined as riding with U_{iso} = 1.2Ueq(C). The N– and O-bound H atoms were located in difference maps and refined with distance restraints: N—H = 0.97 (1)/%A, O—H = 0.82 (2)/%A, H···H = 1.38 (2)/%A.
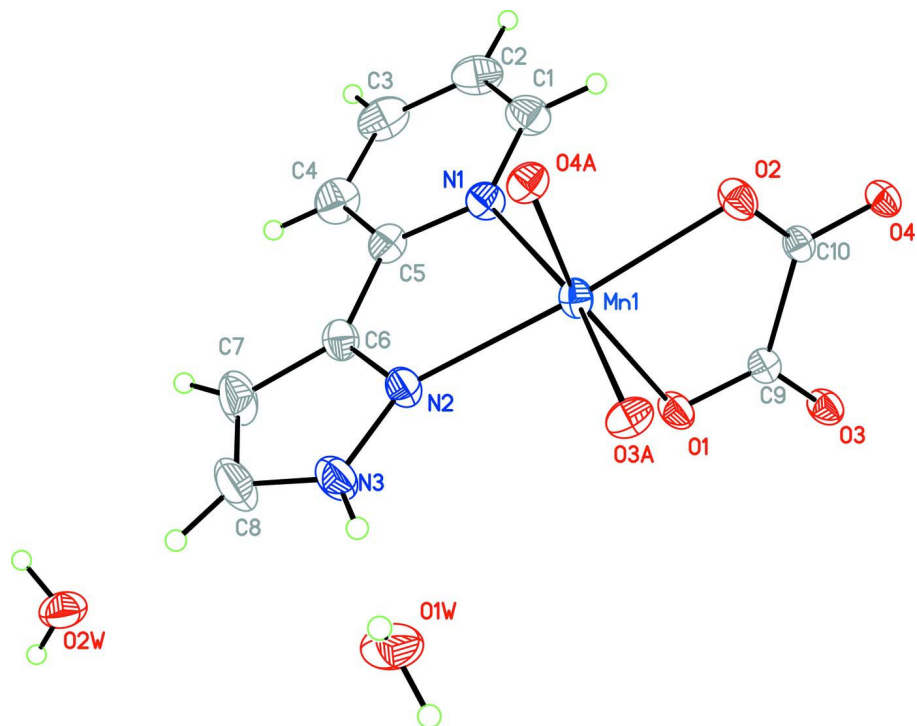
Figure 1

A view of (I) with the unique-atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.
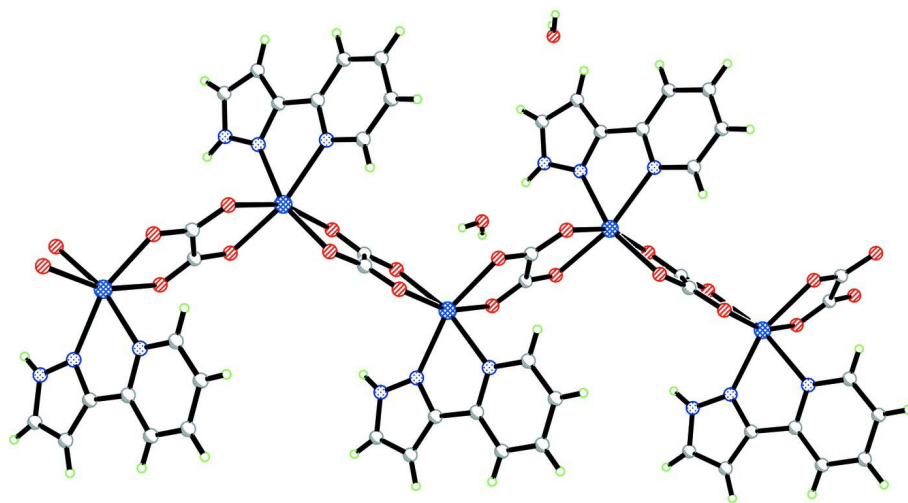
Figure 2

A view of (I) showing the extended chain strcuture.
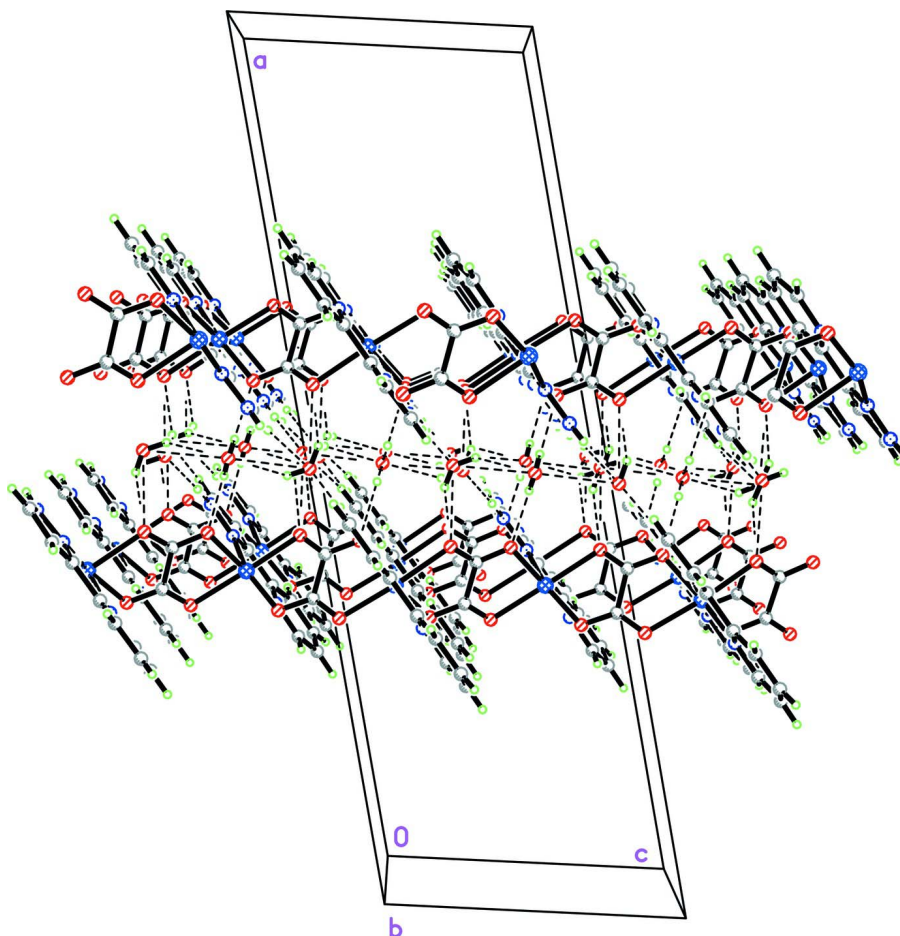
Figure 3

A view of (I) showing the packing.

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Crystal data

[Mn(C₂O₄)(C₈H₇N₃)]·1.5H₂O	$F(000) = 1280$
$M_r = 315.15$	$D_x = 1.597$ Mg m⁻³
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 2634 reflections
$a = 29.460\ (8)$ Å	$\theta = 2.8–25.4°$
$b = 9.236\ (3)$ Å	$\mu = 1.03$ mm⁻¹
$c = 9.875\ (3)$ Å	$T = 296$ K
$\beta = 102.706\ (5)°$	Block, pink
$V = 2621.0\ (13)$ Å³	$0.43 \times 0.28 \times 0.22$ mm
$Z = 8$	

Data collection

Bruker APEXII CCD diffractometer	Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
Radiation source: fine-focus sealed tube	$T_{min} = 0.665$, $T_{max} = 0.805$
Graphite monochromator	6809 measured reflections
φ and ω scans	2438 independent reflections
	2004 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\text{max}} = 25.5°$, $\theta_{\text{min}} = 2.3°$

$h = -35 \rightarrow 35$

$k = -10 \rightarrow 11$

$l = -9 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.027$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.078$	
$S = 1.00$	H atoms treated by a mixture of independent and constrained refinement
2438 reflections	
186 parameters	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.7224P]$ where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{\text{max}} = 0.001$
	$\Delta\rho_{\text{max}} = 0.22$ e Å^{-3}
	$\Delta\rho_{\text{min}} = -0.17$ e Å^{-3}

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.2903 (2)	0.3204 (7)	0.3530 (6)	0.0620 (16)
H1	0.2780	0.2284	0.3594	0.074*
C2	0.2697 (2)	0.4365 (8)	0.4029 (7)	0.0732 (19)
H2	0.2441	0.4229	0.4423	0.088*
C3	0.2872 (2)	0.5721 (8)	0.3938 (7)	0.077 (2)
H3	0.2740	0.6518	0.4279	0.092*
C4	0.3246 (2)	0.5889 (7)	0.3340 (7)	0.0685 (17)
H4	0.3367	0.6806	0.3257	0.082*
C5	0.34421 (19)	0.4681 (6)	0.2858 (5)	0.0483 (13)
C6	0.3844 (2)	0.4772 (6)	0.2209 (6)	0.0506 (13)
C7	0.4082 (3)	0.5950 (7)	0.1822 (8)	0.079 (2)
H7	0.4024	0.6926	0.1940	0.095*
C8	0.4416 (3)	0.5372 (7)	0.1235 (8)	0.085 (2)
H8	0.4632	0.5886	0.0868	0.102*
C9	0.39499 (16)	0.0253 (5)	0.5065 (5)	0.0374 (11)
C10	0.34569 (16)	−0.0362 (5)	0.4432 (5)	0.0367 (11)
N1	0.32730 (15)	0.3343 (5)	0.2955 (5)	0.0472 (11)
N2	0.40299 (15)	0.3533 (4)	0.1877 (5)	0.0470 (11)
N3	0.43793 (17)	0.3939 (6)	0.1279 (5)	0.0628 (13)
H3A	0.4556	0.3346	0.0965	0.075*
Mn1	0.36805 (2)	0.14892 (8)	0.22637 (7)	0.0395 (3)

O1	0.41292 (12)	0.1050 (4)	0.4304 (4)	0.0476 (9)
O2	0.32916 (13)	−0.0076 (4)	0.3189 (4)	0.0514 (9)
O3	0.41261 (12)	−0.0083 (4)	0.6295 (3)	0.0477 (9)
O4	0.32667 (11)	−0.1102 (4)	0.5215 (3)	0.0433 (8)
O1W	0.49441 (17)	0.2150 (6)	0.0153 (6)	0.0849 (14)
O2W	0.5000	0.8860 (7)	0.2500	0.0754 (19)
H1W	0.5197 (14)	0.181 (7)	0.056 (5)	0.080*
H2W	0.485 (2)	0.183 (7)	−0.063 (4)	0.080*
H3W	0.4792 (17)	0.944 (6)	0.222 (7)	0.080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.055 (3)	0.068 (4)	0.070 (4)	0.001 (3)	0.027 (3)	−0.007 (3)
C2	0.054 (4)	0.092 (5)	0.080 (5)	0.015 (4)	0.028 (3)	−0.012 (4)
C3	0.074 (4)	0.079 (5)	0.078 (5)	0.028 (4)	0.019 (4)	−0.021 (4)
C4	0.079 (4)	0.049 (3)	0.076 (4)	0.008 (3)	0.016 (4)	−0.018 (3)
C5	0.054 (3)	0.043 (3)	0.046 (3)	0.004 (2)	0.007 (2)	−0.007 (2)
C6	0.057 (3)	0.040 (3)	0.055 (3)	−0.003 (2)	0.012 (3)	−0.002 (2)
C7	0.101 (5)	0.041 (3)	0.104 (6)	−0.009 (3)	0.039 (5)	0.007 (3)
C8	0.091 (5)	0.065 (4)	0.112 (6)	−0.022 (4)	0.047 (5)	0.013 (4)
C9	0.042 (3)	0.035 (3)	0.037 (3)	−0.002 (2)	0.013 (2)	−0.003 (2)
C10	0.043 (3)	0.032 (2)	0.038 (3)	−0.003 (2)	0.013 (2)	−0.004 (2)
N1	0.048 (2)	0.046 (3)	0.051 (3)	0.0022 (19)	0.017 (2)	−0.0065 (19)
N2	0.051 (3)	0.041 (2)	0.053 (3)	−0.0033 (19)	0.021 (2)	0.0016 (19)
N3	0.061 (3)	0.063 (3)	0.074 (3)	−0.006 (2)	0.035 (3)	0.008 (3)
Mn1	0.0490 (5)	0.0355 (5)	0.0370 (5)	0.0002 (3)	0.0160 (3)	−0.0001 (3)
O1	0.046 (2)	0.055 (2)	0.043 (2)	−0.0140 (16)	0.0116 (16)	0.0073 (16)
O2	0.056 (2)	0.059 (2)	0.037 (2)	−0.0187 (18)	0.0051 (16)	0.0048 (16)
O3	0.046 (2)	0.057 (2)	0.039 (2)	−0.0124 (16)	0.0069 (16)	0.0062 (16)
O4	0.0449 (19)	0.0467 (19)	0.0401 (19)	−0.0105 (15)	0.0132 (16)	0.0017 (15)
O1W	0.060 (3)	0.103 (4)	0.097 (4)	0.016 (3)	0.027 (3)	−0.002 (3)
O2W	0.047 (4)	0.069 (4)	0.102 (5)	0.000	−0.002 (4)	0.000

Geometric parameters (Å, º)

C1—N1	1.342 (7)	C9—O3	1.250 (6)
C1—C2	1.376 (8)	C9—C10	1.557 (7)
C1—H1	0.9300	C10—O2	1.245 (6)
C2—C3	1.365 (10)	C10—O4	1.253 (5)
C2—H2	0.9300	N2—N3	1.348 (6)
C3—C4	1.367 (9)	N3—H3A	0.8600
C3—H3	0.9300	Mn1—N1	2.280 (4)
C4—C5	1.388 (8)	Mn1—N2	2.223 (4)
C4—H4	0.9300	Mn1—O4^i	2.150 (3)
C5—N1	1.344 (6)	Mn1—O2	2.168 (3)
C5—C6	1.468 (8)	Mn1—O1	2.191 (4)
C6—N2	1.339 (7)	Mn1—O3^i	2.208 (3)

C6—C7	1.392 (8)	O3—Mn1ⁱⁱ	2.208 (3)
C7—C8	1.357 (10)	O4—Mn1ⁱⁱ	2.150 (3)
C7—H7	0.9300	O1W—H1W	0.83 (5)
C8—N3	1.329 (8)	O1W—H2W	0.82 (4)
C8—H8	0.9300	O2W—H3W	0.82 (5)
C9—O1	1.250 (6)		
N1—C1—C2	122.7 (6)	C1—N1—C5	117.8 (5)
N1—C1—H1	118.7	C1—N1—Mn1	125.8 (4)
C2—C1—H1	118.7	C5—N1—Mn1	116.2 (3)
C3—C2—C1	119.2 (6)	C6—N2—N3	105.2 (4)
C3—C2—H2	120.4	C6—N2—Mn1	117.0 (3)
C1—C2—H2	120.4	N3—N2—Mn1	137.6 (4)
C2—C3—C4	119.0 (6)	C8—N3—N2	111.5 (5)
C2—C3—H3	120.5	C8—N3—H3A	124.2
C4—C3—H3	120.5	N2—N3—H3A	124.2
C3—C4—C5	119.5 (6)	O4ⁱ—Mn1—O2	92.44 (13)
C3—C4—H4	120.3	O4ⁱ—Mn1—O1	159.58 (14)
C5—C4—H4	120.3	O2—Mn1—O1	75.93 (13)
N1—C5—C4	121.7 (5)	O4ⁱ—Mn1—O3ⁱ	76.27 (12)
N1—C5—C6	115.5 (4)	O2—Mn1—O3ⁱ	102.10 (16)
C4—C5—C6	122.8 (5)	O1—Mn1—O3ⁱ	89.63 (13)
N2—C6—C7	110.1 (5)	O4ⁱ—Mn1—N2	99.67 (15)
N2—C6—C5	118.1 (4)	O2—Mn1—N2	161.17 (16)
C7—C6—C5	131.8 (5)	O1—Mn1—N2	96.12 (15)
C8—C7—C6	105.4 (6)	O3ⁱ—Mn1—N2	94.79 (14)
C8—C7—H7	127.3	O4ⁱ—Mn1—N1	100.36 (14)
C6—C7—H7	127.3	O2—Mn1—N1	90.74 (16)
N3—C8—C7	107.8 (6)	O1—Mn1—N1	96.58 (15)
N3—C8—H8	126.1	O3ⁱ—Mn1—N1	166.79 (15)
C7—C8—H8	126.1	N2—Mn1—N1	73.01 (16)
O1—C9—O3	126.2 (4)	C9—O1—Mn1	114.4 (3)
O1—C9—C10	117.0 (4)	C10—O2—Mn1	115.4 (3)
O3—C9—C10	116.8 (4)	C9—O3—Mn1ⁱⁱ	114.0 (3)
O2—C10—O4	126.4 (4)	C10—O4—Mn1ⁱⁱ	115.7 (3)
O2—C10—C9	116.5 (4)	H1W—O1W—H2W	114 (4)
O4—C10—C9	117.1 (4)		

Symmetry codes: (i) *x*, −*y*, *z*−1/2; (ii) *x*, −*y*, *z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3*A*···O1*W*	0.86	1.89	2.748 (7)	175
O1*W*—H1*W*···O1ⁱⁱⁱ	0.83 (5)	2.08 (4)	2.851 (6)	155 (6)
O1*W*—H2*W*···O2*W*ⁱᵛ	0.82 (4)	2.10 (5)	2.819 (6)	148 (6)
O2*W*—H3*W*···O3ᵛ	0.82 (5)	2.06 (4)	2.823 (4)	156 (6)

Symmetry codes: (iii) −*x*+1, *y*, −*z*+1/2; (iv) −*x*+1, −*y*+1, −*z*; (v) *x*, −*y*+1, *z*−1/2.