Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis{μ-2,2′-[1,1′-(ethane-1,2-diyldinitrilo)-diethylidyne]diphenolato}bis[(benzoato-κO)manganese(III)] dihydrate

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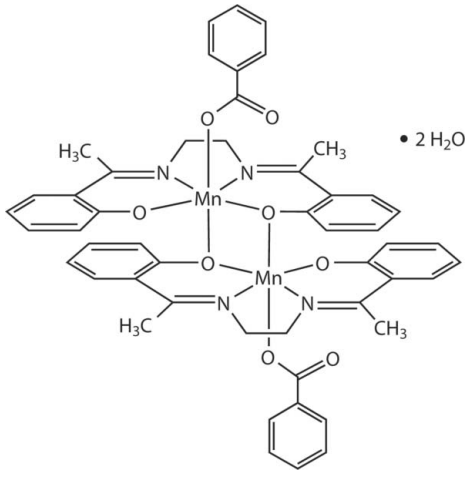
Received 22 November 2007; accepted 29 November 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.026; wR factor = 0.068; data-to-parameter ratio = 9.3.

The title compound, $[Mn_2(C_{18}H_{18}N_2O_2)_2(C_7H_5O_2)_2]\cdot 2H_2O$, was synthesized by the reaction between manganese(II) benzoate and the Schiff base generated *in situ* by the condensation of ethane-1,2-diamine and *o*-hydroxyacetophenone. The Jahn–Teller-distorted manganese(III) ions of the centrosymmetric dimer are connected through phenoxy bridges. Hydrogen-bonding interactions between the uncoordinated C=O of the benzoate and uncoordinated water molecules link the dimers into a chain running parallel to the *c* axis.

Related literature

For related literature, see: Antonyuk *et al.* (2000); Aurengzeb *et al.* (1992); Aurengzeb *et al.* (1994); Barynin *et al.* (2001); Christou (1989); Hulme *et al.* (1997); Meier *et al.* (1996); Pecoraro & Hsieh (2000); Yocum & Pecoraro (1999); Stemmler *et al.* (1997); Zhang & Janiak (2001); Zouni *et al.* (2001).



Experimental

Crystal data

$[Mn_2(C_{18}H_{18}N_2O_2)_2(C_7H_5O_2)_2]\cdot 2H_2O$
M_r = 976.82
Monoclinic, $P2_1/c$
a = 12.9376 (4) Å
b = 12.3983 (4) Å
c = 13.8470 (4) Å
β = 103.702 (2)°
V = 2157.91 (11) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 5.33 mm^{-1}
T = 100 (2) K
0.23 × 0.22 × 0.03 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: numerical (*SADABS*; Sheldrick, 2004)
T_{min} = 0.374, T_{max} = 0.857
21968 measured reflections
3711 independent reflections
3465 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.068
S = 1.03
3711 reflections
398 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H1W···O4^{i}	0.83 (3)	2.02 (3)	2.8452 (19)	173 (2)
O5—H2W···O4^{ii}	0.88 (3)	1.89 (3)	2.7579 (18)	171 (3)

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

We acknowledge the authorities of SN College, Varkala, Kerala, India for providing the facilities of the college for this research. We also acknowledge the NSF (CHE-0443345) and the College of William and Mary for the purchase of the X-ray equipment.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HJ2002).

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supporting information

Acta Cryst. (2008). E**64**, m150–m151 [https://doi.org/10.1107/S160053680706446X]

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V. S Thampidas, T. Radhakrishnan and Robert D. Pike

S1. Comment

The role played by manganese in biological systems like the oxygen-evolving complex (OEC) of photosystem II (Zouni et al.,2001) and enzymes like superoxide dismutase, catalase, arginase etc. is now well-recognized (Pecoraro & Yocum, 2004). Inorganic model complexes have made significant contributions to the progress in delineating the structural and functional aspects of the active-sites of these systems. An enormous number of such manganese complexes have been reported during the last few decades (Christou, 1989; Pecoraro & Hsieh, 2000). One class of high-valent manganese complexes which has received considerable attention in this connection recently is those involving carboxylic acid and Schiff base ligands (Aurengzeb et al., 1992; Aurengzeb et al. 1994; Hulme et al., 1997; Zhang et al., 2001). Crystallographic studies on the active sites of a relatively rare class of manganese catalases found in bacteria-like Thermus thermophilus and Lactobacillus plantarum point to a dinuclear manganese core with an Mn···Mn separation of 3.13 Å (reduced state) and 3.03 Å (oxidized state) respectively (Antonyuk et al., 2000; Barynin et al., 2001). The Mn···Mn distances derived from the EPR and EXAFS data provide complementary structural parameters with the Mn···Mn distances being 3.4 Å and 3.54 Å, respectively (Meier et al., 1996; Stemmler et al., 1997). Here we report the crystal structure of a dimeric manganese complex with a Mn···Mn distance of 3.4616 (5)Å, I (Figure 1).

Compound I crystallizes in the monoclinic space group $P2_1/c$. The two manganese(III) ions, which are in slightly distorted octahedral environments, are linked by phenoxy bridges using the phenolic oxygen atoms of each ligand. The formation of the phenoxy bridges and the nearly planar nature of the tetradentate Schiff base ligand lead the carboxylates to adopt a relatively rare unidentate bonding mode. Each manganese(III) ion is at the centre of an approximate square plane consisting of two Mn–N bonds [Mn1-N1 = 1.9903 (13) Å and Mn1-N2 = 2.0091 (13) Å] and two Mn–O bonds [Mn1-O2 = 1.8673 (11) Å and Mn1-O1= 1.9324 (11) Å]. An axial elongation, of the Mn–Ocarb bond [Mn1–O3 = 2.1306 (11)Å], nearly orthogonal to the plane of the Schiff base, is indicative of the Jahn-Teller distortion anticipated of a high-spin manganese(III) ion in octahedral surroundings. This also causes a considerable weakening of the Mn–O bond along the phenoxy bridge [Mn1-O1$^{(i)}$ = 2.4399 (11)Å; Symmetry codes: (i) -x+1, -y+1, -z+1], leading to an asymmetric Mn1–O–Mn1$^{(i)}$ bridge. The Mn···Mn separation [Mn1···Mn1$^{(i)}$] of 3.4616 (5)Å is comparable to 3.485 (7)Å and 3.529 (4)Å, the corresponding Mn···Mn separations of the previously reported complexes,[{Mn(msalen)($EtCO_2$)}$_2$] and [{Mn(msalen)(Bu^nCO_2)}$_2$] respectively. [H_2msalen = N,N-bis(3-methoxysalicylidene)-1,2-diaminoethane] (Hulme et al., 1997). The non-coordinated C-O of the benzoate and lattice water molecules interact through hydrogen producing chains of the dimers running parallel to the c-axis (Figure 2).

S2. Experimental

To a solution of $Mn(C_6H_5CO_2)_2.2H_2O$ (1.00 g, 3.00 mmol) and *o*-hydroxyacetophenone (0.82 g, 6.00 mmol) in methanol (40 ml), ethane-1,2-diamine (0.18 g, 3.00 mmol) was added. The solution was stirred for 20 minutes, filtered and left to evaporation in an open conical flask. Greenish brown crystals were deposited in 2–3 days. These were collected by filtration, washed with methanol, and dried in air. Yield of **1** is 1.20 g (82.0%) based on manganese.

S3. Refinement

All hydrogen atoms were located in the difference map and refined isotropically.

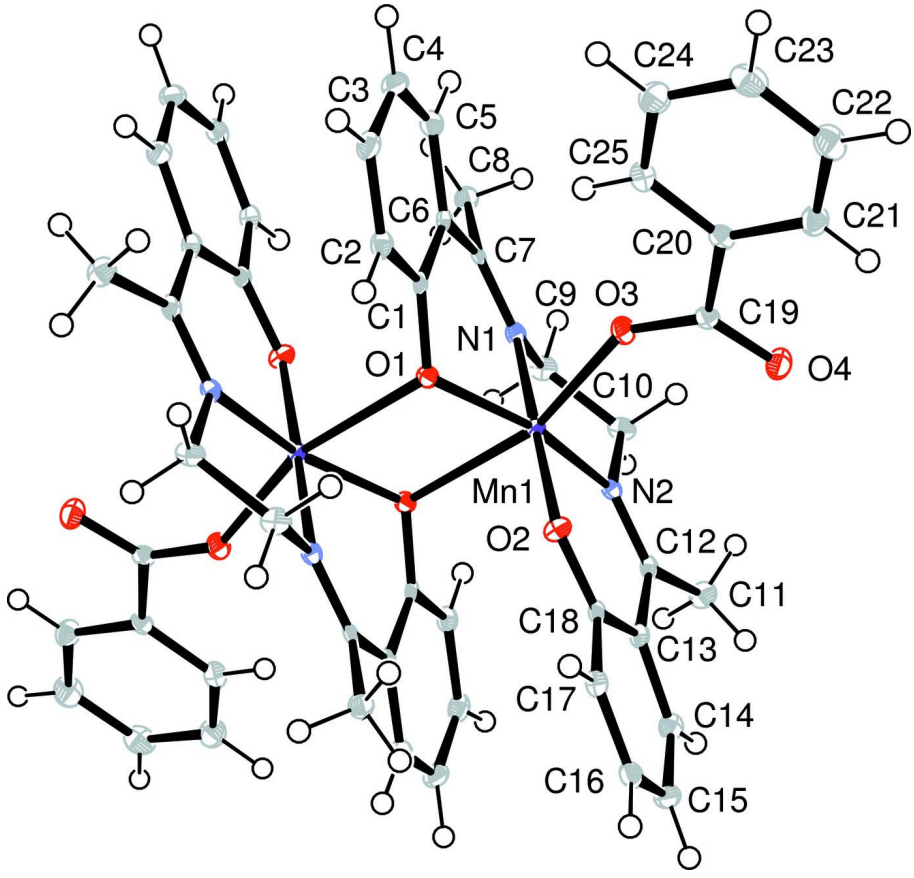

Figure 1

ORTEP picture (Farrugia, 1997) of (1) Displacement ellipsoids have been drawn at the 50% probability level.

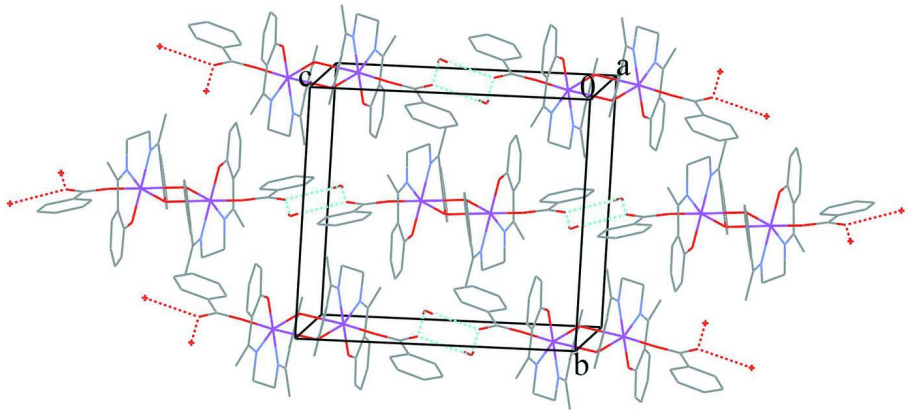

Figure 2

Mercury ball and stick packing diagram (Macrae *et al.*, 2006) of (1) showing hydrogen-bonding chains.

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Crystal data

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$M_r = 976.82$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 12.9376\ (4)$ Å
$b = 12.3983\ (4)$ Å
$c = 13.8470\ (4)$ Å
$\beta = 103.702\ (2)°$
$V = 2157.91\ (11)$ Å^3
$Z = 2$
$F(000) = 1016$
$D_x = 1.503$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 218 reflections
$\theta = 9.6–70.3°$
$\mu = 5.33$ mm^{-1}
$T = 100$ K
Plate, green
0.23 × 0.22 × 0.03 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and Phi scans
Absorption correction: numerical (*SADABS*; Sheldrick, 2004)
$T_{min} = 0.374$, $T_{max} = 0.857$
21968 measured reflections
3711 independent reflections
3465 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 67.0°$, $\theta_{min} = 4.9°$
$h = -15\rightarrow15$
$k = -14\rightarrow14$
$l = -15\rightarrow12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.068$
$S = 1.03$
3711 reflections
398 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 0.9845P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.509469 (18)	0.482743 (19)	0.625826 (18)	0.00737 (9)
O1	0.59764 (8)	0.54044 (9)	0.54335 (8)	0.0097 (2)
O2	0.44338 (8)	0.61250 (8)	0.64417 (8)	0.0115 (2)
O3	0.63962 (9)	0.50305 (9)	0.75151 (8)	0.0141 (3)
O4	0.60249 (9)	0.50899 (10)	0.90102 (9)	0.0171 (3)
O5	0.59404 (11)	0.57505 (11)	0.09578 (10)	0.0243 (3)
N1	0.56577 (10)	0.33741 (10)	0.60493 (9)	0.0097 (3)
N2	0.39511 (10)	0.40011 (10)	0.66981 (9)	0.0093 (3)
C1	0.69961 (12)	0.51025 (13)	0.55995 (11)	0.0095 (3)
C2	0.77582 (13)	0.58879 (14)	0.55177 (12)	0.0123 (3)
C3	0.88167 (13)	0.56196 (15)	0.56395 (12)	0.0149 (4)
C4	0.91550 (14)	0.45594 (15)	0.58562 (12)	0.0165 (4)
C5	0.84191 (13)	0.37768 (14)	0.59350 (12)	0.0146 (4)
C6	0.73315 (12)	0.40178 (13)	0.58058 (11)	0.0103 (3)
C7	0.65666 (12)	0.31506 (13)	0.58595 (11)	0.0100 (3)
C8	0.68401 (14)	0.19971 (14)	0.56750 (13)	0.0133 (3)
C9	0.48612 (13)	0.25258 (13)	0.60535 (13)	0.0134 (3)
C10	0.42002 (13)	0.28324 (13)	0.67791 (13)	0.0129 (3)
C11	0.23512 (14)	0.35696 (14)	0.72628 (14)	0.0155 (4)
C12	0.30861 (12)	0.43524 (13)	0.69174 (11)	0.0102 (3)
C13	0.27896 (12)	0.54987 (13)	0.68234 (11)	0.0109 (3)
C14	0.17770 (13)	0.58263 (14)	0.69292 (12)	0.0134 (3)
C15	0.14654 (13)	0.68915 (14)	0.68857 (12)	0.0148 (3)
C16	0.21835 (13)	0.76876 (14)	0.67560 (12)	0.0135 (3)
C17	0.31734 (13)	0.74033 (13)	0.66321 (12)	0.0119 (3)
C18	0.34894 (12)	0.63105 (13)	0.66258 (11)	0.0097 (3)
C19	0.66321 (13)	0.52194 (12)	0.84366 (12)	0.0106 (3)
C20	0.77494 (12)	0.56330 (12)	0.88745 (12)	0.0110 (3)
C21	0.80612 (14)	0.59426 (14)	0.98683 (13)	0.0164 (4)
C22	0.90820 (14)	0.63329 (15)	1.02608 (14)	0.0213 (4)
C23	0.98022 (14)	0.64194 (15)	0.96662 (14)	0.0204 (4)
C24	0.95039 (14)	0.60999 (15)	0.86776 (14)	0.0193 (4)
C25	0.84822 (13)	0.57172 (13)	0.82813 (13)	0.0146 (3)
H1W	0.5942 (18)	0.551 (2)	0.040 (2)	0.037 (7)*
H2W	0.533 (2)	0.551 (3)	0.104 (2)	0.063 (9)*

H2	0.7503 (14)	0.6633 (16)	0.5367 (13)	0.014 (5)*
H3	0.9297 (16)	0.6167 (16)	0.5540 (14)	0.018 (5)*
H4	0.9887 (17)	0.4374 (17)	0.5946 (15)	0.024 (5)*
H5	0.8668 (14)	0.3032 (16)	0.6101 (13)	0.016 (5)*
H8A	0.6937 (16)	0.1564 (17)	0.6265 (16)	0.026 (5)*
H8B	0.6257 (15)	0.1675 (16)	0.5194 (15)	0.017 (5)*
H8C	0.7486 (16)	0.1934 (16)	0.5453 (14)	0.020 (5)*
H9A	0.5200 (15)	0.1837 (17)	0.6237 (13)	0.018 (5)*
H9B	0.4416 (14)	0.2485 (15)	0.5379 (13)	0.011 (4)*
H10A	0.4591 (15)	0.2663 (16)	0.7458 (15)	0.020 (5)*
H10B	0.3541 (15)	0.2407 (16)	0.6621 (13)	0.016 (5)*
H11A	0.1945 (16)	0.3951 (17)	0.7646 (16)	0.026 (5)*
H11B	0.1857 (17)	0.3241 (18)	0.6685 (16)	0.029 (6)*
H11C	0.2752 (16)	0.3009 (17)	0.7682 (15)	0.023 (5)*
H14	0.1268 (17)	0.5287 (17)	0.7030 (15)	0.022 (5)*
H15	0.0770 (15)	0.7067 (15)	0.6954 (13)	0.012 (4)*
H16	0.1971 (15)	0.8440 (17)	0.6749 (14)	0.018 (5)*
H17	0.3653 (15)	0.7921 (16)	0.6531 (14)	0.016 (5)*
H21	0.7569 (15)	0.5871 (15)	1.0269 (14)	0.016 (5)*
H22	0.9271 (16)	0.6530 (17)	1.0948 (16)	0.028 (6)*
H23	1.0513 (18)	0.6677 (18)	0.9934 (16)	0.032 (6)*
H24	1.0010 (16)	0.6136 (16)	0.8257 (15)	0.024 (5)*
H25	0.8267 (14)	0.5498 (15)	0.7629 (15)	0.014 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.00810 (14)	0.00576 (14)	0.00858 (15)	−0.00092 (9)	0.00260 (10)	0.00002 (9)
O1	0.0091 (5)	0.0097 (5)	0.0101 (6)	−0.0008 (4)	0.0022 (4)	0.0011 (4)
O2	0.0117 (6)	0.0078 (5)	0.0165 (6)	−0.0014 (4)	0.0061 (4)	−0.0006 (4)
O3	0.0144 (6)	0.0169 (6)	0.0100 (6)	−0.0008 (5)	0.0010 (5)	−0.0019 (4)
O4	0.0162 (6)	0.0227 (7)	0.0134 (6)	−0.0035 (5)	0.0052 (5)	−0.0022 (5)
O5	0.0229 (7)	0.0358 (8)	0.0151 (7)	−0.0116 (6)	0.0064 (5)	−0.0064 (6)
N1	0.0119 (7)	0.0080 (7)	0.0089 (7)	−0.0009 (5)	0.0016 (5)	0.0011 (5)
N2	0.0106 (6)	0.0080 (7)	0.0084 (7)	−0.0010 (5)	0.0004 (5)	0.0005 (5)
C1	0.0114 (8)	0.0140 (8)	0.0032 (8)	−0.0020 (6)	0.0020 (6)	−0.0024 (6)
C2	0.0136 (8)	0.0137 (9)	0.0093 (8)	−0.0031 (7)	0.0022 (6)	−0.0010 (6)
C3	0.0130 (8)	0.0213 (9)	0.0110 (8)	−0.0054 (7)	0.0040 (6)	−0.0021 (7)
C4	0.0108 (8)	0.0252 (10)	0.0137 (9)	0.0013 (7)	0.0034 (6)	−0.0026 (7)
C5	0.0156 (8)	0.0175 (9)	0.0105 (8)	0.0026 (7)	0.0026 (6)	−0.0007 (6)
C6	0.0128 (8)	0.0136 (8)	0.0045 (7)	0.0003 (7)	0.0021 (6)	−0.0011 (6)
C7	0.0125 (8)	0.0122 (8)	0.0038 (7)	0.0014 (6)	−0.0009 (6)	0.0010 (6)
C8	0.0162 (9)	0.0114 (8)	0.0127 (9)	0.0023 (7)	0.0044 (7)	−0.0005 (7)
C9	0.0133 (8)	0.0083 (8)	0.0180 (9)	−0.0021 (7)	0.0025 (7)	−0.0010 (6)
C10	0.0121 (8)	0.0077 (8)	0.0184 (9)	−0.0005 (7)	0.0029 (7)	0.0031 (6)
C11	0.0160 (8)	0.0129 (9)	0.0190 (10)	−0.0016 (7)	0.0069 (7)	0.0011 (7)
C12	0.0114 (8)	0.0126 (8)	0.0057 (8)	−0.0031 (6)	0.0002 (6)	−0.0023 (6)
C13	0.0132 (8)	0.0116 (8)	0.0077 (8)	−0.0015 (7)	0.0022 (6)	−0.0014 (6)

C14	0.0121 (8)	0.0158 (9)	0.0118 (8)	−0.0026 (7)	0.0020 (6)	−0.0022 (6)
C15	0.0120 (8)	0.0180 (9)	0.0139 (9)	0.0022 (7)	0.0023 (6)	−0.0024 (7)
C16	0.0176 (8)	0.0122 (8)	0.0098 (8)	0.0029 (7)	0.0012 (6)	−0.0004 (6)
C17	0.0151 (8)	0.0110 (8)	0.0094 (8)	−0.0019 (7)	0.0027 (6)	−0.0003 (6)
C18	0.0119 (8)	0.0114 (8)	0.0052 (8)	−0.0001 (6)	0.0009 (6)	−0.0017 (6)
C19	0.0131 (8)	0.0062 (8)	0.0121 (9)	0.0027 (6)	0.0024 (6)	0.0000 (6)
C20	0.0132 (8)	0.0069 (8)	0.0122 (8)	0.0015 (6)	0.0015 (6)	0.0007 (6)
C21	0.0162 (9)	0.0192 (9)	0.0141 (9)	−0.0020 (7)	0.0041 (7)	−0.0027 (7)
C22	0.0203 (9)	0.0251 (10)	0.0162 (10)	−0.0039 (8)	−0.0006 (7)	−0.0050 (7)
C23	0.0146 (9)	0.0205 (9)	0.0234 (10)	−0.0054 (7)	−0.0008 (7)	0.0008 (7)
C24	0.0173 (9)	0.0212 (10)	0.0205 (10)	−0.0025 (7)	0.0064 (7)	0.0028 (7)
C25	0.0171 (9)	0.0145 (9)	0.0120 (9)	−0.0004 (7)	0.0030 (7)	0.0006 (7)

Geometric parameters (Å, º)

Mn1—O2	1.8673 (11)	C9—C10	1.514 (2)
Mn1—O1	1.9324 (11)	C9—H9A	0.97 (2)
Mn1—N1	1.9903 (13)	C9—H9B	0.976 (18)
Mn1—N2	2.0091 (13)	C10—H10A	0.98 (2)
Mn1—O3	2.1306 (11)	C10—H10B	0.982 (19)
Mn1—O1^{i}	2.4399 (11)	C11—C12	1.513 (2)
O1—C1	1.3377 (19)	C11—H11A	0.96 (2)
O1—Mn1^{i}	2.4398 (11)	C11—H11B	0.99 (2)
O2—C18	1.3259 (19)	C11—H11C	0.97 (2)
O3—C19	1.262 (2)	C12—C13	1.470 (2)
O4—C19	1.253 (2)	C13—C14	1.412 (2)
O5—H1W	0.83 (3)	C13—C18	1.423 (2)
O5—H2W	0.88 (3)	C14—C15	1.378 (2)
N1—C7	1.294 (2)	C14—H14	0.97 (2)
N1—C9	1.473 (2)	C15—C16	1.396 (2)
N2—C12	1.302 (2)	C15—H15	0.951 (18)
N2—C10	1.483 (2)	C16—C17	1.378 (2)
C1—C2	1.409 (2)	C16—H16	0.97 (2)
C1—C6	1.421 (2)	C17—C18	1.416 (2)
C2—C3	1.380 (2)	C17—H17	0.93 (2)
C2—H2	0.987 (19)	C19—C20	1.518 (2)
C3—C4	1.395 (3)	C20—C21	1.393 (2)
C3—H3	0.95 (2)	C20—C25	1.398 (2)
C4—C5	1.382 (3)	C21—C22	1.391 (2)
C4—H4	0.95 (2)	C21—H21	0.94 (2)
C5—C6	1.408 (2)	C22—C23	1.386 (3)
C5—H5	0.99 (2)	C22—H22	0.96 (2)
C6—C7	1.475 (2)	C23—C24	1.389 (3)
C7—C8	1.509 (2)	C23—H23	0.96 (2)
C8—H8A	0.96 (2)	C24—C25	1.389 (2)
C8—H8B	0.97 (2)	C24—H24	0.97 (2)
C8—H8C	0.96 (2)	C25—H25	0.92 (2)

O2—Mn1—O1	96.60 (5)	N1—C9—H9B	106.7 (11)
O2—Mn1—N1	174.25 (5)	C10—C9—H9B	110.5 (10)
O1—Mn1—N1	87.80 (5)	H9A—C9—H9B	109.5 (15)
O2—Mn1—N2	90.25 (5)	N2—C10—C9	109.99 (13)
O1—Mn1—N2	161.46 (5)	N2—C10—H10A	109.6 (12)
N1—Mn1—N2	84.46 (5)	C9—C10—H10A	109.8 (11)
O2—Mn1—O3	94.93 (5)	N2—C10—H10B	110.3 (11)
O1—Mn1—O3	88.63 (5)	C9—C10—H10B	108.3 (11)
N1—Mn1—O3	88.86 (5)	H10A—C10—H10B	108.8 (15)
N2—Mn1—O3	107.99 (5)	C12—C11—H11A	109.1 (13)
O2—Mn1—O1^{i}	93.32 (4)	C12—C11—H11B	110.1 (13)
O1—Mn1—O1^{i}	75.92 (4)	H11A—C11—H11B	108.5 (17)
N1—Mn1—O1^{i}	84.14 (4)	C12—C11—H11C	111.2 (12)
N2—Mn1—O1^{i}	86.53 (4)	H11A—C11—H11C	107.9 (17)
O3—Mn1—O1^{i}	163.22 (4)	H11B—C11—H11C	109.9 (17)
C1—O1—Mn1	119.41 (9)	N2—C12—C13	121.56 (14)
C1—O1—Mn1^{i}	116.41 (9)	N2—C12—C11	119.88 (15)
Mn1—O1—Mn1^{i}	104.08 (4)	C13—C12—C11	118.55 (14)
C18—O2—Mn1	130.40 (10)	C14—C13—C18	117.69 (15)
C19—O3—Mn1	143.43 (11)	C14—C13—C12	119.87 (14)
H1W—O5—H2W	101 (2)	C18—C13—C12	122.44 (14)
C7—N1—C9	121.19 (14)	C15—C14—C13	122.70 (16)
C7—N1—Mn1	127.22 (11)	C15—C14—H14	117.7 (12)
C9—N1—Mn1	111.42 (10)	C13—C14—H14	119.6 (12)
C12—N2—C10	119.51 (13)	C14—C15—C16	119.12 (16)
C12—N2—Mn1	129.45 (11)	C14—C15—H15	119.2 (11)
C10—N2—Mn1	111.03 (10)	C16—C15—H15	121.7 (11)
O1—C1—C2	118.23 (14)	C17—C16—C15	120.11 (16)
O1—C1—C6	122.75 (14)	C17—C16—H16	120.9 (12)
C2—C1—C6	118.94 (15)	C15—C16—H16	119.0 (12)
C3—C2—C1	121.10 (16)	C16—C17—C18	121.60 (15)
C3—C2—H2	121.6 (11)	C16—C17—H17	121.2 (12)
C1—C2—H2	117.3 (11)	C18—C17—H17	117.2 (12)
C2—C3—C4	120.32 (16)	O2—C18—C17	116.60 (14)
C2—C3—H3	118.2 (12)	O2—C18—C13	124.85 (14)
C4—C3—H3	121.4 (12)	C17—C18—C13	118.55 (14)
C5—C4—C3	119.44 (16)	O4—C19—O3	125.43 (15)
C5—C4—H4	120.1 (13)	O4—C19—C20	118.09 (14)
C3—C4—H4	120.5 (13)	O3—C19—C20	116.48 (14)
C4—C5—C6	121.85 (16)	C21—C20—C25	118.81 (15)
C4—C5—H5	118.8 (11)	C21—C20—C19	120.87 (15)
C6—C5—H5	119.3 (11)	C25—C20—C19	120.32 (14)
C5—C6—C1	118.34 (15)	C22—C21—C20	120.53 (16)
C5—C6—C7	120.08 (15)	C22—C21—H21	120.9 (12)
C1—C6—C7	121.56 (14)	C20—C21—H21	118.5 (12)
N1—C7—C6	120.45 (14)	C23—C22—C21	120.30 (17)
N1—C7—C8	119.86 (14)	C23—C22—H22	121.5 (13)
C6—C7—C8	119.68 (14)	C21—C22—H22	118.2 (13)

C7—C8—H8A	112.0 (12)	C22—C23—C24	119.63 (16)
C7—C8—H8B	109.4 (11)	C22—C23—H23	120.9 (13)
H8A—C8—H8B	106.2 (16)	C24—C23—H23	119.5 (13)
C7—C8—H8C	112.9 (12)	C25—C24—C23	120.20 (16)
H8A—C8—H8C	106.1 (17)	C25—C24—H24	119.3 (12)
H8B—C8—H8C	110.0 (16)	C23—C24—H24	120.5 (12)
N1—C9—C10	109.20 (13)	C24—C25—C20	120.51 (16)
N1—C9—H9A	111.0 (11)	C24—C25—H25	121.7 (12)
C10—C9—H9A	109.9 (11)	C20—C25—H25	117.7 (12)

O2—Mn1—O1—C1	136.33 (11)	O1—C1—C6—C7	−0.6 (2)
N1—Mn1—O1—C1	−47.38 (11)	C2—C1—C6—C7	−177.45 (14)
N2—Mn1—O1—C1	−112.66 (17)	C9—N1—C7—C6	176.72 (14)
O3—Mn1—O1—C1	41.53 (11)	Mn1—N1—C7—C6	1.8 (2)
O1^{i}—Mn1—O1—C1	−131.89 (12)	C9—N1—C7—C8	−2.3 (2)
O2—Mn1—O1—Mn1^{i}	−91.78 (5)	Mn1—N1—C7—C8	−177.14 (11)
N1—Mn1—O1—Mn1^{i}	84.51 (5)	C5—C6—C7—N1	158.58 (15)
N2—Mn1—O1—Mn1^{i}	19.23 (17)	C1—C6—C7—N1	−23.0 (2)
O3—Mn1—O1—Mn1^{i}	173.42 (5)	C5—C6—C7—C8	−22.4 (2)
O1^{i}—Mn1—O1—Mn1^{i}	0.0	C1—C6—C7—C8	155.94 (15)
O1—Mn1—O2—C18	153.11 (13)	C7—N1—C9—C10	150.24 (14)
N2—Mn1—O2—C18	−9.62 (13)	Mn1—N1—C9—C10	−34.14 (15)
O3—Mn1—O2—C18	−117.70 (13)	C12—N2—C10—C9	152.00 (14)
O1^{i}—Mn1—O2—C18	76.92 (13)	Mn1—N2—C10—C9	−28.88 (15)
O2—Mn1—O3—C19	52.96 (17)	N1—C9—C10—N2	40.92 (17)
O1—Mn1—O3—C19	149.46 (17)	C10—N2—C12—C13	−178.33 (13)
N1—Mn1—O3—C19	−122.71 (17)	Mn1—N2—C12—C13	2.7 (2)
N2—Mn1—O3—C19	−38.91 (18)	C10—N2—C12—C11	0.7 (2)
O1^{i}—Mn1—O3—C19	172.10 (15)	Mn1—N2—C12—C11	−178.26 (11)
O1—Mn1—N1—C7	26.94 (13)	N2—C12—C13—C14	170.91 (15)
N2—Mn1—N1—C7	−169.93 (14)	C11—C12—C13—C14	−8.1 (2)
O3—Mn1—N1—C7	−61.73 (13)	N2—C12—C13—C18	−9.0 (2)
O1^{i}—Mn1—N1—C7	103.00 (13)	C11—C12—C13—C18	171.94 (15)
O1—Mn1—N1—C9	−148.35 (11)	C18—C13—C14—C15	−2.5 (2)
N2—Mn1—N1—C9	14.78 (10)	C12—C13—C14—C15	177.56 (15)
O3—Mn1—N1—C9	122.98 (11)	C13—C14—C15—C16	−1.6 (2)
O1^{i}—Mn1—N1—C9	−72.29 (10)	C14—C15—C16—C17	2.7 (2)
O2—Mn1—N2—C12	4.96 (14)	C15—C16—C17—C18	0.4 (2)
O1—Mn1—N2—C12	−107.01 (19)	Mn1—O2—C18—C17	−174.08 (10)
N1—Mn1—N2—C12	−172.79 (14)	Mn1—O2—C18—C13	6.5 (2)
O3—Mn1—N2—C12	100.22 (13)	C16—C17—C18—O2	176.07 (14)
O1^{i}—Mn1—N2—C12	−88.34 (13)	C16—C17—C18—C13	−4.5 (2)
O2—Mn1—N2—C10	−174.04 (10)	C14—C13—C18—O2	−175.22 (14)
O1—Mn1—N2—C10	73.98 (19)	C12—C13—C18—O2	4.7 (2)
N1—Mn1—N2—C10	8.21 (10)	C14—C13—C18—C17	5.4 (2)
O3—Mn1—N2—C10	−78.78 (10)	C12—C13—C18—C17	−174.64 (14)
O1^{i}—Mn1—N2—C10	92.65 (10)	Mn1—O3—C19—O4	20.1 (3)
Mn1—O1—C1—C2	−140.61 (12)	Mn1—O3—C19—C20	−160.12 (12)

Mn1^{i}—O1—C1—C2	93.12 (14)	O4—C19—C20—C21	−5.1 (2)
Mn1—O1—C1—C6	42.54 (18)	O3—C19—C20—C21	175.11 (15)
Mn1^{i}—O1—C1—C6	−83.74 (15)	O4—C19—C20—C25	175.36 (15)
O1—C1—C2—C3	−177.31 (14)	O3—C19—C20—C25	−4.4 (2)
C6—C1—C2—C3	−0.3 (2)	C25—C20—C21—C22	0.3 (3)
C1—C2—C3—C4	−0.6 (2)	C19—C20—C21—C22	−179.22 (15)
C2—C3—C4—C5	0.8 (2)	C20—C21—C22—C23	0.1 (3)
C3—C4—C5—C6	−0.2 (2)	C21—C22—C23—C24	−0.9 (3)
C4—C5—C6—C1	−0.7 (2)	C22—C23—C24—C25	1.4 (3)
C4—C5—C6—C7	177.73 (15)	C23—C24—C25—C20	−1.0 (3)
O1—C1—C6—C5	177.78 (14)	C21—C20—C25—C24	0.2 (2)
C2—C1—C6—C5	0.9 (2)	C19—C20—C25—C24	179.70 (15)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H1*W*···O4^{ii}	0.83 (3)	2.02 (3)	2.8452 (19)	173 (2)
O5—H2*W*···O4^{i}	0.88 (3)	1.89 (3)	2.7579 (18)	171 (3)

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