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Aqua{2,2-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}(3-nitrobenzoato)manganese(III)

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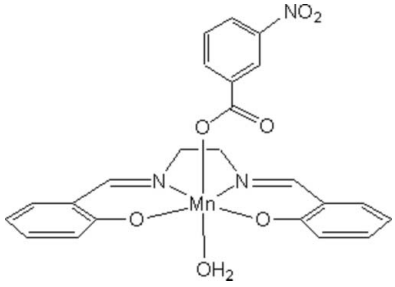
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.035; wR factor = 0.093; data-to-parameter ratio = 11.8.

The title compound, $[Mn(C_{16}H_{14}N_2O_2)(C_7H_4NO_4)(H_2O)]$, is a Jahn–Teller-distorted manganese(III) monomer with an octahedral geometry. The tetradentate Schiff base accommodates the Mn^{III} ion at the centre of a nearly planar square. The axial positions are occupied by a monodentate carboxylate group and a water molecule. Adjacent monomers interact through hydrogen bonding between the noncoordinated C=O group of the carboxylate and the coordinated water molecule to produce chains extending parallel to the b axis.

Related literature

For related literature, see: Christou (1989); Pecoraro & Hsieh (2000); Yocum & Pecoraro (2004); Zhang & Janiak (2001); Zouni *et al.* (2001); Aurangzeb *et al.* (1994); Hulme *et al.* (1997).



Experimental

Crystal data

$[Mn(C_{16}H_{14}N_2O_2)(C_7H_4NO_4)(H_2O)]$
M_r = 505.36
Monoclinic, $P2_1/n$
a = 6.7297 (1) Å
b = 10.5793 (2) Å
c = 29.228 (5) Å
β = 95.188 (1)°
V = 2072.4 (4) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 5.66 mm^{-1}
T = 100 (2) K
0.35 × 0.29 × 0.09 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.245, T_{max} = 0.624
21257 measured reflections
3640 independent reflections
3492 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.092
S = 1.11
3640 reflections
308 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	1.8879 (15)	Mn1—N1	1.9980 (18)
Mn1—O2	1.9113 (15)	Mn1—O3	2.1513 (15)
Mn1—N2	1.9946 (18)	Mn1—O7	2.3250 (16)
O1—Mn1—O2	97.25 (7)	N2—Mn1—O3	91.40 (7)
O1—Mn1—N2	171.26 (7)	N1—Mn1—O3	89.75 (7)
O2—Mn1—N2	91.15 (7)	O1—Mn1—O7	90.07 (6)
O1—Mn1—N1	90.20 (7)	O2—Mn1—O7	91.54 (6)
O2—Mn1—N1	172.54 (7)	N2—Mn1—O7	87.29 (6)
N2—Mn1—N1	81.42 (7)	N1—Mn1—O7	88.85 (6)
O1—Mn1—O3	91.05 (6)	O3—Mn1—O7	178.21 (6)
O2—Mn1—O3	89.70 (6)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H2W···O2^{i}	0.77	2.31	3.074 (2)	172
O7—H1W···O4^{ii}	0.84	1.89	2.710 (2)	166

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, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *XSHELL* (Bruker, 2004); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.* 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2096).

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supplementary materials

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Aqua{2,2-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}(3-nitrobenzoato)manganese(III)

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Comment

Manganese plays a vital role in several biological systems like the oxygen-evolving complex (OEC) of photosystem II (Zouni *et al.*, 2001) and enzymes like superoxide dismutase, catalase, arginase etc. (Yocum & Pecoraro, 2004). The progress in elucidating the structural and functional aspects of the active-sites of these manganese-containing systems, has essentially been connected to the vast number of inorganic model complexes reported during the last few decades (Christou, 1989; Pecoraro & Hsieh, 2000). Recent reports include a few Schiff base complexes of manganese(III) with ancillary carboxylate ligands (Aurangzeb *et al.*, 1994, Hulme *et al.*, 1997; Zhang & Janiak, 2001). Generally, symmetrical N_2O_2 Schiff base ligands like the salen(H_2salen = N,N'-bis(salicylidene)-1,2-diaminoethane), with aromatic rings amenable to π-π overlap, tend to stabilize μ-phenoxy dimers. Here we report a very rare structural type among such complexes, where the trans coordination positions in an octahedral manganese(III) monomer are occupied by a neutral ligand (H_2O) and a monodentate carboxylate group (Fig. 1).

In the title compound, the salen ligand holds the manganese(III) ion at the centre of a nearly planar tetragon consisting of two Mn–O bonds [Mn(1)-O(1) = 1.8879 (15) Å and Mn(1)-O(2) = 1.9113 (15) Å] and two Mn–N bonds [Mn(1)-N(1) = 1.9980 (18) Å and Mn(1)-N(2) = 1.9946 (18)Å]. These bond lengths are comparable to those in complexes containing similar MnN_2O_2 cores (Aurangzeb *et al.*, 1994; Hulme *et al.*, 1997). Jahn-Teller distortion causes an elongation of the Mn–Ocarb [Mn(1)-O(3) = 2.1513 (15) Å] and the Mn–Oaq [Mn(1)-O(7) = 2.3250 (16) Å] axial bonds (Table 1). Chains running parallel to the *b*-axis arise from H-bonding interactions between the non-coordinated O atom of the carboxylate and coordinated water molecules on adjacent molecules (Fig.2, Table 2).

Experimental

To a solution of Mn(m—$NO_2C_6H_4CO_2)_2.2H_2O$ (1.00 g, 2.36 mmol) and salicylaldehyde (0.58 g, 4.72 mmol) in methanol (40 ml), ethane-1,2-diamine (0.14 g, 2.36 mmol) was added. The solution was stirred for 20 minutes, filtered and left to evaporation in an open conical flask. Brown crystals were deposited in 2–3 days. These were collected by filtration, washed with methanol, and dried in air. Yield of the title compound was 0.82 g (75.50%) based on manganese.

Refinement

All hydrogen atoms were initially located in the difference map and then were placed in theoretical positions using a riding model for all but the water H atoms which were allowed to rotate freely, O–H = 0.77 and 0.84 Å. Csp^2–H = 0.95 Å, Csp^3–H = 0.99 Å, U_{iso}(H) = 1.2U_{eq}(C,O).

Figures

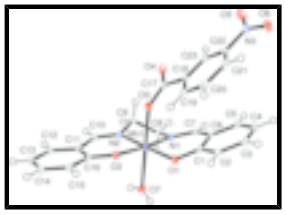

Fig. 1. *ORTEP* picture (Farrugia, 1997) of the title compound. Displacement ellipsoids have been drawn at the 50% probability level.

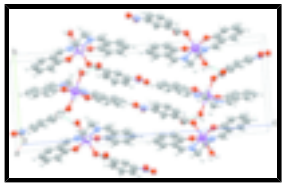

Fig. 2. Mercury (Macrae *et al.* 2006) ball and stick packing diagram of the title compound showing hydrogen-bonding chains.

Aqua{2,2-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}(3- nitrobenzoato)manganese(III)

Crystal data

$[Mn(C_{16}H_{14}N_2O_2)(C_7H_4NO_4)(H_2O)]$	F_{000} = 1040
M_r = 505.36	D_x = 1.620 Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation λ = 1.54178 Å
a = 6.7297 (1) Å	Cell parameters from 256 reflections
b = 10.5793 (2) Å	θ = 9.7–70.9º
c = 29.228 (5) Å	μ = 5.66 mm^{-1}
β = 95.188 (1)º	T = 100 (2) K
V = 2072.4 (4) Å^3	Plate, brown
Z = 4	0.35 × 0.29 × 0.09 mm

Data collection

Bruker SMART APEXII CCD diffractometer	3640 independent reflections
Radiation source: fine-focus sealed tube	3492 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.046
T = 100(2) K	θ_{max} = 67.0º
ω and ψ scans	θ_{min} = 3.0º
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	h = −7→7
T_{min} = 0.245, T_{max} = 0.624	k = −10→12
21257 measured reflections	l = −31→34

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.035$	H-atom parameters constrained
$wR(F^2) = 0.092$	$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 2.1055P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
3640 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
308 parameters	$\Delta\rho_{min} = -0.51$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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}
Mn1	−0.00146 (5)	0.54194 (3)	0.229187 (11)	0.01142 (12)
O1	−0.2188 (2)	0.55831 (14)	0.18400 (5)	0.0155 (3)
O2	−0.1396 (2)	0.45279 (14)	0.27355 (5)	0.0147 (3)
O3	0.0816 (2)	0.36457 (14)	0.20036 (5)	0.0171 (3)
O4	0.3542 (2)	0.32126 (15)	0.16477 (5)	0.0197 (4)
O5	0.2710 (3)	0.15274 (18)	0.00870 (6)	0.0311 (4)
O6	−0.0245 (3)	0.12490 (17)	−0.02568 (5)	0.0282 (4)
O7	−0.0810 (2)	0.73579 (15)	0.26027 (5)	0.0190 (3)
H1W	0.0052	0.7545	0.2818	0.023*
H2W	−0.1592	0.7863	0.2531	0.023*
N1	0.1747 (3)	0.63243 (16)	0.18849 (6)	0.0133 (4)
N2	0.2479 (3)	0.54511 (16)	0.27161 (6)	0.0129 (4)
N3	0.0896 (3)	0.15170 (18)	0.00848 (6)	0.0220 (5)
C1	−0.2066 (3)	0.5574 (2)	0.13906 (8)	0.0149 (5)
C2	−0.3747 (3)	0.5194 (2)	0.11019 (8)	0.0171 (5)
H2	−0.4930	0.4950	0.1233	0.020*
C3	−0.3700 (4)	0.5173 (2)	0.06299 (8)	0.0223 (5)
H3	−0.4848	0.4907	0.0442	0.027*
C4	−0.1991 (4)	0.5536 (2)	0.04252 (8)	0.0239 (5)
H4	−0.1976	0.5519	0.0101	0.029*
C5	−0.0333 (4)	0.5917 (2)	0.06989 (8)	0.0202 (5)
H5	0.0831	0.6167	0.0561	0.024*
C6	−0.0331 (3)	0.5945 (2)	0.11816 (7)	0.0150 (4)
C7	0.1445 (3)	0.63864 (19)	0.14441 (7)	0.0141 (4)

H7	0.2464	0.6748	0.1281	0.017*
C8	0.3601 (3)	0.6801 (2)	0.21297 (7)	0.0159 (5)
H8A	0.3362	0.7622	0.2278	0.019*
H8B	0.4639	0.6920	0.1914	0.019*
C9	0.4256 (3)	0.5815 (2)	0.24879 (7)	0.0153 (4)
H9A	0.4818	0.5070	0.2341	0.018*
H9B	0.5291	0.6168	0.2715	0.018*
C10	0.2631 (3)	0.5163 (2)	0.31447 (7)	0.0138 (4)
H10	0.3899	0.5276	0.3310	0.017*
C11	0.1053 (3)	0.46869 (19)	0.33948 (7)	0.0143 (4)
C12	0.1515 (4)	0.4424 (2)	0.38667 (8)	0.0173 (5)
H12	0.2813	0.4611	0.4006	0.021*
C13	0.0131 (4)	0.3906 (2)	0.41291 (7)	0.0197 (5)
H13	0.0454	0.3749	0.4447	0.024*
C14	−0.1764 (4)	0.3614 (2)	0.39192 (8)	0.0184 (5)
H14	−0.2734	0.3258	0.4098	0.022*
C15	−0.2250 (3)	0.3835 (2)	0.34569 (7)	0.0157 (4)
H15	−0.3541	0.3615	0.3322	0.019*
C16	−0.0877 (3)	0.43777 (19)	0.31824 (7)	0.0134 (4)
C17	0.1704 (3)	0.32348 (19)	0.16688 (7)	0.0142 (4)
C18	0.0387 (3)	0.26862 (19)	0.12698 (7)	0.0140 (4)
C19	−0.1613 (3)	0.2428 (2)	0.13095 (8)	0.0173 (5)
H19	−0.2185	0.2639	0.1585	0.021*
C20	−0.2791 (4)	0.1861 (2)	0.09498 (8)	0.0200 (5)
H20	−0.4151	0.1676	0.0984	0.024*
C21	−0.1988 (4)	0.1569 (2)	0.05438 (8)	0.0197 (5)
H21	−0.2780	0.1188	0.0296	0.024*
C22	−0.0006 (3)	0.1846 (2)	0.05094 (7)	0.0166 (5)
C23	0.1219 (3)	0.2390 (2)	0.08636 (7)	0.0155 (4)
H23	0.2586	0.2556	0.0830	0.019*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0138 (2)	0.01245 (19)	0.00759 (19)	−0.00076 (13)	−0.00106 (13)	0.00132 (12)
O1	0.0173 (8)	0.0190 (8)	0.0097 (8)	0.0005 (6)	−0.0012 (6)	0.0015 (6)
O2	0.0182 (8)	0.0155 (8)	0.0099 (7)	−0.0004 (6)	−0.0023 (6)	0.0019 (6)
O3	0.0262 (9)	0.0129 (8)	0.0121 (8)	0.0011 (6)	0.0018 (6)	−0.0013 (6)
O4	0.0206 (9)	0.0241 (9)	0.0137 (8)	−0.0041 (7)	−0.0018 (6)	0.0007 (6)
O5	0.0317 (11)	0.0424 (11)	0.0198 (9)	0.0022 (8)	0.0059 (7)	−0.0056 (8)
O6	0.0443 (11)	0.0275 (9)	0.0113 (8)	−0.0043 (8)	−0.0053 (7)	−0.0036 (7)
O7	0.0211 (9)	0.0181 (8)	0.0161 (8)	0.0047 (6)	−0.0063 (6)	−0.0028 (6)
N1	0.0163 (9)	0.0107 (9)	0.0128 (9)	0.0004 (7)	0.0004 (7)	0.0000 (7)
N2	0.0162 (10)	0.0096 (9)	0.0128 (9)	0.0004 (7)	−0.0003 (7)	−0.0009 (7)
N3	0.0357 (13)	0.0190 (10)	0.0109 (10)	0.0011 (9)	−0.0007 (8)	−0.0005 (8)
C1	0.0208 (12)	0.0104 (10)	0.0130 (11)	0.0025 (8)	−0.0016 (9)	0.0014 (8)
C2	0.0195 (12)	0.0153 (11)	0.0156 (11)	0.0006 (9)	−0.0025 (9)	0.0019 (9)
C3	0.0275 (13)	0.0222 (12)	0.0153 (12)	0.0000 (10)	−0.0081 (9)	−0.0016 (9)

C4	0.0343 (14)	0.0269 (13)	0.0096 (11)	0.0018 (10)	−0.0026 (10)	−0.0007 (9)
C5	0.0283 (13)	0.0180 (12)	0.0146 (11)	0.0027 (10)	0.0036 (9)	0.0015 (9)
C6	0.0224 (12)	0.0106 (10)	0.0117 (10)	0.0024 (9)	−0.0010 (8)	0.0009 (8)
C7	0.0201 (12)	0.0076 (10)	0.0151 (11)	0.0013 (8)	0.0042 (8)	0.0016 (8)
C8	0.0192 (11)	0.0124 (11)	0.0160 (11)	−0.0031 (8)	0.0008 (9)	−0.0005 (8)
C9	0.0142 (11)	0.0150 (11)	0.0165 (11)	−0.0004 (9)	0.0001 (8)	−0.0003 (9)
C10	0.0172 (11)	0.0099 (10)	0.0131 (11)	0.0003 (8)	−0.0042 (8)	−0.0022 (8)
C11	0.0215 (12)	0.0105 (10)	0.0106 (11)	0.0011 (8)	−0.0011 (8)	−0.0017 (8)
C12	0.0244 (12)	0.0136 (11)	0.0128 (11)	0.0005 (9)	−0.0043 (9)	−0.0009 (8)
C13	0.0337 (14)	0.0159 (11)	0.0088 (10)	−0.0018 (10)	−0.0022 (9)	0.0000 (8)
C14	0.0281 (13)	0.0134 (11)	0.0141 (11)	−0.0028 (9)	0.0046 (9)	−0.0009 (8)
C15	0.0201 (11)	0.0128 (10)	0.0140 (11)	0.0004 (9)	−0.0002 (8)	−0.0010 (8)
C16	0.0222 (12)	0.0083 (10)	0.0093 (10)	0.0026 (8)	−0.0001 (8)	−0.0011 (8)
C17	0.0230 (13)	0.0092 (10)	0.0100 (10)	−0.0020 (8)	−0.0008 (8)	0.0021 (8)
C18	0.0215 (12)	0.0091 (10)	0.0108 (10)	0.0015 (8)	−0.0024 (8)	0.0013 (8)
C19	0.0218 (12)	0.0135 (11)	0.0166 (11)	0.0022 (9)	0.0022 (9)	0.0004 (8)
C20	0.0165 (11)	0.0191 (12)	0.0237 (12)	−0.0005 (9)	−0.0024 (9)	0.0009 (9)
C21	0.0260 (13)	0.0158 (11)	0.0158 (11)	−0.0019 (9)	−0.0073 (9)	−0.0013 (9)
C22	0.0260 (12)	0.0124 (11)	0.0108 (10)	0.0019 (9)	−0.0016 (9)	−0.0003 (8)
C23	0.0191 (11)	0.0129 (10)	0.0140 (11)	−0.0006 (8)	−0.0018 (8)	0.0014 (8)

Geometric parameters (Å, °)

Mn1—O1	1.8879 (15)	C7—H7	0.9500
Mn1—O2	1.9113 (15)	C8—C9	1.515 (3)
Mn1—N2	1.9946 (18)	C8—H8A	0.9900
Mn1—N1	1.9980 (18)	C8—H8B	0.9900
Mn1—O3	2.1513 (15)	C9—H9A	0.9900
Mn1—O7	2.3250 (16)	C9—H9B	0.9900
O1—C1	1.324 (3)	C10—C11	1.434 (3)
O2—C16	1.331 (3)	C10—H10	0.9500
O3—C17	1.269 (3)	C11—C12	1.414 (3)
O4—C17	1.244 (3)	C11—C16	1.426 (3)
O5—N3	1.220 (3)	C12—C13	1.373 (3)
O6—N3	1.236 (3)	C12—H12	0.9500
O7—H1W	0.8400	C13—C14	1.399 (3)
O7—H2W	0.7659	C13—H13	0.9500
N1—C7	1.288 (3)	C14—C15	1.381 (3)
N1—C8	1.471 (3)	C14—H14	0.9500
N2—C10	1.284 (3)	C15—C16	1.400 (3)
N2—C9	1.472 (3)	C15—H15	0.9500
N3—C22	1.472 (3)	C17—C18	1.515 (3)
C1—C2	1.408 (3)	C18—C19	1.389 (3)
C1—C6	1.421 (3)	C18—C23	1.393 (3)
C2—C3	1.383 (3)	C19—C20	1.394 (3)
C2—H2	0.9500	C19—H19	0.9500
C3—C4	1.397 (4)	C20—C21	1.383 (3)
C3—H3	0.9500	C20—H20	0.9500
C4—C5	1.374 (3)	C21—C22	1.378 (3)

C4—H4	0.9500	C21—H21	0.9500
C5—C6	1.411 (3)	C22—C23	1.389 (3)
C5—H5	0.9500	C23—H23	0.9500
C6—C7	1.439 (3)		
O1—Mn1—O2	97.25 (7)	C9—C8—H8A	110.5
O1—Mn1—N2	171.26 (7)	N1—C8—H8B	110.5
O2—Mn1—N2	91.15 (7)	C9—C8—H8B	110.5
O1—Mn1—N1	90.20 (7)	H8A—C8—H8B	108.7
O2—Mn1—N1	172.54 (7)	N2—C9—C8	107.21 (17)
N2—Mn1—N1	81.42 (7)	N2—C9—H9A	110.3
O1—Mn1—O3	91.05 (6)	C8—C9—H9A	110.3
O2—Mn1—O3	89.70 (6)	N2—C9—H9B	110.3
N2—Mn1—O3	91.40 (7)	C8—C9—H9B	110.3
N1—Mn1—O3	89.75 (7)	H9A—C9—H9B	108.5
O1—Mn1—O7	90.07 (6)	N2—C10—C11	125.7 (2)
O2—Mn1—O7	91.54 (6)	N2—C10—H10	117.2
N2—Mn1—O7	87.29 (6)	C11—C10—H10	117.2
N1—Mn1—O7	88.85 (6)	C12—C11—C16	119.4 (2)
O3—Mn1—O7	178.21 (6)	C12—C11—C10	117.3 (2)
C1—O1—Mn1	125.44 (14)	C16—C11—C10	123.1 (2)
C16—O2—Mn1	128.63 (14)	C13—C12—C11	121.5 (2)
C17—O3—Mn1	139.29 (14)	C13—C12—H12	119.2
Mn1—O7—H1W	109.5	C11—C12—H12	119.2
Mn1—O7—H2W	133.3	C12—C13—C14	118.7 (2)
H1W—O7—H2W	116.8	C12—C13—H13	120.6
C7—N1—C8	121.31 (19)	C14—C13—H13	120.6
C7—N1—Mn1	124.86 (15)	C15—C14—C13	121.2 (2)
C8—N1—Mn1	113.44 (13)	C15—C14—H14	119.4
C10—N2—C9	120.50 (19)	C13—C14—H14	119.4
C10—N2—Mn1	126.20 (16)	C14—C15—C16	121.3 (2)
C9—N2—Mn1	113.27 (13)	C14—C15—H15	119.3
O5—N3—O6	123.7 (2)	C16—C15—H15	119.3
O5—N3—C22	118.83 (19)	O2—C16—C15	118.9 (2)
O6—N3—C22	117.5 (2)	O2—C16—C11	123.2 (2)
O1—C1—C2	118.6 (2)	C15—C16—C11	117.8 (2)
O1—C1—C6	123.5 (2)	O4—C17—O3	125.8 (2)
C2—C1—C6	117.9 (2)	O4—C17—C18	118.00 (19)
C3—C2—C1	120.9 (2)	O3—C17—C18	116.17 (19)
C3—C2—H2	119.6	C19—C18—C23	119.6 (2)
C1—C2—H2	119.6	C19—C18—C17	121.01 (19)
C2—C3—C4	121.1 (2)	C23—C18—C17	119.3 (2)
C2—C3—H3	119.4	C18—C19—C20	120.8 (2)
C4—C3—H3	119.4	C18—C19—H19	119.6
C5—C4—C3	119.2 (2)	C20—C19—H19	119.6
C5—C4—H4	120.4	C21—C20—C19	120.3 (2)
C3—C4—H4	120.4	C21—C20—H20	119.9
C4—C5—C6	121.0 (2)	C19—C20—H20	119.9
C4—C5—H5	119.5	C22—C21—C20	118.1 (2)
C6—C5—H5	119.5	C22—C21—H21	121.0

C5—C6—C1	119.9 (2)	C20—C21—H21	121.0
C5—C6—C7	117.7 (2)	C21—C22—C23	123.2 (2)
C1—C6—C7	122.4 (2)	C21—C22—N3	119.2 (2)
N1—C7—C6	124.4 (2)	C23—C22—N3	117.6 (2)
N1—C7—H7	117.8	C22—C23—C18	118.1 (2)
C6—C7—H7	117.8	C22—C23—H23	121.0
N1—C8—C9	106.32 (17)	C18—C23—H23	121.0
N1—C8—H8A	110.5		
O2—Mn1—O1—C1	−146.55 (16)	C2—C1—C6—C7	178.0 (2)
N2—Mn1—O1—C1	49.5 (5)	C8—N1—C7—C6	−179.76 (19)
N1—Mn1—O1—C1	33.04 (17)	Mn1—N1—C7—C6	7.9 (3)
O3—Mn1—O1—C1	−56.72 (16)	C5—C6—C7—N1	−171.5 (2)
O7—Mn1—O1—C1	121.89 (16)	C1—C6—C7—N1	10.2 (3)
O1—Mn1—O2—C16	−161.93 (17)	C7—N1—C8—C9	−136.1 (2)
N2—Mn1—O2—C16	15.66 (17)	Mn1—N1—C8—C9	37.1 (2)
N1—Mn1—O2—C16	21.3 (6)	C10—N2—C9—C8	−145.69 (19)
O3—Mn1—O2—C16	107.05 (17)	Mn1—N2—C9—C8	35.9 (2)
O7—Mn1—O2—C16	−71.66 (17)	N1—C8—C9—N2	−45.6 (2)
O1—Mn1—O3—C17	78.3 (2)	C9—N2—C10—C11	−174.05 (19)
O2—Mn1—O3—C17	175.5 (2)	Mn1—N2—C10—C11	4.1 (3)
N2—Mn1—O3—C17	−93.3 (2)	N2—C10—C11—C12	180.0 (2)
N1—Mn1—O3—C17	−11.9 (2)	N2—C10—C11—C16	5.2 (3)
O7—Mn1—O3—C17	−50.6 (19)	C16—C11—C12—C13	−1.6 (3)
O1—Mn1—N1—C7	−24.13 (18)	C10—C11—C12—C13	−176.7 (2)
O2—Mn1—N1—C7	152.7 (5)	C11—C12—C13—C14	1.2 (3)
N2—Mn1—N1—C7	158.36 (18)	C12—C13—C14—C15	0.2 (3)
O3—Mn1—N1—C7	66.92 (18)	C13—C14—C15—C16	−1.0 (3)
O7—Mn1—N1—C7	−114.20 (18)	Mn1—O2—C16—C15	171.22 (14)
O1—Mn1—N1—C8	162.98 (14)	Mn1—O2—C16—C11	−11.9 (3)
O2—Mn1—N1—C8	−20.2 (6)	C14—C15—C16—O2	177.58 (19)
N2—Mn1—N1—C8	−14.53 (14)	C14—C15—C16—C11	0.5 (3)
O3—Mn1—N1—C8	−105.98 (14)	C12—C11—C16—O2	−176.14 (19)
O7—Mn1—N1—C8	72.91 (14)	C10—C11—C16—O2	−1.4 (3)
O1—Mn1—N2—C10	152.3 (4)	C12—C11—C16—C15	0.8 (3)
O2—Mn1—N2—C10	−11.72 (18)	C10—C11—C16—C15	175.50 (19)
N1—Mn1—N2—C10	169.01 (19)	Mn1—O3—C17—O4	77.7 (3)
O3—Mn1—N2—C10	−101.45 (18)	Mn1—O3—C17—C18	−104.5 (2)
O7—Mn1—N2—C10	79.77 (18)	O4—C17—C18—C19	165.9 (2)
O1—Mn1—N2—C9	−29.4 (5)	O3—C17—C18—C19	−12.1 (3)
O2—Mn1—N2—C9	166.56 (14)	O4—C17—C18—C23	−11.5 (3)
N1—Mn1—N2—C9	−12.70 (14)	O3—C17—C18—C23	170.54 (19)
O3—Mn1—N2—C9	76.84 (14)	C23—C18—C19—C20	0.8 (3)
O7—Mn1—N2—C9	−101.95 (14)	C17—C18—C19—C20	−176.6 (2)
Mn1—O1—C1—C2	154.51 (16)	C18—C19—C20—C21	−1.2 (3)
Mn1—O1—C1—C6	−26.4 (3)	C19—C20—C21—C22	0.4 (3)
O1—C1—C2—C3	179.8 (2)	C20—C21—C22—C23	0.7 (3)
C6—C1—C2—C3	0.6 (3)	C20—C21—C22—N3	178.6 (2)
C1—C2—C3—C4	−0.5 (4)	O5—N3—C22—C21	−165.6 (2)
C2—C3—C4—C5	0.1 (4)	O6—N3—C22—C21	14.7 (3)

C3—C4—C5—C6	0.1 (4)	O5—N3—C22—C23	12.4 (3)
C4—C5—C6—C1	0.0 (3)	O6—N3—C22—C23	−167.3 (2)
C4—C5—C6—C7	−178.4 (2)	C21—C22—C23—C18	−1.0 (3)
O1—C1—C6—C5	−179.4 (2)	N3—C22—C23—C18	−178.95 (18)
C2—C1—C6—C5	−0.3 (3)	C19—C18—C23—C22	0.3 (3)
O1—C1—C6—C7	−1.1 (3)	C17—C18—C23—C22	177.69 (19)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H2W···O2^{i}	0.77	2.31	3.074 (2)	172
O7—H1W···O4^{ii}	0.84	1.89	2.710 (2)	166

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

Fig. 1

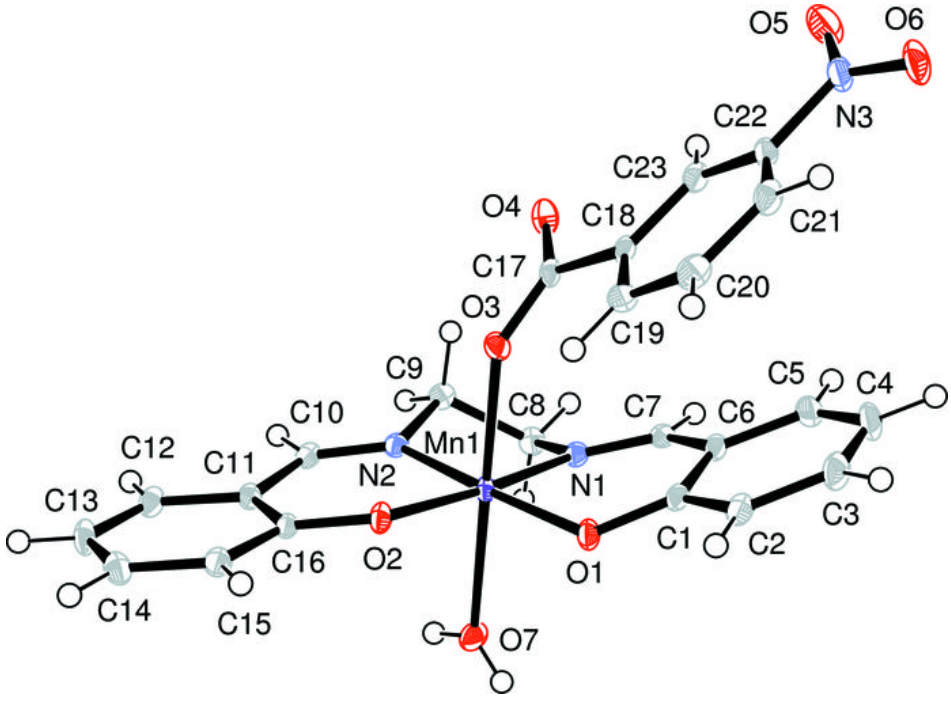
O5
O6
N3
C22
C23
C21
O4
C18
C17
C20
O3
C19
C9
C5
C4
C8
C7
C6
C10
Mn1
C12
C11
N2
N1
C13
C3
C1
C2
C16
O2
O1
C14
C15
O7

Fig. 2