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# Aqua{6,6′-dimethoxy-2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}-(4-hydroxybenzoato)manganese(III)

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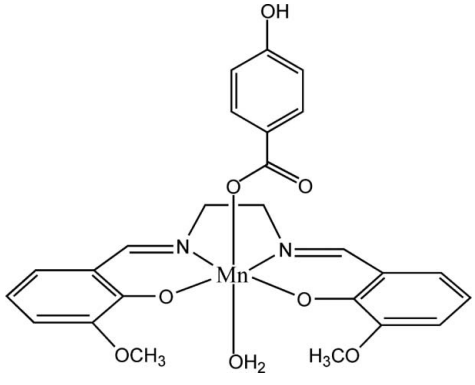
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.029; $wR$ factor = 0.082; data-to-parameter ratio = 12.9.

The title compound, $[Mn(C_{18}H_{18}N_2O_4)(C_7H_5O_3)(H_2O)]$, was synthesized by a template reaction of ethane-1,2-diamine and 3-methoxysalicylaldehyde in presence of manganese(II) 4-hydroxybenzoate. The Jahn–Teller-distorted manganese(III) centre has an octahedral geometry. Extensive O—H···O hydrogen-bonding interactions generate a two-dimensional sheet structure parallel to (103).

## Related literature

For background to the coordination chemistry of manganese, see: Christou (2005); Yocum & Pecoraro (1999); McEvoy & Brudvig (2006); Pecoraro (1992). For the structures of manganese complexes containing Schiff base and carboxylate ligands, see: Bermejo *et al.* (2006); Hulme *et al.* (1997); Zhang & Janiak (2001).




## Experimental

### Crystal data

$[Mn(C_{18}H_{18}N_2O_4)(C_7H_5O_3)(H_2O)]$
$M_r$ = 536.41
Monoclinic, $P2_1/c$
$a$ = 8.5988 (3) Å
$b$ = 13.5524 (5) Å
$c$ = 21.1335 (8) Å
$\beta$ = 93.280 (2)°
$V$ = 2458.75 (16) Å$^3$
$Z$ = 4
Cu $K\alpha$ radiation
$\mu$ = 4.82 mm$^{-1}$
$T$ = 100 K
0.43 × 0.38 × 0.24 mm

### Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: numerical (*SADABS*; Sheldrick, 2004)
$T_{min}$ = 0.229, $T_{max}$ = 0.388
26252 measured reflections
4259 independent reflections
3766 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.033

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.082
$S$ = 1.04
4259 reflections
329 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.31 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O8—H8···O5$^{i}$ | 0.84 | 1.79 | 2.599 (2) | 161 |
| O3—H2$W$···O7$^{ii}$ | 0.84 | 2.32 | 3.0025 (19) | 139 |
| O3—H2$W$···O2$^{ii}$ | 0.84 | 2.11 | 2.8711 (17) | 150 |
| O3—H1$W$···O6$^{ii}$ | 0.84 | 2.29 | 3.000 (2) | 142 |
| O3—H1$W$···O1$^{ii}$ | 0.84 | 2.21 | 2.9475 (18) | 147 |

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

We acknowledge the generosity of the Principal of SN College, Varkala, Kerala, 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: BT5032).

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# supplementary materials

*Acta Cryst.* (2009). E**65**, m1110-m1111 [ **doi:10.1107/S1600536809032553** ]

# Aqua{6,6'-dimethoxy-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}(4-hydroxybenzoato)manganese(III)

**R. Reshma, P. V. Soumya, S. M. Simi, V. S. Thampidas and R. D. Pike**

## Comment

Recent advances in the coordination chemistry of manganese have been mainly associated with (i) manganese clusters and the phenomenon of single-molecule magnetism (Christou, 2005) and (ii) its biological importance (Pecoraro, 1992). With its accessible oxidation states ranging from (II) to (V), and a propensity for coordination with N and O donor atoms, manganese exhibits rich redox and structural chemistry in biological systems like the oxygen-evolvingcomplex (OEC) of photosystem II (McEvoy & Brudvig, 2006), superoxide dismutase, catalase, arginase etc. (Yocum & Pecoraro, 1999). We have been interested in inorganic modeling of the active sites of these manganese-containing systems using complexes containing Schiff base and carboxylate ligands. The structural diversity displayed in such complexes has been amply demonstrated in previous reports (Hulme *et al.*, 1997; Zhang & Janiak, 2001; Bermejo *et al.*, 2006). In this paper, we report the crystal structure of a new manganese(III) complex with the Schiff base, m-salen [$H_2$msalen = N,N'-bis(3-methoxysalicylidene)-ethane-1,2-diamine] and 4-hydroxyobenzoate as an ancillary ligand (Figure 1).

The $N_2O_2$ donor set of the m-salen ligand holds the manganese(III) ion at the centre of an approximate square plane [Mn(1)-O(1) = 1.8848 (12) Å and Mn(1)-O(2) = 1.8821 (11) Å ;Mn(1)-N(1) = 1.9774 (15) Å and Mn(1)-N(2) = 1.9930 (14) Å]. Jahn-Teller distortion elongate of the axial Mn–$O_{carb}$ [Mn(1)-O(4) = 2.1164 (13) Å] and the Mn–$O_{aq}$ [Mn(1)-O(3) = 2.3257 (12) Å]. H-bonding interactions between the non-coordinated O atom of the carboxylate and the para O-H group of the carboxylate of an adjacent molecule produce chains progressing along a screw ($2_1$) axis parallel to the b-axis. Axial $H_2O$ ligands and the m-salen ligands of neighboring molecules are involved in multiple H-bond interactions resulting in chains. These two interactions together produce a 2-dimensional sheet structure parallel to the (1 0 3) plane (Figure 2).

## Experimental

To a solution of [Mn(4-$OHC_6H_4CO_2$)($H_2O$)$_2$].$H_2O$ (1.00 g, 2.61 mmol), and 3-methoxysalicylaldehyde (0.76 g, 5.22 mmol) in methanol (40 ml), ethane-1,2-diamine (0.16 g, 2.61 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. Crystals were grown from a DMF solution.

## Refinement

All hydrogen atoms were initially located in the difference map and then were placed in theoretical positions using a riding model. The methyl groups and the O-H groups were allowed to rotate but not to tip. C$sp^2$—H = 0.95 Å, C$sp^3$—H = 0.99 Å, $U_{iso}$(H) = 1.2Ueq(C,O).

## Figures

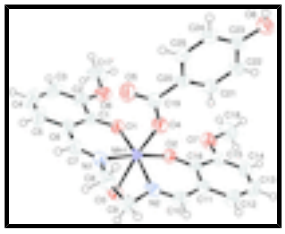

Fig. 1. *ORTEP* picture (Farrugia, 1997) of the title compound. Displacement ellipsoids have been drawn at the 50% probability level.

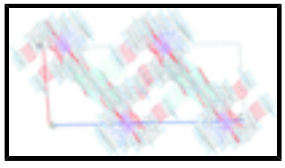

Fig. 2. Mercury capped-stick packing diagram (Macrae *et al.*, 2006) of the title compound showing hydrogen-bonding chains and the 2-dimensional sheet structure.

## Aqua{6,6'-dimethoxy-2,2'-[ethane-1,2- diylbis(nitrilomethylidyne)]diphenolato}(4-hydroxybenzoato)manganese(III)

*Crystal data*

| | |
|---|---|
| $[Mn(C_{18}H_{18}N_2O_4)(C_7H_5O_3)(H_2O)]$ | $F_{000}$ = 1112 |
| $M_r$ = 536.41 | $D_x$ = 1.449 Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Cu $K\alpha$ radiation, λ = 1.54178 Å |
| Hall symbol: -P 2ybc | Cell parameters from 305 reflections |
| $a$ = 8.5988 (3) Å | θ = 9.7–72.7º |
| $b$ = 13.5524 (5) Å | μ = 4.82 mm$^{-1}$ |
| $c$ = 21.1335 (8) Å | $T$ = 100 K |
| β = 93.280 (2)º | Block, red |
| $V$ = 2458.75 (16) Å$^3$ | 0.43 × 0.38 × 0.24 mm |
| $Z$ = 4 | |

*Data collection*

| | |
|---|---|
| Bruker SMART APEXII CCD diffractometer | 4259 independent reflections |
| Radiation source: fine-focus sealed tube | 3766 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.033 |
| $T$ = 100 K | $\theta_{max}$ = 67.0º |
| ω and ψ scans | $\theta_{min}$ = 3.9º |
| Absorption correction: numerical (SADABS; Sheldrick, 2004) | $h$ = −10→10 |
| $T_{min}$ = 0.229, $T_{max}$ = 0.388 | $k$ = −16→16 |
| 26252 measured reflections | $l$ = −25→23 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.082$

$S = 1.04$

4259 reflections

329 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.482P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.17$ e Å$^{-3}$

$\Delta\rho_{min} = -0.31$ e Å$^{-3}$

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 | 0.00260 (3) | 0.572439 (18) | 0.395095 (12) | 0.03435 (10) |
| O1 | 0.16793 (14) | 0.49020 (9) | 0.42468 (6) | 0.0441 (3) |
| O2 | 0.00908 (13) | 0.65071 (8) | 0.46877 (5) | 0.0385 (3) |
| O3 | −0.17820 (15) | 0.46814 (10) | 0.43826 (6) | 0.0462 (3) |
| H1W | −0.2082 | 0.4929 | 0.4719 | 0.069* |
| H2W | −0.1324 | 0.4183 | 0.4539 | 0.069* |
| O4 | 0.13396 (16) | 0.68020 (10) | 0.34910 (7) | 0.0579 (4) |
| O5 | 0.2768 (2) | 0.61403 (11) | 0.27687 (9) | 0.0759 (5) |
| O6 | 0.38532 (16) | 0.39868 (11) | 0.49052 (8) | 0.0605 (4) |
| O7 | 0.11387 (16) | 0.74947 (10) | 0.56553 (6) | 0.0552 (4) |
| O8 | 0.56714 (18) | 1.04617 (10) | 0.31546 (7) | 0.0569 (4) |
| H8 | 0.6043 | 1.0592 | 0.2805 | 0.085* |
| N1 | −0.03465 (18) | 0.49221 (11) | 0.31755 (7) | 0.0437 (4) |
| N2 | −0.18769 (17) | 0.64264 (11) | 0.36080 (7) | 0.0404 (3) |
| C1 | 0.2130 (2) | 0.40534 (13) | 0.40135 (9) | 0.0434 (4) |
| C2 | 0.3325 (2) | 0.35296 (14) | 0.43583 (10) | 0.0504 (5) |
| C3 | 0.3854 (3) | 0.26389 (16) | 0.41349 (13) | 0.0669 (7) |
| H3A | 0.4667 | 0.2299 | 0.4367 | 0.080* |
| C4 | 0.3210 (3) | 0.22341 (17) | 0.35735 (13) | 0.0716 (7) |
| H4 | 0.3571 | 0.1617 | 0.3428 | 0.086* |
| C5 | 0.2069 (3) | 0.27213 (16) | 0.32360 (12) | 0.0648 (6) |
| H5 | 0.1640 | 0.2442 | 0.2852 | 0.078* |

| | | | | |
|---|---|---|---|---|
| C6 | 0.1502 (2) | 0.36359 (14) | 0.34428 (9) | 0.0486 (5) |
| C7 | 0.0319 (3) | 0.41113 (14) | 0.30509 (9) | 0.0503 (5) |
| H7 | 0.0001 | 0.3795 | 0.2664 | 0.060* |
| C8 | −0.1493 (3) | 0.53742 (16) | 0.27184 (9) | 0.0567 (5) |
| H8A | −0.1983 | 0.4862 | 0.2439 | 0.068* |
| H8B | −0.0976 | 0.5861 | 0.2451 | 0.068* |
| C9 | −0.2707 (2) | 0.58766 (16) | 0.30925 (9) | 0.0528 (5) |
| H9A | −0.3339 | 0.6332 | 0.2817 | 0.063* |
| H9B | −0.3410 | 0.5381 | 0.3268 | 0.063* |
| C10 | −0.2353 (2) | 0.72627 (14) | 0.37993 (9) | 0.0438 (4) |
| H10 | −0.3219 | 0.7552 | 0.3569 | 0.053* |
| C11 | −0.1684 (2) | 0.77993 (13) | 0.43343 (9) | 0.0418 (4) |
| C12 | −0.2294 (3) | 0.87431 (15) | 0.44637 (11) | 0.0568 (5) |
| H12 | −0.3083 | 0.9018 | 0.4184 | 0.068* |
| C13 | −0.1765 (3) | 0.92618 (15) | 0.49826 (12) | 0.0620 (6) |
| H13 | −0.2186 | 0.9895 | 0.5063 | 0.074* |
| C14 | −0.0609 (3) | 0.88696 (15) | 0.53968 (10) | 0.0554 (5) |
| H14 | −0.0246 | 0.9235 | 0.5759 | 0.067* |
| C15 | 0.0010 (2) | 0.79578 (13) | 0.52835 (9) | 0.0431 (4) |
| C16 | −0.05175 (19) | 0.73910 (12) | 0.47489 (8) | 0.0363 (4) |
| C17 | 0.5190 (2) | 0.35790 (19) | 0.52483 (14) | 0.0759 (8) |
| H17A | 0.4945 | 0.2914 | 0.5395 | 0.114* |
| H17B | 0.5477 | 0.3999 | 0.5614 | 0.114* |
| H17C | 0.6063 | 0.3546 | 0.4970 | 0.114* |
| C18 | 0.1804 (3) | 0.8014 (2) | 0.61902 (12) | 0.0785 (7) |
| H18A | 0.2285 | 0.8625 | 0.6049 | 0.118* |
| H18B | 0.2598 | 0.7601 | 0.6411 | 0.118* |
| H18C | 0.0988 | 0.8173 | 0.6479 | 0.118* |
| C19 | 0.2422 (2) | 0.68274 (13) | 0.31186 (9) | 0.0416 (4) |
| C20 | 0.33056 (19) | 0.77892 (12) | 0.31102 (8) | 0.0363 (4) |
| C21 | 0.3153 (2) | 0.84743 (13) | 0.35946 (8) | 0.0418 (4) |
| H21 | 0.2480 | 0.8334 | 0.3924 | 0.050* |
| C22 | 0.3962 (2) | 0.93532 (14) | 0.36026 (9) | 0.0443 (4) |
| H22 | 0.3863 | 0.9805 | 0.3942 | 0.053* |
| C23 | 0.4923 (2) | 0.95794 (13) | 0.31152 (9) | 0.0404 (4) |
| C24 | 0.5079 (2) | 0.89109 (13) | 0.26270 (8) | 0.0408 (4) |
| H24 | 0.5728 | 0.9061 | 0.2291 | 0.049* |
| C25 | 0.4281 (2) | 0.80217 (13) | 0.26320 (8) | 0.0392 (4) |
| H25 | 0.4407 | 0.7561 | 0.2300 | 0.047* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Mn1 | 0.03304 (16) | 0.03382 (16) | 0.03536 (16) | −0.00183 (11) | −0.00532 (11) | −0.00038 (11) |
| O1 | 0.0386 (7) | 0.0387 (7) | 0.0539 (7) | 0.0051 (5) | −0.0062 (6) | −0.0046 (6) |
| O2 | 0.0397 (6) | 0.0372 (6) | 0.0374 (6) | 0.0035 (5) | −0.0080 (5) | −0.0011 (5) |
| O3 | 0.0461 (7) | 0.0452 (7) | 0.0467 (7) | −0.0033 (6) | −0.0027 (6) | 0.0103 (6) |
| O4 | 0.0593 (9) | 0.0451 (7) | 0.0719 (9) | −0.0112 (6) | 0.0266 (7) | −0.0016 (7) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O5 | 0.0862 (12) | 0.0505 (9) | 0.0951 (12) | −0.0120 (8) | 0.0399 (10) | −0.0203 (9) |
| O6 | 0.0405 (8) | 0.0569 (8) | 0.0830 (11) | 0.0106 (6) | −0.0075 (7) | 0.0137 (8) |
| O7 | 0.0569 (8) | 0.0565 (8) | 0.0497 (7) | −0.0026 (7) | −0.0175 (6) | −0.0100 (6) |
| O8 | 0.0603 (9) | 0.0460 (7) | 0.0651 (9) | −0.0143 (7) | 0.0111 (7) | −0.0042 (7) |
| N1 | 0.0502 (9) | 0.0412 (8) | 0.0392 (8) | −0.0086 (7) | −0.0021 (7) | −0.0021 (7) |
| N2 | 0.0379 (8) | 0.0449 (9) | 0.0371 (7) | −0.0047 (6) | −0.0085 (6) | 0.0066 (6) |
| C1 | 0.0378 (9) | 0.0355 (9) | 0.0581 (11) | 0.0001 (7) | 0.0132 (8) | 0.0047 (8) |
| C2 | 0.0412 (10) | 0.0435 (10) | 0.0679 (13) | 0.0014 (8) | 0.0146 (9) | 0.0104 (9) |
| C3 | 0.0585 (13) | 0.0509 (12) | 0.0944 (18) | 0.0176 (10) | 0.0311 (13) | 0.0254 (13) |
| C4 | 0.0944 (18) | 0.0417 (12) | 0.0826 (17) | 0.0110 (12) | 0.0400 (15) | 0.0024 (12) |
| C5 | 0.0864 (17) | 0.0414 (11) | 0.0694 (14) | −0.0010 (11) | 0.0304 (13) | −0.0017 (10) |
| C6 | 0.0570 (12) | 0.0366 (9) | 0.0541 (11) | −0.0043 (8) | 0.0186 (9) | −0.0033 (8) |
| C7 | 0.0621 (13) | 0.0444 (11) | 0.0449 (10) | −0.0118 (9) | 0.0073 (9) | −0.0065 (8) |
| C8 | 0.0667 (14) | 0.0609 (12) | 0.0401 (10) | −0.0046 (11) | −0.0168 (10) | −0.0015 (9) |
| C9 | 0.0493 (12) | 0.0608 (12) | 0.0458 (10) | −0.0047 (9) | −0.0201 (9) | 0.0019 (9) |
| C10 | 0.0368 (9) | 0.0456 (10) | 0.0481 (10) | 0.0038 (8) | −0.0059 (8) | 0.0119 (8) |
| C11 | 0.0382 (9) | 0.0382 (9) | 0.0487 (10) | 0.0010 (7) | −0.0006 (8) | 0.0060 (8) |
| C12 | 0.0538 (12) | 0.0460 (11) | 0.0704 (14) | 0.0108 (9) | 0.0013 (10) | 0.0096 (10) |
| C13 | 0.0704 (15) | 0.0392 (11) | 0.0774 (15) | 0.0079 (10) | 0.0126 (12) | −0.0028 (10) |
| C14 | 0.0654 (13) | 0.0431 (11) | 0.0581 (12) | −0.0072 (10) | 0.0063 (10) | −0.0081 (10) |
| C15 | 0.0423 (10) | 0.0422 (10) | 0.0448 (10) | −0.0070 (8) | 0.0008 (8) | −0.0009 (8) |
| C16 | 0.0333 (8) | 0.0353 (9) | 0.0404 (9) | −0.0037 (7) | 0.0031 (7) | 0.0027 (7) |
| C17 | 0.0381 (12) | 0.0765 (16) | 0.112 (2) | 0.0059 (10) | −0.0078 (12) | 0.0371 (15) |
| C18 | 0.0805 (17) | 0.0893 (18) | 0.0625 (14) | −0.0134 (14) | −0.0233 (13) | −0.0233 (13) |
| C19 | 0.0412 (10) | 0.0394 (9) | 0.0440 (10) | 0.0015 (8) | 0.0007 (8) | 0.0025 (8) |
| C20 | 0.0319 (8) | 0.0391 (9) | 0.0374 (9) | 0.0023 (7) | −0.0010 (7) | 0.0045 (7) |
| C21 | 0.0402 (10) | 0.0481 (10) | 0.0374 (9) | −0.0012 (8) | 0.0049 (7) | 0.0027 (8) |
| C22 | 0.0486 (11) | 0.0456 (10) | 0.0387 (9) | −0.0015 (8) | 0.0012 (8) | −0.0048 (8) |
| C23 | 0.0354 (9) | 0.0396 (9) | 0.0455 (10) | −0.0014 (7) | −0.0028 (8) | 0.0044 (8) |
| C24 | 0.0346 (9) | 0.0463 (10) | 0.0420 (9) | 0.0024 (8) | 0.0055 (7) | 0.0066 (8) |
| C25 | 0.0383 (9) | 0.0406 (9) | 0.0386 (9) | 0.0033 (7) | 0.0031 (7) | −0.0004 (7) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Mn1—O2 | 1.8821 (11) | C8—C9 | 1.507 (3) |
| Mn1—O1 | 1.8848 (12) | C8—H8A | 0.9900 |
| Mn1—N1 | 1.9774 (15) | C8—H8B | 0.9900 |
| Mn1—N2 | 1.9930 (14) | C9—H9A | 0.9900 |
| Mn1—O4 | 2.1164 (13) | C9—H9B | 0.9900 |
| Mn1—O3 | 2.3257 (12) | C10—C11 | 1.437 (3) |
| O1—C1 | 1.318 (2) | C10—H10 | 0.9500 |
| O2—C16 | 1.316 (2) | C11—C16 | 1.407 (2) |
| O3—H1W | 0.8400 | C11—C12 | 1.415 (3) |
| O3—H2W | 0.8401 | C12—C13 | 1.359 (3) |
| O4—C19 | 1.253 (2) | C12—H12 | 0.9500 |
| O5—C19 | 1.236 (2) | C13—C14 | 1.392 (3) |
| O6—C2 | 1.366 (3) | C13—H13 | 0.9500 |
| O6—C17 | 1.435 (2) | C14—C15 | 1.372 (3) |
| O7—C15 | 1.366 (2) | C14—H14 | 0.9500 |

| | | | |
|---|---|---|---|
| O7—C18 | 1.424 (2) | C15—C16 | 1.419 (2) |
| O8—C23 | 1.358 (2) | C17—H17A | 0.9800 |
| O8—H8 | 0.8400 | C17—H17B | 0.9800 |
| N1—C7 | 1.274 (2) | C17—H17C | 0.9800 |
| N1—C8 | 1.474 (2) | C18—H18A | 0.9800 |
| N2—C10 | 1.278 (2) | C18—H18B | 0.9800 |
| N2—C9 | 1.470 (2) | C18—H18C | 0.9800 |
| C1—C6 | 1.411 (3) | C19—C20 | 1.509 (2) |
| C1—C2 | 1.416 (3) | C20—C25 | 1.386 (2) |
| C2—C3 | 1.383 (3) | C20—C21 | 1.394 (2) |
| C3—C4 | 1.393 (4) | C21—C22 | 1.379 (3) |
| C3—H3A | 0.9500 | C21—H21 | 0.9500 |
| C4—C5 | 1.352 (4) | C22—C23 | 1.391 (3) |
| C4—H4 | 0.9500 | C22—H22 | 0.9500 |
| C5—C6 | 1.410 (3) | C23—C24 | 1.385 (3) |
| C5—H5 | 0.9500 | C24—C25 | 1.387 (3) |
| C6—C7 | 1.428 (3) | C24—H24 | 0.9500 |
| C7—H7 | 0.9500 | C25—H25 | 0.9500 |
| O2—Mn1—O1 | 94.17 (5) | C8—C9—H9A | 110.3 |
| O2—Mn1—N1 | 172.37 (6) | N2—C9—H9B | 110.3 |
| O1—Mn1—N1 | 91.90 (6) | C8—C9—H9B | 110.3 |
| O2—Mn1—N2 | 90.95 (6) | H9A—C9—H9B | 108.5 |
| O1—Mn1—N2 | 172.26 (6) | N2—C10—C11 | 125.20 (16) |
| N1—Mn1—N2 | 82.56 (6) | N2—C10—H10 | 117.4 |
| O2—Mn1—O4 | 89.99 (5) | C11—C10—H10 | 117.4 |
| O1—Mn1—O4 | 98.52 (6) | C16—C11—C12 | 119.61 (18) |
| N1—Mn1—O4 | 93.68 (6) | C16—C11—C10 | 122.03 (16) |
| N2—Mn1—O4 | 87.26 (6) | C12—C11—C10 | 118.25 (17) |
| O2—Mn1—O3 | 90.40 (5) | C13—C12—C11 | 120.9 (2) |
| O1—Mn1—O3 | 91.09 (5) | C13—C12—H12 | 119.6 |
| N1—Mn1—O3 | 84.87 (6) | C11—C12—H12 | 119.6 |
| N2—Mn1—O3 | 83.08 (5) | C12—C13—C14 | 120.26 (19) |
| O4—Mn1—O3 | 170.33 (5) | C12—C13—H13 | 119.9 |
| C1—O1—Mn1 | 128.61 (12) | C14—C13—H13 | 119.9 |
| C16—O2—Mn1 | 126.94 (10) | C15—C14—C13 | 120.29 (19) |
| Mn1—O3—H1W | 109.5 | C15—C14—H14 | 119.9 |
| Mn1—O3—H2W | 109.5 | C13—C14—H14 | 119.9 |
| H1W—O3—H2W | 98.5 | O7—C15—C14 | 125.68 (17) |
| C19—O4—Mn1 | 137.94 (13) | O7—C15—C16 | 113.16 (15) |
| C2—O6—C17 | 118.09 (18) | C14—C15—C16 | 121.16 (18) |
| C15—O7—C18 | 118.02 (17) | O2—C16—C11 | 124.73 (15) |
| C23—O8—H8 | 109.5 | O2—C16—C15 | 117.41 (15) |
| C7—N1—C8 | 120.99 (16) | C11—C16—C15 | 117.83 (16) |
| C7—N1—Mn1 | 126.33 (14) | O6—C17—H17A | 109.5 |
| C8—N1—Mn1 | 112.66 (12) | O6—C17—H17B | 109.5 |
| C10—N2—C9 | 122.20 (16) | H17A—C17—H17B | 109.5 |
| C10—N2—Mn1 | 125.41 (12) | O6—C17—H17C | 109.5 |
| C9—N2—Mn1 | 112.39 (12) | H17A—C17—H17C | 109.5 |
| O1—C1—C6 | 124.27 (17) | H17B—C17—H17C | 109.5 |

| | | | |
|---|---|---|---|
| O1—C1—C2 | 117.72 (18) | O7—C18—H18A | 109.5 |
| C6—C1—C2 | 118.01 (18) | O7—C18—H18B | 109.5 |
| O6—C2—C3 | 125.8 (2) | H18A—C18—H18B | 109.5 |
| O6—C2—C1 | 113.84 (17) | O7—C18—H18C | 109.5 |
| C3—C2—C1 | 120.4 (2) | H18A—C18—H18C | 109.5 |
| C2—C3—C4 | 120.8 (2) | H18B—C18—H18C | 109.5 |
| C2—C3—H3A | 119.6 | O5—C19—O4 | 124.60 (18) |
| C4—C3—H3A | 119.6 | O5—C19—C20 | 120.33 (16) |
| C5—C4—C3 | 119.9 (2) | O4—C19—C20 | 115.06 (16) |
| C5—C4—H4 | 120.0 | C25—C20—C21 | 118.07 (16) |
| C3—C4—H4 | 120.0 | C25—C20—C19 | 122.08 (16) |
| C4—C5—C6 | 121.3 (2) | C21—C20—C19 | 119.86 (15) |
| C4—C5—H5 | 119.4 | C22—C21—C20 | 121.03 (16) |
| C6—C5—H5 | 119.4 | C22—C21—H21 | 119.5 |
| C5—C6—C1 | 119.7 (2) | C20—C21—H21 | 119.5 |
| C5—C6—C7 | 117.6 (2) | C21—C22—C23 | 120.13 (17) |
| C1—C6—C7 | 122.67 (17) | C21—C22—H22 | 119.9 |
| N1—C7—C6 | 125.66 (18) | C23—C22—H22 | 119.9 |
| N1—C7—H7 | 117.2 | O8—C23—C24 | 123.75 (16) |
| C6—C7—H7 | 117.2 | O8—C23—C22 | 116.63 (17) |
| N1—C8—C9 | 107.53 (16) | C24—C23—C22 | 119.62 (16) |
| N1—C8—H8A | 110.2 | C23—C24—C25 | 119.58 (16) |
| C9—C8—H8A | 110.2 | C23—C24—H24 | 120.2 |
| N1—C8—H8B | 110.2 | C25—C24—H24 | 120.2 |
| C9—C8—H8B | 110.2 | C20—C25—C24 | 121.55 (16) |
| H8A—C8—H8B | 108.5 | C20—C25—H25 | 119.2 |
| N2—C9—C8 | 107.24 (16) | C24—C25—H25 | 119.2 |
| N2—C9—H9A | 110.3 | | |

| | | | |
|---|---|---|---|
| O2—Mn1—O1—C1 | 167.31 (14) | Mn1—N1—C7—C6 | −1.8 (3) |
| N1—Mn1—O1—C1 | −8.07 (15) | C5—C6—C7—N1 | 177.95 (19) |
| O4—Mn1—O1—C1 | −102.08 (15) | C1—C6—C7—N1 | −3.2 (3) |
| O3—Mn1—O1—C1 | 76.83 (14) | C7—N1—C8—C9 | 145.79 (18) |
| O1—Mn1—O2—C16 | 162.00 (13) | Mn1—N1—C8—C9 | −35.67 (19) |
| N2—Mn1—O2—C16 | −23.80 (14) | C10—N2—C9—C8 | 143.81 (18) |
| O4—Mn1—O2—C16 | 63.46 (14) | Mn1—N2—C9—C8 | −35.78 (19) |
| O3—Mn1—O2—C16 | −106.88 (13) | N1—C8—C9—N2 | 45.1 (2) |
| O2—Mn1—O4—C19 | 140.4 (2) | C9—N2—C10—C11 | 174.25 (17) |
| O1—Mn1—O4—C19 | 46.2 (2) | Mn1—N2—C10—C11 | −6.2 (3) |
| N1—Mn1—O4—C19 | −46.3 (2) | N2—C10—C11—C16 | −7.3 (3) |
| N2—Mn1—O4—C19 | −128.6 (2) | N2—C10—C11—C12 | 176.57 (18) |
| O1—Mn1—N1—C7 | 6.06 (17) | C16—C11—C12—C13 | 0.2 (3) |
| N2—Mn1—N1—C7 | −168.52 (17) | C10—C11—C12—C13 | 176.4 (2) |
| O4—Mn1—N1—C7 | 104.73 (16) | C11—C12—C13—C14 | 0.0 (3) |
| O3—Mn1—N1—C7 | −84.86 (16) | C12—C13—C14—C15 | 0.2 (3) |
| O1—Mn1—N1—C8 | −172.39 (13) | C18—O7—C15—C14 | −3.6 (3) |
| N2—Mn1—N1—C8 | 13.03 (13) | C18—O7—C15—C16 | 177.24 (18) |
| O4—Mn1—N1—C8 | −73.72 (13) | C13—C14—C15—O7 | −179.66 (19) |
| O3—Mn1—N1—C8 | 96.69 (13) | C13—C14—C15—C16 | −0.6 (3) |
| O2—Mn1—N2—C10 | 17.80 (15) | Mn1—O2—C16—C11 | 18.7 (2) |

| | | | |
|---|---|---|---|
| N1—Mn1—N2—C10 | −166.21 (16) | Mn1—O2—C16—C15 | −163.44 (12) |
| O4—Mn1—N2—C10 | −72.14 (15) | C12—C11—C16—O2 | 177.39 (17) |
| O3—Mn1—N2—C10 | 108.09 (15) | C10—C11—C16—O2 | 1.3 (3) |
| O2—Mn1—N2—C9 | −162.63 (13) | C12—C11—C16—C15 | −0.5 (3) |
| N1—Mn1—N2—C9 | 13.36 (13) | C10—C11—C16—C15 | −176.59 (16) |
| O4—Mn1—N2—C9 | 107.43 (13) | O7—C15—C16—O2 | 1.9 (2) |
| O3—Mn1—N2—C9 | −72.34 (13) | C14—C15—C16—O2 | −177.34 (17) |
| Mn1—O1—C1—C6 | 5.9 (3) | O7—C15—C16—C11 | 179.91 (15) |
| Mn1—O1—C1—C2 | −174.29 (12) | C14—C15—C16—C11 | 0.7 (3) |
| C17—O6—C2—C3 | 7.6 (3) | Mn1—O4—C19—O5 | 21.3 (3) |
| C17—O6—C2—C1 | −172.48 (17) | Mn1—O4—C19—C20 | −159.68 (14) |
| O1—C1—C2—O6 | 0.6 (2) | O5—C19—C20—C25 | 14.1 (3) |
| C6—C1—C2—O6 | −179.62 (16) | O4—C19—C20—C25 | −164.99 (17) |
| O1—C1—C2—C3 | −179.53 (17) | O5—C19—C20—C21 | −165.88 (18) |
| C6—C1—C2—C3 | 0.3 (3) | O4—C19—C20—C21 | 15.1 (2) |
| O6—C2—C3—C4 | 178.98 (19) | C25—C20—C21—C22 | −0.8 (3) |
| C1—C2—C3—C4 | −0.9 (3) | C19—C20—C21—C22 | 179.17 (17) |
| C2—C3—C4—C5 | 1.0 (3) | C20—C21—C22—C23 | 1.5 (3) |
| C3—C4—C5—C6 | −0.4 (3) | C21—C22—C23—O8 | 179.52 (17) |
| C4—C5—C6—C1 | −0.2 (3) | C21—C22—C23—C24 | −0.9 (3) |
| C4—C5—C6—C7 | 178.7 (2) | O8—C23—C24—C25 | 179.18 (16) |
| O1—C1—C6—C5 | −179.94 (17) | C22—C23—C24—C25 | −0.4 (3) |
| C2—C1—C6—C5 | 0.2 (3) | C21—C20—C25—C24 | −0.5 (3) |
| O1—C1—C6—C7 | 1.3 (3) | C19—C20—C25—C24 | 179.53 (15) |
| C2—C1—C6—C7 | −178.54 (17) | C23—C24—C25—C20 | 1.1 (3) |
| C8—N1—C7—C6 | 176.51 (19) | | |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O8—H8···O5$^{i}$ | 0.84 | 1.79 | 2.599 (2) | 161 |
| O3—H2W···O7$^{ii}$ | 0.84 | 2.32 | 3.0025 (19) | 139 |
| O3—H2W···O2$^{ii}$ | 0.84 | 2.11 | 2.8711 (17) | 150 |
| O3—H1W···O6$^{ii}$ | 0.84 | 2.29 | 3.000 (2) | 142 |
| O3—H1W···O1$^{ii}$ | 0.84 | 2.21 | 2.9475 (18) | 147 |

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

**Fig. 1**

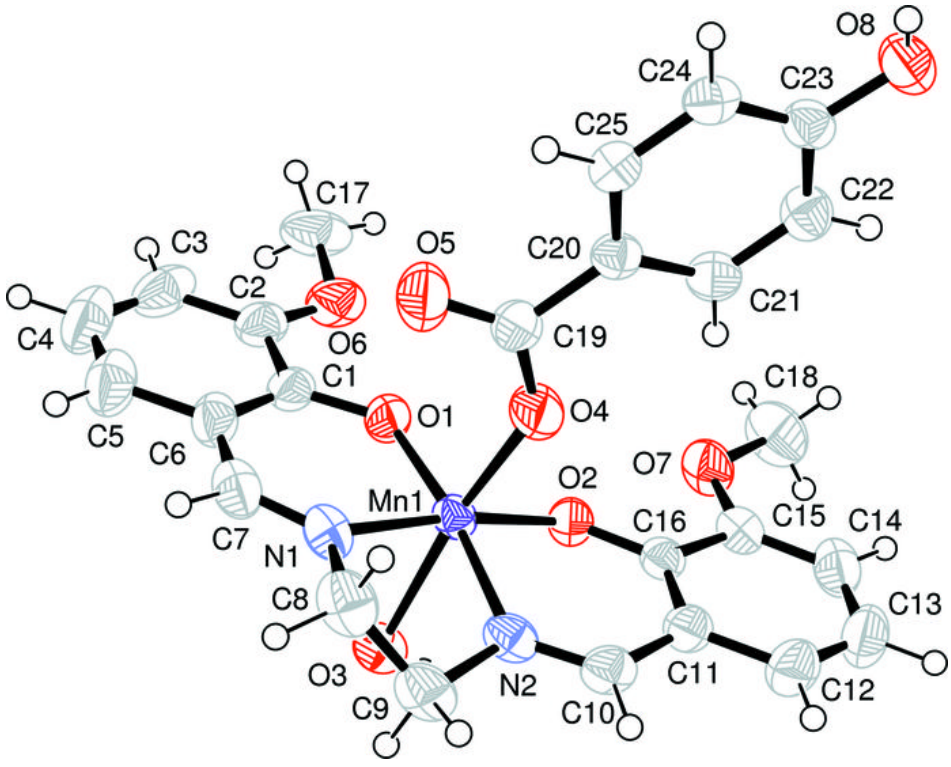
O8
C24
C23
C25
C22
C17
C3
O5
C20
C2
C21
C4
O6
C19
C1
C18
O1
O4
C5
C6
O7
O2
Mn1
C15
C14
C7
N1
C16
C8
C13
O3
N2
C11
C9
C10
C12

**Fig. 2**