

Bis[μ -2,2'-[1,1'-(ethane-1,2-diyl)dinitrilo]-diethylidene]diphenolato}bis[(benzoato- κ O)manganese(III)] dihydrate

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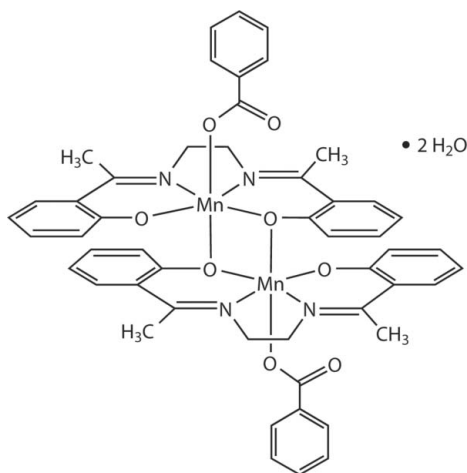
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.026; wR factor = 0.068; data-to-parameter ratio = 9.3.

The title compound, $[\text{Mn}_2(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2)_2(\text{C}_7\text{H}_5\text{O}_2)_2] \cdot 2\text{H}_2\text{O}$, 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

$[\text{Mn}_2(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2)_2(\text{C}_7\text{H}_5\text{O}_2)_2] \cdot 2\text{H}_2\text{O}$
 $M_r = 976.82$
 Monoclinic, $P2_1/c$
 $a = 12.9376$ (4) Å
 $b = 12.3983$ (4) Å
 $c = 13.8470$ (4) Å
 $\beta = 103.702$ (2)°
 $V = 2157.91$ (11) Å³
 $Z = 2$
 Cu $K\alpha$ radiation
 $\mu = 5.33$ mm⁻¹
 $T = 100$ (2) K
 $0.23 \times 0.22 \times 0.03$ 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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$

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
 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.36$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|----------------------------------------------|----------|--------------|--------------|----------------|
| $\text{O5}-\text{H1W} \cdots \text{O4}^i$ | 0.83 (3) | 2.02 (3) | 2.8452 (19) | 173 (2) |
| $\text{O5}-\text{H2W} \cdots \text{O4}^{ii}$ | 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).

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

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Bis{ μ -2,2'-[1,1'-(ethane-1,2-diylidinitrilo)diethyldiyne]diphenolato}bis[(benzoato- κ O)manganese(III)] dihydrate

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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 \cdots 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 \cdots Mn distances derived from the EPR and EXAFS data provide complementary structural parameters with the Mn \cdots 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 \cdots 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 \cdots Mn separation [Mn1 \cdots Mn1⁽ⁱ⁾] of 3.4616 (5)Å is comparable to 3.485 (7)Å and 3.529 (4)Å, the corresponding Mn \cdots Mn separations of the previously reported complexes, [{Mn(msalen)(EtCO₂)₂ }₂] and [{Mn(msalen)(BuⁿCO₂)₂ }₂] respectively. [H₂msalen = 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).

Experimental

To a solution of Mn(C₆H₅CO₂)₂·2H₂O (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

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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.

Refinement

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

Figures

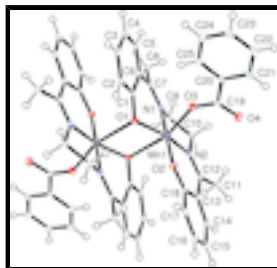


Fig. 1. ORTEP picture (Farrugia, 1997) of (1) Displacement ellipsoids have been drawn at the 50% probability level.

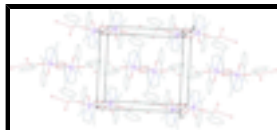


Fig. 2. Mercury ball and stick packing diagram (Macrae *et al.*, 2006) of (1) showing hydrogen-bonding chains.

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$[\text{Mn}_2(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2)_2(\text{C}_7\text{H}_5\text{O}_2)_2] \cdot 2\text{H}_2\text{O}$

$M_r = 976.82$

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) Å³

$Z = 2$

$F(000) = 1016$

$D_x = 1.503$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 218 reflections

$\theta = 9.6\text{--}70.3^\circ$

$\mu = 5.33$ mm⁻¹

$T = 100$ K

Plate, green

$0.23 \times 0.22 \times 0.03$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

ω and Φ scans

Absorption correction: numerical
(*SADABS*; Sheldrick, 2004)

$T_{\min} = 0.374$, $T_{\max} = 0.857$

3711 independent reflections

3465 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.041$

$\theta_{\text{max}} = 67.0^\circ$, $\theta_{\text{min}} = 4.9^\circ$

$h = -15 \rightarrow 15$

$k = -14 \rightarrow 14$

21968 measured reflections

$l = -15 \rightarrow 12$

Refinement

Refinement on F^2

Primary atom site location: structure-invariant direct methods

Least-squares matrix: full

Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.027$

Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.068$

All H-atom parameters refined

$S = 1.03$

$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 0.9845P]$

where $P = (F_o^2 + 2F_c^2)/3$

3711 reflections

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

398 parameters

$\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$

0 restraints

$\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|---------------|---------------|----------------------------------|
| 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) |

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| | | | | |
|------|--------------|--------------|--------------|------------|
| 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 (\AA^2)

| | 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, °)

| | | | |
|---------------------|-------------|----------|------------|
| 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) |

supplementary materials

| | | | |
|-------------------------|-------------|---------------|-------------|
| 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) |

supplementary materials

| | | | |
|-----------------------------|--------------|-----------------|--------------|
| 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 codes: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|----------|-------------|-------------|---------------|
| O5—H1W \cdots O4 ⁱⁱ | 0.83 (3) | 2.02 (3) | 2.8452 (19) | 173 (2) |
| O5—H2W \cdots O4 ⁱ | 0.88 (3) | 1.89 (3) | 2.7579 (18) | 171 (3) |

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

Fig. 1

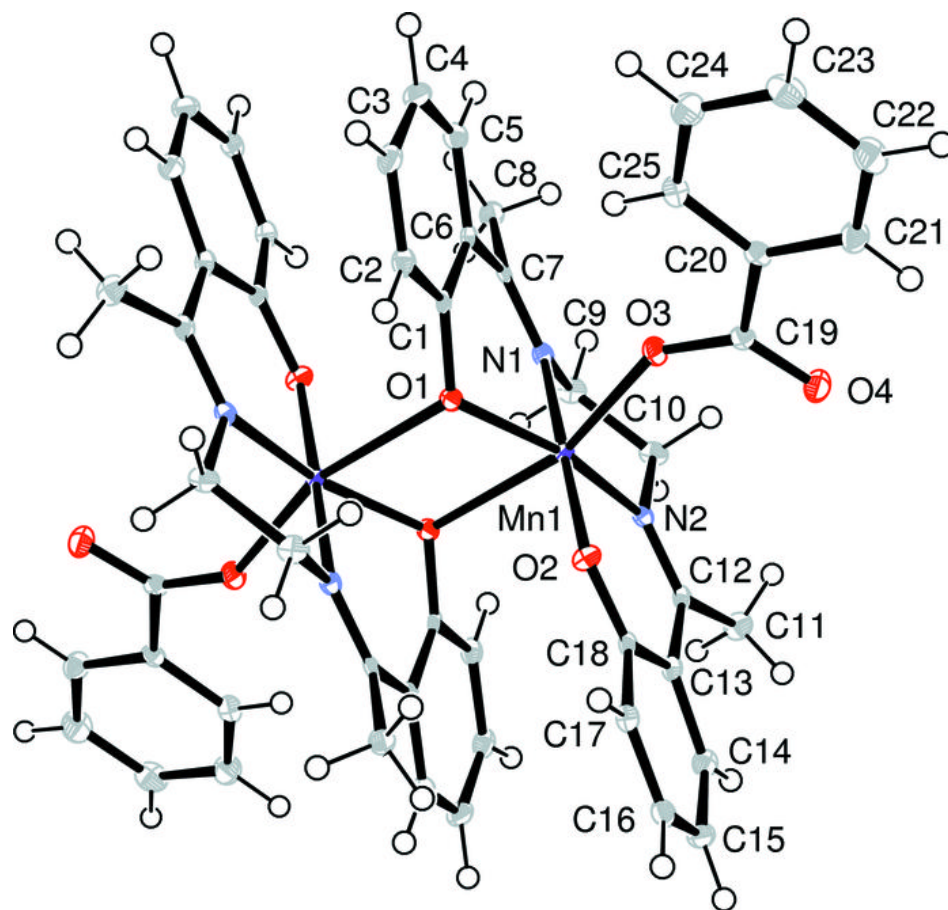


Fig. 2

