

# Diaquabis(2-chlorobenzoato- $\kappa$ O)bis- (*N,N*-diethylnicotinamide- $\kappa$ N<sup>1</sup>)- manganese(II)

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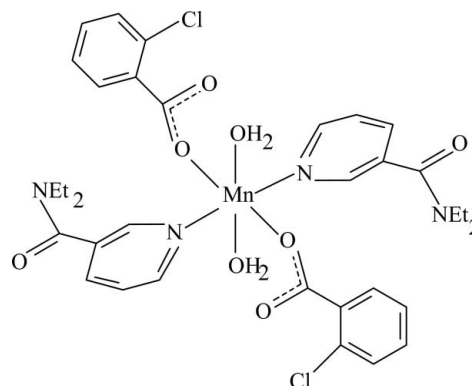
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.033;  $wR$  factor = 0.091; data-to-parameter ratio = 19.9.

In the monomeric title complex,  $[\text{Mn}(\text{C}_7\text{H}_4\text{ClO}_2)_2(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$ , the  $\text{Mn}^{\text{II}}$  atom is located on a crystallographic centre of inversion. The asymmetric unit contains one 2-chlorobenzoate (CB) ligand, one diethylnicotinamide (DNA) ligand and one coordinated water molecule, all ligands being monodentate. The four O atoms in the equatorial plane around the Mn atom form a slightly distorted square-planar arrangement, while the slightly distorted octahedral coordination is completed by the two pyridine N atoms of the DNA ligands in the axial positions. The dihedral angle between the carboxyl group and the adjacent benzene ring is  $77.9$  (11)°, while the pyridine and benzene rings are oriented at a dihedral angle of  $45.94$  (5)°. In the crystal structure, intermolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds link the molecules into infinite chains.

## Related literature

For general background to transition metal complexes with biochemically active ligands, see: Antolini *et al.* (1982); Bigoli *et al.* (1972); Nadzhafov *et al.* (1981); Shnulin *et al.* (1981). For related structures, see: Hökelek *et al.* (1995, 1997, 2007, 2008); Hökelek & Necefoğlu (1996, 1997, 2007).



## Experimental

### Crystal data

$[\text{Mn}(\text{C}_7\text{H}_4\text{ClO}_2)_2(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$

$M_r = 758.54$

Monoclinic,  $P2_1/n$

$a = 13.2840$  (2) Å

$b = 10.2499$  (3) Å

$c = 15.0023$  (4) Å

$\beta = 114.988$  (1)°

$V = 1851.50$  (8) Å<sup>3</sup>

$Z = 2$

Mo  $K\alpha$  radiation

$\mu = 0.55$  mm<sup>-1</sup>

$T = 100$  K

$0.46 \times 0.44 \times 0.27$  mm

### Data collection

Bruker Kappa APEXII CCD area-detector diffractometer

Absorption correction: multi-scan

(*SADABS*; Bruker, 2005)

$T_{\text{min}} = 0.778$ ,  $T_{\text{max}} = 0.864$

16951 measured reflections

4635 independent reflections

3984 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.048$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.091$

$S = 1.07$

4635 reflections

233 parameters

3 restraints

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 1.17$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.38$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$                              | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{O4}-\text{H41}\cdots\text{O2}^{\text{i}}$  | 0.90 (2)     | 1.83 (2)           | 2.666 (2)   | 154 (2)              |
| $\text{O4}-\text{H42}\cdots\text{O3}^{\text{ii}}$ | 0.89 (2)     | 1.86 (2)           | 2.729 (1)   | 166 (2)              |

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2110).

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## supporting information

*Acta Cryst.* (2009). E65, m513–m514 [doi:10.1107/S160053680901318X]

## Diaquabis(2-chlorobenzoato- $\kappa$ O)bis(*N,N*-diethylnicotinamide- $\kappa$ N<sup>1</sup>)manganese(II)

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### S1. Comment

Transition metal complexes with biochemically active ligands frequently show interesting physical and/or chemical properties, as a result they may find applications in biological systems (Antolini *et al.*, 1982). The structural functions and coordination relationships of the arylcarboxylate ion in transition metal complexes of benzoic acid derivatives change depending on the nature and position of the substituent groups on the benzene ring, the nature of the additional ligand molecule or solvent, and the medium of the synthesis (Nadzhafov *et al.*, 1981; Shnulin *et al.*, 1981). The nicotinic acid derivative *N,N*-diethylnicotinamide (DENA) is an important respiratory stimulant (Bigoli *et al.*, 1972).

The structure determination of the title compound, (I), a manganese complex with two 2-chlorobenzoate (CB), two diethylnicotinamide (DENA) ligands and two water molecules, was undertaken in order to determine the properties of the ligands and also to compare the results obtained with those reported previously.

Compound (I) is a monomeric complex, with the Mn atom on a centre of symmetry. It contains two CB, two DENA ligands and two water molecules (Fig. 1). All ligands are monodentate. The four O atoms (O1, O4, and the symmetry-related atoms, O1', O4') in the equatorial plane around the Mn atom form a slightly distorted square-planar arrangement, while the slightly distorted octahedral coordination is completed by the two pyridine N atoms of the DENA ligands (N1, N1') in the axial positions (Fig. 1).

The near equality of the C1—O1 [1.260 (2) Å] and C1—O2 [1.238 (2) Å] bonds in the carboxylate group indicates a delocalized bonding arrangement, rather than localized single and double bonds, and may be compared with the corresponding distances: 1.256 (6) and 1.245 (6) Å in [Mn(DENA)<sub>2</sub>(C<sub>7</sub>H<sub>4</sub>ClO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (Hökelek *et al.*, 2008), 1.265 (6) and 1.275 (6) Å in [Mn(C<sub>9</sub>H<sub>10</sub>NO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] × 2 H<sub>2</sub>O (Hökelek & Necefoğlu, 2007), 1.260 (4) and 1.252 (4) Å in [Zn(DENA)<sub>2</sub>(C<sub>7</sub>H<sub>4</sub>FO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (Hökelek *et al.*, 2007), 1.259 (9) and 1.273 (9) Å in [Cu<sub>2</sub>(DENA)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>COO)<sub>4</sub>] (Hökelek *et al.*, 1995), 1.279 (4) and 1.246 (4) Å in [Zn<sub>2</sub>(DENA)<sub>2</sub>(C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>)<sub>4</sub>] × 2 H<sub>2</sub>O (Hökelek & Necefoğlu, 1996), 1.251 (6) and 1.254 (7) Å in [Co(DENA)<sub>2</sub>(C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (Hökelek & Necefoğlu, 1997) and 1.278 (3) and 1.246 (3) Å in [Cu(DENA)<sub>2</sub>(C<sub>7</sub>H<sub>4</sub>NO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (Hökelek *et al.*, 1997). In the title compound, the average Mn—O bond length is 2.161 (1) Å and the Mn atom is displaced out of the least-squares plane of the carboxylate group (O1/C1/O2) by -0.544 (1) Å. The dihedral angle between the planar carboxylate group and the benzene ring A (C2—C7) is 77.9 (1)°, while that between rings A and B (N1/C8—C12) is 45.94 (5)°.

In the crystal structure, intermolecular O—H...O hydrogen bonds (Table 1) link the molecules into infinite chains.

### S2. Experimental

The title compound was prepared by the reaction of MnSO<sub>4</sub> × H<sub>2</sub>O (0.85 g, 5 mmol) in H<sub>2</sub>O (20 ml) and DENA (1.78 g, 10 mmol) in H<sub>2</sub>O (20 ml) with sodium 2-chlorobenzoate (1.785 g, 10 mmol) in H<sub>2</sub>O (50 ml). The mixture was filtered and set aside to crystallize at ambient temperature for 4 d, giving colorless single crystals.

## S3. Refinement

H atoms of water molecule were located in difference Fourier maps and refined isotropically, with restrains of O4—H41 = 0.896 (12) and O4—H42 = 0.890 (15) Å and H41—O4—H42 = 105.1 (19)°. The remaining H atoms were positioned geometrically with C—H = 0.93, 0.97 and 0.96 Å, for aromatic, methylene and methyl H atoms and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$ , where  $x = 1.5$  for methyl H and  $x = 1.2$  for all other H atoms.

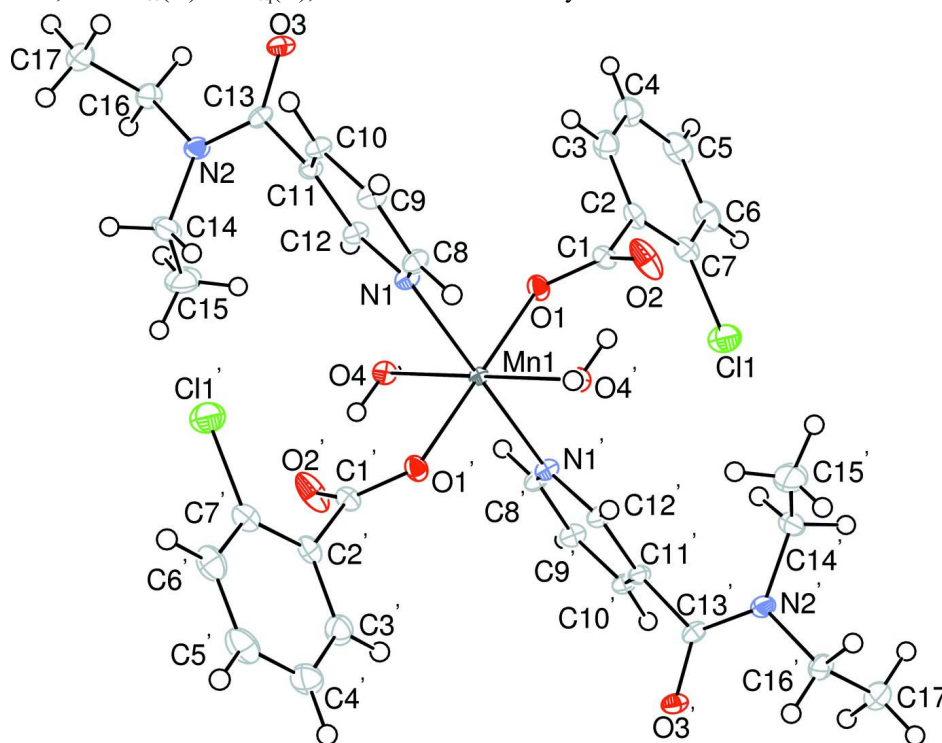


Figure 1

The molecular structure of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Primed atoms are generated by the symmetry operator (1 - x, -y, -z).

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## Crystal data

$[\text{Mn}(\text{C}_7\text{H}_4\text{ClO}_2)_2(\text{C}_{10}\text{H}_{14}\text{N}_2\text{O})_2(\text{H}_2\text{O})_2]$

$M_r = 758.54$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$a = 13.2840$  (2) Å

$b = 10.2499$  (3) Å

$c = 15.0023$  (4) Å

$\beta = 114.988$  (1)°

$V = 1851.50$  (8) Å<sup>3</sup>

$Z = 2$

$F(000) = 790$

$D_x = 1.361$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 8796 reflections

$\theta = 2.5$ – $28.4$ °

$\mu = 0.55$  mm<sup>-1</sup>

$T = 100$  K

Block, colorless

$0.46 \times 0.44 \times 0.27$  mm

## Data collection

Bruker Kappa APEXII CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2005)

$T_{\text{min}} = 0.778$ ,  $T_{\text{max}} = 0.864$

16951 measured reflections  
 4635 independent reflections  
 3984 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.048$

$\theta_{\text{max}} = 28.4^\circ$ ,  $\theta_{\text{min}} = 1.7^\circ$   
 $h = -17 \rightarrow 17$   
 $k = -13 \rightarrow 13$   
 $l = -18 \rightarrow 20$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.091$   
 $S = 1.07$   
 4635 reflections  
 233 parameters  
 3 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 0.6941P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 1.17 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{\AA}^{-3}$

*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 ( $\text{\AA}^2$ )*

|     | $x$          | $y$           | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|--------------|----------------------------------|
| Mn1 | 0.5000       | 0.0000        | 0.0000       | 0.01025 (9)                      |
| Cl1 | 0.18512 (4)  | -0.13983 (4)  | 0.08159 (3)  | 0.02988 (11)                     |
| O1  | 0.46966 (9)  | -0.04216 (10) | 0.12506 (7)  | 0.0170 (2)                       |
| O2  | 0.35458 (12) | 0.11652 (11)  | 0.12485 (10) | 0.0316 (3)                       |
| O3  | 0.93810 (8)  | 0.11259 (9)   | 0.39721 (7)  | 0.0163 (2)                       |
| O4  | 0.61938 (8)  | -0.16212 (10) | 0.03910 (7)  | 0.0146 (2)                       |
| H41 | 0.634 (2)    | -0.173 (2)    | -0.0135 (13) | 0.053 (7)*                       |
| H42 | 0.6079 (18)  | -0.2422 (16)  | 0.0558 (15)  | 0.038 (6)*                       |
| N1  | 0.64747 (10) | 0.13022 (11)  | 0.09437 (8)  | 0.0142 (2)                       |
| N2  | 0.98935 (11) | 0.00083 (12)  | 0.29330 (9)  | 0.0175 (3)                       |
| C1  | 0.40228 (12) | 0.01065 (14)  | 0.15298 (10) | 0.0158 (3)                       |
| C2  | 0.38071 (12) | -0.06704 (14) | 0.22885 (10) | 0.0168 (3)                       |
| C3  | 0.45941 (14) | -0.07053 (16) | 0.32641 (11) | 0.0230 (3)                       |
| H3  | 0.5231       | -0.0196       | 0.3459       | 0.028*                           |
| C4  | 0.44378 (15) | -0.14936 (17) | 0.39502 (12) | 0.0274 (4)                       |
| H4  | 0.4965       | -0.1505       | 0.4600       | 0.033*                           |
| C5  | 0.34943 (15) | -0.22608 (17) | 0.36617 (13) | 0.0279 (4)                       |
| H5  | 0.3396       | -0.2800       | 0.4117       | 0.033*                           |
| C6  | 0.26970 (15) | -0.22309 (16) | 0.26997 (12) | 0.0247 (3)                       |
| H6  | 0.2061       | -0.2742       | 0.2506       | 0.030*                           |

|      |              |               |              |            |
|------|--------------|---------------|--------------|------------|
| C7   | 0.28603 (13) | -0.14272 (15) | 0.20293 (11) | 0.0198 (3) |
| C8   | 0.64781 (12) | 0.26020 (14)  | 0.08373 (10) | 0.0161 (3) |
| H8   | 0.5867       | 0.2994        | 0.0340       | 0.019*     |
| C9   | 0.73522 (12) | 0.33862 (14)  | 0.14366 (10) | 0.0167 (3) |
| H9   | 0.7324       | 0.4284        | 0.1340       | 0.020*     |
| C10  | 0.82671 (12) | 0.28205 (13)  | 0.21802 (10) | 0.0150 (3) |
| H10  | 0.8856       | 0.3329        | 0.2601       | 0.018*     |
| C11  | 0.82833 (11) | 0.14699 (13)  | 0.22827 (10) | 0.0136 (3) |
| C12  | 0.73728 (12) | 0.07548 (14)  | 0.16547 (10) | 0.0146 (3) |
| H12  | 0.7385       | -0.0147       | 0.1730       | 0.017*     |
| C13  | 0.92349 (11) | 0.08431 (13)  | 0.31200 (10) | 0.0134 (3) |
| C14  | 0.98096 (15) | -0.03017 (19) | 0.19502 (12) | 0.0299 (4) |
| H14A | 1.0537       | -0.0218       | 0.1951       | 0.036*     |
| H14B | 0.9320       | 0.0323        | 0.1482       | 0.036*     |
| C15  | 0.93702 (17) | -0.1674 (2)   | 0.16204 (15) | 0.0459 (6) |
| H15A | 0.9385       | -0.1857       | 0.0998       | 0.069*     |
| H15B | 0.8621       | -0.1737       | 0.1555       | 0.069*     |
| H15C | 0.9828       | -0.2294       | 0.2100       | 0.069*     |
| C16  | 1.08576 (12) | -0.05400 (15) | 0.37696 (11) | 0.0192 (3) |
| H16A | 1.1004       | -0.1414       | 0.3606       | 0.023*     |
| H16B | 1.0688       | -0.0601       | 0.4337       | 0.023*     |
| C17  | 1.18844 (14) | 0.02997 (17)  | 0.40244 (12) | 0.0259 (4) |
| H17A | 1.2498       | -0.0080       | 0.4570       | 0.039*     |
| H17B | 1.1745       | 0.1161        | 0.4198       | 0.039*     |
| H17C | 1.2059       | 0.0350        | 0.3466       | 0.039*     |

Atomic displacement parameters ( $\text{\AA}^2$ )

|     | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$      | $U^{13}$     | $U^{23}$      |
|-----|--------------|--------------|--------------|---------------|--------------|---------------|
| Mn1 | 0.01013 (14) | 0.01034 (14) | 0.00924 (14) | -0.00008 (10) | 0.00310 (11) | 0.00017 (10)  |
| Cl1 | 0.0296 (2)   | 0.0346 (2)   | 0.0235 (2)   | -0.00607 (17) | 0.00939 (16) | -0.00069 (15) |
| O1  | 0.0177 (5)   | 0.0201 (5)   | 0.0156 (5)   | 0.0057 (4)    | 0.0093 (4)   | 0.0049 (4)    |
| O2  | 0.0518 (8)   | 0.0195 (6)   | 0.0413 (7)   | 0.0159 (5)    | 0.0369 (7)   | 0.0131 (5)    |
| O3  | 0.0187 (5)   | 0.0141 (5)   | 0.0116 (5)   | 0.0021 (4)    | 0.0019 (4)   | -0.0019 (4)   |
| O4  | 0.0170 (5)   | 0.0107 (5)   | 0.0161 (5)   | 0.0004 (4)    | 0.0068 (4)   | 0.0007 (4)    |
| N1  | 0.0140 (6)   | 0.0132 (6)   | 0.0127 (5)   | -0.0008 (4)   | 0.0030 (5)   | 0.0004 (4)    |
| N2  | 0.0168 (6)   | 0.0199 (6)   | 0.0127 (6)   | 0.0039 (5)    | 0.0031 (5)   | -0.0002 (4)   |
| C1  | 0.0193 (7)   | 0.0144 (7)   | 0.0163 (7)   | -0.0006 (5)   | 0.0099 (6)   | -0.0003 (5)   |
| C2  | 0.0211 (7)   | 0.0145 (7)   | 0.0197 (7)   | 0.0043 (6)    | 0.0135 (6)   | 0.0028 (5)    |
| C3  | 0.0220 (8)   | 0.0259 (8)   | 0.0227 (8)   | 0.0017 (6)    | 0.0111 (6)   | 0.0043 (6)    |
| C4  | 0.0296 (9)   | 0.0337 (9)   | 0.0204 (8)   | 0.0064 (7)    | 0.0121 (7)   | 0.0087 (6)    |
| C5  | 0.0381 (10)  | 0.0270 (9)   | 0.0276 (8)   | 0.0046 (7)    | 0.0226 (8)   | 0.0100 (7)    |
| C6  | 0.0293 (9)   | 0.0221 (8)   | 0.0303 (8)   | -0.0027 (7)   | 0.0198 (7)   | 0.0022 (6)    |
| C7  | 0.0242 (8)   | 0.0198 (7)   | 0.0191 (7)   | 0.0017 (6)    | 0.0125 (6)   | 0.0006 (5)    |
| C8  | 0.0147 (6)   | 0.0157 (7)   | 0.0142 (6)   | 0.0016 (5)    | 0.0025 (5)   | 0.0023 (5)    |
| C9  | 0.0196 (7)   | 0.0111 (6)   | 0.0166 (7)   | -0.0005 (5)   | 0.0050 (6)   | 0.0010 (5)    |
| C10 | 0.0150 (6)   | 0.0141 (7)   | 0.0134 (6)   | -0.0028 (5)   | 0.0035 (5)   | -0.0020 (5)   |
| C11 | 0.0136 (6)   | 0.0147 (6)   | 0.0102 (6)   | 0.0008 (5)    | 0.0029 (5)   | 0.0001 (5)    |

|     |             |             |             |             |            |             |
|-----|-------------|-------------|-------------|-------------|------------|-------------|
| C12 | 0.0155 (6)  | 0.0120 (6)  | 0.0132 (6)  | -0.0001 (5) | 0.0031 (5) | 0.0002 (5)  |
| C13 | 0.0125 (6)  | 0.0099 (6)  | 0.0140 (6)  | -0.0027 (5) | 0.0018 (5) | -0.0001 (5) |
| C14 | 0.0262 (9)  | 0.0466 (11) | 0.0154 (7)  | 0.0147 (8)  | 0.0072 (6) | -0.0029 (7) |
| C15 | 0.0322 (10) | 0.0573 (13) | 0.0357 (10) | 0.0100 (9)  | 0.0022 (8) | -0.0289 (9) |
| C16 | 0.0181 (7)  | 0.0180 (7)  | 0.0174 (7)  | 0.0069 (6)  | 0.0037 (6) | 0.0022 (5)  |
| C17 | 0.0189 (8)  | 0.0314 (9)  | 0.0235 (8)  | 0.0012 (7)  | 0.0051 (6) | -0.0036 (6) |

*Geometric parameters (Å, °)*

|                                      |             |             |             |
|--------------------------------------|-------------|-------------|-------------|
| Mn1—O1                               | 2.1233 (10) | C6—H6       | 0.9300      |
| Mn1—O1 <sup>i</sup>                  | 2.1233 (10) | C7—C2       | 1.386 (2)   |
| Mn1—O4 <sup>i</sup>                  | 2.1987 (10) | C7—C6       | 1.386 (2)   |
| Mn1—O4                               | 2.1987 (10) | C8—C9       | 1.3859 (19) |
| Mn1—N1 <sup>i</sup>                  | 2.2980 (12) | C8—H8       | 0.9300      |
| Mn1—N1                               | 2.2980 (12) | C9—C10      | 1.3828 (19) |
| Cl1—C7                               | 1.7464 (16) | C9—H9       | 0.9300      |
| O1—C1                                | 1.2595 (18) | C10—H10     | 0.9300      |
| O2—C1                                | 1.2375 (18) | C11—C10     | 1.3920 (19) |
| O3—C13                               | 1.2435 (17) | C11—C12     | 1.3875 (19) |
| O4—H41                               | 0.896 (12)  | C12—H12     | 0.9300      |
| O4—H42                               | 0.890 (15)  | C13—C11     | 1.4991 (18) |
| N1—C8                                | 1.3420 (18) | C14—C15     | 1.523 (3)   |
| N1—C12                               | 1.3419 (17) | C14—H14A    | 0.9700      |
| N2—C13                               | 1.3355 (19) | C14—H14B    | 0.9700      |
| N2—C14                               | 1.466 (2)   | C15—H15A    | 0.9600      |
| N2—C16                               | 1.4742 (18) | C15—H15B    | 0.9600      |
| C2—C1                                | 1.512 (2)   | C15—H15C    | 0.9600      |
| C2—C3                                | 1.394 (2)   | C16—C17     | 1.519 (2)   |
| C3—C4                                | 1.392 (2)   | C16—H16A    | 0.9700      |
| C3—H3                                | 0.9300      | C16—H16B    | 0.9700      |
| C4—C5                                | 1.385 (3)   | C17—H17A    | 0.9600      |
| C4—H4                                | 0.9300      | C17—H17B    | 0.9600      |
| C5—H5                                | 0.9300      | C17—H17C    | 0.9600      |
| C6—C5                                | 1.384 (2)   |             |             |
| O1—Mn1—O1 <sup>i</sup>               | 180.00 (8)  | C6—C7—C11   | 118.68 (13) |
| O1—Mn1—O4 <sup>i</sup>               | 90.28 (4)   | C6—C7—C2    | 122.05 (15) |
| O1 <sup>i</sup> —Mn1—O4 <sup>i</sup> | 89.72 (4)   | N1—C8—C9    | 122.86 (13) |
| O1—Mn1—O4                            | 89.72 (4)   | N1—C8—H8    | 118.6       |
| O1 <sup>i</sup> —Mn1—O4              | 90.28 (4)   | C9—C8—H8    | 118.6       |
| O1—Mn1—N1 <sup>i</sup>               | 89.75 (4)   | C8—C9—H9    | 120.3       |
| O1 <sup>i</sup> —Mn1—N1 <sup>i</sup> | 90.25 (4)   | C10—C9—C8   | 119.35 (13) |
| O1—Mn1—N1                            | 90.25 (4)   | C10—C9—H9   | 120.3       |
| O1 <sup>i</sup> —Mn1—N1              | 89.75 (4)   | C9—C10—C11  | 118.26 (13) |
| O4 <sup>i</sup> —Mn1—O4              | 180.00 (6)  | C9—C10—H10  | 120.9       |
| O4 <sup>i</sup> —Mn1—N1 <sup>i</sup> | 86.76 (4)   | C11—C10—H10 | 120.9       |
| O4—Mn1—N1 <sup>i</sup>               | 93.24 (4)   | C12—C11—C10 | 118.82 (13) |
| O4 <sup>i</sup> —Mn1—N1              | 93.24 (4)   | C12—C11—C13 | 121.82 (12) |

|                             |              |               |              |
|-----------------------------|--------------|---------------|--------------|
| O4—Mn1—N1                   | 86.76 (4)    | C10—C11—C13   | 119.15 (12)  |
| N1 <sup>i</sup> —Mn1—N1     | 180.00 (10)  | N1—C12—C11    | 123.10 (13)  |
| Mn1—O4—H41                  | 105.2 (15)   | N1—C12—H12    | 118.5        |
| Mn1—O4—H42                  | 125.6 (14)   | C11—C12—H12   | 118.5        |
| H41—O4—H42                  | 105.1 (19)   | O3—C13—N2     | 122.25 (12)  |
| C1—O1—Mn1                   | 129.29 (9)   | O3—C13—C11    | 118.14 (13)  |
| C8—N1—Mn1                   | 123.24 (9)   | N2—C13—C11    | 119.60 (12)  |
| C12—N1—Mn1                  | 119.15 (9)   | N2—C14—C15    | 112.51 (16)  |
| C12—N1—C8                   | 117.59 (12)  | N2—C14—H14A   | 109.1        |
| C13—N2—C14                  | 124.89 (12)  | N2—C14—H14B   | 109.1        |
| C13—N2—C16                  | 118.42 (12)  | C15—C14—H14A  | 109.1        |
| C14—N2—C16                  | 116.32 (13)  | C15—C14—H14B  | 109.1        |
| O1—C1—C2                    | 114.28 (12)  | H14A—C14—H14B | 107.8        |
| O2—C1—O1                    | 126.65 (14)  | C14—C15—H15A  | 109.5        |
| O2—C1—C2                    | 119.07 (13)  | C14—C15—H15B  | 109.5        |
| C3—C2—C1                    | 120.47 (14)  | C14—C15—H15C  | 109.5        |
| C7—C2—C1                    | 121.43 (13)  | H15A—C15—H15B | 109.5        |
| C7—C2—C3                    | 117.99 (14)  | H15A—C15—H15C | 109.5        |
| C2—C3—H3                    | 119.6        | H15B—C15—H15C | 109.5        |
| C4—C3—C2                    | 120.76 (16)  | N2—C16—C17    | 111.28 (13)  |
| C4—C3—H3                    | 119.6        | N2—C16—H16A   | 109.4        |
| C3—C4—H4                    | 120.1        | N2—C16—H16B   | 109.4        |
| C5—C4—C3                    | 119.78 (15)  | C17—C16—H16A  | 109.4        |
| C5—C4—H4                    | 120.1        | C17—C16—H16B  | 109.4        |
| C4—C5—H5                    | 119.8        | H16A—C16—H16B | 108.0        |
| C6—C5—C4                    | 120.42 (15)  | C16—C17—H17A  | 109.5        |
| C6—C5—H5                    | 119.8        | C16—C17—H17B  | 109.5        |
| C5—C6—C7                    | 118.98 (16)  | C16—C17—H17C  | 109.5        |
| C5—C6—H6                    | 120.5        | H17A—C17—H17B | 109.5        |
| C7—C6—H6                    | 120.5        | H17A—C17—H17C | 109.5        |
| C2—C7—C11                   | 119.26 (11)  | H17B—C17—H17C | 109.5        |
| O1—Mn1—N1—C8                | -112.21 (12) | C3—C2—C1—O1   | 75.74 (18)   |
| O1 <sup>i</sup> —Mn1—N1—C8  | 67.79 (12)   | C3—C2—C1—O2   | -104.05 (18) |
| O1—Mn1—N1—C12               | 66.18 (11)   | C7—C2—C1—O1   | -100.36 (17) |
| O1 <sup>i</sup> —Mn1—N1—C12 | -113.82 (11) | C7—C2—C1—O2   | 79.85 (19)   |
| O4 <sup>i</sup> —Mn1—O1—C1  | 2.94 (12)    | C1—C2—C3—C4   | -175.23 (15) |
| O4—Mn1—O1—C1                | -177.06 (12) | C7—C2—C3—C4   | 1.0 (2)      |
| O4 <sup>i</sup> —Mn1—N1—C8  | -21.92 (12)  | C2—C3—C4—C5   | 0.5 (3)      |
| O4—Mn1—N1—C8                | 158.08 (12)  | C3—C4—C5—C6   | -1.1 (3)     |
| O4 <sup>i</sup> —Mn1—N1—C12 | 156.47 (11)  | C7—C6—C5—C4   | 0.3 (3)      |
| O4—Mn1—N1—C12               | -23.53 (11)  | C6—C7—C2—C1   | 174.34 (14)  |
| N1 <sup>i</sup> —Mn1—O1—C1  | -83.82 (12)  | C6—C7—C2—C3   | -1.8 (2)     |
| N1—Mn1—O1—C1                | 96.18 (12)   | C11—C7—C2—C1  | -4.3 (2)     |
| Mn1—O1—C1—O2                | -16.0 (2)    | C11—C7—C2—C3  | 179.50 (12)  |
| Mn1—O1—C1—C2                | 164.20 (9)   | C2—C7—C6—C5   | 1.2 (2)      |
| Mn1—N1—C8—C9                | 177.23 (11)  | C11—C7—C6—C5  | 179.86 (13)  |
| C12—N1—C8—C9                | -1.2 (2)     | N1—C8—C9—C10  | 0.0 (2)      |



|                |              |                |              |
|----------------|--------------|----------------|--------------|
| Mn1—N1—C12—C11 | -177.57 (11) | C8—C9—C10—C11  | 1.5 (2)      |
| C8—N1—C12—C11  | 0.9 (2)      | C12—C11—C10—C9 | -1.7 (2)     |
| C14—N2—C13—O3  | -175.90 (15) | C13—C11—C10—C9 | -176.41 (13) |
| C16—N2—C13—O3  | -3.2 (2)     | C10—C11—C12—N1 | 0.5 (2)      |
| C14—N2—C13—C11 | 4.1 (2)      | C13—C11—C12—N1 | 175.09 (13)  |
| C16—N2—C13—C11 | 176.82 (12)  | O3—C13—C11—C10 | 62.17 (19)   |
| C13—N2—C14—C15 | -108.92 (18) | O3—C13—C11—C12 | -112.38 (16) |
| C16—N2—C14—C15 | 78.20 (18)   | N2—C13—C11—C10 | -117.81 (15) |
| C13—N2—C16—C17 | -90.68 (17)  | N2—C13—C11—C12 | 67.64 (19)   |
| C14—N2—C16—C17 | 82.69 (17)   |                |              |

Symmetry code: (i)  $-x+1, -y, -z$ .

*Hydrogen-bond geometry (Å, °)*

| <i>D—H...A</i>            | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|---------------------------|------------|--------------|--------------|----------------|
| O4—H41...O2 <sup>i</sup>  | 0.90 (2)   | 1.83 (2)     | 2.666 (2)    | 154 (2)        |
| O4—H42...O3 <sup>ii</sup> | 0.89 (2)   | 1.86 (2)     | 2.729 (1)    | 166 (2)        |

Symmetry codes: (i)  $-x+1, -y, -z$ ; (ii)  $-x+3/2, y-1/2, -z+1/2$ .