



Crystal structure of aquachlorido(nitrato- κ^2O,O')-[1-(pyridin-2-ylmethylidene- κN)-2-(pyridin-2-yl- κN)hydrazine- κN^1]manganese(II)

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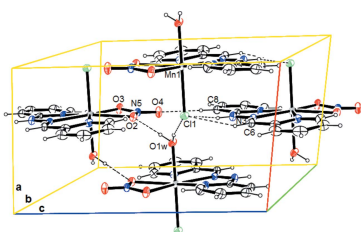
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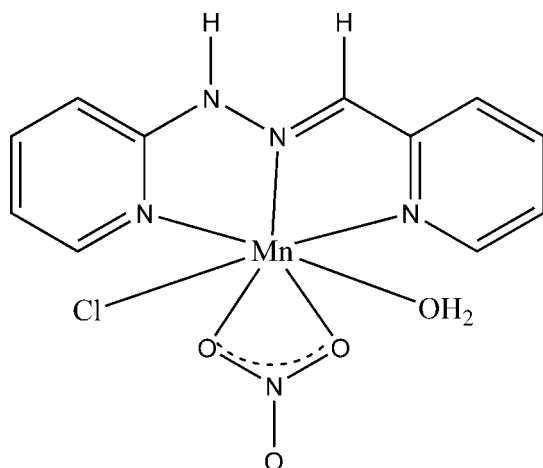
The search for novel manganese(II) compounds having interesting magnetic properties, using 1-(pyridin-2-ylmethylidene)-2-(pyridin-2-yl)hydrazine (HL) as a tridentate ligand, led to the preparation of the title mononuclear material, [MnCl(NO₃)(C₁₁H₁₀N₄)(H₂O)], and the determination of its structure by XRD. The asymmetric unit comprises a discrete molecule in which the cation Mn^{II} is heptacoordinated. The environment around the cation is an almost perfect pentagonal bipyramid. The base is defined by the two N atoms of the pyridine rings, the N atom of the imino function of the ligand and the two O atoms of the chelating bidentate nitrate ligand. The apical positions are occupied by a Cl atom and a water molecule. In the crystal, there are numerous hydrogen bonds of the types Ow—H···ONO₂ and C—H···ONO₂, which generate layers parallel to the *bc* plane in which the ligands in the axial positions point into the interlayer space. These axial ligands give rise to hydrogen bonds of the types Ow—H···ONO₂, Ow—H···Cl, N—H···Cl and C—H···Cl, leading to a three-dimensional framework. The chain bridging the two pyridine rings is disordered over two sets of sites in a 0.53 (2):0.47 (2) ratio.

1. Chemical context

Although very much studied, the coordination chemistry of manganese remains very interesting as this metal can have several degrees of oxidation and its complexes can display different coordination numbers and geometries that are not always easily predicted (Chiswell *et al.*, 1987; Baldeau *et al.*, 2004; Mikuriya *et al.*, 1997). Although the coordination numbers four and six are the most common in the coordination chemistry of manganese, the coordination numbers five, seven and eight are also observed (Louloudi *et al.*, 1999). As a result of the multiple degrees of oxidation of this metal, interest in the coordination chemistry of manganese complexes is considerable. The involvement of manganese in various important biological processes such as oxidation of water by photosynthetic enzymes (Whittaker & Whittaker, 1997), hydrogen peroxide disproportionation by catalase (Meier *et al.*, 1996), superoxide dismutase (SOD) (Schwartz *et al.*, 2000), ribonucleotide reductase and lipoxygenase (Baffert *et al.*, 2003) increases the interest of scientists in this metal. These examples from nature inspire chemists to search for biomimetic catalysts of these metalloenzymes that are highly selective and cause little damage to the environment



(Krishnan & Vancheesan, 1999). Manganese complexes are also used as catalysts in many processes such as epoxidation of alkene (Castaman *et al.*, 2009), oxidation (Wegermann *et al.*, 2014) and hydrogenation of ketones (Bruneau-Voisine *et al.*, 2017). The involvement of the metal center in these processes depends as much on its degree of oxidation as on its coordination number in the complex. The synthetic procedures adopted are essential for yielding complexes with specific properties. In this context, for the synthesis of the hepta-coordinated Mn^{II} title complex, we use a one-pot synthesis method, which is an efficient approach to prepare a large variety of coordination compounds (Oyaizu *et al.*, 2000). Manganese dichloride tetrahydrate is mixed with the synthesized organic ligand (HL), which provides three soft nitrogen-binding sites in the presence of nitrate anions that can act with hard oxygen-binding sites to yield a mononuclear hepta-coordinated manganese(II) complex.



2. Structural commentary

The structure of the title complex is shown in Fig. 1. The asymmetric unit comprises a discrete molecule in which the cation Mn^{II} is hepta-coordinated. The coordination polyhedron of the Mn^{II} center is best described as a distorted pentagonal bipyramid with an MnN₃O₃Cl chromophore. The basal plane is occupied by two nitrogen atoms from the pyridine rings, one nitrogen atom from the imino function and two oxygen atoms from the chelating bidentate nitrate group. The metal-bound ligand nitrogen atoms exhibit angles of 69.85 (7)° (N1—Mn1—N2) and 69.62 (7)° (N2—Mn1—N4) which are slightly different from the ideal angle for a regular pentagon (72°). The sum of the equatorial angles around Mn^{II} [Cl1—Mn1—O1W = 179.07 (4)°] is very close to the ideal value of 180°. The Mn—O/N bond lengths (Table 1) are longer than those observed in the heptadentate manganese complex [Mn(L)(NO₃)₂] [L is 2,6-bis(1-butyl-1*H*-benzo[*d*]imidazol-2-yl)pyridine; Kose & McKee *et al.*, 2014]. The apical bond Mn1—Cl1 [2.4999 (6) Å] is the longest and is comparable to those found for the complex [Mn(L)(Cl)₂].MeOH [Mn1—Cl1 = 2.4849 (7), Mn1—Cl2 = 2.5465 (7) Å] [L is 2,6-bis[(2-*h*-

Table 1
Selected bond lengths (Å).

Mn1—O1W	2.2239 (14)	N2—N3A	1.288 (11)
Mn1—N2	2.2750 (16)	N2—C6	1.325 (13)
Mn1—N4	2.3292 (16)	N2—C6A	1.465 (10)
Mn1—N1	2.3300 (16)	N3—C7	1.566 (9)
Mn1—O2	2.3372 (14)	C5—C6	1.398 (15)
Mn1—O3	2.3635 (15)	C5—N3A	1.450 (11)
Mn1—Cl1	2.4999 (6)	C7—C6A	1.180 (11)
N2—N3	1.217 (7)		

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

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H1WA...Cl1 ⁱ	0.91	2.23	3.1225 (15)	170
O1W—H1WB...O2 ⁱⁱ	0.87	1.92	2.7969 (19)	177
O1W—H1WB...N5 ⁱⁱ	0.87	2.68	3.506 (2)	157
N3—H3N...Cl1 ⁱⁱⁱ	0.86	2.71	3.501 (7)	153
C1—H1...O2	0.93	2.53	3.140 (3)	124
C6—H6...Cl1 ⁱⁱⁱ	0.93	2.66	3.489 (11)	149
C8—H8...O4 ^{iv}	0.93	2.54	3.290 (3)	138
C10—H10...Cl1 ^v	0.93	2.83	3.669 (3)	152
C11—H11...O3	0.93	2.44	3.062 (3)	125

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 2, -y + 1, -z + 2$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $x, y, z - 1$; (v) $-x + 1, -y, -z + 1$.

droxyphenylimino)methyl]pyridine; Kose *et al.*, 2015}. The second axial bond is the shortest distance in the structure [Mn1—O1W = 2.2239 (14) Å]. The two pyridine rings are connected by a disordered chain C—CH=N—NH—C in which the bond lengths are slightly different from those observed in similar complexes; this may be related to the observed disorder. Two intramolecular hydrogen bonds, C1—H1...O2 and C11—H11...O3, are also observed in the structure (Table 2, Fig. 1).

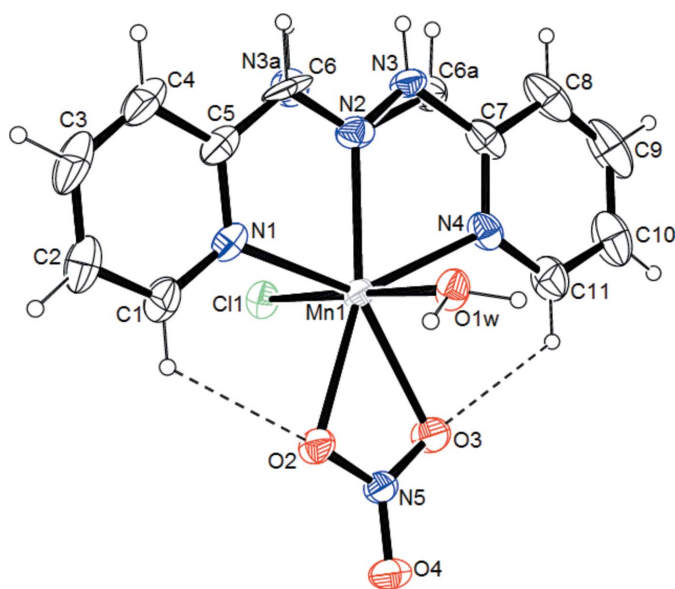


Figure 1
An ORTEP view of the title compound, showing the atom-numbering scheme and intramolecular hydrogen bonds as dashed lines. Displacement ellipsoids are plotted at the 50% probability level.

3. Supramolecular features

In the crystal, the complex molecules are linked by hydrogen bonds, giving rise to a three-dimensional network (Fig. 2, Table 2). The structure is built up from pentagonal bipyramids around the Mn^{II} atom, which are assembled in layers parallel to the *bc* plane. These layers are interconnected by hydrogen bonds. The coordinating axial water molecule points into the interlayer space and act as a hydrogen-bond donor towards oxygen atom O2-NO₂ and chlorine atom Cl1 (Fig. 2) *via* the hydrogen bonds O1W–H1WB···O2ⁱⁱ and O1W–H1WA···Cl1ⁱ, [symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 2, -y + 1, -z + 2$]. The axial Cl1 atom points also in the interlayer space and acts as a hydrogen-bond acceptor toward N3–H3N···Cl1ⁱⁱⁱ and C6–H6···Cl1ⁱⁱⁱ [symmetry code: (iii) $-x + 1, -y + 1, -z + 1$]. The combined hydrogen bonds link the layers into a three-dimensional framework. Within a layer, the molecules are interconnected by hydrogen bonds of the type C–H···ONO₂ [C8–H8···O4^{iv}–NO₂; symmetry code: (iv) $x, y, z - 1$].

4. Database survey

The ligand 1-(2-pyridylmethylidene)-2-(pyridin-2-yl)hydrazine has been widely used in coordination chemistry. The current release of the CSD (Version 5.39, last update Nov 2017; Groom *et al.*, 2016) affords 22 hits. Seven examples of complexes with the above ligand with *f*-block metal ions appear in the literature (Baraniak *et al.*, 1976; Ndiaye-Gueye, Dieng, Thiam, Sow *et al.*, 2017; Ndiaye-Gueye, Dieng, Thiam, Lo *et al.*, 2017; Ndiaye-Gueye, Dieng, Lo *et al.*, 2017; Gueye *et al.*, 2017). The other entries are for complexes with *p*- and *d*-block metal ions. Structures are available for Ca^{II} (Vantomme *et al.*, 2014), Cu^{II} (Mesa *et al.*, 1988, 1989; Rojo *et al.*, 1988;

Ainscough *et al.*, 1996; Chowdhury *et al.*, 2009; Mukherjee *et al.*, 2010; Chang *et al.*, 2011), Co^{II} (Gerloch *et al.*, 1966), Ni^{II} (Chiumia *et al.*, 1999) and Zn^{II} (Dumitru *et al.*, 2005; Vantomme *et al.*, 2014). In all cases, the ligand behaves as a tridentate ligand acting through the soft nitrogen donor atoms from the two pyridine rings and the imino function. The hard protonated nitrogen atom remains uncoordinated in all complexes.

5. Synthesis and crystallization

A mixture of 2-hydrazinopyridine (1 mmol) and 2-pyridine-carbaldehyde (1 mmol) in ethanol (10 mL) was stirred under reflux for 30 min. A mixture of ammonium nitrate (3 mmol) and MnCl₂·4H₂O (1 mmol) in ethanol (10 mL) was added to the solution. The mixture was stirred for 30 min and the resulting yellow solution was filtered and the filtrate was kept at 298 K. A yellow powder appeared after one day and was collected by filtration, yield 65%. Analysis calculated for [C₁₁H₁₂ClMnN₅O₄] C, 32.41; H, 3.26; N, 22.67. Found: C, 32.37; H, 3.19; N, 22.60%. $\mu_{\text{eff}}(\mu_{\text{B}})$: 5.98 Λ_{M} (S cm² mol⁻¹): 14. IR (cm⁻¹): 3233, 1609, 1560, 1521, 1465, 1422, 1289, 1148, 776, 673.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms (=CH, NH and OH₂ groups) were optimized geometrically (C–H = 0.93, N–H = 0.86 and O–H = 0.87–0.91 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O})$. The chain bridging the two pyridine rings is disordered. This disorder may be explained by the fact that the sequence of atoms C(Py)–CH=N–NH–C(py) overlaps with the sequence C(py)–NH–N=CH–C(py), meaning two orientations of the ligand. In

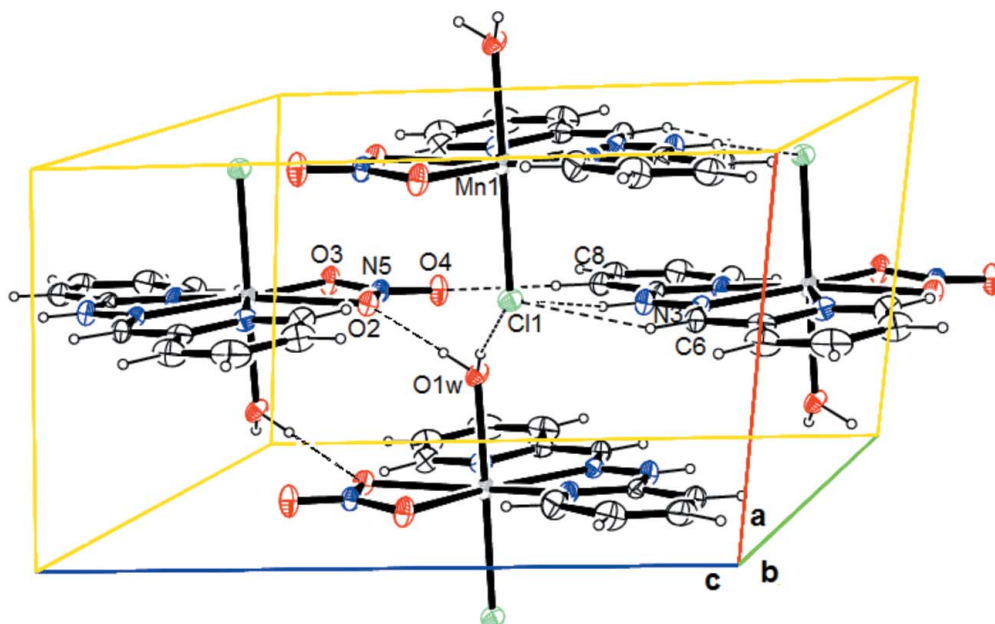


Figure 2 Representation of the title compound, showing the intermolecular hydrogen bonds as dashed lines.

Table 3

Experimental details.

Crystal data	
Chemical formula	[MnCl(NO ₃)(C ₁₁ H ₁₀ N ₄)(H ₂ O)]
<i>M_r</i>	368.65
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.9698 (1), 10.6055 (2), 10.8476 (2)
α , β , γ (°)	98.784 (2), 97.636 (2), 108.308 (2)
<i>V</i> (Å ³)	738.21 (2)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.10
Crystal size (mm)	0.09 × 0.08 × 0.06
Data collection	
Diffraction	Bruker KappaCCD
Absorption correction	–
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	22026, 3571, 2905
<i>R</i> _{int}	0.038
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.034, 0.091, 1.06
No. of reflections	3571
No. of parameters	209
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.31, –0.46

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *ORTEP-3 for Windows* (Farrugia, 2012).

such a case, for the refinement it was assumed that the C atom of the CH group from one chain and the NH atoms from the second chain occupy the same position. The same relates inversely. The occupancy factor refined to 0.53 (2):0.47 (2).

Funding information

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supporting information

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Crystal structure of aquachlorido(nitrato- κ^2O,O')[1-(pyridin-2-yl- κN)-2-(pyridin-2-ylmethylidene- κN)hydrazine- κN^2]manganese(II)

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b).

Aquachlorido(nitrato- κ^2O,O')[1-(pyridin-2-yl- κN)-2-(pyridin-2-ylmethylidene- κN)hydrazine- κN^2]manganese(II)

Crystal data

[MnCl(NO₃)(C₁₁H₁₀N₄)(H₂O)]

$M_r = 368.65$

Triclinic, $P\bar{1}$

$a = 6.9698$ (1) Å

$b = 10.6055$ (2) Å

$c = 10.8476$ (2) Å

$\alpha = 98.784$ (2)°

$\beta = 97.636$ (2)°

$\gamma = 108.308$ (2)°

$V = 738.21$ (2) Å³

$Z = 2$

$F(000) = 374$

$D_x = 1.658$ Mg m⁻³

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

Cell parameters from 9920 reflections

$\theta = 2.4$ – 28.6 °

$\mu = 1.10$ mm⁻¹

$T = 293$ K

Prismatic, yellow

$0.09 \times 0.08 \times 0.06$ mm

Data collection

Bruker KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Detector resolution: 9 pixels mm⁻¹

CCD scans

22026 measured reflections

3571 independent reflections

2905 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\text{max}} = 29.1$ °, $\theta_{\text{min}} = 3.6$ °

$h = -9 \rightarrow 9$

$k = -14 \rightarrow 14$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.091$

$S = 1.06$

3571 reflections

209 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.1976P]$

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

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

$$\Delta\rho_{\max} = 0.31 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Mn1	0.71914 (4)	0.39182 (3)	0.74637 (2)	0.04153 (11)	
Cl1	0.33417 (8)	0.30415 (5)	0.69679 (5)	0.05511 (14)	
O1W	1.0615 (2)	0.46771 (14)	0.79278 (13)	0.0541 (3)	
H1WA	1.140892	0.416765	0.774402	0.081*	
H1WB	1.118139	0.516748	0.869134	0.081*	
O2	0.7483 (2)	0.38248 (13)	0.96166 (13)	0.0529 (3)	
O3	0.7175 (3)	0.19991 (15)	0.83256 (13)	0.0631 (4)	
O4	0.7546 (3)	0.20477 (18)	1.03568 (15)	0.0728 (5)	
N1	0.7321 (3)	0.61349 (16)	0.81806 (18)	0.0528 (4)	
N2	0.7448 (2)	0.50621 (19)	0.58471 (17)	0.0519 (4)	
N3	0.7437 (8)	0.4569 (8)	0.4755 (5)	0.0484 (13)	0.53 (2)
H3N	0.742706	0.499635	0.414304	0.058*	0.53 (2)
N4	0.7511 (3)	0.25742 (19)	0.56463 (15)	0.0550 (4)	
N5	0.7400 (3)	0.25956 (16)	0.94508 (15)	0.0474 (4)	
C1	0.7239 (4)	0.6682 (2)	0.9358 (2)	0.0651 (6)	
H1	0.706417	0.613021	0.995278	0.078*	
C2	0.7400 (4)	0.8019 (2)	0.9744 (3)	0.0810 (8)	
H2	0.735126	0.835887	1.057767	0.097*	
C3	0.7630 (5)	0.8828 (3)	0.8875 (4)	0.0962 (11)	
H3	0.773464	0.973219	0.910758	0.115*	
C4	0.7707 (4)	0.8300 (3)	0.7648 (4)	0.0840 (9)	
H4	0.787019	0.884113	0.704332	0.101*	
C5	0.7536 (3)	0.6938 (2)	0.7329 (3)	0.0593 (6)	
C6	0.757 (2)	0.6350 (13)	0.6090 (13)	0.072 (6)	0.53 (2)
H6	0.766705	0.684993	0.545312	0.087*	0.53 (2)
C7	0.7444 (3)	0.3077 (3)	0.45798 (19)	0.0605 (6)	
C8	0.7378 (4)	0.2313 (4)	0.3399 (2)	0.0898 (10)	
H8	0.732275	0.267981	0.267437	0.108*	
C9	0.7394 (5)	0.1032 (4)	0.3320 (3)	0.1050 (13)	
H9	0.732556	0.050255	0.253735	0.126*	
C10	0.7511 (5)	0.0521 (3)	0.4395 (3)	0.0934 (10)	
H10	0.754750	-0.035280	0.435722	0.112*	
C11	0.7575 (4)	0.1323 (3)	0.5545 (2)	0.0744 (7)	
H11	0.766778	0.097228	0.627718	0.089*	
C6A	0.7462 (14)	0.4203 (12)	0.4658 (9)	0.051 (2)*	0.47 (2)
H6A	0.748686	0.456233	0.392738	0.061*	0.47 (2)

N3A	0.755 (2)	0.6312 (11)	0.6045 (10)	0.057 (4)*	0.47 (2)
H3NA	0.761514	0.675558	0.544192	0.069*	0.47 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.05255 (18)	0.03866 (16)	0.03561 (16)	0.02057 (12)	0.00415 (12)	0.00731 (11)
Cl1	0.0516 (3)	0.0560 (3)	0.0593 (3)	0.0232 (2)	0.0087 (2)	0.0079 (2)
O1W	0.0570 (8)	0.0574 (8)	0.0463 (7)	0.0285 (7)	-0.0016 (6)	-0.0033 (6)
O2	0.0720 (9)	0.0401 (7)	0.0464 (7)	0.0235 (6)	0.0058 (7)	0.0038 (6)
O3	0.0995 (12)	0.0490 (8)	0.0421 (8)	0.0330 (8)	0.0078 (8)	0.0023 (6)
O4	0.1101 (13)	0.0758 (10)	0.0518 (9)	0.0480 (10)	0.0203 (9)	0.0308 (8)
N1	0.0537 (9)	0.0395 (8)	0.0670 (11)	0.0204 (7)	0.0041 (8)	0.0132 (8)
N2	0.0423 (8)	0.0652 (11)	0.0491 (10)	0.0171 (8)	0.0027 (7)	0.0224 (8)
N3	0.069 (3)	0.046 (3)	0.034 (2)	0.026 (2)	0.0046 (15)	0.014 (2)
N4	0.0540 (9)	0.0652 (11)	0.0392 (9)	0.0180 (8)	0.0063 (7)	-0.0017 (7)
N5	0.0609 (10)	0.0437 (8)	0.0407 (8)	0.0230 (7)	0.0073 (7)	0.0091 (7)
C1	0.0751 (15)	0.0483 (11)	0.0736 (15)	0.0301 (11)	0.0082 (12)	0.0037 (10)
C2	0.0791 (16)	0.0505 (13)	0.111 (2)	0.0316 (12)	0.0110 (15)	-0.0054 (14)
C3	0.0790 (18)	0.0406 (12)	0.170 (3)	0.0292 (12)	0.019 (2)	0.0101 (17)
C4	0.0739 (16)	0.0532 (13)	0.139 (3)	0.0303 (12)	0.0211 (17)	0.0425 (17)
C5	0.0462 (11)	0.0481 (11)	0.0895 (18)	0.0194 (9)	0.0080 (11)	0.0286 (11)
C6	0.067 (5)	0.071 (6)	0.095 (9)	0.028 (3)	0.003 (3)	0.067 (7)
C7	0.0391 (10)	0.0915 (18)	0.0366 (10)	0.0094 (10)	0.0041 (8)	0.0010 (10)
C8	0.0651 (15)	0.134 (3)	0.0410 (13)	0.0061 (17)	0.0118 (11)	-0.0108 (15)
C9	0.0724 (18)	0.132 (3)	0.0646 (19)	-0.0014 (18)	0.0206 (14)	-0.0446 (19)
C10	0.091 (2)	0.0782 (18)	0.091 (2)	0.0175 (15)	0.0285 (17)	-0.0271 (16)
C11	0.0906 (18)	0.0643 (14)	0.0637 (15)	0.0286 (13)	0.0194 (13)	-0.0085 (11)

Geometric parameters (Å, °)

Mn1—O1W	2.2239 (14)	C1—C2	1.380 (3)
Mn1—N2	2.2750 (16)	C1—H1	0.9300
Mn1—N4	2.3292 (16)	C2—C3	1.361 (5)
Mn1—N1	2.3300 (16)	C2—H2	0.9300
Mn1—O2	2.3372 (14)	C3—C4	1.378 (5)
Mn1—O3	2.3635 (15)	C3—H3	0.9300
Mn1—Cl1	2.4999 (6)	C4—C5	1.396 (3)
O1W—H1WA	0.9067	C4—H4	0.9300
O1W—H1WB	0.8745	C5—C6	1.398 (15)
O2—N5	1.270 (2)	C5—N3A	1.450 (11)
O3—N5	1.251 (2)	C6—H6	0.9300
O4—N5	1.224 (2)	C7—C6A	1.180 (11)
N1—C1	1.337 (3)	C7—C8	1.394 (3)
N1—C5	1.341 (3)	C8—C9	1.352 (5)
N2—N3	1.217 (7)	C8—H8	0.9300
N2—N3A	1.288 (11)	C9—C10	1.362 (5)
N2—C6	1.325 (13)	C9—H9	0.9300

N2—C6A	1.465 (10)	C10—C11	1.386 (3)
N3—C7	1.566 (9)	C10—H10	0.9300
N3—H3N	0.8600	C11—H11	0.9300
N4—C11	1.330 (3)	C6A—H6A	0.9300
N4—C7	1.347 (3)	N3A—H3NA	0.8600
O1W—Mn1—N2	87.38 (6)	N1—C1—C2	123.8 (3)
O1W—Mn1—N4	85.96 (6)	N1—C1—H1	118.1
N2—Mn1—N4	69.62 (7)	C2—C1—H1	118.1
O1W—Mn1—N1	87.94 (5)	C3—C2—C1	118.4 (3)
N2—Mn1—N1	69.85 (7)	C3—C2—H2	120.8
N4—Mn1—N1	139.23 (7)	C1—C2—H2	120.8
O1W—Mn1—O2	83.70 (5)	C2—C3—C4	119.6 (2)
N2—Mn1—O2	152.55 (6)	C2—C3—H3	120.2
N4—Mn1—O2	135.11 (6)	C4—C3—H3	120.2
N1—Mn1—O2	83.90 (6)	C3—C4—C5	118.7 (3)
O1W—Mn1—O3	89.13 (6)	C3—C4—H4	120.6
N2—Mn1—O3	151.72 (6)	C5—C4—H4	120.6
N4—Mn1—O3	82.14 (6)	N1—C5—C4	122.1 (3)
N1—Mn1—O3	138.06 (6)	N1—C5—C6	117.1 (4)
O2—Mn1—O3	54.21 (5)	C4—C5—C6	120.8 (5)
O1W—Mn1—C11	179.07 (4)	N1—C5—N3A	116.5 (5)
N2—Mn1—C11	93.54 (4)	C4—C5—N3A	121.4 (5)
N4—Mn1—C11	94.25 (5)	N2—C6—C5	118.3 (7)
N1—Mn1—C11	92.48 (4)	N2—C6—H6	120.9
O2—Mn1—C11	95.52 (4)	C5—C6—H6	120.9
O3—Mn1—C11	90.00 (5)	C6A—C7—N4	118.6 (5)
Mn1—O1W—H1WA	124.5	C6A—C7—C8	119.5 (5)
Mn1—O1W—H1WB	116.1	N4—C7—C8	122.0 (3)
H1WA—O1W—H1WB	105.9	N4—C7—N3	115.6 (2)
N5—O2—Mn1	95.09 (10)	C8—C7—N3	122.4 (3)
N5—O3—Mn1	94.39 (10)	C9—C8—C7	119.1 (3)
C1—N1—C5	117.34 (19)	C9—C8—H8	120.4
C1—N1—Mn1	126.26 (14)	C7—C8—H8	120.4
C5—N1—Mn1	116.38 (16)	C8—C9—C10	119.5 (3)
N3—N2—C6	116.9 (6)	C8—C9—H9	120.2
N3A—N2—C6A	128.2 (6)	C10—C9—H9	120.2
N3—N2—Mn1	124.8 (4)	C9—C10—C11	119.0 (3)
N3A—N2—Mn1	120.1 (5)	C9—C10—H10	120.5
C6—N2—Mn1	118.4 (6)	C11—C10—H10	120.5
C6A—N2—Mn1	111.7 (5)	N4—C11—C10	122.7 (3)
N2—N3—C7	113.2 (4)	N4—C11—H11	118.6
N2—N3—H3N	123.4	C10—C11—H11	118.6
C7—N3—H3N	123.4	C7—C6A—N2	123.3 (8)
C11—N4—C7	117.6 (2)	C7—C6A—H6A	118.4
C11—N4—Mn1	126.03 (15)	N2—C6A—H6A	118.4
C7—N4—Mn1	116.15 (16)	N2—N3A—C5	117.1 (8)
O4—N5—O3	122.94 (16)	N2—N3A—H3NA	121.5

O4—N5—O2	120.77 (16)	C5—N3A—H3NA	121.5
O3—N5—O2	116.29 (15)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1 <i>W</i> —H1 <i>WA</i> ...C11 ⁱ	0.91	2.23	3.1225 (15)	170
O1 <i>W</i> —H1 <i>WB</i> ...O2 ⁱⁱ	0.87	1.92	2.7969 (19)	177
O1 <i>W</i> —H1 <i>WB</i> ...N5 ⁱⁱ	0.87	2.68	3.506 (2)	157
N3—H3 <i>N</i> ...C11 ⁱⁱⁱ	0.86	2.71	3.501 (7)	153
C1—H1...O2	0.93	2.53	3.140 (3)	124
C6—H6...C11 ⁱⁱⁱ	0.93	2.66	3.489 (11)	149
C8—H8...O4 ^{iv}	0.93	2.54	3.290 (3)	138
C10—H10...C11 ^v	0.93	2.83	3.669 (3)	152
C11—H11...O3	0.93	2.44	3.062 (3)	125

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+2, -y+1, -z+2$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, y, z-1$; (v) $-x+1, -y, -z+1$.