

# Redetermination of diaqua[*N,N'*-bis(3-methoxy-2-oxidobenzylidene)ethylenediamine- $\kappa^4$ O,*N,N',O'*]-manganese(III) perchlorate at 100 K

Shabana Noor,<sup>a\*</sup> Rüdiger W. Seidel,<sup>b</sup> Richard Goddard,<sup>b</sup> Sarvendra Kumar<sup>c\*</sup> and Suhail Sabir<sup>a</sup>

Received 19 October 2016

Accepted 28 October 2016

Edited by M. Weil, Vienna University of Technology, Austria

**Keywords:** crystal structure; redetermination; Jahn–Teller effect; manganese(III) coordination complex.

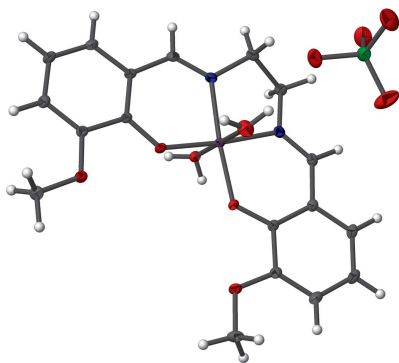
CCDC reference: 1512691

**Structural data:** full structural data are available from iucrdata.iucr.org

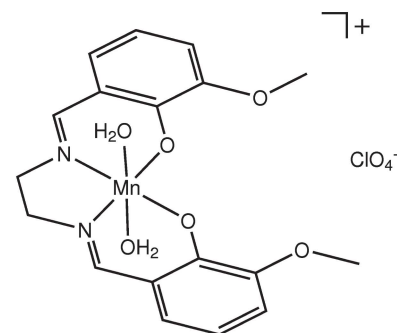
<sup>a</sup>Department of Chemistry, Aligarh Muslim University, Aligarh 202 002, India, <sup>b</sup>Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany, and <sup>c</sup>Faculty of Pharmaceutical Science, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan. \*Correspondence e-mail: shabanachem0711@gmail.com, s.kumar@msn.com

The crystal structure of the organic–inorganic title salt,  $[\text{Mn}(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4)(\text{H}_2\text{O})_2]\text{ClO}_4$ , has been redetermined at 100 K. In contrast to the crystal structure determinations at room temperature [Akitsu *et al.* (2005). *Acta Cryst. C* **61**, m324–m328; Bermejo *et al.* (2007). *Eur. J. Inorg. Chem.* pp. 3789–3797], positional disorder of the ethylene bridge in the Schiff base ligand and the perchlorate anion is not observed at 100 K. The  $\text{Mn}^{\text{III}}$  ion is six-coordinated with the tetradentate Schiff base chelate ligand *N,N'*-bis(3-methoxy-2-oxobenzylidene)ethylenediamine occupying coordination sites in the equatorial plane and the aqua ligands residing in the two axial positions. The octahedral coordination sphere of the  $\text{Mn}^{\text{III}}$  ion exhibits an axial elongation due to the Jahn–Teller effect, which is characteristic of a  $d^4$  high-spin electronic configuration.

## 3D view



## Chemical scheme



## Structure description

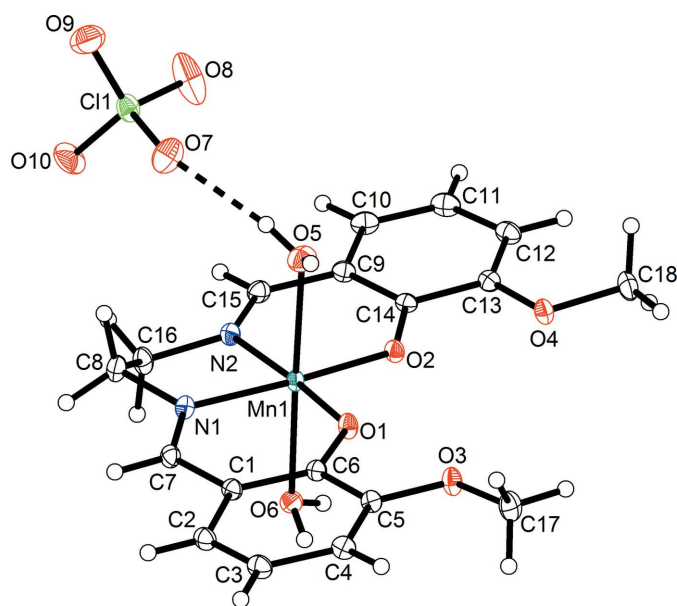
Transition metal complexes of Schiff bases show an interesting chemistry, including various aspects of organometallic and bioinorganic chemistry (Yamada, 1999). Schiff base complexes find application in a variety of catalytic transformations as they have the ability to coordinate to metal ions and stabilize unusual oxidation states. Metal complexes containing salen-type Schiff bases are important owing to their resemblance to metalloproteins with respect to their electronic structure and catalytic activities in the way that they mimic enzymatic oxidations (Groves, 2005). Interest in the coordination chemistry of manganese complexes in high oxidation states is largely centred on the

preparation of functional models of manganese-containing biological systems, such as SOD (Bull *et al.*, 1991) and azide-sensitive catalases (Dismukes, 1996). In addition, the catalytic properties of manganese complexes in organic processes, *e.g.* in the enantioselective epoxidation of olefins (Zhang *et al.*, 1990) make manganese chemistry an attractive area of research.

The cationic complex in the title salt shows a distorted octahedral environment around the Mn<sup>III</sup> ion. The Schiff base ligand behaves as a tetradentate chelate ligand with two nitrogen atoms, N1 and N2, and two oxygen atoms, O1 and O2, occupying the equatorial plane (Fig. 1). O5 and O6 of the coordinating water molecules occupy the two axial positions, whereby the axial Mn–O bonds are elongated owing to the Jahn–Teller effect, which is characteristic of the *d*<sup>4</sup> electronic configuration. Magnetochemical characterization revealed a *d*<sup>4</sup> high-spin configuration (*S* = 2) of the complex (Akitsu *et al.*, 2005).

In the crystal, two cationic complexes form a centrosymmetric hydrogen-bonded dimer, in which an aqua ligand of one complex forms two bifurcated hydrogen bonds to the oxygen atoms of the chelate ligand in the symmetry-related complex (Fig. 2). The second aqua ligand forms hydrogen bonds to the oxygen atoms of two perchlorate anions. Hydrogen-bond details are listed in Table 1.

The structure of the title compound has been previously determined at room temperature by others [Akitsu *et al.*, 2005; Bermejo *et al.*, 2007; refcodes in the Cambridge Structural Database (CSD; Groom *et al.*, 2016): TAPSOT and TAPSOT01, respectively]. It should be noted that the authors of TAPSOT01 (Bermejo *et al.*, 2007) described the compound as a monohydrate in the experimental section of the corresponding article ('compound 2'), although TAPSOT in the CSD



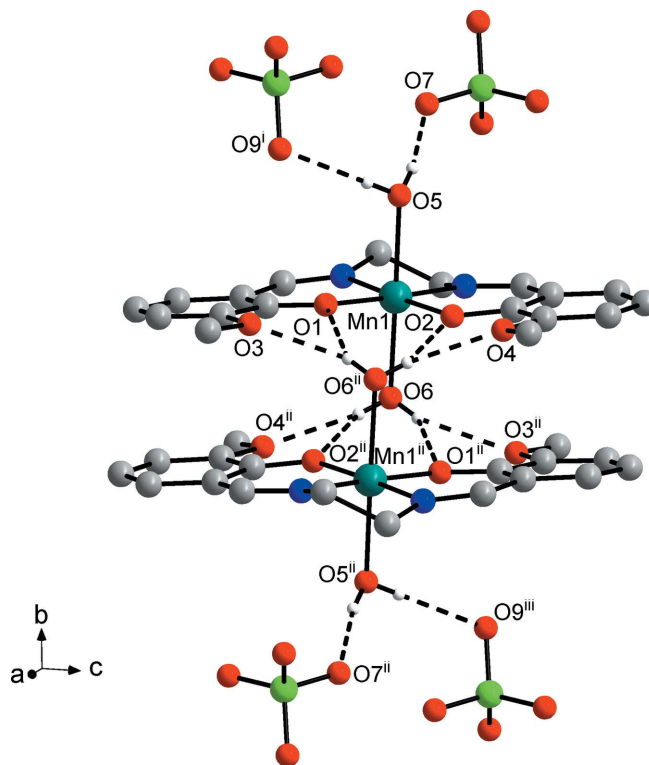
**Figure 1**  
The structures of the molecular components, with displacement ellipsoids drawn at the 50% probability level. H atoms are represented by small spheres of arbitrary radii. The dashed line represents a hydrogen bond.

**Table 1**  
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>
O5–H5A···O7	0.81 (2)	1.95 (2)	2.7505 (16)	169 (2)
O5–H5B···O9 <sup>i</sup>	0.82 (2)	2.29 (2)	3.1089 (18)	175 (2)
O6–H6A···O1 <sup>ii</sup>	0.80 (1)	2.29 (2)	2.9426 (13)	140 (2)
O6–H6B···O2 <sup>ii</sup>	0.80 (1)	2.23 (2)	2.9109 (13)	143 (2)
O6–H6A···O3 <sup>ii</sup>	0.80 (1)	2.23 (2)	2.9454 (13)	151 (2)
O6–H6B···O4 <sup>ii</sup>	0.80 (1)	2.23 (2)	2.9341 (13)	147 (2)

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

and also the crystallographic data listed in the article clearly correspond to the unsolvated complex. The crystal structure of the corresponding monohydrate (CSD refcode: MAXSEJ) was, however, reported by Zhang *et al.* (2000), although these authors inconsistently described the compound as a dihydrate. At room temperature, *i.e.* in TAPSOT and TAPSOT01, the ethylene bridge exhibits positional disorder, which is not observed at 100 K. The perchlorate anion was also found to be disordered at room temperature. The authors of TAPSOT (Akitsu *et al.*, 2005) treated the disorder with elongated atom displacement ellipsoids, whereas the authors of TAPSOT01 (Bermejo *et al.*, 2007) preferred to use a split-atom model. At 100 K there is also no evidence for significant disorder of the perchlorate anion. Apart from the non-observed disorder, the redetermination of the crystal structure at 100 K led to a



**Figure 2**  
The hydrogen-bonded centrosymmetric dimer of two cationic complexes in the crystal structure. Carbon-bound H atoms have been omitted for clarity. Hydrogen bonds are represented by dashed lines. [Symmetry codes: (i)  $-x, -y + 1, -z$ ; (ii)  $-x, -y, -z$ ; (iii)  $x, y - 1, z$ .]

Table 2

Experimental details.

Crystal data	
Chemical formula	[Mn(C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> )(H <sub>2</sub> O) <sub>2</sub> ]ClO <sub>4</sub>
<i>M<sub>r</sub></i>	516.76
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.978 (2), 13.2080 (19), 22.137 (3)
<i>V</i> (Å <sup>3</sup> )	4086.8 (10)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm <sup>-1</sup> )	0.84
Crystal size (mm)	0.06 × 0.06 × 0.04
Data collection	
Diffractometer	Bruker Kappa Mach3 APEXII
Absorption correction	Gaussian ( <i>SADABS</i> ; Bruker, 2013)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.957, 0.978
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	139974, 8570, 6786
<i>R<sub>int</sub></i>	0.068
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.794
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.034, 0.088, 1.06
No. of reflections	8570
No. of parameters	303
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.57, -0.57

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 2014) and *publCIF* (Westrip, 2010).

significant improvement of the quality indicators and bond precision as compared with TAPSOT, *R*<sub>1</sub>[*I* > 2σ(*I*)] = 0.0559; bond precision C—C 0.0051 Å, and TAPSOT01, *R*<sub>1</sub>[*I* > 2σ(*I*)] = 0.0444; bond precision C—C = 0.0070 Å.

### Synthesis and crystallization

Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.362 g, 1.0 mmol) was mixed with *N,N*-bis(3-methoxy-2-oxybenzylidene)ethylenediamine (0.328 g, 1.0 mmol) (Bermejo *et al.*, 2007) and triethylamine (2 mmol, 0.28 ml) in 30 ml of a 2:1 (v/v) acetonitrile/methanol mixture. The reaction mixture was stirred for 6 h at room temperature. Subsequently, the brown solution was left at room tempera-

ture, while the solvents were allowed to evaporate slowly. After 3–4 days, brown crystals suitable for X-ray analysis appeared. The crystals were filtered off and washed with cold methanol. Caution: perchlorates are potentially explosive and should be handled in small quantities with care.

### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

### Acknowledgements

This work was supported by grants from the Department of Science and Technology, SERB, New Delhi, India (SERB/F/815/2014–15). SN would like to thank Professor Mohammad Shakir, Chairman of the Department of Chemistry, Aligarh Muslim University, India, who supported this research.

### References

- Akitsu, T., Takeuchi, Y. & Einaga, Y. (2005). *Acta Cryst.* **C61**, m324–m328.
- Bermejo, M. R., Fernández, M. I., Gómez-Fórneas, E., González-Noya, A., Maneiro, M., Pedrido, R. & Rodríguez, M. (2007). *Eur. J. Inorg. Chem.* pp. 3789–3797.
- Brandenburg, K. (2014). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2013). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bull, C., Niederhoffer, E. C., Yoshida, T. & Fee, J. A. (1991). *J. Am. Chem. Soc.* **113**, 4069–4076.
- Dismukes, G. C. (1996). *Chem. Rev.* **96**, 2909–2926.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Groves, J. T. (2005). *Cytochrome P450: Structure, Mechanism and Biochemistry*, 3rd ed., edited by P. R. Ortiz de Montellano, pp. 1–43. New York: Kluwer Academic/Plenum Publishers.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yamada, S. (1999). *Coord. Chem. Rev.* **190–192**, 537–555.
- Zhang, W., Loebach, J. L., Wilson, S. R. & Jacobsen, E. N. (1990). *J. Am. Chem. Soc.* **112**, 2801–2803.
- Zhang, C.-G., Tian, G.-H., Ma, Z.-F. & Yan, D.-Y. (2000). *Transition Met. Chem.* **25**, 270–273.

## full crystallographic data

*IUCrData* (2016). **1**, x161735 [<https://doi.org/10.1107/S2414314616017351>]

## Redetermination of diaqua[*N,N'*-bis(3-methoxy-2-oxidobenzylidene)ethylenediamine- $\kappa^4$ O,*N,N',O'*]manganese(III) perchlorate at 100 K

Shabana Noor, Rüdiger W. Seidel, Richard Goddard, Sarvendra Kumar and Suhail Sabir

Diaqua[*N,N'*-bis(3-methoxy-2-oxidobenzylidene)ethylenediamine- $\kappa^4$ O,*N,N',O'*]manganese(III) perchlorate

### Crystal data

[Mn(C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub>

$M_r = 516.76$

Orthorhombic, *Pbca*

$a = 13.978$  (2) Å

$b = 13.2080$  (19) Å

$c = 22.137$  (3) Å

$V = 4086.8$  (10) Å<sup>3</sup>

$Z = 8$

$F(000) = 2128$

$D_x = 1.680$  Mg m<sup>-3</sup>

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

Cell parameters from 9815 reflections

$\theta = 3.2\text{--}33.8^\circ$

$\mu = 0.84$  mm<sup>-1</sup>

$T = 100$  K

Plate, brown

0.06 × 0.06 × 0.04 mm

### Data collection

Bruker Kappa Mach3 APEXII  
diffractometer

Radiation source: microfocus X-ray tube,  
Incoatec  $I\mu$ S

Incoatec Helios mirrors monochromator

Detector resolution: 16.67 pixels mm<sup>-1</sup>

$\varphi$ - and  $\omega$ -scans

Absorption correction: gaussian  
(*SADABS*; Bruker, 2013)

$T_{\min} = 0.957$ ,  $T_{\max} = 0.978$

139974 measured reflections

8570 independent reflections

6786 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.068$

$\theta_{\max} = 34.4^\circ$ ,  $\theta_{\min} = 3.1^\circ$

$h = -22 \rightarrow 22$

$k = -20 \rightarrow 20$

$l = -35 \rightarrow 35$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

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

$wR(F^2) = 0.088$

$S = 1.06$

8570 reflections

303 parameters

4 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 2.5037P]$

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

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

$\Delta\rho_{\max} = 0.57$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.57$  e Å<sup>-3</sup>

*Special details*

**Experimental.** Crystal mounted on a MiTeGen loop using Perfluoropolyether PFO-XR75

**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.

**Refinement.** Two low-angle reflections were shadowed by the beamstop (002 and 200) and omitted in the final refinement cycles.

The positions of aromatic, imine and methylene H atoms were calculated geometrically and refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The C—H bond lengths were set to 0.95 Å for aromatic and imine H atoms and to 0.99 Å for methylene H atoms. For the methyl groups C—H = 0.98 Å was set. The torsion angles of the methyl groups were initially determined using a circular Fourier search and subsequently refined while maintaining the tetrahedral structure. For the methyl groups,  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  was applied. The water H atoms were located in a difference Fourier map. The O—H bond lengths were restrained to a target value of 0.84 (2) Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$  was set.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.05507 (2)	0.16542 (2)	0.02662 (2)	0.01032 (4)
O1	0.01911 (6)	0.13705 (7)	−0.05304 (4)	0.01327 (16)
O3	−0.06422 (6)	0.07741 (8)	−0.15036 (4)	0.01552 (17)
O2	−0.05860 (6)	0.11266 (7)	0.05868 (4)	0.01282 (16)
O4	−0.23082 (6)	0.05403 (7)	0.07137 (4)	0.01419 (16)
O5	−0.02462 (8)	0.31470 (8)	0.01391 (5)	0.02090 (19)
H5A	−0.0067 (14)	0.3651 (13)	0.0316 (8)	0.025*
H5B	−0.0344 (15)	0.3299 (15)	−0.0214 (7)	0.025*
O6	0.13121 (7)	0.01671 (7)	0.03740 (4)	0.01389 (16)
H6A	0.1025 (12)	−0.0212 (13)	0.0587 (8)	0.017*
H6B	0.1363 (13)	−0.0126 (13)	0.0058 (7)	0.017*
N1	0.17881 (7)	0.22395 (8)	0.00093 (5)	0.01278 (18)
N2	0.10243 (7)	0.20154 (8)	0.10813 (5)	0.01314 (18)
C1	0.16738 (8)	0.17524 (9)	−0.10433 (5)	0.01203 (19)
C2	0.21723 (9)	0.17554 (9)	−0.15978 (6)	0.0142 (2)
H2	0.2823	0.1962	−0.1608	0.017*
C3	0.17257 (9)	0.14629 (10)	−0.21217 (6)	0.0156 (2)
H3	0.2065	0.1478	−0.2493	0.019*
C4	0.07678 (9)	0.11406 (10)	−0.21103 (6)	0.0144 (2)
H4	0.0458	0.0947	−0.2474	0.017*
C5	0.02787 (8)	0.11054 (9)	−0.15713 (5)	0.01208 (19)
C6	0.07152 (8)	0.14179 (9)	−0.10239 (5)	0.01138 (19)
C7	0.21595 (8)	0.21480 (9)	−0.05204 (6)	0.0131 (2)
H7	0.2805	0.2358	−0.0570	0.016*
C8	0.23024 (9)	0.27754 (10)	0.04970 (6)	0.0160 (2)
H8A	0.2104	0.3495	0.0510	0.019*
H8B	0.3001	0.2747	0.0425	0.019*
C9	−0.04245 (9)	0.16141 (9)	0.16346 (5)	0.0131 (2)
C10	−0.08533 (10)	0.16185 (10)	0.22139 (6)	0.0159 (2)
H10	−0.0507	0.1872	0.2551	0.019*
C11	−0.17650 (10)	0.12588 (10)	0.22909 (6)	0.0173 (2)

H11	-0.2044	0.1258	0.2682	0.021*
C12	-0.22881 (9)	0.08926 (10)	0.17972 (6)	0.0155 (2)
H12	-0.2925	0.0661	0.1853	0.019*
C13	-0.18793 (8)	0.08685 (9)	0.12310 (5)	0.0124 (2)
C14	-0.09280 (8)	0.12115 (9)	0.11373 (5)	0.01138 (19)
C15	0.05446 (9)	0.19643 (10)	0.15778 (6)	0.0142 (2)
H15	0.0859	0.2176	0.1937	0.017*
C16	0.20569 (9)	0.22573 (11)	0.10871 (6)	0.0165 (2)
H16A	0.2437	0.1629	0.1132	0.020*
H16B	0.2206	0.2709	0.1431	0.020*
C17	-0.11436 (9)	0.05085 (11)	-0.20418 (6)	0.0181 (2)
H17A	-0.1187	0.1101	-0.2307	0.027*
H17B	-0.1789	0.0277	-0.1938	0.027*
H17C	-0.0800	-0.0035	-0.2251	0.027*
C18	-0.32985 (9)	0.02778 (11)	0.07497 (7)	0.0185 (2)
H18A	-0.3383	-0.0274	0.1041	0.028*
H18B	-0.3524	0.0059	0.0351	0.028*
H18C	-0.3668	0.0869	0.0881	0.028*
Cl1	0.07410 (2)	0.52382 (3)	0.12199 (2)	0.01738 (6)
O7	0.05549 (8)	0.48739 (9)	0.06149 (5)	0.0266 (2)
O8	0.00029 (9)	0.48986 (13)	0.16163 (6)	0.0404 (3)
O9	0.07464 (9)	0.63287 (9)	0.11931 (6)	0.0325 (3)
O10	0.16496 (8)	0.48708 (10)	0.14218 (6)	0.0288 (2)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Mn1	0.00933 (7)	0.01206 (8)	0.00956 (8)	-0.00203 (6)	0.00013 (6)	-0.00028 (6)
O1	0.0120 (4)	0.0182 (4)	0.0096 (4)	-0.0041 (3)	0.0015 (3)	0.0006 (3)
O3	0.0123 (4)	0.0229 (4)	0.0113 (4)	-0.0044 (3)	-0.0005 (3)	0.0000 (3)
O2	0.0114 (4)	0.0165 (4)	0.0105 (4)	-0.0026 (3)	0.0026 (3)	-0.0017 (3)
O4	0.0102 (4)	0.0183 (4)	0.0142 (4)	-0.0026 (3)	0.0007 (3)	0.0004 (3)
O5	0.0237 (5)	0.0151 (4)	0.0240 (5)	0.0021 (4)	-0.0028 (4)	0.0011 (4)
O6	0.0146 (4)	0.0139 (4)	0.0132 (4)	-0.0011 (3)	0.0025 (3)	-0.0005 (3)
N1	0.0119 (4)	0.0127 (4)	0.0137 (4)	-0.0024 (3)	-0.0007 (3)	0.0006 (4)
N2	0.0117 (4)	0.0143 (4)	0.0134 (4)	-0.0007 (3)	-0.0015 (3)	-0.0015 (4)
C1	0.0118 (5)	0.0113 (5)	0.0129 (5)	-0.0008 (4)	0.0017 (4)	0.0017 (4)
C2	0.0129 (5)	0.0144 (5)	0.0155 (5)	-0.0007 (4)	0.0035 (4)	0.0017 (4)
C3	0.0156 (5)	0.0172 (5)	0.0140 (5)	0.0000 (4)	0.0047 (4)	0.0016 (4)
C4	0.0154 (5)	0.0155 (5)	0.0123 (5)	0.0005 (4)	0.0010 (4)	0.0013 (4)
C5	0.0118 (4)	0.0131 (5)	0.0114 (5)	-0.0004 (4)	0.0001 (4)	0.0011 (4)
C6	0.0120 (5)	0.0111 (5)	0.0110 (5)	-0.0005 (4)	0.0013 (4)	0.0014 (4)
C7	0.0118 (5)	0.0118 (5)	0.0156 (5)	-0.0017 (4)	0.0003 (4)	0.0021 (4)
C8	0.0145 (5)	0.0174 (5)	0.0161 (5)	-0.0047 (4)	-0.0017 (4)	-0.0015 (4)
C9	0.0141 (5)	0.0137 (5)	0.0114 (5)	0.0013 (4)	0.0004 (4)	0.0000 (4)
C10	0.0205 (5)	0.0168 (5)	0.0104 (5)	0.0026 (4)	0.0008 (4)	-0.0001 (4)
C11	0.0214 (6)	0.0179 (6)	0.0127 (5)	0.0029 (5)	0.0050 (4)	0.0022 (4)
C12	0.0154 (5)	0.0157 (5)	0.0155 (5)	0.0017 (4)	0.0041 (4)	0.0026 (4)

C13	0.0128 (5)	0.0117 (5)	0.0127 (5)	0.0007 (4)	0.0006 (4)	0.0019 (4)
C14	0.0120 (5)	0.0108 (5)	0.0114 (5)	0.0016 (4)	0.0013 (4)	0.0009 (4)
C15	0.0153 (5)	0.0147 (5)	0.0126 (5)	0.0005 (4)	-0.0019 (4)	-0.0018 (4)
C16	0.0123 (5)	0.0226 (6)	0.0145 (5)	-0.0028 (4)	-0.0025 (4)	-0.0011 (4)
C17	0.0149 (5)	0.0261 (6)	0.0131 (5)	-0.0027 (5)	-0.0036 (4)	0.0004 (5)
C18	0.0109 (5)	0.0213 (6)	0.0233 (6)	-0.0031 (4)	0.0005 (4)	0.0033 (5)
Cl1	0.01365 (12)	0.02412 (15)	0.01436 (12)	-0.00049 (10)	-0.00314 (10)	-0.00031 (11)
O7	0.0345 (6)	0.0301 (6)	0.0152 (4)	-0.0050 (5)	-0.0071 (4)	-0.0021 (4)
O8	0.0211 (5)	0.0764 (10)	0.0235 (6)	-0.0062 (6)	-0.0018 (4)	0.0216 (6)
O9	0.0349 (6)	0.0236 (5)	0.0391 (7)	0.0044 (5)	-0.0056 (5)	-0.0082 (5)
O10	0.0179 (5)	0.0391 (6)	0.0295 (6)	0.0088 (4)	-0.0084 (4)	-0.0041 (5)

*Geometric parameters (Å, °)*

Mn1—O1	1.8714 (9)	C5—C6	1.4181 (17)
Mn1—O2	1.8745 (9)	C7—H7	0.9500
Mn1—N1	1.9780 (11)	C8—C16	1.5142 (18)
Mn1—N2	1.9803 (11)	C8—H8A	0.9900
Mn1—O6	2.2466 (10)	C8—H8B	0.9900
Mn1—O5	2.2820 (11)	C9—C14	1.4107 (17)
O1—C6	1.3170 (14)	C9—C10	1.4156 (17)
O3—C5	1.3678 (14)	C9—C15	1.4369 (17)
O3—C17	1.4260 (15)	C10—C11	1.3707 (19)
O2—C14	1.3138 (14)	C10—H10	0.9500
O4—C13	1.3634 (15)	C11—C12	1.4012 (19)
O4—C18	1.4292 (15)	C11—H11	0.9500
O5—H5A	0.811 (15)	C12—C13	1.3779 (17)
O5—H5B	0.819 (15)	C12—H12	0.9500
O6—H6A	0.795 (14)	C13—C14	1.4200 (17)
O6—H6B	0.804 (14)	C15—H15	0.9500
N1—C7	1.2880 (16)	C16—H16A	0.9900
N1—C8	1.4775 (16)	C16—H16B	0.9900
N2—C15	1.2891 (16)	C17—H17A	0.9800
N2—C16	1.4783 (16)	C17—H17B	0.9800
C1—C2	1.4113 (17)	C17—H17C	0.9800
C1—C6	1.4116 (16)	C18—H18A	0.9800
C1—C7	1.4401 (17)	C18—H18B	0.9800
C2—C3	1.3727 (18)	C18—H18C	0.9800
C2—H2	0.9500	Cl1—O8	1.4267 (12)
C3—C4	1.4052 (18)	Cl1—O10	1.4312 (11)
C3—H3	0.9500	Cl1—O9	1.4416 (13)
C4—C5	1.3758 (17)	Cl1—O7	1.4467 (11)
C4—H4	0.9500		
O1—Mn1—O2	93.13 (4)	N1—C8—C16	107.68 (10)
O1—Mn1—N1	92.42 (4)	N1—C8—H8A	110.2
O2—Mn1—N1	174.44 (4)	C16—C8—H8A	110.2
O1—Mn1—N2	175.23 (4)	N1—C8—H8B	110.2

O2—Mn1—N2	91.60 (4)	C16—C8—H8B	110.2
N1—Mn1—N2	82.85 (4)	H8A—C8—H8B	108.5
O1—Mn1—O6	93.00 (4)	C14—C9—C10	119.82 (11)
O2—Mn1—O6	92.08 (4)	C14—C9—C15	121.56 (11)
N1—Mn1—O6	87.60 (4)	C10—C9—C15	118.50 (11)
N2—Mn1—O6	87.45 (4)	C11—C10—C9	120.33 (12)
O1—Mn1—O5	85.74 (4)	C11—C10—H10	119.8
O2—Mn1—O5	87.37 (4)	C9—C10—H10	119.8
N1—Mn1—O5	93.08 (4)	C10—C11—C12	120.52 (12)
N2—Mn1—O5	93.86 (4)	C10—C11—H11	119.7
O6—Mn1—O5	178.59 (4)	C12—C11—H11	119.7
C6—O1—Mn1	128.52 (8)	C13—C12—C11	120.08 (12)
C5—O3—C17	116.72 (10)	C13—C12—H12	120.0
C14—O2—Mn1	128.90 (8)	C11—C12—H12	120.0
C13—O4—C18	117.14 (10)	O4—C13—C12	126.08 (11)
Mn1—O5—H5A	119.9 (15)	O4—C13—C14	112.99 (10)
Mn1—O5—H5B	114.3 (15)	C12—C13—C14	120.92 (11)
H5A—O5—H5B	108 (2)	O2—C14—C9	125.06 (11)
Mn1—O6—H6A	112.0 (13)	O2—C14—C13	116.68 (10)
Mn1—O6—H6B	111.8 (13)	C9—C14—C13	118.26 (11)
H6A—O6—H6B	104.9 (18)	N2—C15—C9	125.58 (11)
C7—N1—C8	120.93 (10)	N2—C15—H15	117.2
C7—N1—Mn1	125.27 (9)	C9—C15—H15	117.2
C8—N1—Mn1	113.74 (8)	N2—C16—C8	108.14 (10)
C15—N2—C16	120.78 (11)	N2—C16—H16A	110.1
C15—N2—Mn1	126.18 (9)	C8—C16—H16A	110.1
C16—N2—Mn1	112.73 (8)	N2—C16—H16B	110.1
C2—C1—C6	119.73 (11)	C8—C16—H16B	110.1
C2—C1—C7	117.73 (11)	H16A—C16—H16B	108.4
C6—C1—C7	122.45 (11)	O3—C17—H17A	109.5
C3—C2—C1	120.63 (11)	O3—C17—H17B	109.5
C3—C2—H2	119.7	H17A—C17—H17B	109.5
C1—C2—H2	119.7	O3—C17—H17C	109.5
C2—C3—C4	120.22 (11)	H17A—C17—H17C	109.5
C2—C3—H3	119.9	H17B—C17—H17C	109.5
C4—C3—H3	119.9	O4—C18—H18A	109.5
C5—C4—C3	119.96 (12)	O4—C18—H18B	109.5
C5—C4—H4	120.0	H18A—C18—H18B	109.5
C3—C4—H4	120.0	O4—C18—H18C	109.5
O3—C5—C4	124.99 (11)	H18A—C18—H18C	109.5
O3—C5—C6	113.85 (10)	H18B—C18—H18C	109.5
C4—C5—C6	121.15 (11)	O8—C11—O10	110.06 (8)
O1—C6—C1	124.62 (11)	O8—C11—O9	110.08 (9)
O1—C6—C5	117.12 (10)	O10—C11—O9	110.30 (8)
C1—C6—C5	118.26 (11)	O8—C11—O7	109.56 (8)
N1—C7—C1	125.16 (11)	O10—C11—O7	109.63 (7)
N1—C7—H7	117.4	O9—C11—O7	107.17 (7)
C1—C7—H7	117.4		



N1—C8—C16—N2	-41.38 (14)	C12—C13—O4—C18	5.73 (18)
C4—C5—O3—C17	-4.17 (18)		

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O5—H5 <i>A</i> $\cdots$ O7	0.81 (2)	1.95 (2)	2.7505 (16)	169 (2)
O5—H5 <i>B</i> $\cdots$ O9 <sup>i</sup>	0.82 (2)	2.29 (2)	3.1089 (18)	175 (2)
O6—H6 <i>A</i> $\cdots$ O1 <sup>ii</sup>	0.80 (1)	2.29 (2)	2.9426 (13)	140 (2)
O6—H6 <i>B</i> $\cdots$ O2 <sup>ii</sup>	0.80 (1)	2.23 (2)	2.9109 (13)	143 (2)
O6—H6 <i>A</i> $\cdots$ O3 <sup>ii</sup>	0.80 (1)	2.23 (2)	2.9454 (13)	151 (2)
O6—H6 <i>B</i> $\cdots$ O4 <sup>ii</sup>	0.80 (1)	2.23 (2)	2.9341 (13)	147 (2)

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