

Crystal structure of bis(2-[[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]-6-methoxyphenolato)-manganese(IV) 0.39-hydrate

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Received 1 October 2015
Accepted 4 October 2015

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Edited by J. Simpson, University of Otago, New Zealand

Keywords: crystal structure; monomeric octahedral Mn^{IV} complex; Schiff base ligand; *o*-vanillin; tris(hydroxymethyl)aminomethane

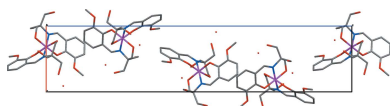
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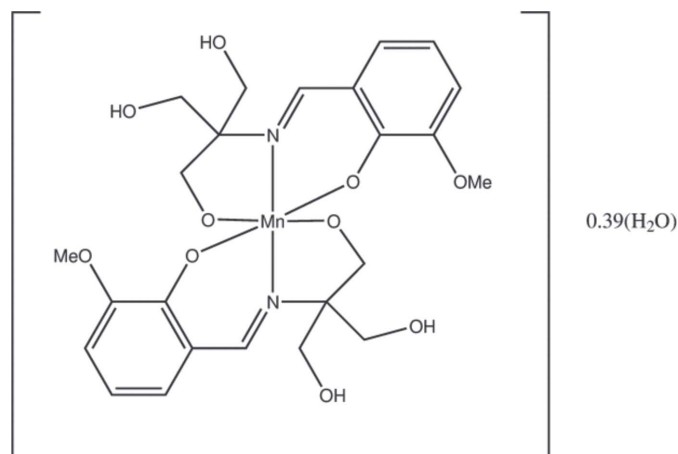
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The title compound, [Mn(C₁₂H₁₅NO₅)₂].0.39H₂O, is a 0.39 hydrate of the isostructural complex bis(2-[[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]-6-methoxyphenolato)manganese(IV) that has previously been reported by Back, Oliveira, Canabarro & Iglesias [*Z. Anorg. Allg. Chem.* (2015), **641**, 941–947], based on room-temperature data. The current structure that was determined at 100 K reveals a lengthening of the *c* cell parameter compared with the published one due to the incorporation of the partial occupancy water molecule. The title compound crystallizes in the tetragonal chiral space group *P*4₁2₁2; the neutral [Mn^{IV}(C₁₂H₁₅NO₅)₂] molecule is situated on a crystallographic *C*₂ axis. The overall geometry about the central manganese ion is octahedral with an N₂O₄ core; each ligand acts as a meridional ONO donor. The coordination environment of Mn^{IV} at 100 K displays a difference in one of the two Mn–O bond lengths, compared with the room-temperature structure. In the crystal, the neutral molecules are stacked in a helical fashion along the *c*-axis direction.

1. Chemical context

The title compound is a hydrate of the isostructural complex bis(2-[[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]-6-methoxyphenolato)manganese(IV) (refcode IGOSII; Back *et al.*, 2015). It was isolated as an unexpected product in an attempt to prepare a heterometallic Mn/Zn compound with the multidentate Schiff base ligand 2-[[2-(2-hydroxy-3-methoxyphenyl)methylene]amino]-2-(hydroxymethyl)-1,3-propanediol (H₄L) (Odabaşoğlu *et al.*, 2003). Zn powder and MnCl₂·4H₂O were reacted with the Schiff base formed *in situ* from the condensation between *o*-vanillin and tris(hydroxymethyl)aminomethane in methanol in a 1:1:2 molar ratio. Metal powders have been successfully applied in *direct synthesis of coordination compounds* to yield a number of novel monometallic (Babich & Kozozay, 1997; Babich *et al.*, 1996; Kovbasyuk *et al.*, 1997) and heterometallic complexes (Nikitina *et al.*, 2008; Nesterov *et al.*, 2011) of various nuclearities and dimensionalities. However, the isolated black microcrystalline product of the reaction studied appeared to be the mononuclear Schiff base complex [Mn^{IV}(H₂L)₂].0.39H₂O (**1**). Oxidation of the manganese(II) atom directly to the manganese(IV) species proceeds easily in open air even in the presence of zerovalent Zn, indicating that the tridentate ligand H₂L²⁻ containing two O⁻ donors effectively stabilizes the Mn^{IV} oxidation state. Stabilization of Mn^{IV} species by similar ligands with phenolate oxygen atoms has been reported previously (Kessissoglou *et al.*, 1987; Pradeep *et al.*, 2004).





Remarkably, the current structure that was determined at 100 K reveals shortening of the *a* cell parameter compared with the published one [8.0953 (2) (**1**), 8.1620 (2) Å (IGOSII)] as expected in the case of low-temperature determination, but lengthening of the *c* cell parameter [37.568 (2) (**1**), 37.4557 (11) Å (IGOSII)] due to the incorporation of the partial occupancy water molecule. Also, (**1**) shows somewhat longer Mn–O bond lengths to the deprotonated hydroxymethyl group [1.871 (4) Å] compared to the corresponding distance in IGOSII [1.849 (2) Å], while the Mn–N bonds stay the same [1.992 (5) (**1**), 1.991 (3) Å (IGOSII)].

2. Structural commentary

The title compound (**1**) crystallizes in the tetragonal chiral space group $P4_12_12$; the neutral $[\text{Mn}^{\text{IV}}(\text{C}_{12}\text{H}_{15}\text{NO}_5)_2]$ molecule is situated on a crystallographic C_2 axis, hence the

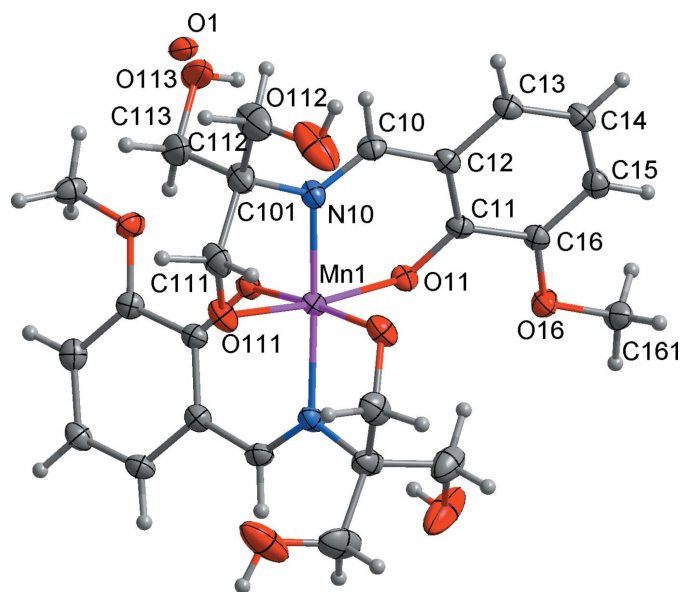


Figure 1

The molecular structure of the title complex, showing the atom-numbering scheme. Non-H atoms are shown with displacement ellipsoids at the 50% probability level. Labelled atoms are related to unlabelled atoms by the symmetry operation $y, x, -z + 1$.

Table 1

Selected geometric parameters (Å, °).

Mn1–O111	1.871 (4)	Mn1–N10	1.992 (5)
Mn1–O11	1.939 (4)		
O111–Mn1–O111 ⁱ	94.0 (3)	O111 ⁱ –Mn1–N10	88.07 (19)
O111–Mn1–O11 ⁱ	89.58 (16)	O11 ⁱ –Mn1–N10	98.44 (18)
O111–Mn1–O11	172.89 (18)	O11–Mn1–N10	89.82 (17)
O11 ⁱ –Mn1–O11	87.6 (2)	N10–Mn1–N10 ⁱ	168.6 (3)
O111–Mn1–N10	84.14 (18)		

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

asymmetric unit comprises one half of the metal complex and the O atom of a water molecule with occupancy 0.195 (15) (Fig. 1). The overall geometry about the central metal ion is distorted octahedral with an N_2O_4 core; each ligand acts as a meridional ONO donor. The $\text{Mn}^{\text{IV}}\text{–N}(\text{imine})$ [1.992 (5) Å], $\text{Mn}^{\text{IV}}\text{–O}(\text{phenolate})$ [1.939 (4) Å] and $\text{Mn}^{\text{IV}}\text{–O}(\text{alkoxo})$ [1.871 (4) Å] bond lengths in (**1**) are strictly comparable to those for several reported Mn^{IV} complexes containing similar ligation (Kessissoglou *et al.*, 1987; Pradeep *et al.*, 2004). The MnO_4 equatorial fragment is approximately square planar, the maximum deviation from the mean plane being about 0.11 Å. The ranges of *cis* and *trans* angles at the metal atom are 84.14 (18)–98.44 (18) and 168.6 (3)–172.89 (18)°, respectively (Table 1). The Mn–N distance is longer than the average Mn–O distance by approximately 0.1 Å. This is significantly larger than the difference in covalent radii of N and O. Thus, the primary distortion of the MnN_2O_4 octahedron is axial elongation along the MnN_2 axis.

The molecular structure of (**1**) closely resembles that of the Mn^{II} complex of the same ligand, $[\text{Mn}^{\text{II}}(\text{H}_3\text{L})_2]\cdot 2\text{CH}_3\text{OH}\cdot 0.5\text{H}_2\text{O}$ (refcode ROMROB; Zhang *et al.*, 2009) (Fig. 2). The latter crystallizes in the monoclinic space group $P2_1/n$ and has no crystallographically imposed symmetry. There is a marked increase in the ROMROB Mn^{II}–O(H) bond length (mean 2.134 Å) when (**1**) is compared to ROMROB which has two additional protons to compensate for the two additional electrons. In ROMROB, the Mn^{II}–O(phenolate) and Mn^{II}–N(imine) bonds are also elongated (mean lengths 2.011 and

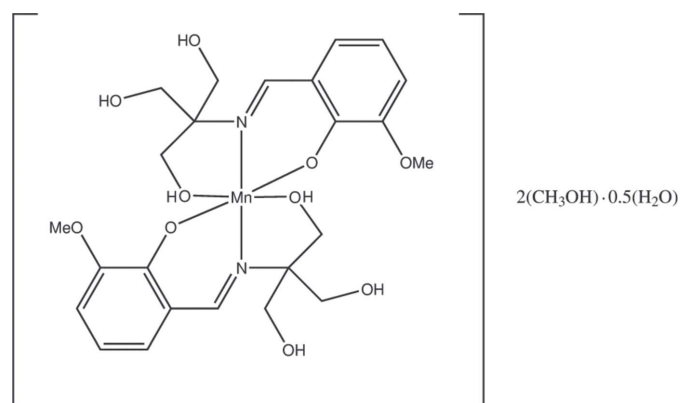


Figure 2

Scheme showing the structure of the closely related ROMROB Mn^{II} complex.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O112—H112 ⁱⁱ ···O11 ⁱⁱ	0.84	2.2	2.850 (7)	134
O112—H112 ⁱⁱ ···O16 ⁱⁱ	0.84	2.1	2.802 (7)	141
O113—H113 ⁱⁱⁱ ···O112 ⁱⁱⁱ	0.84	2.3	2.965 (12)	137

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

2.027 Å, respectively). **(1)** thus provides a rare structural example of variations in the metal coordination sphere to accommodate change in the metal oxidation state. The flexibility of the lattice, formed using the partly deprotonated H_4L ligand, permits distortion of the structure in the solid state to allow for changes in the charge and spin state of the Mn atom without disrupting the integrity of the crystal structure.

3. Supramolecular features

In the crystal lattice, individual $[Mn^{IV}(H_2L)_2]$ molecules are stacked in a helical fashion along the c axis, as shown in Fig. 3, with the minimum Mn···Mn distances inside a column being 10.28 Å. Molecules that are translated by one unit cell in the a -axis direction [Mn···Mn distance equals the a -axial length, 8.0953 (2) Å] are intertwined by intermolecular hydrogen bonds between the hydroxyl groups and phenolic and methoxy oxygen atoms. There is also a possible hydrogen-bonding interaction between one hydroxyl group (O113) and the solvent water molecule (O1) considering the O113···O1 distance of 2.17 (2) but as the H atoms on O1 could not be located this contact could not be confirmed. Details of the hydrogen bonding are given in Table 2.

4. Database survey

A search of the Cambridge Structural Database (CSD Version 5.36 with one update; Groom & Allen, 2014) for metal complexes of this ligand reveals the crystal structures of above 30 compounds, mostly comprising polynuclear homo- Co^{II} , Co^{III} , V_2 , Cu_4 , Mn_4 , Ni_4 , Ln_9 and Ln_{10} and heterometallic $1s-3d$ and $3d-4f$ assemblies of 4–20 nuclearity. Mononuclear complexes of this ligand are limited to five Mn, Ni and Mo structures. The ligand molecules exist in either doubly or triply

deprotonated forms, adopt a chelating-bridging mode and form five- and six-membered rings. The H_4L ligand can stabilize manganese in various oxidation states. Apart from Mn^{II} (ROMROB) and Mn^{IV} [**(1)**; IGOSII] complexes, the structure of the Mn^{III} derivative, $[Mn_4(HL)_2(H_2L)_2 \cdot (CH_3OH)_4](ClO_4)_2 \cdot 4CH_3OH$ has also been reported (Zhu *et al.*, 2014). Stabilization of Mn^{IV} species by similar ligands with phenolate oxygen atoms has been reported previously with details of three structures of $[Mn^{IV}N_2O_4]$ complexes with tridentate Schiff base ligands similar to H_4L (Kessissoglou *et al.*, 1987; Chandra *et al.*, 1990; Pradeep *et al.*, 2004).

5. Synthesis and crystallization

2-Hydroxy-3-methoxy-benzaldehyde (0.30 g, 2 mmol) and tris(hydroxymethyl)aminomethane (0.24 g, 2 mmol), were added to methanol (20 ml) and stirred magnetically for 30 min. Next zinc powder (0.07 g, 1 mmol) and $MnCl_2 \cdot 4H_2O$ (0.20 g, 1 mmol) were added to the yellow solution and the mixture was heated to 323 K under stirring until total dissolution of the zinc powder was observed (1 h). The resulting brown solution was filtered and allowed to stand at room temperature. Black microcrystals of the title compound were formed in several days. They were collected by filter-suction, washed with dry Pr^iOH and finally dried *in vacuo* (yield: 43%).

The IR spectrum of powdered **(1)** in the range 4000–400 cm^{-1} shows all the characteristic Schiff base vibration bands: $\nu(OH)$, $\nu(CH)$ and $\nu(C=N)$ at 3400, 3000–2840, and 1602 cm^{-1} , respectively (see Supplementary data). A strong peak at 1618 cm^{-1} is due to the bending of the H_2O molecule, providing evidence of the presence of water in **(1)**. The major feature of the X-band solid-state EPR spectrum of **(1)** at 77 K is a strong and broad signal at $g \sim 4$ and a weak but resolved response at $g \sim 2$ (see Supplementary data). This corresponds to strong axial distortion with small zero-field splitting, $2D \gg hv$ (hv 0.31 cm^{-1} at the X-band frequency) in agreement with structural findings. The ^{55}Mn hyperfine structure is not resolved.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The solvent was modelled as a water molecule with the site occupancy refined to 0.195 (15).

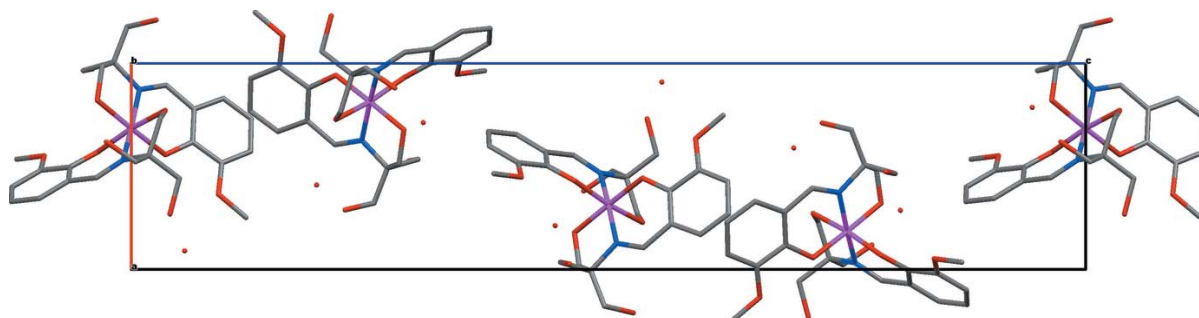


Figure 3
Crystal packing of **(1)** showing the helical arrangement of $Mn^{IV}(H_2L)_2$ molecules in the c -axis direction. H atoms are not shown.

Table 3
Experimental details.

Crystal data	
Chemical formula	[Mn(C ₁₂ H ₁₅ NO ₅) ₂].0.39H ₂ O
<i>M_r</i>	568.46
Crystal system, space group	Tetragonal, <i>P</i> 4 ₁ 2 ₁ 2
Temperature (K)	100
<i>a</i> , <i>c</i> (Å)	8.0953 (2), 37.568 (2)
<i>V</i> (Å ³)	2461.97 (18)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	4.92
Crystal size (mm)	0.09 × 0.08 × 0.01
Data collection	
Diffraction	Oxford Diffraction Gemini
Absorption correction	Analytical [<i>CrysAlis PRO</i> (Agilent, 2014) using an expression derived by Clark & Reid (1995)]
<i>T</i> _{min} , <i>T</i> _{max}	0.695, 0.946
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	18553, 2214, 1885
<i>R</i> _{int}	0.103
(sin θ/λ) _{max} (Å ⁻¹)	0.600
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.052, 0.136, 1.05
No. of reflections	2214
No. of parameters	181
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.54, -0.34
Absolute structure	Flack <i>x</i> determined using 584 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013).
Absolute structure parameter	-0.007 (6)

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SIR92* (Altomare *et al.*, 1993), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1999) and *WinGX* (Farrugia, 2012).

Associated hydrogen atoms were not located. The OH hydrogen atoms H112 and H113 were refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. All hydrogen atoms bound to carbon were included in calculated positions and refined using a riding model with isotropic displacement parameters based on those of the parent atom [$\text{C}-\text{H} = 0.95 \text{ \AA}$, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH and CH₂, $1.5U_{\text{eq}}(\text{C})$ for CH₃].

Acknowledgements

The authors acknowledge the facilities, scientific and technical assistance of the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy, Characterization & Analysis, the University of Western Australia, a facility funded by the University, State and Commonwealth Governments.

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supporting information

Acta Cryst. (2015). E71, 1307-1310 [https://doi.org/10.1107/S2056989015018551]

Crystal structure of bis(2-[[1,1-bis(hydroxymethyl)-2-oxidoethyl]imino-methyl]-6-methoxyphenolato)manganese(IV) 0.39-hydrate

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Bis(2-[[1,1-bis(hydroxymethyl)-2-oxidoethyl]iminomethyl]-6-methoxyphenolato)manganese(IV) 0.39 hydrate

Crystal data

[Mn(C₁₂H₁₅NO₅)₂]·0.39H₂O

M_r = 568.46

Tetragonal, *P*4₁2₁2

Hall symbol: P 4abw 2nw

a = 8.0953 (2) Å

c = 37.568 (2) Å

V = 2461.97 (18) Å³

Z = 4

F(000) = 1188

D_x = 1.534 Mg m⁻³

Cu *Kα* radiation, λ = 1.54178 Å

Cell parameters from 2851 reflections

θ = 3.5–67.6°

μ = 4.92 mm⁻¹

T = 100 K

Plate, black

0.09 × 0.08 × 0.01 mm

Data collection

Oxford Diffraction Gemini diffractometer

Graphite monochromator

Detector resolution: 10.4738 pixels mm⁻¹

ω scans

Absorption correction: analytical

[*CrysAlis Pro* (Agilent, 2014) using an expression derived by Clark & Reid (1995)]

T_{min} = 0.695, *T_{max}* = 0.946

18553 measured reflections

2214 independent reflections

1885 reflections with *I* > 2σ(*I*)

R_{int} = 0.103

θ_{max} = 67.7°, θ_{min} = 4.7°

h = -9→9

k = -6→9

l = -42→44

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.052

wR(*F*²) = 0.136

S = 1.05

2214 reflections

181 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0691*P*)² + 1.3653*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.54 e Å⁻³

Δρ_{min} = -0.34 e Å⁻³

Absolute structure: Flack x determined using
584 quotients $[(I^-)-(I)]/[(I^+)+(I)]$ (Parsons *et al.*,
2013).
Absolute structure parameter: -0.007 (6)

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.

Refinement. The solvent was modelled as a water molecule with a site occupancy refined to 0.195 (15). Associated hydrogen atoms were not located.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Mn1	0.68511 (10)	0.68511 (10)	0.5	0.0286 (3)	
C11	0.6187 (6)	0.4968 (6)	0.56423 (15)	0.0308 (12)	
O11	0.5567 (4)	0.5690 (5)	0.53567 (9)	0.0333 (8)	
C12	0.7784 (6)	0.4298 (7)	0.56576 (14)	0.0330 (13)	
C13	0.8302 (7)	0.3446 (7)	0.59647 (14)	0.0365 (13)	
H13	0.9372	0.2963	0.5969	0.044*	
C14	0.7305 (7)	0.3297 (7)	0.62568 (16)	0.0385 (13)	
H14	0.7677	0.2721	0.6462	0.046*	
C15	0.5729 (7)	0.4005 (7)	0.62492 (15)	0.0394 (13)	
H15	0.5037	0.393	0.6453	0.047*	
C16	0.5167 (7)	0.4815 (7)	0.59479 (14)	0.0329 (11)	
O16	0.3648 (5)	0.5520 (5)	0.59131 (11)	0.0414 (10)	
C161	0.2522 (8)	0.5349 (8)	0.62010 (18)	0.0443 (15)	
H16A	0.2355	0.4174	0.6253	0.066*	
H16B	0.1462	0.5854	0.6137	0.066*	
H16C	0.2971	0.5901	0.6412	0.066*	
C10	0.8942 (7)	0.4456 (7)	0.53655 (15)	0.0364 (13)	
H10	0.9951	0.3863	0.5385	0.044*	
N10	0.8733 (5)	0.5316 (6)	0.50849 (12)	0.0349 (11)	
C101	1.0070 (8)	0.5533 (9)	0.48146 (17)	0.0502 (17)	
C111	0.9865 (8)	0.7342 (9)	0.46941 (19)	0.0508 (17)	
H11A	1.0338	0.8087	0.4876	0.061*	
H11B	1.0475	0.7518	0.4469	0.061*	
O111	0.8214 (5)	0.7719 (5)	0.46438 (11)	0.0444 (10)	
C112	1.1779 (9)	0.5228 (11)	0.4957 (2)	0.072 (2)	
H11C	1.1897	0.4044	0.5018	0.087*	
H11D	1.26	0.5492	0.477	0.087*	
O112	1.2110 (7)	0.6187 (10)	0.52604 (19)	0.096 (2)	
H112	1.2848	0.5727	0.5382	0.143*	
C113	0.9654 (11)	0.4419 (9)	0.44961 (19)	0.065 (2)	
H11E	0.8528	0.4678	0.441	0.078*	
H11F	1.044	0.464	0.43	0.078*	
O113	0.9740 (11)	0.2689 (7)	0.45943 (17)	0.105 (3)	

H113	0.9002	0.2478	0.4745	0.157*	
O1	0.787 (3)	0.090 (3)	0.4441 (6)	0.048 (9)	0.195 (15)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0282 (4)	0.0282 (4)	0.0293 (6)	−0.0008 (5)	−0.0022 (4)	0.0022 (4)
C11	0.031 (3)	0.025 (3)	0.036 (3)	−0.002 (2)	−0.005 (2)	0.000 (2)
O11	0.026 (2)	0.039 (2)	0.034 (2)	−0.0011 (15)	−0.0036 (16)	0.0023 (17)
C12	0.034 (3)	0.030 (3)	0.035 (3)	−0.005 (2)	−0.003 (2)	0.002 (2)
C13	0.031 (3)	0.037 (3)	0.042 (3)	−0.001 (2)	−0.006 (2)	0.003 (2)
C14	0.043 (3)	0.035 (3)	0.037 (3)	−0.005 (3)	−0.007 (2)	0.008 (2)
C15	0.046 (3)	0.035 (3)	0.037 (3)	−0.008 (3)	0.002 (3)	0.001 (2)
C16	0.032 (3)	0.029 (3)	0.037 (3)	−0.005 (2)	0.001 (2)	0.003 (2)
O16	0.032 (2)	0.052 (2)	0.041 (2)	0.0051 (17)	0.0082 (17)	0.0053 (19)
C161	0.038 (3)	0.043 (4)	0.052 (4)	0.002 (3)	0.011 (3)	0.007 (3)
C10	0.026 (3)	0.041 (3)	0.042 (3)	0.002 (2)	−0.002 (2)	0.000 (3)
N10	0.028 (2)	0.045 (3)	0.032 (2)	−0.002 (2)	−0.0006 (18)	0.007 (2)
C101	0.036 (3)	0.067 (5)	0.047 (4)	0.008 (3)	0.007 (3)	0.012 (3)
C111	0.045 (4)	0.060 (4)	0.047 (4)	−0.008 (3)	0.004 (3)	0.016 (3)
O111	0.043 (2)	0.048 (2)	0.041 (2)	−0.010 (2)	−0.0092 (19)	0.0110 (18)
C112	0.039 (4)	0.098 (6)	0.080 (6)	0.006 (4)	0.019 (4)	0.035 (5)
O112	0.049 (3)	0.142 (6)	0.096 (5)	−0.025 (4)	−0.025 (3)	0.055 (4)
C113	0.085 (6)	0.056 (4)	0.055 (4)	0.015 (4)	0.024 (4)	0.012 (4)
O113	0.184 (8)	0.053 (3)	0.077 (4)	0.048 (4)	0.067 (5)	0.025 (3)
O1	0.055 (16)	0.037 (13)	0.052 (15)	0.017 (11)	0.016 (11)	0.008 (10)

Geometric parameters (Å, °)

Mn1—O111	1.871 (4)	C161—H16B	0.98
Mn1—O111 ⁱ	1.871 (4)	C161—H16C	0.98
Mn1—O11 ⁱ	1.939 (4)	C10—N10	1.275 (7)
Mn1—O11	1.939 (4)	C10—H10	0.95
Mn1—N10	1.992 (5)	N10—C101	1.495 (7)
Mn1—N10 ⁱ	1.992 (5)	C101—C112	1.504 (10)
C11—O11	1.321 (6)	C101—C113	1.536 (10)
C11—C12	1.403 (8)	C101—C111	1.542 (10)
C11—C16	1.420 (8)	C111—O111	1.384 (8)
C12—C13	1.408 (7)	C111—H11A	0.99
C12—C10	1.449 (8)	C111—H11B	0.99
C13—C14	1.368 (8)	C112—O112	1.405 (11)
C13—H13	0.95	C112—H11C	0.99
C14—C15	1.399 (9)	C112—H11D	0.99
C14—H14	0.95	O112—H112	0.84
C15—C16	1.384 (8)	C113—O113	1.450 (9)
C15—H15	0.95	C113—H11E	0.99
C16—O16	1.362 (7)	C113—H11F	0.99
O16—C161	1.421 (7)	O113—H113	0.84

C161—H16A	0.98		
O111—Mn1—O111 ⁱ	94.0 (3)	H16A—C161—H16B	109.5
O111—Mn1—O11 ⁱ	89.58 (16)	O16—C161—H16C	109.5
O111 ⁱ —Mn1—O11 ⁱ	172.89 (19)	H16A—C161—H16C	109.5
O111—Mn1—O11	172.89 (18)	H16B—C161—H16C	109.5
O111 ⁱ —Mn1—O11	89.58 (16)	N10—C10—C12	126.0 (5)
O11 ⁱ —Mn1—O11	87.6 (2)	N10—C10—H10	117
O111—Mn1—N10	84.14 (18)	C12—C10—H10	117
O111 ⁱ —Mn1—N10	88.07 (19)	C10—N10—C101	122.0 (5)
O11 ⁱ —Mn1—N10	98.44 (18)	C10—N10—Mn1	125.1 (4)
O11—Mn1—N10	89.82 (17)	C101—N10—Mn1	111.8 (4)
O111—Mn1—N10 ⁱ	88.07 (19)	N10—C101—C112	113.9 (5)
O111 ⁱ —Mn1—N10 ⁱ	84.14 (18)	N10—C101—C113	107.5 (6)
O11 ⁱ —Mn1—N10 ⁱ	89.82 (17)	C112—C101—C113	112.5 (7)
O11—Mn1—N10 ⁱ	98.44 (18)	N10—C101—C111	103.5 (5)
N10—Mn1—N10 ⁱ	168.6 (3)	C112—C101—C111	111.1 (6)
O11—C11—C12	123.7 (5)	C113—C101—C111	107.8 (5)
O11—C11—C16	118.3 (5)	O111—C111—C101	110.7 (5)
C12—C11—C16	118.0 (5)	O111—C111—H11A	109.5
C11—O11—Mn1	124.9 (3)	C101—C111—H11A	109.5
C11—C12—C13	119.8 (5)	O111—C111—H11B	109.5
C11—C12—C10	122.1 (5)	C101—C111—H11B	109.5
C13—C12—C10	118.1 (5)	H11A—C111—H11B	108.1
C14—C13—C12	121.6 (5)	C111—O111—Mn1	112.9 (4)
C14—C13—H13	119.2	O112—C112—C101	111.9 (7)
C12—C13—H13	119.2	O112—C112—H11C	109.2
C13—C14—C15	119.0 (5)	C101—C112—H11C	109.2
C13—C14—H14	120.5	O112—C112—H11D	109.2
C15—C14—H14	120.5	C101—C112—H11D	109.2
C16—C15—C14	120.7 (5)	H11C—C112—H11D	107.9
C16—C15—H15	119.7	C112—O112—H112	109.5
C14—C15—H15	119.7	O113—C113—C101	111.0 (6)
O16—C16—C15	125.0 (5)	O113—C113—H11E	109.4
O16—C16—C11	114.3 (5)	C101—C113—H11E	109.4
C15—C16—C11	120.7 (5)	O113—C113—H11F	109.4
C16—O16—C161	117.7 (5)	C101—C113—H11F	109.4
O16—C161—H16A	109.5	H11E—C113—H11F	108
O16—C161—H16B	109.5	C113—O113—H113	109.5

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O112—H112 ⁱⁱⁱ —O11 ⁱⁱ	0.84	2.2	2.850 (7)	134

O112—H112...O16 ⁱⁱ	0.84	2.1	2.802 (7)	141
O113—H113...O112 ⁱⁱⁱ	0.84	2.3	2.965 (12)	137

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