Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Bis(μ-2-carboxymethyl-2-hydroxybutanedioato)bis[diaquamanganese(II)]–1,2-bis(pyridin-4-yl)ethane–water (1/1/2)

In Hong Hwang,[a] Pan-Gi Kim,[b] Cheal Kim[a]* and Youngmee Kim[c]*

[a]Department of Fine Chemistry, Seoul National University of Science & Technology, Seoul 139-743, Republic of Korea, [b]Department of Forest & Environment Resources, Kyungpook National University, Sangju 742-711, Republic of Korea, and [c]Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Republic of Korea
Correspondence e-mail: chealkim@seoultech.ac.kr, ymeekim@ewha.ac.kr

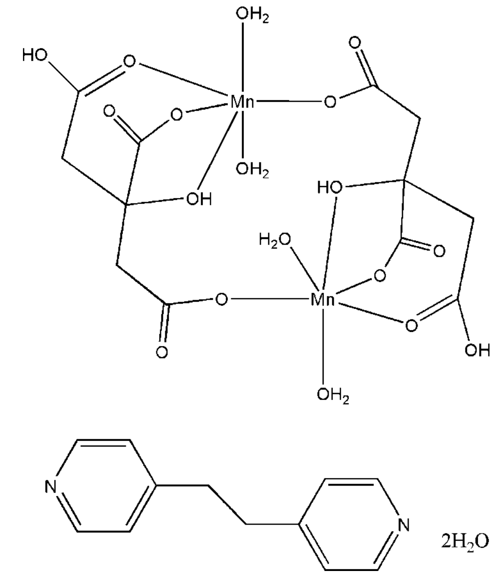
Received 17 July 2012; accepted 19 July 2012

Key indicators: single-crystal X-ray study; *T* = 293 K; mean σ(C–C) = 0.004 Å; *R* factor = 0.033; *wR* factor = 0.092; data-to-parameter ratio = 12.8.

The asymmetric unit of the title compound, $[Mn_2(C_6H_6O_7)_2(H_2O)_4]\cdot C_{12}H_{12}N_2\cdot 2H_2O$, comprises half of a centrosymmetric dimer, half of a 1,2-bis(pyridin-4-yl)ethane and one water molecule. Two citrate ligands bridge two Mn^{II} ions, the Mn^{II} ion being coordinated by four O atoms from the citrate(2−) ligands and two water O atoms, forming a distorted octahedral environment. In the crystal, O—H$\cdots$O hydrogen bonds link the centrosymmetric dimers and lattice water molecules into a three-dimensional structure which is further stabilized by intermolecular π–π interactions [centroid–centroid distance = 3.792 (2) Å].

Related literature

For interactions of metal ions with biologically active molecules, see: Daniele *et al.* (2008); Parkin (2004); Tshuva & Lippard (2004); Stoumpos *et al.* (2009). For related complexes, see: Lee *et al.* (2008); Park *et al.* (2008); Shin *et al.* (2009); Song *et al.* (2009); Yu *et al.* (2008, 2009); Kim *et al.* (2011).



Experimental

Crystal data

$[Mn_2(C_6H_6O_7)_2(H_2O)_4]\cdot$-
$C_{12}H_{12}N_2\cdot 2H_2O$
M_r = 782.43
Triclinic, $P\overline{1}$
a = 9.3950 (19) Å
b = 9.5880 (19) Å
c = 10.252 (2) Å
α = 68.90 (3)°
β = 67.74 (3)°
γ = 78.16 (3)°
V = 794.8 (3) Å^3
Z = 1
Mo *K*α radiation
μ = 0.88 mm^{-1}
T = 293 K
0.40 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.719, T_{max} = 0.843
4449 measured reflections
3048 independent reflections
2780 reflections with $I > 2\sigma(I)$
R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.092
S = 1.05
3048 reflections
239 parameters
7 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O1*W*—H1*WA*$\cdots$O3	0.96 (1)	1.91 (1)	2.869 (3)	175 (3)
O1—H1*O*$\cdots$O6	0.93 (1)	1.74 (1)	2.6020 (19)	153 (2)
O1*W*—H1*WB*$\cdots$O7^{i}	0.96 (1)	2.02 (2)	2.903 (3)	152 (3)
O5—H5$\cdots$N11^{ii}	0.82	1.84	2.649 (2)	171
O8—H8*A*$\cdots$O5^{ii}	0.86 (1)	1.84 (1)	2.694 (2)	170 (2)
O8—H8*B*$\cdots$O7^{iii}	0.86 (1)	2.06 (1)	2.872 (2)	158 (2)
O8—H8*B*$\cdots$O7^{iv}	0.86 (1)	2.56 (2)	3.075 (3)	119 (2)
O9—H9*A*$\cdots$O1*W*^{iii}	0.86 (1)	1.88 (1)	2.722 (3)	168 (3)
O9—H9*B*$\cdots$O2^{v}	0.86 (1)	1.97 (1)	2.829 (2)	173 (3)

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Financial support from the Forest Science & Technology Projects (S121012L080111) and the Converging Research Center Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012001725) is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2421).

References

Bruker (1997). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Daniele, P. G., Foti, C., Gianguzza, A., Prenesti, E. & Sammartano, S. (2008). *Coord. Chem. Rev.* **252**, 1093–1107.
Kim, J. H., Kim, C. & Kim, Y. (2011). *Acta Cryst.* E**67**, m3–m4.
Lee, E. Y., Park, B. K., Kim, C., Kim, S.-J. & Kim, Y. (2008). *Acta Cryst.* E**64**, m286.
Park, B. K., Jang, K.-H., Kim, P.-G., Kim, C. & Kim, Y. (2008). *Acta Cryst.* E**64**, m1141.
Parkin, G. (2004). *Chem. Rev.* **104**, 699–767.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Shin, D. H., Han, S.-H., Kim, P.-G., Kim, C. & Kim, Y. (2009). *Acta Cryst.* E**65**, m658–m659.
Song, Y. J., Lee, S.-W., Jang, K. H., Kim, C. & Kim, Y. (2009). *Acta Cryst.* E**65**, m1495–m1496.
Stoumpos, C. C., Gass, I. A., Milios, C. J., Lalioti, N., Terzis, A., Aromi, G., Teat, S. J., Brechin, E. K. & Perlepes, S. P. (2009). *Dalton Trans.* pp. 307–317.
Tshuva, E. Y. & Lippard, S. J. (2004). *Chem. Rev.* **104**, 987–1012.
Yu, S. M., Park, C.-H., Kim, P.-G., Kim, C. & Kim, Y. (2008). *Acta Cryst.* E**64**, m881–m882.
Yu, S. M., Shin, D. H., Kim, P.-G., Kim, C. & Kim, Y. (2009). *Acta Cryst.* E**65**, m1045–m1046.

supporting information

Acta Cryst. (2012). E**68**, m1116–m1117   [https://doi.org/10.1107/S1600536812032771]

Bis(*µ*-2-carboxymethyl-2-hydroxybutanedioato)bis[diaquamanganese(II)]–1,2-bis(pyridin-4-yl)ethane–water (1/1/2)

In Hong Hwang, Pan-Gi Kim, Cheal Kim and Youngmee Kim

S1. Comment

As models to examine the interaction between transition metal ions with biologically active molecules (Daniele, *et al.*, 2008; Parkin, 2004; Tshuva & Lippard, 2004; Stoumpos, *et al.*, 2009), we have intensively studied the interaction of the transition metal ions with the various acids such as benzoic acid, citric acid, and amino acids. Therefore, we have reported a variety of structures of copper(II), cadmium(II), nickel(II), cobalt(II), and zinc(II) benzoates with quinoxaline, 6-methylquinoline, 3-methylquinoline, *trans*-1-(2-pyridyl)-2-(pyridin-4-yl)ethylene, and di-2-pyridyl ketone (Lee, *et al.*, 2008; Yu, *et al.*, 2008; Park, *et al.*, 2008; Shin, *et al.*, 2009; Song, *et al.*, 2009; Yu, *et al.*, 2008, 2009; Kim, *et al.*, 2011). However, manganese as a metal ion source was rarely used. In this work, we have employed manganese(II) nitrate as a building block and citric acid as a ligand. We report here on the structure of new tetraaquadicitratodimanganese(II)-1,2-bis(pyridin-4-yl)ethane-dihydrate, $[Mn_2(H_2O)_4(C_6H_8O_7)_2].(C_{12}H_{12}N_2).2(H_2O)$. The molecular structure of the title compound is shown in Fig. 1. The asymmetric unit of the title compound, $C_{24}H_{36}Mn_2N_2O_{20}$, comprises half of a centrosymmetric dimer , half of a 1,2-bis(pyridin-4-yl)ethane ligand and one water molecule. Two citrate ligands bridge two Mn^{II} ions, and each Mn^{II} is coordinated by four oxygen atoms from the citrates ligand and two water oxygen atoms, forming a distorted octahedral environment. In the crystal, O—H···O hydrogen bonds link the cetrosymmetric dimer and free H_2O components into a three-dimensional structure. The crystal structure is further stabilized by intermolecular π-π interactions [centroid = C11–C15/N11; centroid–centroid distance = 3.792 (2) Å symmetry code: 1-x, -y, 2-z].

S2. Experimental

Citric acid (19.4 mg,0.1 mmol) and $Mn(NO_3)_2.H_2O$(18.3 mg, 0.1 mmol) were dissolved in 4 ml H_2O and carefully layered by 4 ml acetonitrile solution of 1,2-bis(pyridin-4-yl)ethane (38.0 mg, 0.2 mmol). Suitable crystals of the title compound were obtained in a month.

S3. Refinement

H atoms bonded to C atoms were placed in calculated positions with C—H distances of 0.93 Å for aromatic C atoms and 0.97 Å for methylene C atoms. They were included in the refinement in riding-motion approximation with U_{iso}(H) = 1.2U_{eq}(C). H atom bonded to O atom was placed in the calculated position with O—H distance of 0.82 Å for carboxylate O atom, and it was included in the refinement in riding-motion approximation with U_{iso}(H) = 1.5U_{eq}(C). The position of O—H atom of the hydroxyl group was refined with O—H = 0.93 Å and U_{iso}(H) = 1.5U_{eq}(N). The positions of O—H atoms of the coordinated water ligands were refined with O—H = 0.86 Å and U_{iso}(H) = 1.2U_{eq}(N). The positions of O—H atoms of the free water molecule were refined with O—H = 0.96 Å and U_{iso}(H) = 1.2U_{eq}(N).

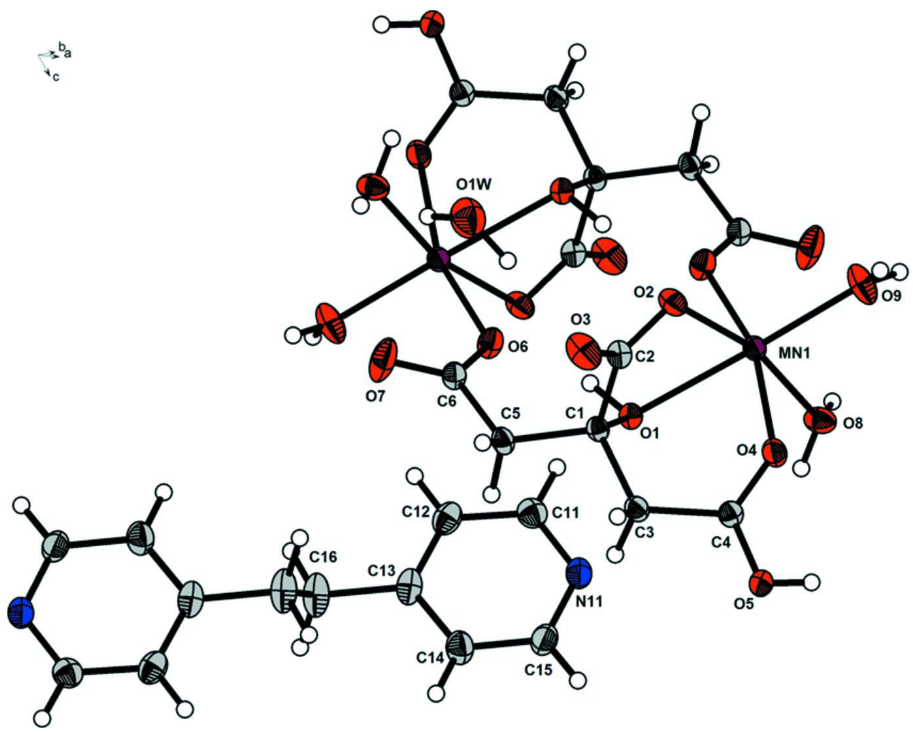


Figure 1

The structure of the title compound showing the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level. The labelled atoms are related with unlabelled atoms by symmetry code: [1-x, 1-y, 1-z] for diaqua- bis-(citrato)di-manganese(II) fragment and [-x, -y, 2-z] for 1,2-bis(pyridin-4-yl)ethane solvate.

Bis(μ-2-carboxymethyl-2-hydroxybutanedioato)bis[diaquamanganese(II)]– 1,2-bis(pyridin-4-yl)ethane–water (1/1/2)

Crystal data

$[Mn_2(C_6H_6O_7)_2(H_2O)_4]\cdot C_{12}H_{12}N_2\cdot 2H_2O$
$M_r = 782.43$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 9.3950$ (19) Å
$b = 9.5880$ (19) Å
$c = 10.252$ (2) Å
$\alpha = 68.90$ (3)°
$\beta = 67.74$ (3)°
$\gamma = 78.16$ (3)°
$V = 794.8$ (3) Å^3
$Z = 1$
$F(000) = 404$
$D_x = 1.635$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 11909 reflections
$\theta = 2.7$–27.6°
$\mu = 0.88$ mm^{-1}
$T = 293$ K
Block, colourless
0.40 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min} = 0.719$, $T_{max} = 0.843$
4449 measured reflections
3048 independent reflections
2780 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.3°$
$h = -11 \rightarrow 11$
$k = -8 \rightarrow 11$
$l = -12 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.092$
$S = 1.05$
3048 reflections
239 parameters
7 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
$w = 1/[\sigma^2(F_o^2) + (0.0603P)^2 + 0.2356P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Mn1	0.59630 (3)	0.69243 (3)	0.60317 (3)	0.02605 (12)
O1	0.42810 (14)	0.50818 (14)	0.71524 (14)	0.0253 (3)
H1O	0.422 (3)	0.467 (2)	0.648 (2)	0.038*
O2	0.38654 (15)	0.79182 (15)	0.54871 (15)	0.0344 (3)
O3	0.13155 (17)	0.80099 (18)	0.6601 (2)	0.0491 (4)
O4	0.47047 (16)	0.73580 (18)	0.81310 (15)	0.0377 (3)
O5	0.34758 (17)	0.66928 (18)	1.05400 (15)	0.0400 (4)
H5	0.4213	0.7042	1.0522	0.060*
O6	0.31979 (15)	0.40470 (17)	0.57203 (15)	0.0355 (3)
O7	0.06796 (18)	0.4110 (3)	0.6235 (2)	0.0632 (6)
O8	0.76699 (16)	0.56448 (18)	0.70557 (16)	0.0389 (3)
H8A	0.738 (3)	0.4919 (19)	0.7866 (15)	0.047*
H8B	0.8528 (15)	0.525 (3)	0.659 (2)	0.047*
O9	0.70528 (19)	0.89824 (18)	0.5069 (2)	0.0498 (4)
H9A	0.8044 (3)	0.892 (3)	0.476 (3)	0.060*
H9B	0.672 (3)	0.9906 (10)	0.498 (3)	0.060*
C1	0.27525 (19)	0.5802 (2)	0.76103 (19)	0.0243 (4)
C2	0.2623 (2)	0.7377 (2)	0.6467 (2)	0.0289 (4)
C3	0.2476 (2)	0.5940 (2)	0.9129 (2)	0.0294 (4)
H3A	0.1475	0.6478	0.9430	0.035*
H3B	0.2421	0.4939	0.9836	0.035*
C4	0.3654 (2)	0.6717 (2)	0.9252 (2)	0.0277 (4)
C5	0.1528 (2)	0.4839 (2)	0.7782 (2)	0.0285 (4)
H5A	0.1468	0.3963	0.8648	0.034*

H5B	0.0535	0.5413	0.7976	0.034*
C6	0.1791 (2)	0.4310 (2)	0.6473 (2)	0.0295 (4)
N11	0.4324 (2)	0.18749 (19)	0.9584 (2)	0.0367 (4)
C11	0.4410 (3)	0.1513 (2)	0.8411 (2)	0.0392 (5)
H11	0.5245	0.1776	0.7540	0.047*
C12	0.3275 (3)	0.0755 (2)	0.8483 (3)	0.0401 (5)
H12	0.3343	0.0505	0.7664	0.048*
C13	0.2026 (2)	0.0363 (2)	0.9784 (3)	0.0397 (5)
C14	0.1958 (3)	0.0774 (3)	1.0979 (3)	0.0433 (5)
H14	0.1126	0.0544	1.1857	0.052*
C15	0.3128 (3)	0.1524 (3)	1.0851 (3)	0.0408 (5)
H15	0.3090	0.1790	1.1652	0.049*
C16	0.0763 (3)	−0.0475 (3)	0.9912 (3)	0.0521 (6)
H16A	0.0643	−0.1376	1.0761	0.062*
H16B	0.1053	−0.0777	0.9032	0.062*
O1W	0.0166 (2)	0.8352 (2)	0.4269 (2)	0.0644 (5)
H1WA	0.061 (3)	0.824 (4)	0.501 (3)	0.077*
H1WB	0.023 (4)	0.7418 (18)	0.410 (4)	0.077*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.02480 (17)	0.02764 (18)	0.02587 (17)	−0.00515 (11)	−0.00565 (12)	−0.00986 (12)
O1	0.0215 (6)	0.0254 (6)	0.0297 (6)	0.0000 (5)	−0.0076 (5)	−0.0114 (5)
O2	0.0298 (7)	0.0293 (7)	0.0357 (7)	−0.0044 (6)	−0.0089 (6)	−0.0016 (6)
O3	0.0295 (8)	0.0379 (9)	0.0649 (11)	0.0061 (6)	−0.0130 (7)	−0.0066 (8)
O4	0.0375 (8)	0.0463 (8)	0.0320 (7)	−0.0179 (6)	−0.0006 (6)	−0.0189 (6)
O5	0.0428 (8)	0.0539 (9)	0.0291 (7)	−0.0222 (7)	−0.0092 (6)	−0.0126 (7)
O6	0.0265 (7)	0.0492 (9)	0.0378 (7)	−0.0015 (6)	−0.0071 (6)	−0.0263 (7)
O7	0.0296 (8)	0.1139 (16)	0.0738 (12)	−0.0066 (9)	−0.0134 (8)	−0.0644 (12)
O8	0.0288 (7)	0.0465 (9)	0.0312 (7)	−0.0008 (6)	−0.0072 (6)	−0.0048 (7)
O9	0.0355 (8)	0.0282 (8)	0.0753 (12)	−0.0089 (7)	−0.0104 (8)	−0.0094 (8)
C1	0.0204 (8)	0.0253 (9)	0.0265 (8)	−0.0026 (7)	−0.0042 (7)	−0.0108 (7)
C2	0.0267 (9)	0.0263 (9)	0.0346 (10)	−0.0004 (7)	−0.0106 (8)	−0.0110 (8)
C3	0.0294 (9)	0.0308 (10)	0.0273 (9)	−0.0082 (8)	−0.0032 (7)	−0.0119 (8)
C4	0.0281 (9)	0.0262 (9)	0.0297 (9)	−0.0019 (7)	−0.0078 (7)	−0.0121 (8)
C5	0.0223 (8)	0.0310 (10)	0.0317 (9)	−0.0056 (7)	−0.0032 (7)	−0.0133 (8)
C6	0.0261 (9)	0.0318 (10)	0.0328 (9)	−0.0038 (7)	−0.0083 (7)	−0.0135 (8)
N11	0.0367 (9)	0.0311 (9)	0.0455 (10)	−0.0044 (7)	−0.0202 (8)	−0.0078 (8)
C11	0.0400 (11)	0.0335 (11)	0.0415 (11)	−0.0017 (9)	−0.0152 (9)	−0.0077 (9)
C12	0.0450 (12)	0.0367 (11)	0.0487 (12)	0.0040 (9)	−0.0244 (10)	−0.0193 (10)
C13	0.0350 (11)	0.0345 (11)	0.0600 (14)	0.0020 (9)	−0.0235 (10)	−0.0209 (10)
C14	0.0341 (11)	0.0492 (13)	0.0496 (13)	−0.0077 (10)	−0.0124 (10)	−0.0180 (11)
C15	0.0446 (12)	0.0429 (12)	0.0438 (12)	−0.0066 (10)	−0.0208 (10)	−0.0154 (10)
C16	0.0394 (13)	0.0454 (14)	0.0871 (19)	0.0007 (11)	−0.0266 (13)	−0.0350 (13)
O1W	0.0568 (11)	0.0585 (12)	0.0768 (13)	−0.0075 (9)	−0.0278 (10)	−0.0126 (11)

Geometric parameters (Å, º)

Mn1—O6^{i}	2.1319 (15)	C3—C4	1.518 (3)
Mn1—O9	2.1395 (17)	C3—H3A	0.9700
Mn1—O4	2.1720 (15)	C3—H3B	0.9700
Mn1—O8	2.1725 (16)	C5—C6	1.519 (3)
Mn1—O2	2.1871 (15)	C5—H5A	0.9700
Mn1—O1	2.2905 (16)	C5—H5B	0.9700
O1—C1	1.440 (2)	N11—C11	1.337 (3)
O1—H1O	0.930 (2)	N11—C15	1.341 (3)
O2—C2	1.275 (2)	C11—C12	1.375 (3)
O3—C2	1.234 (2)	C11—H11	0.9300
O4—C4	1.246 (2)	C12—C13	1.389 (3)
O5—C4	1.259 (2)	C12—H12	0.9300
O5—H5	0.8200	C13—C14	1.392 (3)
O6—C6	1.280 (2)	C13—C16	1.506 (3)
O6—Mn1^{i}	2.1319 (15)	C14—C15	1.375 (3)
O7—C6	1.223 (2)	C14—H14	0.9300
O8—H8A	0.860 (2)	C15—H15	0.9300
O8—H8B	0.859 (2)	C16—C16^{ii}	1.518 (5)
O9—H9A	0.860 (2)	C16—H16A	0.9700
O9—H9B	0.860 (2)	C16—H16B	0.9700
C1—C3	1.529 (3)	O1W—H1WA	0.960 (2)
C1—C5	1.540 (2)	O1W—H1WB	0.959 (2)
C1—C2	1.558 (3)		
O6^{i}—Mn1—O9	103.57 (7)	C1—C3—H3A	108.0
O6^{i}—Mn1—O4	163.30 (6)	C4—C3—H3B	108.0
O9—Mn1—O4	93.05 (7)	C1—C3—H3B	108.0
O6^{i}—Mn1—O8	93.96 (6)	H3A—C3—H3B	107.2
O9—Mn1—O8	95.36 (7)	O4—C4—O5	122.97 (17)
O4—Mn1—O8	85.97 (6)	O4—C4—C3	121.25 (16)
O6^{i}—Mn1—O2	92.00 (6)	O5—C4—C3	115.76 (16)
O9—Mn1—O2	94.89 (6)	C6—C5—C1	116.30 (15)
O4—Mn1—O2	84.89 (6)	C6—C5—H5A	108.2
O8—Mn1—O2	166.60 (5)	C1—C5—H5A	108.2
O6^{i}—Mn1—O1	83.80 (6)	C6—C5—H5B	108.2
O9—Mn1—O1	166.66 (6)	C1—C5—H5B	108.2
O4—Mn1—O1	79.57 (6)	H5A—C5—H5B	107.4
O8—Mn1—O1	95.19 (6)	O7—C6—O6	124.37 (18)
O2—Mn1—O1	73.53 (5)	O7—C6—C5	119.40 (17)
C1—O1—Mn1	107.05 (10)	O6—C6—C5	116.17 (16)
C1—O1—H1O	101.9 (14)	C11—N11—C15	121.11 (18)
Mn1—O1—H1O	112.3 (14)	N11—C11—C12	120.5 (2)
C2—O2—Mn1	114.86 (12)	N11—C11—H11	119.7
C4—O4—Mn1	132.39 (13)	C12—C11—H11	119.7
C4—O5—H5	109.5	C11—C12—C13	119.8 (2)
C6—O6—Mn1^{i}	127.51 (12)	C11—C12—H12	120.1

Mn1—O8—H8A	118.4 (17)	C13—C12—H12	120.1
Mn1—O8—H8B	123.3 (17)	C12—C13—C14	118.3 (2)
H8A—O8—H8B	101 (2)	C12—C13—C16	121.5 (2)
Mn1—O9—H9A	117.2 (19)	C14—C13—C16	120.2 (2)
Mn1—O9—H9B	134 (2)	C15—C14—C13	119.5 (2)
H9A—O9—H9B	109 (3)	C15—C14—H14	120.2
O1—C1—C3	106.79 (14)	C13—C14—H14	120.2
O1—C1—C5	110.98 (14)	N11—C15—C14	120.7 (2)
C3—C1—C5	108.23 (15)	N11—C15—H15	119.7
O1—C1—C2	110.46 (14)	C14—C15—H15	119.7
C3—C1—C2	110.69 (15)	C13—C16—C16^{ii}	111.7 (2)
C5—C1—C2	109.64 (15)	C13—C16—H16A	109.3
O3—C2—O2	125.25 (18)	C16^{ii}—C16—H16A	109.3
O3—C2—C1	116.81 (17)	C13—C16—H16B	109.3
O2—C2—C1	117.94 (16)	C16^{ii}—C16—H16B	109.3
C4—C3—C1	117.19 (15)	H16A—C16—H16B	107.9
C4—C3—H3A	108.0	H1WA—O1W—H1WB	111 (3)

O6^{i}—Mn1—O1—C1	−128.46 (11)	C5—C1—C2—O2	−134.76 (17)
O9—Mn1—O1—C1	−4.0 (3)	O1—C1—C3—C4	54.5 (2)
O4—Mn1—O1—C1	53.18 (11)	C5—C1—C3—C4	174.00 (15)
O8—Mn1—O1—C1	138.10 (11)	C2—C1—C3—C4	−65.8 (2)
O2—Mn1—O1—C1	−34.53 (10)	Mn1—O4—C4—O5	150.23 (16)
O6^{i}—Mn1—O2—C2	113.17 (14)	Mn1—O4—C4—C3	−31.3 (3)
O9—Mn1—O2—C2	−143.02 (14)	C1—C3—C4—O4	7.7 (3)
O4—Mn1—O2—C2	−50.38 (14)	C1—C3—C4—O5	−173.68 (17)
O8—Mn1—O2—C2	−3.2 (3)	O1—C1—C5—C6	−51.4 (2)
O1—Mn1—O2—C2	30.23 (13)	C3—C1—C5—C6	−168.30 (16)
O6^{i}—Mn1—O4—C4	−3.7 (3)	C2—C1—C5—C6	70.9 (2)
O9—Mn1—O4—C4	170.83 (19)	Mn1^{i}—O6—C6—O7	−4.3 (3)
O8—Mn1—O4—C4	−94.01 (19)	Mn1^{i}—O6—C6—C5	172.89 (12)
O2—Mn1—O4—C4	76.19 (19)	C1—C5—C6—O7	−150.0 (2)
O1—Mn1—O4—C4	2.03 (18)	C1—C5—C6—O6	32.6 (3)
Mn1—O1—C1—C3	−85.32 (13)	C15—N11—C11—C12	−0.6 (3)
Mn1—O1—C1—C5	156.92 (12)	N11—C11—C12—C13	0.1 (3)
Mn1—O1—C1—C2	35.10 (15)	C11—C12—C13—C14	0.8 (3)
Mn1—O2—C2—O3	158.86 (17)	C11—C12—C13—C16	−179.6 (2)
Mn1—O2—C2—C1	−20.1 (2)	C12—C13—C14—C15	−1.2 (3)
O1—C1—C2—O3	168.78 (17)	C16—C13—C14—C15	179.2 (2)
C3—C1—C2—O3	−73.2 (2)	C11—N11—C15—C14	0.2 (3)
C5—C1—C2—O3	46.2 (2)	C13—C14—C15—N11	0.7 (4)
O1—C1—C2—O2	−12.2 (2)	C12—C13—C16—C16^{ii}	−113.7 (3)
C3—C1—C2—O2	105.91 (19)	C14—C13—C16—C16^{ii}	65.8 (4)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O3	0.96 (1)	1.91 (1)	2.869 (3)	175 (3)
O1—H1*O*···O6	0.93 (1)	1.74 (1)	2.6020 (19)	153 (2)
O1*W*—H1*WB*···O7^{iii}	0.96 (1)	2.02 (2)	2.903 (3)	152 (3)
O5—H5···N11^{iv}	0.82	1.84	2.649 (2)	171
O8—H8*A*···O5^{iv}	0.86 (1)	1.84 (1)	2.694 (2)	170 (2)
O8—H8*B*···O7^{v}	0.86 (1)	2.06 (1)	2.872 (2)	158 (2)
O8—H8*B*···O7^{i}	0.86 (1)	2.56 (2)	3.075 (3)	119 (2)
O9—H9*A*···O1*W*^{v}	0.86 (1)	1.88 (1)	2.722 (3)	168 (3)
O9—H9*B*···O2^{vi}	0.86 (1)	1.97 (1)	2.829 (2)	173 (3)
C5—H5*B*···O3	0.97	2.48	2.834 (3)	101
C14—H14···O1*W*^{vii}	0.93	2.59	3.357 (4)	141
C15—H15···O4^{iv}	0.93	2.49	3.114 (3)	125

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*, −*y*+1, −*z*+1; (iv) −*x*+1, −*y*+1, −*z*+2; (v) *x*+1, *y*, *z*; (vi) −*x*+1, −*y*+2, −*z*+1; (vii) *x*, *y*−1, *z*+1.