Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis(μ-pyridinium-2-carboxylato-κ^2O:O')-bis[triaqua(sulfato-κO)manganese(II)]

Hossein Ali Rasekh* and Bohlul Bahrami

Department of Chemistry, Islamic Azad University, Firoozabad Branch, Firoozabad, Fars, Iran
Correspondence e-mail: Dr.H.A.Rasekh@gmail.com

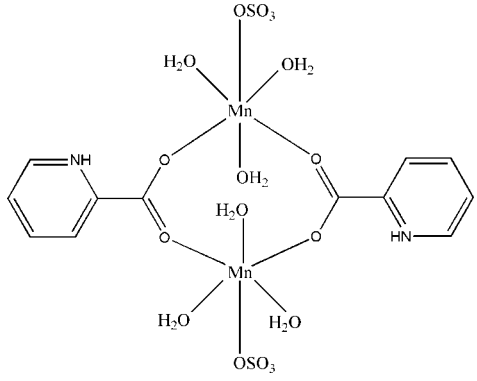
Received 11 December 2011; accepted 19 December 2011

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.005 Å; R factor = 0.028; wR factor = 0.075; data-to-parameter ratio = 10.7.

The asymmetric unit of the title compound, $[Mn_2(SO_4)_2(C_6H_5NO_2)_2(H_2O)_6]$, comprises half of a centrosymmetric dimer. The Mn^{II} atom is coordinated by two O atoms of the monodentate carboxylate ligand, an O atom of the sulfate anion in axial position and three water molecules in a distorted octahedral geometry. In the crystal, molecules are connected through N—H···O and O—H···O hydrogen bonds, forming a three-dimensional network. The crystal structure is further stabilized by intermolecular π–π interactions [centroid–centroid distance = 3.842 (2) Å].

Related literature

For standard bond lengths, see: Allen *et al.* (1987). For background to the applications of Mn^{II} complexes, see: Lee *et al.* (2004); Mautner *et al.* (1997).



Experimental

Crystal data

$[Mn_2(SO_4)_2(C_6H_5NO_2)_2(H_2O)_6]$ M_r = 656.32
Orthorhombic, *Pbca*
a = 16.886 (3) Å
b = 7.6022 (15) Å
c = 18.070 (4) Å
V = 2319.6 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.36 mm^{-1}
T = 291 K
0.28 × 0.22 × 0.18 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.702, T_{max} = 0.792
5787 measured reflections
1945 independent reflections
1386 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.075
S = 1.26
1944 reflections
181 parameters
9 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O5^{i}	0.86	1.97	2.799 (3)	161
O1W—H11···O5^{ii}	0.81 (2)	2.06 (2)	2.856 (3)	168 (3)
O1W—H12···O5^{i}	0.84 (2)	1.91 (2)	2.735 (3)	173 (3)
O2W—H21···O4^{ii}	0.82 (2)	1.90 (2)	2.704 (3)	167 (4)
O2W—H22···O4^{iii}	0.83 (2)	1.97 (2)	2.758 (3)	158 (3)
O3W—H31···O6^{ii}	0.82 (2)	1.92 (2)	2.736 (3)	177 (4)
O3W—H32···O6^{iv}	0.83 (2)	1.84 (2)	2.660 (3)	172 (3)

Symmetry codes: (i) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, y-1, z$; (iii) $-x+2, -y+1, -z+1$; (iv) $-x+\frac{5}{2}, y-\frac{1}{2}, z$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

HAR and BB thank Islamic Azad University, Firoozabad Branch. BB thanks Dr Reza Kia for the data collection, structure determination, refinement and manuscript preparation.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2328).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Lee, S., Shin, D. M. & Chung, Y. K. (2004). *Chem. Eur. J.* **10**, 3158–3163.
Mautner, F. A., Abu-Youssef, M. A. M. & Goher, M. A. S. (1997). *Polyhedron*, **16**, 235–241.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2012). E**68**, m88 [doi:10.1107/S1600536811054596]

Bis(*μ*-pyridinium-2-carboxylato-*κ*^{2}*O*:*O*′)bis[triaqua(sulfato-*κO*)manganese(II)]

Hossein Ali Rasekh and Bohlul Bahrami

S1. Comment

As a part of a synthetic work on synthesis and characterization and applications (Lee *et al.,* 2004; Mautner *et al.,* 1997), of new Mn(II) complexes with aromatic carboxylic acid, we determined the X-ray structure of the title compound.

The molecule structure of the title compound (Fig. 1) is composed of a centerosymmetric dimer of a Mn(II) complex with pyridine-2-carboxylic acid. The bond lengths (Allen *et al.,* 1987) and angles are within the normal ranges. The geometry around the Mn^{II} is a distorted octahedron which is coordinated by two oxygen atoms of the carboxylic ligand, an oxygen atom of the sulfate anion, and three oxygen atoms of the coordinated water molecules. Intermolecular N—H···O and O—H···O hydrogen bonds (Table 1), link neighboring molecules, forming three dimensional network (Fig. 2). The crystal structure is further stabilized by the intermolecular *π*-*π* interaction [Cg1···Cg1^{i} = 3.842 (2) Å, (i) 3/2 - *x*, -1/2 + *y*, *z*; Cg1 is the centroid of the (N1/C1–C5) ring.

S2. Experimental

The title compound was synthesized by adding 10 ml solution of pyridine-2-carboxylic acid (1.456 g, 11.832 mmol) to a 10 ml solution of manganese sulfate (2g, 11.832 mmol). The mixture was stirred for 24 h. Light-brown single crystals of the title compound suitable for *X*-ray structure determination were obtained by slow evaporation of the solvents at room temperature after 4 days.

S3. Refinement

All hydrogen atoms of C were positioned geometrically with C—H = 0.93 Å and included in a riding model approximation with U_{iso} (H) = 1.2 U_{eq}(C). The N-bound H atom was located in a difference Fourier map and constrained to refine with the parent atom by U_{iso} (H) = 1.2 U_{eq}(N). The hydrogen atoms of the water molecules were located in a difference Fourier map and constrained to refine with the parent atoms by U_{iso} (H) = 1.5 U_{eq}(O).

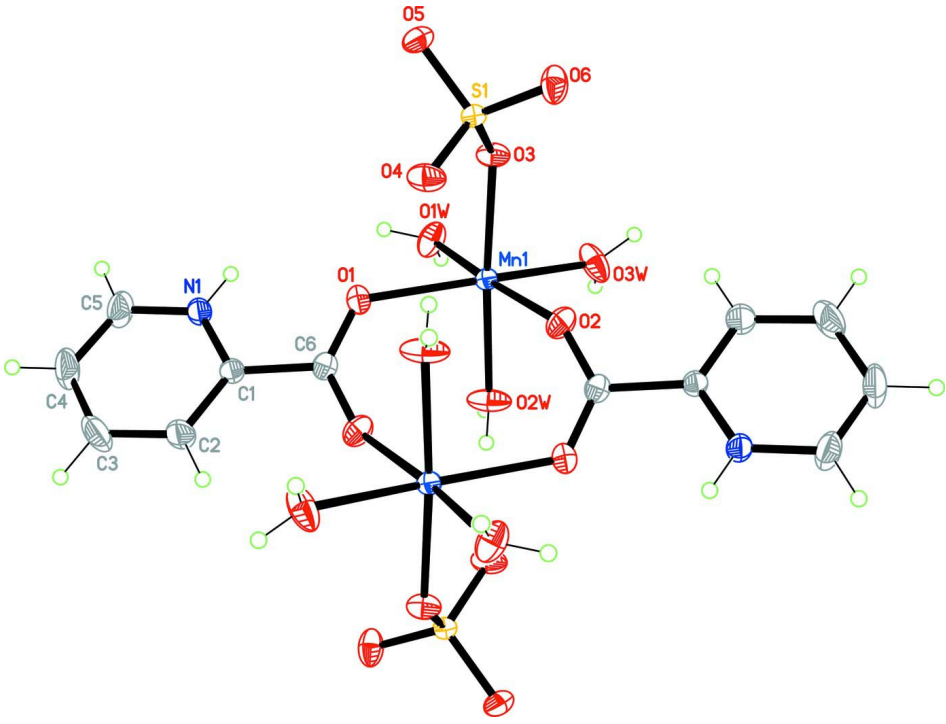


Figure 1

The molecular structure of the title compound, with 40% probability displacement ellipsoids. Symmetry code for the unlabeled atoms: -*x* + *2*, -*y* + 1, -*z* + 1

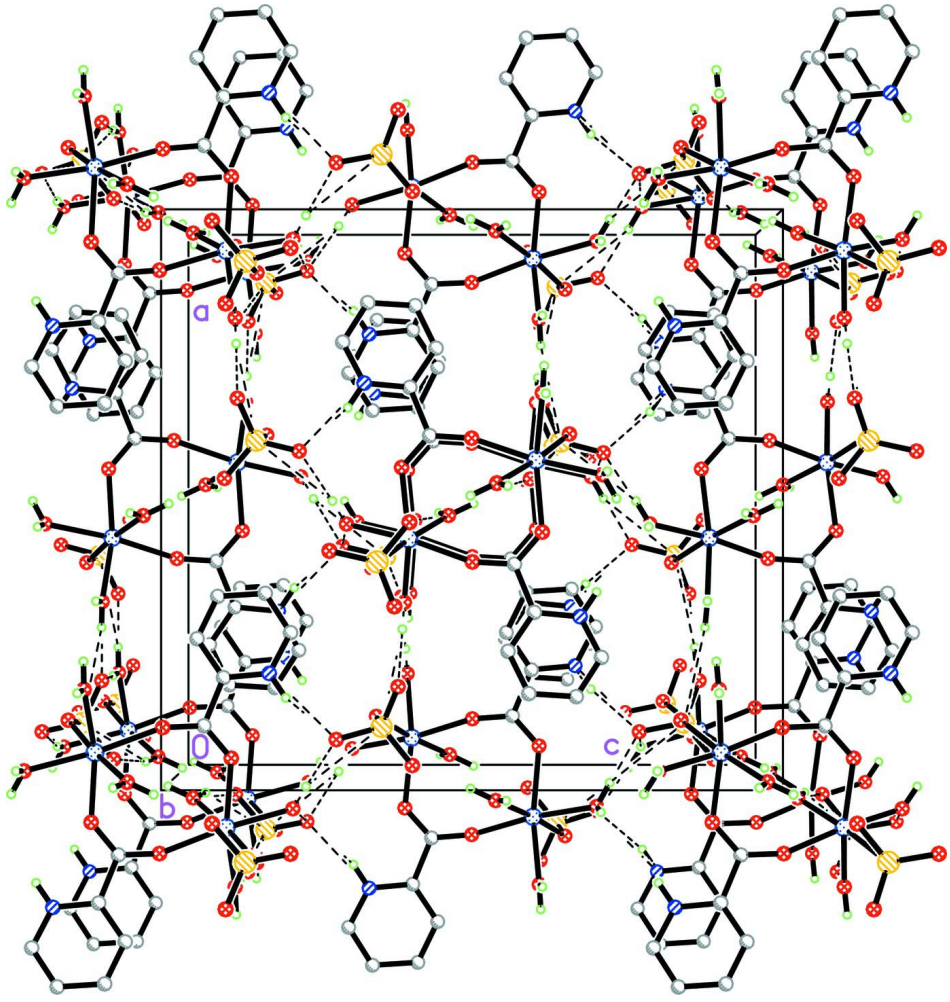


Figure 2

The packing diagram of the title compound viewed down the *b*-axis showing three dimensional networks. The dashed lines show the intermolecular interactions.

Bis(*μ*-pyridinium-2-carboxylato-κ^2*O*:*O*′)bis[triaqua(sulfato- κ*O*)manganese(II)]

Crystal data

$[Mn_2(SO_4)_2(C_6H_5NO_2)_2(H_2O)_6]$
M_r = 656.32
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 16.886 (3) Å
b = 7.6022 (15) Å
c = 18.070 (4) Å
V = 2319.6 (8) Å^3
Z = 4
F(000) = 1336
D_x = 1.879 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 2525 reflections
θ = 2.5–27.4°
μ = 1.36 mm^{-1}
T = 291 K
Block, light-brown
0.28 × 0.22 × 0.18 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.702, T_{max} = 0.792
5787 measured reflections
1945 independent reflections
1386 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 25.0°, θ_{min} = 2.4°
h = −17→20
k = −8→9
l = −21→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.075
S = 1.26
1944 reflections
181 parameters
9 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
$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-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.

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 $F^2 > 2$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.
the reflection "2 0 0" was removed because it was affected by the beam stop

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.80634 (14)	0.4943 (3)	0.39991 (16)	0.0274 (6)
C2	0.73913 (18)	0.5011 (4)	0.44213 (18)	0.0441 (8)
H2	0.7429	0.5010	0.4935	0.053*
C3	0.66613 (19)	0.5082 (5)	0.4087 (2)	0.0608 (10)
H3	0.6204	0.5132	0.4373	0.073*
C4	0.66096 (19)	0.5077 (5)	0.3323 (2)	0.0580 (10)
H4	0.6119	0.5134	0.3089	0.070*
C5	0.72870 (19)	0.4990 (4)	0.29191 (19)	0.0513 (9)
H5	0.7263	0.4971	0.2405	0.062*
C6	0.88940 (16)	0.4876 (3)	0.43176 (16)	0.0281 (6)
Mn1	1.06804 (2)	0.42796 (5)	0.39782 (2)	0.02431 (11)
N1	0.79903 (13)	0.4929 (3)	0.32634 (13)	0.0341 (6)
H1	0.8413	0.4879	0.2999	0.041*
O1	0.94438 (10)	0.5098 (3)	0.38689 (11)	0.0369 (5)
O2	1.10645 (13)	0.5419 (2)	0.50058 (11)	0.0407 (5)

O3	1.11498 (11)	0.6541 (2)	0.34100 (11)	0.0326 (5)
O4	1.03729 (12)	0.8763 (2)	0.40293 (11)	0.0413 (5)
O5	1.08436 (11)	0.9258 (2)	0.28009 (10)	0.0364 (5)
O6	1.17596 (11)	0.9245 (2)	0.38020 (12)	0.0439 (6)
S1	1.10322 (4)	0.84382 (8)	0.35237 (4)	0.02353 (15)
O1W	1.04261 (13)	0.2883 (3)	0.29403 (12)	0.0443 (6)
H11	1.0473 (18)	0.183 (2)	0.2892 (18)	0.066*
H12	1.0020 (14)	0.322 (3)	0.2717 (18)	0.066*
O2W	1.02785 (15)	0.2033 (3)	0.46116 (13)	0.0499 (6)
H21	1.023 (2)	0.104 (3)	0.4449 (17)	0.075*
H22	1.007 (2)	0.208 (4)	0.5024 (12)	0.075*
O3W	1.18013 (11)	0.2837 (3)	0.38886 (16)	0.0541 (7)
H31	1.1775 (19)	0.177 (2)	0.385 (2)	0.081*
H32	1.2266 (12)	0.317 (4)	0.386 (2)	0.081*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0269 (15)	0.0338 (14)	0.0214 (16)	0.0010 (10)	0.0006 (13)	−0.0029 (13)
C2	0.0358 (19)	0.069 (2)	0.0275 (18)	0.0012 (15)	0.0040 (15)	−0.0017 (15)
C3	0.0265 (17)	0.092 (3)	0.064 (3)	0.0010 (16)	0.0128 (19)	−0.004 (2)
C4	0.0307 (19)	0.084 (3)	0.060 (3)	0.0043 (16)	−0.0178 (18)	−0.008 (2)
C5	0.041 (2)	0.079 (2)	0.034 (2)	0.0091 (16)	−0.0136 (16)	−0.0051 (17)
C6	0.0309 (16)	0.0268 (15)	0.0268 (17)	−0.0002 (11)	−0.0045 (14)	−0.0049 (12)
Mn1	0.02487 (19)	0.0253 (2)	0.0228 (2)	−0.00078 (16)	0.0004 (2)	0.0016 (2)
N1	0.0271 (13)	0.0522 (15)	0.0231 (14)	0.0037 (10)	0.0008 (10)	−0.0015 (11)
O1	0.0254 (11)	0.0471 (12)	0.0381 (13)	0.0007 (8)	−0.0027 (10)	0.0033 (9)
O2	0.0474 (13)	0.0493 (14)	0.0254 (12)	−0.0007 (10)	−0.0098 (10)	−0.0025 (10)
O3	0.0453 (13)	0.0190 (10)	0.0336 (12)	−0.0011 (8)	0.0102 (9)	−0.0012 (9)
O4	0.0517 (12)	0.0352 (12)	0.0369 (12)	0.0031 (8)	0.0185 (11)	−0.0012 (10)
O5	0.0460 (12)	0.0352 (11)	0.0280 (11)	−0.0014 (9)	−0.0035 (9)	0.0077 (9)
O6	0.0364 (11)	0.0309 (11)	0.0643 (16)	0.0000 (9)	−0.0172 (10)	−0.0037 (11)
S1	0.0258 (3)	0.0226 (3)	0.0222 (4)	−0.0006 (3)	0.0009 (3)	0.0009 (3)
O1W	0.0555 (14)	0.0397 (12)	0.0376 (13)	0.0123 (10)	−0.0153 (11)	−0.0104 (11)
O2W	0.0808 (17)	0.0247 (12)	0.0441 (15)	−0.0037 (11)	0.0313 (13)	0.0021 (11)
O3W	0.0279 (10)	0.0296 (11)	0.105 (2)	0.0007 (8)	0.0048 (14)	−0.0058 (14)

Geometric parameters (Å, º)

C1—N1	1.335 (3)	Mn1—O1	2.1878 (18)
C1—C2	1.368 (4)	Mn1—O3W	2.1934 (19)
C1—C6	1.517 (3)	Mn1—O1W	2.198 (2)
C2—C3	1.374 (4)	N1—H1	0.8600
C2—H2	0.9300	O2—C6^{i}	1.245 (3)
C3—C4	1.383 (5)	O3—S1	1.4703 (17)
C3—H3	0.9300	O4—S1	1.4613 (19)
C4—C5	1.358 (5)	O5—S1	1.4817 (19)
C4—H4	0.9300	O6—S1	1.4622 (19)

C5—N1	1.342 (4)	O1W—H11	0.811 (17)
C5—H5	0.9300	O1W—H12	0.835 (17)
C6—O1	1.244 (3)	O2W—H21	0.817 (17)
C6—O2^{i}	1.245 (3)	O2W—H22	0.827 (17)
Mn1—O2	2.1492 (19)	O3W—H31	0.818 (17)
Mn1—O3	2.1536 (18)	O3W—H32	0.826 (17)
Mn1—O2W	2.1652 (19)		

N1—C1—C2	118.6 (3)	O1—Mn1—O3W	163.57 (8)
N1—C1—C6	117.6 (2)	O2—Mn1—O1W	172.34 (8)
C2—C1—C6	123.8 (3)	O3—Mn1—O1W	92.91 (8)
C1—C2—C3	120.0 (3)	O2W—Mn1—O1W	90.50 (9)
C1—C2—H2	120.0	O1—Mn1—O1W	82.76 (8)
C3—C2—H2	120.0	O3W—Mn1—O1W	82.19 (9)
C2—C3—C4	119.7 (3)	C1—N1—C5	122.9 (3)
C2—C3—H3	120.1	C1—N1—H1	118.5
C4—C3—H3	120.1	C5—N1—H1	118.5
C5—C4—C3	118.9 (3)	C6—O1—Mn1	127.94 (18)
C5—C4—H4	120.6	C6^{i}—O2—Mn1	142.42 (18)
C3—C4—H4	120.6	S1—O3—Mn1	131.82 (11)
N1—C5—C4	119.9 (3)	O4—S1—O6	110.72 (12)
N1—C5—H5	120.1	O4—S1—O3	110.86 (10)
C4—C5—H5	120.1	O6—S1—O3	110.26 (11)
O1—C6—O2^{i}	128.5 (3)	O4—S1—O5	108.44 (12)
O1—C6—C1	116.0 (2)	O6—S1—O5	107.90 (12)
O2^{i}—C6—C1	115.5 (3)	O3—S1—O5	108.57 (11)
O2—Mn1—O3	88.79 (7)	Mn1—O1W—H11	123 (2)
O2—Mn1—O2W	87.48 (9)	Mn1—O1W—H12	115 (2)
O3—Mn1—O2W	175.65 (9)	H11—O1W—H12	109 (2)
O2—Mn1—O1	104.56 (8)	Mn1—O2W—H21	125 (2)
O3—Mn1—O1	94.65 (7)	Mn1—O2W—H22	125 (2)
O2W—Mn1—O1	88.46 (9)	H21—O2W—H22	109 (2)
O2—Mn1—O3W	90.28 (9)	Mn1—O3W—H31	117 (2)
O3—Mn1—O3W	92.65 (8)	Mn1—O3W—H32	132 (2)
O2W—Mn1—O3W	85.13 (9)	H31—O3W—H32	111 (3)

N1—C1—C2—C3	−0.7 (4)	O3—Mn1—O1—C6	−145.0 (2)
C6—C1—C2—C3	179.5 (3)	O2W—Mn1—O1—C6	32.0 (2)
C1—C2—C3—C4	0.2 (5)	O3W—Mn1—O1—C6	98.9 (4)
C2—C3—C4—C5	0.5 (5)	O1W—Mn1—O1—C6	122.7 (2)
C3—C4—C5—N1	−0.8 (5)	O3—Mn1—O2—C6^{i}	−176.0 (3)
N1—C1—C6—O1	11.2 (3)	O2W—Mn1—O2—C6^{i}	1.7 (3)
C2—C1—C6—O1	−169.0 (3)	O1—Mn1—O2—C6^{i}	89.5 (3)
N1—C1—C6—O2^{i}	−167.9 (2)	O3W—Mn1—O2—C6^{i}	−83.4 (3)
C2—C1—C6—O2^{i}	11.9 (4)	O2—Mn1—O3—S1	−51.74 (16)
C2—C1—N1—C5	0.4 (4)	O1—Mn1—O3—S1	52.77 (16)
C6—C1—N1—C5	−179.8 (2)	O3W—Mn1—O3—S1	−141.97 (17)
C4—C5—N1—C1	0.3 (5)	O1W—Mn1—O3—S1	135.73 (16)

O2^{i}—C6—O1—Mn1	21.0 (4)	Mn1—O3—S1—O4	−12.1 (2)
C1—C6—O1—Mn1	−157.90 (17)	Mn1—O3—S1—O6	110.89 (16)
O2—Mn1—O1—C6	−55.0 (2)	Mn1—O3—S1—O5	−131.11 (14)

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O5^{ii}	0.86	1.97	2.799 (3)	161
O1*W*—H11···O5^{iii}	0.81 (2)	2.06 (2)	2.856 (3)	168 (3)
O1*W*—H12···O5^{ii}	0.84 (2)	1.91 (2)	2.735 (3)	173 (3)
O2*W*—H21···O4^{iii}	0.82 (2)	1.90 (2)	2.704 (3)	167 (4)
O2*W*—H22···O4^{i}	0.83 (2)	1.97 (2)	2.758 (3)	158 (3)
O3*W*—H31···O6^{iii}	0.82 (2)	1.92 (2)	2.736 (3)	177 (4)
O3*W*—H32···O6^{iv}	0.83 (2)	1.84 (2)	2.660 (3)	172 (3)

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+2, *y*−1/2, −*z*+1/2; (iii) *x*, *y*−1, *z*; (iv) −*x*+5/2, *y*−1/2, *z*.