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catena-Poly[[[bis(1,10-phenanthroline-κ^2N,N')manganese(II)]-μ-9,10-dioxoanthracene-1,5-disulfonato-κ^2O^1:O^5] tetrahydrate]

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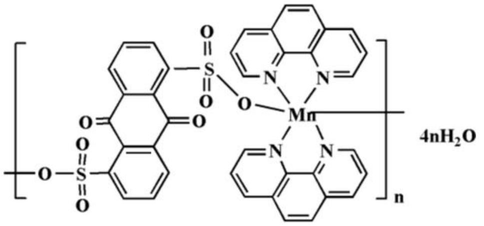
Key indicators: single-crystal X-ray study; *T* = 294 K; mean σ(C–C) = 0.003 Å; *R* factor = 0.030; *wR* factor = 0.086; data-to-parameter ratio = 11.7.

The title complex, $\{[\mathrm{Mn}(\mathrm{C_{14}H_6O_8S_2})(\mathrm{C_{12}H_8N_2})_2]\cdot4\mathrm{H_2O}\}_n$, exhibits a chain-like polymeric structure with 9,10-dioxoanthracene-1,5-disulfonate anions bridging Mn^{II} atoms in a bis-monodentate mode. The unique Mn^{II} atom is located on a crystallographic centre of inversion. Four N atoms from two chelating 1,10-phenanthroline ligands and two sulfonate O atoms from two symmetry-related 9,10-dioxoanthracene-1,5-disulfonate anions give rise to a slightly distorted octahedral coordination environment around the Mn^{II} centre. The centroid of the central ring of the anthraquinone ligand represents another crystallographic centre of inversion. In the crystal structure, interligand π–π stacking [centroid-to-centroid distances 3.532 (1) and 3.497 (3) Å] and intermolecular O—H⋯O hydrogen-bonding interactions assemble the chains into a three-dimensional supramolecular network.

Related literature

For applications of organosulfonate-based metal complexes, see: Côté & Shimizu (2003); Cai (2004). For synthetic procedure, see: Cui *et al.* (2007); Dai *et al.* (2006); Zhao *et al.* (2007). For related structures, see: Cai *et al.* (2001); Du *et al.* (2006); Gándara *et al.* (2006); Wu *et al.* (2007).



Experimental

Crystal data

$[\mathrm{Mn}(\mathrm{C_{14}H_6O_8S_2})(\mathrm{C_{12}H_8N_2})_2]\cdot4\mathrm{H_2O}$
M_r = 853.74
Triclinic, $P\bar{1}$
a = 8.8882 (9) Å
b = 9.578 (1) Å
c = 11.016 (1) Å
α = 105.962 (1)°
β = 103.050 (1)°
γ = 93.120 (1)°
V = 871.5 (2) Å^3
Z = 1
Mo *K*α radiation
μ = 0.58 mm^{-1}
T = 294 K
0.32 × 0.28 × 0.26 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.838, $T_{\max}$ = 0.865
4767 measured reflections
3042 independent reflections
2751 reflections with $I > 2\sigma(I)$
R_{int} = 0.011

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.086
S = 1.05
3042 reflections
259 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.36 e Å^{-3}
$\Delta\rho_{\min}$ = −0.32 e Å^{-3}

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O5*W*—H5*A*⋯O2$^{\mathrm{i}}$	0.85	2.03	2.826 (2)	156
O5*W*—H5*B*⋯O2$^{\mathrm{ii}}$	0.85	2.10	2.948 (2)	172
O6*W*—H6*A*⋯O5*W*$^{\mathrm{iii}}$	0.85	2.13	2.868 (3)	145
O6*W*—H6*B*⋯O3$^{\mathrm{iv}}$	0.85	2.12	2.922 (3)	157

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

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2001); 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) and *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2118).

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supporting information

Acta Cryst. (2009). E**65**, m695–m696   [doi:10.1107/S1600536809019503]

catena-Poly[[[bis(1,10-phenanthroline-κ^2N,N')manganese(II)]-μ-9,10-dioxoanthracene-1,5-disulfonato-$\kappa^2O^1:O^5$] tetrahydrate]

Jia Jia, Wen Feng, Hong-Kun Zhao and En-Cui Yang

S1. Comment

Recently, organosulfonate-based metal complexes have drawn intense interest due to their adjustable coordination ability and interesting applications as functional materials [Cai, 2004; Côté & Shimizu, 2003; Zhao *et al.*, 2007]. By introducing popular nitrogen-containing functional organic molecules as coligands, a series of sulfonate-based complexes have successfully been synthesized, which exhibit diverse structures ranging from discrete zero-dimensional (0D) to infinite high-dimensional structures [Cai *et al.*, 2001; Gándara *et al.*, 2006; Du *et al.*, 2006]. As part of our continuous investigation on the coordination chemistry of mixed-ligand systems [Dai *et al.*, 2006; Cui *et al.*, 2007; Wu *et al.*, 2007], we herein report the crystal structure of a Mn^{II} complex with 1,10-phenanthroline and 9,10-dioxoanthracene-1,5-disulfonate ligands (**I**).

The local coordination environment of Mn^{II} atom in **I** is shown in Fig. 1. The unique Mn^{II} atom is situated on a crystallodraphic centre of inversion and is six-coordinated by four N atoms from two chelating 1,10-phenanthroline ligands and two sulfonate O atoms from two independent 9,10-dioxoanthracene-1,5-disulfonate anions, exhibiting a slightly distorted octahedral coordination mode. The centrosymmetric 9,10-dioxoanthracene-1,5-disulfonate anion adopts a bis-monodentate mode, linking the adjacent Mn^{II} atoms into a one-dimensional infinite chain along the *c*-axis (Fig. 2). Two interligand π–π stacking interactions between the intrachain 1,10-phenanthroline and anthraquinone ring as well as between the two interchain 1,10-phenanthroline rings were observed (Fig. 1 and 2), which stabilize the one-dimensional chain and further extend the chains into a two-dimensional plane. The centroid–centroid distance and the dihedral angle between the 1,10-phenanthroline and anthraquinone ring measures to 3.532 (1) Å and 2.704 (4)°. In contrast, the π-stacking parameters between the interchain 1,10-phenanthroline rings are 3.497 (3) Å and 0.0°, respectively.

Additionally, the adjacent two-dimensional planes are extended into a three-dimensional supramolecular network by fourfold O—H···O hydrogen-bonding interactions between the sulfonate O atoms and the lattice water molecules (Table 1 and Fig. 2).

S2. Experimental

A mixture of disodium 9,10-dioxoanthracene-1,5-disulfonate (164.8 mg, 0.4 mmol), $Mn(OAc)_2.4H_2O$ (98.0 mg, 0.4 mmol), 1,10-phenanthroline (79.3 mg, 0.4 mmol), and H_2O (20 ml) was sealed in a 23 ml teflon lined stainless steel vessel. The vessel was heated to 413 K for 2 d under autogenous pressure and then cooled to room temperature at a rate of 2.4 K/h. Yellow block-shaped crystals suitable for X-ray analysis were obtained in a 41% yield. Analysis calculated for $C_{19}H_{15}Mn_{0.50}N_2O_6S$: C 53.46, H 3.54, N 6.56%; found: C 53.56, H 3.50, N 6.70%.

S3. Refinement

H atoms were located from difference Fourier maps, but were subsequently placed in calculated positions and treated as riding, with C—H = 0.93 Å and O—H = 0.85 Å. All H atoms were allocated displacement parameters related to those of their parent atoms [U_{iso}(H) = 1.2Ueq(C,O)].

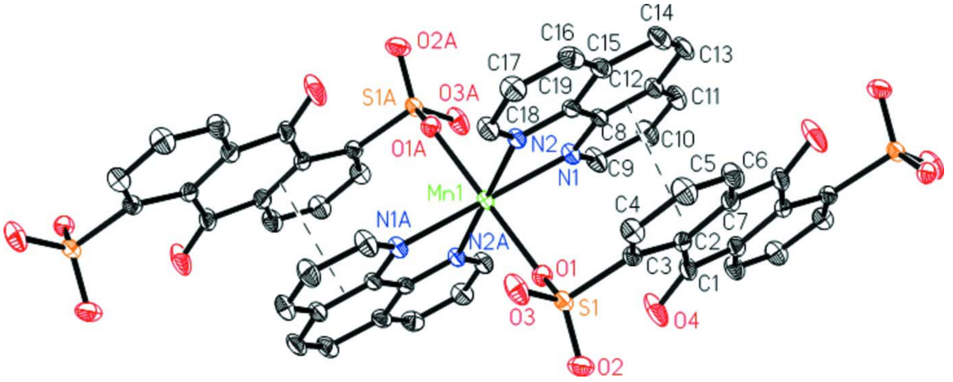

Figure 1

The local coordination environment of Mn^{II} in **I**) drawn with 30% probability displacement ellipsoids. H atoms were omitted for clarity. The short dashed lines indicate interligand *π*-*π* stacking interactions [Symmetry code: (A) 1 - *x*, 1 - *y*, 1 - *z*.]

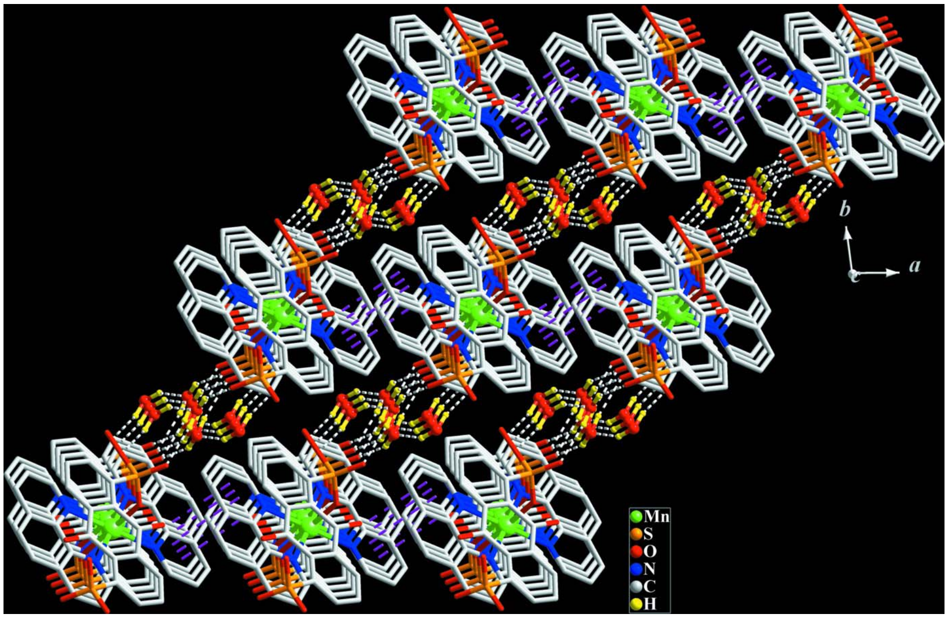

Figure 2

The three-dimensional supramolecular network of (**I**) produced by hydrogen-bonding and *π*–*π* stacking interactions.

catena-Poly[[[bis(1,10-phenanthroline- *κ*^{2}N,N′)manganese(II)]-*μ*-9,10-dioxoanthracene-1,5- disulfonato-*κ*^{2}O^1: \<i>O^5] tetrahydrate]

Crystal data

[Mn($C_{14}H_6O_8S_2$)($C_{12}H_8N_2$)$_2$]·4H_2O	Triclinic, $P\overline{1}$
M_r = 853.74	Hall symbol: -P 1

$a = 8.8882$ (9) Å
$b = 9.578$ (1) Å
$c = 11.016$ (1) Å
$\alpha = 105.962$ (1)°
$\beta = 103.050$ (1)°
$\gamma = 93.120$ (1)°
$V = 871.5$ (2) Å^3
$Z = 1$
$F(000) = 439$

$D_x = 1.627$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3691 reflections
$\theta = 2.2$–27.9°
$\mu = 0.58$ mm^{-1}
$T = 294$ K
Block, yellow
0.32 × 0.28 × 0.26 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.838$, $T_{\max} = 0.865$

4767 measured reflections
3042 independent reflections
2751 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.011$
$\theta_{\max} = 25.0°$, $\theta_{\min} = 2.0°$
$h = -9 \rightarrow 10$
$k = -11 \rightarrow 8$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.086$
$S = 1.05$
3042 reflections
259 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.3551P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ 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	0.5000	0.5000	0.5000	0.02553 (13)
S1	0.34382 (5)	0.24029 (5)	0.21379 (4)	0.03110 (14)
O1	0.34939 (15)	0.38120 (14)	0.30894 (12)	0.0344 (3)
O2	0.19137 (17)	0.18841 (18)	0.12816 (15)	0.0506 (4)
O3	0.40672 (19)	0.13426 (17)	0.27693 (17)	0.0532 (4)
O4	0.2494 (2)	0.4691 (2)	0.0881 (2)	0.0710 (6)
N1	0.59998 (18)	0.65125 (17)	0.40181 (15)	0.0323 (3)
N2	0.71074 (17)	0.40323 (16)	0.44201 (15)	0.0294 (3)

C1	0.3690 (2)	0.4857 (2)	0.05604 (19)	0.0388 (5)
C2	0.4839 (2)	0.3789 (2)	0.05903 (17)	0.0307 (4)
C3	0.4760 (2)	0.2649 (2)	0.11671 (17)	0.0306 (4)
C4	0.5807 (2)	0.1633 (2)	0.1047 (2)	0.0389 (5)
H4	0.5756	0.0884	0.1429	0.047*
C5	0.6932 (3)	0.1712 (2)	0.0368 (2)	0.0448 (5)
H5	0.7597	0.0995	0.0264	0.054*
C6	0.7061 (2)	0.2844 (2)	−0.0148 (2)	0.0425 (5)
H6	0.7838	0.2916	−0.0576	0.051*
C7	0.6032 (2)	0.3891 (2)	−0.00353 (18)	0.0338 (4)
C8	0.7230 (2)	0.60542 (19)	0.35365 (17)	0.0284 (4)
C9	0.5491 (3)	0.7727 (2)	0.3818 (2)	0.0454 (5)
H9	0.4652	0.8050	0.4142	0.055*
C10	0.6133 (3)	0.8547 (2)	0.3155 (2)	0.0486 (5)
H10	0.5727	0.9391	0.3041	0.058*
C11	0.7358 (3)	0.8100 (2)	0.2677 (2)	0.0448 (5)
H11	0.7806	0.8639	0.2235	0.054*
C12	0.7950 (2)	0.6821 (2)	0.28506 (19)	0.0351 (4)
C13	0.9234 (2)	0.6277 (2)	0.2369 (2)	0.0436 (5)
H13	0.9702	0.6779	0.1911	0.052*
C14	0.9780 (2)	0.5056 (2)	0.2565 (2)	0.0435 (5)
H14	1.0616	0.4724	0.2239	0.052*
C15	0.9090 (2)	0.4258 (2)	0.32685 (19)	0.0345 (4)
C16	0.9640 (2)	0.2989 (2)	0.3505 (2)	0.0419 (5)
H16	1.0480	0.2634	0.3200	0.050*
C17	0.8938 (2)	0.2278 (2)	0.4183 (2)	0.0431 (5)
H17	0.9290	0.1436	0.4348	0.052*
C18	0.7684 (2)	0.2839 (2)	0.4623 (2)	0.0383 (5)
H18	0.7217	0.2349	0.5090	0.046*
C19	0.7815 (2)	0.47471 (19)	0.37489 (17)	0.0281 (4)
O5W	0.9995 (2)	0.9273 (2)	0.12804 (18)	0.0708 (5)
H5A	0.9520	0.8694	0.0539	0.106*
H5B	1.0469	1.0073	0.1289	0.106*
O6W	0.7867 (3)	0.0448 (3)	0.6265 (2)	0.0998 (8)
H6A	0.8658	0.0844	0.6892	0.150*
H6B	0.7305	−0.0255	0.6340	0.150*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0264 (2)	0.0268 (2)	0.0277 (2)	0.00381 (15)	0.01252 (15)	0.01015 (15)
S1	0.0332 (3)	0.0287 (2)	0.0334 (3)	−0.00064 (18)	0.0137 (2)	0.00874 (19)
O1	0.0354 (7)	0.0363 (7)	0.0301 (7)	0.0033 (5)	0.0105 (6)	0.0061 (5)
O2	0.0369 (8)	0.0589 (10)	0.0456 (9)	−0.0125 (7)	0.0110 (7)	0.0018 (7)
O3	0.0627 (10)	0.0451 (9)	0.0749 (11)	0.0172 (7)	0.0383 (9)	0.0358 (8)
O4	0.0518 (10)	0.1099 (15)	0.1036 (15)	0.0435 (10)	0.0535 (10)	0.0824 (13)
N1	0.0336 (8)	0.0312 (8)	0.0380 (9)	0.0052 (6)	0.0160 (7)	0.0138 (7)
N2	0.0286 (8)	0.0310 (8)	0.0330 (8)	0.0038 (6)	0.0120 (6)	0.0128 (6)

C1	0.0334 (10)	0.0589 (13)	0.0369 (11)	0.0142 (9)	0.0180 (8)	0.0259 (10)
C2	0.0282 (9)	0.0396 (10)	0.0251 (9)	0.0035 (8)	0.0082 (7)	0.0095 (8)
C3	0.0305 (9)	0.0329 (9)	0.0269 (9)	0.0003 (7)	0.0098 (7)	0.0046 (7)
C4	0.0430 (11)	0.0329 (10)	0.0435 (11)	0.0057 (8)	0.0177 (9)	0.0100 (9)
C5	0.0461 (12)	0.0413 (11)	0.0546 (13)	0.0159 (9)	0.0245 (10)	0.0148 (10)
C6	0.0395 (11)	0.0510 (12)	0.0467 (12)	0.0136 (9)	0.0250 (10)	0.0171 (10)
C7	0.0304 (9)	0.0446 (11)	0.0308 (10)	0.0083 (8)	0.0123 (8)	0.0137 (8)
C8	0.0267 (9)	0.0315 (9)	0.0269 (9)	−0.0024 (7)	0.0092 (7)	0.0074 (7)
C9	0.0479 (12)	0.0411 (11)	0.0634 (14)	0.0145 (9)	0.0302 (11)	0.0265 (10)
C10	0.0555 (14)	0.0404 (11)	0.0653 (15)	0.0115 (10)	0.0261 (12)	0.0304 (11)
C11	0.0519 (13)	0.0416 (11)	0.0509 (12)	−0.0002 (10)	0.0215 (10)	0.0240 (10)
C12	0.0357 (10)	0.0366 (10)	0.0346 (10)	−0.0039 (8)	0.0121 (8)	0.0120 (8)
C13	0.0407 (11)	0.0512 (12)	0.0470 (12)	−0.0032 (9)	0.0247 (10)	0.0180 (10)
C14	0.0362 (11)	0.0507 (12)	0.0494 (12)	0.0034 (9)	0.0246 (10)	0.0132 (10)
C15	0.0284 (9)	0.0385 (10)	0.0359 (10)	0.0016 (8)	0.0132 (8)	0.0062 (8)
C16	0.0315 (10)	0.0453 (12)	0.0501 (12)	0.0103 (9)	0.0180 (9)	0.0089 (10)
C17	0.0405 (11)	0.0395 (11)	0.0550 (13)	0.0138 (9)	0.0162 (10)	0.0182 (10)
C18	0.0366 (10)	0.0396 (11)	0.0482 (12)	0.0095 (8)	0.0182 (9)	0.0211 (9)
C19	0.0248 (9)	0.0314 (9)	0.0261 (9)	−0.0012 (7)	0.0075 (7)	0.0055 (7)
O5W	0.0725 (12)	0.0829 (13)	0.0555 (10)	−0.0218 (10)	0.0079 (9)	0.0305 (10)
O6W	0.1002 (17)	0.1057 (18)	0.0955 (16)	−0.0265 (14)	−0.0050 (13)	0.0642 (14)

Geometric parameters (Å, º)

Mn1—O1^{i}	2.1820 (12)	C7—C1^{ii}	1.499 (3)
Mn1—O1	2.1820 (12)	C8—C12	1.412 (3)
Mn1—N2	2.2758 (15)	C8—C19	1.438 (3)
Mn1—N2^{i}	2.2758 (15)	C9—C10	1.390 (3)
Mn1—N1^{i}	2.2834 (15)	C9—H9	0.9300
Mn1—N1	2.2834 (15)	C10—C11	1.353 (3)
S1—O2	1.4368 (15)	C10—H10	0.9300
S1—O3	1.4499 (16)	C11—C12	1.403 (3)
S1—O1	1.4539 (13)	C11—H11	0.9300
S1—C3	1.8042 (18)	C12—C13	1.429 (3)
O4—C1	1.210 (2)	C13—C14	1.343 (3)
N1—C9	1.326 (3)	C13—H13	0.9300
N1—C8	1.362 (2)	C14—C15	1.432 (3)
N2—C18	1.331 (2)	C14—H14	0.9300
N2—C19	1.361 (2)	C15—C16	1.402 (3)
C1—C2	1.485 (3)	C15—C19	1.406 (3)
C1—C7^{ii}	1.499 (3)	C16—C17	1.362 (3)
C2—C7	1.401 (2)	C16—H16	0.9300
C2—C3	1.412 (3)	C17—C18	1.390 (3)
C3—C4	1.383 (3)	C17—H17	0.9300
C4—C5	1.388 (3)	C18—H18	0.9300
C4—H4	0.9300	O5W—H5A	0.8502
C5—C6	1.366 (3)	O5W—H5B	0.8502
C5—H5	0.9300	O6W—H6A	0.8503

C6—C7	1.393 (3)	O6W—H6B	0.8500
C6—H6	0.9300		

O1^{i}—Mn1—O1	180.0	C5—C6—H6	119.9
O1^{i}—Mn1—N2	88.86 (5)	C7—C6—H6	119.9
O1—Mn1—N2	91.14 (5)	C6—C7—C2	120.69 (18)
O1^{i}—Mn1—N2^{i}	91.14 (5)	C6—C7—C1^{ii}	116.82 (17)
O1—Mn1—N2^{i}	88.86 (5)	C2—C7—C1^{ii}	122.43 (17)
N2—Mn1—N2^{i}	180.00 (7)	N1—C8—C12	122.37 (17)
O1^{i}—Mn1—N1^{i}	87.76 (5)	N1—C8—C19	118.36 (15)
O1—Mn1—N1^{i}	92.24 (5)	C12—C8—C19	119.27 (16)
N2—Mn1—N1^{i}	106.48 (5)	N1—C9—C10	124.2 (2)
N2^{i}—Mn1—N1^{i}	73.52 (5)	N1—C9—H9	117.9
O1^{i}—Mn1—N1	92.24 (5)	C10—C9—H9	117.9
O1—Mn1—N1	87.76 (5)	C11—C10—C9	119.0 (2)
N2—Mn1—N1	73.52 (5)	C11—C10—H10	120.5
N2^{i}—Mn1—N1	106.48 (5)	C9—C10—H10	120.5
N1^{i}—Mn1—N1	179.999 (2)	C10—C11—C12	119.77 (19)
O2—S1—O3	112.74 (10)	C10—C11—H11	120.1
O2—S1—O1	112.54 (9)	C12—C11—H11	120.1
O3—S1—O1	111.06 (9)	C11—C12—C8	117.56 (18)
O2—S1—C3	108.28 (9)	C11—C12—C13	122.97 (18)
O3—S1—C3	104.66 (9)	C8—C12—C13	119.46 (19)
O1—S1—C3	107.04 (8)	C14—C13—C12	121.33 (19)
S1—O1—Mn1	135.36 (8)	C14—C13—H13	119.3
C9—N1—C8	117.14 (16)	C12—C13—H13	119.3
C9—N1—Mn1	128.11 (13)	C13—C14—C15	120.80 (19)
C8—N1—Mn1	114.68 (12)	C13—C14—H14	119.6
C18—N2—C19	117.16 (16)	C15—C14—H14	119.6
C18—N2—Mn1	127.72 (12)	C16—C15—C19	117.87 (18)
C19—N2—Mn1	115.07 (12)	C16—C15—C14	122.40 (18)
O4—C1—C2	121.34 (19)	C19—C15—C14	119.73 (19)
O4—C1—C7^{ii}	119.27 (19)	C17—C16—C15	119.72 (18)
C2—C1—C7^{ii}	119.26 (16)	C17—C16—H16	120.1
C7—C2—C3	118.43 (17)	C15—C16—H16	120.1
C7—C2—C1	117.76 (17)	C16—C17—C18	118.60 (19)
C3—C2—C1	123.77 (16)	C16—C17—H17	120.7
C4—C3—C2	119.42 (17)	C18—C17—H17	120.7
C4—C3—S1	114.57 (15)	N2—C18—C17	124.23 (18)
C2—C3—S1	125.96 (14)	N2—C18—H18	117.9
C3—C4—C5	121.22 (19)	C17—C18—H18	117.9
C3—C4—H4	119.4	N2—C19—C15	122.41 (17)
C5—C4—H4	119.4	N2—C19—C8	118.19 (15)
C6—C5—C4	119.86 (19)	C15—C19—C8	119.40 (16)
C6—C5—H5	120.1	H5A—O5W—H5B	117.0
C4—C5—H5	120.1	H6A—O6W—H6B	117.0
C5—C6—C7	120.25 (18)		

O2—S1—O1—Mn1	157.33 (11)	C4—C5—C6—C7	−2.3 (3)
O3—S1—O1—Mn1	29.85 (14)	C5—C6—C7—C2	−0.9 (3)
C3—S1—O1—Mn1	−83.83 (12)	C5—C6—C7—C1^{ii}	176.6 (2)
O1^{i}—Mn1—O1—S1	163 (13)	C3—C2—C7—C6	3.5 (3)
N2—Mn1—O1—S1	33.35 (11)	C1—C2—C7—C6	−174.07 (19)
N2^{i}—Mn1—O1—S1	−146.65 (11)	C3—C2—C7—C1^{ii}	−173.82 (17)
N1^{i}—Mn1—O1—S1	−73.20 (11)	C1—C2—C7—C1^{ii}	8.6 (3)
N1—Mn1—O1—S1	106.81 (11)	C9—N1—C8—C12	0.0 (3)
O1^{i}—Mn1—N1—C9	−91.40 (18)	Mn1—N1—C8—C12	177.27 (14)
O1—Mn1—N1—C9	88.60 (18)	C9—N1—C8—C19	179.47 (18)
N2—Mn1—N1—C9	−179.54 (19)	Mn1—N1—C8—C19	−3.2 (2)
N2^{i}—Mn1—N1—C9	0.45 (19)	C8—N1—C9—C10	0.0 (3)
N1^{i}—Mn1—N1—C9	−37 (8)	Mn1—N1—C9—C10	−176.90 (18)
O1^{i}—Mn1—N1—C8	91.68 (13)	N1—C9—C10—C11	−0.1 (4)
O1—Mn1—N1—C8	−88.32 (13)	C9—C10—C11—C12	0.4 (4)
N2—Mn1—N1—C8	3.53 (12)	C10—C11—C12—C8	−0.4 (3)
N2^{i}—Mn1—N1—C8	−176.47 (12)	C10—C11—C12—C13	179.7 (2)
N1^{i}—Mn1—N1—C8	146 (8)	N1—C8—C12—C11	0.2 (3)
O1^{i}—Mn1—N2—C18	86.18 (16)	C19—C8—C12—C11	−179.24 (17)
O1—Mn1—N2—C18	−93.82 (16)	N1—C8—C12—C13	−179.86 (18)
N2^{i}—Mn1—N2—C18	36 (17)	C19—C8—C12—C13	0.7 (3)
N1^{i}—Mn1—N2—C18	−1.15 (17)	C11—C12—C13—C14	179.3 (2)
N1—Mn1—N2—C18	178.85 (17)	C8—C12—C13—C14	−0.6 (3)
O1^{i}—Mn1—N2—C19	−96.18 (12)	C12—C13—C14—C15	−0.2 (3)
O1—Mn1—N2—C19	83.82 (12)	C13—C14—C15—C16	−179.2 (2)
N2^{i}—Mn1—N2—C19	−146 (17)	C13—C14—C15—C19	0.8 (3)
N1^{i}—Mn1—N2—C19	176.49 (12)	C19—C15—C16—C17	−0.1 (3)
N1—Mn1—N2—C19	−3.51 (12)	C14—C15—C16—C17	179.9 (2)
O4—C1—C2—C7	167.4 (2)	C15—C16—C17—C18	0.1 (3)
C7^{ii}—C1—C2—C7	−8.3 (3)	C19—N2—C18—C17	−0.8 (3)
O4—C1—C2—C3	−10.0 (3)	Mn1—N2—C18—C17	176.82 (16)
C7^{ii}—C1—C2—C3	174.24 (17)	C16—C17—C18—N2	0.4 (3)
C7—C2—C3—C4	−3.0 (3)	C18—N2—C19—C15	0.7 (3)
C1—C2—C3—C4	174.46 (18)	Mn1—N2—C19—C15	−177.20 (13)
C7—C2—C3—S1	174.29 (14)	C18—N2—C19—C8	−178.94 (17)
C1—C2—C3—S1	−8.3 (3)	Mn1—N2—C19—C8	3.2 (2)
O2—S1—C3—C4	−108.81 (16)	C16—C15—C19—N2	−0.3 (3)
O3—S1—C3—C4	11.67 (17)	C14—C15—C19—N2	179.75 (18)
O1—S1—C3—C4	129.62 (14)	C16—C15—C19—C8	179.36 (17)
O2—S1—C3—C2	73.81 (18)	C14—C15—C19—C8	−0.6 (3)
O3—S1—C3—C2	−165.72 (16)	N1—C8—C19—N2	0.1 (2)
O1—S1—C3—C2	−47.77 (18)	C12—C8—C19—N2	179.57 (16)
C2—C3—C4—C5	−0.2 (3)	N1—C8—C19—C15	−179.58 (16)
S1—C3—C4—C5	−177.72 (16)	C12—C8—C19—C15	−0.1 (3)
C3—C4—C5—C6	2.8 (3)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5*W*—H5*A*···O2^{ii}	0.85	2.03	2.826 (2)	156
O5*W*—H5*B*···O2^{iii}	0.85	2.10	2.948 (2)	172
O6*W*—H6*A*···O5*W*^{iv}	0.85	2.13	2.868 (3)	145
O6*W*—H6*B*···O3^{v}	0.85	2.12	2.922 (3)	157

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