

Tetraaqua(2,2'-bipyridine- κ^2N,N')-manganese(II) di- μ -aqua-bis[aqua(2,2'-bipyridine- κ^2N,N')(5-sulfonatoisophthalato- κO)manganate(II)] tetrahydrate

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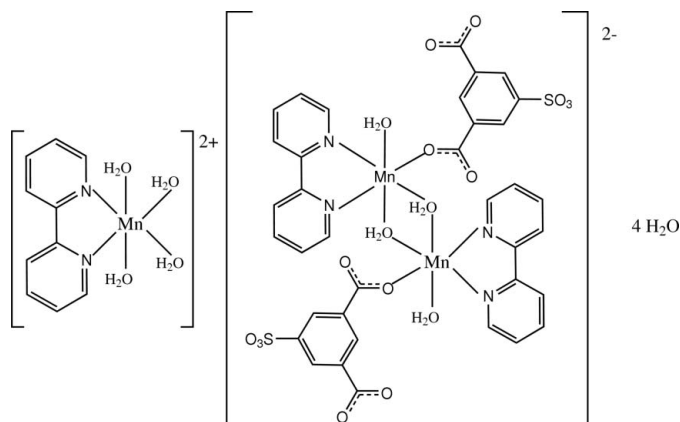
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(C-C) = 0.005$ Å; R factor = 0.048; wR factor = 0.123; data-to-parameter ratio = 16.5.

The crystal structure of the title salt, $[Mn(C_{10}H_8N_2)(H_2O)_4][Mn_2(C_8H_3O_7S)_2(C_{10}H_8N_2)_2(H_2O)_4] \cdot 4H_2O$, consists of mononuclear manganese(II) cations, dinuclear manganate(II) dianions and uncoordinated water molecules. The dianion is located about an inversion center; the Mn^{II} atom is coordinated by a 2,2'-bipyridine ligand, a sulfonatoisophthalate group, a water molecule along with two bridging water molecules in an octahedral geometry. The cation lies on a twofold rotation axis; the Mn^{II} atom is coordinated by four water molecules and a chelating 2,2'-bipyridine ligand in a distorted octahedral geometry. A partially overlapped arrangement between the bipyridine ligands and the aromatic ring of the sulfoisophthalate group of adjacent anions is observed; the distance (3.357 Å) indicates π - π stacking. Hydrogen bonds, with the water molecules serving as hydrogen-bond donors, lead to a three-dimensional network architecture.

Related literature

For general background, see: Deisenhofer & Michel (1989); Pan *et al.* (2006); Su & Xu (2004). For a related structure, see: Zhang *et al.* (2008). For the thickness of the aromatic ring, see: Cotton & Wilkinson (1972).



Experimental

Crystal data

$[Mn(C_{10}H_8N_2)(H_2O)_4][Mn_2(C_8H_3O_7S)_2(C_{10}H_8N_2)_2(H_2O)_4] \cdot 4H_2O$
 $M_r = 1335.89$
 Monoclinic, $C2/c$
 $a = 19.656$ (4) Å
 $b = 9.1286$ (17) Å
 $c = 32.035$ (6) Å

$\beta = 96.584$ (7)°
 $V = 5710.1$ (18) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.82$ mm⁻¹
 $T = 295$ (2) K
 0.40 × 0.36 × 0.20 mm

Data collection

Rigaku R-Axis RAPID IP diffractometer
 Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
 $T_{min} = 0.742$, $T_{max} = 0.850$

32384 measured reflections
 6179 independent reflections
 4071 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.071$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.123$
 $S = 1.09$
 6179 reflections

375 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.96$ e Å⁻³
 $\Delta\rho_{min} = -0.41$ e Å⁻³

Table 1

Selected bond lengths (Å).

Mn1—N1	2.253 (3)	Mn1—O2W	2.161 (2)
Mn1—N2	2.212 (3)	Mn2—N3	2.282 (3)
Mn1—O1	2.116 (2)	Mn2—O3W	2.145 (2)
Mn1—O1W	2.278 (2)	Mn2—O4W	2.1707 (19)
Mn1—O1W ⁱ	2.305 (2)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H1A \cdots O5W	0.85	1.87	2.701 (3)	164
O1W—H1B \cdots O2	0.93	1.62	2.548 (3)	173
O2W—H2A \cdots O3 ⁱⁱ	0.85	1.87	2.716 (3)	170
O2W—H2B \cdots O6 ⁱⁱⁱ	0.89	1.91	2.789 (3)	167
O3W—H3A \cdots O5 ^{iv}	0.90	1.85	2.746 (3)	176
O3W—H3B \cdots O4 ⁱⁱ	0.95	1.68	2.621 (3)	170
O4W—H4A \cdots O3 ^v	0.95	1.82	2.727 (3)	157
O4W—H4B \cdots O7 ^{iv}	0.89	1.90	2.780 (3)	168
O5W—H5A \cdots O7 ⁱⁱⁱ	0.95	1.83	2.770 (4)	170

metal-organic compounds

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O5W-H5B\cdots O6W^i$	0.95	2.04	2.749 (5)	131
$O6W-H6A\cdots O6^{vi}$	0.91	2.26	3.128 (5)	160
$O6W-H6B\cdots O3$	0.92	2.27	3.109 (5)	151

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2471).

References

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supporting information

Acta Cryst. (2008). E64, m1003–m1004 [doi:10.1107/S1600536808020540]

Tetraaqua(2,2'-bipyridine- κ^2N,N')manganese(II) di- μ -aqua-bis[aqua(2,2'-bipyridine- κ^2N,N')(5-sulfonatoisophthalato- κO)manganate(II)] tetrahydrate

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S1. Comment

As π - π stacking between aromatic rings plays an important role in electron transfer process in some biological system (Deisenhofer & Michel, 1989), π - π stacking has attracted our much attention in past years (Su & Xu, 2004; Pan *et al.*, 2006). In order to investigate the influence of substituents of the aromatic compounds on stacking between parallel aromatic rings, the title Mn^{II} compound incorporating sulfoisophthalate ligand has recently been prepared and its crystal structure is reported here.

The crystal structure of the title compound consists of dimeric Mn^{II} complex anions, monomeric Mn^{II} complex cations and lattice water molecules (Fig. 1).

The complex anion is located across on an inversion center, two independent parts are bridged by two water molecules with approximately identical Mn—O(bridge) bond distances (Table 1) and a normal Mn—O—Mnⁱ bond angle of 103.85 (8)° [symmetry code: (i) 1 - x, -y, 1 - z]. Each Mn^{II} ion is coordinated by one 2,2'-bipyridine (bipy) ligand, one sulfoisophthalate anion, two bridge water molecules and one terminal water molecule in a distorted octahedral geometry. The Mn—O(bridge) bond distances are significantly longer than Mn—O(terminal) bond distances. In the Mn₂O₂ core the Mn \cdots Mn and O \cdots O distances are 3.6071 (11) and 2.826 (4) Å, respectively. The benzene ring of sulfoisophthalate and bipy ring system coordinated to the same Mn^{II} ion are nearly co-planar, the dihedral angle being 2.62 (14)°.

The complex cation has twofold rotation symmetry, with the Mn2 and the mid-point of the C23—C23ⁱⁱ bond located on the twofold rotation axis [symmetry code: (ii) 1 - x, y, 3/2 - z]. The Mn2 ion is coordinated by four water molecules and chelated by one bipy in a distorted octahedral geometry.

Partially overlapped arrangement between nearly parallel [dihedral angle 3.49 (19)°] bipy and benzene ring of sulfoisophthalate of the adjacent complex anion is observed in the crystal structure (Fig. 2). The perpendicular distance of the centroid of the N2-pyridine ring on the C6ⁱⁱⁱ-benzene ring is 3.357 Å, and the perpendicular distance of the centroid of the C6ⁱⁱⁱ-benzene ring on the N2-pyridine ring is 3.425 Å, they are significantly shorter than the van der Waals thickness of the aromatic ring (Cotton & Wilkinson, 1972) and indicate the existence of π - π stacking involving sulfoisophthalate anion, similar to that found in a related Co^{II} complex with sulfoisophthalate ligand (Zhang *et al.*, 2008).

The extensive O—H \cdots O and C—H \cdots O hydrogen bonding network presents in the crystal structure (Table 2), which helps to stabilize the crystal structure.

S2. Experimental

The monosodium 5-sulfoisophthalate (0.27 g, 1 mmol), sodium carbonate (0.11 g, 1 mmol), 2,2'-bipyridine (0.16 g, 1 mmol), manganese chloride tetrahydrate (0.20 g, 1 mmol), water (8 ml) and ethanol (2 ml) were sealed in a 20-ml Teflon-lined, stainless-steel autoclave. The autoclave was heated to 398 K for 36 h and then cooled to room temperature over 24 h. The solution was filtered and the single crystals of the title compound were obtained from the filtrate after 10 d.

S3. Refinement

Water H atoms were located in a difference Fourier map and refined as riding in as-found relative positions with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. Aromatic H atoms were placed in calculated positions with $\text{C}-\text{H} = 0.93 \text{ \AA}$ and refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

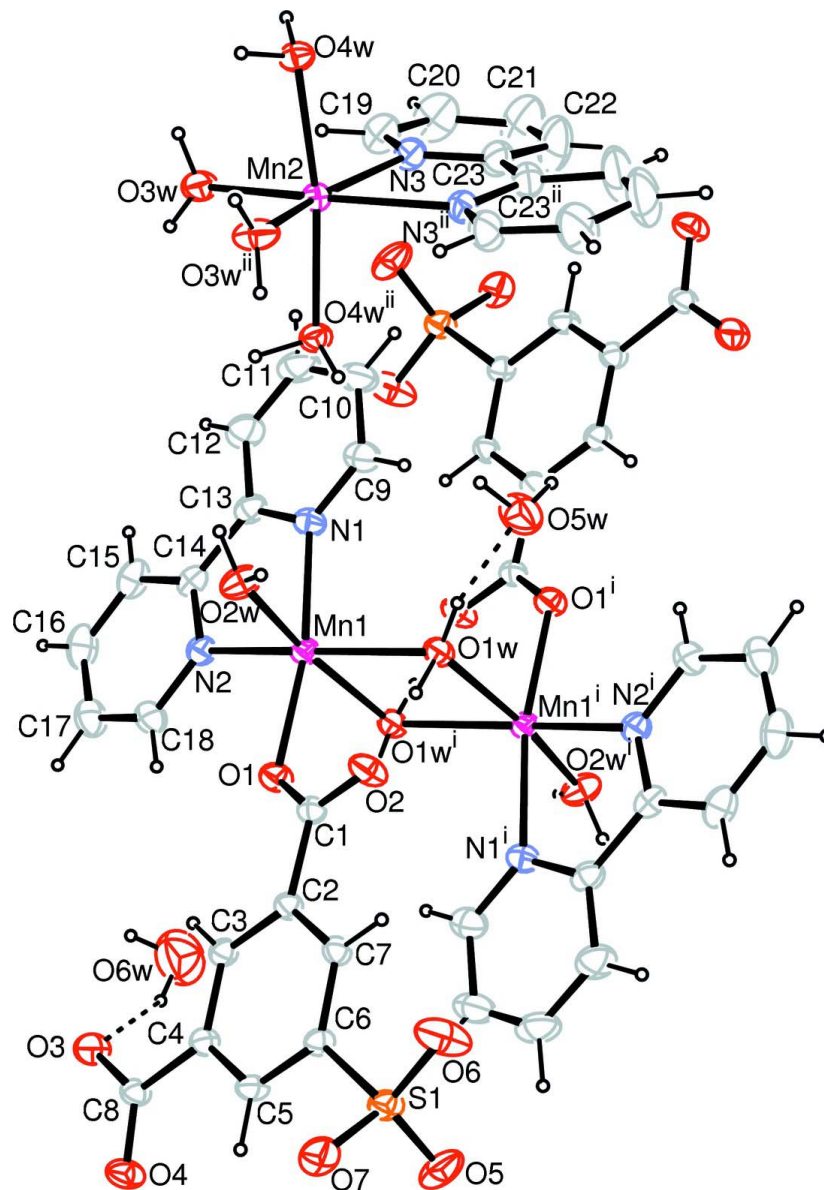


Figure 1

The molecular structure of the title compound with 30% probability displacement (arbitrary spheres for H atoms). Dashed lines indicate hydrogen bonding [symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, y, 3/2 - z$].

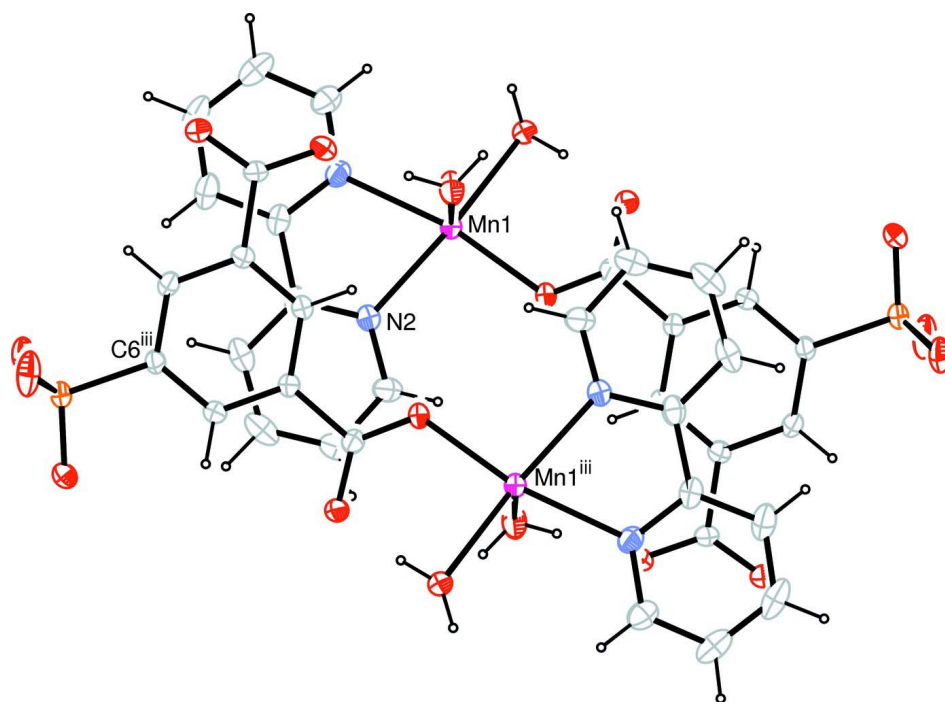
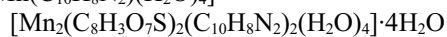


Figure 2

A diagram showing π - π stacking between aromatic rings [symmetry code: (iii) 1 - x, 1 - y, 1 - z].

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Crystal data



$M_r = 1335.89$

Monoclinic, C2/c

Hall symbol: -C 2yc

$a = 19.656$ (4) Å

$b = 9.1286$ (17) Å

$c = 32.035$ (6) Å

$\beta = 96.584$ (7)°

$V = 5710.1$ (18) Å³

$Z = 4$

$F(000) = 2748$

$D_x = 1.554$ Mg m⁻³

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

Cell parameters from 8728 reflections

$\theta = 2.2$ – 24.5 °

$\mu = 0.82$ mm⁻¹

$T = 295$ K

Plate, yellow

$0.40 \times 0.36 \times 0.20$ mm

Data collection

Rigaku R-AXIS RAPID IP

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 10.0 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.742$, $T_{\max} = 0.850$

32384 measured reflections

6179 independent reflections

4071 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.071$

$\theta_{\max} = 27.0$ °, $\theta_{\min} = 2.1$ °

$h = -24$ → 23

$k = -11$ → 11

$l = -40$ → 40

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.123$
 $S = 1.09$
 6179 reflections
 375 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
 $w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 1.8129P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.97 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.52324 (2)	0.17373 (5)	0.524402 (13)	0.03219 (14)
Mn2	0.5000	0.11071 (7)	0.7500	0.03035 (18)
S1	0.17116 (4)	0.28491 (9)	0.36332 (2)	0.0385 (2)
N1	0.60400 (14)	0.1056 (3)	0.57642 (7)	0.0367 (6)
N2	0.61544 (13)	0.3064 (3)	0.51746 (8)	0.0357 (6)
N3	0.56862 (14)	-0.0915 (3)	0.75678 (8)	0.0390 (6)
O1	0.46005 (11)	0.2725 (2)	0.47425 (6)	0.0380 (5)
O2	0.36256 (11)	0.1687 (2)	0.48870 (7)	0.0441 (6)
O3	0.45078 (12)	0.6278 (3)	0.35348 (7)	0.0494 (6)
O4	0.35555 (11)	0.6315 (3)	0.30833 (6)	0.0458 (6)
O5	0.17450 (13)	0.2000 (3)	0.32526 (8)	0.0640 (8)
O6	0.14849 (13)	0.1983 (4)	0.39683 (9)	0.0785 (10)
O7	0.13200 (11)	0.4188 (3)	0.35423 (7)	0.0495 (6)
O1W	0.44697 (10)	-0.0134 (2)	0.52604 (6)	0.0350 (5)
H1A	0.4411	-0.0471	0.5501	0.052*
H1B	0.4137	0.0501	0.5136	0.052*
O2W	0.47816 (11)	0.2970 (3)	0.57186 (7)	0.0479 (6)
H2A	0.5042	0.3135	0.5946	0.072*
H2B	0.4371	0.2837	0.5806	0.072*
O3W	0.58479 (12)	0.2600 (3)	0.75394 (6)	0.0511 (7)
H3A	0.6123	0.2751	0.7779	0.077*
H3B	0.6103	0.3029	0.7338	0.077*
O4W	0.49868 (11)	0.1280 (2)	0.81748 (6)	0.0368 (5)
H4A	0.4857	0.2251	0.8238	0.055*
H4B	0.5394	0.1176	0.8327	0.055*

O5W	0.40641 (16)	-0.1425 (3)	0.59492 (8)	0.0703 (8)
H5A	0.3967	-0.0709	0.6149	0.105*
H5B	0.4381	-0.2183	0.6027	0.105*
O6W	0.5729 (2)	0.4097 (4)	0.36611 (13)	0.1194 (13)
H6A	0.6043	0.4786	0.3758	0.179*
H6B	0.5384	0.4658	0.3524	0.179*
C1	0.39638 (16)	0.2497 (3)	0.46703 (8)	0.0308 (7)
C2	0.35851 (15)	0.3205 (3)	0.42861 (8)	0.0291 (6)
C3	0.39081 (16)	0.4194 (3)	0.40419 (8)	0.0306 (7)
H3	0.4362	0.4450	0.4122	0.037*
C4	0.35618 (15)	0.4800 (3)	0.36818 (8)	0.0311 (7)
C5	0.28809 (16)	0.4397 (3)	0.35622 (9)	0.0337 (7)
H5	0.2643	0.4794	0.3321	0.040*
C6	0.25587 (15)	0.3399 (3)	0.38050 (8)	0.0291 (6)
C7	0.29045 (15)	0.2815 (3)	0.41659 (9)	0.0311 (7)
H7	0.2684	0.2164	0.4329	0.037*
C8	0.39040 (17)	0.5872 (3)	0.34085 (9)	0.0340 (7)
C9	0.59329 (19)	0.0111 (4)	0.60721 (10)	0.0471 (9)
H9	0.5513	-0.0367	0.6058	0.056*
C10	0.6419 (2)	-0.0177 (4)	0.64070 (11)	0.0588 (11)
H10	0.6327	-0.0828	0.6617	0.071*
C11	0.7038 (2)	0.0510 (5)	0.64246 (12)	0.0635 (12)
H11	0.7378	0.0317	0.6644	0.076*
C12	0.7155 (2)	0.1487 (4)	0.61154 (11)	0.0555 (10)
H12	0.7574	0.1966	0.6126	0.067*
C13	0.66478 (17)	0.1759 (4)	0.57867 (9)	0.0383 (8)
C14	0.67202 (16)	0.2851 (3)	0.54492 (9)	0.0361 (7)
C15	0.73194 (18)	0.3614 (4)	0.54134 (12)	0.0479 (9)
H15	0.7706	0.3448	0.5603	0.057*
C16	0.7340 (2)	0.4622 (4)	0.50942 (13)	0.0569 (10)
H16	0.7736	0.5155	0.5070	0.068*
C17	0.6765 (2)	0.4829 (4)	0.48121 (12)	0.0519 (9)
H17	0.6768	0.5489	0.4591	0.062*
C18	0.61831 (19)	0.4036 (4)	0.48648 (10)	0.0453 (8)
H18	0.5793	0.4185	0.4676	0.054*
C19	0.6369 (2)	-0.0855 (4)	0.76152 (11)	0.0535 (10)
H19	0.6576	0.0059	0.7651	0.064*
C20	0.6783 (2)	-0.2072 (5)	0.76141 (15)	0.0759 (13)
H20	0.7258	-0.1990	0.7653	0.091*
C21	0.6470 (3)	-0.3405 (5)	0.75534 (18)	0.0976 (18)
H21	0.6730	-0.4251	0.7542	0.117*
C22	0.5767 (3)	-0.3485 (5)	0.75088 (16)	0.0856 (15)
H22	0.5551	-0.4390	0.7471	0.103*
C23	0.53805 (18)	-0.2222 (4)	0.75198 (11)	0.0481 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0267 (3)	0.0370 (3)	0.0316 (2)	−0.0038 (2)	−0.00182 (19)	0.00509 (19)
Mn2	0.0315 (4)	0.0302 (3)	0.0292 (3)	0.000	0.0031 (3)	0.000
S1	0.0252 (5)	0.0501 (5)	0.0383 (4)	−0.0054 (4)	−0.0040 (3)	0.0078 (4)
N1	0.0360 (17)	0.0400 (15)	0.0335 (13)	0.0056 (13)	0.0015 (12)	0.0044 (11)
N2	0.0313 (16)	0.0383 (15)	0.0367 (14)	−0.0040 (12)	0.0003 (12)	0.0006 (11)
N3	0.0380 (18)	0.0372 (16)	0.0403 (14)	0.0053 (13)	−0.0016 (12)	−0.0037 (12)
O1	0.0245 (13)	0.0469 (13)	0.0404 (12)	−0.0055 (10)	−0.0051 (10)	0.0116 (10)
O2	0.0263 (13)	0.0559 (14)	0.0490 (13)	−0.0031 (11)	0.0002 (10)	0.0247 (11)
O3	0.0418 (15)	0.0621 (15)	0.0428 (12)	−0.0237 (12)	−0.0021 (11)	0.0143 (11)
O4	0.0379 (14)	0.0610 (15)	0.0378 (12)	−0.0096 (11)	0.0011 (10)	0.0182 (11)
O5	0.0496 (17)	0.0700 (18)	0.0650 (16)	0.0079 (14)	−0.0254 (13)	−0.0247 (14)
O6	0.0302 (15)	0.128 (3)	0.0738 (18)	−0.0267 (16)	−0.0079 (13)	0.0576 (18)
O7	0.0284 (14)	0.0553 (15)	0.0616 (15)	0.0062 (11)	−0.0093 (11)	−0.0033 (12)
O1W	0.0324 (13)	0.0365 (12)	0.0355 (11)	−0.0016 (10)	0.0011 (9)	0.0079 (9)
O2W	0.0325 (14)	0.0698 (17)	0.0408 (12)	−0.0003 (12)	0.0010 (10)	−0.0106 (11)
O3W	0.0553 (17)	0.0643 (16)	0.0326 (11)	−0.0299 (13)	0.0005 (11)	0.0056 (11)
O4W	0.0344 (13)	0.0441 (13)	0.0310 (10)	0.0056 (10)	−0.0006 (9)	−0.0009 (9)
O5W	0.104 (2)	0.0568 (16)	0.0541 (15)	0.0119 (16)	0.0275 (16)	0.0038 (12)
O6W	0.113 (3)	0.105 (3)	0.139 (3)	−0.016 (2)	0.010 (2)	0.022 (2)
C1	0.0299 (19)	0.0316 (16)	0.0299 (15)	0.0009 (14)	0.0000 (13)	0.0020 (12)
C2	0.0247 (17)	0.0316 (16)	0.0306 (14)	−0.0001 (13)	0.0008 (12)	0.0031 (12)
C3	0.0256 (17)	0.0344 (16)	0.0312 (15)	−0.0035 (13)	0.0001 (12)	0.0011 (12)
C4	0.0285 (18)	0.0361 (17)	0.0291 (15)	−0.0032 (13)	0.0044 (13)	0.0024 (12)
C5	0.0297 (19)	0.0428 (18)	0.0272 (14)	0.0005 (14)	−0.0023 (13)	0.0056 (13)
C6	0.0210 (16)	0.0363 (16)	0.0293 (14)	−0.0010 (13)	0.0007 (12)	0.0011 (12)
C7	0.0285 (18)	0.0319 (16)	0.0329 (15)	−0.0038 (13)	0.0029 (13)	0.0052 (12)
C8	0.035 (2)	0.0394 (18)	0.0280 (15)	−0.0066 (15)	0.0036 (14)	0.0077 (13)
C9	0.054 (2)	0.051 (2)	0.0368 (18)	0.0071 (18)	0.0062 (16)	0.0033 (15)
C10	0.083 (3)	0.055 (2)	0.0367 (19)	0.023 (2)	−0.001 (2)	0.0066 (16)
C11	0.069 (3)	0.067 (3)	0.048 (2)	0.025 (2)	−0.021 (2)	−0.003 (2)
C12	0.044 (2)	0.061 (2)	0.057 (2)	0.0091 (19)	−0.0145 (18)	−0.0003 (19)
C13	0.034 (2)	0.0420 (18)	0.0368 (16)	0.0072 (15)	−0.0032 (14)	−0.0067 (14)
C14	0.0298 (19)	0.0402 (18)	0.0376 (16)	0.0011 (14)	0.0015 (14)	−0.0100 (13)
C15	0.029 (2)	0.049 (2)	0.065 (2)	−0.0034 (16)	0.0048 (17)	−0.0138 (18)
C16	0.044 (3)	0.047 (2)	0.083 (3)	−0.0121 (18)	0.023 (2)	−0.011 (2)
C17	0.055 (3)	0.046 (2)	0.058 (2)	−0.0078 (18)	0.019 (2)	0.0038 (17)
C18	0.049 (2)	0.0446 (19)	0.0428 (18)	−0.0084 (17)	0.0074 (16)	0.0079 (15)
C19	0.045 (2)	0.051 (2)	0.063 (2)	0.0116 (19)	−0.0021 (18)	−0.0091 (18)
C20	0.049 (3)	0.079 (3)	0.097 (3)	0.024 (2)	−0.002 (2)	−0.019 (3)
C21	0.083 (4)	0.060 (3)	0.143 (5)	0.035 (3)	−0.016 (3)	−0.030 (3)
C22	0.085 (4)	0.038 (2)	0.129 (4)	0.013 (2)	−0.010 (3)	−0.017 (2)
C23	0.055 (2)	0.0366 (19)	0.050 (2)	0.0049 (17)	−0.0065 (19)	−0.0032 (15)

Geometric parameters (Å, °)

Mn1—N1	2.253 (3)	O6W—H6B	0.9184
Mn1—N2	2.212 (3)	C1—C2	1.509 (4)
Mn1—O1	2.116 (2)	C2—C3	1.394 (4)
Mn1—O1W	2.278 (2)	C2—C7	1.395 (4)
Mn1—O1W ⁱ	2.305 (2)	C3—C4	1.386 (4)
Mn1—O2W	2.161 (2)	C3—H3	0.9300
Mn2—N3 ⁱⁱ	2.282 (3)	C4—C5	1.398 (4)
Mn2—N3	2.282 (3)	C4—C8	1.521 (4)
Mn2—O3W	2.145 (2)	C5—C6	1.396 (4)
Mn2—O3W ⁱⁱ	2.145 (2)	C5—H5	0.9300
Mn2—O4W ⁱⁱ	2.1707 (19)	C6—C7	1.379 (4)
Mn2—O4W	2.1707 (19)	C7—H7	0.9300
S1—O6	1.444 (2)	C9—C10	1.378 (5)
S1—O5	1.452 (3)	C9—H9	0.9300
S1—O7	1.456 (2)	C10—C11	1.364 (6)
S1—C6	1.765 (3)	C10—H10	0.9300
N1—C9	1.345 (4)	C11—C12	1.372 (5)
N1—C13	1.351 (4)	C11—H11	0.9300
N2—C18	1.337 (4)	C12—C13	1.387 (5)
N2—C14	1.351 (4)	C12—H12	0.9300
N3—C19	1.334 (4)	C13—C14	1.490 (4)
N3—C23	1.337 (4)	C14—C15	1.384 (4)
O1—C1	1.263 (3)	C15—C16	1.380 (5)
O2—C1	1.255 (3)	C15—H15	0.9300
O3—C8	1.265 (4)	C16—C17	1.377 (5)
O4—C8	1.247 (3)	C16—H16	0.9300
O1W—Mn1 ⁱ	2.305 (2)	C17—C18	1.380 (5)
O1W—H1A	0.8508	C17—H17	0.9300
O1W—H1B	0.9294	C18—H18	0.9300
O2W—H2A	0.8554	C19—C20	1.378 (5)
O2W—H2B	0.8930	C19—H19	0.9300
O3W—H3A	0.8964	C20—C21	1.368 (6)
O3W—H3B	0.9466	C20—H20	0.9300
O4W—H4A	0.9507	C21—C22	1.375 (7)
O4W—H4B	0.8932	C21—H21	0.9300
O5W—H5A	0.9496	C22—C23	1.383 (5)
O5W—H5B	0.9445	C22—H22	0.9300
O6W—H6A	0.9118	C23—C23 ⁱⁱ	1.486 (7)
O1—Mn1—O2W	93.44 (9)	C3—C2—C7	119.6 (3)
O1—Mn1—N2	96.13 (9)	C3—C2—C1	121.4 (3)
O2W—Mn1—N2	101.09 (9)	C7—C2—C1	118.9 (2)
O1—Mn1—N1	168.94 (9)	C4—C3—C2	120.9 (3)
O2W—Mn1—N1	86.24 (9)	C4—C3—H3	119.5
N2—Mn1—N1	73.13 (9)	C2—C3—H3	119.5
O1—Mn1—O1W	90.36 (8)	C3—C4—C5	119.1 (3)

O2W—Mn1—O1W	92.89 (8)	C3—C4—C8	121.9 (3)
N2—Mn1—O1W	164.17 (8)	C5—C4—C8	119.0 (3)
N1—Mn1—O1W	100.70 (9)	C6—C5—C4	120.0 (3)
O1—Mn1—O1W ⁱ	84.97 (8)	C6—C5—H5	120.0
O2W—Mn1—O1W ⁱ	168.90 (8)	C4—C5—H5	120.0
N2—Mn1—O1W ⁱ	90.01 (8)	C7—C6—C5	120.5 (3)
N1—Mn1—O1W ⁱ	97.42 (8)	C7—C6—S1	120.6 (2)
O1W—Mn1—O1W ⁱ	76.15 (8)	C5—C6—S1	118.9 (2)
O3W—Mn2—O3W ⁱⁱ	101.14 (14)	C6—C7—C2	119.9 (3)
O3W—Mn2—O4W ⁱⁱ	85.10 (8)	C6—C7—H7	120.1
O3W ⁱⁱ —Mn2—O4W ⁱⁱ	89.62 (8)	C2—C7—H7	120.1
O3W—Mn2—O4W	89.62 (8)	O4—C8—O3	125.3 (3)
O3W ⁱⁱ —Mn2—O4W	85.10 (8)	O4—C8—C4	116.9 (3)
O4W ⁱⁱ —Mn2—O4W	171.68 (12)	O3—C8—C4	117.7 (3)
O3W—Mn2—N3 ⁱⁱ	165.06 (10)	N1—C9—C10	122.7 (4)
O3W ⁱⁱ —Mn2—N3 ⁱⁱ	93.52 (10)	N1—C9—H9	118.6
O4W ⁱⁱ —Mn2—N3 ⁱⁱ	92.20 (8)	C10—C9—H9	118.6
O4W—Mn2—N3 ⁱⁱ	94.54 (9)	C11—C10—C9	118.7 (4)
O3W—Mn2—N3	93.52 (10)	C11—C10—H10	120.7
O3W ⁱⁱ —Mn2—N3	165.06 (10)	C9—C10—H10	120.7
O4W ⁱⁱ —Mn2—N3	94.54 (8)	C10—C11—C12	119.5 (3)
O4W—Mn2—N3	92.20 (8)	C10—C11—H11	120.3
N3 ⁱⁱ —Mn2—N3	72.01 (14)	C12—C11—H11	120.3
O6—S1—O5	112.31 (19)	C11—C12—C13	119.9 (4)
O6—S1—O7	114.02 (17)	C11—C12—H12	120.0
O5—S1—O7	110.72 (14)	C13—C12—H12	120.0
O6—S1—C6	106.50 (14)	N1—C13—C12	120.6 (3)
O5—S1—C6	106.36 (14)	N1—C13—C14	115.9 (3)
O7—S1—C6	106.37 (14)	C12—C13—C14	123.4 (3)
C9—N1—C13	118.5 (3)	N2—C14—C15	121.2 (3)
C9—N1—Mn1	124.3 (2)	N2—C14—C13	115.4 (3)
C13—N1—Mn1	116.87 (19)	C15—C14—C13	123.4 (3)
C18—N2—C14	118.5 (3)	C16—C15—C14	119.6 (3)
C18—N2—Mn1	122.9 (2)	C16—C15—H15	120.2
C14—N2—Mn1	118.6 (2)	C14—C15—H15	120.2
C19—N3—C23	118.9 (3)	C17—C16—C15	119.1 (3)
C19—N3—Mn2	123.6 (2)	C17—C16—H16	120.4
C23—N3—Mn2	117.3 (2)	C15—C16—H16	120.4
C1—O1—Mn1	123.47 (18)	C16—C17—C18	118.5 (3)
Mn1—O1W—Mn1 ⁱ	103.85 (8)	C16—C17—H17	120.8
Mn1—O1W—H1A	116.7	C18—C17—H17	120.8
Mn1 ⁱ —O1W—H1A	118.6	N2—C18—C17	123.0 (3)
Mn1—O1W—H1B	87.4	N2—C18—H18	118.5
Mn1 ⁱ —O1W—H1B	108.5	C17—C18—H18	118.5
H1A—O1W—H1B	117.0	N3—C19—C20	123.6 (4)
Mn1—O2W—H2A	116.0	N3—C19—H19	118.2
Mn1—O2W—H2B	127.5	C20—C19—H19	118.2
H2A—O2W—H2B	103.2	C21—C20—C19	117.4 (4)

Mn2—O3W—H3A	122.4	C21—C20—H20	121.3
Mn2—O3W—H3B	133.7	C19—C20—H20	121.3
H3A—O3W—H3B	101.9	C20—C21—C22	119.6 (4)
Mn2—O4W—H4A	108.2	C20—C21—H21	120.2
Mn2—O4W—H4B	115.0	C22—C21—H21	120.2
H4A—O4W—H4B	103.2	C21—C22—C23	120.0 (4)
H5A—O5W—H5B	120.3	C21—C22—H22	120.0
H6A—O6W—H6B	102.3	C23—C22—H22	120.0
O2—C1—O1	124.9 (3)	N3—C23—C22	120.4 (4)
O2—C1—C2	117.4 (3)	N3—C23—C23 ⁱⁱ	116.40 (19)
O1—C1—C2	117.7 (2)	C22—C23—C23 ⁱⁱ	123.2 (3)

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x+1, y, -z+3/2$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1A \cdots O5W	0.85	1.87	2.701 (3)	164
O1W—H1B \cdots O2	0.93	1.62	2.548 (3)	173
O2W—H2A \cdots O3 ⁱⁱⁱ	0.85	1.87	2.716 (3)	170
O2W—H2B \cdots O6 ^{iv}	0.89	1.91	2.789 (3)	167
O3W—H3A \cdots O5 ^v	0.90	1.85	2.746 (3)	176
O3W—H3B \cdots O4 ⁱⁱⁱ	0.95	1.68	2.621 (3)	170
O4W—H4A \cdots O3 ^{vi}	0.95	1.82	2.727 (3)	157
O4W—H4B \cdots O7 ^v	0.89	1.90	2.780 (3)	168
O5W—H5A \cdots O7 ^{iv}	0.95	1.83	2.770 (4)	170
O5W—H5B \cdots O6W ⁱ	0.95	2.04	2.749 (5)	131
O6W—H6A \cdots O6 ^{vii}	0.91	2.26	3.128 (5)	160
O6W—H6B \cdots O3	0.92	2.27	3.109 (5)	151
C16—H16 \cdots O2 ^{vii}	0.93	2.36	3.281 (4)	169
C17—H17 \cdots O6 ^{vii}	0.93	2.43	3.337 (5)	166

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