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catena-Poly[[[aquamanganese(II)]-di-μ-sulfato-[aquamanganese(II)]-μ-*N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-hexane-1,6-diamine] hexahydrate]

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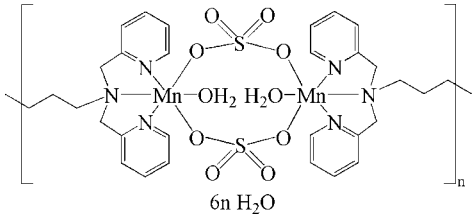
Key indicators: single-crystal X-ray study; T = 243 K; mean σ(C–C) = 0.008 Å; disorder in main residue; R factor = 0.079; wR factor = 0.145; data-to-parameter ratio = 15.4.

In the polymeric title compound, $\{[Mn_2(SO_4)_2(C_{30}H_{36}N_6)(H_2O)_2]\cdot 6H_2O\}_n$, the two Mn^{2+} ions are bridged by two sulfate anions to form dinuclear complexes, and these dinuclear species are linked by the hexadentate ligand *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)hexane-1,6-diamine (tphn), forming a one-dimensional chain structure running in the [101] direction. The repeat unit of the polymer, $Mn_2(SO_4)_2(H_2O)_2$(tphn), is disposed about a twofold axis passing through the centre of the dinuclear unit. The coordination geometry around the Mn centre is distorted octahedral. Two methylene groups are each disordered equally over two positions.

Related literature

For a related Mn-complex involving the tphn ligand, see: Hwang & Ha (2007).



Experimental

Crystal data

$[Mn_2(SO_4)_2(C_{30}H_{36}N_6)(H_2O)_2]\cdot 6H_2O$
M_r = 926.78
Monoclinic, $C2/c$
a = 20.910 (3) Å
b = 12.5820 (17) Å
c = 15.752 (2) Å
β = 99.888 (3)°
V = 4082.7 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.80 mm^{-1}
T = 243 (2) K
0.21 × 0.20 × 0.15 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.734, T_{max} = 0.888
11793 measured reflections
4165 independent reflections
3158 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.079
$wR(F^2)$ = 0.145
S = 1.22
4165 reflections
271 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.67 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O5*W*—H5*W*1···O7*W*^{i}	0.96	1.76	2.703 (5)	166
O5*W*—H5*W*2···O3^{ii}	0.94	1.85	2.727 (4)	153
O6*W*—H6*W*1···O2^{iii}	0.96	1.91	2.865 (5)	171
O6*W*—H6*W*2···O3^{iv}	0.86	2.26	2.899 (5)	130
O7*W*—H7*W*1···O8*W*	1.00	1.85	2.829 (6)	165
O7*W*—H7*W*2···O6*W*	0.93	2.53	3.044 (6)	115
O7*W*—H7*W*2···O6*W*^{v}	0.93	2.35	3.162 (6)	146
O8*W*—H8*W*1···O3^{vi}	1.03	1.91	2.860 (5)	152
O8*W*—H8*W*2···O1^{vii}	0.97	1.96	2.913 (5)	166
O8*W*—H8*W*2···O3^{vii}	0.97	2.59	3.317 (5)	132

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LN2016).

References

Bruker (2000). *SADABS* (Version 2.03), *SMART* (Version 5.618) and *SAINT* (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Hwang, I.-C. & Ha, K. (2007). *Acta Cryst.* E**63**, m2302.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

Acta Cryst. (2008). E**64**, m44 [**doi:10.1107/S1600536807063313**]

catena-Poly[[[aquamanganese(II)]-di-μ-sulfato-[aquamanganese(II)]-μ-*N*,*N*,*N*',*N*'-tetrakis(2-pyridylmethyl)hexane-1,6-diamine] hexahydrate]

A.-R. Song, I.-C. Hwang and K. Ha

Comment

The title compound consists of a Mn^{II} complex polymer with solvent H_2O molecules. In the polymer, two Mn^{2+} ions are first bridged by two SO_4 anion ligands to form dinuclear complexes (Fig. 1), and these dinuclear species are anew bridged by the hexadentate ligand *N*,*N*,*N*',*N*'-tetrakis(2-pyridylmethyl)hexane-1,6-diamine (tphn) to form a one-dimensional chain structure running in the [101] direction (Fig. 2). The Mn ion is six-coordinated in a distorted octahedral structure by three N atoms from the tphn ligand in the facial position, two O atoms from the two SO_4 ligands and an O atom from H_2O ligand. The constitutional repeating unit of the polymer, $Mn_2(SO_4)_2(H_2O)_2$(tphn), is disposed about a twofold axis passing through the centre of the dinuclear unit. As the twofold axis is parallel to the *b* axis, the unit lies in the (010) plane. The Mn—*N*(amine) bond length [2.360 (4) Å] is slightly longer than the Mn—N(pyridyl) bond lengths [2.300 (4) and 2.256 (4) Å], and the Mn—O(H_2O) bond length [2.206 (3) Å] is slightly longer than the Mn—O(SO_4) bond lengths [2.139 (3) and 2.143 (3) Å]. The geometry of the bridging SO_4 ligand is nearly tetrahedral with the O—S—O bond angles of 107.96 (18)–110.23 (18)°, and the S—O bond distances are almost equal [1.456 (3)–1.486 (3) Å]. The compound displays intra- and intermolecular O—H···O hydrogen bonds among the H_2O ligand, solvent molecules and SO_4 anions (Fig. 2, Table 1).

Experimental

To a solution of $MnSO_4.5H_2O$ (0.25 g, 1.04 mmol) in H_2O (10 ml) was added a solution of *N*,*N*,*N*',*N*'-tetrakis(2-pyridylmethyl)hexane-1,6-diamine (0.50 g, 1.04 mmol) in EtOH (10 ml) and stirred for 1 h at room temparature, and then filtered. The solvent was removed under vacuum, the residue washed with EtOH/acetone and dried, to give a pale yellow powder (0.41 g). Crystals suitable for X-ray analysis were obtained by slow evaporation from an aqueous solution. MS (FAB): m/*z* 632 (Mn(tphn)HSO_4^+); IR (KBr): 3405 cm^{-1} (broad).

Refinement

H atoms bonded to C atoms were positioned geometrically and allowed to ride on their respective carrier atoms [C—H = 0.94 Å (aromatic) or 0.98 Å (CH_2) and U_{iso}(H) = 1.2U_{eq}(C)]. The H atoms of the water ligand and solvent molecules were located from Fourier difference maps, but their positions were not refined and U_{iso}(H) was fixed at 0.08. The hexylene chain of the tphn ligand displayed relatively large displacement factors so that the chain appears to be partially disordered. Atoms C14 and C15 were modelled anisotropically as disordered over two sites, with a site occupancy factor of 0.5. The disorder of the hexylene chain and the relatively large displacement factors of the solvent water molecules result in the large value of the *R* factor.

Figures

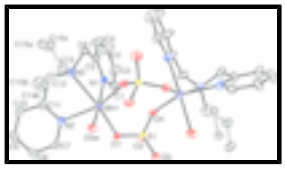

Fig. 1. The structure of the constitutional repeating unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level. H atoms and the solvent H_2O molecules have been omitted for clarity. The bonds of the disordered hexylene chains are shown with dashed lines.

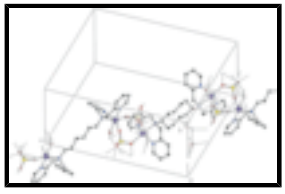

Fig. 2. View of the unit-cell contents and chain structure of the title compound. H atoms at C atoms have been omitted for clarity. Hydrogen-bond interactions are drawn with dashed lines.

catena-Poly[[[aquamanganese(II)]-di-μ-sulfato-[aquamanganese(II)]-μ- *N*,*N*,*N*',*N*'-tetrakis(2-pyridylmethyl)hexane-1,6-diamine] hexahydrate]

Crystal data

$[Mn_2(SO_4)_2(C_{30}H_{36}N_6)(H_2O)_2]\cdot 6H_2O$	F_{000} = 1936
M_r = 926.78	D_x = 1.508 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 2250 reflections
a = 20.910 (3) Å	θ = 2.2–24.3°
b = 12.5820 (17) Å	μ = 0.80 mm^{-1}
c = 15.752 (2) Å	*T* = 243 (2) K
β = 99.888 (3)°	Block, colorless
V = 4082.7 (10) Å^3	0.21 × 0.20 × 0.15 mm
Z = 4	

Data collection

Bruker SMART 1000 CCD diffractometer	4165 independent reflections
Radiation source: fine-focus sealed tube	3158 reflections with $I > 2\sigma s(I)$
Monochromator: graphite	R_{int} = 0.050
T = 243(2) K	θ_{max} = 26.4°
φ and ω scans	θ_{min} = 1.9°
Absorption correction: multi-scan (SADABS; Bruker, 2000)	*h* = −26→20
T_{min} = 0.734, T_{max} = 0.888	*k* = −15→15
11793 measured reflections	*l* = −18→19

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.079$	H-atom parameters constrained
$wR(F^2) = 0.145$	$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.22$	$(\Delta/\sigma)_{max} < 0.001$
4165 reflections	$\Delta\rho_{max} = 0.56$ e Å^{-3}
271 parameters	$\Delta\rho_{min} = -0.67$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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}	Occ. (<1)
Mn1	0.39214 (3)	0.24391 (5)	0.21343 (4)	0.0214 (2)	
N1	0.41270 (18)	0.4176 (3)	0.1814 (2)	0.0258 (9)	
N2	0.28972 (18)	0.2294 (3)	0.1407 (2)	0.0263 (9)	
N3	0.32712 (19)	0.3532 (3)	0.2857 (2)	0.0275 (9)	
C1	0.4377 (2)	0.4535 (4)	0.1136 (3)	0.0317 (12)	
H1	0.4496	0.4033	0.0749	0.038*	
C2	0.4467 (3)	0.5585 (4)	0.0978 (4)	0.0515 (16)	
H2	0.4644	0.5802	0.0497	0.062*	
C3	0.4295 (4)	0.6309 (4)	0.1537 (5)	0.082 (3)	
H3	0.4347	0.7040	0.1446	0.098*	
C4	0.4040 (4)	0.5958 (4)	0.2244 (4)	0.072 (2)	
H4	0.3923	0.6449	0.2641	0.086*	
C5	0.3960 (2)	0.4891 (4)	0.2360 (3)	0.0329 (12)	
C6	0.3681 (2)	0.4466 (4)	0.3113 (3)	0.0334 (12)	
H6A	0.4034	0.4269	0.3579	0.040*	
H6B	0.3421	0.5020	0.3330	0.040*	
C7	0.2691 (2)	0.1531 (4)	0.0829 (3)	0.0310 (12)	
H7	0.3000	0.1055	0.0678	0.037*	
C8	0.2056 (3)	0.1406 (4)	0.0446 (3)	0.0376 (13)	
H8	0.1934	0.0860	0.0043	0.045*	
C9	0.1602 (3)	0.2099 (4)	0.0664 (3)	0.0419 (14)	
H9	0.1162	0.2034	0.0411	0.050*	

C10	0.1798 (3)	0.2889 (4)	0.1256 (3)	0.0375 (13)	
H10	0.1496	0.3373	0.1411	0.045*	
C11	0.2447 (2)	0.2960 (4)	0.1620 (3)	0.0283 (11)	
C12	0.2683 (2)	0.3835 (4)	0.2250 (3)	0.0349 (12)	
H12A	0.2775	0.4469	0.1931	0.042*	
H12B	0.2338	0.4016	0.2576	0.042*	
C13	0.3108 (3)	0.2990 (4)	0.3633 (3)	0.0414 (13)	
H13A	0.2808	0.2414	0.3420	0.050*	0.50
H13B	0.3509	0.2651	0.3922	0.050*	0.50
H13C	0.3506	0.2664	0.3945	0.050*	0.50
H13D	0.2973	0.3533	0.4011	0.050*	0.50
C14A	0.2846 (6)	0.3505 (7)	0.4266 (6)	0.039 (3)	0.50
H14A	0.2435	0.3831	0.4000	0.047*	0.50
H14B	0.3141	0.4079	0.4500	0.047*	0.50
C15A	0.2719 (5)	0.2795 (8)	0.5022 (6)	0.033 (2)	0.50
H15A	0.2409	0.2235	0.4800	0.040*	0.50
H15B	0.3125	0.2453	0.5288	0.040*	0.50
C14B	0.2607 (5)	0.2176 (8)	0.3489 (6)	0.038 (3)	0.50
H14C	0.2708	0.1673	0.3056	0.046*	0.50
H14D	0.2189	0.2511	0.3260	0.046*	0.50
C15B	0.2545 (6)	0.1568 (7)	0.4313 (6)	0.042 (3)	0.50
H15C	0.2262	0.0953	0.4157	0.050*	0.50
H15D	0.2975	0.1299	0.4569	0.050*	0.50
S1	0.50266 (6)	0.19295 (9)	0.09722 (7)	0.0224 (3)	
O1	0.43452 (15)	0.1790 (2)	0.11052 (18)	0.0311 (8)	
O2	0.50341 (16)	0.2496 (2)	0.01682 (18)	0.0340 (8)	
O3	0.53263 (16)	0.0869 (2)	0.09408 (18)	0.0304 (8)	
O4	0.53755 (16)	0.2547 (2)	0.17063 (18)	0.0332 (8)	
O5W	0.37252 (16)	0.0856 (2)	0.26352 (19)	0.0335 (8)	
H5W1	0.3706	0.0210	0.2304	0.080*	
H5W2	0.3952	0.0746	0.3200	0.080*	
O6W	0.0222 (2)	0.3660 (3)	0.1421 (2)	0.0555 (11)	
H6W1	0.0116	0.3339	0.0860	0.080*	
H6W2	0.0000	0.4224	0.1267	0.080*	
O7W	0.11759 (19)	0.3934 (3)	0.3098 (3)	0.0633 (12)	
H7W1	0.1173	0.4122	0.3717	0.080*	
H7W2	0.0723	0.3913	0.2988	0.080*	
O8W	0.1124 (2)	0.4811 (3)	0.4739 (3)	0.0716 (14)	
H8W1	0.0798	0.4383	0.5024	0.080*	
H8W2	0.0897	0.5429	0.4459	0.080*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0244 (4)	0.0200 (4)	0.0213 (3)	0.0010 (3)	0.0082 (3)	0.0018 (3)
N1	0.026 (2)	0.025 (2)	0.029 (2)	0.0012 (17)	0.0125 (18)	−0.0024 (17)
N2	0.026 (2)	0.030 (2)	0.0251 (19)	0.0024 (17)	0.0088 (17)	0.0064 (17)
N3	0.031 (2)	0.032 (2)	0.0216 (19)	−0.0001 (18)	0.0123 (18)	0.0043 (17)

C1	0.040 (3)	0.029 (3)	0.031 (3)	0.003 (2)	0.019 (2)	0.003 (2)
C2	0.064 (4)	0.034 (3)	0.067 (4)	0.000 (3)	0.041 (3)	0.015 (3)
C3	0.130 (7)	0.022 (3)	0.117 (6)	−0.007 (4)	0.084 (6)	0.003 (3)
C4	0.113 (6)	0.026 (3)	0.095 (5)	−0.008 (3)	0.072 (5)	−0.014 (3)
C5	0.040 (3)	0.028 (3)	0.035 (3)	−0.002 (2)	0.018 (2)	−0.004 (2)
C6	0.046 (3)	0.030 (3)	0.030 (3)	0.000 (2)	0.020 (2)	−0.007 (2)
C7	0.035 (3)	0.029 (3)	0.029 (3)	0.000 (2)	0.006 (2)	−0.002 (2)
C8	0.042 (4)	0.040 (3)	0.029 (3)	−0.012 (3)	0.000 (3)	0.006 (2)
C9	0.027 (3)	0.061 (4)	0.037 (3)	−0.004 (3)	0.001 (2)	0.018 (3)
C10	0.034 (3)	0.047 (3)	0.034 (3)	0.009 (3)	0.012 (2)	0.015 (2)
C11	0.029 (3)	0.035 (3)	0.023 (2)	0.003 (2)	0.012 (2)	0.013 (2)
C12	0.036 (3)	0.038 (3)	0.035 (3)	0.010 (2)	0.017 (2)	0.004 (2)
C13	0.046 (4)	0.054 (3)	0.027 (3)	−0.004 (3)	0.013 (3)	0.006 (2)
C14A	0.056 (8)	0.024 (5)	0.042 (6)	0.004 (5)	0.023 (6)	0.004 (5)
C15A	0.041 (7)	0.035 (6)	0.026 (5)	−0.002 (4)	0.012 (5)	0.003 (4)
C14B	0.058 (8)	0.036 (6)	0.024 (5)	0.009 (5)	0.021 (5)	0.004 (4)
C15B	0.055 (8)	0.030 (6)	0.042 (6)	0.014 (5)	0.016 (6)	0.012 (5)
S1	0.0259 (7)	0.0213 (6)	0.0212 (6)	0.0008 (5)	0.0076 (5)	−0.0024 (5)
O1	0.033 (2)	0.0322 (18)	0.0319 (18)	−0.0025 (15)	0.0158 (16)	−0.0072 (14)
O2	0.043 (2)	0.0343 (19)	0.0269 (16)	−0.0004 (17)	0.0138 (16)	0.0022 (15)
O3	0.035 (2)	0.0259 (17)	0.0302 (17)	0.0045 (15)	0.0063 (15)	−0.0066 (14)
O4	0.039 (2)	0.0248 (17)	0.0328 (17)	0.0084 (16)	−0.0009 (15)	−0.0086 (14)
O5W	0.042 (2)	0.0243 (17)	0.0338 (18)	−0.0047 (16)	0.0057 (16)	0.0018 (14)
O6W	0.074 (3)	0.048 (2)	0.046 (2)	−0.003 (2)	0.015 (2)	−0.0042 (18)
O7W	0.054 (3)	0.045 (2)	0.095 (3)	0.011 (2)	0.026 (3)	0.025 (2)
O8W	0.060 (3)	0.069 (3)	0.096 (3)	0.022 (2)	0.044 (3)	0.041 (2)

Geometric parameters (Å, °)

Mn1—O1	2.139 (3)	C11—C12	1.507 (6)
Mn1—O4^{i}	2.143 (3)	C12—H12A	0.9800
Mn1—O5W	2.206 (3)	C12—H12B	0.9800
Mn1—N2	2.256 (4)	C13—C14A	1.379 (10)
Mn1—N1	2.300 (4)	C13—C14B	1.456 (11)
Mn1—N3	2.360 (4)	C13—H13A	0.9800
N1—C5	1.332 (5)	C13—H13B	0.9800
N1—C1	1.345 (5)	C13—H13C	0.9800
N2—C7	1.342 (5)	C13—H13D	0.9800
N2—C11	1.346 (6)	C14A—C15A	1.547 (12)
N3—C6	1.468 (6)	C14A—H14A	0.9800
N3—C12	1.473 (6)	C14A—H14B	0.9800
N3—C13	1.489 (5)	C15A—C15B^{ii}	1.499 (13)
C1—C2	1.364 (6)	C15A—H15A	0.9800
C1—H1	0.9400	C15A—H15B	0.9800
C2—C3	1.358 (7)	C14B—C15B	1.531 (12)
C2—H2	0.9400	C14B—H14C	0.9800
C3—C4	1.387 (7)	C14B—H14D	0.9800
C3—H3	0.9400	C15B—H15C	0.9800
C4—C5	1.370 (7)	C15B—H15D	0.9800

C4—H4	0.9400	S1—O2	1.456 (3)
C5—C6	1.507 (6)	S1—O4	1.477 (3)
C6—H6A	0.9800	S1—O3	1.479 (3)
C6—H6B	0.9800	S1—O1	1.486 (3)
C7—C8	1.370 (7)	O5W—H5W1	0.963
C7—H7	0.9400	O5W—H5W2	0.944
C8—C9	1.376 (7)	O6W—H6W1	0.962
C8—H8	0.9400	O6W—H6W2	0.860
C9—C10	1.377 (7)	O7W—H7W1	1.004
C9—H9	0.9400	O7W—H7W2	0.933
C10—C11	1.381 (7)	O8W—H8W1	1.030
C10—H10	0.9400	O8W—H8W2	0.977
O1—Mn1—O4^{i}	110.92 (13)	C10—C11—C12	120.5 (4)
O1—Mn1—O5W	93.05 (11)	N3—C12—C11	112.4 (4)
O4^{i}—Mn1—O5W	83.96 (11)	N3—C12—H12A	109.1
O1—Mn1—N2	93.72 (12)	C11—C12—H12A	109.1
O4^{i}—Mn1—N2	152.92 (13)	N3—C12—H12B	109.1
O5W—Mn1—N2	83.68 (12)	C11—C12—H12B	109.1
O1—Mn1—N1	94.54 (12)	H12A—C12—H12B	107.9
O4^{i}—Mn1—N1	90.01 (12)	C14A—C13—C14B	94.5 (7)
O5W—Mn1—N1	171.62 (12)	C14A—C13—N3	123.6 (6)
N2—Mn1—N1	99.36 (13)	C14B—C13—N3	117.1 (5)
O1—Mn1—N3	159.47 (12)	C14A—C13—H13A	106.4
O4^{i}—Mn1—N3	85.39 (13)	N3—C13—H13A	106.4
O5W—Mn1—N3	101.28 (12)	C14A—C13—H13B	106.4
N2—Mn1—N3	73.57 (13)	C14B—C13—H13B	107.5
N1—Mn1—N3	72.36 (12)	N3—C13—H13B	106.4
C5—N1—C1	117.8 (4)	H13A—C13—H13B	106.5
C5—N1—Mn1	114.9 (3)	C14A—C13—H13C	104.0
C1—N1—Mn1	127.3 (3)	C14B—C13—H13C	108.0
C7—N2—C11	117.3 (4)	N3—C13—H13C	108.0
C7—N2—Mn1	124.6 (3)	H13A—C13—H13C	107.5
C11—N2—Mn1	117.8 (3)	C14B—C13—H13D	108.0
C6—N3—C12	110.7 (4)	N3—C13—H13D	108.0
C6—N3—C13	110.2 (3)	H13A—C13—H13D	119.2
C12—N3—C13	111.6 (4)	H13B—C13—H13D	109.6
C6—N3—Mn1	104.0 (3)	H13C—C13—H13D	107.3
C12—N3—Mn1	108.9 (3)	C13—C14A—C15A	115.3 (8)
C13—N3—Mn1	111.2 (3)	C13—C14A—H14A	108.4
N1—C1—C2	123.7 (4)	C15A—C14A—H14A	108.4
N1—C1—H1	118.2	C13—C14A—H14B	108.4
C2—C1—H1	118.2	C15A—C14A—H14B	108.4
C3—C2—C1	118.2 (5)	H14A—C14A—H14B	107.5
C3—C2—H2	120.9	C15B^{ii}—C15A—C14A	111.2 (8)
C1—C2—H2	120.9	C15B^{ii}—C15A—H15A	109.4
C2—C3—C4	119.2 (5)	C14A—C15A—H15A	109.4
C2—C3—H3	120.4	C15B^{ii}—C15A—H15B	109.4

C4—C3—H3	120.4	C14A—C15A—H15B	109.4
C5—C4—C3	119.5 (5)	H15A—C15A—H15B	108.0
C5—C4—H4	120.3	C13—C14B—C15B	112.5 (8)
C3—C4—H4	120.3	C13—C14B—H14C	109.1
N1—C5—C4	121.6 (5)	C15B—C14B—H14C	109.1
N1—C5—C6	116.7 (4)	C13—C14B—H14D	109.1
C4—C5—C6	121.7 (4)	C15B—C14B—H14D	109.1
N3—C6—C5	110.7 (3)	H14C—C14B—H14D	107.8
N3—C6—H6A	109.5	C15A^{ii}—C15B—C14B	114.9 (8)
C5—C6—H6A	109.5	C15A^{ii}—C15B—H15C	108.5
N3—C6—H6B	109.5	C14B—C15B—H15C	108.5
C5—C6—H6B	109.5	C15A^{ii}—C15B—H15D	108.5
H6A—C6—H6B	108.1	C14B—C15B—H15D	108.5
N2—C7—C8	123.7 (5)	H15C—C15B—H15D	107.5
N2—C7—H7	118.2	O2—S1—O4	110.23 (18)
C8—C7—H7	118.2	O2—S1—O3	110.17 (18)
C7—C8—C9	118.5 (5)	O4—S1—O3	110.21 (18)
C7—C8—H8	120.8	O2—S1—O1	109.54 (19)
C9—C8—H8	120.8	O4—S1—O1	107.96 (18)
C8—C9—C10	119.1 (5)	O3—S1—O1	108.69 (18)
C8—C9—H9	120.4	S1—O1—Mn1	126.45 (18)
C10—C9—H9	120.4	S1—O4—Mn1^{i}	143.91 (19)
C9—C10—C11	119.1 (5)	H5W1—O5W—H5W2	110.7
C9—C10—H10	120.5	H6W1—O6W—H6W2	93.4
C11—C10—H10	120.5	H7W1—O7W—H7W2	90.7
N2—C11—C10	122.3 (5)	H8W1—O8W—H8W2	107.8
N2—C11—C12	117.1 (4)		
O1—Mn1—N1—C5	−176.5 (3)	C12—N3—C6—C5	−67.5 (5)
O4^{i}—Mn1—N1—C5	−65.5 (3)	C13—N3—C6—C5	168.5 (4)
N2—Mn1—N1—C5	88.9 (3)	Mn1—N3—C6—C5	49.3 (4)
N3—Mn1—N1—C5	19.6 (3)	N1—C5—C6—N3	−36.5 (6)
O1—Mn1—N1—C1	5.3 (4)	C4—C5—C6—N3	143.6 (6)
O4^{i}—Mn1—N1—C1	116.3 (4)	C11—N2—C7—C8	0.6 (6)
N2—Mn1—N1—C1	−89.2 (4)	Mn1—N2—C7—C8	174.5 (3)
N3—Mn1—N1—C1	−158.5 (4)	N2—C7—C8—C9	−0.1 (7)
O1—Mn1—N2—C7	31.8 (3)	C7—C8—C9—C10	−0.1 (7)
O4^{i}—Mn1—N2—C7	−124.2 (4)	C8—C9—C10—C11	−0.4 (7)
O5W—Mn1—N2—C7	−60.9 (3)	C7—N2—C11—C10	−1.1 (6)
N1—Mn1—N2—C7	127.0 (3)	Mn1—N2—C11—C10	−175.4 (3)
N3—Mn1—N2—C7	−164.6 (4)	C7—N2—C11—C12	−178.3 (4)
O1—Mn1—N2—C11	−154.4 (3)	Mn1—N2—C11—C12	7.4 (5)
O4^{i}—Mn1—N2—C11	49.7 (4)	C9—C10—C11—N2	1.0 (7)
O5W—Mn1—N2—C11	113.0 (3)	C9—C10—C11—C12	178.1 (4)
N1—Mn1—N2—C11	−59.1 (3)	C6—N3—C12—C11	148.8 (4)
N3—Mn1—N2—C11	9.2 (3)	C13—N3—C12—C11	−88.0 (5)
O1—Mn1—N3—C6	−88.2 (4)	Mn1—N3—C12—C11	35.0 (4)
O4^{i}—Mn1—N3—C6	55.5 (3)	N2—C11—C12—N3	−29.7 (6)

O5W—Mn1—N3—C6	138.4 (3)	C10—C11—C12—N3	153.1 (4)
N2—Mn1—N3—C6	−141.7 (3)	C6—N3—C13—C14A	52.1 (8)
N1—Mn1—N3—C6	−35.9 (3)	C12—N3—C13—C14A	−71.4 (8)
O1—Mn1—N3—C12	29.9 (5)	Mn1—N3—C13—C14A	166.8 (7)
O4^{i}—Mn1—N3—C12	173.6 (3)	C6—N3—C13—C14B	168.5 (6)
O5W—Mn1—N3—C12	−103.5 (3)	C12—N3—C13—C14B	45.0 (7)
N2—Mn1—N3—C12	−23.6 (3)	Mn1—N3—C13—C14B	−76.8 (7)
N1—Mn1—N3—C12	82.1 (3)	C14B—C13—C14A—C15A	53.7 (10)
O1—Mn1—N3—C13	153.2 (3)	N3—C13—C14A—C15A	−179.5 (7)
O4^{i}—Mn1—N3—C13	−63.1 (3)	C13—C14A—C15A—C15B^{ii}	178.2 (9)
O5W—Mn1—N3—C13	19.8 (3)	C14A—C13—C14B—C15B	−56.4 (9)
N2—Mn1—N3—C13	99.7 (3)	N3—C13—C14B—C15B	172.1 (6)
N1—Mn1—N3—C13	−154.5 (3)	C13—C14B—C15B—C15A^{ii}	68.7 (12)
C5—N1—C1—C2	−0.1 (7)	O2—S1—O1—Mn1	−116.8 (2)
Mn1—N1—C1—C2	178.1 (4)	O4—S1—O1—Mn1	3.3 (3)
N1—C1—C2—C3	−0.1 (9)	O3—S1—O1—Mn1	122.8 (2)
C1—C2—C3—C4	0.5 (11)	O4^{i}—Mn1—O1—S1	−32.5 (3)
C2—C3—C4—C5	−0.8 (11)	O5W—Mn1—O1—S1	−117.2 (2)
C1—N1—C5—C4	−0.2 (8)	N2—Mn1—O1—S1	158.9 (2)
Mn1—N1—C5—C4	−178.6 (5)	N1—Mn1—O1—S1	59.2 (2)
C1—N1—C5—C6	179.9 (4)	N3—Mn1—O1—S1	108.3 (4)
Mn1—N1—C5—C6	1.5 (5)	O2—S1—O4—Mn1^{i}	−134.1 (3)
C3—C4—C5—N1	0.6 (10)	O3—S1—O4—Mn1^{i}	−12.3 (4)
C3—C4—C5—C6	−179.5 (6)	O1—S1—O4—Mn1^{i}	106.3 (4)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5W—H5W1···O7W^{iii}	0.963	1.758	2.703 (5)	166
O5W—H5W2···O3^{i}	0.944	1.852	2.727 (4)	153
O6W—H6W1···O2^{iv}	0.962	1.911	2.865 (5)	171
O6W—H6W2···O3^{v}	0.860	2.266	2.899 (5)	130
O7W—H7W1···O8W	1.004	1.847	2.829 (6)	165
O7W—H7W2···O6W	0.933	2.530	3.044 (6)	115
O7W—H7W2···O6W^{vi}	0.933	2.347	3.162 (6)	146
O8W—H8W1···O3^{vii}	1.030	1.910	2.860 (5)	152
O8W—H8W2···O1^{viii}	0.977	1.956	2.913 (5)	166
O8W—H8W2···O3^{viii}	0.977	2.587	3.317 (5)	132

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

Fig. 1

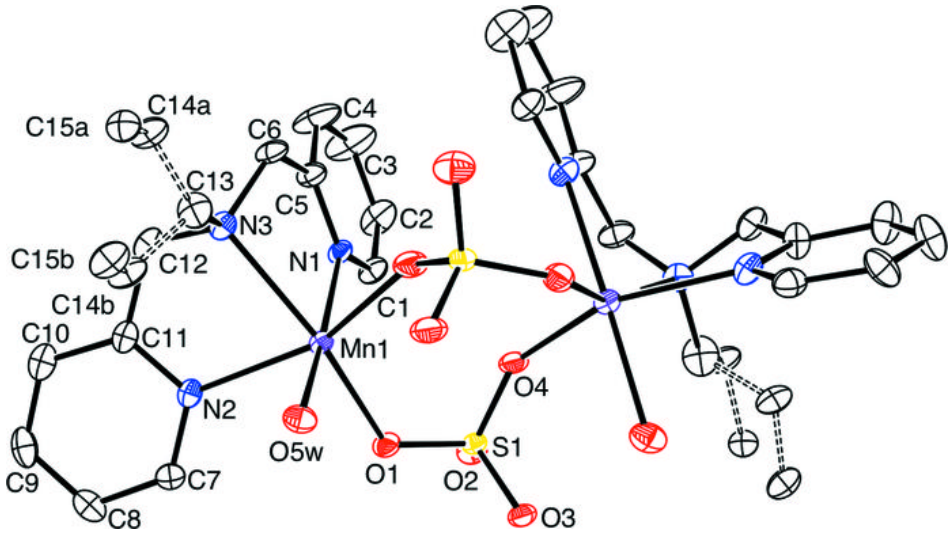
C14a
C15a
C6
C4
C13
C3
C5
N3
C2
C15b
C12
N1
C14b
C1
C10
C11
Mn1
O4
N2
O5w
O1
S1
O2
C9
C7
C8
O3

Fig. 2