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Diaquabromido[*N*,*N*′-bis(2-pyridylmethylidene)cyclohexane-1,2-diamine]manganese(II) bromide dibromido[*N*,*N*′-bis(2-pyridylmethylidene)cyclohexane-1,2-diamine]manganese(II)

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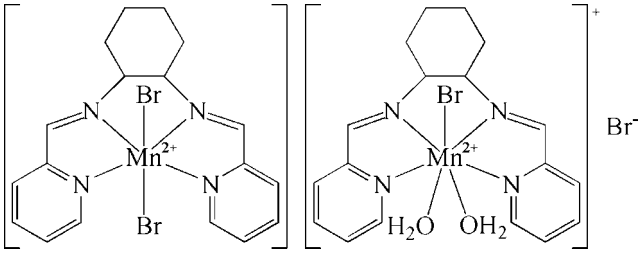
Key indicators: single-crystal X-ray study; T = 243 K; mean σ(C–C) = 0.009 Å; R factor = 0.044; wR factor = 0.137; data-to-parameter ratio = 17.4.

The crystal structure of the title compound, [MnBr($C_{18}H_{20}N_4$)(H_2O)$_2$]Br·[$MnBr_2(C_{18}H_{20}N_4)$], contains two different Mn^{II} complexes in the asymmetric unit. In the neutral complex, the Mn^{2+} ion is six-coordinated in a distorted octahedral environment by four N atoms from the tetradentate ligand *N*,*N*′-bis(2-pyridylmethylidene)cyclohexane-1,2-diamine (bpic) and two Br atoms. In the cationic complex, the Mn^{2+} ion is seven-coordinated in an approximately pentagonal–bipyramidal environment by four N atoms from bpic, one Br atom and two O atoms from water ligands. The compound displays intermolecular O—H···Br hydrogen bonding. There are also intermolecular π–π interactions between adjacent pyridine rings, with centroid-to-centroid distances of 3.604 and 3.680 Å, and with dihedral angles between the ring planes of 4.7 and 5.0°.

Related literature

For some other Mn(bpic) complexes, see: Lu *et al.* (2006); Schoumacker *et al.* (2003).



Experimental

Crystal data

[MnBr($C_{18}H_{20}N_4$)(H_2O)$_2$]Br·[$MnBr_2(C_{18}H_{20}N_4)$]
M_r = 1050.27
Triclinic, $P\overline{1}$
a = 11.8283 (9) Å
b = 12.4842 (9) Å
c = 14.134 (1) Å
α = 97.971 (1)°
β = 91.017 (1)°
γ = 98.036 (1)°
V = 2045.2 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 4.57 mm^{-1}
T = 243 (2) K
0.15 × 0.10 × 0.10 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.520, T_{max} = 0.633
12149 measured reflections
8169 independent reflections
5661 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.137
S = 1.00
8169 reflections
469 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.85 e Å^{-3}
$\Delta\rho_{min}$ = −0.70 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*W*···Br1^{i}	0.942	2.38	3.320 (4)	172.3
O1—H2*W*···Br4^{ii}	0.855	2.46	3.291 (4)	165.0
O2—H3*W*···Br4	0.907	2.53	3.413 (4)	163.8
O2—H4*W*···Br4^{ii}	0.840	2.47	3.303 (4)	169.2

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

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: *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: RK2035).

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supplementary materials

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Diaquabromido[*N*,*N*'-bis(2-pyridylmethylidene)cyclohexane-1,2-diamine]manganese(II) bromide dibromido[*N*,*N*'-bis(2-pyridylmethylidene)cyclohexane-1,2-diamine]manganese(II)

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Comment

The crystal structure of the title compound, $[MnBr_2(C_{18}H_{20}N_4)][MnBr(C_{18}H_{20}N_4)(H_2O)_2]Br$, consists of two different Mn^{II} complexes in an asymmetric unit (Fig. 1). In one neutral complex, Mn^{2+} ion is six-coordinated in a distorted octahedral environment by four N atoms from the tetradentate ligand *N*,*N*'-bis(2-pyridylmethylidene)-1,2-diiminocyclohexane (bpic) occupying equatorial positions and two Br atoms occupying axial positions. Within the equatorial plane, the chelating angles lie in the range of 70.69 (16)–71.98 (16)°. The apical Br1—Mn1—Br2 bond angle is 151.60 (4)°. In the other cation complex, Mn^{2+} ion is seven-coordinated in an approximately pentagonal bipyramidal structure by four N atoms from bpic, one Br atom and two O atoms from water ligands. The four N atoms and one O atom occupy the equatorial positions, and the Br atom and one O atom lie in the axial positions. Within the equatorial plane, the chelating angles lie in the range of 68.66 (17)–69.23 (16)°. The apical Br3—Mn2—O1 bond angle is 170.10 (10)°. The compound displays intermolecular hydrogen bonds between the O atoms and the Br atoms (Br1, Br4) (Fig. 2). Moreover, there are intermolecular π–π interactions between the adjacent pyridine rings. The distances between *Cg*1 (the centroid of six-membered ring N1–C5) and *Cg*4^{iii} [ring N8–C36; symmetry code: (iii) 1 − *x*, 1 − *y*, −*z*], and between *Cg*2 (ring N4–C18) and *Cg*3^{iv} [ring N5–C23; symmetry code: (iv) 1 − *x*, 2 − *y*, 1 − *z*] are 3.604 Å and 3.680 Å, repectively, with the respective dihedral angles between the ring planes 4.7° and 5.0°.

Experimental

A solution of $MnBr_2$ (0.37 g, 1.72 mmol) and *N*,*N*'-bis(2-pyridylmethylidene)-1,2-diiminocyclohexane (0.50 g, 1.71 mmol) in EtOH (30 ml) was stirred for 1 h at room temparature. After add of diethyl ether to the solution, the formed precipitate was separated by filtration and washed with acetone and dried under vacuum, to give a dark yellow powder (0.45 g). Crystals suitable for X-ray analysis were obtained by slow evaporation from a EtOH solution. MS (FAB): m/*z* 426, 428 [$Mn(bpic)Br^+$]; IR (KBr): 3376 cm^{-1} (broad).

Refinement

H atoms were positioned geometrically and allowed to ride on their respective carrier atoms [C—H = 0.94, 0.98 or 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. The H atoms of the water ligands were located from Fourier difference maps, but not refined [$U_{iso}(H) = 0.08$ Å^2].

The CIF check program indicates a high ratio of the maximum and minimum residual density (4.07) in the structure and solvent accessible voids of 79 Å^3. All these factors indicate a strong likelihood of disordered solvent molecule MeOH in the structure. However, the solvent molecule could neither be located nor refined, because the highest difference peak

(2.85 e Å^{-3}) lies on a special position (0, 0, 0) with the site occupation factor 0.5. The distance between this peak and the nearest atom is 1.433 Å.

Figures

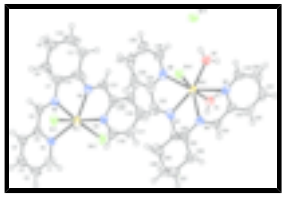

Fig. 1. The structure of the title compound with the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The H atoms are presented as a spheres of arbitrary radius.

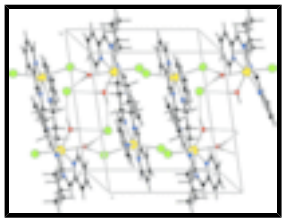

Fig. 2. View of the unit-cell contents of the title compound. Hydrogen-bond interactions are drawn with dashed lines.

Diaquabromido[*N*,*N*'-bis(2-pyridylmethylidene)cyclohexane-1,2- diamine]manganese(II) bromide dibromido[*N*,*N*'-bis(2-pyridylmethylidene)cyclohexane-1,2-diamine]manganese(II)

Crystal data

$[MnBr(C_{18}H_{20}N_4)(H_2O)_2]Br\cdot[MnBr_2(C_{18}H_{20}N_4)]$	$Z = 2$
$M_r = 1050.27$	$F_{000} = 1044$
Triclinic, $P\overline{1}$	$D_x = 1.706$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 11.8283$ (9) Å	Cell parameters from 4110 reflections
$b = 12.4842$ (9) Å	$\theta = 2.2$–26.3°
$c = 14.1340$ (10) Å	$\mu = 4.57$ mm^{-1}
$\alpha = 97.971$ (1)°	$T = 243$ (2) K
$\beta = 91.017$ (1)°	Plate, yellow
$\gamma = 98.036$ (1)°	0.15 × 0.10 × 0.10 mm
$V = 2045.2$ (3) Å^3	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	8169 independent reflections
Radiation source: fine-focus sealed tube	5661 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.019$
$T = 243(2)$ K	$\theta_{max} = 26.4^\circ$
φ and ω scans	$\theta_{min} = 1.5^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$h = -14\rightarrow13$
$T_{min} = 0.520$, $T_{max} = 0.633$	$k = -15\rightarrow15$

12149 measured reflections	$l = -17 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H-atom parameters constrained
$wR(F^2) = 0.137$	$w = 1/[\sigma^2(F_o^2) + (0.0737P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
8169 reflections	$\Delta\rho_{max} = 2.85$ e Å^{-3}
469 parameters	$\Delta\rho_{min} = -0.70$ 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 $F^2 > 2\sigma(F^2)$ 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	0.76129 (7)	0.66873 (7)	0.07222 (6)	0.0291 (2)
Br1	0.97942 (5)	0.75164 (5)	0.12675 (4)	0.03992 (17)
Br2	0.56467 (5)	0.68502 (6)	−0.00236 (4)	0.04501 (18)
N1	0.8298 (4)	0.6500 (4)	−0.0837 (3)	0.0302 (10)
N2	0.8074 (4)	0.5001 (4)	0.0341 (3)	0.0385 (12)
N3	0.7153 (4)	0.5746 (4)	0.1928 (3)	0.0358 (11)
N4	0.7117 (4)	0.7889 (4)	0.1988 (3)	0.0314 (10)
C1	0.8331 (5)	0.7196 (5)	−0.1462 (4)	0.0418 (15)
H1	0.8147	0.7899	−0.1260	0.050*
C2	0.8623 (5)	0.6940 (6)	−0.2398 (5)	0.0487 (17)
H2	0.8610	0.7451	−0.2826	0.058*
C3	0.8929 (5)	0.5949 (5)	−0.2694 (4)	0.0441 (15)
H3	0.9143	0.5764	−0.3327	0.053*
C4	0.8921 (5)	0.5211 (5)	−0.2047 (4)	0.0376 (14)
H4	0.9141	0.4519	−0.2226	0.045*
C5	0.8588 (4)	0.5516 (4)	−0.1147 (4)	0.0310 (12)
C6	0.8508 (5)	0.4744 (5)	−0.0451 (4)	0.0370 (14)

H6	0.8775	0.4067	−0.0594	0.044*
C7	0.8060 (7)	0.4325 (6)	0.1111 (5)	0.068 (2)
H7	0.8790	0.4593	0.1478	0.081*
C8	0.8103 (6)	0.3115 (5)	0.0798 (5)	0.0511 (17)
H8A	0.7484	0.2820	0.0323	0.061*
H8B	0.8831	0.3024	0.0497	0.061*
C9	0.7984 (8)	0.2488 (7)	0.1641 (6)	0.089 (3)
H9A	0.7780	0.1711	0.1394	0.107*
H9B	0.8734	0.2577	0.1971	0.107*
C10	0.7176 (8)	0.2776 (6)	0.2329 (6)	0.084 (3)
H10A	0.7332	0.2456	0.2904	0.101*
H10B	0.6415	0.2434	0.2075	0.101*
C11	0.7136 (5)	0.3963 (5)	0.2621 (4)	0.0383 (14)
H11A	0.7776	0.4269	0.3072	0.046*
H11B	0.6425	0.4055	0.2949	0.046*
C12	0.7199 (7)	0.4588 (6)	0.1767 (5)	0.064 (2)
H12	0.6478	0.4288	0.1398	0.077*
C13	0.6838 (4)	0.6249 (5)	0.2698 (4)	0.0324 (13)
H13	0.6667	0.5880	0.3226	0.039*
C14	0.6747 (4)	0.7403 (5)	0.2754 (4)	0.0328 (13)
C15	0.6282 (4)	0.7954 (5)	0.3528 (4)	0.0360 (13)
H15	0.6035	0.7593	0.4044	0.043*
C16	0.6186 (5)	0.9029 (5)	0.3537 (4)	0.0411 (15)
H16	0.5872	0.9424	0.4059	0.049*
C17	0.6555 (5)	0.9524 (5)	0.2770 (5)	0.0426 (15)
H17	0.6496	1.0265	0.2755	0.051*
C18	0.7022 (5)	0.8907 (5)	0.2007 (4)	0.0398 (14)
H18	0.7278	0.9254	0.1484	0.048*
Mn2	0.25348 (7)	0.76805 (6)	0.42552 (6)	0.0291 (2)
Br3	0.42980 (5)	0.81252 (5)	0.54720 (4)	0.03697 (16)
Br4	0.12914 (5)	0.36444 (5)	0.52829 (5)	0.04494 (18)
N5	0.1501 (4)	0.8781 (4)	0.5369 (3)	0.0335 (11)
N6	0.2646 (4)	0.9444 (4)	0.3879 (3)	0.0326 (11)
N7	0.3127 (4)	0.7766 (4)	0.2688 (3)	0.0364 (11)
N8	0.3411 (4)	0.6112 (4)	0.3653 (4)	0.0376 (12)
C19	0.0984 (5)	0.8510 (5)	0.6154 (4)	0.0404 (14)
H19	0.0938	0.7783	0.6273	0.048*
C20	0.0512 (5)	0.9247 (6)	0.6804 (5)	0.0453 (15)
H20	0.0175	0.9019	0.7353	0.054*
C21	0.0538 (5)	1.0317 (5)	0.6639 (5)	0.0420 (15)
H21	0.0215	1.0826	0.7065	0.050*
C22	0.1053 (5)	1.0610 (5)	0.5828 (4)	0.0393 (14)
H22	0.1074	1.1326	0.5685	0.047*
C23	0.1544 (4)	0.9839 (5)	0.5219 (4)	0.0332 (13)
C24	0.2162 (4)	1.0140 (5)	0.4385 (4)	0.0345 (13)
H24	0.2196	1.0852	0.4229	0.041*
C25	0.3296 (5)	0.9712 (5)	0.3049 (4)	0.0364 (14)
H25	0.4117	0.9753	0.3224	0.044*
C26	0.3135 (5)	1.0776 (5)	0.2695 (5)	0.0504 (17)

H26A	0.2326	1.0770	0.2530	0.061*
H26B	0.3372	1.1390	0.3203	0.061*
C27	0.3832 (6)	1.0917 (7)	0.1833 (6)	0.069 (2)
H27A	0.3719	1.1604	0.1609	0.083*
H27B	0.4644	1.0962	0.2011	0.083*
C28	0.3511 (7)	0.9993 (6)	0.1042 (5)	0.066 (2)
H28A	0.3979	1.0110	0.0490	0.079*
H28B	0.2707	0.9962	0.0844	0.079*
C29	0.3693 (6)	0.8919 (6)	0.1379 (5)	0.0551 (18)
H29A	0.4505	0.8932	0.1537	0.066*
H29B	0.3458	0.8311	0.0866	0.066*
C30	0.2990 (5)	0.8754 (5)	0.2262 (4)	0.0376 (14)
H30	0.2172	0.8716	0.2076	0.045*
C31	0.3557 (5)	0.6978 (5)	0.2261 (4)	0.0422 (15)
H31	0.3795	0.6999	0.1632	0.051*
C32	0.3693 (4)	0.6028 (5)	0.2731 (4)	0.0373 (14)
C33	0.4082 (5)	0.5137 (5)	0.2263 (5)	0.0474 (17)
H33	0.4260	0.5104	0.1615	0.057*
C34	0.4213 (5)	0.4281 (6)	0.2752 (6)	0.058 (2)
H34	0.4455	0.3643	0.2438	0.069*
C35	0.3987 (5)	0.4372 (5)	0.3691 (6)	0.0561 (19)
H35	0.4105	0.3812	0.4046	0.067*
C36	0.3580 (5)	0.5294 (5)	0.4122 (5)	0.0437 (15)
H36	0.3415	0.5346	0.4774	0.052*
O1	0.0812 (3)	0.7290 (3)	0.3424 (3)	0.0405 (10)
H1W	0.0595	0.7353	0.2792	0.080*
H2W	0.0187	0.7035	0.3659	0.080*
O2	0.1481 (3)	0.6340 (3)	0.5022 (3)	0.0424 (10)
H3W	0.1576	0.5634	0.5037	0.080*
H4W	0.0767	0.6311	0.5019	0.080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0353 (5)	0.0276 (5)	0.0254 (5)	0.0090 (4)	0.0041 (3)	0.0021 (3)
Br1	0.0350 (3)	0.0481 (4)	0.0344 (3)	0.0081 (3)	0.0011 (2)	−0.0039 (3)
Br2	0.0384 (3)	0.0614 (4)	0.0355 (4)	0.0150 (3)	−0.0011 (3)	0.0000 (3)
N1	0.033 (2)	0.031 (3)	0.027 (3)	0.006 (2)	0.0000 (19)	0.005 (2)
N2	0.054 (3)	0.029 (3)	0.036 (3)	0.012 (2)	0.016 (2)	0.008 (2)
N3	0.051 (3)	0.031 (3)	0.028 (3)	0.013 (2)	0.006 (2)	0.003 (2)
N4	0.032 (2)	0.031 (3)	0.031 (3)	0.009 (2)	0.002 (2)	−0.002 (2)
C1	0.045 (4)	0.043 (4)	0.040 (4)	0.009 (3)	0.006 (3)	0.012 (3)
C2	0.051 (4)	0.063 (5)	0.037 (4)	0.004 (3)	0.005 (3)	0.025 (3)
C3	0.042 (4)	0.061 (4)	0.028 (3)	0.004 (3)	0.006 (3)	0.002 (3)
C4	0.037 (3)	0.045 (4)	0.030 (3)	0.008 (3)	0.005 (3)	0.000 (3)
C5	0.030 (3)	0.031 (3)	0.030 (3)	0.003 (2)	0.002 (2)	0.001 (2)
C6	0.046 (3)	0.029 (3)	0.037 (4)	0.012 (3)	0.010 (3)	−0.001 (3)
C7	0.118 (7)	0.042 (4)	0.056 (5)	0.034 (4)	0.041 (5)	0.023 (4)

C8	0.080 (5)	0.035 (4)	0.044 (4)	0.020 (3)	0.021 (3)	0.011 (3)
C9	0.148 (9)	0.050 (5)	0.091 (7)	0.047 (5)	0.056 (6)	0.039 (5)
C10	0.153 (9)	0.041 (4)	0.067 (6)	0.019 (5)	0.039 (6)	0.026 (4)
C11	0.041 (3)	0.038 (3)	0.037 (4)	0.006 (3)	0.002 (3)	0.010 (3)
C12	0.119 (6)	0.039 (4)	0.041 (4)	0.029 (4)	0.024 (4)	0.012 (3)
C13	0.034 (3)	0.039 (3)	0.023 (3)	0.002 (2)	0.002 (2)	0.003 (3)
C14	0.022 (3)	0.042 (3)	0.031 (3)	0.006 (2)	−0.002 (2)	−0.007 (3)
C15	0.028 (3)	0.044 (4)	0.033 (3)	0.004 (3)	0.000 (2)	−0.006 (3)
C16	0.027 (3)	0.051 (4)	0.040 (4)	0.008 (3)	−0.003 (3)	−0.012 (3)
C17	0.036 (3)	0.035 (3)	0.053 (4)	0.013 (3)	−0.012 (3)	−0.010 (3)
C18	0.041 (3)	0.038 (4)	0.039 (4)	0.009 (3)	−0.001 (3)	−0.001 (3)
Mn2	0.0316 (4)	0.0273 (5)	0.0282 (5)	0.0064 (3)	0.0025 (3)	0.0012 (4)
Br3	0.0360 (3)	0.0412 (4)	0.0322 (3)	0.0084 (3)	−0.0008 (2)	−0.0028 (3)
Br4	0.0395 (3)	0.0471 (4)	0.0506 (4)	0.0006 (3)	−0.0001 (3)	0.0213 (3)
N5	0.034 (3)	0.032 (3)	0.034 (3)	0.007 (2)	−0.002 (2)	0.000 (2)
N6	0.028 (2)	0.036 (3)	0.033 (3)	0.002 (2)	−0.001 (2)	0.006 (2)
N7	0.032 (3)	0.043 (3)	0.030 (3)	0.001 (2)	0.004 (2)	−0.004 (2)
N8	0.035 (3)	0.033 (3)	0.042 (3)	0.005 (2)	0.003 (2)	−0.006 (2)
C19	0.043 (3)	0.036 (4)	0.039 (4)	0.003 (3)	0.004 (3)	0.001 (3)
C20	0.038 (3)	0.058 (4)	0.037 (4)	0.005 (3)	0.005 (3)	0.000 (3)
C21	0.033 (3)	0.041 (4)	0.047 (4)	0.010 (3)	−0.001 (3)	−0.013 (3)
C22	0.037 (3)	0.033 (3)	0.046 (4)	0.014 (3)	−0.013 (3)	−0.007 (3)
C23	0.030 (3)	0.032 (3)	0.037 (3)	0.009 (2)	−0.006 (2)	−0.001 (3)
C24	0.030 (3)	0.030 (3)	0.043 (4)	0.002 (2)	−0.006 (3)	0.006 (3)
C25	0.030 (3)	0.042 (4)	0.039 (4)	0.004 (3)	−0.001 (3)	0.013 (3)
C26	0.042 (4)	0.053 (4)	0.061 (5)	0.004 (3)	0.004 (3)	0.029 (4)
C27	0.048 (4)	0.086 (6)	0.086 (6)	0.011 (4)	0.007 (4)	0.056 (5)
C28	0.079 (5)	0.079 (6)	0.041 (4)	0.000 (4)	0.010 (4)	0.025 (4)
C29	0.055 (4)	0.075 (5)	0.031 (4)	0.000 (4)	0.005 (3)	0.007 (3)
C30	0.034 (3)	0.049 (4)	0.029 (3)	0.001 (3)	−0.001 (2)	0.008 (3)
C31	0.034 (3)	0.056 (4)	0.031 (3)	0.000 (3)	0.005 (3)	−0.007 (3)
C32	0.027 (3)	0.039 (4)	0.039 (4)	−0.002 (2)	−0.001 (3)	−0.012 (3)
C33	0.030 (3)	0.048 (4)	0.056 (4)	0.003 (3)	0.007 (3)	−0.022 (3)
C34	0.035 (4)	0.041 (4)	0.088 (6)	0.006 (3)	0.009 (4)	−0.021 (4)
C35	0.041 (4)	0.035 (4)	0.090 (6)	0.003 (3)	0.002 (4)	0.006 (4)
C36	0.040 (3)	0.034 (4)	0.056 (4)	0.008 (3)	0.005 (3)	0.001 (3)
O1	0.037 (2)	0.049 (3)	0.034 (2)	−0.0017 (19)	0.0005 (17)	0.0084 (19)
O2	0.038 (2)	0.034 (2)	0.058 (3)	0.0068 (18)	0.004 (2)	0.011 (2)

Geometric parameters (Å, °)

Mn1—N3	2.234 (4)	Mn2—N7	2.346 (5)
Mn1—N2	2.245 (5)	Mn2—N8	2.403 (5)
Mn1—N4	2.309 (4)	Mn2—N5	2.408 (5)
Mn1—N1	2.354 (4)	Mn2—Br3	2.6268 (10)
Mn1—Br2	2.5818 (10)	N5—C19	1.338 (7)
Mn1—Br1	2.6988 (10)	N5—C23	1.361 (7)
N1—C1	1.320 (7)	N6—C24	1.256 (7)
N1—C5	1.339 (7)	N6—C25	1.465 (7)

N2—C6	1.259 (7)	N7—C31	1.256 (7)
N2—C7	1.466 (8)	N7—C30	1.473 (7)
N3—C13	1.268 (7)	N8—C36	1.327 (7)
N3—C12	1.441 (8)	N8—C32	1.345 (7)
N4—C18	1.289 (7)	C19—C20	1.389 (8)
N4—C14	1.363 (7)	C19—H19	0.9400
C1—C2	1.379 (9)	C20—C21	1.384 (9)
C1—H1	0.9400	C20—H20	0.9400
C2—C3	1.350 (9)	C21—C22	1.377 (8)
C2—H2	0.9400	C21—H21	0.9400
C3—C4	1.384 (8)	C22—C23	1.395 (8)
C3—H3	0.9400	C22—H22	0.9400
C4—C5	1.358 (7)	C23—C24	1.464 (8)
C4—H4	0.9400	C24—H24	0.9400
C5—C6	1.466 (7)	C25—C30	1.515 (8)
C6—H6	0.9400	C25—C26	1.517 (8)
C7—C12	1.431 (9)	C25—H25	0.9900
C7—C8	1.522 (9)	C26—C27	1.501 (9)
C7—H7	0.9900	C26—H26A	0.9800
C8—C9	1.513 (9)	C26—H26B	0.9800
C8—H8A	0.9800	C27—C28	1.493 (11)
C8—H8B	0.9800	C27—H27A	0.9800
C9—C10	1.421 (10)	C27—H27B	0.9800
C9—H9A	0.9800	C28—C29	1.524 (9)
C9—H9B	0.9800	C28—H28A	0.9800
C10—C11	1.490 (9)	C28—H28B	0.9800
C10—H10A	0.9800	C29—C30	1.534 (8)
C10—H10B	0.9800	C29—H29A	0.9800
C11—C12	1.523 (8)	C29—H29B	0.9800
C11—H11A	0.9800	C30—H30	0.9900
C11—H11B	0.9800	C31—C32	1.463 (9)
C12—H12	0.9900	C31—H31	0.9400
C13—C14	1.450 (8)	C32—C33	1.356 (8)
C13—H13	0.9400	C33—C34	1.374 (10)
C14—C15	1.375 (7)	C33—H33	0.9400
C15—C16	1.361 (8)	C34—C35	1.351 (10)
C15—H15	0.9400	C34—H34	0.9400
C16—C17	1.369 (8)	C35—C36	1.379 (9)
C16—H16	0.9400	C35—H35	0.9400
C17—C18	1.405 (8)	C36—H36	0.9400
C17—H17	0.9400	O1—H1W	0.942
C18—H18	0.9400	O1—H2W	0.855
Mn2—O1	2.291 (4)	O2—H3W	0.907
Mn2—N6	2.322 (4)	O2—H4W	0.840
Mn2—O2	2.344 (4)		
N3—Mn1—N2	71.68 (16)	O1—Mn2—N8	100.81 (15)
N3—Mn1—N4	71.98 (16)	N6—Mn2—N8	134.05 (16)
N2—Mn1—N4	142.60 (17)	O2—Mn2—N8	79.55 (15)
N3—Mn1—N1	142.22 (16)	N7—Mn2—N8	68.79 (17)

N2—Mn1—N1	70.69 (16)	O1—Mn2—N5	83.30 (15)
N4—Mn1—N1	145.68 (16)	N6—Mn2—N5	69.23 (16)
N3—Mn1—Br2	102.99 (12)	O2—Mn2—N5	78.73 (14)
N2—Mn1—Br2	111.61 (14)	N7—Mn2—N5	134.79 (16)
N4—Mn1—Br2	84.99 (11)	N8—Mn2—N5	156.11 (16)
N1—Mn1—Br2	87.70 (11)	O1—Mn2—Br3	170.10 (10)
N3—Mn1—Br1	99.48 (13)	N6—Mn2—Br3	95.07 (11)
N2—Mn1—Br1	91.76 (13)	O2—Mn2—Br3	97.15 (11)
N4—Mn1—Br1	85.68 (11)	N7—Mn2—Br3	110.61 (12)
N1—Mn1—Br1	85.05 (11)	N8—Mn2—Br3	84.23 (12)
Br2—Mn1—Br1	151.60 (4)	N5—Mn2—Br3	88.70 (11)
C1—N1—C5	116.7 (5)	C19—N5—C23	116.6 (5)
C1—N1—Mn1	128.4 (4)	C19—N5—Mn2	128.2 (4)
C5—N1—Mn1	114.6 (3)	C23—N5—Mn2	114.9 (4)
C6—N2—C7	122.4 (5)	C24—N6—C25	121.7 (5)
C6—N2—Mn1	119.7 (4)	C24—N6—Mn2	120.0 (4)
C7—N2—Mn1	116.8 (4)	C25—N6—Mn2	118.3 (3)
C13—N3—C12	124.0 (5)	C31—N7—C30	123.4 (5)
C13—N3—Mn1	118.6 (4)	C31—N7—Mn2	118.6 (4)
C12—N3—Mn1	117.4 (4)	C30—N7—Mn2	118.0 (3)
C18—N4—C14	117.6 (5)	C36—N8—C32	117.2 (5)
C18—N4—Mn1	128.0 (4)	C36—N8—Mn2	126.4 (4)
C14—N4—Mn1	113.9 (3)	C32—N8—Mn2	116.2 (4)
N1—C1—C2	122.9 (6)	N5—C19—C20	123.4 (6)
N1—C1—H1	118.5	N5—C19—H19	118.3
C2—C1—H1	118.5	C20—C19—H19	118.3
C3—C2—C1	119.5 (6)	C21—C20—C19	119.8 (6)
C3—C2—H2	120.3	C21—C20—H20	120.1
C1—C2—H2	120.3	C19—C20—H20	120.1
C2—C3—C4	118.6 (6)	C22—C21—C20	117.7 (6)
C2—C3—H3	120.7	C22—C21—H21	121.1
C4—C3—H3	120.7	C20—C21—H21	121.1
C5—C4—C3	118.2 (6)	C21—C22—C23	119.7 (6)
C5—C4—H4	120.9	C21—C22—H22	120.2
C3—C4—H4	120.9	C23—C22—H22	120.2
N1—C5—C4	124.0 (5)	N5—C23—C22	122.8 (5)
N1—C5—C6	115.8 (5)	N5—C23—C24	116.1 (5)
C4—C5—C6	120.2 (5)	C22—C23—C24	121.1 (5)
N2—C6—C5	118.9 (5)	N6—C24—C23	119.7 (5)
N2—C6—H6	120.5	N6—C24—H24	120.1
C5—C6—H6	120.5	C23—C24—H24	120.1
C12—C7—N2	109.7 (6)	N6—C25—C30	106.7 (4)
C12—C7—C8	116.5 (6)	N6—C25—C26	116.5 (5)
N2—C7—C8	115.7 (6)	C30—C25—C26	110.7 (5)
C12—C7—H7	104.5	N6—C25—H25	107.5
N2—C7—H7	104.5	C30—C25—H25	107.5
C8—C7—H7	104.5	C26—C25—H25	107.5
C9—C8—C7	110.9 (6)	C27—C26—C25	110.0 (6)
C9—C8—H8A	109.5	C27—C26—H26A	109.7

C7—C8—H8A	109.5	C25—C26—H26A	109.7
C9—C8—H8B	109.5	C27—C26—H26B	109.7
C7—C8—H8B	109.5	C25—C26—H26B	109.7
H8A—C8—H8B	108.1	H26A—C26—H26B	108.2
C10—C9—C8	117.2 (6)	C28—C27—C26	111.7 (6)
C10—C9—H9A	108.0	C28—C27—H27A	109.3
C8—C9—H9A	108.0	C26—C27—H27A	109.3
C10—C9—H9B	108.0	C28—C27—H27B	109.3
C8—C9—H9B	108.0	C26—C27—H27B	109.3
H9A—C9—H9B	107.2	H27A—C27—H27B	107.9
C9—C10—C11	117.2 (6)	C27—C28—C29	109.8 (6)
C9—C10—H10A	108.0	C27—C28—H28A	109.7
C11—C10—H10A	108.0	C29—C28—H28A	109.7
C9—C10—H10B	108.0	C27—C28—H28B	109.7
C11—C10—H10B	108.0	C29—C28—H28B	109.7
H10A—C10—H10B	107.2	H28A—C28—H28B	108.2
C10—C11—C12	111.9 (6)	C28—C29—C30	109.7 (6)
C10—C11—H11A	109.2	C28—C29—H29A	109.7
C12—C11—H11A	109.2	C30—C29—H29A	109.7
C10—C11—H11B	109.2	C28—C29—H29B	109.7
C12—C11—H11B	109.2	C30—C29—H29B	109.7
H11A—C11—H11B	107.9	H29A—C29—H29B	108.2
C7—C12—N3	111.6 (6)	N7—C30—C25	106.3 (4)
C7—C12—C11	114.3 (6)	N7—C30—C29	115.4 (5)
N3—C12—C11	118.8 (6)	C25—C30—C29	110.8 (5)
C7—C12—H12	103.3	N7—C30—H30	108.0
N3—C12—H12	103.3	C25—C30—H30	108.0
C11—C12—H12	103.3	C29—C30—H30	108.0
N3—C13—C14	119.0 (5)	N7—C31—C32	120.8 (5)
N3—C13—H13	120.5	N7—C31—H31	119.6
C14—C13—H13	120.5	C32—C31—H31	119.6
N4—C14—C15	122.6 (5)	N8—C32—C33	123.0 (6)
N4—C14—C13	116.1 (5)	N8—C32—C31	115.2 (5)
C15—C14—C13	121.3 (5)	C33—C32—C31	121.9 (6)
C16—C15—C14	119.2 (6)	C32—C33—C34	119.0 (6)
C16—C15—H15	120.4	C32—C33—H33	120.5
C14—C15—H15	120.4	C34—C33—H33	120.5
C15—C16—C17	118.6 (6)	C35—C34—C33	118.9 (6)
C15—C16—H16	120.7	C35—C34—H34	120.6
C17—C16—H16	120.7	C33—C34—H34	120.6
C16—C17—C18	118.9 (6)	C34—C35—C36	119.3 (7)
C16—C17—H17	120.5	C34—C35—H35	120.3
C18—C17—H17	120.5	C36—C35—H35	120.3
N4—C18—C17	123.1 (6)	N8—C36—C35	122.5 (6)
N4—C18—H18	118.4	N8—C36—H36	118.7
C17—C18—H18	118.4	C35—C36—H36	118.7
O1—Mn2—N6	87.55 (15)	Mn2—O1—H1W	132.4
O1—Mn2—O2	75.62 (14)	Mn2—O1—H2W	124.1
N6—Mn2—O2	145.34 (14)	H1W—O1—H2W	103.6

O1—Mn2—N7	79.24 (15)	Mn2—O2—H3W	130.0
N6—Mn2—N7	68.66 (17)	Mn2—O2—H4W	118.0
O2—Mn2—N7	134.59 (16)	H3W—O2—H4W	102.6
N3—Mn1—N1—C1	168.5 (4)	N8—Mn2—N5—C19	−6.7 (7)
N2—Mn1—N1—C1	174.0 (5)	Br3—Mn2—N5—C19	−79.2 (5)
N4—Mn1—N1—C1	−17.5 (6)	O1—Mn2—N5—C23	−91.6 (4)
Br2—Mn1—N1—C1	60.1 (5)	N6—Mn2—N5—C23	−1.7 (4)
Br1—Mn1—N1—C1	−92.4 (5)	O2—Mn2—N5—C23	−168.2 (4)
N3—Mn1—N1—C5	−4.7 (5)	N7—Mn2—N5—C23	−24.0 (5)
N2—Mn1—N1—C5	0.8 (4)	N8—Mn2—N5—C23	166.8 (4)
N4—Mn1—N1—C5	169.3 (3)	Br3—Mn2—N5—C23	94.3 (4)
Br2—Mn1—N1—C5	−113.1 (4)	O1—Mn2—N6—C24	84.1 (4)
Br1—Mn1—N1—C5	94.4 (4)	O2—Mn2—N6—C24	24.1 (6)
N3—Mn1—N2—C6	179.6 (5)	N7—Mn2—N6—C24	163.5 (5)
N4—Mn1—N2—C6	−166.2 (4)	N8—Mn2—N6—C24	−173.2 (4)
N1—Mn1—N2—C6	3.1 (5)	N5—Mn2—N6—C24	0.4 (4)
Br2—Mn1—N2—C6	82.5 (5)	Br3—Mn2—N6—C24	−86.3 (4)
Br1—Mn1—N2—C6	−81.0 (5)	O1—Mn2—N6—C25	−96.3 (4)
N3—Mn1—N2—C7	−12.1 (5)	O2—Mn2—N6—C25	−156.4 (3)
N4—Mn1—N2—C7	2.1 (6)	N7—Mn2—N6—C25	−16.9 (4)
N1—Mn1—N2—C7	171.4 (5)	N8—Mn2—N6—C25	6.4 (5)
Br2—Mn1—N2—C7	−109.2 (5)	N5—Mn2—N6—C25	180.0 (4)
Br1—Mn1—N2—C7	87.3 (5)	Br3—Mn2—N6—C25	93.3 (4)
N2—Mn1—N3—C13	171.8 (5)	O1—Mn2—N7—C31	−103.1 (4)
N4—Mn1—N3—C13	0.8 (4)	N6—Mn2—N7—C31	165.3 (5)
N1—Mn1—N3—C13	177.2 (4)	O2—Mn2—N7—C31	−46.0 (5)
Br2—Mn1—N3—C13	−79.5 (4)	N8—Mn2—N7—C31	3.0 (4)
Br1—Mn1—N3—C13	83.1 (4)	N5—Mn2—N7—C31	−172.3 (4)
N2—Mn1—N3—C12	−10.2 (5)	Br3—Mn2—N7—C31	77.9 (4)
N4—Mn1—N3—C12	178.8 (5)	O1—Mn2—N7—C30	77.8 (4)
N1—Mn1—N3—C12	−4.8 (6)	N6—Mn2—N7—C30	−13.7 (4)
Br2—Mn1—N3—C12	98.6 (5)	O2—Mn2—N7—C30	135.0 (4)
Br1—Mn1—N3—C12	−98.9 (5)	N8—Mn2—N7—C30	−176.0 (4)
N3—Mn1—N4—C18	−175.0 (5)	N5—Mn2—N7—C30	8.7 (5)
N2—Mn1—N4—C18	170.8 (4)	Br3—Mn2—N7—C30	−101.1 (4)
N1—Mn1—N4—C18	8.9 (6)	O1—Mn2—N8—C36	−107.4 (5)
Br2—Mn1—N4—C18	−69.6 (5)	N6—Mn2—N8—C36	155.4 (4)
Br1—Mn1—N4—C18	83.6 (5)	O2—Mn2—N8—C36	−34.4 (5)
N3—Mn1—N4—C14	−3.9 (3)	N7—Mn2—N8—C36	178.7 (5)
N2—Mn1—N4—C14	−18.1 (5)	N5—Mn2—N8—C36	−9.5 (7)
N1—Mn1—N4—C14	180.0 (3)	Br3—Mn2—N8—C36	64.0 (5)
Br2—Mn1—N4—C14	101.5 (3)	O1—Mn2—N8—C32	68.2 (4)
Br1—Mn1—N4—C14	−105.3 (3)	N6—Mn2—N8—C32	−28.9 (5)
C5—N1—C1—C2	1.3 (8)	O2—Mn2—N8—C32	141.2 (4)
Mn1—N1—C1—C2	−171.8 (4)	N7—Mn2—N8—C32	−5.6 (4)
N1—C1—C2—C3	−2.3 (10)	N5—Mn2—N8—C32	166.1 (4)
C1—C2—C3—C4	1.0 (9)	Br3—Mn2—N8—C32	−120.4 (4)
C2—C3—C4—C5	1.0 (9)	C23—N5—C19—C20	−0.4 (8)
C1—N1—C5—C4	0.9 (8)	Mn2—N5—C19—C20	173.0 (4)

Mn1—N1—C5—C4	175.0 (4)	N5—C19—C20—C21	1.7 (9)
C1—N1—C5—C6	−178.0 (5)	C19—C20—C21—C22	−0.8 (9)
Mn1—N1—C5—C6	−4.0 (6)	C20—C21—C22—C23	−1.3 (8)
C3—C4—C5—N1	−2.1 (8)	C19—N5—C23—C22	−1.7 (8)
C3—C4—C5—C6	176.8 (5)	Mn2—N5—C23—C22	−176.0 (4)
C7—N2—C6—C5	−174.0 (6)	C19—N5—C23—C24	177.0 (5)
Mn1—N2—C6—C5	−6.4 (7)	Mn2—N5—C23—C24	2.7 (6)
N1—C5—C6—N2	6.9 (8)	C21—C22—C23—N5	2.6 (8)
C4—C5—C6—N2	−172.0 (6)	C21—C22—C23—C24	−176.0 (5)
C6—N2—C7—C12	−159.9 (7)	C25—N6—C24—C23	−178.7 (5)
Mn1—N2—C7—C12	32.1 (9)	Mn2—N6—C24—C23	0.9 (7)
C6—N2—C7—C8	−25.6 (10)	N5—C23—C24—N6	−2.5 (8)
Mn1—N2—C7—C8	166.4 (5)	C22—C23—C24—N6	176.3 (5)
C12—C7—C8—C9	−44.1 (10)	C24—N6—C25—C30	−137.7 (5)
N2—C7—C8—C9	−175.2 (7)	Mn2—N6—C25—C30	42.7 (5)
C7—C8—C9—C10	40.7 (12)	C24—N6—C25—C26	−13.6 (8)
C8—C9—C10—C11	−42.9 (13)	Mn2—N6—C25—C26	166.9 (4)
C9—C10—C11—C12	43.4 (11)	N6—C25—C26—C27	−178.6 (6)
N2—C7—C12—N3	−39.5 (10)	C30—C25—C26—C27	−56.6 (7)
C8—C7—C12—N3	−173.4 (6)	C25—C26—C27—C28	58.7 (8)
N2—C7—C12—C11	−177.8 (6)	C26—C27—C28—C29	−59.5 (8)
C8—C7—C12—C11	48.3 (10)	C27—C28—C29—C30	57.6 (8)
C13—N3—C12—C7	−150.9 (7)	C31—N7—C30—C25	−139.5 (5)
Mn1—N3—C12—C7	31.2 (9)	Mn2—N7—C30—C25	39.5 (5)
C13—N3—C12—C11	−14.7 (10)	C31—N7—C30—C29	−16.2 (8)
Mn1—N3—C12—C11	167.4 (5)	Mn2—N7—C30—C29	162.7 (4)
C10—C11—C12—C7	−45.7 (10)	N6—C25—C30—N7	−49.9 (5)
C10—C11—C12—N3	179.1 (7)	C26—C25—C30—N7	−177.6 (4)
C12—N3—C13—C14	−175.5 (6)	N6—C25—C30—C29	−176.0 (5)
Mn1—N3—C13—C14	2.4 (7)	C26—C25—C30—C29	56.3 (6)
C18—N4—C14—C15	0.2 (8)	C28—C29—C30—N7	−177.4 (5)
Mn1—N4—C14—C15	−171.8 (4)	C28—C29—C30—C25	−56.6 (7)
C18—N4—C14—C13	178.5 (5)	C30—N7—C31—C32	178.7 (5)
Mn1—N4—C14—C13	6.4 (6)	Mn2—N7—C31—C32	−0.3 (7)
N3—C13—C14—N4	−6.0 (7)	C36—N8—C32—C33	3.1 (8)
N3—C13—C14—C15	172.2 (5)	Mn2—N8—C32—C33	−172.9 (4)
N4—C14—C15—C16	−0.1 (8)	C36—N8—C32—C31	−176.4 (5)
C13—C14—C15—C16	−178.2 (5)	Mn2—N8—C32—C31	7.5 (6)
C14—C15—C16—C17	0.1 (8)	N7—C31—C32—N8	−5.0 (8)
C15—C16—C17—C18	−0.2 (8)	N7—C31—C32—C33	175.4 (5)
C14—N4—C18—C17	−0.4 (8)	N8—C32—C33—C34	−0.9 (9)
Mn1—N4—C18—C17	170.4 (4)	C31—C32—C33—C34	178.7 (5)
C16—C17—C18—N4	0.4 (9)	C32—C33—C34—C35	−2.3 (9)
O1—Mn2—N5—C19	94.9 (5)	C33—C34—C35—C36	3.1 (10)
N6—Mn2—N5—C19	−175.2 (5)	C32—N8—C36—C35	−2.3 (8)
O2—Mn2—N5—C19	18.3 (5)	Mn2—N8—C36—C35	173.4 (4)
N7—Mn2—N5—C19	162.5 (4)	C34—C35—C36—N8	−0.8 (10)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1W···Br1^{i}	0.942	2.38	3.320 (4)	172.3
O1—H2W···Br4^{ii}	0.855	2.46	3.291 (4)	165.0
O2—H3W···Br4	0.907	2.53	3.413 (4)	163.8
O2—H4W···Br4^{ii}	0.840	2.47	3.303 (4)	169.2

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

Fig. 1

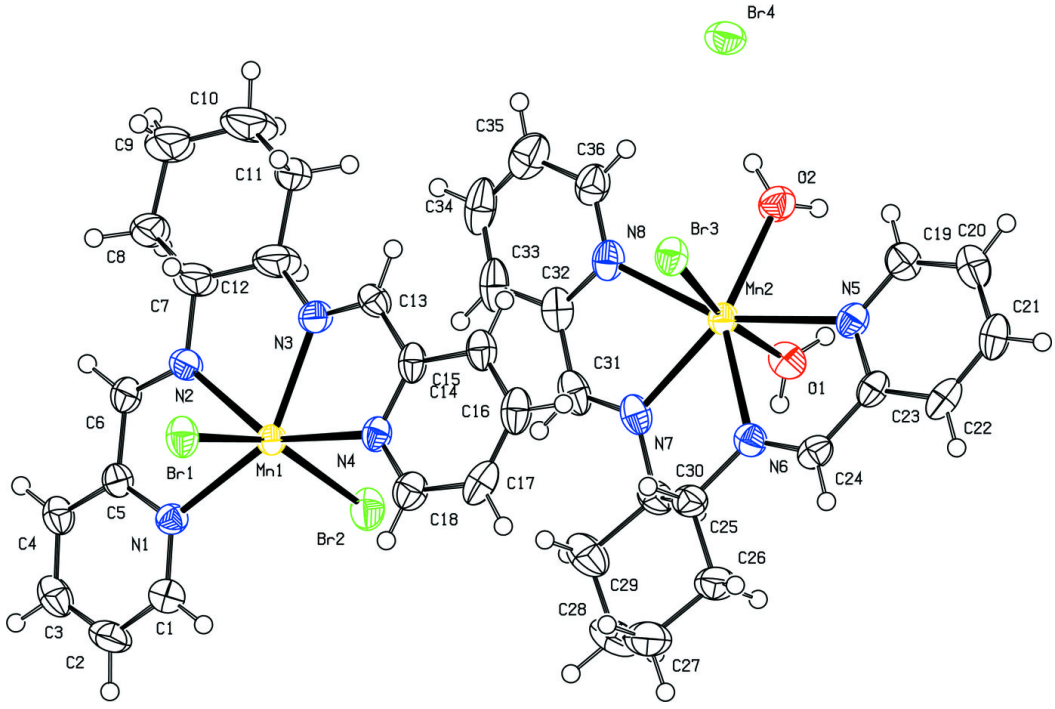
Br4
C10
C9
C11
C35
C36
O2
C34
N8
Br3
C19
C20
C8
C33
C32
Mn2
N5
C21
C7
C12
C13
N3
C31
O1
N2
C15
C14
C16
C23
C6
N7
C22
Br1
Mn1
N4
N6
C24
C30
C17
C5
C18
C25
C4
N1
Br2
C26
C29
C28
C3
C1
C27
C2

Fig. 2