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cis-Bis(2,2′-bipyrimidine-$\kappa^2N^1,N^{1'}$)-dibromidomanganese(II) nitromethane monosolvate

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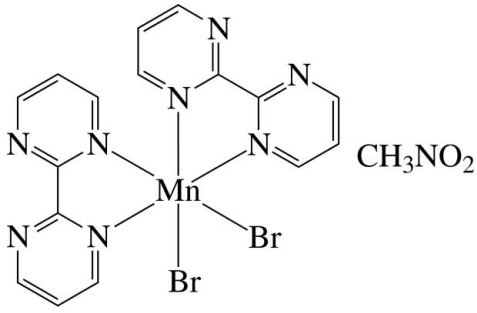
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.008 Å; R factor = 0.043; wR factor = 0.078; data-to-parameter ratio = 18.2.

The asymmetric unit of the title compound, $[MnBr_2(C_8H_6N_4)_2]\cdot CH_3NO_2$, contains one half of a neutral Mn^{II} complex and one half of a nitromethane solvent molecule, the complete molecules being generated by the application of twofold symmetry. In the complex, the Mn^{II} ion has a distorted *cis*-Br_2N_4 octahedral coordination geometry defined by four N atoms of the two chelating 2,2′-bipyrimidine ligands and two Br^- ions. There are intra- and intermolecular C—H···Br and C—H···N contacts.

Related literature

For the crystal structures of mononuclear 2,2′-bipyrimidine Mn^{II} complexes, see: Hong *et al.* (1996); Smith *et al.* (2001).



Experimental

Crystal data

$[MnBr_2(C_8H_6N_4)_2]\cdot CH_3NO_2$
M_r = 592.14
Orthorhombic, $C222_1$
a = 8.3876 (4) Å
b = 12.1772 (6) Å
c = 20.7479 (11) Å
V = 2119.14 (18) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.43 mm^{-1}
T = 200 K
0.17 × 0.10 × 0.07 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.825, T_{max} = 1.000
7872 measured reflections
2608 independent reflections
1818 reflections with $I > 2\sigma(I)$
R_{int} = 0.069

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.078
S = 1.02
2608 reflections
143 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.87 e Å^{-3}
$\Delta\rho_{min}$ = −0.86 e Å^{-3}
Absolute structure: Flack (1983), 1121 Friedel pairs
Flack parameter: −0.003 (16)

Table 1
Selected geometric parameters (Å, °).

Mn1—Br1	2.6140 (9)	Mn1—N3	2.306 (5)
Mn1—N1	2.292 (5)		
N1^i—Mn1—N1	158.0 (2)	Br1—Mn1—Br1^i	98.66 (5)
N3—Mn1—N3^i	89.5 (2)		

Symmetry code: (i) $-x, y, -z+\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···Br1	0.95	2.87	3.542 (6)	129
C2—H2···Br1^{ii}	0.95	2.91	3.802 (6)	156
C6—H6···Br1^{iii}	0.95	2.86	3.752 (5)	157
C9—H9*C*···N2^{iv}	0.98	2.57	3.430 (5)	147

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); 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: TK2729).

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Acta Cryst. (2011). E**67**, m474 [doi:10.1107/S1600536811010075]

cis-Bis(2,2′-bipyrimidine-$\kappa^2N^1,N^{1'}$)dibromidomanganese(II) nitromethane monosolvate

Kwang Ha

S1. Comment

Mononuclear Mn^{II} complexes of 2,2′-bipyrimidine ligand have been investigated previously (Hong *et al.*, 1996; Smith *et al.*, 2001). The asymmetric unit of the title compound, $[MnBr_2(bpym)_2].CH_3NO_2$ (where bpym is 2,2′-bipyrimidine; $C_8H_6N_4$), contains half of a neutral Mn(II) complex and half of a nitromethane solvent molecule (Fig. 1). The complex is disposed about a twofold rotation axis running in the [010] direction passing through the Mn1 atom with the special position at (0, *y*, 1/4) (Wyckoff letter b). The solvent molecule is also located on a twofold rotation axis, but the axis is running along the [100] direction passing through the N5 and C9 atoms, which lie on the special positions of (*x*, 1/2, 0) (Wyckoff letter a). Because of the symmetry of the twofold rotation, the methyl group of the nitromethane molecule was modelled as disordered over two sites.

In the complex, the Mn^{II} ion is six-coordinated in a distorted octahedral environment defined by four N atoms of the two chelating 2,2′-bipyrimidine ligands and two Br^- anions, Table 1, which define a *cis*-Br_2N_4 donor set. The main contributions to the distortion are the tight N—Mn—N chelate angle and the Br—Br repulsion (N1—Mn1—$N3^a$ = 71.1 (2) ° and Br1—Mn1—$Br1^a$ = 98.66 (5) °; symmetry code a: -*x*, *y*, 1/2 - *z*), which result in non-linear *trans* axes (<N3—Mn1—$Br1^a$ = 163.6 (1) ° and <N1—Mn1—$N1^a$ = 158.0 (2) °). The Mn—N bond lengths are almost equivalent (Table 1) and the dihedral angle between the least-squares planes of the two bpym ligands is 73.05 (7) °.

In the crystal structure, the complexes are stacked in columns along the *a* axis. When viewed down the *c* axis, the successive complexes are stacked in the opposite direction. In the columns, several inter- and intramolecular π-π interactions between adjacent pyrimidine rings are present. The shortest distance between *Cg*1 (the centroid of ring N1—C4) and $Cg2^i$ (ring N3—C8, symmetry code i: 1/2 - *x*, 1/2 + *y*, 1/2 - *z*) is 4.411 (3) Å, and the dihedral angle between the ring planes is 4.7 (3) °. Moreover, there are intra- and inter-molecular C—H···Br and C—H···N contacts with d(C···Br) = 3.542 (6)–3.802 (6) Å, and d(C···N) = 3.430 (5) Å (Fig. 2, Table 2).

S2. Experimental

To a solution of $MnBr_2.4H_2O$ (0.2867 g, 1.000 mmol) in EtOH (30 ml) was added 2,2′-bipyrimidine (0.1584 g, 1.002 mmol) followed by stirring for 3 h. The precipitate was separated by filtration, washed with EtOH and dried at 323 K to give a yellow powder (0.3441 g). Crystals suitable for X-ray analysis were obtained by slow evaporation from a CH_3NO_2 solution.

S3. Refinement

H atoms were positioned geometrically and allowed to ride on their respective parent atoms [C—H = 0.95 Å (CH) or 0.98 Å (CH_3), and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C)]. The H atoms of the methyl group of the nitromethane solvent molecule were modelled as disordered over two sites rotated by 60° from one another, with an occupancy ratio of

0.5:0.5.

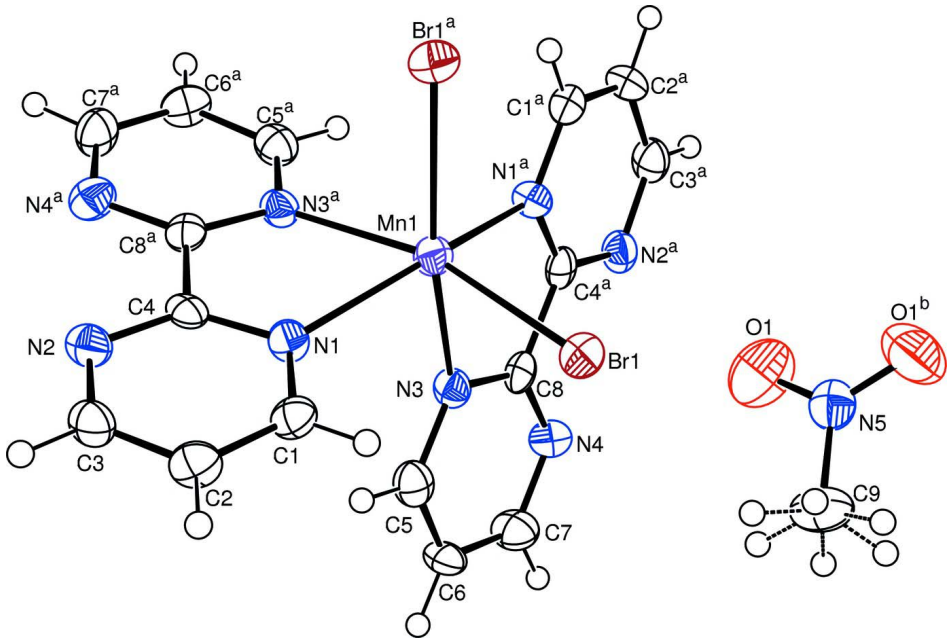

Figure 1

Molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level for non-H atoms [Symmetry codes: (*a*) -*x*, *y*, 1/2 - *z*, (*b*) *x*, 1 - *y*, -*z*]. H atoms are shown as small circles of arbitrary radius and the bonds of the disordered methyl group are shown with dashed lines.

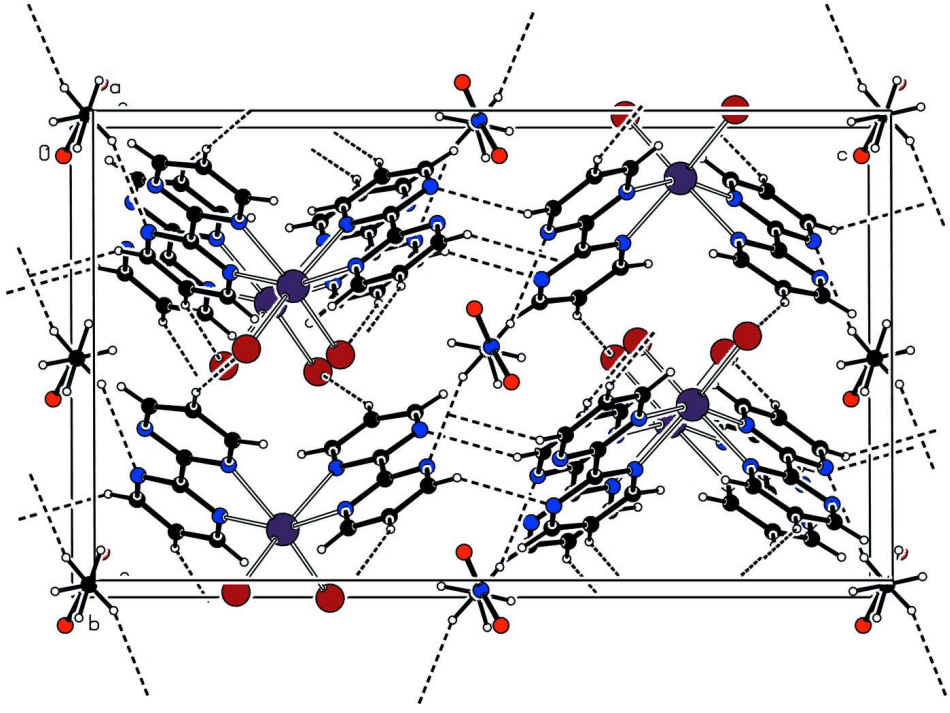

Figure 2

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

Bis(2,2′-bipyrimidine-κ^2N,N')dibromidomanganese(II) nitromethane monosolvate

Crystal data

$[MnBr_2(C_8H_6N_4)_2]\cdot CH_3NO_2$
$M_r = 592.14$
Orthorhombic, $C222_1$
Hall symbol: C 2c 2
$a = 8.3876$ (4) Å
$b = 12.1772$ (6) Å
$c = 20.7479$ (11) Å
$V = 2119.14$ (18) Å^3
$Z = 4$
$F(000) = 1164$
$D_x = 1.856$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2401 reflections
$\theta = 3.0$–$25.5°$
$\mu = 4.43$ mm^{-1}
$T = 200$ K
Block, yellow
0.17 × 0.10 × 0.07 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.825$, $T_{max} = 1.000$
7872 measured reflections
2608 independent reflections
1818 reflections with $I > 2\sigma(I)$
$R_{int} = 0.069$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.0°$
$h = -10 \rightarrow 11$
$k = -16 \rightarrow 15$
$l = -24 \rightarrow 27$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.078$
$S = 1.02$
2608 reflections
143 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
$w = 1/[\sigma^2(F_o^2) + (0.010P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.87$ e Å^{-3}
$\Delta\rho_{min} = -0.86$ e Å^{-3}
Absolute structure: Flack (1983), 1121 Friedel pairs
Absolute structure parameter: −0.003 (16)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Br1	0.17577 (6)	0.51358 (4)	0.18610 (3)	0.03361 (16)	
Mn1	0.0000	0.37369 (10)	0.2500	0.0262 (3)	
N1	0.1984 (5)	0.3378 (3)	0.3230 (2)	0.0258 (11)	

N2	0.2612 (6)	0.2496 (4)	0.4234 (2)	0.0306 (12)	
N3	0.0862 (5)	0.2392 (4)	0.1799 (3)	0.0261 (10)	
N4	0.0382 (6)	0.1601 (4)	0.0767 (2)	0.0341 (13)	
C1	0.3439 (6)	0.3827 (4)	0.3225 (3)	0.0288 (12)	
H1	0.3728	0.4299	0.2880	0.035*	
C2	0.4533 (6)	0.3625 (5)	0.3707 (3)	0.0323 (15)	
H2	0.5572	0.3935	0.3694	0.039*	
C3	0.4059 (7)	0.2952 (5)	0.4210 (3)	0.0331 (16)	
H3	0.4789	0.2809	0.4550	0.040*	
C4	0.1658 (7)	0.2722 (4)	0.3736 (3)	0.0246 (12)	
C5	0.2306 (6)	0.1925 (4)	0.1809 (3)	0.0324 (14)	
H5	0.2971	0.2028	0.2175	0.039*	
C6	0.2853 (6)	0.1295 (5)	0.1300 (3)	0.0332 (15)	
H6	0.3876	0.0960	0.1308	0.040*	
C7	0.1849 (8)	0.1177 (5)	0.0783 (3)	0.0373 (14)	
H7	0.2214	0.0775	0.0420	0.045*	
C8	−0.0027 (7)	0.2208 (4)	0.1271 (3)	0.0255 (12)	
O1	−0.0029 (7)	0.4220 (4)	0.0230 (2)	0.0712 (16)	
N5	0.0678 (8)	0.5000	0.0000	0.0372 (18)	
C9	0.2426 (8)	0.5000	0.0000	0.046 (3)	
H9A	0.2815	0.4843	0.0436	0.069*	0.50
H9B	0.2815	0.5721	−0.0138	0.069*	0.50
H9C	0.2815	0.4435	−0.0297	0.069*	0.50

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0310 (3)	0.0361 (3)	0.0337 (3)	−0.0004 (3)	0.0036 (3)	0.0056 (3)
Mn1	0.0250 (6)	0.0294 (7)	0.0240 (7)	0.000	−0.0007 (6)	0.000
N1	0.024 (2)	0.025 (2)	0.028 (3)	−0.002 (2)	−0.002 (2)	0.002 (2)
N2	0.028 (3)	0.036 (3)	0.028 (3)	0.003 (2)	−0.004 (2)	−0.007 (3)
N3	0.023 (2)	0.030 (2)	0.025 (3)	−0.0023 (19)	−0.004 (2)	0.002 (2)
N4	0.031 (3)	0.038 (3)	0.034 (3)	0.004 (2)	0.005 (2)	0.000 (3)
C1	0.030 (3)	0.032 (3)	0.025 (3)	0.000 (3)	0.002 (3)	−0.004 (3)
C2	0.024 (3)	0.035 (4)	0.038 (4)	−0.009 (3)	−0.001 (3)	−0.002 (3)
C3	0.030 (4)	0.041 (4)	0.028 (4)	0.004 (3)	−0.007 (3)	−0.005 (3)
C4	0.025 (3)	0.025 (3)	0.024 (3)	0.009 (3)	−0.002 (3)	−0.008 (2)
C5	0.034 (3)	0.030 (3)	0.033 (4)	−0.003 (3)	−0.003 (3)	0.004 (3)
C6	0.027 (3)	0.031 (3)	0.042 (4)	0.011 (3)	0.006 (3)	0.004 (3)
C7	0.037 (4)	0.039 (4)	0.036 (4)	0.006 (4)	0.003 (3)	−0.009 (3)
C8	0.033 (3)	0.021 (3)	0.022 (3)	−0.004 (3)	0.002 (3)	0.006 (2)
O1	0.070 (3)	0.066 (4)	0.077 (4)	−0.027 (3)	0.007 (3)	0.002 (3)
N5	0.046 (5)	0.033 (5)	0.032 (5)	0.000	0.000	−0.003 (4)
C9	0.032 (4)	0.065 (7)	0.040 (6)	0.000	0.000	−0.017 (6)

Geometric parameters (Å, º)

Mn1—Br1	2.6140 (9)	C2—C3	1.386 (8)
Mn1—N1^{i}	2.292 (5)	C2—H2	0.9500
Mn1—N1	2.292 (5)	C3—H3	0.9500
Mn1—N3	2.306 (5)	C4—C8^{i}	1.505 (8)
Mn1—N3^{i}	2.306 (5)	C5—C6	1.385 (8)
Mn1—Br1^{i}	2.6140 (9)	C5—H5	0.9500
N1—C1	1.338 (6)	C6—C7	1.370 (8)
N1—C4	1.347 (7)	C6—H6	0.9500
N2—C3	1.336 (6)	C7—H7	0.9500
N2—C4	1.336 (7)	C8—C4^{i}	1.505 (8)
N3—C5	1.338 (6)	O1—N5	1.217 (5)
N3—C8	1.344 (7)	N5—O1^{ii}	1.217 (5)
N4—C8	1.326 (7)	N5—C9	1.466 (9)
N4—C7	1.334 (7)	C9—H9A	0.9800
C1—C2	1.379 (7)	C9—H9B	0.9800
C1—H1	0.9500	C9—H9C	0.9800
N1^{i}—Mn1—N1	158.0 (2)	C3—C2—H2	121.3
N1^{i}—Mn1—N3	71.06 (16)	N2—C3—C2	122.3 (6)
N1—Mn1—N3	93.09 (15)	N2—C3—H3	118.8
N1^{i}—Mn1—N3^{i}	93.09 (15)	C2—C3—H3	118.8
N1—Mn1—N3^{i}	71.06 (16)	N2—C4—N1	127.2 (5)
N3—Mn1—N3^{i}	89.5 (2)	N2—C4—C8^{i}	117.8 (5)
N1^{i}—Mn1—Br1	101.45 (11)	N1—C4—C8^{i}	115.1 (5)
N1—Mn1—Br1	92.87 (11)	N3—C5—C6	121.6 (6)
N3—Mn1—Br1	88.07 (11)	N3—C5—H5	119.2
N3^{i}—Mn1—Br1	163.59 (10)	C6—C5—H5	119.2
N1^{i}—Mn1—Br1^{i}	92.87 (11)	C7—C6—C5	116.8 (5)
N1—Mn1—Br1^{i}	101.45 (11)	C7—C6—H6	121.6
N3—Mn1—Br1^{i}	163.59 (10)	C5—C6—H6	121.6
N3^{i}—Mn1—Br1^{i}	88.07 (11)	N4—C7—C6	123.1 (6)
Br1—Mn1—Br1^{i}	98.66 (5)	N4—C7—H7	118.4
C1—N1—C4	115.6 (5)	C6—C7—H7	118.4
C1—N1—Mn1	125.4 (4)	N4—C8—N3	126.3 (6)
C4—N1—Mn1	118.7 (4)	N4—C8—C4^{i}	117.4 (5)
C3—N2—C4	115.4 (5)	N3—C8—C4^{i}	116.2 (5)
C5—N3—C8	116.3 (5)	O1—N5—O1^{ii}	121.6 (8)
C5—N3—Mn1	125.1 (4)	O1—N5—C9	119.2 (4)
C8—N3—Mn1	117.3 (4)	O1^{ii}—N5—C9	119.2 (4)
C8—N4—C7	115.7 (5)	N5—C9—H9A	109.5
N1—C1—C2	122.0 (5)	N5—C9—H9B	109.5
N1—C1—H1	119.0	H9A—C9—H9B	109.5
C2—C1—H1	119.0	N5—C9—H9C	109.5
C1—C2—C3	117.4 (5)	H9A—C9—H9C	109.5
C1—C2—H2	121.3	H9B—C9—H9C	109.5

N1^{i}—Mn1—N1—C1	130.5 (4)	Mn1—N1—C1—C2	175.5 (4)
N3—Mn1—N1—C1	87.8 (4)	N1—C1—C2—C3	−1.4 (8)
N3^{i}—Mn1—N1—C1	176.2 (4)	C4—N2—C3—C2	0.8 (8)
Br1—Mn1—N1—C1	−0.4 (4)	C1—C2—C3—N2	0.8 (9)
Br1^{i}—Mn1—N1—C1	−99.9 (4)	C3—N2—C4—N1	−2.1 (8)
N1^{i}—Mn1—N1—C4	−54.4 (4)	C3—N2—C4—C8^{i}	178.5 (5)
N3—Mn1—N1—C4	−97.1 (4)	C1—N1—C4—N2	1.6 (8)
N3^{i}—Mn1—N1—C4	−8.7 (4)	Mn1—N1—C4—N2	−174.0 (4)
Br1—Mn1—N1—C4	174.7 (4)	C1—N1—C4—C8^{i}	−179.0 (4)
Br1^{i}—Mn1—N1—C4	75.3 (4)	Mn1—N1—C4—C8^{i}	5.4 (6)
N1^{i}—Mn1—N3—C5	178.2 (5)	C8—N3—C5—C6	0.5 (7)
N1—Mn1—N3—C5	−17.4 (4)	Mn1—N3—C5—C6	−166.5 (4)
N3^{i}—Mn1—N3—C5	−88.4 (5)	N3—C5—C6—C7	0.3 (8)
Br1—Mn1—N3—C5	75.4 (4)	C8—N4—C7—C6	3.8 (9)
Br1^{i}—Mn1—N3—C5	−169.8 (3)	C5—C6—C7—N4	−2.6 (9)
N1^{i}—Mn1—N3—C8	11.3 (4)	C7—N4—C8—N3	−3.0 (9)
N1—Mn1—N3—C8	175.7 (4)	C7—N4—C8—C4^{i}	178.6 (5)
N3^{i}—Mn1—N3—C8	104.7 (4)	C5—N3—C8—N4	0.9 (8)
Br1—Mn1—N3—C8	−91.5 (4)	Mn1—N3—C8—N4	168.9 (4)
Br1^{i}—Mn1—N3—C8	23.3 (7)	C5—N3—C8—C4^{i}	179.3 (4)
C4—N1—C1—C2	0.3 (7)	Mn1—N3—C8—C4^{i}	−12.7 (6)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···Br1	0.95	2.87	3.542 (6)	129
C2—H2···Br1^{iii}	0.95	2.91	3.802 (6)	156
C6—H6···Br1^{iv}	0.95	2.86	3.752 (5)	157
C9—H9*C*···N2^{v}	0.98	2.57	3.430 (5)	147

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