Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

Kwang Ha

School of Applied Chemical Engineering, The Research Institute of Catalysis, Chonnam National University, Gwangju 500-757, Republic of Korea
Correspondence e-mail: hakwang@chonnam.ac.kr

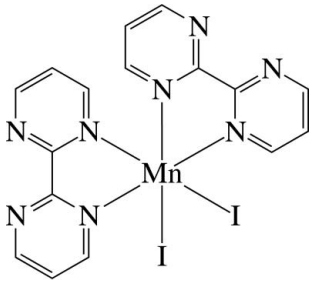
Received 25 November 2011; accepted 25 November 2011

Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.006 Å; R factor = 0.027; wR factor = 0.064; data-to-parameter ratio = 20.1.

The asymmetric unit of the title complex, $[MnI_2(C_8H_6N_4)_2]$, contains one half of a neutral Mn^{II} complex, with the entire molecule completed by the application of twofold symmetry. The Mn^{II} ion is six-coordinated in a distorted octahedral environment defined by four N atoms of the two chelating 2,2′-bipyrimidine (bpym) ligands and two I^- anions in a *cis*-N_4I_2 coordination geometry. The dihedral angle between the least-squares planes of the two bpym ligands (r.m.s deviation for all non-H atoms = 0.063 Å) is 85.04 (6)°. In the crystal, complex molecules are connected by C—H···N and C—H···I hydrogen bonds, forming a three-dimensional network. Molecules are stacked in columns along the *a* axis. Along the *c* axis, successive molecules stack in the opposite directions.

Related literature

For related crystal structures of $[MnI(bpym)_2(H_2O)]I\cdot xH_2O$ (x = 2, 1), see: Ha (2011*a*,*b*).



Experimental

Crystal data

$[MnI_2(C_8H_6N_4)_2]$
M_r = 625.08
Monoclinic, $C2/c$
a = 8.2841 (4) Å
b = 13.8442 (7) Å
c = 17.8243 (9) Å
β = 97.822 (1)°
V = 2025.19 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.72 mm^{-1}
T = 200 K
0.34 × 0.22 × 0.17 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.863, T_{max} = 1.000
7130 measured reflections
2477 independent reflections
1923 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.064
S = 1.10
2477 reflections
123 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.94 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—N4	2.289 (3)	Mn1—I1	2.8410 (5)
Mn1—N1	2.305 (3)		
N4^{i}—Mn1—N1	71.78 (10)	I1—Mn1—I1^{i}	104.19 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···N3^{ii}	0.95	2.60	3.151 (5)	117
C6—H6···N2^{iii}	0.95	2.62	3.554 (5)	166
C7—H7···I1^{iv}	0.95	2.97	3.917 (4)	173

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

This work was supported by the Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010–0029626).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5729).

References

Bruker (2000). *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Ha, K. (2011*a*). *Acta Cryst.* E**67**, m1414.
Ha, K. (2011*b*). *Acta Cryst.* E**67**, m1453.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2012). E**68**, m1 [doi:10.1107/S160053681105080X]

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

Kwang Ha

S1. Comment

The asymmetric unit of the title complex, [$MnI_2(bpym)_2$] (bpym = 2,2′-bipyrimidine, $C_8H_6N_4$), contains one half of a neutral Mn^{II} complex (Fig. 1). The complex is disposed about a twofold rotation axis running in the [010] direction passing through the Mn1 atom. The Mn^{II} ion is six-coordinated in a distorted octahedral environment defined by four N atoms of the two chelating bpym ligands and two I^- anions in a *cis*-N_4I_2 coordination geometry. The structure is quite different from the previously reported complexes [$MnI(bpym)_2(H_2O)$]I.xH_2O obtained from a methanol (x = 2; Ha, 2011*a*) or a 2-butanone solution (x = 1; Ha, 2011*b*) of the same reaction product, in which two bpym ligands, an I^- anion and a water ligand are coordinated to the Mn^{II} ion, respectively.

The tight N—Mn—N chelating angles and I—I repelling (Table 1) contribute the distortion of ocataheron, which results in non-linear *trans* axes (<N1—Mn1—N1^i = 156.60 (15)° and <I1—Mn1—N4 = 164.40 (8)°; symmetry code i: 1 - x, y, 1/2 - z). Because the Mn—N bond lengths are nearly equivalent (Table 1), the different *trans* effects of the I and N atoms cannot be observed reliably. The dihedral angle between the least-squares planes of the two bpym ligands [maximum deviation = 0.098 (3) Å] is 85.04 (6)°. In the crystal, the complex molecules are connected by intermolecular C—H···N and C—H···I hydrogen bonds, forming a three-dimensional network (Fig. 2, Table 2). Molecules are stacked in columns along the *a* axis. When viewed down the *c* axis, successive molecules stack in the opposite directions. In the columns, several inter- and intramolecular π-π interactions between adjacent pyrimidine rings are present, the shortest ring centroid-centroid distance being 3.853 (2) Å.

S2. Experimental

To a solution of 2,2′-bipyrimidine (0.1587 g, 1.003 mmol) in acetone (40 ml) was added MnI_2 (0.1540 g, 0.499 mmol) and refluxed for 3 h. The formed precipitate was separated by filtration, washed with acetone and dried at 50 °C, to give a yellow powder (0.0701 g). Crystals suitable for X-ray analysis were obtained by slow evaporation from a dimethyl sulfoxide (DMSO) solution at 90 °C.

S3. Refinement

H atoms were positioned geometrically and allowed to ride on their respective parent atoms [C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C)]. The highest peak (0.94 e Å^{-3}) and the deepest hole (-0.50 e Å^{-3}) in the difference Fourier map are located 1.35 Å and 0.83 Å from the atoms N3 and C2, respectively.

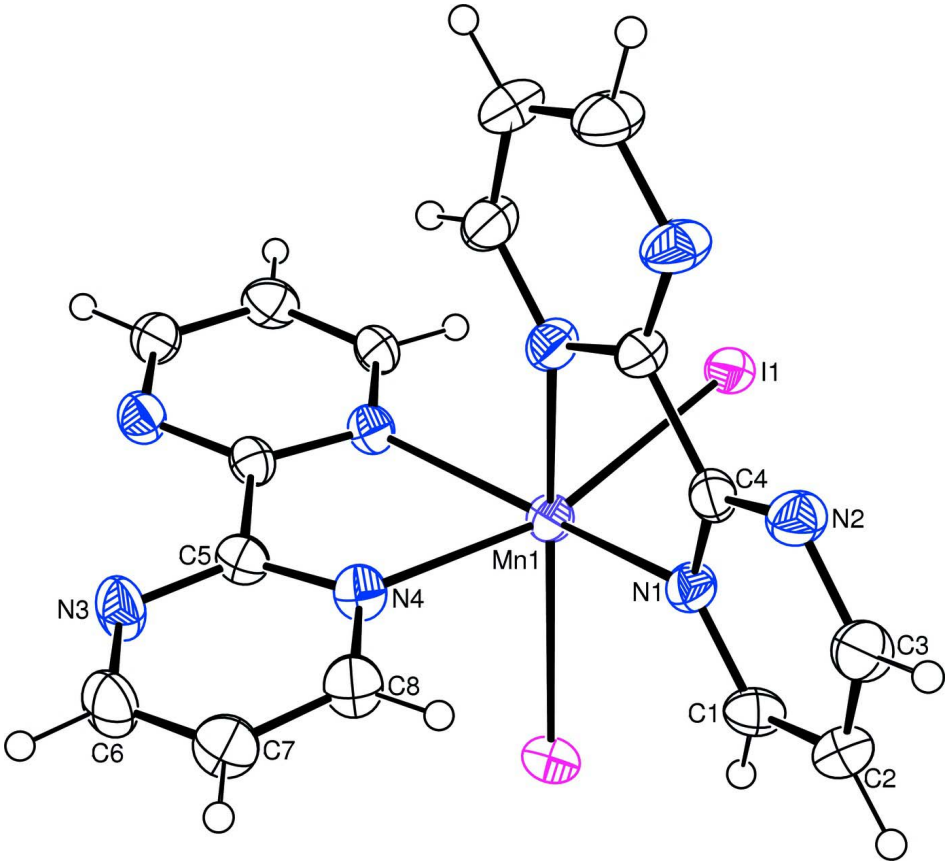


Figure 1

The structure of the title complex, with displacement ellipsoids drawn at the 40% probability level for non-H atoms. Unlabelled atoms are related to the reference atoms by the (1 - *x*, *y*, 1/2 - *z*) symmetry transformation.

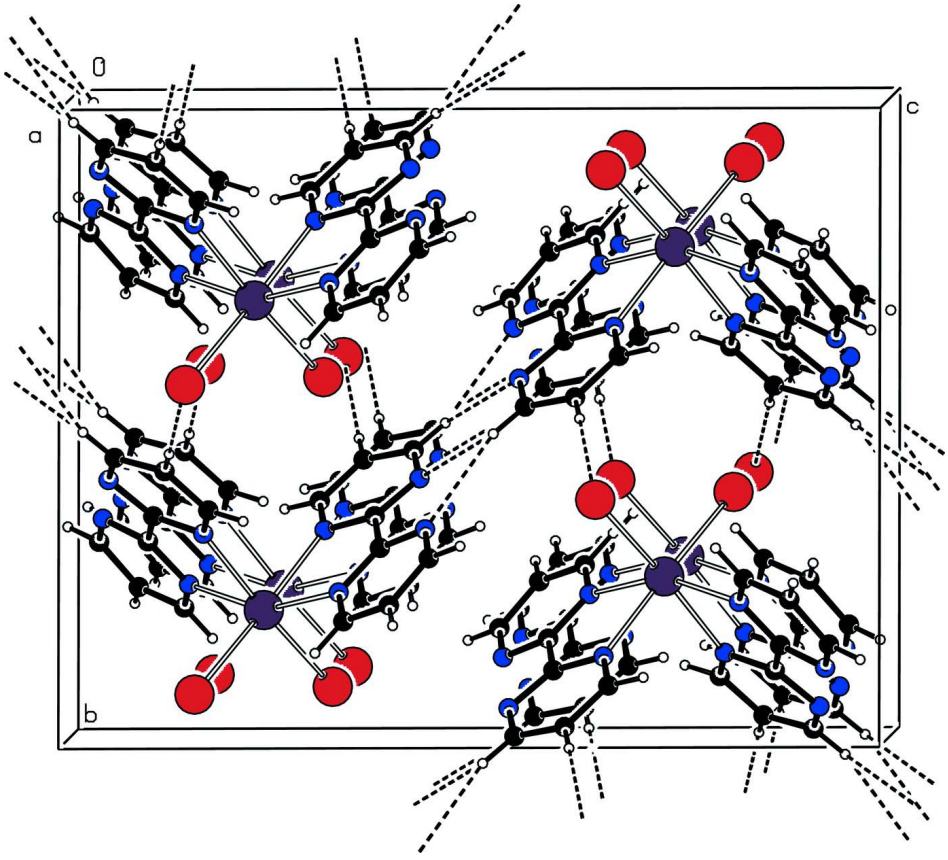


Figure 2

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

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

Crystal data

$[MnI_2(C_8H_6N_4)_2]$
M_r = 625.08
Monoclinic, $C2/c$
Hall symbol: -C 2yc
a = 8.2841 (4) Å
b = 13.8442 (7) Å
c = 17.8243 (9) Å
β = 97.822 (1)°
V = 2025.19 (17) Å^3
Z = 4
$F(000)$ = 1180
D_x = 2.050 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3917 reflections
θ = 2.9–28.1°
μ = 3.72 mm^{-1}
T = 200 K
Block, yellow
0.34 × 0.22 × 0.17 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} = 0.863, T_{max} = 1.000
7130 measured reflections
2477 independent reflections
1923 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 28.3°, θ_{min} = 2.3°
$h = -10 \rightarrow 11$
$k = -18 \rightarrow 18$
$l = -23 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.064$
$S = 1.10$
2477 reflections
123 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
$w = 1/[\sigma^2(F_o^2) + (0.0197P)^2 + 5.0272P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.94$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ 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	0.28328 (5)	0.2500	0.03038 (18)
I1	0.68736 (3)	0.409360 (18)	0.170347 (15)	0.03768 (9)
N1	0.2923 (4)	0.2495 (2)	0.15380 (16)	0.0316 (7)
N2	0.2149 (4)	0.1486 (2)	0.04676 (18)	0.0372 (7)
N3	0.4761 (4)	0.0785 (2)	0.4388 (2)	0.0444 (9)
N4	0.4157 (4)	0.1610 (2)	0.32184 (18)	0.0349 (7)
C1	0.1449 (5)	0.2901 (3)	0.1444 (2)	0.0359 (8)
H1	0.1204	0.3392	0.1783	0.043*
C2	0.0271 (5)	0.2616 (3)	0.0861 (2)	0.0421 (10)
H2	−0.0780	0.2903	0.0789	0.051*
C3	0.0689 (5)	0.1895 (3)	0.0387 (2)	0.0408 (9)
H3	−0.0105	0.1682	−0.0013	0.049*
C4	0.3207 (4)	0.1809 (2)	0.10433 (19)	0.0302 (8)
C5	0.5128 (4)	0.1365 (3)	0.3852 (2)	0.0322 (8)
C6	0.3261 (5)	0.0392 (3)	0.4279 (3)	0.0478 (11)
H6	0.2938	−0.0021	0.4657	0.057*
C7	0.2193 (5)	0.0569 (3)	0.3644 (2)	0.0448 (10)
H7	0.1152	0.0271	0.3563	0.054*
C8	0.2688 (5)	0.1201 (3)	0.3123 (2)	0.0411 (9)
H8	0.1956	0.1349	0.2680	0.049*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0302 (4)	0.0301 (4)	0.0306 (4)	0.000	0.0034 (3)	0.000

I1	0.03561 (15)	0.03743 (15)	0.04207 (16)	0.00468 (11)	0.01272 (11)	0.00650 (11)
N1	0.0328 (16)	0.0308 (16)	0.0310 (16)	0.0042 (13)	0.0041 (13)	−0.0004 (13)
N2	0.0335 (17)	0.0430 (18)	0.0345 (18)	0.0038 (14)	0.0031 (14)	−0.0054 (14)
N3	0.0395 (19)	0.049 (2)	0.044 (2)	−0.0127 (16)	0.0022 (16)	0.0159 (16)
N4	0.0351 (17)	0.0333 (16)	0.0356 (18)	−0.0060 (14)	0.0023 (14)	−0.0003 (14)
C1	0.035 (2)	0.036 (2)	0.038 (2)	0.0031 (17)	0.0107 (16)	−0.0092 (17)
C2	0.030 (2)	0.051 (2)	0.045 (2)	0.0079 (18)	0.0051 (17)	0.003 (2)
C3	0.035 (2)	0.051 (2)	0.035 (2)	−0.0030 (18)	0.0010 (17)	−0.0035 (18)
C4	0.036 (2)	0.0299 (18)	0.0252 (18)	0.0017 (15)	0.0047 (15)	0.0020 (15)
C5	0.0315 (19)	0.0300 (18)	0.036 (2)	−0.0062 (15)	0.0064 (16)	−0.0026 (16)
C6	0.048 (3)	0.045 (2)	0.051 (3)	−0.013 (2)	0.009 (2)	0.013 (2)
C7	0.035 (2)	0.042 (2)	0.056 (3)	−0.0135 (18)	0.004 (2)	0.001 (2)
C8	0.038 (2)	0.042 (2)	0.042 (2)	−0.0096 (18)	−0.0002 (18)	0.0008 (18)

Geometric parameters (Å, º)

Mn1—N4^{i}	2.289 (3)	N4—C5	1.338 (5)
Mn1—N4	2.289 (3)	C1—C2	1.383 (5)
Mn1—N1	2.305 (3)	C1—H1	0.9500
Mn1—N1^{i}	2.305 (3)	C2—C3	1.381 (6)
Mn1—I1	2.8410 (5)	C2—H2	0.9500
Mn1—I1^{i}	2.8410 (5)	C3—H3	0.9500
N1—C1	1.334 (5)	C4—C5^{i}	1.498 (5)
N1—C4	1.339 (4)	C5—C4^{i}	1.498 (5)
N2—C3	1.325 (5)	C6—C7	1.361 (6)
N2—C4	1.332 (5)	C6—H6	0.9500
N3—C5	1.315 (5)	C7—C8	1.378 (6)
N3—C6	1.347 (5)	C7—H7	0.9500
N4—C8	1.332 (5)	C8—H8	0.9500
N4^{i}—Mn1—N4	84.55 (16)	N1—C1—H1	119.5
N4^{i}—Mn1—N1	71.78 (10)	C2—C1—H1	119.5
N4—Mn1—N1	90.72 (11)	C3—C2—C1	117.1 (4)
N4^{i}—Mn1—N1^{i}	90.72 (11)	C3—C2—H2	121.4
N4—Mn1—N1^{i}	71.78 (10)	C1—C2—H2	121.4
N1—Mn1—N1^{i}	156.60 (15)	N2—C3—C2	122.9 (4)
N4^{i}—Mn1—I1	86.90 (8)	N2—C3—H3	118.5
N4—Mn1—I1	164.40 (8)	C2—C3—H3	118.5
N1—Mn1—I1	98.98 (7)	N2—C4—N1	126.1 (3)
N1^{i}—Mn1—I1	95.35 (7)	N2—C4—C5^{i}	117.2 (3)
N4^{i}—Mn1—I1^{i}	164.40 (8)	N1—C4—C5^{i}	116.7 (3)
N4—Mn1—I1^{i}	86.90 (8)	N3—C5—N4	126.6 (3)
N1—Mn1—I1^{i}	95.35 (7)	N3—C5—C4^{i}	117.4 (3)
N1^{i}—Mn1—I1^{i}	98.98 (7)	N4—C5—C4^{i}	116.0 (3)
I1—Mn1—I1^{i}	104.19 (3)	N3—C6—C7	122.0 (4)
C1—N1—C4	117.1 (3)	N3—C6—H6	119.0
C1—N1—Mn1	125.8 (2)	C7—C6—H6	119.0
C4—N1—Mn1	117.0 (2)	C6—C7—C8	117.2 (4)

C3—N2—C4	115.8 (3)	C6—C7—H7	121.4
C5—N3—C6	116.2 (3)	C8—C7—H7	121.4
C8—N4—C5	115.7 (3)	N4—C8—C7	122.2 (4)
C8—N4—Mn1	125.9 (3)	N4—C8—H8	118.9
C5—N4—Mn1	117.7 (2)	C7—C8—H8	118.9
N1—C1—C2	120.9 (3)		

N4^{i}—Mn1—N1—C1	176.2 (3)	Mn1—N1—C1—C2	−177.5 (3)
N4—Mn1—N1—C1	92.1 (3)	N1—C1—C2—C3	0.3 (6)
N1^{i}—Mn1—N1—C1	132.8 (3)	C4—N2—C3—C2	0.5 (6)
I1—Mn1—N1—C1	−100.1 (3)	C1—C2—C3—N2	−0.7 (6)
I1^{i}—Mn1—N1—C1	5.2 (3)	C3—N2—C4—N1	0.1 (6)
N4^{i}—Mn1—N1—C4	−1.6 (2)	C3—N2—C4—C5^{i}	−179.7 (3)
N4—Mn1—N1—C4	−85.6 (3)	C1—N1—C4—N2	−0.5 (5)
N1^{i}—Mn1—N1—C4	−44.9 (2)	Mn1—N1—C4—N2	177.4 (3)
I1—Mn1—N1—C4	82.1 (2)	C1—N1—C4—C5^{i}	179.4 (3)
I1^{i}—Mn1—N1—C4	−172.6 (2)	Mn1—N1—C4—C5^{i}	−2.7 (4)
N4^{i}—Mn1—N4—C8	−90.9 (3)	C6—N3—C5—N4	0.8 (6)
N1—Mn1—N4—C8	−19.2 (3)	C6—N3—C5—C4^{i}	−179.7 (4)
N1^{i}—Mn1—N4—C8	176.6 (3)	C8—N4—C5—N3	−1.6 (6)
I1—Mn1—N4—C8	−148.0 (3)	Mn1—N4—C5—N3	169.7 (3)
I1^{i}—Mn1—N4—C8	76.1 (3)	C8—N4—C5—C4^{i}	178.9 (3)
N4^{i}—Mn1—N4—C5	98.8 (3)	Mn1—N4—C5—C4^{i}	−9.8 (4)
N1—Mn1—N4—C5	170.5 (3)	C5—N3—C6—C7	1.2 (7)
N1^{i}—Mn1—N4—C5	6.3 (3)	N3—C6—C7—C8	−2.3 (7)
I1—Mn1—N4—C5	41.8 (5)	C5—N4—C8—C7	0.3 (6)
I1^{i}—Mn1—N4—C5	−94.2 (3)	Mn1—N4—C8—C7	−170.1 (3)
C4—N1—C1—C2	0.2 (5)	C6—C7—C8—N4	1.5 (7)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···N3^{ii}	0.95	2.60	3.151 (5)	117
C6—H6···N2^{iii}	0.95	2.62	3.554 (5)	166
C7—H7···I1^{iv}	0.95	2.97	3.917 (4)	173

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