

trans-Dibromidotetrakis(5-methyl-1*H*-pyrazole- κN^2)manganese(II)

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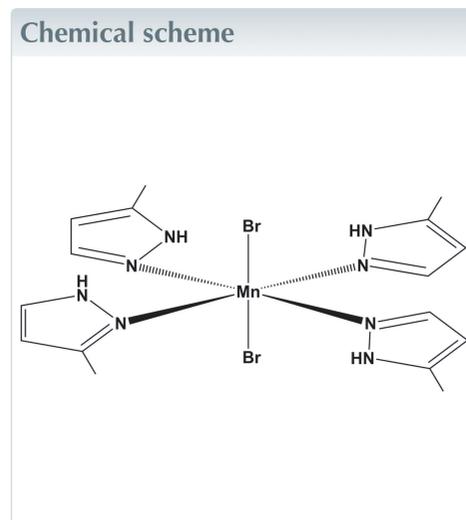
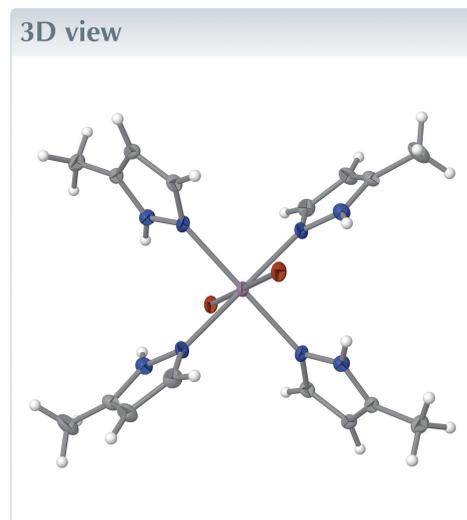
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Keywords: manganese; coordination compound; crystal structure; heteroleptic complex; herringbone pattern; polymorphism.

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Structural data: full structural data are available from iucrdata.iucr.org

The title compound, *trans*-dibromidotetrakis(5-methyl-1*H*-pyrazole- κN^2)manganese(II), [MnBr₂(C₄H₆N₂)₄] or [Mn(3-MePzH)₄Br₂] (**1**) crystallizes in the triclinic $P\bar{1}$ space group with the cell parameters $a = 7.6288$ (3), $b = 8.7530$ (4), $c = 9.3794$ (4) Å and $\alpha = 90.707$ (4), $\beta = 106.138$ (4), $\gamma = 114.285$ (5)°, $V = 542.62$ (5) Å³, $T = 120$ K. The asymmetric unit contains only half the molecule with the manganese atom is situated on a crystallographic inversion center. The 3-MePzH ligands are present in an *AABB* type manner with two methyl groups pointing up and the other two down. The supramolecular architecture is characterized by several intermolecular C—H...N, N—H...Br, and C—H... π interactions. Earlier, a polymorphic structure of [Mn(3-MePzH)₄Br₂] (**2**) with a similar geometry and also an *AABB* arrangement for the pyrazole ligands was described [Reedijk *et al.* (1971). *Inorg. Chem.* **10**, 2594–2599; $a = 8.802$ (6), $b = 9.695$ (5), $c = 7.613$ (8) Å and $\alpha = 105.12$ (4), $\beta = 114.98$ (4), $\gamma = 92.90$ (3)°, $V = 558.826$ (5) Å³, $T = 295$ K]. A varying supramolecular pattern was reported, with the structure of **1** featuring a herringbone type pattern while that of structure **2** shows a pillared network type of arrangement along the a axis. A nickel complex [Ni(3-MePzH)₄Br₂] isomorphous to **1** and the analogous chloro derivatives of Fe^{II}, Co^{II} and Cu^{II} are also known.



Structure description

Earth-abundant transition metals such as manganese have received much attention owing to their numerous applications in biological, industrial, and material sciences (Constable *et al.*, 2021; Rice *et al.*, 2017; Zhang *et al.*, 2007; Dell, 2000). Apart from these applications, several mixed-valent multinuclear manganese cages have been assembled to understand their single molecular magnetism (SMM) behavior (Zabala-Lekuona *et al.*,

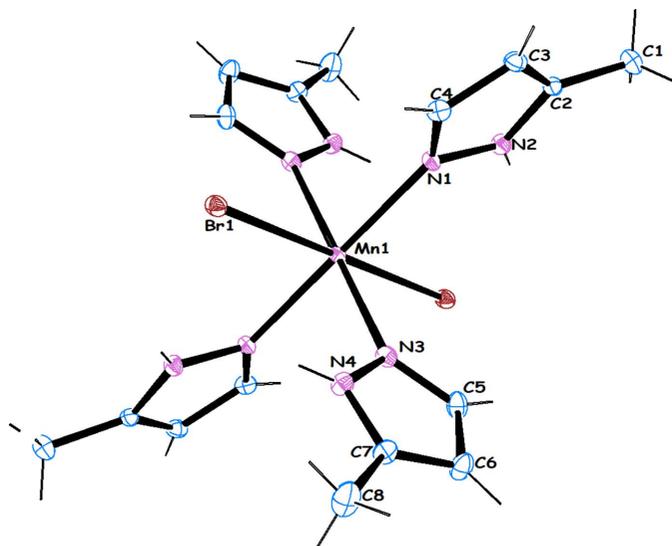


Figure 1
The molecular structure of the title compound **1** with 50% probability displacement ellipsoids. The unlabeled atoms are related by symmetry.

2021). In addition, the famous Jacobson catalyst consisting of an Mn^{II}–salen complex was developed for the enantioselective epoxidation of alkenes (Zhang *et al.*, 1990) while Mn^I carbonyls containing imidazolyl-based ligands have been used for the electrocatalytic-disproportionation of CO₂ (Myren *et al.*, 2020). Likewise, many Mn^I carbonyls containing various *N*-heterocyclic ligands were developed as biomimicking models for hydrogenase enzymes (Xu *et al.*, 2016; Pan *et al.*, 2020.) and as CO-releasing molecules (Mann, 2012; Cheng & Hu, 2021). Pyrazoles are one of the important classes of organic ligands used in many facets of coordination and organometallic chemistry (Trofimenko, 1972; Halcrow, 2009).

We aim to synthesize various CO-releasing molecules of the manganese family containing pyrazoles as primary ligands. In one such an attempt, a simple room-temperature stirring reaction involving the combination of Mn(CO)₅Br, 5-methyl-1*H*-pyrazole and triethylamine base (1:2:4) was found to release all CO molecules and afforded yellow-colored crystals suitable for single-crystal X-ray diffraction analysis (SCXRD) from a dichloromethane-ethanol mixture (1:1) in quantitative yield. The SCXRD analysis reveals that it is *trans*-dibromo tetrakis(5-methyl-1*H*-pyrazole-*κ*²*N*)manganese(II) (**1**). In other words, Mn^I was oxidized *in situ* to Mn^{II} and an octahedral heteroleptic complex containing two bromo ligands *trans* to each other in the axial position and four neutral 5-methyl-1*H*-pyrazoles in the equatorial position was obtained (Fig. 1). The asymmetric unit contains half the molecule with the manganese atom located on a crystallographic inversion center. The 3-MePzH ligands of the asymmetric unit are arranged in an *AABB* pattern with two neighboring pyrazole pointing upwards and the other two (their counterparts by inversion) downwards. The analysis reveals that it is a distorted octahedral complex with the axial distances to the larger bromine atoms [Mn1–Br1 = 2.7274 (3) Å] longer than the equatorial distances [Mn1–N1 = 2.251 (2) Å and Mn1–N3 = 2.261 (2) Å]. Angles at the manganese atom are

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

Cg1 and Cg2 are the centroids of the N1/N2/C2–C4 and N3/N4/ C5–C7 rings, respectively.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N2–H2···Br1	0.84 (3)	2.70 (3)	3.343 (2)	134 (2)
C1–H1C···Br1 ⁱ	0.98	3.11	3.951 (3)	145
N2–H2···Br1	0.84 (3)	2.70 (3)	3.343 (2)	134 (2)
N2–H2···Br1 ⁱ	0.84 (3)	3.05 (3)	3.704 (2)	137 (2)
N4–H7···Br1 ⁱⁱⁱ	0.80 (3)	3.00 (3)	3.636 (2)	138 (3)
N4–H7···Br1 ⁱⁱⁱ	0.80 (3)	2.76 (3)	3.351 (2)	132 (3)
C3–H3···N4 ^{iv}	0.95	2.76	3.659 (3)	158
C8–H8A···N2 ^v	0.98	2.86	3.744 (3)	151
C8–H8A···Cg1 ^v	0.98	2.61	3.586 (3)	173
C3–H3···Cg2 ^{vi}	0.95	2.84	3.667 (4)	146

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

close to 90° [N1–Mn1–Br1 = 89.10 (5)° and N3–Mn1–Br1 = 91.45 (5)°] and neighboring 3-MePzH rings are mutually perpendicular to each other with the dihedral angle between their planes being 87.08 (2)°.

Earlier, many transition-metal pyrazoles were reported (Reedijk *et al.*, 1971; Bieller *et al.*, 2006; Cotton *et al.*, 2002; Nelana *et al.*, 2004; Khan *et al.*, 2014; Al Isawi *et al.*, 2023). In particular, Reedijk *et al.* (1971) synthesized many of the first transition-metal 5-methyl-1*H*-pyrazole complexes, including a polymorphic form of the title compound [Mn(3-MePzH)₄Br₂] (**2**), which was synthesized using MnBr₂ and ethyl orthoformate as a dehydrating agent. It is interesting to note that the crystal data for compound **1** were collected at 120 K [$a = 7.6288$ (3), $b = 8.7530$ (4), $c = 9.3794$ (4) Å and $\alpha = 90.707$ (4), $\beta = 106.138$ (4), $\gamma = 114.285$ (5)°, $V = 542.62$ (5) Å³] while compound **2** data were collected at 295 K [$a = 8.802$ (6), $b = 9.695$ (5), $c = 7.613$ (8) Å and $\alpha = 105.12$ (4), $\beta = 114.98$ (4), $\gamma = 92.90$ (3)°, $V = 558.826$ (5) Å³]. A root-mean-square (r.m.s.) overlay of the molecules of **1** and **2** using Mercury 4.0 (Macrae *et al.*, 2020) is shown in Fig. 2 and reveals that in Reedijk’s polymorphic form, the 3-MePzH units are also placed in an

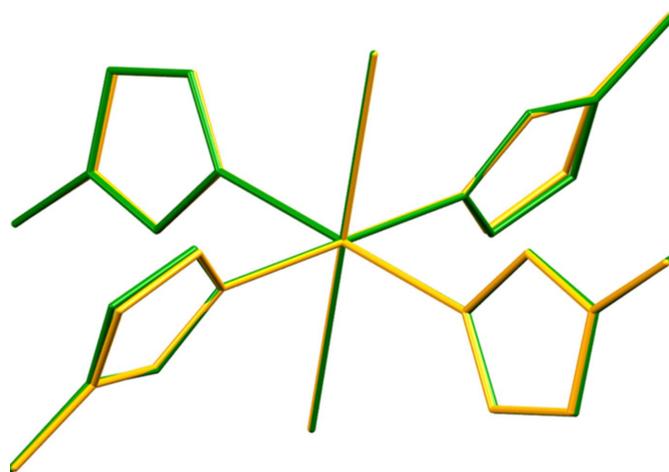


Figure 2
Overlay of the compounds **1** and **2** showing a slight deviation of 0.0612 Å (Mercury; Macrae *et al.*, 2020).

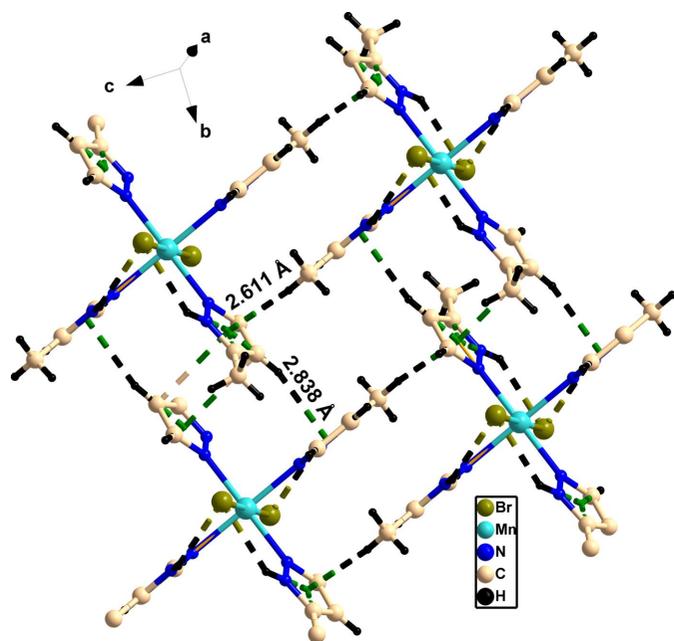


Figure 3
Perspective view of the supramolecular pattern of compound **1** showing the presence of intermolecular C–H··· π interactions.

AABB pattern with an r.m.s. deviation of 0.0612 Å. The analogous Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} bromo complexes isomorphous with Reedijk's polymorph **2** were reported (Cotton *et al.*, 2002; Nelana *et al.*, 2004; Khan *et al.*, 2014) and the bond parameters of **1** and **2** are both in good agreement with those reported structures. Interestingly, the Ni^{II} bromo complex (Nelana *et al.*, 2004) is isomorphous with compound **1**. It was synthesized using (1,2-dimethoxyethane)₂NiBr₂ as the metal source.

Compound **1** contains various intra- and intermolecular interactions in the form of N–H···Br and C–H···N interactions as well as C–H··· π interactions (see Table 1). A perspective view of the supramolecular architecture of **1** is given in Fig. 3, which shows the presence of the various C–H··· π interactions, leading to the formation of a

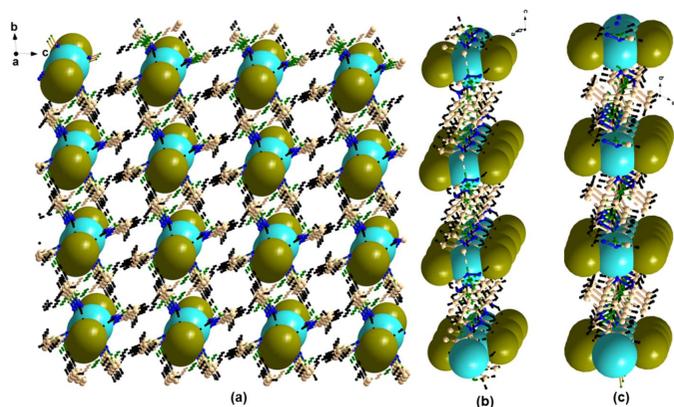


Figure 4
Supramolecular architecture of compound **1**. (a) View along the *a* axis showing a herringbone-type arrangement; (b) and (c) the stacking of Br–Mn–Br along the respective axes.

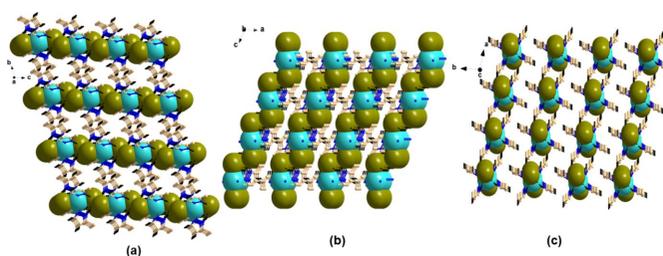


Figure 5
Supramolecular architecture of compound **2**. (a) View along the *a* axis showing a pillared network arrangement; (b) a view along the *b* axis showing the zigzag pattern of Br–Mn–Br and (c) a view along the *c* axis.

herringbone-type of arrangement (Fig. 4a) along the *a* axis. In contrast, a pillared network along the *a* axis is seen in the structure of **2** (Fig. 5a). Further investigation reveals that along the *b* axis, the Br–Mn–Br moieties are stacked one over another in compound **1** while in **2**, they are arranged in a zigzag fashion (Fig. 4b and 5b). The view along *c* axis is also different in both the compounds (Fig. 4c and 5c). Overall, the supramolecular architectures clearly distinguish the two polymorphic forms **1** and **2**.

Synthesis and crystallization

50 mg (0.19 mmol) of Mn(CO)₅Br [bromopentacarbonylmanganese(I)] and 30.6 μ L (0.38 mmol) of 5-methyl-1*H*-pyrazole were dissolved in 20 ml of ethanol. After stirring for a few minutes, 105 μ L (0.76 mmol) of triethylamine were added to the reaction mixture and the resultant straw-yellow-colored solution was stirred at room temperature for 20 h. Light-yellow crystals were obtained by the slow evaporation method of a 1:1 dichloromethane–ethanol solvent mixture. Crystal yield 60%. ESI–MS data: *m/z* 540.53290 [*M* – H]⁺.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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Table 2

Experimental details.

Crystal data	
Chemical formula	[MnBr ₂ (C ₄ H ₆ N ₂) ₄]
<i>M_r</i>	543.19
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.6288 (3), 8.7530 (4), 9.3794 (4)
α , β , γ (°)	90.707 (4), 106.138 (4), 114.285 (5)
<i>V</i> (Å ³)	542.62 (5)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.31
Crystal size (mm)	0.17 × 0.14 × 0.12
Data collection	
Diffractometer	XtaLAB AFC12 (RINC): Kappa single
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2017)
<i>T_{min}</i> , <i>T_{max}</i>	0.706, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	11690, 2574, 2115
<i>R_{int}</i>	0.060
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.680
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.032, 0.064, 1.04
No. of reflections	2574
No. of parameters	134
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.50, -0.38

Computer programs: *CrysAlis PRO* (Rigaku OD, 2017), *SHELXT* (Sheldrick, 2015a), *SHELXL2019/3* (Sheldrick, 2015b), *ORTEP-3 for Windows2020* (Farrugia, 2012), *Diamond* (Brandenburg *et al.*, 2014) and *publCIF* (Westrip, 2010).

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full crystallographic data

IUCrData (2024). **9**, x240237 [https://doi.org/10.1107/S2414314624002372]

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trans-Dibromidotetrakis(5-methyl-1*H*-pyrazole- κN^2)\ manganese(II)*Crystal data*

[MnBr₂(C₄H₆N₂)₄]

$M_r = 543.19$

Triclinic, $P\bar{1}$

$a = 7.6288$ (3) Å

$b = 8.7530$ (4) Å

$c = 9.3794$ (4) Å

$\alpha = 90.707$ (4)°

$\beta = 106.138$ (4)°

$\gamma = 114.285$ (5)°

$V = 542.62$ (5) Å³

$Z = 1$

$F(000) = 271$

$D_x = 1.662$ Mg m⁻³

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

Cell parameters from 4000 reflections

$\theta = 3.1$ – 28.0 °

$\mu = 4.31$ mm⁻¹

$T = 120$ K

Block, yellow

$0.17 \times 0.14 \times 0.12$ mm

Data collection

XtaLAB AFC12 (RINC): Kappa single diffractometer

Radiation source: fine-focus sealed X-ray tube
0 scans

Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2017)

$T_{\min} = 0.706$, $T_{\max} = 1.000$

11690 measured reflections

2574 independent reflections

2115 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.060$

$\theta_{\max} = 28.9$ °, $\theta_{\min} = 3.1$ °

$h = -10$ → 10

$k = -10$ → 11

$l = -12$ → 11

3 standard reflections every 20 reflections

intensity decay: none

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.064$

$S = 1.04$

2574 reflections

134 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0225P)^2 + 0.1264P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.50$ e Å⁻³

$\Delta\rho_{\min} = -0.37$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.8781 (4)	-0.4193 (4)	0.2379 (3)	0.0248 (6)
H1A	0.841583	-0.535204	0.195589	0.037*
H1B	0.924272	-0.407646	0.347700	0.037*
H1C	0.986772	-0.339348	0.203390	0.037*
C2	0.6971 (4)	-0.3823 (3)	0.1878 (3)	0.0177 (5)
C3	0.5014 (4)	-0.4665 (3)	0.1909 (3)	0.0196 (6)
H3	0.443446	-0.571543	0.225950	0.024*
C4	0.4061 (4)	-0.3654 (3)	0.1319 (3)	0.0191 (5)
H4	0.268506	-0.392289	0.120452	0.023*
C5	0.6662 (4)	0.1767 (4)	0.3552 (3)	0.0234 (6)
H5	0.803196	0.199834	0.368271	0.028*
C6	0.5970 (4)	0.2174 (4)	0.4670 (3)	0.0251 (6)
H6	0.675254	0.271808	0.566727	0.030*
C7	0.3930 (4)	0.1625 (3)	0.4026 (3)	0.0201 (6)
C8	0.2336 (4)	0.1681 (4)	0.4618 (3)	0.0329 (7)
H8A	0.264306	0.152549	0.567683	0.049*
H8B	0.101977	0.077534	0.404452	0.049*
H8C	0.229412	0.278049	0.452166	0.049*
Br1	0.91038 (4)	0.16217 (3)	0.06734 (3)	0.01922 (10)
Mn1	0.500000	0.000000	0.000000	0.01496 (13)
N1	0.5313 (3)	-0.2264 (3)	0.0935 (2)	0.0169 (4)
N2	0.7090 (3)	-0.2395 (3)	0.1301 (2)	0.0177 (5)
N3	0.5156 (3)	0.1016 (3)	0.2283 (2)	0.0175 (5)
N4	0.3507 (3)	0.0941 (3)	0.2610 (2)	0.0193 (5)
H2	0.804 (4)	-0.166 (4)	0.106 (3)	0.013 (7)*
H7	0.244 (5)	0.058 (4)	0.196 (3)	0.025 (8)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0248 (15)	0.0259 (15)	0.0293 (15)	0.0154 (13)	0.0098 (12)	0.0085 (12)
C2	0.0219 (13)	0.0169 (13)	0.0145 (12)	0.0100 (11)	0.0038 (10)	0.0005 (10)
C3	0.0258 (14)	0.0163 (13)	0.0177 (13)	0.0092 (11)	0.0079 (11)	0.0036 (10)
C4	0.0184 (13)	0.0187 (14)	0.0208 (13)	0.0069 (11)	0.0088 (10)	0.0018 (10)
C5	0.0165 (13)	0.0293 (16)	0.0253 (14)	0.0116 (12)	0.0052 (11)	0.0054 (12)
C6	0.0237 (14)	0.0349 (17)	0.0161 (13)	0.0124 (13)	0.0058 (11)	0.0008 (11)
C7	0.0216 (14)	0.0229 (14)	0.0165 (13)	0.0086 (11)	0.0087 (11)	0.0027 (10)
C8	0.0276 (16)	0.055 (2)	0.0204 (14)	0.0201 (15)	0.0104 (12)	0.0017 (13)
Br1	0.01626 (14)	0.01839 (15)	0.02480 (15)	0.00854 (11)	0.00746 (10)	0.00161 (10)
Mn1	0.0161 (3)	0.0151 (3)	0.0174 (3)	0.0090 (2)	0.0070 (2)	0.0023 (2)
N1	0.0180 (11)	0.0168 (11)	0.0181 (11)	0.0106 (9)	0.0042 (9)	0.0020 (8)
N2	0.0148 (11)	0.0175 (12)	0.0208 (12)	0.0061 (10)	0.0065 (9)	0.0040 (9)
N3	0.0163 (11)	0.0204 (12)	0.0203 (11)	0.0098 (9)	0.0092 (9)	0.0030 (9)
N4	0.0159 (12)	0.0201 (12)	0.0195 (12)	0.0054 (10)	0.0056 (10)	0.0013 (9)

Geometric parameters (Å, °)

C1—C2	1.497 (3)	C7—N4	1.346 (3)
C1—H1A	0.9800	C7—C8	1.488 (4)
C1—H1B	0.9800	C8—H8A	0.9800
C1—H1C	0.9800	C8—H8B	0.9800
C2—N2	1.348 (3)	C8—H8C	0.9800
C2—C3	1.376 (4)	Br1—Br1	0.0000 (10)
C3—C4	1.391 (4)	Br1—Mn1	2.7274 (3)
C3—H3	0.9500	Mn1—N1	2.251 (2)
C4—N1	1.330 (3)	Mn1—N1 ⁱ	2.251 (2)
C4—H4	0.9500	Mn1—N3	2.2612 (19)
C5—N3	1.330 (3)	Mn1—N3 ⁱ	2.2613 (19)
C5—C6	1.400 (4)	N1—N2	1.356 (3)
C5—H5	0.9500	N2—H2	0.84 (3)
C6—C7	1.368 (4)	N3—N4	1.352 (3)
C6—H6	0.9500	N4—H7	0.80 (3)
C2—C1—H1A	109.5	N1—Mn1—N3	89.74 (7)
C2—C1—H1B	109.5	N1 ⁱ —Mn1—N3	90.26 (7)
H1A—C1—H1B	109.5	N1—Mn1—N3 ⁱ	90.26 (7)
C2—C1—H1C	109.5	N1 ⁱ —Mn1—N3 ⁱ	89.74 (7)
H1A—C1—H1C	109.5	N3—Mn1—N3 ⁱ	180.0
H1B—C1—H1C	109.5	N1—Mn1—Br1	89.10 (5)
N2—C2—C3	105.9 (2)	N1 ⁱ —Mn1—Br1	90.90 (5)
N2—C2—C1	121.2 (2)	N3—Mn1—Br1	91.45 (5)
C3—C2—C1	132.9 (2)	N3 ⁱ —Mn1—Br1	88.55 (5)
C2—C3—C4	105.5 (2)	N1—Mn1—Br1	89.10 (5)
C2—C3—H3	127.3	N1 ⁱ —Mn1—Br1	90.90 (5)
C4—C3—H3	127.3	N3—Mn1—Br1	91.45 (5)
N1—C4—C3	111.7 (2)	N3 ⁱ —Mn1—Br1	88.55 (5)
N1—C4—H4	124.1	Br1—Mn1—Br1	0.000 (16)
C3—C4—H4	124.1	N1—Mn1—Br1 ⁱ	90.90 (5)
N3—C5—C6	111.3 (2)	N1 ⁱ —Mn1—Br1 ⁱ	89.10 (5)
N3—C5—H5	124.3	N3—Mn1—Br1 ⁱ	88.55 (5)
C6—C5—H5	124.3	N3 ⁱ —Mn1—Br1 ⁱ	91.45 (5)
C7—C6—C5	105.6 (2)	Br1—Mn1—Br1 ⁱ	180.0
C7—C6—H6	127.2	Br1—Mn1—Br1 ⁱ	180.0
C5—C6—H6	127.2	C4—N1—N2	104.0 (2)
N4—C7—C6	105.9 (2)	C4—N1—Mn1	133.75 (17)
N4—C7—C8	122.0 (2)	N2—N1—Mn1	122.16 (16)
C6—C7—C8	132.1 (2)	C2—N2—N1	112.9 (2)
C7—C8—H8A	109.5	C2—N2—H2	129.5 (18)
C7—C8—H8B	109.5	N1—N2—H2	117.2 (18)
H8A—C8—H8B	109.5	C5—N3—N4	104.0 (2)
C7—C8—H8C	109.5	C5—N3—Mn1	133.35 (17)
H8A—C8—H8C	109.5	N4—N3—Mn1	122.65 (15)
H8B—C8—H8C	109.5	C7—N4—N3	113.2 (2)

Br1—Br1—Mn1	0.00 (2)	C7—N4—H7	127 (2)
N1—Mn1—N1 ⁱ	180.0	N3—N4—H7	119 (2)
N2—C2—C3—C4	0.4 (3)	C1—C2—N2—N1	-178.9 (2)
C1—C2—C3—C4	178.2 (3)	C4—N1—N2—C2	0.8 (3)
C2—C3—C4—N1	0.1 (3)	Mn1—N1—N2—C2	178.32 (15)
N3—C5—C6—C7	0.3 (3)	C6—C5—N3—N4	-0.4 (3)
C5—C6—C7—N4	0.0 (3)	C6—C5—N3—Mn1	179.66 (18)
C5—C6—C7—C8	-180.0 (3)	C6—C7—N4—N3	-0.3 (3)
C3—C4—N1—N2	-0.5 (3)	C8—C7—N4—N3	179.7 (2)
C3—C4—N1—Mn1	-177.60 (16)	C5—N3—N4—C7	0.4 (3)
C3—C2—N2—N1	-0.8 (3)	Mn1—N3—N4—C7	-179.64 (17)

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

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

*Cg*1 and *Cg*2 are the centroids of the N1/N2/C2–C4 and N3/N4/ C5–C7 rings, respectively.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H2 \cdots Br1	0.84 (3)	2.70 (3)	3.343 (2)	134 (2)
C1—H1C \cdots Br1 ⁱⁱ	0.98	3.11	3.951 (3)	145
N2—H2 \cdots Br1	0.84 (3)	2.70 (3)	3.343 (2)	134 (2)
N2—H2 \cdots Br1 ⁱⁱ	0.84 (3)	3.05 (3)	3.704 (2)	137 (2)
N4—H7 \cdots Br1 ⁱⁱⁱ	0.80 (3)	3.00 (3)	3.636 (2)	138 (3)
N4—H7 \cdots Br1 ⁱ	0.80 (3)	2.76 (3)	3.351 (2)	132 (3)
C3—H3 \cdots N4 ^{iv}	0.95	2.76	3.659 (3)	158
C8—H8A \cdots N2 ^v	0.98	2.86	3.744 (3)	151
C8—H8A \cdots Cg1 ^v	0.98	2.61	3.586 (3)	173
C3—H3 \cdots Cg2 ^{vi}	0.95	2.84	3.667 (4)	146

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