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catena-Poly[[*trans*-bis(1,3-benzothiazole- κ N)manganese(II)]-di- μ -chlorido]Hasna Bouchareb,^a Sabrina Benmebarek,^a Sofiane Bouacida,^{a,b,*} Hocine Merazig^a and Mhamed Boudraa^a^aUnité de Recherche de Chimie de l'Environnement et Moléculaire Structurale, CHEMS, Université Constantine 1, 25000, Algeria, and ^bDépartement Sciences de la Matière, Faculté des Sciences Exactes et Sciences de la Nature et de la Vie, Université Oum El Bouaghi, Algeria

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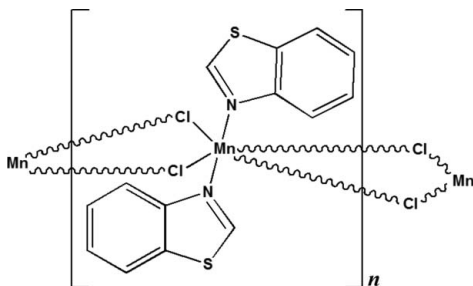
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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.042; wR factor = 0.092; data-to-parameter ratio = 14.3.

In the title coordination polymer, $[\text{MnCl}_2(\text{C}_7\text{H}_5\text{NS})_2]_n$, the Mn^{II} ion is located on the intersection of a twofold rotation axis and a mirror plane and adopts an octahedral coordination geometry defined by two mutually *trans* N atoms from benzothiazole ligands which occupy the axial positions, and four Cl atoms which form the equatorial sites. The Mn^{II} ions are connected by two bridging Cl atoms, forming chains parallel to the c axis. The crystal packing can be described as alternating layers parallel to (001) featuring π - π stacking interactions with a centroid-centroid distance of 3.6029 (15) Å.

Related literature

For applications of benzothiazole and its derivatives, see: Petkova *et al.* (2000); Karisson *et al.* (2003); Khan *et al.* (2011). For related structures see: Bouchareb *et al.* (2013); Roh & Jeong (2007); Popović *et al.* (2003); Maniukiewicz (2004).



Experimental

Crystal data

 $[\text{MnCl}_2(\text{C}_7\text{H}_5\text{NS})_2]$ $M_r = 396.22$

Tetragonal, $P4_2/mbc$
 $a = 14.761$ (6) Å
 $c = 7.170$ (3) Å
 $V = 1562.3$ (14) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 1.45$ mm⁻¹
 $T = 150$ K
 $0.19 \times 0.14 \times 0.12$ mm

Data collection

Bruker APEXII diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2002)
 $T_{\text{min}} = 0.674$, $T_{\text{max}} = 0.746$

15714 measured reflections
 918 independent reflections
 685 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.117$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.092$
 $S = 1.14$
 918 reflections

64 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.55$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.46$ e Å⁻³

Data collection: APEX2 (Bruker, 2011); cell refinement: SAINT (Bruker, 2011); data reduction: SAINT; program(s) used to solve structure: SIR2002 (Burla *et al.*, 2005); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and DIAMOND (Brandenburg & Berndt, 2001); software used to prepare material for publication: WinGX (Farrugia, 2012).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: LH5716).

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supporting information

Acta Cryst. (2014). E70, m275 [doi:10.1107/S1600536814014159]

catena-Poly[[*trans*-bis(1,3-benzothiazole- κ N)manganese(II)]-di- μ -chlorido]

Hasna Bouchareb, Sabrina Benmebarek, Sofiane Bouacida, Hocine Merazig and Mhamed Boudraa

1. Comment

In recent years, benzothiazole and its derivatives have attracted more attention because they exhibit interesting optical and biological activities (Petkova *et al.*, 2000; Karisson *et al.*, 2003; Khan *et al.* 2011). Related structural studies are partly focused on the fact that the benzothiazole ring contains N, S and O as potential donor atoms, which exhibit good coordination capacity, and so are propitious to build novel complexes (Roh *et al.* 2007, Popović *et al.* 2003, Maniukiewicz 2004). As part of our ongoing studies of benzothiazole-based coordination networks (Bouchareb *et al.* 2013), we report herein the structure of a coordination polymer of manganese and a benzothiazole ligand (I). The molecular geometry and the atom-numbering scheme are shown in Fig 1.

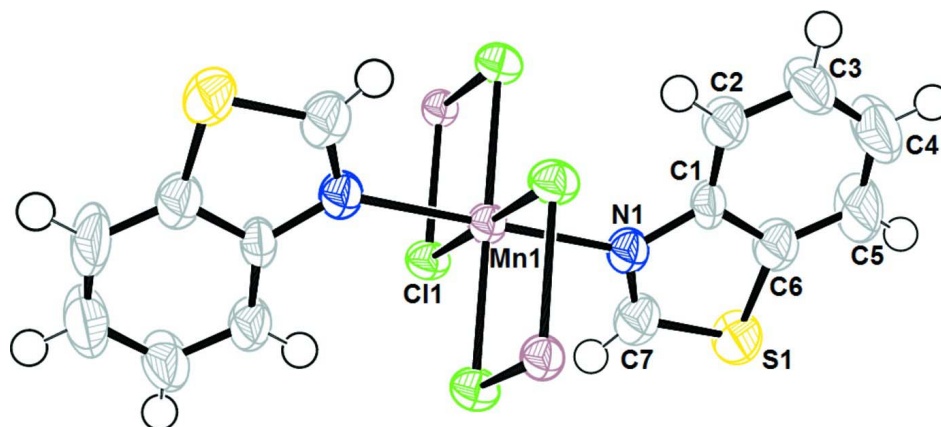
In the title compound, the Mn^{II} cation is located on the intersection of a twofold rotation axis and a mirror plane. The coordination sphere is defined by two mutually *trans* N atoms from two neutral monodentate benzothiazole ligands occupying the axial positions, and four Cl atoms lying in the equatorial plane. All Mn–Cl bond lengths are identical [2.5232 (10)] Å by symmetry and the Mn–N bond lengths are 2.307 (4) Å. In the coordination octahedron, all N–Mn–Cl and Cl–Mn–Cl bond angles are in the range of 89.40 (7) – 90.60 (7)°. The Mn^{II} ions are connected by two bridging Cl atoms, resulting in a chain of octahedra parallel to the *c* axis (Fig. 2). The crystal packing can be described as alternating layers parallel to (001) (Fig. 3). The crystal structure features two π – π stacking interactions: $Cg1$ – $Cg1 = 3.6029$ (15) Å and $Cg1$ – $Cg2 = 4.048$ (2) Å, Where, $Cg1$ is the centroid of the imidazole ring (N1/C7/S1/C6/C1) and $Cg2$ is the centroid of the fused benzene ring (C1/C2/C3/C4/C5/C6). No hydrogen bonds are observed in the structure.

2. Experimental

Benzothiazole (1 ml) and ethanol (1 ml) were added to a solution of MnCl₂·4H₂O (39.5 mg, 0.2 mmol) in water (10 ml). The mixture was then refluxed with stirring for 3 h and the resulting solution was left to stand at room temperature. After several days, single crystals suitable for X-ray diffraction were obtained.

3. Refinement

All non-H atoms were refined with anisotropic displacement parameters. Approximate positions for all H atoms were first obtained from the difference electron density map. However, the H atoms were placed in idealized positions and refined in a riding-model approximation. The applied constraints were as follow: C–H = 0.93 Å and $U_{iso} = 1.2U_{eq}(C)$.

**Figure 1**

The molecular structure of, (I), with displacement ellipsoids drawn at the 50% probability level. Only the contents of the asymmetric unit are numbered. H atoms are represented as small spheres of arbitrary radii.

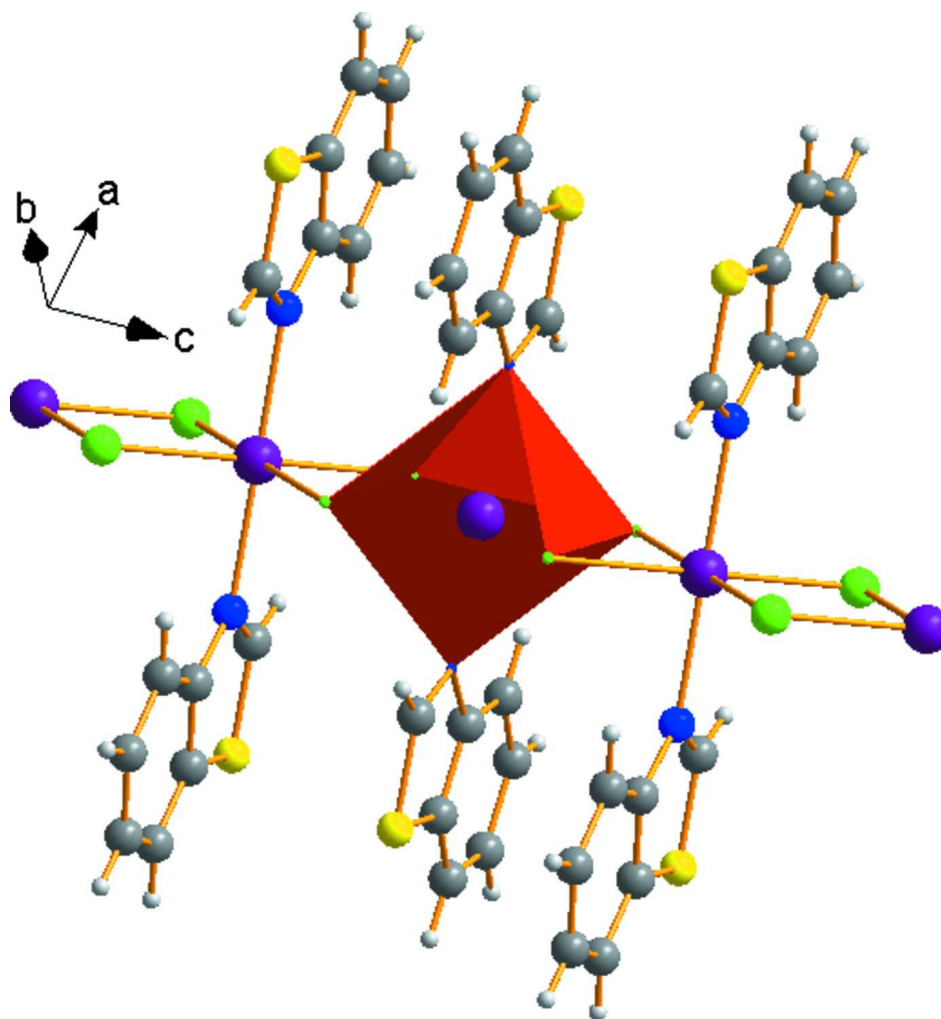
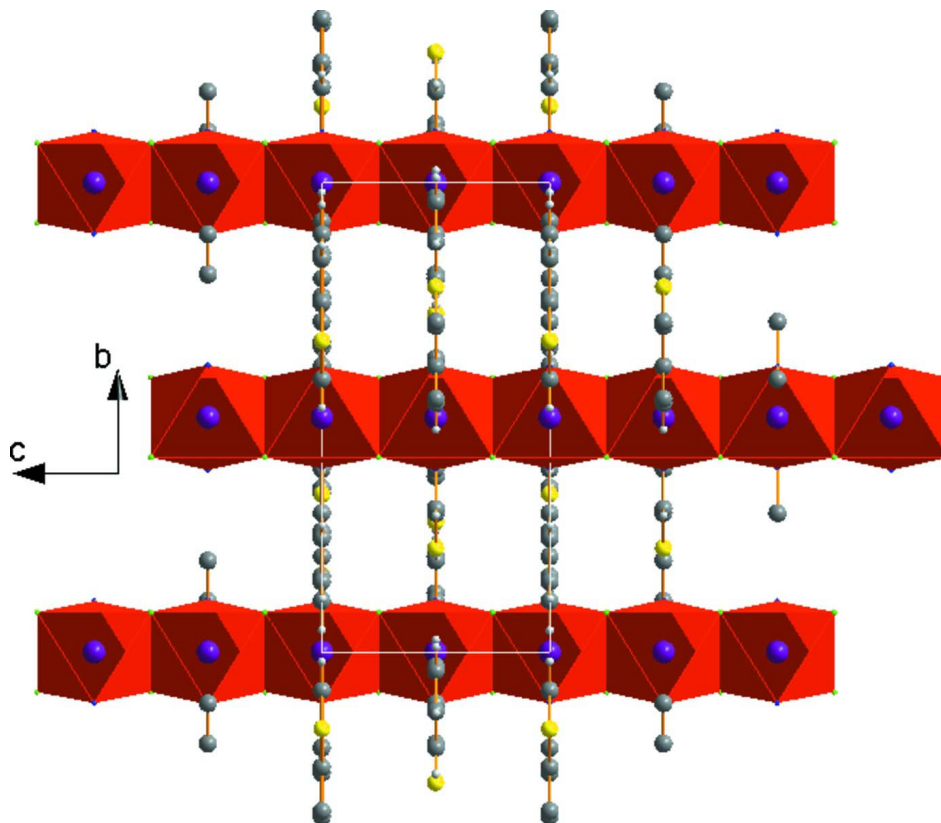


Figure 2

 The coordination around the Mn^{II} ion in a chain of octahedra parallel to the *c* axis

Figure 3

 Packing diagram of (I) viewed along the *a* axis showing alternating layers parallel to (001).

catena-Poly[[*trans*-bis(1,3-benzothiazole- κ N)manganese(II)]-di- μ -chlorido]
Crystal data
 $[\text{MnCl}_2(\text{C}_7\text{H}_5\text{NS})_2]$
 $M_r = 396.22$

 Tetragonal, $P4_2/mbc$

 Hall symbol: $-P\ 4c\ 2ab$
 $a = 14.761\ (6)\ \text{\AA}$
 $c = 7.170\ (3)\ \text{\AA}$
 $V = 1562.3\ (14)\ \text{\AA}^3$
 $Z = 4$
 $F(000) = 796$
 $D_x = 1.685\ \text{Mg m}^{-3}$

 Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1270 reflections

 $\theta = 3.1\text{--}25.2^\circ$
 $\mu = 1.45\ \text{mm}^{-1}$
 $T = 150\ \text{K}$

Block, colorless

 $0.19 \times 0.14 \times 0.12\ \text{mm}$
Data collection

Bruker APEXII

diffractometer

Radiation source: sealed tube

Graphite monochromator

 φ and ω scans

Absorption correction: multi-scan

 (*SADABS*; Sheldrick, 2002)

 $T_{\min} = 0.674$, $T_{\max} = 0.746$

15714 measured reflections

918 independent reflections

 685 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.117$
 $\theta_{\max} = 27.0^\circ$, $\theta_{\min} = 2.8^\circ$
 $h = -18 \rightarrow 18$
 $k = -18 \rightarrow 18$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.092$
 $S = 1.14$
 918 reflections
 64 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
 $w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 1.2805P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.007$
 $\Delta\rho_{\max} = 0.55 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.46 \text{ e } \text{Å}^{-3}$

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	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.8908 (3)	0.2962 (3)	1	0.0160 (9)
C2	0.9693 (3)	0.2427 (3)	1	0.0242 (11)
H2	1.0264	0.2692	1	0.029*
C3	0.9597 (3)	0.1501 (3)	1	0.0337 (13)
H3	1.0112	0.1137	1	0.04*
C4	0.8742 (3)	0.1096 (3)	1	0.0423 (16)
H4	0.8697	0.0468	1	0.051*
C5	0.7963 (3)	0.1612 (3)	1	0.0398 (15)
H5	0.7395	0.134	1	0.048*
C6	0.8050 (3)	0.2547 (3)	1	0.0226 (10)
C7	0.8052 (3)	0.4183 (3)	1	0.0225 (11)
H7	0.7909	0.4796	1	0.027*
N1	0.8879 (2)	0.3912 (2)	1	0.0167 (7)
S1	0.72177 (8)	0.33651 (9)	1	0.0284 (3)
Cl1	0.91494 (5)	0.58506 (5)	0.75	0.0163 (2)
Mn1	1	0.5	1	0.0135 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.018 (2)	0.012 (2)	0.018 (2)	-0.0047 (18)	0	0
C2	0.014 (2)	0.018 (2)	0.041 (3)	-0.0029 (18)	0	0
C3	0.018 (2)	0.016 (2)	0.067 (4)	0.002 (2)	0	0
C4	0.026 (3)	0.016 (3)	0.084 (5)	-0.004 (2)	0	0
C5	0.020 (3)	0.023 (3)	0.077 (4)	-0.012 (2)	0	0

C6	0.018 (2)	0.020 (2)	0.030 (3)	-0.0039 (19)	0	0
C7	0.019 (2)	0.023 (3)	0.026 (3)	-0.004 (2)	0	0
N1	0.015 (2)	0.016 (2)	0.0192 (18)	-0.0017 (14)	0	0
S1	0.0122 (6)	0.0245 (7)	0.0484 (8)	-0.0023 (5)	0	0
Cl1	0.0161 (3)	0.0161 (3)	0.0167 (5)	0.0030 (4)	0.0004 (4)	0.0004 (4)
Mn1	0.0128 (5)	0.0128 (5)	0.0150 (4)	-0.0003 (3)	0	0

Geometric parameters (Å, °)

C1—C2	1.402 (6)	C6—S1	1.723 (5)
C1—N1	1.402 (5)	C7—N1	1.284 (6)
C1—C6	1.406 (6)	C7—S1	1.724 (5)
C2—C3	1.374 (6)	C7—H7	0.93
C2—H2	0.93	N1—Mn1	2.307 (4)
C3—C4	1.397 (7)	Cl1—Mn1 ⁱ	2.5232 (10)
C3—H3	0.93	Cl1—Mn1	2.5232 (10)
C4—C5	1.379 (7)	Mn1—N1 ⁱⁱ	2.307 (4)
C4—H4	0.93	Mn1—Cl1 ⁱⁱⁱ	2.5232 (10)
C5—C6	1.386 (7)	Mn1—Cl1 ⁱⁱ	2.5232 (10)
C5—H5	0.93	Mn1—Cl1 ^{iv}	2.5232 (10)
C2—C1—N1	126.1 (4)	C7—N1—C1	109.9 (4)
C2—C1—C6	119.9 (4)	C7—N1—Mn1	117.7 (3)
N1—C1—C6	114.1 (4)	C1—N1—Mn1	132.4 (3)
C3—C2—C1	118.4 (4)	C6—S1—C7	88.9 (2)
C3—C2—H2	120.8	Mn1 ⁱ —Cl1—Mn1	90.54 (4)
C1—C2—H2	120.8	N1 ⁱⁱ —Mn1—N1	180
C2—C3—C4	121.2 (5)	N1 ⁱⁱ —Mn1—Cl1 ⁱⁱⁱ	89.40 (7)
C2—C3—H3	119.4	N1—Mn1—Cl1 ⁱⁱⁱ	90.60 (7)
C4—C3—H3	119.4	N1 ⁱⁱ —Mn1—Cl1 ⁱⁱ	89.40 (7)
C5—C4—C3	121.1 (5)	N1—Mn1—Cl1 ⁱⁱ	90.60 (7)
C5—C4—H4	119.4	Cl1 ⁱⁱⁱ —Mn1—Cl1 ⁱⁱ	90.54 (4)
C3—C4—H4	119.4	N1 ⁱⁱ —Mn1—Cl1	90.60 (7)
C4—C5—C6	118.2 (5)	N1—Mn1—Cl1	89.40 (7)
C4—C5—H5	120.9	Cl1 ⁱⁱⁱ —Mn1—Cl1	89.46 (4)
C6—C5—H5	120.9	Cl1 ⁱⁱ —Mn1—Cl1	180
C5—C6—C1	121.1 (4)	N1 ⁱⁱ —Mn1—Cl1 ^{iv}	90.60 (7)
C5—C6—S1	129.2 (4)	N1—Mn1—Cl1 ^{iv}	89.40 (7)
C1—C6—S1	109.7 (3)	Cl1 ⁱⁱⁱ —Mn1—Cl1 ^{iv}	180
N1—C7—S1	117.4 (4)	Cl1 ⁱⁱ —Mn1—Cl1 ^{iv}	89.46 (4)
N1—C7—H7	121.3	Cl1—Mn1—Cl1 ^{iv}	90.54 (4)
S1—C7—H7	121.3		
N1—C1—C2—C3	180	C6—C1—N1—Mn1	180
C6—C1—C2—C3	0	C5—C6—S1—C7	180
C1—C2—C3—C4	0	C1—C6—S1—C7	0
C2—C3—C4—C5	0	N1—C7—S1—C6	0
C3—C4—C5—C6	0	C7—N1—Mn1—Cl1 ⁱⁱⁱ	-134.72 (2)

C4—C5—C6—C1	0	C1—N1—Mn1—C11 ⁱⁱⁱ	45.28 (2)
C4—C5—C6—S1	180	C7—N1—Mn1—C11 ⁱⁱ	134.72 (2)
C2—C1—C6—C5	0	C1—N1—Mn1—C11 ⁱⁱ	-45.28 (2)
N1—C1—C6—C5	180	C7—N1—Mn1—C11	-45.28 (2)
C2—C1—C6—S1	180	C1—N1—Mn1—C11	134.72 (2)
N1—C1—C6—S1	0	C7—N1—Mn1—C11 ^{iv}	45.28 (2)
S1—C7—N1—C1	0	C1—N1—Mn1—C11 ^{iv}	-134.72 (2)
S1—C7—N1—Mn1	180	Mn1 ⁱ —C11—Mn1—N1 ⁱⁱ	89.39 (7)
C2—C1—N1—C7	180	Mn1 ⁱ —C11—Mn1—N1	-90.61 (7)
C6—C1—N1—C7	0	Mn1 ⁱ —C11—Mn1—C11 ^{iv}	180
C2—C1—N1—Mn1	0		

Symmetry codes: (i) $y+1/2, x-1/2, -z+3/2$; (ii) $-x+2, -y+1, -z+2$; (iii) $-x+2, -y+1, z$; (iv) $x, y, -z+2$.