Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Poly[bis(μ_2-azido-κ^2N^1:N^3)(μ_2-3,5-di-2-pyridyl-1,2,4-triazole-κ^4N^1,N^5:N^2,N^3)-manganese(II)]

Sheng Hu, Shu-Hua Zhang and Ming-Hua Zeng*

School of Chemistry and Chemical Engineering, Guangxi Normal University, Guilin, 541004, People's Republic of China
Correspondence e-mail: zmh@mailbox.gxnu.edu.cn

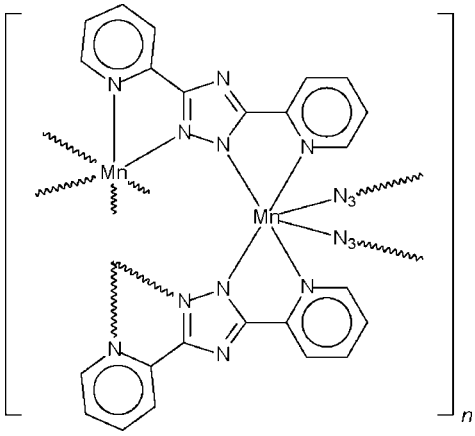
Received 9 September 2007; accepted 10 September 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.035; wR factor = 0.076; data-to-parameter ratio = 12.3.

In the crystal structure of the polymeric title compound, $[Mn_2(N_3)_2(C_{12}H_8N_5)_2]_n$, the Mn^{II} atom exists in an octahedral geometry owing to coordination by four N atoms from two 3,5-bis(pyridin-2-yl)-1,2,4-triazolate ligands and by two azide ligands. The heterocyclic ligand binds in a chelating mode. The bidentate bridging mode of both anions leads to a linear ribbon motif.

Related literature

For related literature, see: Prins *et al.* (1995); Chen *et al.* (2006); Wang *et al.* (2006).



Experimental

Crystal data

$[Mn_2(N_3)_2(C_{12}H_8N_5)_2]$
M_r = 638.38
Monoclinic, $P2_1$
a = 8.6965 (9) Å
b = 6.5597 (7) Å
c = 11.8601 (13) Å
β = 109.245 (2)°
V = 638.77 (12) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.04 mm^{-1}
T = 293 (2) K
0.31 × 0.26 × 0.22 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.732, T_{max} = 0.796
3598 measured reflections
2337 independent reflections
2207 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.076
S = 1.05
2337 reflections
190 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), with 825 Friedel pairs
Flack parameter: 0.02 (2)

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

The authors acknowledge financial support by the Natural Science Foundation of China (grant No. 20561001) and the Patent Special Foundation of the Ministry of Education of Guangxi Province (grant No. 2006-26).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2325).

References

Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2001). *SAINT* (Version 6.45) and *SMART* (Version 5.0). Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, J.-C., Hu, S., Zhou, A.-J., Tong, M.-L. & Tong, Y.-X. (2006). *Z. Anorg. Allg. Chem.* **632**, 475–481.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Prins, R., Birker, P. J. M. W., Haasnoot, J. G., Verschoor, G. C. & Reedijk, J. (1995). *Inorg. Chem.* **24**, 4128–4133.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Wang, X.-Y., Wang, L., Wang, Z.-M. & Gao, S. (2006). *J. Am. Chem. Soc.* **128**, 674–675.

supplementary materials

Acta Cryst. (2007). E**63**, m2543 [**doi:10.1107/S1600536807044066**]

Poly[bis(μ_2-azido-$\kappa^2N^1:N^3$)(μ_2-3,5-di-2-pyridyl-1,2,4-triazole-$\kappa^4N^1,N^5:N^2,N^3$)manganese(II)]

S. Hu, S.-H. Zhang and M.-H. Zeng

Comment

1,2,4-triazole derivatives are a class of azole compounds that can act as either 2,4- or 1,2-bridging nitrogen donor ligands. 3,5-bis(pyridin-2-yl)-1,2,4-triazole can act as tetradentate ligands and are therefore very suitable for studying exchange-coupled pairs of transition-metal ions. (Prins *et al.*, 1995; Chen *et al.*, 2006). However, only small part of mononuclear and dinuclear complexes were characterized by X-ray crystallography. On the other hand, azide was widely used to connect metal ions, and the correlation between the structure and magnetic properties of different coordination modes was observed (Wang *et al.*, 2006). In this paper, solvothermal technique has been successfully applied in the Mn^{2+}/bpt^{-}/N_3^{-} system to synthesize the title compound.

There are one Mn^{II} atom, one bpt^{-} ligand and one azide ligand in the asymmetric unit. The Mn^{II} atom has an octahedral environment, formed by four N atoms from two different bpt^{-} ligand and two N atoms belonging to two azide ligands. The bpt^{-} ligand binds to manganese in a *cis-bis*(chelate) mode, through two pyridine and two triazole nitrogen atoms, linking the Mn^{II} atoms into a helical chain that runs along the *b* axis. Each pair of Mn^{II} ions from adjacent chains are additionally bridged by two azide lingds in the EE mode and further linked the $[Mn(bpt)]^{+}$ chains into a two-dimensional (4,4) net.

Experimental

A mixture of manganese sulfate monohydrate (0.169 g, 1 mmol), sodium azide (0.065 g, 1 mmol) 3,5-bis(pyridin-2-yl)-1,2,4-triazole (0.223 g, 1 mmol) and methanol (10 ml) was heated in a Teflon-lined stainless steel autoclave (25 ml) for 120 h at 393 K, after which the autoclave was cooled to room temperature over a period of 8 h at a rate of 10 K h^{-1}. Pale yellow block single crystals of (I) were collected in about 15% yield. Elemental analysis, calcd (%) for $C_{12}H_8MnN_8$: C, 45.16; H, 2.53; N, 35.11; found (%): C, 45.19; H, 2.50; N, 35.07.

Refinement

All other H atoms were positioned geometrically and refined as riding, with C–H distances of 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C).

Figures

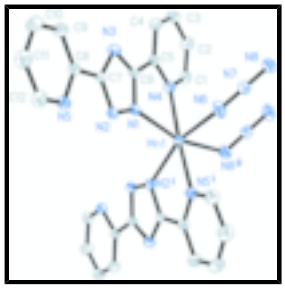


Fig. 1. The asymmetric unit of (I), showing displacement ellipsoids drawn at the 30% probability level for non-H atoms. Hydrogen atoms have been omitted. Symmetry codes: (i) −*x*, *y* − 1/2, −*z*; (ii) 1 − *x*, *y*-1/2,-*z*.

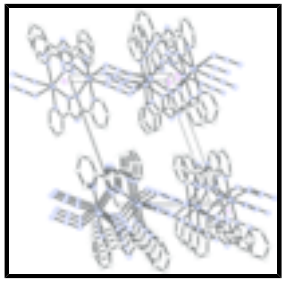


Fig. 2. 3-D Packing diagram of title complex; Hydrogen atoms have been omitted.

Poly[bis(μ$_2$-azido-κ^2*N*^{1}:*N*^{3})(μ$_2$-3,5-di-2-pyridyl- 1,2,4-triazole-κ^4*N*^{1},*N*^{5}:*N*^{2},*N*^{3})manganese(II)]

Crystal data

$[Mn_2(N_3)_2(C_{12}H_8N_5)_2]$	F_{000} = 322
M_r = 638.38	D_x = 1.660 Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 8.6965 (9) Å	Cell parameters from 2337 reflections
b = 6.5597 (7) Å	θ = 1.8–27.0º
c = 11.8601 (13) Å	μ = 1.04 mm^{-1}
β = 109.245 (2)º	T = 293 (2) K
V = 638.77 (12) Å^3	Block, pale yellow
Z = 1	0.31 × 0.26 × 0.22 mm

Data collection

Bruker APEX area-detector diffractometer	2337 independent reflections
Radiation source: fine-focus sealed tube	2207 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.019
T = 293(2) K	θ_{max} = 27.0º
φ and ω scans	θ_{min} = 1.8º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −8→11
T_{min} = 0.732, T_{max} = 0.796	k = −6→8
3598 measured reflections	l = −15→11

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.035$	$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.076$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.40$ e Å^{-3}
2337 reflections	$\Delta\rho_{min} = -0.23$ e Å^{-3}
190 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), with 825 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.02 (2)
Secondary atom site location: difference Fourier map	

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	0.20518 (4)	0.28461 (8)	0.01852 (3)	0.02671 (12)
C1	0.2386 (4)	−0.0499 (5)	−0.1771 (3)	0.0378 (8)
H1A	0.2845	−0.1357	−0.1123	0.045*
C2	0.2498 (4)	−0.1043 (6)	−0.2863 (3)	0.0432 (9)
H2A	0.3023	−0.2240	−0.2948	0.052*
C3	0.1817 (4)	0.0222 (6)	−0.3828 (3)	0.0433 (9)
H3A	0.1896	−0.0090	−0.4572	0.052*
C4	0.1025 (4)	0.1938 (6)	−0.3673 (3)	0.0398 (8)
H4A	0.0545	0.2800	−0.4316	0.048*
C5	0.0938 (3)	0.2397 (5)	−0.2553 (3)	0.0301 (8)
C6	0.0090 (3)	0.4189 (5)	−0.2304 (2)	0.0279 (6)
C7	−0.1260 (4)	0.6830 (5)	−0.2408 (3)	0.0271 (6)
C8	−0.2227 (4)	0.8677 (5)	−0.2788 (3)	0.0298 (7)
C9	−0.2739 (4)	0.9397 (6)	−0.3957 (3)	0.0412 (8)
H9A	−0.2508	0.8674	−0.4556	0.049*

C10	−0.3587 (5)	1.1186 (6)	−0.4209 (3)	0.0492 (10)
H10A	−0.3943	1.1689	−0.4985	0.059*
C11	−0.3914 (4)	1.2242 (6)	−0.3312 (3)	0.0475 (9)
H11A	−0.4469	1.3477	−0.3463	0.057*
C12	−0.3394 (4)	1.1413 (6)	−0.2185 (3)	0.0418 (8)
H12A	−0.3627	1.2112	−0.1579	0.050*
N1	0.0114 (3)	0.4542 (4)	−0.1192 (2)	0.0277 (6)
N2	−0.0767 (3)	0.6266 (4)	−0.1258 (2)	0.0272 (6)
N3	−0.0742 (3)	0.5565 (4)	−0.3107 (2)	0.0311 (6)
N4	0.1652 (3)	0.1196 (4)	−0.1599 (2)	0.0305 (6)
N5	−0.2582 (3)	0.9683 (4)	−0.1913 (2)	0.0315 (6)
N6	0.3757 (3)	0.4973 (5)	−0.0301 (3)	0.0504 (8)
N7	0.4788 (3)	0.5367 (4)	−0.0680 (2)	0.0302 (6)
N8	0.5818 (3)	0.5817 (5)	−0.1066 (3)	0.0400 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0275 (2)	0.0289 (2)	0.0258 (2)	0.0011 (2)	0.01163 (15)	0.0022 (2)
C1	0.0392 (18)	0.0314 (19)	0.0395 (18)	0.0030 (16)	0.0084 (15)	0.0001 (15)
C2	0.0461 (19)	0.035 (2)	0.048 (2)	0.0058 (17)	0.0147 (16)	−0.0104 (17)
C3	0.053 (2)	0.048 (2)	0.0321 (18)	0.0030 (18)	0.0171 (16)	−0.0110 (16)
C4	0.0419 (18)	0.046 (2)	0.0304 (17)	0.0092 (16)	0.0112 (15)	0.0016 (15)
C5	0.0306 (14)	0.032 (2)	0.0277 (14)	0.0035 (13)	0.0100 (12)	−0.0002 (12)
C6	0.0285 (15)	0.0312 (18)	0.0261 (15)	0.0018 (13)	0.0119 (12)	−0.0001 (13)
C7	0.0259 (14)	0.0311 (17)	0.0256 (15)	0.0003 (13)	0.0104 (12)	−0.0005 (12)
C8	0.0281 (15)	0.0306 (16)	0.0317 (16)	−0.0023 (13)	0.0113 (13)	0.0007 (13)
C9	0.049 (2)	0.042 (2)	0.0333 (17)	0.0043 (18)	0.0149 (15)	0.0046 (16)
C10	0.055 (2)	0.049 (2)	0.040 (2)	0.008 (2)	0.0101 (18)	0.0164 (17)
C11	0.050 (2)	0.033 (2)	0.057 (2)	0.0087 (16)	0.0147 (18)	0.0102 (16)
C12	0.0446 (19)	0.034 (2)	0.048 (2)	0.0056 (16)	0.0171 (17)	−0.0014 (16)
N1	0.0283 (13)	0.0302 (15)	0.0286 (13)	0.0021 (11)	0.0148 (10)	0.0009 (11)
N2	0.0248 (12)	0.0300 (15)	0.0282 (13)	0.0021 (11)	0.0106 (10)	0.0027 (11)
N3	0.0363 (14)	0.0314 (15)	0.0275 (13)	0.0038 (12)	0.0133 (11)	0.0021 (11)
N4	0.0329 (13)	0.0275 (15)	0.0305 (14)	0.0015 (12)	0.0098 (11)	0.0016 (11)
N5	0.0350 (14)	0.0289 (15)	0.0326 (14)	0.0023 (12)	0.0140 (12)	0.0003 (12)
N6	0.0377 (16)	0.050 (2)	0.068 (2)	−0.0082 (15)	0.0233 (15)	0.0086 (17)
N7	0.0313 (13)	0.0225 (13)	0.0353 (14)	0.0001 (11)	0.0089 (12)	0.0024 (11)
N8	0.0380 (15)	0.0431 (19)	0.0441 (17)	−0.0086 (13)	0.0207 (13)	−0.0045 (14)

Geometric parameters (Å, °)

Mn1—N2^{i}	2.208 (2)	C7—N2	1.340 (4)
Mn1—N1	2.221 (2)	C7—N3	1.351 (4)
Mn1—N8^{ii}	2.240 (3)	C7—C8	1.459 (4)
Mn1—N6	2.245 (3)	C8—N5	1.348 (4)
Mn1—N5^{i}	2.289 (3)	C8—C9	1.392 (4)
Mn1—N4	2.299 (3)	C9—C10	1.365 (5)

C1—N4	1.331 (4)	C9—H9A	0.9300
C1—C2	1.377 (5)	C10—C11	1.375 (5)
C1—H1A	0.9300	C10—H10A	0.9300
C2—C3	1.380 (5)	C11—C12	1.374 (5)
C2—H2A	0.9300	C11—H11A	0.9300
C3—C4	1.363 (5)	C12—N5	1.319 (4)
C3—H3A	0.9300	C12—H12A	0.9300
C4—C5	1.389 (4)	N1—N2	1.354 (3)
C4—H4A	0.9300	N2—Mn1^{iii}	2.208 (2)
C5—N4	1.351 (4)	N5—Mn1^{iii}	2.289 (3)
C5—C6	1.468 (4)	N6—N7	1.157 (4)
C6—N1	1.333 (4)	N7—N8	1.170 (4)
C6—N3	1.339 (4)	N8—Mn1^{iv}	2.240 (3)
N2^{i}—Mn1—N1	104.67 (9)	N2—C7—C8	120.1 (3)
N2^{i}—Mn1—N8^{ii}	87.13 (10)	N3—C7—C8	126.5 (3)
N1—Mn1—N8^{ii}	162.01 (9)	N5—C8—C9	121.5 (3)
N2^{i}—Mn1—N6	160.37 (11)	N5—C8—C7	115.1 (3)
N1—Mn1—N6	84.57 (10)	C9—C8—C7	123.5 (3)
N8^{ii}—Mn1—N6	88.54 (11)	C10—C9—C8	118.8 (3)
N2^{i}—Mn1—N5^{i}	73.88 (9)	C10—C9—H9A	120.6
N1—Mn1—N5^{i}	105.95 (9)	C8—C9—H9A	120.6
N8^{ii}—Mn1—N5^{i}	90.21 (10)	C9—C10—C11	119.9 (3)
N6—Mn1—N5^{i}	87.01 (11)	C9—C10—H10A	120.1
N2^{i}—Mn1—N4	110.94 (9)	C11—C10—H10A	120.1
N1—Mn1—N4	73.20 (9)	C12—C11—C10	117.9 (3)
N8^{ii}—Mn1—N4	90.03 (10)	C12—C11—H11A	121.1
N6—Mn1—N4	88.19 (11)	C10—C11—H11A	121.1
N5^{i}—Mn1—N4	175.18 (10)	N5—C12—C11	123.8 (3)
N4—C1—C2	123.2 (3)	N5—C12—H12A	118.1
N4—C1—H1A	118.4	C11—C12—H12A	118.1
C2—C1—H1A	118.4	C6—N1—N2	105.3 (2)
C1—C2—C3	118.7 (3)	C6—N1—Mn1	113.65 (19)
C1—C2—H2A	120.7	N2—N1—Mn1	137.63 (19)
C3—C2—H2A	120.7	C7—N2—N1	105.9 (2)
C4—C3—C2	118.9 (3)	C7—N2—Mn1^{iii}	113.8 (2)
C4—C3—H3A	120.6	N1—N2—Mn1^{iii}	137.99 (19)
C2—C3—H3A	120.6	C6—N3—C7	100.9 (2)
C3—C4—C5	119.8 (3)	C1—N4—C5	118.0 (3)
C3—C4—H4A	120.1	C1—N4—Mn1	126.9 (2)
C5—C4—H4A	120.1	C5—N4—Mn1	112.7 (2)
N4—C5—C4	121.4 (3)	C12—N5—C8	118.2 (3)
N4—C5—C6	114.9 (3)	C12—N5—Mn1^{iii}	127.3 (2)
C4—C5—C6	123.7 (3)	C8—N5—Mn1^{iii}	113.7 (2)
N1—C6—N3	114.5 (3)	N7—N6—Mn1	154.2 (3)
N1—C6—C5	119.6 (3)	N6—N7—N8	178.3 (4)

N3—C6—C5	125.9 (2)	N7—N8—Mn1^{iv}	126.1 (2)
N2—C7—N3	113.3 (3)		

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

Fig. 1

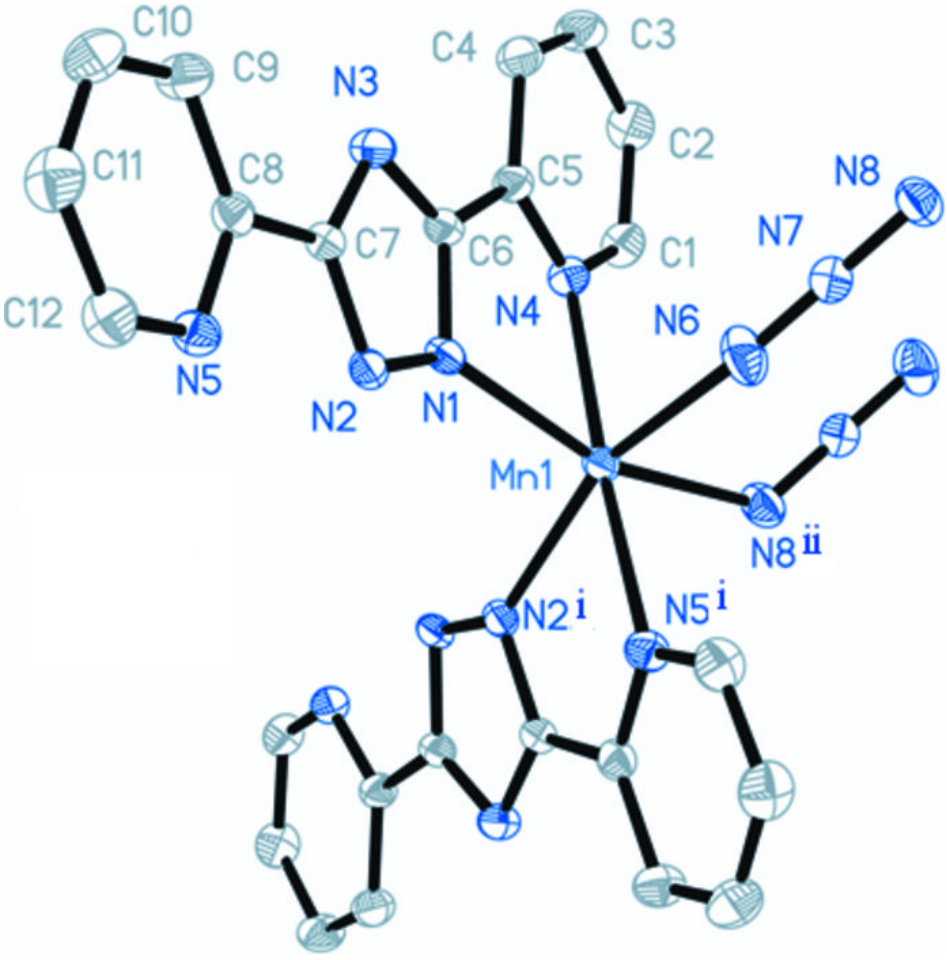

C10
C9
N3
C4
C3
C11
C8
C5
C2
N8
C7
C6
C1
N7
C12
N4
N6
N5
N2
N1
Mn1
N8ii
N2i
N5i

Fig. 2