

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

# Bis{2-[6-(1*H*-benzimidazol-2-yl)- $\kappa$ N<sup>3</sup>]-2-pyridyl- $\kappa$ N]benzimidazolato- $\kappa$ N}-manganese(II)

 Xian-Qun Bai<sup>a,b</sup> and Shu-Hua Zhang<sup>a\*</sup>

<sup>a</sup>Key Laboratory of Non-ferrous Metal Materials and Processing Technology, Department of Materials and Chemistry Engineering, Guilin University of Technology, Ministry of Education, Guilin 541004, People's Republic of China, and <sup>b</sup>College of Pharmacy, Guilin Medical University, Guilin 541004, People's Republic of China

Correspondence e-mail: zsh720108@21cn.com

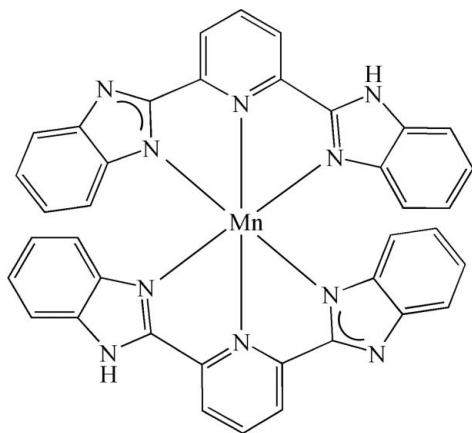
Received 11 February 2009; accepted 7 March 2009

Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.035;  $wR$  factor = 0.095; data-to-parameter ratio = 14.2.

In the title compound,  $[\text{Mn}(\text{C}_{19}\text{H}_{12}\text{N}_5)_2]$ , each  $\text{Mn}^{\text{II}}$  atom lies on a position of site symmetry 222 and has a distorted octahedral coordination geometry made up from six N atoms of two tridentate 2-[6-(1*H*-benzimidazol-2-yl)-2-pyridyl]benzimidazolato ligands. The complex molecules are linked into layers parallel to (001) by  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds, with the H atoms disordered over four symmetry-equivalent non-coordinated N atoms.

## Related literature

For a previous report of this complex, see: Shi *et al.* (2003). For other comparable transition-metal complexes, see: Harvey *et al.* (2003); Wang *et al.* (1994); Yue *et al.* (2006); Zhang *et al.* (2007).



## Experimental

## Crystal data

$[\text{Mn}(\text{C}_{19}\text{H}_{12}\text{N}_5)_2]$   
 $M_r = 675.61$   
 Tetragonal,  $P4n2$   
 $a = 10.1225$  (14) Å  
 $c = 15.865$  (3) Å  
 $V = 1625.6$  (5) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.45$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.45 \times 0.44 \times 0.31$  mm

## Data collection

Bruker SMART 2K CCD diffractometer  
 Absorption correction: none  
 6803 measured reflections

1599 independent reflections  
 1226 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.040$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.095$   
 $S = 1.04$   
 1599 reflections  
 113 parameters  
 H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.18$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.21$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983),  
 701 Friedel pairs  
 Flack parameter: 0.00 (1)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N3}-\text{H1}\cdots\text{N3}^i$	0.91	1.89	2.736 (4)	154

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

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

We acknowledge financial support by Guangxi Key Laboratory for Advanced Materials and New Preparation Technology (grant No. 0842003-25) and the Young Science Foundation of Guangxi Province of China (grant No. 0832085).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2351).

## References

- Bruker (2003). *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Harvey, M. A., Baggio, S., Muñoz, J. C. & Baggio, R. (2003). *Acta Cryst.* **C59**, m283–m285.  
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
 Shi, W., Li, W., Shen, P.-P., Xu, Y.-K., Wang, H.-M., Shi, M. & Liu, Y. (2003). *Chin. J. Chem.* **21**, 659–664.  
 Wang, S., Cui, Y., Ran, R. & Luo, A. (1994). *Polyhedron*, **13**, 1661–1668.  
 Yue, S.-M., Xu, H.-B., Ma, J.-F., Su, Z.-M., Kan, Y.-H. & Zhang, H.-J. (2006). *Polyhedron*, **25**, 635–644.  
 Zhang, S.-H., Zeng, M.-H. & Liang, H. (2007). *Acta Cryst.* **E63**, m1055–m1056.

## supporting information

*Acta Cryst.* (2009). E65, m397 [doi:10.1107/S1600536809008411]

**Bis{2-[6-(1*H*-benzimidazol-2-yl- $\kappa$ N<sup>3</sup>)-2-pyridyl- $\kappa$ N]benzimidazolato- $\kappa$ N}manganese(II)****Xian-Qun Bai and Shu-Hua Zhang****S1. Comment**

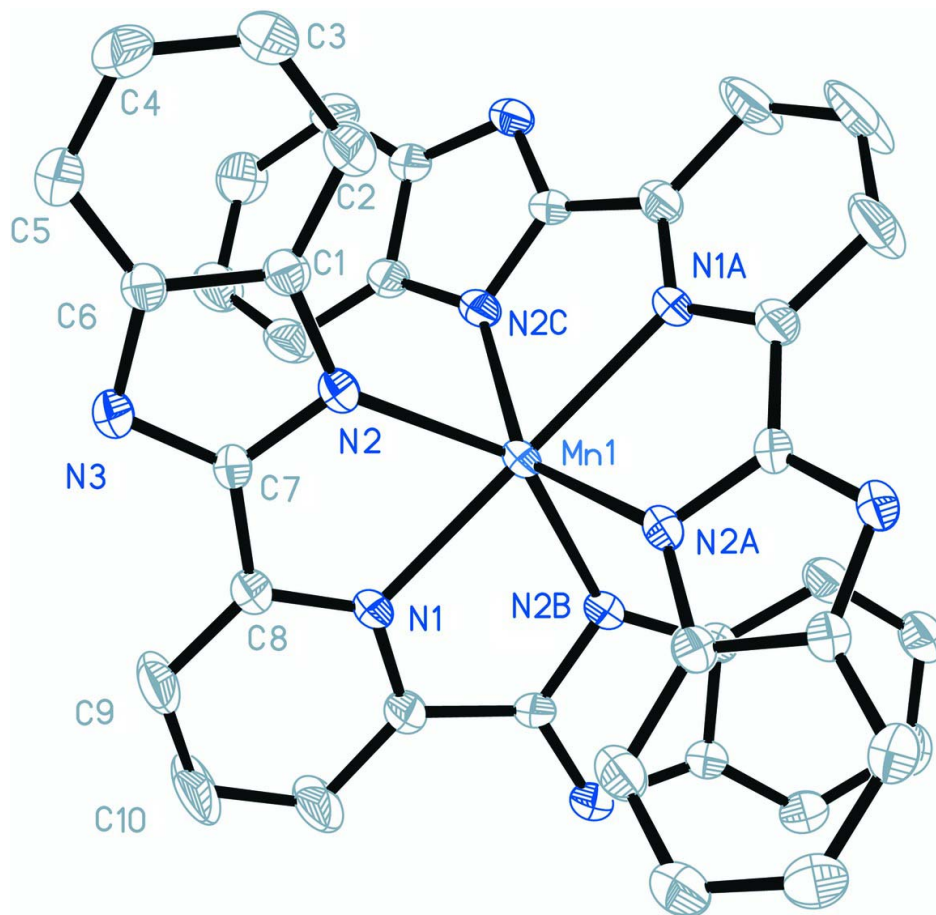
The 2,6-bis(1*H*-benzimidazol-2-yl)pyridine ligand is known to form complexes with various transition metal atoms (Harvey *et al.*, 2003; Wang *et al.*, 1994; Yue *et al.*, 2006; Zhang *et al.*, 2007). The title compound, containing Mn<sup>II</sup>, has been reported previously (Shi *et al.*, 2003), with closely comparable cell parameters but refined in space group *Pn*. Atomic coordinates were not reported and they are not available in the Cambridge Structural Database. However, diagrams of the structure in the paper of Shi *et al.* (2003) suggest it to be closely comparable to the current reported structure, and it is probable that the previous refinement in *Pn* is an instance of "missed symmetry".

**S2. Experimental**

Manganese nitrate hexahydrate (0.144 g, 0.5 mmol) and 2,6-bis(1*H*-benzimidazol-2-yl)pyridine (0.1536 g, 1 mmol) were dissolved in ethanol (8 ml). The solution was placed in a 15 ml Teflon-lined stainless steel bomb and heated at 423 K for 96 h. The cooled mixture yielded red block-shaped crystals in about 41% yield. The crystals were washed with ethanol and dried in air.

**S3. Refinement**

All H atoms were positioned geometrically (C—H = 0.93 Å, N—H = 0.91 Å) and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C or N})$ . The site occupancy of H1 was constrained to 0.5 so that it sums to a total of 2 H atoms disordered over the four symmetry-equivalent N3 atoms.

**Figure 1**

Molecular structure showing 30% probability displacement ellipsoids. H atoms are omitted. Symmetry codes: (A)  $-x + 2, -y, z$ ; (B)  $-y + 1, -x + 1, -z$ ; (C)  $y + 1, x - 1, -z$ .

### Bis{2-[6-(1*H*-benzimidazol-2-yl- $\kappa$ N<sup>3</sup>)-2-pyridyl- $\kappa$ N]benzimidazolato- $\kappa$ N}manganese(II)

#### Crystal data

[Mn(C<sub>19</sub>H<sub>12</sub>N<sub>5</sub>)<sub>2</sub>]

$M_r = 675.61$

Tetragonal,  $P4n2$

Hall symbol:  $P -4 -2n$

$a = 10.1225 (14) \text{ \AA}$

$c = 15.865 (3) \text{ \AA}$

$V = 1625.6 (5) \text{ \AA}^3$

$Z = 2$

$F(000) = 694$

$D_x = 1.380 \text{ Mg m}^{-3}$

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

Cell parameters from 6803 reflections

$\theta = 2.4\text{--}26.0^\circ$

$\mu = 0.45 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Block, red

$0.45 \times 0.44 \times 0.31 \text{ mm}$

#### Data collection

Bruker SMART 2K CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

6803 measured reflections

1599 independent reflections

1226 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\text{max}} = 26.0^\circ$ ,  $\theta_{\text{min}} = 2.4^\circ$

$h = -10 \rightarrow 12$   
 $k = -12 \rightarrow 11$

$l = -19 \rightarrow 12$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.095$   
 $S = 1.04$   
 1599 reflections  
 113 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.3361P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$   
 Absolute structure: Flack (1983), 701 Friedel  
 pairs  
 Absolute structure parameter: 0.00 (1)

*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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Mn1	0.5000	0.0000	0.2500	0.0372 (2)	
C1	0.3191 (3)	0.1985 (3)	0.12293 (17)	0.0379 (6)	
C2	0.2023 (3)	0.1312 (3)	0.1090 (2)	0.0542 (9)	
H2	0.1913	0.0448	0.1279	0.065*	
C3	0.1031 (4)	0.1952 (4)	0.0668 (3)	0.0626 (10)	
H3	0.0234	0.1520	0.0575	0.075*	
C4	0.1195 (3)	0.3226 (4)	0.0376 (2)	0.0625 (10)	
H4	0.0511	0.3624	0.0078	0.075*	
C5	0.2336 (3)	0.3919 (3)	0.0513 (2)	0.0540 (9)	
H5	0.2432	0.4782	0.0321	0.065*	
C6	0.3348 (3)	0.3286 (3)	0.09494 (19)	0.0406 (7)	
C7	0.5083 (3)	0.2688 (3)	0.16267 (18)	0.0366 (7)	
C8	0.6350 (3)	0.2666 (3)	0.2067 (2)	0.0471 (8)	
C9	0.7292 (4)	0.3650 (4)	0.2072 (3)	0.0915 (16)	
H9	0.7147	0.4441	0.1789	0.110*	
C10	0.8439 (3)	0.3439 (3)	0.2500	0.128 (3)	
H10	0.9089	0.4089	0.2500	0.154*	
N1	0.65540 (18)	0.15540 (18)	0.2500	0.0381 (7)	
N2	0.4325 (2)	0.1611 (2)	0.16468 (16)	0.0388 (6)	
N3	0.4560 (2)	0.3722 (2)	0.12179 (17)	0.0437 (6)	
H1	0.5082	0.4448	0.1157	0.066*	0.50

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Mn1	0.0277 (3)	0.0277 (3)	0.0560 (5)	-0.0078 (3)	0.000	0.000
C1	0.0366 (16)	0.0338 (16)	0.0435 (15)	-0.0021 (11)	-0.0031 (14)	-0.0071 (14)
C2	0.0514 (19)	0.0429 (18)	0.068 (2)	-0.0116 (14)	-0.0116 (18)	-0.0014 (17)
C3	0.049 (2)	0.056 (2)	0.083 (3)	-0.0112 (17)	-0.016 (2)	-0.003 (2)
C4	0.0494 (19)	0.062 (2)	0.076 (3)	0.0047 (18)	-0.0231 (18)	0.0033 (19)
C5	0.053 (2)	0.0375 (17)	0.071 (2)	0.0038 (15)	-0.0036 (17)	0.0058 (18)
C6	0.0381 (16)	0.0316 (16)	0.0520 (18)	-0.0011 (12)	-0.0007 (14)	-0.0043 (14)
C7	0.0358 (15)	0.0240 (13)	0.0501 (18)	-0.0011 (11)	0.0004 (15)	0.0004 (12)
C8	0.0367 (16)	0.0352 (16)	0.069 (2)	-0.0057 (12)	-0.0053 (16)	0.0089 (15)
C9	0.066 (2)	0.051 (2)	0.158 (4)	-0.0324 (18)	-0.046 (3)	0.047 (2)
C10	0.078 (3)	0.078 (3)	0.229 (8)	-0.058 (3)	-0.083 (5)	0.083 (5)
N1	0.0292 (9)	0.0292 (9)	0.0559 (19)	-0.0071 (11)	0.0007 (15)	-0.0007 (15)
N2	0.0347 (13)	0.0285 (11)	0.0531 (15)	-0.0063 (10)	-0.0047 (11)	-0.0010 (11)
N3	0.0402 (13)	0.0285 (12)	0.0623 (16)	-0.0045 (10)	-0.0046 (13)	0.0033 (13)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Mn1—N1 <sup>i</sup>	2.225 (3)	C5—C6	1.393 (4)
Mn1—N1	2.225 (3)	C5—H5	0.930
Mn1—N2 <sup>ii</sup>	2.226 (2)	C6—N3	1.372 (4)
Mn1—N2 <sup>i</sup>	2.226 (2)	C7—N2	1.333 (3)
Mn1—N2	2.226 (2)	C7—N3	1.341 (4)
Mn1—N2 <sup>iii</sup>	2.226 (2)	C7—C8	1.461 (4)
C1—N2	1.378 (3)	C8—N1	1.334 (3)
C1—C2	1.382 (4)	C8—C9	1.379 (4)
C1—C6	1.399 (4)	C9—C10	1.362 (4)
C2—C3	1.370 (5)	C9—H9	0.930
C2—H2	0.930	C10—C9 <sup>iii</sup>	1.362 (4)
C3—C4	1.380 (5)	C10—H10	0.930
C3—H3	0.930	N1—C8 <sup>iii</sup>	1.334 (3)
C4—C5	1.369 (5)	N3—H1	0.910
C4—H4	0.930		
N1 <sup>i</sup> —Mn1—N1	180.00 (13)	C4—C5—C6	117.7 (3)
N1 <sup>i</sup> —Mn1—N2 <sup>ii</sup>	72.49 (5)	C4—C5—H5	121.2
N1—Mn1—N2 <sup>ii</sup>	107.51 (5)	C6—C5—H5	121.2
N1 <sup>i</sup> —Mn1—N2 <sup>i</sup>	72.49 (5)	N3—C6—C5	131.7 (3)
N1—Mn1—N2 <sup>i</sup>	107.51 (5)	N3—C6—C1	107.8 (3)
N2 <sup>ii</sup> —Mn1—N2 <sup>i</sup>	144.99 (11)	C5—C6—C1	120.5 (3)
N1 <sup>i</sup> —Mn1—N2	107.51 (5)	N2—C7—N3	115.0 (2)
N1—Mn1—N2	72.49 (5)	N2—C7—C8	118.8 (2)
N2 <sup>ii</sup> —Mn1—N2	85.43 (12)	N3—C7—C8	126.1 (2)
N2 <sup>i</sup> —Mn1—N2	105.11 (12)	N1—C8—C9	120.0 (3)
N1 <sup>i</sup> —Mn1—N2 <sup>iii</sup>	107.51 (5)	N1—C8—C7	113.2 (2)
N1—Mn1—N2 <sup>iii</sup>	72.49 (5)	C9—C8—C7	126.8 (3)

N2 <sup>ii</sup> —Mn1—N2 <sup>iii</sup>	105.11 (12)	C10—C9—C8	118.6 (4)
N2 <sup>i</sup> —Mn1—N2 <sup>iii</sup>	85.43 (12)	C10—C9—H9	120.7
N2—Mn1—N2 <sup>iii</sup>	144.99 (11)	C8—C9—H9	120.7
N2—C1—C2	130.8 (3)	C9—C10—C9 <sup>iii</sup>	121.0 (4)
N2—C1—C6	108.5 (2)	C9—C10—H10	119.5
C2—C1—C6	120.7 (3)	C9 <sup>iii</sup> —C10—H10	119.5
C3—C2—C1	118.1 (3)	C8—N1—C8 <sup>iii</sup>	121.7 (3)
C3—C2—H2	120.9	C8—N1—Mn1	119.15 (16)
C1—C2—H2	120.9	C8 <sup>iii</sup> —N1—Mn1	119.15 (16)
C2—C3—C4	121.2 (3)	C7—N2—C1	104.0 (2)
C2—C3—H3	119.4	C7—N2—Mn1	115.90 (18)
C4—C3—H3	119.4	C1—N2—Mn1	138.51 (18)
C5—C4—C3	121.8 (3)	C7—N3—C6	104.6 (2)
C5—C4—H4	119.1	C7—N3—H1	116.9
C3—C4—H4	119.1	C6—N3—H1	138.2

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

*Hydrogen-bond geometry (Å, °)*

<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>
N3—H1 $\cdots$ N3 <sup>iv</sup>	0.91	1.89	2.736 (4)	154

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