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Bis{2-[6-(1*H*-benzimidazol-2-yl-κN^3)-2-pyridyl-κN]benzimidazolato-κN}-manganese(II)

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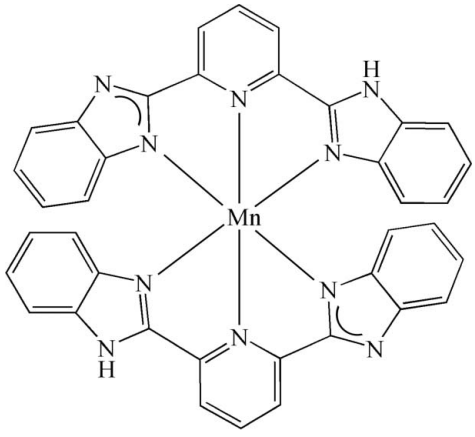
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.035; wR factor = 0.095; data-to-parameter ratio = 14.2.

In the title compound, $[Mn(C_{19}H_{12}N_5)_2]$, each Mn^{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]benzimidazolate ligands. The complex molecules are linked into layers parallel to (001) by N—H···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

$[Mn(C_{19}H_{12}N_5)_2]$
M_r = 675.61
Tetragonal, $P\bar{4}n2$
a = 10.1225 (14) Å
c = 15.865 (3) Å
V = 1625.6 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.45 mm^{-1}
T = 298 K
0.45 × 0.44 × 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_{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
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Absolute structure: Flack (1983), 701 Friedel pairs
Flack parameter: 0.00 (1)

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H1···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: *SAINT* (Bruker, 2003); data reduction: *SAINT*; 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*.

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

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supplementary materials

Acta Cryst. (2009). E**65**, m397 [**doi:10.1107/S1600536809008411**]

Bis{2-[6-(1*H*-benzimidazol-2-yl-κN^3)-2-pyridyl-κN]benzimidazolato-κN}manganese(II)

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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^{II}, 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".

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.

Refinement

All H atoms were positioned geometrically (C—H = 0.93 Å, N—H = 0.91 Å) and refined as riding with U_{iso}(H) = 1.2 U_{eq}(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.

Figures

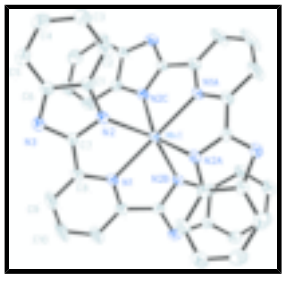

Fig. 1. Molecular structure showing 30% probability displacement ellipsoids. H atoms are omitted. Symmetry codes: (A) -*x* + 2, -*y*, *z*; (B) -*y* + 1, -*x* + 1, -*z*; (C) *y* + 1, *x* - 1, -*z*.

Bis{2-[6-(1*H*-benzimidazol-2-yl-κN^3)-2-pyridyl- κ*N*]benzimidazolato-κ*N*}manganese(II)

Crystal data

$[Mn(C_{19}H_{12}N_5)_2]$ $Z = 2$

M_r = 675.61	F_{000} = 694
Tetragonal, $P\bar{4}n2$	D_x = 1.380 Mg m^{-3}
Hall symbol: P -4 -2n	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 10.1225 (14) Å	Cell parameters from 6803 reflections
b = 10.1225 (14) Å	θ = 2.4–26.0º
c = 15.865 (3) Å	μ = 0.45 mm^{-1}
α = 90º	T = 298 K
β = 90º	Block, red
γ = 90º	0.45 × 0.44 × 0.31 mm
V = 1625.6 (5) Å^3	

Data collection

Bruker SMART 2K CCD diffractometer	1226 reflections with $I > 2<s(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.040
Monochromator: graphite	θ_{max} = 26.0º
T = 293 K	θ_{min} = 2.4º
φ and ω scans	h = −10→12
Absorption correction: none	k = −12→11
6803 measured reflections	l = −19→12
1599 independent reflections	

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	$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.3361P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.095	$(\Delta/\sigma)_{max} < 0.001$
S = 1.04	$\Delta\rho_{max}$ = 0.18 e Å^{-3}
1599 reflections	$\Delta\rho_{min}$ = −0.21 e Å^{-3}
113 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 701 Friedel pairs
Secondary atom site location: difference Fourier map	Flack 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{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 (Å^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 (Å, °)

Mn1—N1^{i}	2.225 (3)	C5—C6	1.393 (4)
Mn1—N1	2.225 (3)	C5—H5	0.930
Mn1—N2^{ii}	2.226 (2)	C6—N3	1.372 (4)
Mn1—N2^{i}	2.226 (2)	C7—N2	1.333 (3)
Mn1—N2	2.226 (2)	C7—N3	1.341 (4)
Mn1—N2^{iii}	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^{iii}	1.362 (4)
C3—C4	1.380 (5)	C10—H10	0.930
C3—H3	0.930	N1—C8^{iii}	1.334 (3)
C4—C5	1.369 (5)	N3—H1	0.910
C4—H4	0.930		
N1^{i}—Mn1—N1	180.00 (13)	C4—C5—C6	117.7 (3)
N1^{i}—Mn1—N2^{ii}	72.49 (5)	C4—C5—H5	121.2
N1—Mn1—N2^{ii}	107.51 (5)	C6—C5—H5	121.2
N1^{i}—Mn1—N2^{i}	72.49 (5)	N3—C6—C5	131.7 (3)
N1—Mn1—N2^{i}	107.51 (5)	N3—C6—C1	107.8 (3)
N2^{ii}—Mn1—N2^{i}	144.99 (11)	C5—C6—C1	120.5 (3)
N1^{i}—Mn1—N2	107.51 (5)	N2—C7—N3	115.0 (2)
N1—Mn1—N2	72.49 (5)	N2—C7—C8	118.8 (2)
N2^{ii}—Mn1—N2	85.43 (12)	N3—C7—C8	126.1 (2)
N2^{i}—Mn1—N2	105.11 (12)	N1—C8—C9	120.0 (3)
N1^{i}—Mn1—N2^{iii}	107.51 (5)	N1—C8—C7	113.2 (2)
N1—Mn1—N2^{iii}	72.49 (5)	C9—C8—C7	126.8 (3)
N2^{ii}—Mn1—N2^{iii}	105.11 (12)	C10—C9—C8	118.6 (4)
N2^{i}—Mn1—N2^{iii}	85.43 (12)	C10—C9—H9	120.7
N2—Mn1—N2^{iii}	144.99 (11)	C8—C9—H9	120.7
N2—C1—C2	130.8 (3)	C9—C10—C9^{iii}	121.0 (4)
N2—C1—C6	108.5 (2)	C9—C10—H10	119.5
C2—C1—C6	120.7 (3)	C9^{iii}—C10—H10	119.5
C3—C2—C1	118.1 (3)	C8—N1—C8^{iii}	121.7 (3)
C3—C2—H2	120.9	C8—N1—Mn1	119.15 (16)
C1—C2—H2	120.9	C8^{iii}—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, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H1···N3^{iv}	0.91	1.89	2.736 (4)	154

Symmetry codes: (iv) −*x*+1, −*y*+1, *z*.

Fig. 1