metal-organic compounds

Dichlorido(dipyrido[3,2-*a*:2′,3′-*c*]-phenazine)manganese(II)

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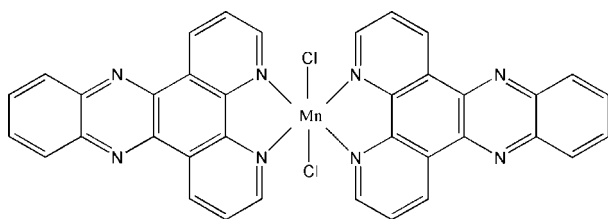Correspondence e-mail: guangbochejl@yahoo.com

The complete molecule of the title compound, [MnCl$_2$-(C$_{18}$H$_{10}$N$_4$)$_2$], is generated by crystallographic twofold symmetry with the Mn atom lying on the rotation axis. The Mn coordination geometry is a distorted *cis*-MnCl$_2$N$_4$ octahedron, arising from two *N*,*N*′-bidentate dipyrido[3,2-*a*:2′,3′-*c*]phenazine (DPPZ) ligands and two chloride ions. In the crystal structure, neighbouring mononuclear units pack together through π–π contacts between the DPPZ rings [shortest centroid–centroid distance = 3.480 (2) Å], leading to a chain-like structure along [001]. C—H$\cdots$Cl hydrogen bonds complete the structure.

Related literature

For background, see: Che *et al.* (2006, 2008); Xu *et al.* (2008).

Experimental

Crystal data

[MnCl$_2$(C$_{18}$H$_{10}$N$_4$)$_2$]
M_r = 690.44
Monoclinic, $C2/c$
a = 8.4017 (17) Å

b = 12.256 (3) Å
c = 28.226 (6) Å
β = 95.09 (3)°
V = 2895.0 (10) Å^3

Z = 4
Mo $K\alpha$ radiation
μ = 0.69 mm^{-1}

T = 292 (2) K
0.38 × 0.24 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.821, T_{max} = 0.864

11873 measured reflections
2866 independent reflections
1748 reflections with $I > 2\sigma(I)$
R_{int} = 0.078

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.120
S = 1.00
2866 reflections
243 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Table 1
Selected bond lengths (Å).

Mn—N1	2.283 (3)	Mn—Cl	2.4644 (12)
Mn—N2	2.316 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots$$A$	D—H$\cdots$$A$
C2—H2$\cdots$Cl^i	1.09 (3)	2.67 (3)	3.737 (4)	168 (2)
C15—H15$\cdots$Cl^{ii}	1.04 (3)	2.64 (3)	3.648 (4)	163 (3)

Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (ii) $-x + \frac{5}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); 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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2884).

References

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Che, G.-B., Liu, C.-B., Liu, B., Wang, Q.-W. & Xu, Z.-L. (2008). *CrystEngComm*, **10**, 184–191.
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supporting information

Dichlorido(dipyrido[3,2-*a*:2′,3′-*c*]phenazine)manganese(II)

Mao-Liang Xu, Shu-Bo Sun, Xiu-Ying Li and Guang-Bo Che

S1. Comment

1,10-Phenanthroline (phen) and its derivatives, as chelating N-containing aromatic ligands, has been extensively studied in the chemistry of coordination polymers (Che *et al.*, 2008). Here, we report the crystal structure of the title compound, [Mn(DPPZ)₂Cl₂] or [Mn($C_{18}H_{10}N_4$)₂Cl₂] (I), based on the dipyrido[3,2 - a:2′,3′-c]-phenazine (DPPZ) ligand (Xu *et al.*, 2008).

In compound (I), the Mn atom (site symmetry 2) is coordinated in a distorted octahedral fashion (Fig. 1) by four N atoms from two DPPZ ligands and two Cl ions (Table 1). The DPPZ ring systems is almost planar and the dihedral angle between the two symmetry-related DPPZ planes is 70.66°.

π-π stacking interactions between the DPPZ ligands assemble mononuclear complex molecules into one-dimensional chains along (001) [centroid-centroid distances = 3.480 (2) Å] (Fig. 2). Finally, C—H···Cl hydrogen bonds involving the hydrogen of aromatic rings and the Cl ions further stabilize the crystal structure (Table 2).

S2. Experimental

The DPPZ ligand was synthesized according to the literature method of Che *et al.* (2006). A mixture of DPPZ, MnCl₂ and water in a molar ratio of 2:1:5000 was sealed in a Teflon-lined autoclave and heated to 423 K for 3 d. Upon cooling and opening the bomb, yellow blocks of (I) were obtained (81% yield based on Mn).

S3. Refinement

The H atoms were located in a difference map and their positions were freely refined with a fixed U_{iso} value of 0.06Å².
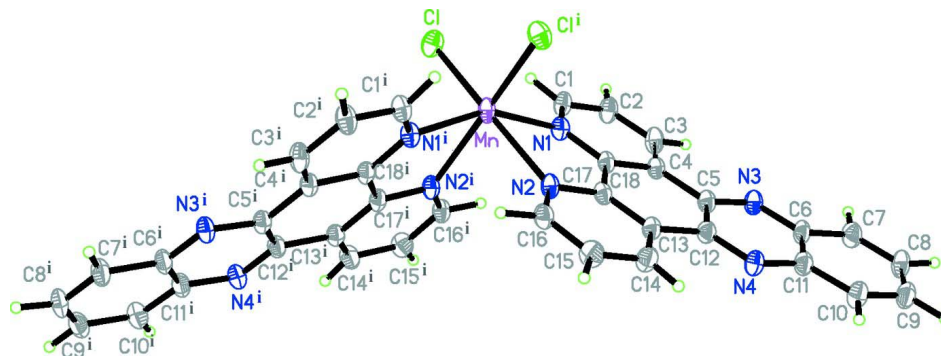

Figure 1

A view of (I). Displacement ellipsoids are drawn at the 30% probability level (arbitrary spheres for the H atoms). [Symmetry code: (i) -x + 2, y, -z + 1/2.]
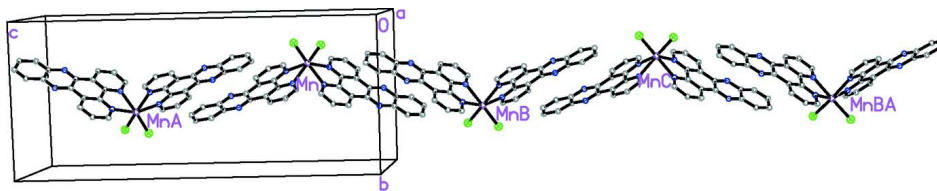
Figure 2

View of the supramolecular chain structure of (I) arising from *π*-*π* stacking. H atoms have been omitted. [Symmetry code: (A) -*x* + 2, *y*, -*z* + 1/2; (B) *x*, -*y* + 1, -*z*; (C) *x*, *y*, -*z* - 1; (BA) *x*, -*y* + 1, -*z* - 1.]

Dichlorido(dipyrido[3,2-a:2′,3′-c]phenazine)manganese(II)

Crystal data

[MnCl$_2$(C$_{18}$H$_{10}$N$_4$)$_2$]	$F(000) = 1404$
$M_r = 690.44$	$D_x = 1.584$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 2001 reflections
$a = 8.4017$ (17) Å	$\theta = 2.9–26.1°$
$b = 12.256$ (3) Å	$\mu = 0.69$ mm^{-1}
$c = 28.226$ (6) Å	$T = 292$ K
$\beta = 95.09$ (3)°	Block, yellow
$V = 2895.0$ (10) Å^3	$0.38 \times 0.24 \times 0.21$ mm
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	11873 measured reflections
Radiation source: fine-focus sealed tube	2866 independent reflections
Graphite monochromator	1748 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.078$
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	$\theta_{max} = 26.1°$, $\theta_{min} = 2.9°$
$T_{min} = 0.821$, $T_{max} = 0.864$	$h = -10→10$
	$k = -15→15$
	$l = -34→34$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.053$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.120$	
$S = 1.00$	H atoms treated by a mixture of independent and constrained refinement
2866 reflections	
243 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} = 0.001$
	$\Delta\rho_{max} = 0.32$ e Å^{-3}
	$\Delta\rho_{min} = -0.43$ e 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_{iso}*/U_{eq}
C1	0.6671 (4)	0.3405 (3)	0.29912 (12)	0.0408 (9)
C2	0.5622 (4)	0.3550 (3)	0.33399 (12)	0.0459 (10)
C3	0.6118 (4)	0.4167 (3)	0.37276 (13)	0.0461 (10)
C4	0.7619 (4)	0.4666 (3)	0.37635 (11)	0.0343 (8)
C5	0.8223 (4)	0.5307 (3)	0.41737 (11)	0.0367 (9)
C7	0.7118 (5)	0.6056 (3)	0.53324 (14)	0.0508 (11)
C8	0.7738 (5)	0.6604 (3)	0.57158 (13)	0.0521 (11)
C9	0.9253 (5)	0.7097 (3)	0.57276 (13)	0.0501 (11)
C10	1.0139 (5)	0.7010 (3)	0.53419 (13)	0.0508 (11)
C11	0.9520 (4)	0.6445 (3)	0.49315 (12)	0.0424 (9)
C12	0.9766 (4)	0.5811 (3)	0.41822 (12)	0.0373 (9)
C13	1.0710 (4)	0.5678 (3)	0.37731 (11)	0.0364 (9)
C14	1.2220 (4)	0.6152 (3)	0.37604 (13)	0.0448 (10)
C15	1.3054 (4)	0.5992 (3)	0.33699 (13)	0.0472 (10)
C16	1.2389 (4)	0.5345 (3)	0.30016 (13)	0.0419 (9)
C17	1.0135 (4)	0.5042 (3)	0.33907 (11)	0.0345 (8)
C18	0.8568 (4)	0.4510 (3)	0.33849 (11)	0.0333 (8)
C6	0.7985 (4)	0.5942 (3)	0.49265 (12)	0.0404 (9)
N1	0.8113 (3)	0.3861 (2)	0.30102 (9)	0.0377 (7)
N2	1.0963 (3)	0.4861 (2)	0.30080 (9)	0.0380 (7)
N3	0.7343 (3)	0.5382 (2)	0.45415 (9)	0.0409 (8)
N4	1.0403 (3)	0.6370 (2)	0.45531 (10)	0.0427 (8)
Mn	1.0000	0.34811 (7)	0.2500	0.0383 (3)
Cl	0.82991 (11)	0.22033 (8)	0.20077 (3)	0.0501 (3)
H1	0.634 (4)	0.289 (3)	0.2722 (13)	0.060*
H2	0.448 (4)	0.313 (3)	0.3296 (12)	0.060*
H3	0.550 (4)	0.427 (3)	0.3977 (13)	0.060*
H7	0.613 (4)	0.566 (3)	0.5315 (12)	0.060*
H8	0.720 (4)	0.663 (3)	0.5996 (13)	0.060*
H9	0.973 (4)	0.751 (3)	0.6018 (14)	0.060*
H10	1.116 (4)	0.738 (3)	0.5341 (13)	0.060*
H14	1.264 (4)	0.661 (3)	0.3997 (13)	0.060*
H15	1.417 (4)	0.634 (3)	0.3341 (12)	0.060*
H16	1.299 (4)	0.524 (3)	0.2703 (12)	0.060*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.036 (2)	0.056 (3)	0.031 (2)	−0.0009 (19)	0.0073 (16)	−0.0062 (19)
C2	0.036 (2)	0.068 (3)	0.035 (2)	−0.003 (2)	0.0089 (17)	−0.006 (2)

C3	0.037 (2)	0.069 (3)	0.035 (2)	0.003 (2)	0.0195 (18)	0.000 (2)
C4	0.0330 (19)	0.043 (2)	0.0278 (19)	0.0012 (17)	0.0080 (15)	0.0006 (16)
C5	0.037 (2)	0.045 (2)	0.0288 (19)	0.0031 (18)	0.0086 (16)	0.0008 (17)
C7	0.058 (3)	0.061 (3)	0.036 (2)	0.005 (2)	0.019 (2)	−0.003 (2)
C8	0.061 (3)	0.069 (3)	0.029 (2)	0.004 (2)	0.0175 (19)	−0.008 (2)
C9	0.060 (3)	0.058 (3)	0.032 (2)	0.012 (2)	0.002 (2)	−0.008 (2)
C10	0.054 (3)	0.061 (3)	0.037 (2)	−0.002 (2)	0.007 (2)	−0.009 (2)
C11	0.049 (2)	0.050 (2)	0.029 (2)	0.005 (2)	0.0079 (17)	−0.0027 (18)
C12	0.041 (2)	0.042 (2)	0.030 (2)	0.0025 (18)	0.0095 (16)	−0.0019 (18)
C13	0.039 (2)	0.042 (2)	0.030 (2)	0.0012 (17)	0.0075 (16)	−0.0004 (17)
C14	0.045 (2)	0.051 (3)	0.039 (2)	−0.010 (2)	0.0098 (18)	−0.0088 (19)
C15	0.038 (2)	0.056 (3)	0.049 (2)	−0.009 (2)	0.0158 (19)	−0.002 (2)
C16	0.044 (2)	0.051 (2)	0.032 (2)	−0.0016 (19)	0.0128 (17)	0.0011 (19)
C17	0.0339 (19)	0.044 (2)	0.0269 (19)	0.0051 (17)	0.0078 (15)	0.0047 (17)
C18	0.0342 (19)	0.041 (2)	0.0257 (19)	0.0034 (17)	0.0065 (15)	0.0021 (17)
C6	0.047 (2)	0.050 (2)	0.025 (2)	0.0076 (19)	0.0090 (16)	−0.0031 (18)
N1	0.0344 (16)	0.049 (2)	0.0300 (17)	−0.0013 (15)	0.0053 (13)	−0.0018 (15)
N2	0.0379 (17)	0.050 (2)	0.0283 (16)	0.0001 (15)	0.0129 (13)	0.0004 (14)
N3	0.0396 (17)	0.054 (2)	0.0307 (17)	0.0027 (15)	0.0128 (14)	−0.0028 (15)
N4	0.0452 (18)	0.052 (2)	0.0317 (17)	0.0017 (15)	0.0091 (14)	−0.0061 (15)
Mn	0.0351 (4)	0.0540 (6)	0.0273 (4)	0.000	0.0113 (3)	0.000
Cl	0.0432 (6)	0.0631 (7)	0.0448 (6)	0.0003 (5)	0.0081 (4)	−0.0096 (5)

Geometric parameters (Å, º)

C1—N1	1.330 (4)	C11—C6	1.429 (5)
C1—C2	1.390 (5)	C12—N4	1.323 (4)
C1—H1	1.01 (4)	C12—C13	1.467 (4)
C2—C3	1.365 (5)	C13—C17	1.383 (4)
C2—H2	1.08 (4)	C13—C14	1.399 (5)
C3—C4	1.397 (5)	C14—C15	1.372 (5)
C3—H3	0.92 (4)	C14—H14	0.92 (4)
C4—C18	1.402 (4)	C15—C16	1.385 (5)
C4—C5	1.453 (4)	C15—H15	1.04 (4)
C5—N3	1.330 (4)	C16—N2	1.339 (4)
C5—C12	1.434 (4)	C16—H16	1.03 (3)
C7—C8	1.339 (5)	C17—N2	1.354 (4)
C7—C6	1.418 (5)	C17—C18	1.468 (4)
C7—H7	0.96 (3)	C18—N1	1.351 (4)
C8—C9	1.406 (5)	C6—N3	1.356 (4)
C8—H8	0.95 (4)	Mn—N1	2.283 (3)
C9—C10	1.377 (5)	Mn—N2	2.316 (3)
C9—H9	1.02 (4)	Mn—Cl	2.4644 (12)
C10—C11	1.409 (5)	Mn—N1[i]	2.283 (3)
C10—H10	0.97 (4)	Mn—N2[i]	2.316 (3)
C11—N4	1.357 (4)	Mn—Cl[i]	2.4644 (12)
N1—C1—C2	123.4 (4)	C14—C15—C16	119.0 (3)

N1—C1—H1	119 (2)	C14—C15—H15	122 (2)
C2—C1—H1	118 (2)	C16—C15—H15	118.7 (19)
C3—C2—C1	118.1 (4)	N2—C16—C15	123.1 (3)
C3—C2—H2	123.9 (19)	N2—C16—H16	117.5 (19)
C1—C2—H2	118.0 (19)	C15—C16—H16	119 (2)
C2—C3—C4	120.7 (3)	N2—C17—C13	123.1 (3)
C2—C3—H3	123 (2)	N2—C17—C18	116.2 (3)
C4—C3—H3	117 (2)	C13—C17—C18	120.6 (3)
C3—C4—C18	117.1 (3)	N1—C18—C4	122.4 (3)
C3—C4—C5	122.9 (3)	N1—C18—C17	117.5 (3)
C18—C4—C5	119.9 (3)	C4—C18—C17	120.1 (3)
N3—C5—C12	121.5 (3)	N3—C6—C7	120.1 (3)
N3—C5—C4	118.7 (3)	N3—C6—C11	121.4 (3)
C12—C5—C4	119.8 (3)	C7—C6—C11	118.5 (3)
C8—C7—C6	120.8 (4)	C1—N1—C18	118.2 (3)
C8—C7—H7	125 (2)	C1—N1—Mn	124.7 (2)
C6—C7—H7	114 (2)	C18—N1—Mn	116.7 (2)
C7—C8—C9	121.4 (4)	C16—N2—C17	117.5 (3)
C7—C8—H8	121 (2)	C16—N2—Mn	125.4 (2)
C9—C8—H8	118 (2)	C17—N2—Mn	116.0 (2)
C10—C9—C8	120.0 (4)	C5—N3—C6	116.8 (3)
C10—C9—H9	118 (2)	C12—N4—C11	116.6 (3)
C8—C9—H9	122 (2)	N1ⁱ—Mn—N1	156.48 (15)
C9—C10—C11	120.1 (4)	N1ⁱ—Mn—N2	91.01 (10)
C9—C10—H10	120 (2)	N1—Mn—N2	71.63 (10)
C11—C10—H10	119 (2)	N1ⁱ—Mn—N2ⁱ	71.63 (10)
N4—C11—C10	119.5 (3)	N1—Mn—N2ⁱ	91.01 (10)
N4—C11—C6	121.3 (3)	N2—Mn—N2ⁱ	86.22 (14)
C10—C11—C6	119.2 (3)	N1ⁱ—Mn—Cl	100.04 (7)
N4—C12—C5	122.5 (3)	N1—Mn—Cl	94.86 (8)
N4—C12—C13	118.1 (3)	N2—Mn—Cl	165.09 (7)
C5—C12—C13	119.3 (3)	N2ⁱ—Mn—Cl	87.79 (8)
C17—C13—C14	118.0 (3)	N1ⁱ—Mn—Clⁱ	94.86 (8)
C17—C13—C12	120.1 (3)	N1—Mn—Clⁱ	100.04 (7)
C14—C13—C12	121.9 (3)	N2—Mn—Clⁱ	87.79 (8)
C15—C14—C13	119.4 (4)	N2ⁱ—Mn—Clⁱ	165.09 (7)
C15—C14—H14	119 (2)	Cl—Mn—Clⁱ	101.09 (6)
C13—C14—H14	122 (2)		

Symmetry code: (i) $-x+2, y, -z+1/2$.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···Clⁱⁱ	1.09 (3)	2.67 (3)	3.737 (4)	168 (2)
C15—H15···Clⁱⁱⁱ	1.04 (3)	2.64 (3)	3.648 (4)	163 (3)

Symmetry codes: (ii) $-x+1, y, -z+1/2$; (iii) $-x+5/2, y+1/2, -z+1/2$.