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Dichlorido[*N*-(2-pyridylmethylidene)-benzene-1,4-diamine]zinc(II)

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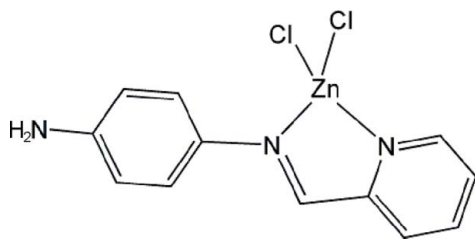
Received 14 April 2010; accepted 25 April 2010

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.038; wR factor = 0.108; data-to-parameter ratio = 17.1.

In the title compound, $[\text{ZnCl}_2(\text{C}_{12}\text{H}_{11}\text{N}_3)]$, the Zn^{II} atom is four-coordinated by two N atoms from an *N*-(2-pyridylmethylidene)benzene-1,4-diamine ligand and two Cl atoms in a distorted tetrahedral geometry. In the crystal, the complex molecules are connected by $\text{N}-\text{H}\cdots\text{Cl}$ and $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonds into a two-dimensional layer structure parallel to (110).

Related literature

For general background to zinc(II) complexes with Schiff base ligands, see: Su *et al.* (1999); Ye *et al.* (2005).



Experimental

Crystal data

$[\text{ZnCl}_2(\text{C}_{12}\text{H}_{11}\text{N}_3)]$
 $M_r = 333.53$

Triclinic, $P\bar{1}$
 $a = 7.5004$ (15) Å

$b = 9.1168$ (18) Å
 $c = 10.186$ (2) Å
 $\alpha = 84.36$ (3)°
 $\beta = 82.27$ (3)°
 $\gamma = 74.19$ (3)°
 $V = 662.7$ (3) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 2.24$ mm⁻¹
 $T = 293$ K
 $0.20 \times 0.18 \times 0.16$ mm

Data collection

Rigaku R-AXIS RAPID
 diffractometer
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
 $T_{\text{min}} = 0.645$, $T_{\text{max}} = 0.699$

6557 measured reflections
 3000 independent reflections
 2345 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.108$
 $S = 0.93$
 3000 reflections
 175 parameters

H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N11}-\text{H10}\cdots\text{Cl4}^{\text{i}}$	0.86	2.60	3.433 (4)	164
$\text{N11}-\text{H11}\cdots\text{Cl2}^{\text{ii}}$	0.86	2.64	3.470 (4)	161
$\text{C3}-\text{H3}\cdots\text{Cl4}^{\text{iii}}$	0.99 (5)	2.89 (5)	3.864 (4)	169 (4)
$\text{C6}-\text{H6}\cdots\text{Cl2}^{\text{iv}}$	0.93	2.83	3.658 (4)	149

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2300).

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supporting information

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Dichlorido[*N*-(2-pyridylmethylidene)benzene-1,4-diamine]zinc(II)**Yun-Fen Shi, Qiao-Hua Feng, Wen-Jie Zhao, Yun-Bo Shi and Peng Zhan****S1. Comment**

Based on the design and syntheses of zinc Schiff-base complexes and the potential applications of these materials as fluorescent probes (Su *et al.*, 1999; Ye *et al.*, 2005), the title compound has been obtained. As shown in Fig. 1, the asymmetric unit contains one Zn^{II} ion, one *N*-(pyridin-2-ylmethylene)benzene-1,4-diamine ligand and two Cl atoms. The Zn^{II} atom exhibits a distorted tetrahedral coordinate geometry formed by two N atoms from the ligand and two Cl atoms, with the Zn—N distances of 2.057 (3) and 2.070 (3) Å and the Zn—Cl distances of 2.2000 (13) and 2.2456 (12) Å. As shown in Fig. 2, the complex molecules are connected into a two-dimensional supramolecular layer-like structure via weak N—H⋯Cl and C—H⋯Cl hydrogen-bonding interactions (Table 1).

S2. Experimental

The ligand was prepared according to the previous method (Ye *et al.*, 2005). 1,4-Diaminobenzene (1.08 g, 10 mmol) was dissolved in methanol (20 ml), followed by addition of 2-pyridine carboxaldehyde (4.24 mg, 40 mmol). The mixture was stirred at room temperature for 2 h and filtered. The resulting yellow crystalline solid was washed with methanol several times and dried in air. A solution of ZnCl₂·2H₂O (14 mg, 0.08 mmol) in acetonitrile (5 ml) was allowed to diffuse slowly into a methylene chloride solution (10 ml) of the ligand (0.179 g, 0.625 mmol) in an H-shaped tube. Colorless crystals were obtained over a week.

S3. Refinement

H atoms bonded to C3, C4 and C11 were located from a difference Fourier map and refined isotropically. The other H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 and N—H = 0.86 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$.

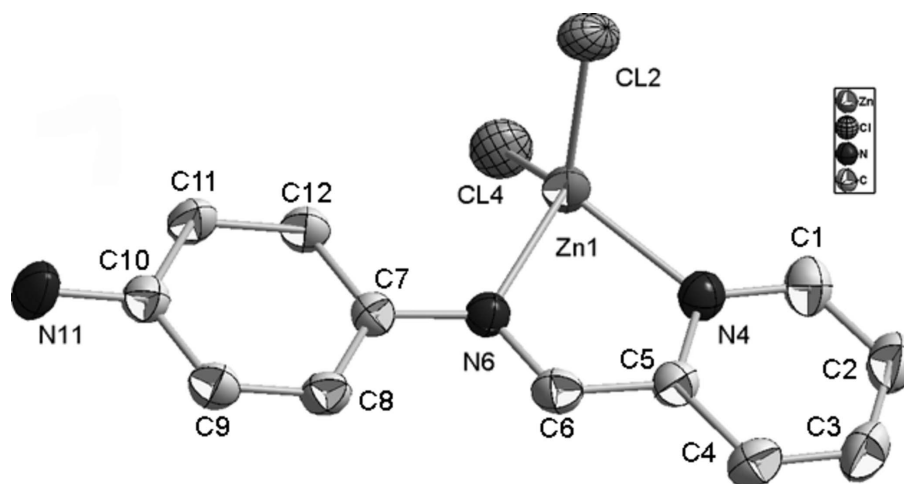


Figure 1
Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

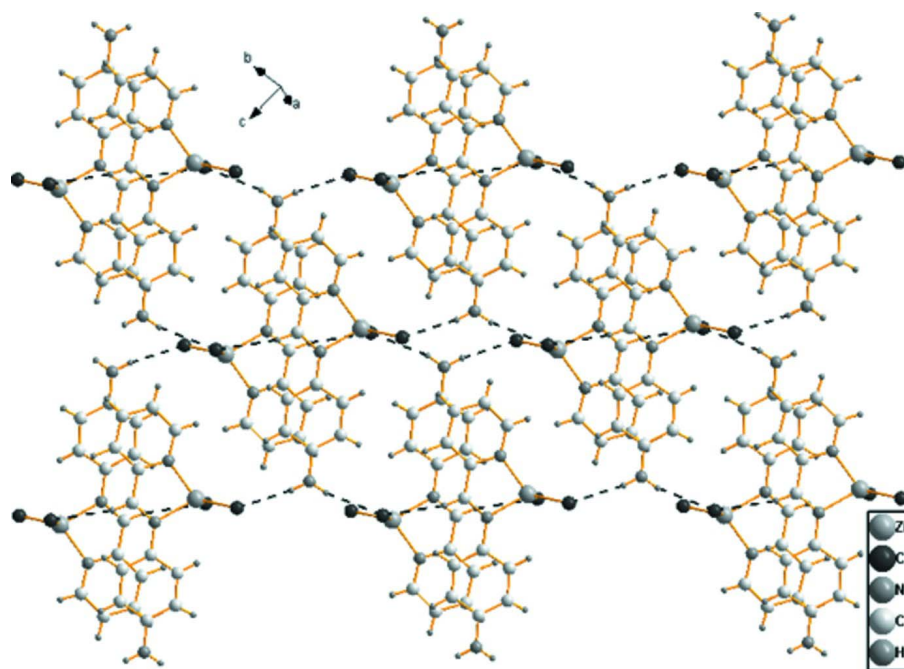


Figure 2
A view of the two-dimensional layer-like structure in the title compound.

Dichlorido[N-(2-pyridylmethylidene)benzene-1,4-diamine]zinc(II)

Crystal data

[ZnCl₂(C₁₂H₁₁N₃)]

M_r = 333.53

Triclinic, *P* $\bar{1}$

Hall symbol: -P 1

a = 7.5004 (15) Å

b = 9.1168 (18) Å

c = 10.186 (2) Å

α = 84.36 (3)°

β = 82.27 (3)°

γ = 74.19 (3)°

V = 662.7 (3) Å³

Z = 2

F(000) = 336

D_x = 1.671 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 2613 reflections

$\theta = 3.2\text{--}26.5^\circ$
 $\mu = 2.24 \text{ mm}^{-1}$
 $T = 293 \text{ K}$

Block, red
 $0.20 \times 0.18 \times 0.16 \text{ mm}$

Data collection

Rigaku R-AXIS RAPID
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.645$, $T_{\max} = 0.699$

6557 measured reflections
 3000 independent reflections
 2345 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.2^\circ$
 $h = -9 \rightarrow 9$
 $k = -11 \rightarrow 11$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.108$
 $S = 0.93$
 3000 reflections
 175 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 atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.9028P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.27968 (6)	0.38462 (4)	0.24431 (4)	0.03673 (14)
Cl2	0.09004 (13)	0.22915 (11)	0.26242 (10)	0.0490 (2)
Cl4	0.55281 (14)	0.29132 (12)	0.13201 (10)	0.0515 (3)
N4	0.1317 (4)	0.6067 (3)	0.2044 (3)	0.0353 (6)
N6	0.2715 (4)	0.4658 (3)	0.4284 (3)	0.0308 (6)
C2	-0.0484 (6)	0.8248 (5)	0.0885 (4)	0.0492 (9)
H2	-0.0941	0.8704	0.0098	0.059*
C3	-0.0912 (6)	0.9047 (5)	0.2008 (4)	0.0508 (10)
C4	-0.0201 (6)	0.8340 (4)	0.3174 (4)	0.0455 (9)
C1	0.0631 (5)	0.6763 (4)	0.0925 (4)	0.0433 (8)
H1	0.0912	0.6232	0.0157	0.052*
C11	0.5458 (6)	0.1380 (4)	0.6210 (4)	0.0422 (8)
N11	0.5896 (5)	0.0970 (4)	0.8533 (3)	0.0536 (9)
H11	0.6555	0.0052	0.8408	0.064*
H10	0.5698	0.1306	0.9314	0.064*
C9	0.4073 (5)	0.3393 (4)	0.7684 (3)	0.0375 (7)
H8	0.3895	0.3764	0.8524	0.045*
C5	0.0910 (5)	0.6854 (4)	0.3156 (3)	0.0342 (7)
C10	0.5160 (5)	0.1897 (4)	0.7488 (3)	0.0366 (7)
C6	0.1730 (5)	0.6044 (4)	0.4344 (3)	0.0357 (7)
H6	0.1536	0.6533	0.5131	0.043*

C8	0.3268 (5)	0.4319 (4)	0.6659 (3)	0.0347 (7)
H7	0.2548	0.5306	0.6812	0.042*
C12	0.4640 (5)	0.2327 (4)	0.5178 (3)	0.0382 (8)
H9	0.4845	0.1973	0.4330	0.046*
C7	0.3523 (4)	0.3789 (4)	0.5390 (3)	0.0312 (7)
H5	0.604 (6)	0.045 (5)	0.601 (4)	0.050 (12)*
H4	-0.030 (7)	0.890 (6)	0.403 (5)	0.070 (14)*
H3	-0.189 (7)	1.002 (6)	0.196 (5)	0.079 (16)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0404 (2)	0.0338 (2)	0.0327 (2)	-0.00136 (17)	-0.00508 (16)	-0.00900 (15)
Cl2	0.0465 (5)	0.0419 (5)	0.0599 (6)	-0.0092 (4)	-0.0042 (4)	-0.0183 (4)
Cl4	0.0469 (5)	0.0540 (5)	0.0475 (5)	-0.0026 (4)	0.0052 (4)	-0.0188 (4)
N4	0.0341 (15)	0.0352 (15)	0.0347 (14)	-0.0062 (12)	-0.0034 (12)	-0.0027 (12)
N6	0.0322 (14)	0.0299 (13)	0.0291 (13)	-0.0059 (11)	-0.0029 (11)	-0.0030 (10)
C2	0.051 (2)	0.047 (2)	0.049 (2)	-0.0123 (18)	-0.0147 (18)	0.0131 (18)
C3	0.045 (2)	0.038 (2)	0.063 (3)	0.0000 (17)	-0.0106 (19)	0.0056 (18)
C4	0.049 (2)	0.0335 (18)	0.052 (2)	-0.0061 (16)	-0.0058 (18)	-0.0070 (16)
C1	0.042 (2)	0.048 (2)	0.0377 (18)	-0.0097 (16)	-0.0052 (15)	0.0034 (16)
C11	0.054 (2)	0.0295 (17)	0.0401 (19)	-0.0002 (16)	-0.0105 (16)	-0.0089 (15)
N11	0.077 (3)	0.0386 (17)	0.0373 (16)	0.0017 (16)	-0.0176 (16)	0.0005 (13)
C9	0.043 (2)	0.0383 (18)	0.0299 (16)	-0.0080 (15)	-0.0015 (14)	-0.0092 (14)
C5	0.0333 (17)	0.0323 (16)	0.0369 (17)	-0.0084 (14)	-0.0036 (14)	-0.0024 (13)
C10	0.0409 (19)	0.0344 (17)	0.0348 (17)	-0.0098 (15)	-0.0049 (14)	-0.0029 (14)
C6	0.0389 (19)	0.0352 (17)	0.0327 (16)	-0.0079 (14)	-0.0017 (14)	-0.0089 (13)
C8	0.0386 (18)	0.0311 (16)	0.0334 (16)	-0.0067 (14)	-0.0006 (14)	-0.0085 (13)
C12	0.045 (2)	0.0345 (17)	0.0333 (16)	-0.0035 (15)	-0.0057 (14)	-0.0109 (14)
C7	0.0309 (16)	0.0320 (16)	0.0314 (15)	-0.0084 (13)	-0.0054 (13)	-0.0026 (12)

Geometric parameters (Å, °)

Zn1—N4	2.057 (3)	C11—C12	1.391 (5)
Zn1—N6	2.070 (3)	C11—C10	1.396 (5)
Zn1—Cl4	2.2000 (13)	C11—H5	0.87 (4)
Zn1—Cl2	2.2456 (12)	N11—C10	1.371 (4)
N4—C1	1.343 (4)	N11—H11	0.8600
N4—C5	1.356 (4)	N11—H10	0.8600
N6—C6	1.281 (4)	C9—C8	1.374 (5)
N6—C7	1.418 (4)	C9—C10	1.403 (5)
C2—C3	1.370 (6)	C9—H8	0.9300
C2—C1	1.384 (5)	C5—C6	1.472 (5)
C2—H2	0.9300	C6—H6	0.9300
C3—C4	1.394 (6)	C8—C7	1.395 (4)
C3—H3	0.99 (5)	C8—H7	0.9300
C4—C5	1.384 (5)	C12—C7	1.387 (5)
C4—H4	1.03 (5)	C12—H9	0.9300

C1—H1	0.9300		
N4—Zn1—N6	81.72 (11)	C10—C11—H5	125 (3)
N4—Zn1—Cl4	120.24 (9)	C10—N11—H11	120.0
N6—Zn1—Cl4	118.70 (9)	C10—N11—H10	120.0
N4—Zn1—Cl2	109.98 (9)	H11—N11—H10	120.0
N6—Zn1—Cl2	108.64 (8)	C8—C9—C10	121.2 (3)
Cl4—Zn1—Cl2	113.46 (4)	C8—C9—H8	119.4
C1—N4—C5	118.7 (3)	C10—C9—H8	119.4
C1—N4—Zn1	130.3 (3)	N4—C5—C4	122.1 (3)
C5—N4—Zn1	110.8 (2)	N4—C5—C6	116.2 (3)
C6—N6—C7	122.8 (3)	C4—C5—C6	121.7 (3)
C6—N6—Zn1	111.6 (2)	N11—C10—C11	121.2 (3)
C7—N6—Zn1	125.5 (2)	N11—C10—C9	120.4 (3)
C3—C2—C1	119.9 (4)	C11—C10—C9	118.4 (3)
C3—C2—H2	120.0	N6—C6—C5	119.3 (3)
C1—C2—H2	120.0	N6—C6—H6	120.3
C2—C3—C4	118.9 (4)	C5—C6—H6	120.3
C2—C3—H3	116 (3)	C9—C8—C7	120.4 (3)
C4—C3—H3	124 (3)	C9—C8—H7	119.8
C5—C4—C3	118.7 (4)	C7—C8—H7	119.8
C5—C4—H4	117 (3)	C7—C12—C11	121.2 (3)
C3—C4—H4	124 (3)	C7—C12—H9	119.4
N4—C1—C2	121.7 (4)	C11—C12—H9	119.4
N4—C1—H1	119.1	C12—C7—C8	118.8 (3)
C2—C1—H1	119.1	C12—C7—N6	117.2 (3)
C12—C11—C10	120.0 (3)	C8—C7—N6	124.0 (3)
C12—C11—H5	115 (3)		
N6—Zn1—N4—C1	179.7 (3)	C3—C4—C5—N4	-0.4 (6)
Cl4—Zn1—N4—C1	61.3 (3)	C3—C4—C5—C6	179.1 (3)
Cl2—Zn1—N4—C1	-73.4 (3)	C12—C11—C10—N11	177.7 (4)
N6—Zn1—N4—C5	-5.4 (2)	C12—C11—C10—C9	-1.9 (6)
Cl4—Zn1—N4—C5	-123.9 (2)	C8—C9—C10—N11	-177.6 (3)
Cl2—Zn1—N4—C5	101.5 (2)	C8—C9—C10—C11	2.0 (5)
N4—Zn1—N6—C6	4.4 (2)	C7—N6—C6—C5	-178.8 (3)
Cl4—Zn1—N6—C6	124.4 (2)	Zn1—N6—C6—C5	-2.7 (4)
Cl2—Zn1—N6—C6	-104.0 (2)	N4—C5—C6—N6	-2.0 (5)
N4—Zn1—N6—C7	-179.7 (3)	C4—C5—C6—N6	178.4 (3)
Cl4—Zn1—N6—C7	-59.6 (3)	C10—C9—C8—C7	-0.3 (5)
Cl2—Zn1—N6—C7	72.0 (3)	C10—C11—C12—C7	0.1 (6)
C1—C2—C3—C4	0.3 (6)	C11—C12—C7—C8	1.7 (5)
C2—C3—C4—C5	-0.1 (6)	C11—C12—C7—N6	-178.6 (3)
C5—N4—C1—C2	-0.5 (5)	C9—C8—C7—C12	-1.6 (5)
Zn1—N4—C1—C2	174.1 (3)	C9—C8—C7—N6	178.8 (3)
C3—C2—C1—N4	0.0 (6)	C6—N6—C7—C12	-176.7 (3)
C1—N4—C5—C4	0.7 (5)	Zn1—N6—C7—C12	7.8 (4)
Zn1—N4—C5—C4	-174.9 (3)	C6—N6—C7—C8	3.0 (5)

C1—N4—C5—C6	-178.8 (3)	Zn1—N6—C7—C8	-172.5 (2)
Zn1—N4—C5—C6	5.6 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N11—H10...C14 ⁱ	0.86	2.60	3.433 (4)	164
N11—H11...C12 ⁱⁱ	0.86	2.64	3.470 (4)	161
C3—H3...C14 ⁱⁱⁱ	0.99 (5)	2.89 (5)	3.864 (4)	169 (4)
C6—H6...C12 ^{iv}	0.93	2.83	3.658 (4)	149

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