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[5-Amino-6,8-dichloro-2,3-bis(2-pyridyl)-quinoxaline]dichlorozinc(II)

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Key indicators

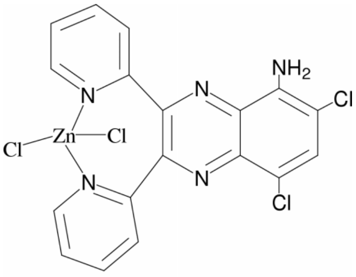
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.007 Å
R factor = 0.046
wR factor = 0.088
Data-to-parameter ratio = 13.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The Zn^{II} atom in the title complex, $[ZnCl_2(C_{18}H_{11}N_5Cl_2)]$, has a distorted tetrahedral environment formed by the N atoms of two quinoxaline *ortho*-pyridyl substituents and two terminal chloro ligands. There is a symmetry-independent intermolecular hydrogen bond in the crystal, which links one of the H atoms of the aniline group with one of the chloro ligands [$Cl\cdots N$ 3.418 (3) Å and $Cl\cdots H—N$ 142°]. This hydrogen bond is responsible for the formation of infinite zigzag chains, which run along the b axis of the crystal.

Comment

Polypyridyl ligands and their transition metal complexes have attracted much interest owing to their potential as building blocks for supramolecular assemblies, as well as their possible use in optical sensors and probes for nucleic acids (Arkin *et al.*, 1996; Holmlin *et al.*, 1999). 2,3-Bis(2-pyridyl)quinoxaline and its derivatives represent an important class of chelating agents which have been extensively studied over the last two decades (Balzani *et al.*, 1996; Scott *et al.*, 1999). However, most of the results were obtained for Ru^{II}, Os^{II}, and Re^{I} complexes, whereas studies on first row transition metals are still quite rare. We report herein the synthesis and crystal structure of the zinc(II) complex [5-amino-6,8-dichloro-2,3-bis(2-pyridyl)-quinoxaline]dichlorozinc(II), (I) (Fig. 1).



(I)

The Zn^{II} atom has a distorted tetrahedral coordination, formed by the N atoms of two *ortho*-pyridyl groups of the chelate system and two chloro ligands. The *ortho*-pyridyl substituents in the quinoxaline system can not be coplanar, either with each other or with the quinoxaline moiety, as a planar conformation would cause sterically unacceptable contacts between the pyridyl rings. In fact, the existence of the adjacent pyridyl substituents causes substantial out-of-plane twist, even within the quinoxaline itself, the torsion angle C1A—C2—C3—C1B being −4.1 (1)°; the mean atomic displacement from the least-squares quinoxaline plane is 0.0345 (2) Å. The two pyridine rings form dihedral angles of

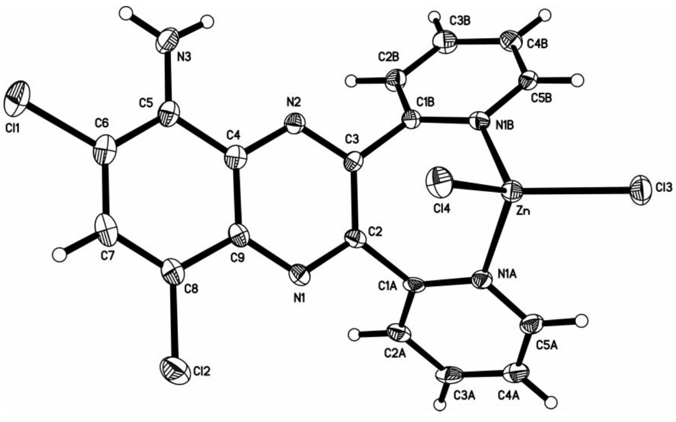


Figure 1
*ORTEP*II view (Johnson, 1976) of the title complex, shown with 30% probability displacement ellipsoids.

115.1 (3) and 53.3 (2)° with the mean quinoxaline plane, and a dihedral angle of 94.4 (3)° with each other.

Selected bond distances and angles are given in Table 1. The C2—N1 and C3—N2 bond distances [1.318 (6) and 1.315 (6) Å, respectively] are noticeably shorter than N1—C9 and N2—C4 [1.354 (6) and 1.351 (6) Å, respectively], which is typical for quinoxaline system geometry (Rasmussen *et al.*, 1990). All N—C bond lengths are well within the range between the ranges normally considered standard for single C—N and double C═N bonds [1.47 Å (Sasada, 1984) and 1.28 Å (Wang *et al.*, 1998), respectively].

Although there are two 'active' H atoms in the structure, only one of them (H3*C*) actually takes part in intermolecular hydrogen bonding. The hydrogen bond N3—H3*C*···Cl4^{i} [N3···Cl3^{i} 3.418 (3) Å and N3—H3*C*···Cl3^{i} 142°; symmetry code: (i) $-x$, $y-1/2$, $1/2-z$] links the molecules of the complex into infinite chains along the *b* axis of the crystal (Fig. 2).

Experimental

The title complex was synthesized by the reaction of 1-nitro-2,3-phenylenediamine and 2,2′-bipyridyl, and then reduced by Pd/C in the presence of concentrated (36%) HCl under reflux. The details will be published elsewhere. A mixture of solutions of equimolecular $ZnCl_2$ (55 mg, 0.4 mmol) in CH_3OH (30 ml) and 5-amino-6,8-dichloro-2,3-bis(2-pyridyl)quinoxaline (147 mg, 0.4 mmol) in $CHCl_3$ (20 ml) was left to stand at room temperature. Yellow crystals precipitated slowly with the evaporation of the solvent. Yield: 75%. FT-IR data (KBr pellet, cm^{-1}): 3490 (*m*), 3380 (*s*), 1602 (*vs*), 1570 (*m*), 1487 (*s*), 1458 (*m*), 1349 (*vs*), 1029 (*s*), 789 (*m*), 755 (*m*). Analysis calculated for the title complex: C 42.85, H 2.20, N 13.89%; found: C 42.81, H 2.40, N 13.83%.

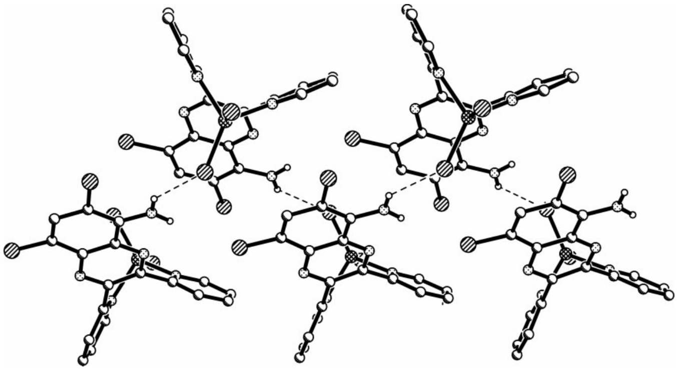


Figure 2
View of the zigzag chain in the crystal of the title complex.

Crystal data

$[ZnCl_2(C_{18}H_{11}N_5Cl_2)]$
M_r = 504.49
Monoclinic, $P2_1/c$
a = 16.097 (9) Å
b = 8.922 (3) Å
c = 13.858 (4) Å
β = 100.04 (3)°
V = 1959.8 (14) Å^3
Z = 4
D_x = 1.710 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10665 reflections
θ = 1.3–25.0°
μ = 1.81 mm^{-1}
T = 193 (2) K
Prism, yellow
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART 1000 diffractometer
ω scans
Absorption correction: multi-scan [*SAINT* (Bruker, 1998) and *SADABS* (Sheldrick, 1997)]
T_{min} = 0.612, T_{max} = 0.713
10833 measured reflections
3451 independent reflections
2107 reflections with $I > 2\sigma(I)$
R_{int} = 0.096
θ_{max} = 25.0°
$h = -19 \rightarrow 10$
$k = -9 \rightarrow 10$
$l = -13 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.088
S = 1.04
3451 reflections
254 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn—N1*A*	2.062 (4)	N1—C9	1.354 (6)
Zn—N1*B*	2.056 (4)	N2—C3	1.315 (6)
Zn—Cl3	2.2218 (18)	N2—C4	1.351 (6)
Zn—Cl4	2.2093 (17)	N3—C5	1.371 (6)
N1—C2	1.318 (6)		
N1*B*—Zn—N1*A*	91.32 (15)	N1*B*—Zn—Cl3	107.47 (12)
N1*B*—Zn—Cl4	113.73 (13)	N1*A*—Zn—Cl3	106.32 (13)
N1*A*—Zn—Cl4	112.42 (12)	Cl4—Zn—Cl3	121.30 (6)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*C*···Cl4^{i}	0.88	2.68	3.418 (3)	142

Symmetry code: (i) $-x, y-\frac{1}{2}, \frac{1}{2}-z$.

All H atoms were placed in geometrically calculated positions and included in the final refinement in the riding-model approximation, with displacement parameters derived from the atoms to which they were bonded. The U_{iso} values for the H atoms were set at $1.2U_{eq}$ of the parent atom values.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine

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structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXTL* (Bruker, 1998).

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