

Dichlorido[(*S*)-(1-phenylethyl)(2-pyridylmethyl)amine- κ^2N,N']zinc(II)

Quang Trung Nguyen and Jong Hwa Jeong*

Department of Chemistry, Kyungpook National University, Taegu 702-701, Republic of Korea

Correspondence e-mail: jeongjh@knu.ac.kr

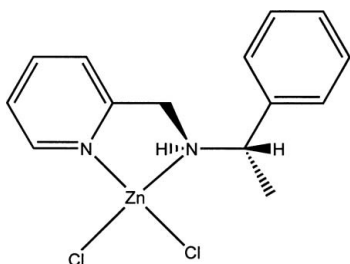
Received 6 January 2008; accepted 1 February 2008

 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.006$ Å; R factor = 0.031; wR factor = 0.081; data-to-parameter ratio = 9.6.

In the title compound, $[ZnCl_2(C_{14}H_{16}N_2)]$, the Zn^{II} atom is coordinated by two N atoms and two Cl atoms in an approximately tetrahedral arrangement. The dihedral angle between the N–Zn–N and Cl–Zn–Cl planes is $88.06(8)^\circ$. The H atoms on the chiral C atom and the adjacent N atom have an *anti* conformation.

Related literature

For the synthesis of (*S*)-2-pyridinal-1-phenylethylimine, see: Kang *et al.* (2006). For related structures, see: Moreau *et al.* (1999); Mizushima *et al.* (1999); Himeda *et al.* (2003).



Experimental

Crystal data

$[ZnCl_2(C_{14}H_{16}N_2)]$
 $M_r = 348.56$
 Orthorhombic, $P2_12_12_1$
 $a = 9.2342(6)$ Å
 $b = 12.5782(10)$ Å
 $c = 13.4032(8)$ Å

$V = 1556.78(18)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.91$ mm⁻¹
 $T = 293(2)$ K
 $0.40 \times 0.40 \times 0.30$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Absorption correction: ψ scan (*ABSCALC*; McArdle & Daly, 1999)
 $T_{min} = 0.485$, $T_{max} = 0.564$
 1705 measured reflections

1659 independent reflections
 1530 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.009$
 3 standard reflections
 frequency: 60 min
 intensity decay: 0.2%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.080$
 $S = 1.07$
 1659 reflections
 173 parameters
 H-atom parameters constrained

$\Delta\rho_{max} = 0.56$ e Å⁻³
 $\Delta\rho_{min} = -0.57$ e Å⁻³
 Absolute structure: Flack (1983), 2
 Friedel pairs
 Flack parameter: 0.018 (19)

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD* (McArdle, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIXIII* (McArdle, 1995); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2180).

References

- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Himeda, Y., Onozawa-Komatsuzaki, N., Sugihara, H., Arakawa, H. & Kasuga, K. (2003). *J. Mol. Catal. A: Chem.* **195**, 95–100.
- Kang, B., Kim, M., Lee, J., Do, Y. & Chang, S. (2006). *J. Org. Chem.* **71**, 6721–6727.
- McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
- McArdle, P. (1999). *XCAD*. National University of Ireland, Galway, Ireland.
- McArdle, P. & Daly, P. (1999). *ABSCALC*. National University of Ireland, Galway, Ireland.
- Mizushima, E., Ohi, H., Yamaguchi, M. & Yamagishi, T. J. (1999). *J. Mol. Catal. A: Chem.* **149**, 43–49.
- Moreau, C., Frost, C. G. & Murrer, B. (1999). *Tetrahedron Lett.* **40**, 5617–5620.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

Acta Cryst. (2008). E64, m457 [doi:10.1107/S1600536808003541]

Dichlorido[(*S*)-(1-phenylethyl)(2-pyridylmethyl)amine- κ^2N,N']zinc(II)

Q. T. Nguyen and J. H. Jeong

Comment

The ligand, (*S*)-(1-Phenylethyl)(2-pyridylmethyl)amine, was obtained from reduction of (*S*)-2-pyridinal-1-phenylethylimine (Kang *et al.*, 2006) with NaBH₄ in methanol solution. The ligand was used as co-ligand with another chiral ligand in Ru or Rh complexes as the catalyst for hydrogenation of ketones (Moreau *et al.*, 1999; Mizushima *et al.*, 1999; Himeda *et al.*, 2003). In the crystal structure, the geometry around the Zn^{II} ion is approximately tetrahedral with bonds being formed by two chloride ions and the pyridyl and amine nitrogen atoms of the ligand (Fig. 1). The dihedral angle between the N—Zn—N and Cl—Zn—Cl planes is 88.06 (8)°. The H atoms on the chiral carbon atom and the adjacent nitrogen atom have an anti conformation.

Experimental

NaBH₄ (0.33 g, 8.8 mmol) was added slowly to a solution of (*S*)-2-pyridinal-1-phenylethylimine (1.79 g, 8.5 mmol) in methanol (15 ml). The mixture was stirred overnight, and the solvent was removed by evaporation. The residue obtained was dissolved in 20 ml distilled water and the organic product was extracted with CH₂Cl₂ (3 x 20 ml) and dried over anhydrous MgSO₄. The solvent was evaporated to give a pale yellow oil; 1.41 g (78% yield). ¹H-NMR (400 MHz, CDCl₃) δ 7.39 (t, 1H, ArH), 7.26 (m, 4H, ArH), 7.17 (m, 1H, ArH), 6.90 (t, 2H, ArH), 3.74 (q, J=6.56 Hz, 1H, CH), 3.59 (s, 2H, CH₂), 2.45 (s, 3H, PyCH₃), 2.19 (br, s, 1H, NH), 1.30 (d, J=6.56 Hz, 3H, CH₃). A solution of the ligand (0.96 g, 4.5 mmol) in ethanol (5 ml) was added dropwise to a solution of ZnCl₂ (0.61 g, 4.5 mmol) in ethanol (10 ml). The mixture was stirred overnight at room temperature. The solvent was removed to yield a white solid product. Colorless crystals were obtained by slowly diffusing diethyl ether into a saturated solution in acetonitrile (1.36 g, 87%). Anal. Calcd. for C₁₄H₁₆Cl₂N₂Zn: C, 48.23; H, 4.63; N, 8.04. Found: C, 48.19; H, 4.70; N, 8.01%. ¹H-NMR (400 MHz, CD₃CN) δ 7.89 (m, 1H, ArH), 7.44 (m, 6H, ArH), 7.16 (d, J=7.79 Hz, 1H, ArH), 4.15 (m, 2H, NH & CH), 3.77 (m, 2H, CH₂), 2.78 (s, 3H, PyCH₃), 1.70 (d, J=3.24 Hz, CH₃).

Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for C(*sp*²)H, C—H = 0.97 Å, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH₂, C—H = 0.96 Å, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for CH₃, and N—H = 0.91 Å, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ for NH atoms.

Figures

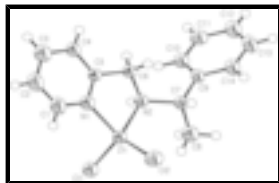


Fig. 1. The molecular structure. Displacement ellipsoids are drawn at the 40% probability level.

Dichlorido[(S)-(1-phenylethyl)(2-pyridylmethyl)amine- κ^2N,N']zinc(II)

Crystal data

[ZnCl₂(C₁₄H₁₆N₂)]

$M_r = 348.56$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 9.2342$ (6) Å

$b = 12.5782$ (10) Å

$c = 13.4032$ (8) Å

$V = 1556.78$ (18) Å³

$Z = 4$

$F_{000} = 712$

$D_x = 1.487$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 9.9\text{--}13.0^\circ$

$\mu = 1.91$ mm⁻¹

$T = 293$ (2) K

Block, colorless

$0.40 \times 0.40 \times 0.30$ mm

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ (2) K

$\omega/2\theta$ scans

Absorption correction: ψ scan
(ABSCALC; McArdle & Daly, 1999)

$T_{\min} = 0.485$, $T_{\max} = 0.564$

1705 measured reflections

1659 independent reflections

1530 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.009$

$\theta_{\max} = 25.5^\circ$

$\theta_{\min} = 2.2^\circ$

$h = 0 \rightarrow 11$

$k = -14 \rightarrow 0$

$l = 0 \rightarrow 15$

3 standard reflections

every 60 min

intensity decay: 0.2%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.080$

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 0.2097P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$S = 1.07$ $\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$
 1659 reflections $\Delta\rho_{\min} = -0.57 \text{ e } \text{\AA}^{-3}$
 173 parameters Extinction correction: none
 Primary atom site location: structure-invariant direct methods Absolute structure: Flack (1983), 2 Friedel pairs
 Secondary atom site location: difference Fourier map Flack parameter: 0.018 (19)

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn	0.04578 (5)	0.93541 (3)	0.73653 (3)	0.04068 (15)
Cl1	-0.15959 (12)	0.94695 (8)	0.65366 (7)	0.0527 (3)
Cl2	0.14716 (13)	1.08625 (8)	0.78507 (9)	0.0584 (3)
N1	0.1861 (4)	0.8349 (3)	0.6668 (2)	0.0464 (8)
N2	0.0324 (3)	0.8129 (2)	0.8414 (2)	0.0339 (6)
H2N	-0.0496	0.7755	0.8279	0.041*
C1	0.2413 (6)	0.8436 (4)	0.5749 (3)	0.0640 (13)
H1	0.2270	0.9068	0.5402	0.077*
C2	0.3170 (7)	0.7649 (4)	0.5300 (4)	0.0749 (15)
H2	0.3525	0.7736	0.4656	0.090*
C3	0.3405 (6)	0.6719 (4)	0.5811 (4)	0.0653 (13)
H3	0.3912	0.6162	0.5517	0.078*
C4	0.2874 (5)	0.6627 (3)	0.6769 (3)	0.0465 (9)
H4	0.3038	0.6013	0.7137	0.056*
C5	0.2098 (4)	0.7455 (3)	0.7174 (3)	0.0359 (8)
C6	0.1564 (4)	0.7408 (3)	0.8239 (3)	0.0378 (8)
H6A	0.1276	0.6685	0.8394	0.045*
H6B	0.2349	0.7601	0.8685	0.045*
C7	0.0213 (4)	0.8512 (3)	0.9465 (3)	0.0371 (8)
H7	0.1060	0.8960	0.9594	0.045*
C8	-0.1117 (5)	0.9209 (4)	0.9566 (3)	0.0579 (11)
H8A	-0.1047	0.9795	0.9110	0.087*
H8B	-0.1180	0.9474	1.0236	0.087*
H8C	-0.1967	0.8799	0.9415	0.087*
C9	0.0207 (4)	0.7636 (3)	1.0248 (3)	0.0367 (8)
C10	-0.0433 (4)	0.6656 (3)	1.0102 (3)	0.0439 (8)
H10	-0.0836	0.6494	0.9485	0.053*
C11	-0.0482 (5)	0.5911 (4)	1.0863 (3)	0.0546 (10)
H11	-0.0918	0.5255	1.0753	0.065*
C12	0.0112 (5)	0.6139 (4)	1.1780 (3)	0.0608 (13)
H12	0.0074	0.5641	1.2293	0.073*

supplementary materials

C13	0.0767 (5)	0.7114 (4)	1.1932 (3)	0.0581 (12)
H13	0.1183	0.7270	1.2547	0.070*
C14	0.0804 (5)	0.7855 (4)	1.1175 (3)	0.0492 (10)
H14	0.1237	0.8511	1.1287	0.059*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn	0.0526 (3)	0.0350 (2)	0.0345 (2)	0.00634 (18)	0.00028 (19)	0.00188 (16)
Cl1	0.0638 (6)	0.0493 (5)	0.0448 (5)	0.0054 (5)	-0.0134 (5)	-0.0018 (4)
Cl2	0.0673 (6)	0.0459 (5)	0.0621 (6)	-0.0077 (5)	-0.0033 (5)	-0.0040 (5)
N1	0.056 (2)	0.0442 (17)	0.0388 (16)	0.0054 (16)	0.0066 (15)	0.0006 (14)
N2	0.0335 (14)	0.0380 (16)	0.0300 (14)	0.0003 (12)	-0.0007 (12)	-0.0015 (11)
C1	0.090 (3)	0.062 (3)	0.040 (2)	0.018 (3)	0.018 (2)	0.015 (2)
C2	0.107 (4)	0.076 (3)	0.042 (2)	0.022 (3)	0.023 (3)	0.008 (2)
C3	0.083 (3)	0.061 (3)	0.051 (3)	0.018 (3)	0.016 (3)	-0.009 (2)
C4	0.062 (2)	0.042 (2)	0.0356 (19)	0.0057 (19)	0.0047 (18)	-0.0014 (16)
C5	0.0412 (18)	0.0338 (16)	0.0327 (17)	-0.0011 (14)	0.0002 (15)	-0.0014 (14)
C6	0.0420 (19)	0.0367 (18)	0.0347 (18)	0.0029 (16)	0.0051 (16)	-0.0003 (15)
C7	0.0389 (18)	0.0400 (18)	0.0324 (17)	0.0009 (15)	0.0027 (15)	-0.0043 (14)
C8	0.068 (3)	0.058 (3)	0.048 (2)	0.025 (2)	0.011 (2)	0.006 (2)
C9	0.0335 (17)	0.046 (2)	0.0304 (17)	0.0053 (15)	0.0034 (15)	0.0004 (15)
C10	0.0431 (19)	0.047 (2)	0.0415 (19)	0.0011 (18)	0.0057 (18)	-0.0013 (16)
C11	0.060 (2)	0.048 (2)	0.056 (2)	0.006 (2)	0.011 (2)	0.0083 (19)
C12	0.065 (3)	0.071 (3)	0.047 (2)	0.027 (2)	0.012 (2)	0.017 (2)
C13	0.063 (3)	0.079 (3)	0.0326 (19)	0.015 (3)	-0.0036 (19)	0.000 (2)
C14	0.046 (2)	0.061 (2)	0.040 (2)	-0.0008 (19)	-0.0015 (18)	-0.0048 (19)

Geometric parameters (\AA , $^\circ$)

Zn—N1	2.037 (3)	C6—H6B	0.970
Zn—N2	2.089 (3)	C7—C8	1.516 (5)
Zn—Cl1	2.2025 (12)	C7—C9	1.522 (5)
Zn—Cl2	2.2134 (11)	C7—H7	0.980
N1—C5	1.332 (5)	C8—H8A	0.960
N1—C1	1.338 (5)	C8—H8B	0.960
N2—C6	1.479 (4)	C8—H8C	0.960
N2—C7	1.492 (4)	C9—C10	1.380 (5)
N2—H2N	0.910	C9—C14	1.387 (5)
C1—C2	1.354 (7)	C10—C11	1.386 (6)
C1—H1	0.930	C10—H10	0.930
C2—C3	1.373 (7)	C11—C12	1.377 (7)
C2—H2	0.930	C11—H11	0.930
C3—C4	1.379 (6)	C12—C13	1.382 (8)
C3—H3	0.930	C12—H12	0.930
C4—C5	1.375 (5)	C13—C14	1.378 (6)
C4—H4	0.930	C13—H13	0.930
C5—C6	1.511 (5)	C14—H14	0.930
C6—H6A	0.970		

N1—Zn—N2	83.58 (12)	N2—C6—H6B	109.2
N1—Zn—C11	110.92 (11)	C5—C6—H6B	109.2
N2—Zn—C11	109.70 (9)	H6A—C6—H6B	107.9
N1—Zn—C12	113.45 (11)	N2—C7—C8	109.1 (3)
N2—Zn—C12	117.35 (9)	N2—C7—C9	114.7 (3)
C11—Zn—C12	117.13 (4)	C8—C7—C9	110.8 (3)
C5—N1—C1	118.4 (4)	N2—C7—H7	107.3
C5—N1—Zn	113.3 (2)	C8—C7—H7	107.3
C1—N1—Zn	127.9 (3)	C9—C7—H7	107.3
C6—N2—C7	113.6 (3)	C7—C8—H8A	109.5
C6—N2—Zn	107.5 (2)	C7—C8—H8B	109.5
C7—N2—Zn	113.7 (2)	H8A—C8—H8B	109.5
C6—N2—H2N	107.3	C7—C8—H8C	109.5
C7—N2—H2N	107.3	H8A—C8—H8C	109.5
Zn—N2—H2N	107.3	H8B—C8—H8C	109.5
N1—C1—C2	123.1 (4)	C10—C9—C14	118.3 (4)
N1—C1—H1	118.4	C10—C9—C7	123.4 (3)
C2—C1—H1	118.4	C14—C9—C7	118.2 (4)
C1—C2—C3	118.9 (4)	C9—C10—C11	120.9 (4)
C1—C2—H2	120.5	C9—C10—H10	119.5
C3—C2—H2	120.5	C11—C10—H10	119.5
C2—C3—C4	118.6 (4)	C12—C11—C10	120.2 (4)
C2—C3—H3	120.7	C12—C11—H11	119.9
C4—C3—H3	120.7	C10—C11—H11	119.9
C3—C4—C5	119.4 (4)	C11—C12—C13	119.4 (4)
C3—C4—H4	120.3	C11—C12—H12	120.3
C5—C4—H4	120.3	C13—C12—H12	120.3
N1—C5—C4	121.6 (3)	C14—C13—C12	120.2 (4)
N1—C5—C6	117.4 (3)	C14—C13—H13	119.9
C4—C5—C6	120.9 (3)	C12—C13—H13	119.9
N2—C6—C5	112.2 (3)	C13—C14—C9	121.0 (4)
N2—C6—H6A	109.2	C13—C14—H14	119.5
C5—C6—H6A	109.2	C9—C14—H14	119.5
N2—Zn—N1—C5	-2.7 (3)	C3—C4—C5—C6	-176.8 (4)
C11—Zn—N1—C5	-111.4 (3)	C7—N2—C6—C5	-152.2 (3)
C12—Zn—N1—C5	114.3 (3)	Zn—N2—C6—C5	-25.6 (3)
N2—Zn—N1—C1	169.4 (5)	N1—C5—C6—N2	26.0 (4)
C11—Zn—N1—C1	60.7 (5)	C4—C5—C6—N2	-157.8 (3)
C12—Zn—N1—C1	-73.5 (5)	C6—N2—C7—C8	-178.0 (3)
N1—Zn—N2—C6	15.9 (2)	Zn—N2—C7—C8	58.7 (4)
C11—Zn—N2—C6	125.8 (2)	C6—N2—C7—C9	-53.2 (4)
C12—Zn—N2—C6	-97.2 (2)	Zn—N2—C7—C9	-176.4 (2)
N1—Zn—N2—C7	142.5 (3)	N2—C7—C9—C10	-34.9 (5)
C11—Zn—N2—C7	-107.6 (2)	C8—C7—C9—C10	89.0 (4)
C12—Zn—N2—C7	29.3 (3)	N2—C7—C9—C14	148.8 (4)
C5—N1—C1—C2	1.7 (8)	C8—C7—C9—C14	-87.2 (4)
Zn—N1—C1—C2	-170.0 (4)	C14—C9—C10—C11	0.2 (6)
N1—C1—C2—C3	-0.9 (10)	C7—C9—C10—C11	-176.1 (4)

supplementary materials

C1—C2—C3—C4	-0.8 (9)	C9—C10—C11—C12	-0.1 (6)
C2—C3—C4—C5	1.6 (8)	C10—C11—C12—C13	-0.5 (7)
C1—N1—C5—C4	-0.8 (6)	C11—C12—C13—C14	0.9 (7)
Zn—N1—C5—C4	172.1 (3)	C12—C13—C14—C9	-0.8 (7)
C1—N1—C5—C6	175.4 (4)	C10—C9—C14—C13	0.2 (6)
Zn—N1—C5—C6	-11.7 (4)	C7—C9—C14—C13	176.7 (4)
C3—C4—C5—N1	-0.8 (6)		

Fig. 1

