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# Dichlorido(2,6-dipyrazol-1-ylpyridine)-zinc(II)

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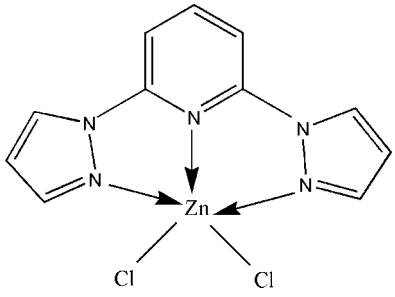
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.029; $wR$ factor = 0.078; data-to-parameter ratio = 16.5.

In the title complex, $[ZnCl_2(C_{11}H_9N_5)]$, the $Zn^{II}$ ion assumes a distorted trigonal–bipyramidal $ZnN_3Cl_2$ coordination geometry [Zn—N = 2.1397 (16)–2.2117 (17) Å, Zn—Cl = 2.2470 (6) and 2.2564 (6) Å]. The crystal packing exhibits $\pi$–$\pi$ stacking interactions between the 2,6-dipyrazol-1-ylpyridine ligands of neighbouring molecules.

## Related literature

For the related crystal structure of dichlorido[2,6-bis-(pyrazolylmethyl)pyridine]zinc(II), see Balamurugan *et al.* (2004).




## Experimental

### Crystal data

$[ZnCl_2(C_{11}H_9N_5)]$
$M_r$ = 347.50
Monoclinic, $P2_1/c$
$a$ = 10.9630 (17) Å
$b$ = 8.0263 (13) Å
$c$ = 14.943 (2) Å
$\beta$ = 93.079 (2)°
$V$ = 1313.0 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 2.27 mm$^{-1}$
$T$ = 298 (2) K
0.48 × 0.42 × 0.29 mm

### Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.409, $T_{max}$ = 0.559
(expected range = 0.379–0.518)
7375 measured reflections
2848 independent reflections
2431 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.078
$S$ = 1.05
2848 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.32 e Å$^{-3}$

**Table 1**
Selected interatomic distances (Å).

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the C4/N1/N4/N5/Zn1, C1–C3/N4/N5 and C4–C8/N1 rings, respectively.

| | | | |
|---|---|---|---|
| $Cg1\cdots Cg2^{i}$ | 3.4087 (12) | $Cg2\cdots Cg3^{i}$ | 3.6253 (13) |

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2454).

## References

Balamurugan, V., Hundal, M. S. & Mukherjee, R. (2004). *Chem. Eur. J.* **10**, 1683–1690.
Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# supplementary materials

*Acta Cryst.* (2008). E**64**, m1374 [ **doi:10.1107/S1600536808031152** ]

# Dichlorido(2,6-dipyrazol-1-ylpyridine)zinc(II)

**Z. N. Yang and T. T. Sun**

## Comment

2,6-Dipyrazol-1-ylpyridine and the relevant homologues as a tridentate ligand play an important role in modern coordination chemistry (Balamurugan *et al.*, 2004), and the interest in complexes with 2,6-dipyrazol-1-ylpyridine ligand stimulted us to prepare the title complex, (I). Herein we report its crystal structure.

In (I) (Fig. 1), each $Zn^{II}$ ion has a distorted trigonal-bipyramidal coordination environment. In the crystal, there exist π-π stacking interactions involving symmetry related 2,6-dipyrazol-1-ylpyridine ligands (Talbe 1).

## Experimental

15 ml me thanol solution containing 2,6-dipyrazol-1-ylpyridine (0.0522 g, 0.247 mmol) and pyrazine-1,4-dioxide (0.0414 g, 0.369 mmol) was added into 5 ml $H_2O$ solution of $ZnCl_2$ (0.0783 g, 0.575 mmol), and the mixed solution was stirred for a few minutes. Colorless single crystals were obtained after the filtrate was allowed to stand at room temperature for 40 days.

## Refinement

All H atoms were placed in calculated positions with C—H = 0.93 Å and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

## Figures

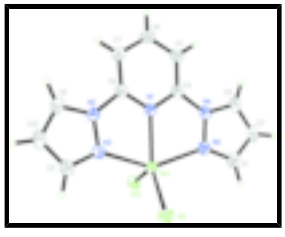

Fig. 1. The molecular structure of (I) showing the atomic numbering and 30% probability displacement ellipsoids.

## Dichlorido(2,6-dipyrazol-1-ylpyridine)zinc(II)

*Crystal data*

| | |
|---|---|
| $[ZnCl_2(C_{11}H_9N_5)]$ | $F_{000} = 696$ |
| $M_r = 347.50$ | $D_x = 1.758$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation<br>λ = 0.71073 Å |
| Hall symbol: -P 2ybc | Cell parameters from 3889 reflections |
| $a = 10.9630$ (17) Å | θ = 2.4–28.2° |

| | |
|---|---|
| $b$ = 8.0263 (13) Å | μ = 2.27 mm$^{-1}$ |
| $c$ = 14.943 (2) Å | $T$ = 298 (2) K |
| β = 93.079 (2)º | Block, colourless |
| $V$ = 1313.0 (4) Å$^3$ | 0.48 × 0.42 × 0.29 mm |
| $Z$ = 4 | |

*Data collection*

| | |
|---|---|
| Bruker SMART APEX CCD diffractometer | 2848 independent reflections |
| Radiation source: fine-focus sealed tube | 2431 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.030 |
| $T$ = 298(2) K | $\theta_{max}$ = 27.0º |
| φ and ω scans | $\theta_{min}$ = 2.9º |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h$ = −9→14 |
| $T_{min}$ = 0.409, $T_{max}$ = 0.559 | $k$ = −9→10 |
| 7375 measured reflections | $l$ = −16→18 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)]$ = 0.029 | $w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 0.0869P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2)$ = 0.078 | $(\Delta/\sigma)_{max}$ = 0.002 |
| $S$ = 1.05 | $\Delta\rho_{max}$ = 0.28 e Å$^{-3}$ |
| 2848 reflections | $\Delta\rho_{min}$ = −0.32 e Å$^{-3}$ |
| 173 parameters | Extinction correction: SHELXTL (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | Extinction coefficient: 0.0167 (11) |
| Secondary atom site location: difference Fourier map | |

*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 | 0.47097 (18) | 0.3058 (2) | 0.04770 (16) | 0.0447 (5) |
| H1 | 0.4465 | 0.3525 | 0.1008 | 0.054* |
| C2 | 0.40961 (19) | 0.3275 (3) | −0.03549 (17) | 0.0478 (5) |
| H2 | 0.3389 | 0.3891 | −0.0481 | 0.057* |
| C3 | 0.47479 (18) | 0.2396 (2) | −0.09475 (16) | 0.0440 (5) |
| H3 | 0.4572 | 0.2292 | −0.1561 | 0.053* |
| C4 | 0.66172 (17) | 0.0609 (2) | −0.07399 (13) | 0.0349 (4) |
| C5 | 0.66885 (19) | 0.0026 (3) | −0.16015 (14) | 0.0448 (5) |
| H5 | 0.6147 | 0.0387 | −0.2062 | 0.054* |
| C6 | 0.7591 (2) | −0.1111 (3) | −0.17553 (16) | 0.0487 (5) |
| H6 | 0.7663 | −0.1533 | −0.2330 | 0.058* |
| C7 | 0.8394 (2) | −0.1637 (3) | −0.10659 (15) | 0.0442 (5) |
| H7 | 0.8998 | −0.2423 | −0.1160 | 0.053* |
| C8 | 0.82578 (17) | −0.0944 (2) | −0.02369 (14) | 0.0357 (4) |
| C9 | 0.99689 (18) | −0.2410 (2) | 0.06325 (16) | 0.0454 (5) |
| H9 | 1.0275 | −0.3088 | 0.0192 | 0.054* |
| C10 | 1.0387 (2) | −0.2314 (3) | 0.14943 (17) | 0.0502 (6) |
| H10 | 1.1036 | −0.2903 | 0.1767 | 0.060* |
| C11 | 0.9647 (2) | −0.1152 (3) | 0.18931 (17) | 0.0491 (6) |
| H11 | 0.9730 | −0.0837 | 0.2492 | 0.059* |
| Cl1 | 0.65199 (5) | 0.06053 (7) | 0.25184 (4) | 0.05045 (17) |
| Cl2 | 0.83525 (5) | 0.37392 (6) | 0.12155 (4) | 0.04545 (15) |
| N1 | 0.74008 (13) | 0.01621 (18) | −0.00710 (10) | 0.0327 (3) |
| N2 | 0.90163 (15) | −0.13336 (19) | 0.05243 (12) | 0.0374 (4) |
| N3 | 0.88095 (15) | −0.0554 (2) | 0.13084 (11) | 0.0417 (4) |
| N4 | 0.57069 (14) | 0.1699 (2) | −0.04655 (11) | 0.0366 (4) |
| N5 | 0.56823 (14) | 0.2105 (2) | 0.04169 (11) | 0.0385 (4) |
| Zn1 | 0.73202 (2) | 0.13073 (3) | 0.121755 (15) | 0.03696 (11) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0377 (11) | 0.0347 (10) | 0.0624 (14) | −0.0040 (8) | 0.0090 (10) | −0.0009 (10) |
| C2 | 0.0347 (10) | 0.0363 (10) | 0.0721 (16) | −0.0005 (9) | −0.0004 (10) | 0.0102 (10) |
| C3 | 0.0360 (10) | 0.0439 (11) | 0.0512 (13) | −0.0045 (9) | −0.0066 (9) | 0.0124 (9) |
| C4 | 0.0329 (10) | 0.0332 (9) | 0.0386 (11) | −0.0072 (7) | 0.0014 (8) | 0.0020 (8) |
| C5 | 0.0441 (11) | 0.0538 (12) | 0.0361 (11) | −0.0052 (10) | −0.0025 (9) | 0.0023 (9) |
| C6 | 0.0539 (13) | 0.0570 (13) | 0.0357 (12) | −0.0052 (10) | 0.0062 (10) | −0.0076 (10) |
| C7 | 0.0428 (12) | 0.0470 (11) | 0.0435 (12) | 0.0032 (9) | 0.0071 (9) | −0.0029 (9) |
| C8 | 0.0338 (10) | 0.0337 (9) | 0.0400 (11) | −0.0062 (8) | 0.0054 (8) | 0.0026 (8) |
| C9 | 0.0392 (11) | 0.0374 (11) | 0.0599 (15) | 0.0031 (9) | 0.0064 (10) | 0.0053 (9) |
| C10 | 0.0414 (11) | 0.0469 (12) | 0.0613 (15) | 0.0030 (9) | −0.0047 (10) | 0.0154 (11) |
| C11 | 0.0458 (12) | 0.0549 (13) | 0.0460 (14) | 0.0010 (10) | −0.0036 (10) | 0.0090 (10) |
| Cl1 | 0.0523 (3) | 0.0611 (4) | 0.0389 (3) | −0.0069 (2) | 0.0112 (2) | −0.0012 (2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Cl2 | 0.0431 (3) | 0.0428 (3) | 0.0500 (3) | −0.0086 (2) | −0.0017 (2) | −0.0035 (2) |
| N1 | 0.0309 (8) | 0.0332 (8) | 0.0338 (9) | −0.0042 (6) | 0.0000 (7) | 0.0014 (7) |
| N2 | 0.0348 (9) | 0.0376 (9) | 0.0400 (10) | 0.0006 (6) | 0.0034 (7) | 0.0025 (7) |
| N3 | 0.0413 (9) | 0.0486 (10) | 0.0351 (9) | 0.0030 (8) | 0.0022 (7) | 0.0011 (7) |
| N4 | 0.0316 (8) | 0.0370 (8) | 0.0407 (10) | −0.0038 (7) | −0.0015 (7) | 0.0037 (7) |
| N5 | 0.0359 (9) | 0.0376 (9) | 0.0419 (10) | −0.0029 (7) | 0.0022 (7) | −0.0007 (7) |
| Zn1 | 0.03632 (16) | 0.04045 (17) | 0.03418 (17) | −0.00377 (9) | 0.00263 (10) | −0.00260 (9) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—N5 | 1.319 (3) | C8—N1 | 1.325 (2) |
| C1—C2 | 1.392 (3) | C8—N2 | 1.408 (3) |
| C1—H1 | 0.9300 | C9—C10 | 1.346 (3) |
| C2—C3 | 1.364 (3) | C9—N2 | 1.358 (2) |
| C2—H2 | 0.9300 | C9—H9 | 0.9300 |
| C3—N4 | 1.362 (2) | C10—C11 | 1.391 (3) |
| C3—H3 | 0.9300 | C10—H10 | 0.9300 |
| C4—N1 | 1.332 (2) | C11—N3 | 1.323 (3) |
| C4—C5 | 1.376 (3) | C11—H11 | 0.9300 |
| C4—N4 | 1.405 (2) | Cl1—Zn1 | 2.2470 (6) |
| C5—C6 | 1.374 (3) | Cl2—Zn1 | 2.2564 (6) |
| C5—H5 | 0.9300 | N1—Zn1 | 2.1397 (16) |
| C6—C7 | 1.385 (3) | N2—N3 | 1.358 (2) |
| C6—H6 | 0.9300 | N3—Zn1 | 2.2117 (17) |
| C7—C8 | 1.374 (3) | N4—N5 | 1.360 (2) |
| C7—H7 | 0.9300 | N5—Zn1 | 2.1988 (16) |
| Cg1···Cg2$^{i}$ | 3.4087 (12) | Cg2···Cg3$^{i}$ | 3.6253 (13) |
| N5—C1—C2 | 111.4 (2) | C11—C10—H10 | 127.1 |
| N5—C1—H1 | 124.3 | N3—C11—C10 | 111.1 (2) |
| C2—C1—H1 | 124.3 | N3—C11—H11 | 124.4 |
| C3—C2—C1 | 105.67 (19) | C10—C11—H11 | 124.4 |
| C3—C2—H2 | 127.2 | C8—N1—C4 | 118.37 (17) |
| C1—C2—H2 | 127.2 | C8—N1—Zn1 | 121.33 (13) |
| N4—C3—C2 | 106.6 (2) | C4—N1—Zn1 | 120.23 (13) |
| N4—C3—H3 | 126.7 | C9—N2—N3 | 110.69 (17) |
| C2—C3—H3 | 126.7 | C9—N2—C8 | 130.90 (18) |
| N1—C4—C5 | 122.93 (18) | N3—N2—C8 | 118.41 (16) |
| N1—C4—N4 | 112.86 (17) | C11—N3—N2 | 105.09 (18) |
| C5—C4—N4 | 124.19 (18) | C11—N3—Zn1 | 140.30 (16) |
| C6—C5—C4 | 117.4 (2) | N2—N3—Zn1 | 114.53 (12) |
| C6—C5—H5 | 121.3 | N5—N4—C3 | 111.07 (17) |
| C4—C5—H5 | 121.3 | N5—N4—C4 | 118.92 (16) |
| C5—C6—C7 | 120.8 (2) | C3—N4—C4 | 129.90 (18) |
| C5—C6—H6 | 119.6 | C1—N5—N4 | 105.25 (17) |
| C7—C6—H6 | 119.6 | C1—N5—Zn1 | 140.46 (15) |
| C8—C7—C6 | 116.84 (19) | N4—N5—Zn1 | 113.56 (11) |
| C8—C7—H7 | 121.6 | N1—Zn1—N5 | 72.99 (6) |
| C6—C7—H7 | 121.6 | N1—Zn1—N3 | 72.49 (6) |

| | | | |
|---|---|---|---|
| N1—C8—C7 | 123.55 (19) | N5—Zn1—N3 | 143.97 (6) |
| N1—C8—N2 | 113.06 (17) | N1—Zn1—Cl1 | 135.05 (4) |
| C7—C8—N2 | 123.38 (18) | N5—Zn1—Cl1 | 101.44 (5) |
| C10—C9—N2 | 107.3 (2) | N3—Zn1—Cl1 | 95.67 (5) |
| C10—C9—H9 | 126.3 | N1—Zn1—Cl2 | 108.99 (4) |
| N2—C9—H9 | 126.3 | N5—Zn1—Cl2 | 98.18 (5) |
| C9—C10—C11 | 105.8 (2) | N3—Zn1—Cl2 | 102.45 (5) |
| C9—C10—H10 | 127.1 | Cl1—Zn1—Cl2 | 115.93 (2) |
| N5—C1—C2—C3 | −0.1 (2) | C5—C4—N4—N5 | 175.69 (18) |
| C1—C2—C3—N4 | −0.1 (2) | N1—C4—N4—C3 | −178.85 (18) |
| N1—C4—C5—C6 | 2.3 (3) | C5—C4—N4—C3 | −0.2 (3) |
| N4—C4—C5—C6 | −176.27 (18) | C2—C1—N5—N4 | 0.2 (2) |
| C4—C5—C6—C7 | −0.2 (3) | C2—C1—N5—Zn1 | 169.07 (15) |
| C5—C6—C7—C8 | −1.3 (3) | C3—N4—N5—C1 | −0.3 (2) |
| C6—C7—C8—N1 | 0.9 (3) | C4—N4—N5—C1 | −176.86 (16) |
| C6—C7—C8—N2 | −178.97 (18) | C3—N4—N5—Zn1 | −172.54 (12) |
| N2—C9—C10—C11 | 0.3 (2) | C4—N4—N5—Zn1 | 10.85 (19) |
| C9—C10—C11—N3 | 0.0 (3) | C8—N1—Zn1—N5 | −173.52 (14) |
| C7—C8—N1—C4 | 1.0 (3) | C4—N1—Zn1—N5 | 9.64 (13) |
| N2—C8—N1—C4 | −179.07 (15) | C8—N1—Zn1—N3 | −4.01 (13) |
| C7—C8—N1—Zn1 | −175.88 (15) | C4—N1—Zn1—N3 | 179.15 (15) |
| N2—C8—N1—Zn1 | 4.0 (2) | C8—N1—Zn1—Cl1 | −84.26 (14) |
| C5—C4—N1—C8 | −2.7 (3) | C4—N1—Zn1—Cl1 | 98.90 (13) |
| N4—C4—N1—C8 | 176.00 (15) | C8—N1—Zn1—Cl2 | 93.49 (13) |
| C5—C4—N1—Zn1 | 174.24 (14) | C4—N1—Zn1—Cl2 | −83.35 (13) |
| N4—C4—N1—Zn1 | −7.1 (2) | C1—N5—Zn1—N1 | −178.6 (2) |
| C10—C9—N2—N3 | −0.4 (2) | N4—N5—Zn1—N1 | −10.30 (11) |
| C10—C9—N2—C8 | 179.88 (19) | C1—N5—Zn1—N3 | 164.27 (19) |
| N1—C8—N2—C9 | 178.77 (18) | N4—N5—Zn1—N3 | −27.46 (18) |
| C7—C8—N2—C9 | −1.3 (3) | C1—N5—Zn1—Cl1 | 47.6 (2) |
| N1—C8—N2—N3 | −0.9 (2) | N4—N5—Zn1—Cl1 | −144.18 (11) |
| C7—C8—N2—N3 | 179.04 (18) | C1—N5—Zn1—Cl2 | −71.1 (2) |
| C10—C11—N3—N2 | −0.3 (2) | N4—N5—Zn1—Cl2 | 97.15 (12) |
| C10—C11—N3—Zn1 | −176.68 (16) | C11—N3—Zn1—N1 | 179.3 (2) |
| C9—N2—N3—C11 | 0.4 (2) | N2—N3—Zn1—N1 | 3.17 (12) |
| C8—N2—N3—C11 | −179.84 (17) | C11—N3—Zn1—N5 | −163.4 (2) |
| C9—N2—N3—Zn1 | 177.92 (12) | N2—N3—Zn1—N5 | 20.38 (19) |
| C8—N2—N3—Zn1 | −2.4 (2) | C11—N3—Zn1—Cl1 | −45.1 (2) |
| C2—C3—N4—N5 | 0.2 (2) | N2—N3—Zn1—Cl1 | 138.76 (12) |
| C2—C3—N4—C4 | 176.33 (18) | C11—N3—Zn1—Cl2 | 73.1 (2) |
| N1—C4—N4—N5 | −3.0 (2) | N2—N3—Zn1—Cl2 | −103.08 (12) |

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

**Fig. 1**