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# Bis[5-(2-amino-3-pyridyl)tetrazolato]-copper(II)

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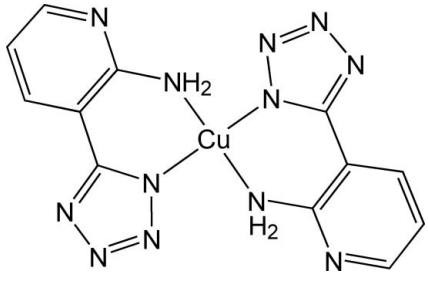
Key indicators: single-crystal X-ray study; $T$ = 294 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.040; $wR$ factor = 0.109; data-to-parameter ratio = 11.9.

In the centrosymmetric title complex, $[Cu(C_6H_5N_6)_2]$, the $Cu^{II}$ ion is coordinated by four N atoms from two symmetry-related bidentate 5-(2-amino-3-pyridyl)tetrazolate ligands in a slightly distorted square-planar environment. There are weak intramolecular N—H···N hydrogen bonds between the two ligands. In the crystal structure, there are significant $\pi$–$\pi$ stacking interactions between symmetry-related tetrazole and pyridine rings, with a centroid–centroid distance of 3.6025 (18)°.

## Related literature

For the coordination chemistry of tetrazole compounds, see: Butler (1984); Zhao *et al.* (2008). For the *in situ* [2 + 3] cycloaddition synthesis of tetrazole coordination polymers, see: Xiong *et al.* (2002); Ye *et al.* (2006); Fu *et al.* (2008). For coordination polymers synthesized with similar organic ligand derivatives, see: Ye *et al.* (2005); Bhandari *et al.* (2000).




## Experimental

### Crystal data

$[Cu(C_6H_5N_6)_2]$
$M_r$ = 385.86
Monoclinic, $P2_1/c$
$a$ = 6.6492 (6) Å
$b$ = 7.9093 (7) Å
$c$ = 13.5581 (12) Å
$\beta$ = 100.692 (2)°
$V$ = 700.65 (11) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 1.59 mm$^{-1}$
$T$ = 294 K
0.15 × 0.13 × 0.09 mm

### Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min}$ = 0.797, $T_{max}$ = 0.870
3743 measured reflections
1363 independent reflections
1228 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.020

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.109
$S$ = 1.07
1363 reflections
115 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.69 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.73 e Å$^{-3}$

**Table 1**
Selected bond angles (°).

| | | | |
|---|---|---|---|
| N5$^i$—Cu1—N5 | 180 | N5—Cu1—N4$^i$ | 90.97 (10) |
| N5—Cu1—N4 | 89.03 (10) | N4—Cu1—N4$^i$ | 180 |

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

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N5—H5$A$···N2$^i$ | 0.90 | 2.50 | 2.902 (4) | 108 |

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2827).

## References

Bhandari, S., Hague, C. E., Mahon, M. F. & Molloy, K. C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 663–669.
Butler, R. N. (1984). In *Comprehensive Heterocyclic Chemistry*, Vol. 5, edited by A. R. Katritzky, pp. 791–838. Amsterdam: Elsevier.
Fu, D. W., Zhang, W. & Xiong, R. G. (2008). *Cryst. Growth Des.* **8**, 3461–3464.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Xiong, R. G., Xue, X., Zhao, H., You, X. Z., Abrahams, B. F. & Xue, Z. L. (2002). *Angew. Chem. Int. Ed.* **41**, 3800–3803.
Ye, Q., Li, Y. H., Song, Y. M., Huang, X. F., Xiong, R. G. & Xue, Z. L. (2005). *Inorg. Chem.* **44**, 3618–3625.
Ye, Q., Song, Y. M., Wang, G. X., Chen, K., Fu, D. W., Chang, P. W. H., Zhu, J. S., Huang, S. P. D. & Xiong, R. G. (2006). *J. Am. Chem. Soc.* **128**, 6554–6555.
Zhao, H., Qu, Z. R., Ye, H. Y. & Xiong, R. G. (2008). *Chem. Soc. Rev.* **37**, 84–100.

# supplementary materials

*Acta Cryst.* (2009). E**65**, m1160 [ **doi:10.1107/S1600536809034369** ]

# Bis[5-(2-amino-3-pyridyl)tetrazolato]copper(II)

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## Comment

In situ [2+3] cycloaddition synthesis of tetrazole coordination polymers under hydrothermal conditions has proved to be a fast and convenient route to explore novel coordination polymers with rich structural diversities and potential physical properties, such as second harmonic generation (SGH), ferroelectric and dielectric responses (Xiong *et al.*, 2002; Ye *et al.*, 2006; Fu *et al.* (2008). The crystal structure of the compound formed by our hydrothermal synthesis is reported herein.

The molecular structure of the title compound is shown in Fig. 1. The $Cu^{II}$ ion lies on an inversion center coordinated by four N atoms from two symmetry related bidentate 3-(2-Amino-pyridyl))tetrazolato ligands in a slightly distorted square-planar environment. In the crystal structure, there are significant π–π stacking interactions between symmetry related tetrazole and pyridine rings with a centroid to centroid distance of 3.6025 (18)°.

## Experimental

The title compound was prepared by hydrothermal treatment of 2-aminonicotinonitrile (2.3 mmol) and $Cu(NO_3)_2$ (1.0 mmol) with excess amount of $NaN_3$ in a sealed Pyrex tuble at 403K for 2–4 days. The resulting green rectangular crystals gave a yield of 75% based on $Cu(NO_3)_2$.

## Refinement

H atoms were placed in caculated positions with C-H = 0.93 and N-H = 0.90Å and refined using a riding-model approximation with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

## Figures

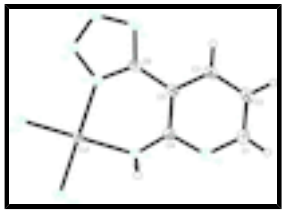

Fig. 1. The molecular structure of the title compound with the atomic numbering scheme. Displacement ellipsoids were drawn at the 30% probability level. Symmetry code: (a) -x+1, -y+1, -z+1. Hydrogen bonds are shown as dashed lines.

## Bis[5-(2-amino-3-pyridyl)tetrazolato]copper(II)

*Crystal data*

| | |
|---|---|
| $[Cu(C_6H_5N_6)_2]$ | $F(000) = 390$ |
| $M_r = 385.86$ | $D_x = 1.829$ Mg m$^{-3}$ |

| | |
|---|---|
| Monoclinic, $P2_1/c$ | Melting point: 723 K |
| Hall symbol: -P 2ybc | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 6.6492$ (6) Å | Cell parameters from 2942 reflections |
| $b = 7.9093$ (7) Å | $\theta = 3.0–27.5°$ |
| $c = 13.5581$ (12) Å | $\mu = 1.59$ mm$^{-1}$ |
| $\beta = 100.692$ (2)° | $T = 294$ K |
| $V = 700.65$ (11) Å$^3$ | Rectangle, green |
| $Z = 2$ | 0.15 × 0.13 × 0.09 mm |

*Data collection*

| | |
|---|---|
| Rigaku Mercury2 diffractometer | 1363 independent reflections |
| Radiation source: fine-focus sealed tube | 1228 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.020$ |
| Detector resolution: 13.6612 pixels mm$^{-1}$ | $\theta_{max} = 26.0°$, $\theta_{min} = 3.0°$ |
| ω scans | $h = -8\rightarrow7$ |
| Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005) | $k = -8\rightarrow9$ |
| $T_{min} = 0.797$, $T_{max} = 0.870$ | $l = -15\rightarrow16$ |
| 3743 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.040$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.109$ | H-atom parameters constrained |
| $S = 1.07$ | $w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 1.0273P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 1363 reflections | $(\Delta/\sigma)_{max} < 0.001$ |
| 115 parameters | $\Delta\rho_{max} = 0.69$ e Å$^{-3}$ |
| 0 restraints | $\Delta\rho_{min} = -0.73$ 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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0.5000 | 0.5000 | 0.5000 | 0.0265 (2) |
| N6 | 1.0060 (4) | 0.1967 (3) | 0.61317 (18) | 0.0302 (6) |
| C6 | 0.7920 (5) | 0.3986 (4) | 0.3685 (2) | 0.0260 (6) |
| C5 | 0.9283 (4) | 0.3088 (4) | 0.4476 (2) | 0.0263 (6) |
| N4 | 0.6177 (4) | 0.4748 (3) | 0.37835 (19) | 0.0294 (6) |
| C4 | 0.8741 (5) | 0.2899 (4) | 0.5446 (2) | 0.0258 (6) |
| N3 | 0.8245 (4) | 0.4167 (4) | 0.27476 (19) | 0.0345 (6) |
| C3 | 1.1079 (5) | 0.2369 (4) | 0.4307 (2) | 0.0322 (7) |
| H3A | 1.1439 | 0.2497 | 0.3680 | 0.039* |
| N2 | 0.5399 (4) | 0.5422 (4) | 0.2875 (2) | 0.0365 (6) |
| C2 | 1.2364 (5) | 0.1461 (4) | 0.5041 (3) | 0.0364 (7) |
| H2A | 1.3576 | 0.0997 | 0.4914 | 0.044* |
| C1 | 1.1816 (5) | 0.1263 (4) | 0.5947 (2) | 0.0349 (7) |
| H1A | 1.2646 | 0.0642 | 0.6446 | 0.042* |
| N1 | 0.6643 (5) | 0.5072 (4) | 0.2266 (2) | 0.0385 (7) |
| N5 | 0.7116 (4) | 0.3534 (3) | 0.56979 (17) | 0.0291 (6) |
| H5A | 0.7585 | 0.4076 | 0.6279 | 0.035* |
| H5B | 0.6431 | 0.2629 | 0.5866 | 0.035* |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0241 (3) | 0.0352 (3) | 0.0227 (3) | 0.00433 (19) | 0.0104 (2) | 0.00138 (19) |
| N6 | 0.0281 (14) | 0.0330 (14) | 0.0300 (13) | 0.0006 (10) | 0.0068 (11) | 0.0029 (10) |
| C6 | 0.0267 (15) | 0.0296 (14) | 0.0243 (13) | −0.0035 (11) | 0.0112 (11) | −0.0035 (11) |
| C5 | 0.0250 (15) | 0.0270 (14) | 0.0292 (15) | −0.0012 (11) | 0.0108 (12) | −0.0019 (11) |
| N4 | 0.0280 (14) | 0.0395 (14) | 0.0223 (12) | 0.0041 (11) | 0.0087 (10) | 0.0012 (10) |
| C4 | 0.0239 (15) | 0.0258 (14) | 0.0286 (14) | −0.0029 (11) | 0.0076 (12) | 0.0000 (11) |
| N3 | 0.0342 (15) | 0.0477 (16) | 0.0248 (12) | 0.0030 (12) | 0.0137 (11) | −0.0019 (11) |
| C3 | 0.0325 (17) | 0.0347 (16) | 0.0328 (16) | 0.0011 (13) | 0.0151 (13) | −0.0031 (13) |
| N2 | 0.0353 (16) | 0.0513 (16) | 0.0245 (13) | 0.0073 (13) | 0.0100 (11) | 0.0046 (12) |
| C2 | 0.0280 (16) | 0.0374 (17) | 0.0464 (18) | 0.0065 (13) | 0.0141 (14) | −0.0028 (14) |
| C1 | 0.0297 (17) | 0.0334 (16) | 0.0393 (17) | 0.0024 (12) | 0.0002 (13) | 0.0015 (13) |
| N1 | 0.0365 (17) | 0.0561 (19) | 0.0242 (13) | 0.0054 (12) | 0.0092 (12) | 0.0040 (11) |
| N5 | 0.0277 (14) | 0.0401 (15) | 0.0229 (11) | 0.0069 (11) | 0.0135 (10) | 0.0056 (10) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cu1—N5$^{i}$ | 1.930 (2) | N4—N2 | 1.354 (4) |
| Cu1—N5 | 1.930 (2) | C4—N5 | 1.293 (4) |
| Cu1—N4 | 1.963 (2) | N3—N1 | 1.348 (4) |
| Cu1—N4$^{i}$ | 1.963 (2) | C3—C2 | 1.386 (5) |
| N6—C1 | 1.358 (4) | C3—H3A | 0.9300 |
| N6—C4 | 1.369 (4) | N2—N1 | 1.302 (4) |

| | | | |
|---|---|---|---|
| C6—N4 | 1.335 (4) | C2—C1 | 1.354 (5) |
| C6—N3 | 1.336 (4) | C2—H2A | 0.9300 |
| C6—C5 | 1.455 (4) | C1—H1A | 0.9300 |
| C5—C3 | 1.380 (4) | N5—H5A | 0.9000 |
| C5—C4 | 1.435 (4) | N5—H5B | 0.9000 |
| N5$^{i}$—Cu1—N5 | 180 | C6—N3—N1 | 105.3 (2) |
| N5$^{i}$—Cu1—N4 | 90.97 (10) | C5—C3—C2 | 122.1 (3) |
| N5—Cu1—N4 | 89.03 (10) | C5—C3—H3A | 118.9 |
| N5$^{i}$—Cu1—N4$^{i}$ | 89.03 (10) | C2—C3—H3A | 118.9 |
| N5—Cu1—N4$^{i}$ | 90.97 (10) | N1—N2—N4 | 108.2 (3) |
| N4—Cu1—N4$^{i}$ | 180 | C1—C2—C3 | 118.5 (3) |
| C1—N6—C4 | 124.1 (3) | C1—C2—H2A | 120.7 |
| N4—C6—N3 | 110.1 (3) | C3—C2—H2A | 120.7 |
| N4—C6—C5 | 125.5 (3) | C2—C1—N6 | 120.3 (3) |
| N3—C6—C5 | 124.4 (3) | C2—C1—H1A | 119.8 |
| C3—C5—C4 | 118.8 (3) | N6—C1—H1A | 119.8 |
| C3—C5—C6 | 121.3 (3) | N2—N1—N3 | 110.1 (3) |
| C4—C5—C6 | 119.9 (3) | C4—N5—Cu1 | 132.2 (2) |
| C6—N4—N2 | 106.2 (2) | C4—N5—H5A | 104.2 |
| C6—N4—Cu1 | 128.3 (2) | Cu1—N5—H5A | 104.2 |
| N2—N4—Cu1 | 125.5 (2) | C4—N5—H5B | 104.2 |
| N5—C4—N6 | 119.4 (3) | Cu1—N5—H5B | 104.2 |
| N5—C4—C5 | 124.5 (3) | H5A—N5—H5B | 105.5 |
| N6—C4—C5 | 116.1 (3) | | |
| N4—C6—C5—C3 | −178.6 (3) | C6—C5—C4—N6 | 176.9 (3) |
| N3—C6—C5—C3 | 1.2 (5) | N4—C6—N3—N1 | 0.1 (3) |
| N4—C6—C5—C4 | 3.1 (4) | C5—C6—N3—N1 | −179.8 (3) |
| N3—C6—C5—C4 | −177.1 (3) | C4—C5—C3—C2 | 0.5 (5) |
| N3—C6—N4—N2 | 0.1 (4) | C6—C5—C3—C2 | −177.8 (3) |
| C5—C6—N4—N2 | 179.9 (3) | C6—N4—N2—N1 | −0.2 (4) |
| N3—C6—N4—Cu1 | −176.5 (2) | Cu1—N4—N2—N1 | 176.5 (2) |
| C5—C6—N4—Cu1 | 3.4 (4) | C5—C3—C2—C1 | 0.8 (5) |
| N5—Cu1—N4—C6 | −7.2 (3) | C3—C2—C1—N6 | −1.1 (5) |
| N5—Cu1—N4—N2 | 176.9 (3) | C4—N6—C1—C2 | 0.1 (5) |
| C1—N6—C4—N5 | −179.3 (3) | N4—N2—N1—N3 | 0.2 (4) |
| C1—N6—C4—C5 | 1.2 (4) | C6—N3—N1—N2 | −0.2 (4) |
| C3—C5—C4—N5 | 179.0 (3) | N6—C4—N5—Cu1 | 175.8 (2) |
| C6—C5—C4—N5 | −2.6 (4) | C5—C4—N5—Cu1 | −4.7 (5) |
| C3—C5—C4—N6 | −1.4 (4) | N4—Cu1—N5—C4 | 8.1 (3) |

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

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N5—H5A···N2$^{i}$ | 0.90 | 2.50 | 2.902 (4) | 108 |

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

**Fig. 1**