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

Min Guo

Ordered Matter Science Research Center, Southeast University, Nanjing 210096, People's Republic of China

Correspondence e-mail: guomin625@yahoo.com.cn

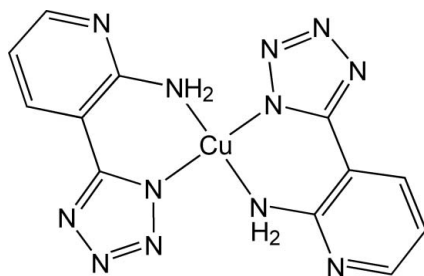
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.040; wR factor = 0.109; data-to-parameter ratio = 11.9.

In the centrosymmetric title complex, $[\text{Cu}(\text{C}_6\text{H}_5\text{N}_6)_2]$, 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 $\text{N}-\text{H}\cdots\text{N}$ 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

$[\text{Cu}(\text{C}_6\text{H}_5\text{N}_6)_2]$
 $M_r = 385.86$
 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) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.59$ mm⁻¹

$T = 294$ K
 $0.15 \times 0.13 \times 0.09$ mm

Data collection

Rigaku Mercury2 diffractometer
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 $T_{\text{min}} = 0.797$, $T_{\text{max}} = 0.870$

3743 measured reflections
 1363 independent reflections
 1228 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

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
 $\Delta\rho_{\text{max}} = 0.69$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.73$ e Å⁻³

Table 1

Selected bond angles (°).

$\text{N5}^i-\text{Cu1}-\text{N5}$	180	$\text{N5}-\text{Cu1}-\text{N4}^i$	90.97 (10)
$\text{N5}-\text{Cu1}-\text{N4}$	89.03 (10)	$\text{N4}-\text{Cu1}-\text{N4}^i$	180

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N5}-\text{H5A}\cdots\text{N2}^i$	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).

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supporting information

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

Min Guo

S1. 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.

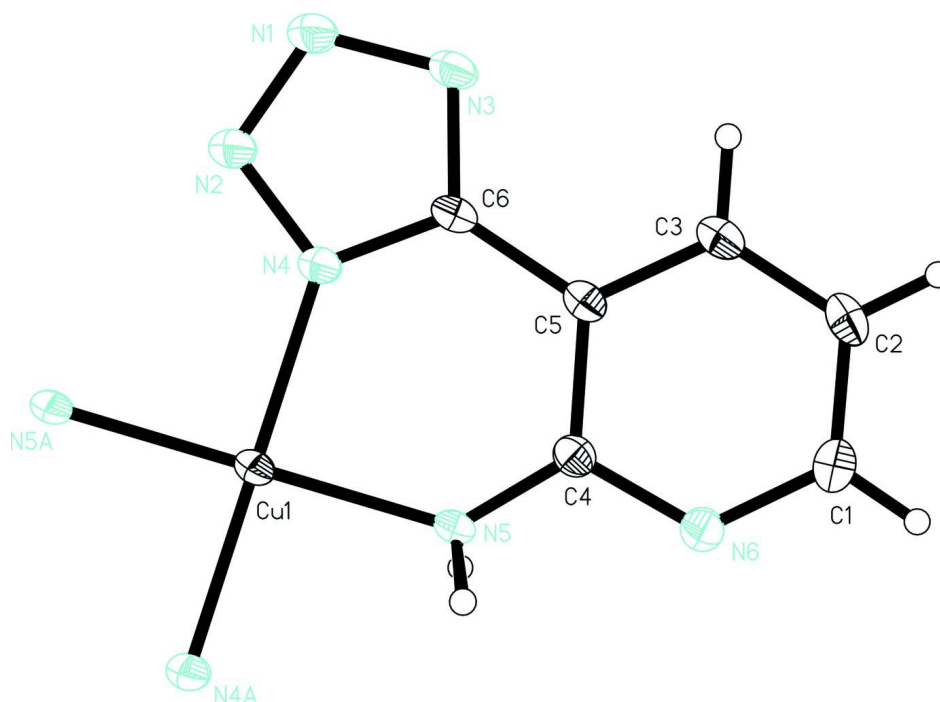
The molecular structure of the title compound is shown in Fig. 1. The Cu^{II} ion lies on an inversion center coordinated by four N atoms from two symmetry related bidentate 3-(2-Amino-pyridyl))tetrazolato ligands in a slightly distorted square-planar environment. In the crystal structure, there are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

S2. Experimental

The title compound was prepared by hydrothermal treatment of 2-aminonicotinonitrile (2.3 mmol) and Cu(NO₃)₂ (1.0 mmol) with excess amount of NaN₃ in a sealed Pyrex tube at 403K for 2–4 days. The resulting green rectangular crystals gave a yield of 75% based on Cu(NO₃)₂.

S3. Refinement

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

**Figure 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

$[\text{Cu}(\text{C}_6\text{H}_5\text{N}_6)_2]$

$M_r = 385.86$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 6.6492(6)\ \text{\AA}$

$b = 7.9093(7)\ \text{\AA}$

$c = 13.5581(12)\ \text{\AA}$

$\beta = 100.692(2)^\circ$

$V = 700.65(11)\ \text{\AA}^3$

$Z = 2$

$F(000) = 390$

$D_x = 1.829\ \text{Mg m}^{-3}$

Melting point: 723 K

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2942 reflections

$\theta = 3.0\text{--}27.5^\circ$

$\mu = 1.59\ \text{mm}^{-1}$

$T = 294\ \text{K}$

Rectangle, green

$0.15 \times 0.13 \times 0.09\ \text{mm}$

Data collection

Rigaku Mercury2
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $13.6612\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)

$T_{\min} = 0.797, T_{\max} = 0.870$

3743 measured reflections

1363 independent reflections

1228 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 26.0^\circ, \theta_{\min} = 3.0^\circ$

$h = -8 \rightarrow 7$

$k = -8 \rightarrow 9$

$l = -15 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.109$

$S = 1.07$

1363 reflections

115 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-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 1.0273P]$

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

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

$\Delta\rho_{\max} = 0.69 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.73 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^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 code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N5—H5 <i>A</i> \cdots N2 ⁱ	0.90	2.50	2.902 (4)	108

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