Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis[5-(pyridin-2-yl-κN)tetrazolido-κN^1]-copper(II)

Jian-Quan Li,[a,b]* Dan Mu[c] and Meng-Bao Fan[a]

[a]School of Mechatronic Engineering, China University of Mining and Technology (Xuzhou), Jiangsu 221116, People's Republic of China, [b]Opto-Electronic Engineering College, Zaozhuang University, Shandong 277160, People's Republic of China, and [c]College of Chemistry Chemical Engineering and Materials Science, Zaozhuang University, Shandong 277160, People's Republic of China
Correspondence e-mail: lijq786@163.com

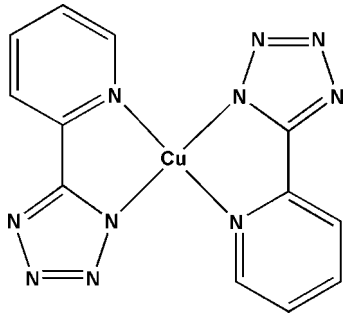
Received 17 January 2014; accepted 29 January 2014

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.003 Å; R factor = 0.034; wR factor = 0.087; data-to-parameter ratio = 11.7.

In the title complex, $[Cu(C_6H_4N_5)_2]$, the Cu^{II} ion lies on an inversion center and is coordinated by two chelating 5-(pyridin-2-yl)tetrazolide ligands in a slightly distorted square-planar coordination geometry. In the crystal, π–π stacking interactions, with centroid–centroid distances in the range 3.4301 (14)–3.4387 (13) Å, link the complex molecules along [101].

Related literature

For background to coordination complexes, see: Lu *et al.* (2011); Yang *et al.* (2012).



Experimental

Crystal data

$[Cu(C_6H_4N_5)_2]$
M_r = 355.82
Monoclinic, $P2_1/c$
a = 5.5391 (9) Å
b = 13.128 (2) Å
c = 8.7950 (15) Å
β = 97.650 (3)°
V = 633.88 (18) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.74 mm^{-1}
T = 291 K
0.44 × 0.35 × 0.30 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.486, T_{max} = 0.593
3328 measured reflections
1241 independent reflections
1063 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.087
S = 1.03
1241 reflections
106 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

This work was supported by the National Natural Science Foundation of China (grant 21203164) and China Postdoctoral Science Foundation funded project (grant 2013M531586).

Supporting information for this paper is available from the IUCr electronic archives (Reference: LH5686).

References

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA
Lu, Z.-Z., Zhang, R., Li, Y.-Z., Guo, Z.-J. & Zheng, H.-G. (2011). *J. Am. Chem. Soc.* pp. 4172–4174.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC. (2006). *CrystalStructure*. Rigaku/MSC, The Woodlands, Texas, USA..
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Yang, S., Lin, X., Lewis, W., Suyetin, M., Bichoutskaia, E., Parker, J. E., Tang, C. C., Allan, D. R., Rizkallah, P. J., Hubberstey, P., Champness, N. R., Thomas, K. M., Blake, A. J. & Schröder, M. (2012). *Nat. Mater.* pp. 710–716.

supporting information

Acta Cryst. (2014). E**70**, m79 [doi:10.1107/S1600536814002062]

Bis[5-(pyridin-2-yl-κN)tetrazolido-κN^1]copper(II)

Jian-Quan Li, Dan Mu and Meng-Bao Fan

S1. Comment

Coordination complexes (polymers) have drawn broad attention in recent decades due to their promising applications in catalysis, sensing and gas adsorption/separation (Yang *et al.*, 2012; Lu *et al.*, 2011). Despite several investigations, a detailed analysis of single crystal structures of coordination complexes is also of importance for the study of specific bonding between supramolecules in the solid state.

We report here a coordination complex, formulated as $Cu(pytz)_2$ (pytz = 5-(pyridin-2-yl)tetrazolide). The molecular structure of the title compound is shown in Fig. 1. The Cu^{II} ion is located on an inversion center. The pytz ligand coordinates to the Cu^{II} ion *via* two symmetry related pyridine N atoms and two symmetry related tetrazolide N atoms. The Cu—N bond distances are 1.956 (2) and 2.021 (2) Å. In the crystal, π–π stacking interactions with centroid–centroid distances of 3.4386 (13)Å for Cg1···Cg3(-x+1, -y+1, -z+1), 3.4387 (14)Å for Cg2···Cg3 (-1+x, y, z) and 3.4301 (14)Å for Cg3–Cg3 (-1+x, -1+y, -1+z) link the complex molecules along [101]. Cg1, Cg2 and Cg3 are the centroids of the Cu1/N1/C5/C6/N2, Cu1/$N1^i$/$C5^i$/$C6^i$/$N2^i$ (symmetry code (i):-x, -y+1, -z+1) and N2/N3/N4/N5/N6 rings, respectively. These stacking interactions allow for intermolecular Cu···N contacts of 2.993 (1)Å (Fig. 2).

S2. Experimental

The title complex was synthesized by the addition of $CuNO_3$ (2 mmol) to an ethanol solution of Hpytz (4 mmol). The mixed solution was allowed to evaporated solwly at room temperature, and blue prismatic crystals were isolated in about 15 days. Analysis calculated for $C_{12}H_8N_{10}Cu$: C 40.51, H 2.27, N 39.37%; Found: C 40.48, H 2,21, N 39.30%.

S3. Refinement

The H atoms on carbon were placed in calculated positions [C—H = 0.93 Å (aromatic), and U_{iso}(H) = 1.2U_{eq}($C_{aromatic}$)] using a riding model approximation.

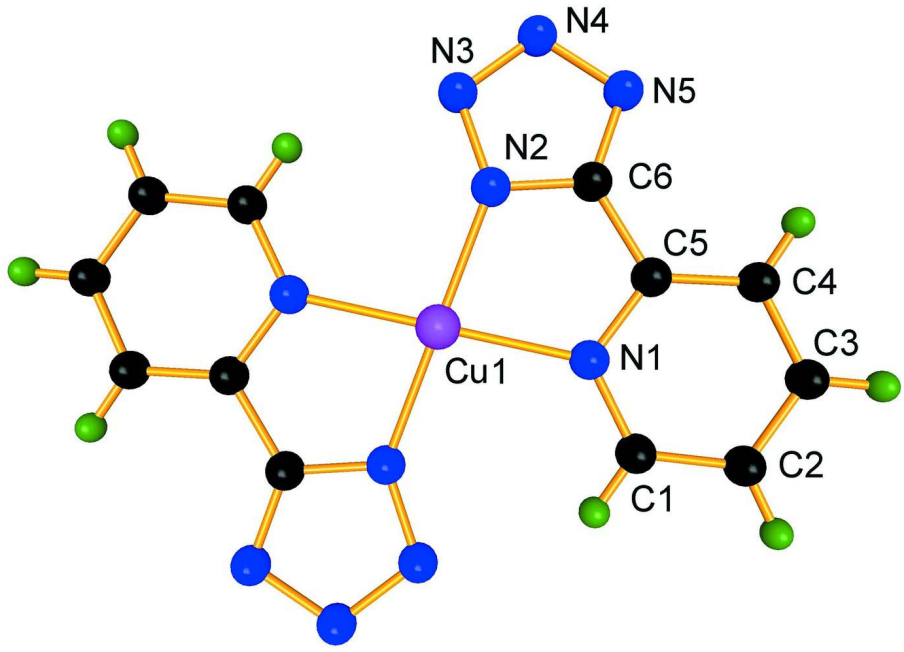


Figure 1

The molecular structure with ellipsoids drawn at the 30% probability level. Unlabeled atoms are related by the symmetry operator (-x, -y+1, -z+1).

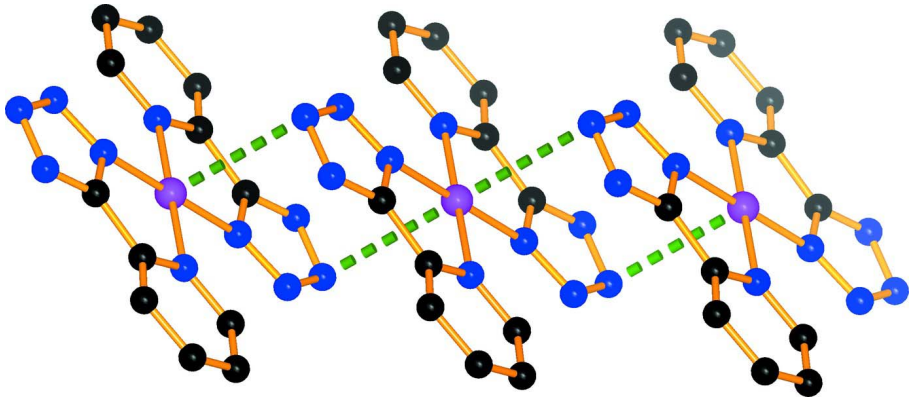


Figure 2

Part of the crystal structure indicating π–π stacking interactions along [101] and dashed lines to show closest intermolecular Cu···N contacts.

Bis[5-(pyridin-2-yl-κN)tetrazolido-κN^1]copper(II)

Crystal data

$[Cu(C_6H_4N_5)_2]$
M_r = 355.82
Monoclinic, $P2_1/c$
a = 5.5391 (9) Å
b = 13.128 (2) Å
c = 8.7950 (15) Å
β = 97.650 (3)°
V = 633.88 (18) Å^3
Z = 2
$F(000)$ = 358
D_x = 1.864 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1641 reflections
θ = 2.3–25.1°

μ = 1.74 mm^{-1}
T = 291 K

Block, blue
0.44 × 0.35 × 0.30 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 10 pixels mm^{-1}
ω scan
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.486, T_{max} = 0.593

3328 measured reflections
1241 independent reflections
1063 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 26.0°, θ_{min} = 2.8°
h = −6→6
k = −9→16
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.087
S = 1.03
1241 reflections
106 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.055P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 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.

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

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.0000	0.5000	0.5000	0.03232 (18)
N3	0.4142 (4)	0.54997 (16)	0.3062 (2)	0.0405 (5)
N5	0.5268 (4)	0.39183 (15)	0.2804 (2)	0.0396 (5)
N1	0.0300 (3)	0.34667 (17)	0.49523 (18)	0.0316 (5)
C5	0.2056 (4)	0.31234 (17)	0.4168 (2)	0.0303 (5)
N2	0.2605 (4)	0.49021 (12)	0.3709 (2)	0.0325 (5)
C6	0.3376 (4)	0.39545 (17)	0.3530 (2)	0.0311 (5)
C4	0.2523 (4)	0.21184 (17)	0.3970 (3)	0.0389 (6)
H4	0.3775	0.1913	0.3433	0.047*
N4	0.5743 (5)	0.49081 (14)	0.2522 (3)	0.0430 (6)
C1	−0.1079 (4)	0.27709 (18)	0.5552 (3)	0.0376 (6)
H1	−0.2307	0.2990	0.6099	0.045*
C3	0.1085 (5)	0.14121 (19)	0.4590 (3)	0.0426 (6)
H3	0.1346	0.0719	0.4471	0.051*
C2	−0.0724 (5)	0.17453 (18)	0.5379 (3)	0.0421 (6)
H2	−0.1714	0.1279	0.5797	0.051*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0308 (3)	0.0254 (3)	0.0450 (3)	0.00163 (14)	0.02087 (19)	0.00056 (15)
N3	0.0396 (12)	0.0350 (12)	0.0520 (13)	−0.0013 (10)	0.0251 (10)	0.0024 (10)
N5	0.0390 (11)	0.0353 (11)	0.0491 (12)	−0.0004 (9)	0.0231 (9)	−0.0020 (9)
N1	0.0297 (10)	0.0279 (11)	0.0393 (11)	0.0002 (7)	0.0128 (9)	0.0002 (7)
C5	0.0277 (11)	0.0298 (12)	0.0351 (11)	−0.0005 (9)	0.0105 (9)	−0.0012 (9)
N2	0.0316 (11)	0.0285 (11)	0.0410 (12)	−0.0005 (7)	0.0180 (9)	0.0007 (7)
C6	0.0301 (12)	0.0283 (11)	0.0369 (12)	0.0000 (9)	0.0119 (9)	−0.0027 (9)
C4	0.0399 (13)	0.0331 (13)	0.0473 (14)	0.0015 (10)	0.0190 (11)	−0.0042 (10)
N4	0.0422 (13)	0.0370 (13)	0.0562 (14)	−0.0011 (8)	0.0298 (11)	−0.0010 (9)
C1	0.0347 (12)	0.0342 (13)	0.0470 (14)	−0.0003 (10)	0.0176 (11)	0.0009 (10)
C3	0.0496 (15)	0.0266 (12)	0.0556 (15)	0.0015 (11)	0.0216 (13)	−0.0033 (11)
C2	0.0461 (14)	0.0324 (14)	0.0512 (15)	−0.0061 (11)	0.0193 (12)	0.0030 (11)

Geometric parameters (Å, º)

Cu1—N2	1.956 (2)	C5—C4	1.360 (3)
Cu1—N2^{i}	1.956 (2)	C5—C6	1.466 (3)
Cu1—N1^{i}	2.021 (2)	N2—C6	1.331 (3)
Cu1—N1	2.021 (2)	C4—C3	1.381 (3)
N3—N4	1.314 (3)	C4—H4	0.9300
N3—N2	1.339 (3)	C1—C2	1.372 (3)
N5—C6	1.299 (3)	C1—H1	0.9300
N5—N4	1.355 (2)	C3—C2	1.364 (4)
N1—C1	1.343 (3)	C3—H3	0.9300
N1—C5	1.343 (3)	C2—H2	0.9300
N2—Cu1—N2^{i}	180.0	N5—C6—N2	112.6 (2)
N2—Cu1—N1^{i}	98.42 (7)	N5—C6—C5	129.6 (2)
N2^{i}—Cu1—N1^{i}	81.58 (7)	N2—C6—C5	117.8 (2)
N2—Cu1—N1	81.58 (7)	C5—C4—C3	118.1 (2)
N2^{i}—Cu1—N1	98.42 (7)	C5—C4—H4	120.9
N1^{i}—Cu1—N1	180.0	C3—C4—H4	120.9
N4—N3—N2	107.76 (19)	N3—N4—N5	110.1 (2)
C6—N5—N4	104.1 (2)	N1—C1—C2	121.8 (2)
C1—N1—C5	117.5 (2)	N1—C1—H1	119.1
C1—N1—Cu1	128.11 (16)	C2—C1—H1	119.1
C5—N1—Cu1	114.33 (15)	C2—C3—C4	119.1 (2)
N1—C5—C4	123.7 (2)	C2—C3—H3	120.4
N1—C5—C6	112.3 (2)	C4—C3—H3	120.4
C4—C5—C6	124.1 (2)	C3—C2—C1	119.8 (2)
C6—N2—N3	105.40 (19)	C3—C2—H2	120.1
C6—N2—Cu1	113.75 (15)	C1—C2—H2	120.1
N3—N2—Cu1	140.20 (15)		

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