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catena-Poly[[[5-(2-pyridyl)tetrazolato-κ^2N^1,N^5]copper(II)]-μ-5-(2-pyridyl)tetrazolato-$\kappa^2N^1,N^5:N^3$]

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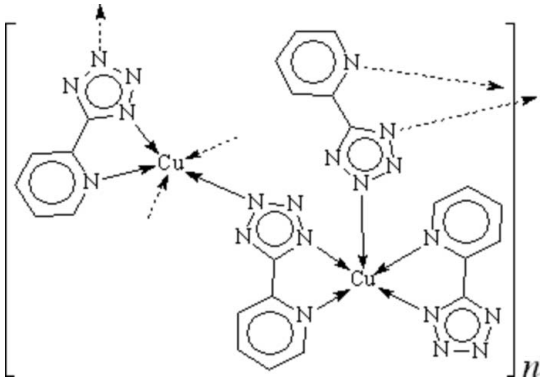
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.004 Å; R factor = 0.025; wR factor = 0.066; data-to-parameter ratio = 11.3.

In the title compound, $[Cu(C_6H_5N_5)_2]_n$, the Cu^{II} atom is coordinated by five N atoms from three distinct pyridyltetrazolate anions in a highly distorted square-pyramidal arrangement. The ligands link adjacent Cu^{II} atoms to form one-dimensional polymeric chains with a Cu···Cu separation of 6.224 (2) Å. The chains are further linked by π–π stacking interactions [centroid–centroid = 3.684 (2) Å and vertical distance = 3.281 (2) Å], forming a three-dimensional supramolecular framework.

Related literature

For the crystal structures of related compounds, see: Andrews *et al.* (2006); Facchetti *et al.* (2004); Mo *et al.* (2004); Wang *et al.* (2003); Zhang *et al.* (2006).



Experimental

Crystal data

$[Cu(C_6H_5N_5)_2]$
M_r = 355.82
Orthorhombic, *Pbca*
a = 8.5905 (9) Å
b = 14.8361 (16) Å
c = 20.905 (2) Å
V = 2664.3 (5) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.66 mm^{-1}
T = 294 (2) K
0.30 × 0.28 × 0.28 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.584, T_{max} = 0.630
12543 measured reflections
2348 independent reflections
1951 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.066
S = 1.05
2348 reflections
208 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.0005 (18)	Cu1—N6	1.9723 (19)
Cu1—N3^{i}	2.2574 (19)	Cu1—N10	2.0355 (19)
Cu1—N5	2.0625 (19)		
N1—Cu1—N3^{i}	94.06 (7)	N6—Cu1—N3^{i}	102.82 (8)
N1—Cu1—N5	79.95 (7)	N6—Cu1—N5	98.08 (8)
N1—Cu1—N10	97.09 (8)	N6—Cu1—N10	81.26 (8)
N5—Cu1—N3^{i}	91.09 (7)	N10—Cu1—N3^{i}	101.01 (7)
N6—Cu1—N1	163.06 (8)	N10—Cu1—N5	167.75 (8)

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2170).

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supplementary materials

Acta Cryst. (2007). E**63**, m2894 [**doi:10.1107/S1600536807053597**]

catena-Poly[[[5-(2-pyridyl)tetrazolato-κ^2N^1,N^5]copper(II)]-μ-5-(2-pyridyl)tetrazolato-$\kappa^2N^1,N^5:N^3$]

Y.-E. Qiu, M.-F. Jin and X.-L. Zhang

Comment

The crystal structures of manganese(II), copper(I, II), zinc(II), lanthanum(III) and gadolinium(III) complexes of the 5-(2-pyridyl)tetrazolate ligand have been reported recently (Andrews *et al.*, 2006; Facchetti *et al.*, 2004; Mo *et al.*, 2004; Wang *et al.*, 2003; Zhang *et al.*, 2006). Except for the copper(I, II) complex, which has a two-dimensional structure with Cl^- ions co-ligated, all other complexes have a mononuclear structure, in which the pyridyltetrazolate anion adopts a chelating coordination mode using its 1-position N atom of the tetrazolate ring and the pyridine N atom. Herein, we report the title complex, $[Cu(C_6H_5N_5)_2]_n$, which has a polymeric one-dimensional structure.

In the title compound, the copper(II) atom is coordinated by five N atoms from three distinct pyridyltetrazolate ligands to form a highly distorted square-pyramidal geometry. The coordination basal plane is provided by two chelating ligands through their 1-position N atoms of the tetrazolate rings and by the pyridine N atoms, while and the apical position is occupied by the third ligand using the 3-position N atoms of its tetrazolate group (Fig. 1). Bond distances and angles around the copper(II) centre are in the range 1.972 (2)–2.257 (2) Å and 79.95 (7)–102.82 (8) °, respectively (Table 1). It is interesting to note that the ligands perform two types of coordination modes: chelating and chelating–bridging. The latter links the metal centres to form polymeric one-dimensional chains running parallel to the *a* axis with an intrachain Cu···Cu separation of 6.224 (2) Å (Fig. 2). In addition, π–π interactions occurring between the pyridine and tetrazolato rings of adjacent chains extend the structure to form a three-dimensional supramolecular framework as shown in Fig. 3 ($Cp1\cdots Cp2^{i}$, 3.684 (3) Å; $Cp3\cdots Cp4^{ii}$, 3.973 (4) Å; Cp1, Cp2, Cp3 and Cp4 are the centroids of the N1–N4/C1, N5/C2–C6, N6–N9/C7 and N10/C8–C12 rings respectively. Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1/2+x, y, 1/2-z$).

Experimental

5-(2-Pyridyl)-1*H*-tetrazole (30 mg, 0.2 mmol) and copper(II) chloride dihydrate (34 mg, 0.2 mmol) were placed in a Teflon-lined stainless-steel Parr bomb along with water (14 ml). The bomb was heated at 431 K for 48 h and then cooled to room temperature over 24 h. Black crystals of the title compound were isolated manually in about 5% yield based on copper(II), with combining light blue crystals which have a mononuclear structure (Mo *et al.*, 2004). Caution: tetrazole derivatives are potentially explosive. Although we have met no problems in this work, only a small amount of them should be prepared and handled with great caution.

Refinement

All H atoms were included in calculated positions and treated in the subsequent refinement as riding atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2\ U_{eq}(C, N)$.

Figures

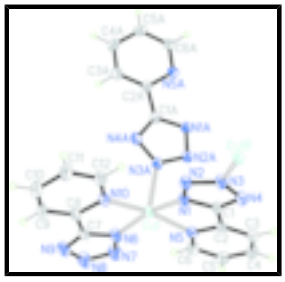

Fig. 1. The molecular structure of the title compound with displacement ellipsoid drawn at the 40% probability level. Symmetry codes: (A) 1/2 + *x*, 3/2 − *y*, 1 − *z*; (B) *x* − 1/2, 3/2 − *y*, 1 − *z*.

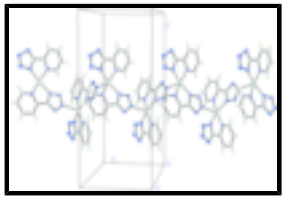

Fig. 2. The polymeric one-dimensional chain structure of the title compound running parallel to the *a* axis. Displacement ellipsoid are drawn at the 40% probability level.

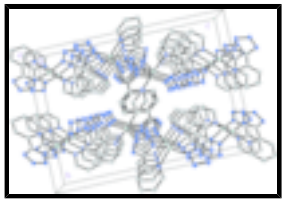

Fig. 3. Packing diagram of the title compound viewed along the *a* axis. Displacement ellipsoid are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

catena-Poly[[[5-(2-pyridyl)tetrazolato-κ^2*N*^{1},*N*^{5}]copper(II)]-μ- 5-(2-pyridyl)tetrazolato-κ^2*N*^{1},*N*^{5}:*N*^{3}]

Crystal data

$[Cu(C_6H_5N_5)_2]$	F_{000} = 1432
M_r = 355.82	D_x = 1.774 Mg m^{-3}
Orthorhombic, *Pbca*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 5746 reflections
a = 8.5905 (9) Å	θ = 2.9–26.3º
b = 14.8361 (16) Å	μ = 1.66 mm^{-1}
c = 20.905 (2) Å	*T* = 294 (2) K
V = 2664.3 (5) Å^3	Block, black
Z = 8	0.30 × 0.28 × 0.28 mm

Data collection

Bruker SMART CCD area-detector diffractometer	2348 independent reflections
Radiation source: fine-focus sealed tube	1951 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.034
T = 294(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 2.0º
Absorption correction: multi-scan (SADABS; Bruker, 1998)	*h* = −10→5

T_{min} = 0.584, T_{max} = 0.630	k = −17→15
12543 measured reflections	l = −24→24

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.025	H-atom parameters constrained
$wR(F^2)$ = 0.066	$w = 1/[\sigma^2(F_o^2) + (0.0285P)^2 + 2.1688P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(\Delta/\sigma)_{max}$ = 0.001
2348 reflections	$\Delta\rho_{max}$ = 0.25 e Å^{-3}
208 parameters	$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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	0.14469 (3)	0.665133 (18)	0.410674 (12)	0.02476 (11)
N1	0.0006 (2)	0.70131 (12)	0.48135 (8)	0.0251 (4)
N2	−0.1087 (2)	0.76313 (13)	0.49385 (9)	0.0283 (5)
N3	−0.1560 (2)	0.74998 (13)	0.55297 (9)	0.0278 (4)
N4	−0.0808 (2)	0.68002 (13)	0.58008 (9)	0.0298 (5)
N5	0.1939 (2)	0.56565 (12)	0.47656 (9)	0.0255 (4)
N6	0.2346 (2)	0.60614 (13)	0.33463 (9)	0.0325 (5)
N7	0.3321 (3)	0.53800 (15)	0.31895 (11)	0.0449 (6)
N8	0.3451 (3)	0.53719 (16)	0.25631 (11)	0.0465 (6)
N9	0.2584 (3)	0.60382 (15)	0.23010 (9)	0.0409 (6)
N10	0.0545 (2)	0.74744 (13)	0.34215 (8)	0.0283 (4)
C1	0.0149 (3)	0.65195 (15)	0.53450 (10)	0.0238 (5)
C2	0.1234 (3)	0.57621 (15)	0.53389 (11)	0.0258 (5)
C3	0.1519 (3)	0.51949 (16)	0.58505 (11)	0.0323 (6)
H3A	0.1013	0.5280	0.6239	0.039*
C4	0.2575 (3)	0.44974 (17)	0.57718 (12)	0.0381 (6)

H4A	0.2803	0.4111	0.6109	0.046*
C5	0.3281 (3)	0.43854 (17)	0.51872 (13)	0.0369 (6)
H5A	0.3986	0.3918	0.5124	0.044*
C6	0.2936 (3)	0.49731 (16)	0.46930 (12)	0.0311 (6)
H6A	0.3413	0.4890	0.4298	0.037*
C7	0.1927 (3)	0.64422 (16)	0.27966 (11)	0.0301 (6)
C8	0.0905 (3)	0.72220 (16)	0.28170 (10)	0.0292 (5)
C9	0.0337 (3)	0.76779 (18)	0.22914 (11)	0.0387 (6)
H9A	0.0582	0.7485	0.1880	0.046*
C10	−0.0593 (3)	0.84200 (18)	0.23832 (12)	0.0410 (6)
H10A	−0.0991	0.8733	0.2034	0.049*
C11	−0.0928 (3)	0.86950 (19)	0.29970 (12)	0.0419 (7)
H11A	−0.1535	0.9204	0.3069	0.050*
C12	−0.0350 (3)	0.82024 (17)	0.35020 (12)	0.0377 (6)
H12A	−0.0592	0.8384	0.3916	0.045*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02785 (17)	0.02881 (17)	0.01762 (16)	0.00286 (12)	0.00096 (12)	−0.00109 (11)
N1	0.0264 (10)	0.0279 (10)	0.0210 (9)	0.0031 (9)	0.0021 (8)	0.0001 (8)
N2	0.0309 (11)	0.0313 (11)	0.0228 (10)	0.0050 (9)	0.0038 (8)	−0.0004 (8)
N3	0.0305 (11)	0.0311 (10)	0.0220 (10)	0.0039 (9)	0.0024 (8)	−0.0012 (8)
N4	0.0326 (11)	0.0351 (11)	0.0217 (10)	0.0017 (9)	0.0011 (9)	−0.0008 (8)
N5	0.0254 (10)	0.0260 (10)	0.0251 (10)	−0.0008 (8)	−0.0009 (8)	−0.0021 (8)
N6	0.0363 (12)	0.0352 (11)	0.0259 (10)	0.0045 (10)	0.0019 (9)	−0.0047 (9)
N7	0.0533 (15)	0.0455 (13)	0.0359 (13)	0.0122 (12)	0.0062 (11)	−0.0072 (10)
N8	0.0541 (15)	0.0503 (14)	0.0352 (13)	0.0064 (12)	0.0087 (11)	−0.0113 (11)
N9	0.0461 (14)	0.0500 (14)	0.0265 (11)	−0.0022 (12)	0.0059 (10)	−0.0100 (10)
N10	0.0316 (11)	0.0346 (11)	0.0187 (9)	−0.0001 (10)	−0.0008 (8)	0.0002 (8)
C1	0.0230 (12)	0.0298 (12)	0.0186 (11)	−0.0030 (10)	−0.0007 (9)	−0.0020 (9)
C2	0.0250 (12)	0.0279 (12)	0.0244 (12)	−0.0036 (10)	−0.0029 (10)	−0.0017 (9)
C3	0.0369 (14)	0.0356 (14)	0.0246 (12)	−0.0007 (12)	−0.0005 (11)	0.0019 (10)
C4	0.0440 (16)	0.0343 (14)	0.0358 (14)	0.0007 (12)	−0.0093 (12)	0.0083 (11)
C5	0.0350 (15)	0.0292 (13)	0.0465 (16)	0.0065 (12)	−0.0070 (12)	0.0008 (11)
C6	0.0279 (13)	0.0323 (13)	0.0330 (13)	0.0024 (11)	0.0009 (11)	−0.0032 (10)
C7	0.0309 (13)	0.0378 (14)	0.0217 (12)	−0.0077 (11)	0.0010 (10)	−0.0056 (10)
C8	0.0280 (13)	0.0389 (14)	0.0208 (12)	−0.0072 (11)	−0.0009 (10)	−0.0005 (10)
C9	0.0432 (16)	0.0538 (16)	0.0191 (12)	−0.0038 (14)	0.0000 (11)	0.0016 (11)
C10	0.0463 (16)	0.0495 (16)	0.0273 (14)	0.0014 (14)	−0.0035 (12)	0.0122 (12)
C11	0.0477 (17)	0.0437 (15)	0.0343 (15)	0.0087 (13)	0.0033 (12)	0.0085 (12)
C12	0.0485 (17)	0.0400 (15)	0.0245 (13)	0.0088 (13)	0.0035 (12)	0.0008 (11)

Geometric parameters (Å, °)

Cu1—N1	2.0005 (18)	N10—C8	1.354 (3)
Cu1—N3^{i}	2.2574 (19)	C1—C2	1.460 (3)
Cu1—N5	2.0625 (19)	C2—C3	1.383 (3)

Cu1—N6	1.9723 (19)	C3—C4	1.386 (4)
Cu1—N10	2.0355 (19)	C3—H3A	0.9300
N1—C1	1.336 (3)	C4—C5	1.375 (4)
N1—N2	1.339 (3)	C4—H4A	0.9300
N2—N3	1.315 (3)	C5—C6	1.384 (3)
N3—N4	1.348 (3)	C5—H5A	0.9300
N3—Cu1^{ii}	2.2574 (19)	C6—H6A	0.9300
N4—C1	1.326 (3)	C7—C8	1.453 (3)
N5—C6	1.336 (3)	C8—C9	1.379 (3)
N5—C2	1.352 (3)	C9—C10	1.374 (4)
N6—C7	1.330 (3)	C9—H9A	0.9300
N6—N7	1.353 (3)	C10—C11	1.377 (4)
N7—N8	1.314 (3)	C10—H10A	0.9300
N8—N9	1.354 (3)	C11—C12	1.377 (4)
N9—C7	1.323 (3)	C11—H11A	0.9300
N10—C12	1.337 (3)	C12—H12A	0.9300
N1—Cu1—N3^{i}	94.06 (7)	N5—C2—C3	122.4 (2)
N1—Cu1—N5	79.95 (7)	N5—C2—C1	112.50 (19)
N1—Cu1—N10	97.09 (8)	C3—C2—C1	125.1 (2)
N5—Cu1—N3^{i}	91.09 (7)	C2—C3—C4	118.6 (2)
N6—Cu1—N1	163.06 (8)	C2—C3—H3A	120.7
N6—Cu1—N3^{i}	102.82 (8)	C4—C3—H3A	120.7
N6—Cu1—N5	98.08 (8)	C5—C4—C3	119.0 (2)
N6—Cu1—N10	81.26 (8)	C5—C4—H4A	120.5
N10—Cu1—N3^{i}	101.01 (7)	C3—C4—H4A	120.5
N10—Cu1—N5	167.75 (8)	C4—C5—C6	119.5 (2)
C1—N1—N2	106.11 (18)	C4—C5—H5A	120.2
C1—N1—Cu1	114.22 (15)	C6—C5—H5A	120.2
N2—N1—Cu1	139.65 (14)	N5—C6—C5	122.1 (2)
N3—N2—N1	107.36 (17)	N5—C6—H6A	119.0
N2—N3—N4	111.19 (17)	C5—C6—H6A	119.0
N2—N3—Cu1^{ii}	117.88 (14)	N9—C7—N6	111.6 (2)
N4—N3—Cu1^{ii}	130.67 (14)	N9—C7—C8	129.9 (2)
C1—N4—N3	103.71 (18)	N6—C7—C8	118.5 (2)
C6—N5—C2	118.4 (2)	N10—C8—C9	121.8 (2)
C6—N5—Cu1	126.76 (16)	N10—C8—C7	112.7 (2)
C2—N5—Cu1	114.68 (15)	C9—C8—C7	125.5 (2)
C7—N6—N7	106.01 (19)	C10—C9—C8	119.2 (2)
C7—N6—Cu1	113.68 (16)	C10—C9—H9A	120.4
N7—N6—Cu1	140.28 (16)	C8—C9—H9A	120.4
N8—N7—N6	107.5 (2)	C9—C10—C11	119.3 (2)
N7—N8—N9	110.5 (2)	C9—C10—H10A	120.3
C7—N9—N8	104.4 (2)	C11—C10—H10A	120.3
C12—N10—C8	118.2 (2)	C12—C11—C10	118.8 (3)
C12—N10—Cu1	127.96 (15)	C12—C11—H11A	120.6
C8—N10—Cu1	113.84 (16)	C10—C11—H11A	120.6
N4—C1—N1	111.6 (2)	N10—C12—C11	122.7 (2)

N4—C1—C2	130.1 (2)	N10—C12—H12A	118.7
N1—C1—C2	118.24 (19)	C11—C12—H12A	118.7

Symmetry codes: (i) *x*+1/2, −*y*+3/2, −*z*+1; (ii) *x*−1/2, −*y*+3/2, −*z*+1.

Fig. 1

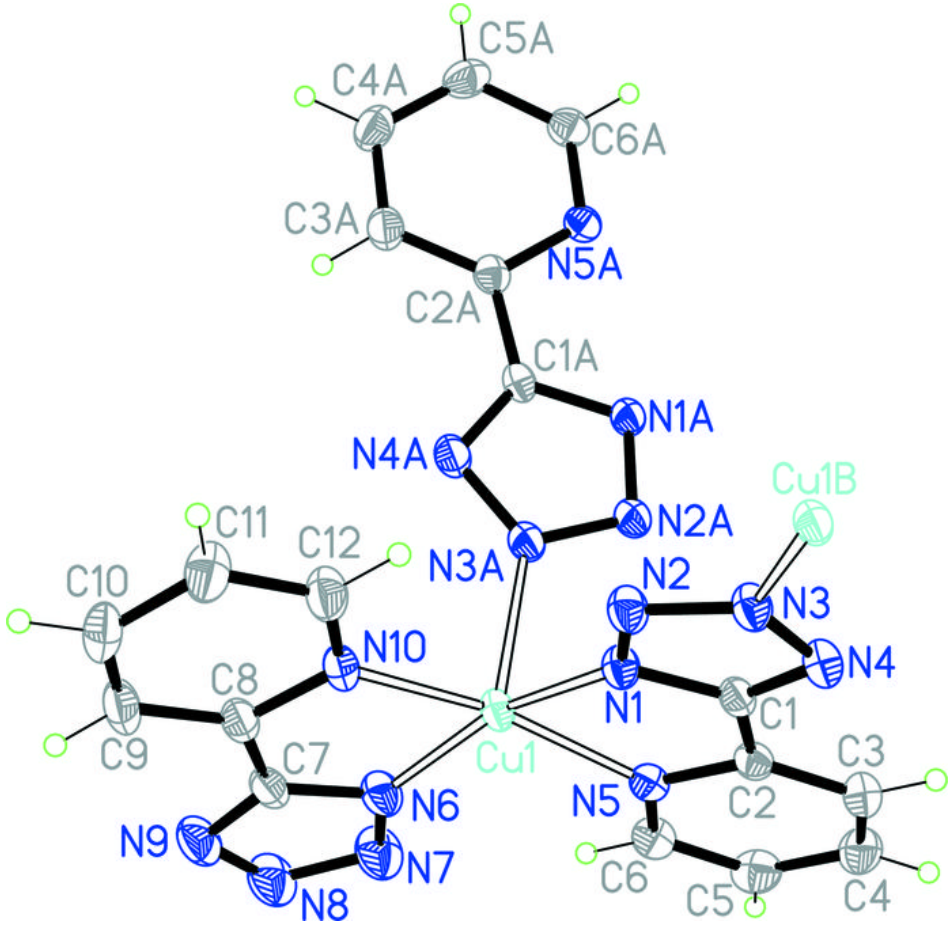
C5A
C4A
C6A
C3A
N5A
C2A
C1A
N1A
N4A
Cu1B
N2A
C11
C12
N3A
N2
N3
C10
N10
N4
C8
N1
C1
C9
C7
Cu1
C3
N6
N5
C2
N9
N7
C6
C5
C4
N8

Fig. 2

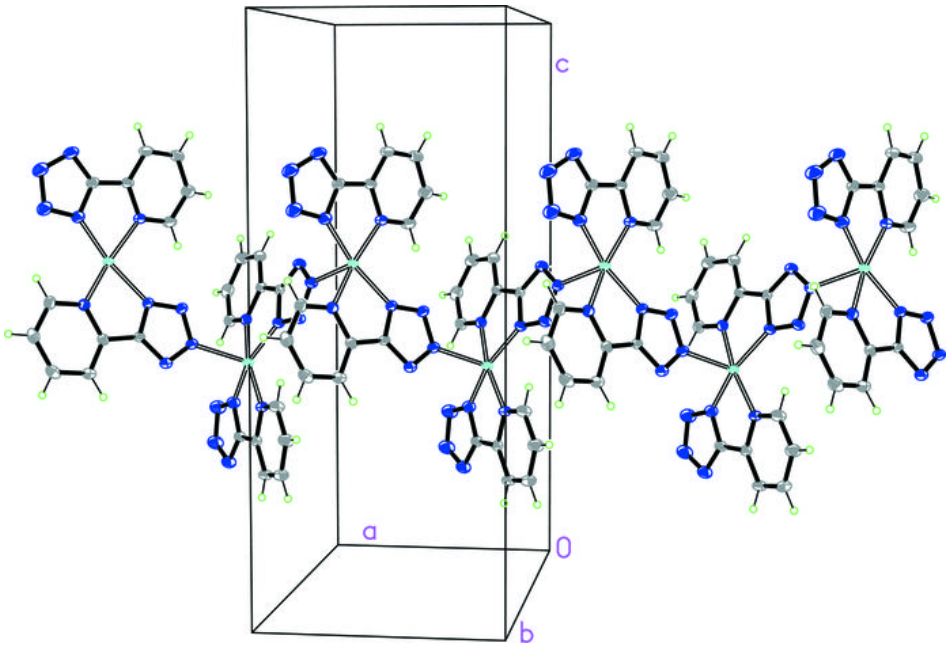

Fig. 3