Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis[μ-5-(pyrazin-2-yl)tetrazol-1-ido]-bis[azido(2,2′-bipyridine)copper(II)]

Yan-Jun Zhang, Xin Fang, Ming-Lei Cao, Hai-Yang Yu and Jun-Dong Wang*

Department of Chemistry, University of Fuzhou, Fuzhou 350002, People's Republic of China, and State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou 350002, People's Republic of China
Correspondence e-mail: wangjd@fzu.edu.cn

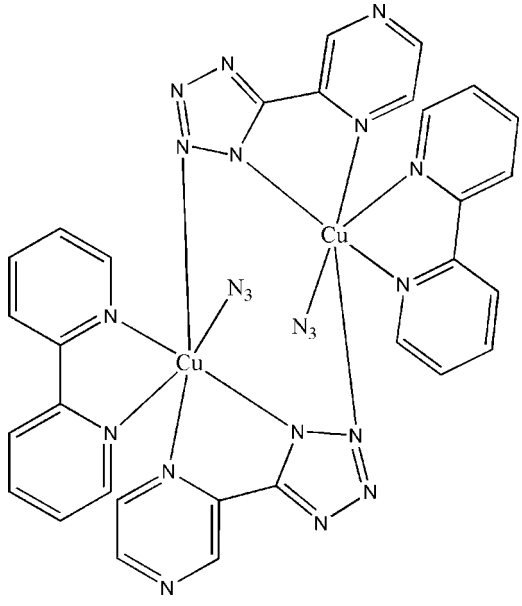
Received 15 September 2007; accepted 23 September 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.006 Å; R factor = 0.062; wR factor = 0.174; data-to-parameter ratio = 14.7.

The title compound, $[Cu_2(C_5H_3N_6)_2(N_3)_2(C_{10}H_8N_2)_2]$, consists of isolated neutral centrosymmetric dinuclear units. Each molecule comprises two Cu atoms, two 2-tzpz$^-$ ligands [2-Htzpz = 2-(1*H*-tetrazol-5-yl)pyrazine], two 2,2′-bipyridine (bpy) ligands and two azide groups. The 2-tzpz$^-$ ligand is tridentate, utilizing N atoms from the tetrazole and pyrazine rings to chelate to one Cu^{2+} ion and a second tetrazole N atom to form a bridge to the second Cu^{2+} ion. The coordination geometry about each Cu^{2+} center is slightly distorted octahedral. The crystal packing is stabilized by intermolecular C—H···N hydrogen bonds.

Related literature

For related literature, see: Demko & Sharpless (2001); Rodriguez-Dieguez *et al.* (2007).



Experimental

Crystal data

$[Cu_2(C_5H_3N_6)_2(N_3)_2(C_{10}H_8N_2)_2]$
M_r = 817.78
Triclinic, $P\overline{1}$
a = 8.189 (2) Å
b = 10.252 (2) Å
c = 11.380 (2) Å
α = 107.629 (2)°
β = 102.061 (2)°
γ = 108.185 (4)°
V = 815.0 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.37 mm^{-1}
T = 298 (2) K
0.1 × 0.1 × 0.1 mm

Data collection

Rigaku R-AXIS SPIDER CCD diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.792, T_{max} = 0.825
(expected range = 0.838–0.872)
7984 measured reflections
3724 independent reflections
3001 reflections with $I > 2\sigma(I)$
R_{int} = 0.084

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.174
S = 1.08
3724 reflections
254 parameters
Only H-atom displacement parameters refined
$\Delta\rho_{max}$ = 1.44 e Å^{-3}
$\Delta\rho_{min}$ = −1.23 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···N11^{i}	0.93	2.54	3.413 (5)	157
C7—H7···N5^{i}	0.93	2.52	3.450 (4)	174

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

Data collection: *RAPID-AUTO* (Rigaku, 2004); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX5* (McArdle, 1996); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Foundations of Fujian Province (No. 2006 F5058) and Fuzhou University (No. XRC-0527).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2359).

References

Demko, Z. P. & Sharpless, B. K. (2001). *J. Org. Chem.* **66**, 7945–7950.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
McArdle, P. (1996). *ORTEX5*. UCG Crystallography Centre, University College Galway, Ireland.
Rigaku (2004). *RAPID-AUTO*. Version 3.0. Rigaku Corporation, Tokyo, Japan.
Rodriguez-Dieguez, A., Cano, J., Kivekas, R., Debdoubi, A. & Colacio, E. (2007). *Inorg. Chem.* **46**, 2503–2510.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

  doi:10.1107/S1600536807046764

supplementary materials

Acta Cryst. (2007). E**63**, m2630 [**doi:10.1107/S1600536807046764**]

Bis[μ-5-(pyrazin-2-yl)tetrazol-1-ido]bis[azido(2,2'-bipyridine)copper(II)]

Y.-J. Zhang, X. Fang, M.-L. Cao, H.-Y. Yu and J.-D. Wang

Comment

Considerable attention has been paid to the tetrazoles complex in recent years not only because of their structural and topological novelty but also because of their potential applications as molecular-based functional materials in fields such as electrical conductivity, molecular magnetism, molecular absorption, catalysis and optical materials (Demko & Sharpless, 2001; Rodriguez-Dieguez *et al.*, 2007).

The structure of the title tetrazole complex consists of isolated neutral dinuclear units (Fig. 1). The dinuclear unit lies about a center of symmetry and is constructed from two Cu atoms, two 5-pztz$^-$ ligands, two bpy ligands and two N_3^- groups. In the compound, two Cu atoms are bridged through 2-N atoms of the tetrazolide, and the 5-pztz$^-$ ligand acts as a tridentate ligand by utilizing its two nitrogen atoms from the tetrazole rings and one nitrogen atom from pyrazine rings to chelate with one Cu^{2+} ion and bridge another Cu^{2+} ion. The Cu^{2+} center is bonded to six nitrogen atoms forming a slightly distorted octahedron, with atoms N1, N4^i, N3 and N7 occupying equatorial positions and N2 and N9 in the axial positions. In the crystal structure of (I), the crystal packing is stabilized by intermolecular C—H···N bonds, Table 1.

Experimental

A mixture of $CuCl_2$ (0.3 mmol), NaN_3 (0.5 mmol), pyrazine-2-carbonitrile (0.3 mmol), 2,2-bipyridine (0.3 mmol) in 3 ml H_2O was heated in a 20 ml Teflon-lined reaction vessel at 130°C for two days. After slowly cooling to room temperature over a period of 12 h, blue block-like crystals of (I) were isolated.

Refinement

All H atoms were located at calculated positions with d(C—H) = 0.93Å and the isotropic displacement parameters refined.

Figures

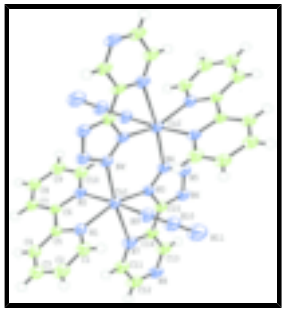


Fig. 1. The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms. Labelled atoms are related to unlabelled atoms by the symmetry operation (i) = $-x$,$-y$ + 1, $-z$

Bis[μ-5-(pyrazin-2-yl)tetrazol-1-*ido*]bis[azido(2,2'-bipyridine)copper(II)]

Crystal data

$[Cu_2(C_5H_3N_6)_2(N_3)_2(C_{10}H_8N_2)_2]$	$Z = 1$
$M_r = 817.78$	$F_{000} = 414$
Triclinic, $P\overline{1}$	$D_x = 1.666$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
$a = 8.189$ (2) Å	Cell parameters from 4727 reflections
$b = 10.252$ (2) Å	$\theta = 6.8$–55.1º
$c = 11.380$ (2) Å	$\mu = 1.37$ mm^{-1}
$\alpha = 107.629$ (2)º	$T = 298$ (2) K
$\beta = 102.061$ (2)º	Block, blue
$\gamma = 108.185$ (4)º	0.1 × 0.1 × 0.1 mm
$V = 815.0$ (3) Å^3	

Data collection

Rigaku R-AXIS SPIDER CCD diffractometer	3724 independent reflections
Radiation source: Rotating Anode	3001 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.084$
$T = 173$(2) K	$\theta_{max} = 27.5$º
ω oscillation scans	$\theta_{min} = 3.4$º
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$h = -10 \rightarrow 10$
$T_{min} = 0.792$, $T_{max} = 0.825$	$k = -13 \rightarrow 12$
7984 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.062$	Only H-atom displacement parameters refined
$wR(F^2) = 0.174$	$w = 1/[\sigma^2(F_o^2) + (0.0895P)^2 +]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.009$
3724 reflections	$\Delta\rho_{max} = 1.44$ e Å^{-3}
254 parameters	$\Delta\rho_{min} = -1.22$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. collimator diameter: 0.800000 mm

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	0.00291 (5)	0.39768 (4)	0.13246 (3)	0.02186 (19)
N1	−0.0628 (4)	0.2191 (3)	0.1846 (3)	0.0228 (6)
N2	0.1729 (4)	0.3079 (3)	0.0730 (2)	0.0205 (6)
N3	0.1679 (4)	0.6080 (3)	0.1614 (2)	0.0195 (6)
N4	0.1678 (4)	0.6840 (3)	0.0839 (3)	0.0213 (6)
N5	0.2890 (4)	0.8210 (3)	0.1493 (3)	0.0249 (6)
N6	0.3733 (4)	0.8393 (3)	0.2721 (3)	0.0266 (6)
N7	0.2331 (4)	0.5307 (4)	0.3744 (3)	0.0275 (7)
N8	0.5066 (5)	0.7371 (4)	0.6118 (3)	0.0321 (7)
N9	−0.1772 (4)	0.4647 (3)	0.1932 (3)	0.0262 (6)
N10	−0.1322 (5)	0.5859 (4)	0.2741 (3)	0.0311 (7)
N11	−0.0945 (7)	0.7022 (4)	0.3530 (4)	0.0528 (11)
C1	−0.1837 (5)	0.1860 (4)	0.2440 (3)	0.0272 (7)
H1	−0.2643	0.2329	0.2465	0.037 (11)*
C2	−0.1948 (6)	0.0842 (4)	0.3025 (3)	0.0313 (8)
H2	−0.2823	0.0618	0.3421	0.038*
C3	−0.0718 (6)	0.0168 (4)	0.3001 (3)	0.0308 (8)
H3	−0.0747	−0.0511	0.3392	0.035 (11)*
C4	0.0549 (5)	0.0516 (4)	0.2391 (3)	0.0251 (7)
H4	0.1388	0.0080	0.2371	0.027 (10)*
C5	0.0553 (5)	0.1530 (4)	0.1807 (3)	0.0222 (7)
C6	0.1808 (5)	0.1949 (4)	0.1098 (3)	0.0208 (7)
C7	0.2976 (5)	0.1272 (4)	0.0789 (3)	0.0248 (7)
H7	0.3023	0.0498	0.1041	0.029 (10)*
C8	0.4063 (5)	0.1762 (4)	0.0106 (3)	0.0263 (7)
H8	0.4884	0.1345	−0.0083	0.028 (10)*
C9	0.3925 (5)	0.2887 (4)	−0.0301 (3)	0.0284 (8)
H9	0.4615	0.3207	−0.0791	0.034 (11)*
C10	0.2753 (5)	0.3506 (4)	0.0035 (3)	0.0269 (8)
H10	0.2663	0.4261	−0.0232	0.021 (9)*
C11	0.2686 (5)	0.4979 (4)	0.4791 (3)	0.0278 (8)

H11	0.2002	0.4032	0.4731	0.018 (9)*
C12	0.4035 (5)	0.5997 (4)	0.5964 (3)	0.0301 (8)
H12	0.4228	0.5714	0.6667	0.032 (11)*
C13	0.4728 (6)	0.7708 (4)	0.5076 (3)	0.0322 (8)
H13	0.5422	0.8653	0.5139	0.034 (11)*
C14	0.3375 (5)	0.6694 (4)	0.3902 (3)	0.0235 (7)
C15	0.2952 (5)	0.7063 (4)	0.2756 (3)	0.0213 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0287 (3)	0.0187 (3)	0.0221 (3)	0.0138 (2)	0.0091 (2)	0.0085 (2)
N1	0.0297 (16)	0.0177 (14)	0.0205 (12)	0.0119 (12)	0.0073 (11)	0.0052 (11)
N2	0.0255 (15)	0.0211 (14)	0.0162 (11)	0.0132 (12)	0.0057 (11)	0.0059 (11)
N3	0.0286 (15)	0.0178 (13)	0.0167 (11)	0.0133 (12)	0.0089 (11)	0.0078 (11)
N4	0.0314 (16)	0.0177 (14)	0.0186 (12)	0.0155 (12)	0.0090 (11)	0.0060 (11)
N5	0.0333 (17)	0.0208 (15)	0.0224 (13)	0.0147 (13)	0.0081 (12)	0.0076 (12)
N6	0.0337 (17)	0.0212 (15)	0.0224 (13)	0.0119 (13)	0.0059 (12)	0.0069 (12)
N7	0.0336 (18)	0.0262 (16)	0.0230 (13)	0.0136 (13)	0.0074 (12)	0.0097 (13)
N8	0.0399 (19)	0.0312 (17)	0.0197 (13)	0.0133 (15)	0.0046 (13)	0.0078 (13)
N9	0.0315 (17)	0.0242 (16)	0.0275 (14)	0.0147 (13)	0.0134 (12)	0.0101 (13)
N10	0.050 (2)	0.0293 (18)	0.0293 (15)	0.0242 (15)	0.0215 (14)	0.0172 (15)
N11	0.094 (4)	0.037 (2)	0.0405 (18)	0.036 (2)	0.035 (2)	0.0137 (18)
C1	0.032 (2)	0.0245 (18)	0.0263 (15)	0.0150 (15)	0.0102 (14)	0.0079 (14)
C2	0.041 (2)	0.032 (2)	0.0262 (16)	0.0176 (17)	0.0165 (15)	0.0112 (16)
C3	0.043 (2)	0.0269 (19)	0.0274 (16)	0.0185 (17)	0.0107 (15)	0.0141 (15)
C4	0.0315 (19)	0.0214 (17)	0.0240 (15)	0.0146 (15)	0.0067 (14)	0.0086 (14)
C5	0.0292 (18)	0.0173 (16)	0.0170 (13)	0.0121 (14)	0.0051 (12)	0.0018 (13)
C6	0.0289 (18)	0.0179 (15)	0.0141 (12)	0.0128 (13)	0.0044 (12)	0.0030 (12)
C7	0.0321 (19)	0.0208 (17)	0.0188 (14)	0.0141 (14)	0.0031 (13)	0.0048 (13)
C8	0.0300 (19)	0.0259 (18)	0.0250 (15)	0.0163 (15)	0.0098 (14)	0.0070 (14)
C9	0.036 (2)	0.0289 (19)	0.0239 (15)	0.0154 (16)	0.0124 (14)	0.0117 (15)
C10	0.038 (2)	0.0248 (17)	0.0258 (15)	0.0186 (16)	0.0109 (14)	0.0133 (15)
C11	0.037 (2)	0.0272 (19)	0.0251 (16)	0.0166 (16)	0.0117 (15)	0.0139 (15)
C12	0.036 (2)	0.036 (2)	0.0228 (15)	0.0215 (17)	0.0102 (14)	0.0115 (16)
C13	0.037 (2)	0.030 (2)	0.0225 (16)	0.0113 (16)	0.0033 (15)	0.0085 (15)
C14	0.0305 (19)	0.0244 (17)	0.0162 (13)	0.0157 (15)	0.0066 (13)	0.0048 (13)
C15	0.0272 (18)	0.0179 (16)	0.0199 (14)	0.0121 (14)	0.0070 (13)	0.0065 (13)

Geometric parameters (Å, °)

Cu1—N9	1.974 (3)	C1—H1	0.9300
Cu1—N2	2.014 (3)	C2—C3	1.388 (5)
Cu1—N3	2.037 (3)	C2—H2	0.9300
Cu1—N1	2.043 (3)	C3—C4	1.380 (5)
Cu1—N4^{i}	2.302 (3)	C3—H3	0.9300
N1—C1	1.327 (5)	C4—C5	1.392 (5)
N1—C5	1.344 (4)	C4—H4	0.9300

N2—C10	1.333 (5)	C5—C6	1.474 (5)
N2—C6	1.360 (4)	C6—C7	1.389 (5)
N3—C15	1.333 (4)	C7—C8	1.378 (5)
N3—N4	1.343 (4)	C7—H7	0.9300
N4—N5	1.304 (4)	C8—C9	1.393 (5)
N4—Cu1^{i}	2.302 (3)	C8—H8	0.9300
N5—N6	1.350 (4)	C9—C10	1.363 (5)
N6—C15	1.329 (5)	C9—H9	0.9300
N7—C11	1.333 (4)	C10—H10	0.9300
N7—C14	1.344 (5)	C11—C12	1.383 (5)
N8—C13	1.331 (4)	C11—H11	0.9300
N8—C12	1.333 (5)	C12—H12	0.9300
N9—N10	1.186 (4)	C13—C14	1.384 (5)
N10—N11	1.153 (5)	C13—H13	0.9300
C1—C2	1.388 (5)	C14—C15	1.468 (4)
N9—Cu1—N2	173.54 (12)	C3—C4—C5	119.0 (3)
N9—Cu1—N3	92.79 (12)	C3—C4—H4	120.5
N2—Cu1—N3	93.43 (12)	C5—C4—H4	120.5
N9—Cu1—N1	93.71 (12)	N1—C5—C4	121.3 (3)
N2—Cu1—N1	79.96 (12)	N1—C5—C6	115.0 (3)
N3—Cu1—N1	152.23 (11)	C4—C5—C6	123.6 (3)
N9—Cu1—N4^{i}	92.15 (11)	N2—C6—C7	120.7 (3)
N2—Cu1—N4^{i}	88.60 (10)	N2—C6—C5	114.3 (3)
N3—Cu1—N4^{i}	98.96 (10)	C7—C6—C5	125.0 (3)
N1—Cu1—N4^{i}	107.74 (10)	C8—C7—C6	119.1 (3)
C1—N1—C5	119.4 (3)	C8—C7—H7	120.5
C1—N1—Cu1	125.3 (2)	C6—C7—H7	120.5
C5—N1—Cu1	113.7 (2)	C7—C8—C9	119.5 (3)
C10—N2—C6	119.2 (3)	C7—C8—H8	120.2
C10—N2—Cu1	125.7 (2)	C9—C8—H8	120.2
C6—N2—Cu1	115.1 (2)	C10—C9—C8	118.4 (3)
C15—N3—N4	104.9 (3)	C10—C9—H9	120.8
C15—N3—Cu1	123.4 (2)	C8—C9—H9	120.8
N4—N3—Cu1	131.4 (2)	N2—C10—C9	123.0 (3)
N5—N4—N3	109.3 (2)	N2—C10—H10	118.5
N5—N4—Cu1^{i}	121.3 (2)	C9—C10—H10	118.5
N3—N4—Cu1^{i}	129.3 (2)	N7—C11—C12	122.3 (4)
N4—N5—N6	109.7 (3)	N7—C11—H11	118.8
C15—N6—N5	104.4 (3)	C12—C11—H11	118.8
C11—N7—C14	115.6 (3)	N8—C12—C11	122.0 (3)
C13—N8—C12	116.2 (3)	N8—C12—H12	119.0
N10—N9—Cu1	121.3 (3)	C11—C12—H12	119.0
N11—N10—N9	177.6 (5)	N8—C13—C14	122.0 (4)
N1—C1—C2	122.7 (3)	N8—C13—H13	119.0
N1—C1—H1	118.7	C14—C13—H13	119.0
C2—C1—H1	118.7	N7—C14—C13	121.9 (3)
C1—C2—C3	118.2 (4)	N7—C14—C15	115.4 (3)

C1—C2—H2	120.9	C13—C14—C15	122.6 (3)
C3—C2—H2	120.9	N6—C15—N3	111.7 (3)
C4—C3—C2	119.4 (3)	N6—C15—C14	125.5 (3)
C4—C3—H3	120.3	N3—C15—C14	122.8 (3)
C2—C3—H3	120.3		

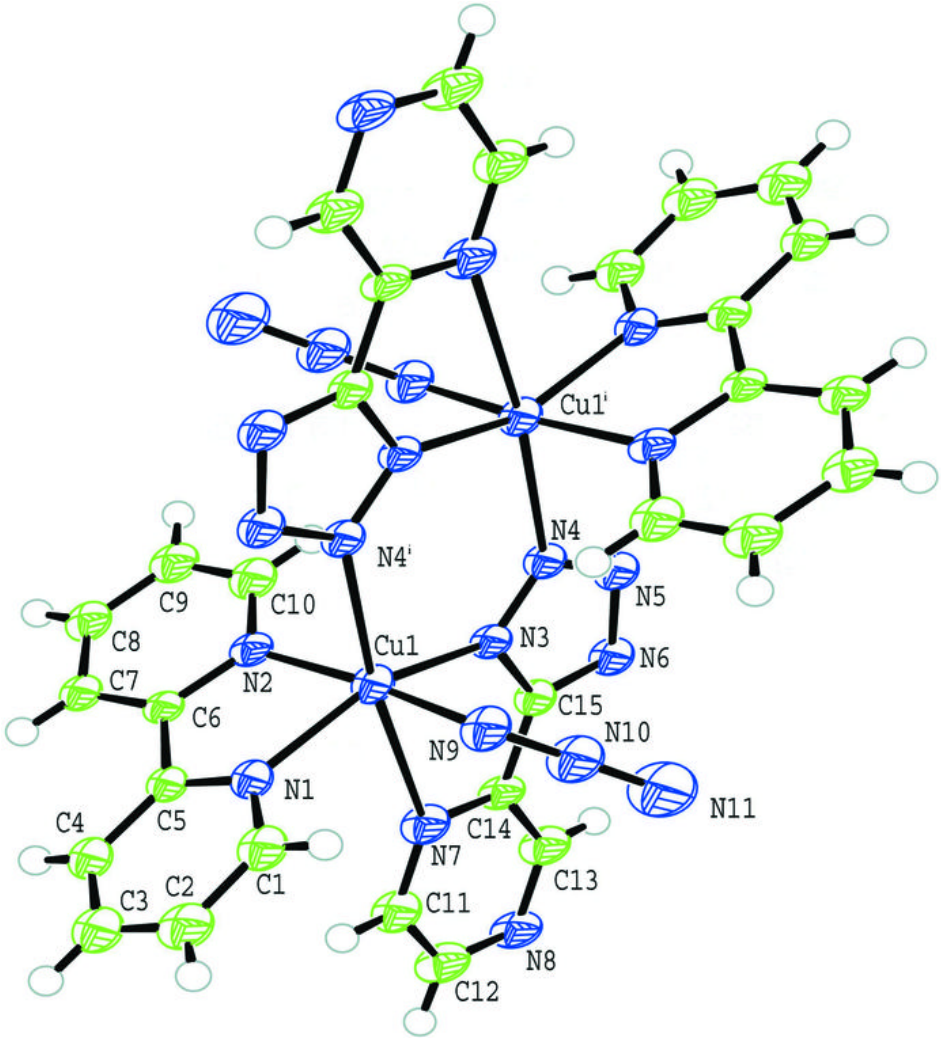
Symmetry codes: (i) −*x*, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···N11^{ii}	0.93	2.54	3.413 (5)	157
C7—H7···N5^{ii}	0.93	2.52	3.450 (4)	174

Symmetry codes: (ii) *x*, *y*−1, *z*.

Fig. 1


Cu1i
N4
N4i
N5
C9
C10
C8
Cu1
N3
N6
C7
N2
C15
C6
N10
N9
N1
N11
C4
C5
C14
N7
C13
C2
C1
C3
C11
N8
C12