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Bis[3-ethyl-4-(4-methylphenyl)-5-(2-pyridyl)-4*H*-1,2,4-triazole-κ^2N,N']-copper(II) bis(perchlorate)

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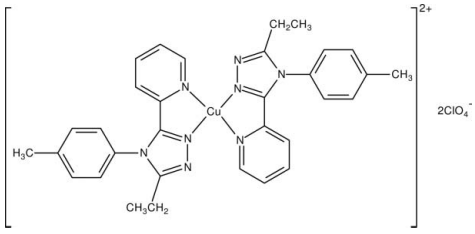
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.006 Å; R factor = 0.058; wR factor = 0.127; data-to-parameter ratio = 14.1.

In the title compound, $[Cu(C_{16}H_{16}N_4)_2](ClO_4)_2$, the Cu^{II} atom lies on an inversion centre and has a distorted square-planar geometry. In each ligand, the dihedral angle between the triazole and pyridine rings is 9.1 (3)°, and that between the triazole and benzene rings is 85.01 (14)°.

Related literature

For related literature, see: Bencini *et al.* (1987); Garcia *et al.* (1997); Kahn & Martinez (1998); Klingele & Brooker (2003); Klingele *et al.* (2005); Koningsbruggen (2004); Koningsbruggen *et al.* (1995); Lavrenova & Larionov (1998); Matouzenko *et al.* (2004); Moliner *et al.* (1998, 2001).



Experimental

Crystal data

$[Cu(C_{16}H_{16}N_4)_2](ClO_4)_2$
M_r = 791.10
Triclinic, $P\overline{1}$
a = 8.0113 (14) Å
b = 8.3126 (14) Å
c = 14.215 (3) Å
α = 99.374 (3)°
β = 102.689 (3)°
γ = 107.041 (2)°
V = 856.4 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.86 mm^{-1}
T = 291 (2) K
0.26 × 0.20 × 0.18 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.808, T_{max} = 0.861
4686 measured reflections
3294 independent reflections
2297 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.127
S = 1.03
3294 reflections
234 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.82 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.982 (3)	Cu1—N1	2.043 (3)
N2—Cu1—N1	80.82 (12)		

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: CF2155).

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supplementary materials

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Bis[3-ethyl-4-(4-methylphenyl)-5-(2-pyridyl)-4*H*-1,2,4-triazole-κ^2N,N']copper(II) bis(perchlorate)

P. Wu, Z. Wang, B. Zhou and L. Huang

Comment

The coordination chemistry of 1,2,4-triazole derivatives has attracted great attention in recent years (Bencini *et al.*, 1987; Koningsbruggen *et al.*, 1995; Moliner *et al.*, 1998; Moliner *et al.*, 2001; Klingele & Brooker 2003; Klingele *et al.*, 2005). Some spin-crossover complexes of 1,2,4-triazoles with iron(II) salts have been reported, which could be used as molecular-based memory devices, displays and optical switches (Garcia *et al.*, 1997; Lavrenova & Larionov, 1998; Kahn & Martinez, 1998; Koningsbruggen, 2004; Matouzenko *et al.*, 2004). We report here the crystal structure analysis of the title compound, (I).

The structure of (I) is shown in Fig.1. In the crystal structure, the Cu^{II} atom lies on an inversion centre and is coordinated by two 3-ethyl-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole ligands in a distorted square-planar geometry. In each ligand, the dihedral angle between the triazole and pyridine rings is 9.1 (3)°, and that between the triazole and benzene rings is 85.01 (14)°.

Experimental

The title compound was prepared by reaction of 3-ethyl-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole with copper(II) perchlorate in acetonitrile and water. To a warm solution of 1.06 grams of 3-ethyl-4-(*p*-methylphenyl)-5-(2-pyridyl)-1,2,4-triazole (4.0 mmol) in 20 ml acetonitrile-water (V/V = 1:1), 0.52 grams of copper(II) perchlorate (2.0 mmol) was added. The filtrate was left to stand at room temperature for several days, and single crystals suitable for X-ray diffraction were collected.

Refinement

All H atoms were located in a difference Fourier map and allowed to ride on their parent atoms at distances of 0.93Å (aromatic), 0.96Å (methyl) and 0.97Å (methylene), and with U_{iso}(H) values of 1.2 or 1.5 times U_{eq}(C).

Figures

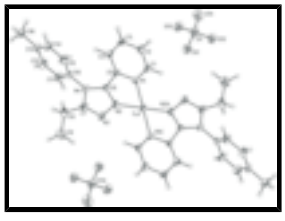


Fig. 1. The molecular structure of the title compound with the atomic labelling. Displacement ellipsoids are shown at the 30% probability level.

Bis[3-ethyl-4-(4-methylphenyl)-5-(2-pyridyl)-4*H*-1,2,4-triazole-\ κ^2*N*,*N*']copper(II) bis(perchlorate)

Crystal data

$[Cu(C_{16}H_{16}N_4)_2](ClO_4)_2$	$Z = 1$
$M_r = 791.10$	$F_{000} = 407$
Triclinic, $P\overline{1}$	$D_x = 1.534$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 8.0113$ (14) Å	Cell parameters from 1954 reflections
$b = 8.3126$ (14) Å	$\theta = 2.6$–25.9º
$c = 14.215$ (3) Å	$\mu = 0.86$ mm^{-1}
$\alpha = 99.374$ (3)º	$T = 291$ (2) K
$\beta = 102.689$ (3)º	Block, blue
$\gamma = 107.041$ (2)º	0.26 × 0.20 × 0.18 mm
$V = 856.4$ (3) Å^3	

Data collection

Bruker SMART APEX CCD diffractometer	3294 independent reflections
Radiation source: sealed tube	2297 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.031$
$T = 291(2)$ K	$\theta_{max} = 26.0$º
φ and ω scans	$\theta_{min} = 2.6$º
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$h = -9 \rightarrow 9$
$T_{min} = 0.808$, $T_{max} = 0.861$	$k = -10 \rightarrow 4$
4686 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.058$	H-atom parameters constrained
$wR(F^2) = 0.127$	$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
3294 reflections	$\Delta\rho_{max} = 0.82$ e Å^{-3}
234 parameters	$\Delta\rho_{min} = -0.47$ e Å^{-3}
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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}
C1	0.2672 (5)	0.8169 (5)	0.4734 (3)	0.0436 (8)
H1	0.2871	0.8753	0.4242	0.052*
C2	0.3614 (5)	0.7036 (5)	0.4944 (3)	0.0464 (9)
H2	0.4479	0.6920	0.4620	0.056*
C3	0.3255 (6)	0.6094 (5)	0.5632 (3)	0.0517 (10)
H3	0.3800	0.5269	0.5741	0.062*
C4	0.2066 (5)	0.6394 (5)	0.6158 (3)	0.0439 (8)
H4	0.1849	0.5829	0.6655	0.053*
C5	0.1218 (4)	0.7550 (4)	0.5924 (2)	0.0346 (7)
C6	−0.0067 (5)	0.8021 (4)	0.6396 (2)	0.0331 (7)
C7	−0.1790 (6)	0.8482 (5)	0.7319 (3)	0.0514 (9)
C8	−0.2685 (6)	0.8364 (6)	0.8112 (3)	0.0594 (11)
H8A	−0.1771	0.8451	0.8711	0.071*
H8B	−0.3578	0.7206	0.7938	0.071*
C9	−0.3609 (7)	0.9592 (7)	0.8374 (4)	0.0722 (14)
H9A	−0.3116	1.0153	0.9070	0.108*
H9B	−0.4889	0.8975	0.8232	0.108*
H9C	−0.3425	1.0448	0.7993	0.108*
C10	0.0172 (5)	0.6772 (5)	0.7884 (2)	0.0405 (7)
C11	0.1746 (6)	0.7618 (6)	0.8615 (3)	0.0551 (10)
H11	0.2371	0.8783	0.8674	0.066*
C12	0.2433 (6)	0.6748 (6)	0.9279 (3)	0.0574 (11)
H12	0.3485	0.7346	0.9800	0.069*
C13	0.1561 (6)	0.5013 (5)	0.9166 (3)	0.0473 (9)
C14	0.0003 (6)	0.4204 (6)	0.8422 (3)	0.0560 (10)
H14	−0.0582	0.3025	0.8342	0.067*
C15	−0.0762 (6)	0.5021 (5)	0.7780 (3)	0.0563 (11)
H15	−0.1862	0.4431	0.7293	0.068*
C16	0.2347 (6)	0.4050 (6)	0.9865 (4)	0.0607 (11)
H16A	0.3107	0.3535	0.9581	0.091*
H16B	0.1373	0.3158	0.9965	0.091*
H16C	0.3057	0.4848	1.0492	0.091*
Cl1	−0.35945 (13)	0.75087 (13)	0.28048 (7)	0.0529 (3)

Cu1	0.0000	1.0000	0.5000	0.03407 (19)
N1	0.1517 (4)	0.8428 (4)	0.5214 (2)	0.0366 (6)
N2	−0.0939 (4)	0.8995 (4)	0.6031 (2)	0.0387 (6)
N3	−0.2055 (5)	0.9288 (5)	0.6598 (2)	0.0503 (8)
N4	−0.0578 (4)	0.7672 (4)	0.7204 (2)	0.0428 (7)
O11	−0.4876 (4)	0.8173 (4)	0.3132 (2)	0.0591 (8)
O12	−0.2782 (4)	0.8561 (4)	0.2241 (2)	0.0564 (7)
O13	−0.2264 (4)	0.7560 (4)	0.3667 (2)	0.0594 (8)
O14	−0.4462 (4)	0.5766 (4)	0.2267 (2)	0.0740 (10)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.058 (2)	0.050 (2)	0.0445 (19)	0.0306 (18)	0.0273 (18)	0.0285 (17)
C2	0.055 (2)	0.057 (2)	0.050 (2)	0.0327 (19)	0.0264 (17)	0.0321 (18)
C3	0.066 (3)	0.060 (2)	0.060 (2)	0.046 (2)	0.029 (2)	0.036 (2)
C4	0.0469 (19)	0.047 (2)	0.055 (2)	0.0257 (17)	0.0234 (17)	0.0300 (18)
C5	0.0441 (17)	0.0351 (17)	0.0335 (15)	0.0162 (15)	0.0167 (14)	0.0193 (14)
C6	0.0402 (15)	0.0269 (15)	0.0345 (16)	0.0145 (13)	0.0089 (13)	0.0101 (12)
C7	0.066 (2)	0.054 (2)	0.061 (2)	0.034 (2)	0.037 (2)	0.0349 (19)
C8	0.060 (2)	0.073 (3)	0.049 (2)	0.017 (2)	0.026 (2)	0.024 (2)
C9	0.075 (3)	0.074 (3)	0.069 (3)	0.021 (3)	0.033 (3)	0.015 (3)
C10	0.0628 (18)	0.0398 (18)	0.0293 (14)	0.0239 (16)	0.0186 (12)	0.0169 (13)
C11	0.059 (2)	0.050 (2)	0.056 (2)	0.0147 (18)	0.0140 (14)	0.0198 (18)
C12	0.058 (2)	0.067 (3)	0.052 (2)	0.026 (2)	0.0083 (19)	0.029 (2)
C13	0.060 (2)	0.055 (2)	0.0360 (18)	0.0219 (19)	0.0214 (17)	0.0206 (17)
C14	0.066 (2)	0.051 (2)	0.057 (2)	0.024 (2)	0.012 (2)	0.028 (2)
C15	0.066 (2)	0.041 (2)	0.056 (2)	0.0145 (19)	0.0016 (19)	0.0248 (19)
C16	0.068 (3)	0.058 (3)	0.071 (3)	0.032 (2)	0.024 (2)	0.031 (2)
Cl1	0.0524 (5)	0.0504 (6)	0.0511 (5)	0.0100 (4)	0.0129 (4)	0.0157 (4)
Cu1	0.0445 (3)	0.0388 (3)	0.0348 (3)	0.0229 (3)	0.0183 (2)	0.0261 (3)
N1	0.0407 (15)	0.0344 (14)	0.0394 (15)	0.0156 (13)	0.0090 (12)	0.0198 (12)
N2	0.0468 (15)	0.0495 (18)	0.0299 (13)	0.0191 (13)	0.0173 (12)	0.0234 (12)
N3	0.065 (2)	0.066 (2)	0.0453 (18)	0.0412 (18)	0.0238 (16)	0.0341 (16)
N4	0.0607 (18)	0.0420 (16)	0.0392 (15)	0.0266 (14)	0.0190 (14)	0.0224 (13)
O11	0.0631 (17)	0.0517 (17)	0.0564 (17)	0.0120 (14)	0.0141 (14)	0.0147 (14)
O12	0.0551 (15)	0.0517 (17)	0.0565 (16)	0.0090 (13)	0.0131 (13)	0.0177 (14)
O13	0.0586 (16)	0.0471 (16)	0.0525 (18)	0.0096 (13)	0.0075 (14)	0.0152 (14)
O14	0.068 (2)	0.0549 (19)	0.066 (2)	−0.0070 (16)	0.0069 (17)	−0.0063 (16)

Geometric parameters (Å, °)

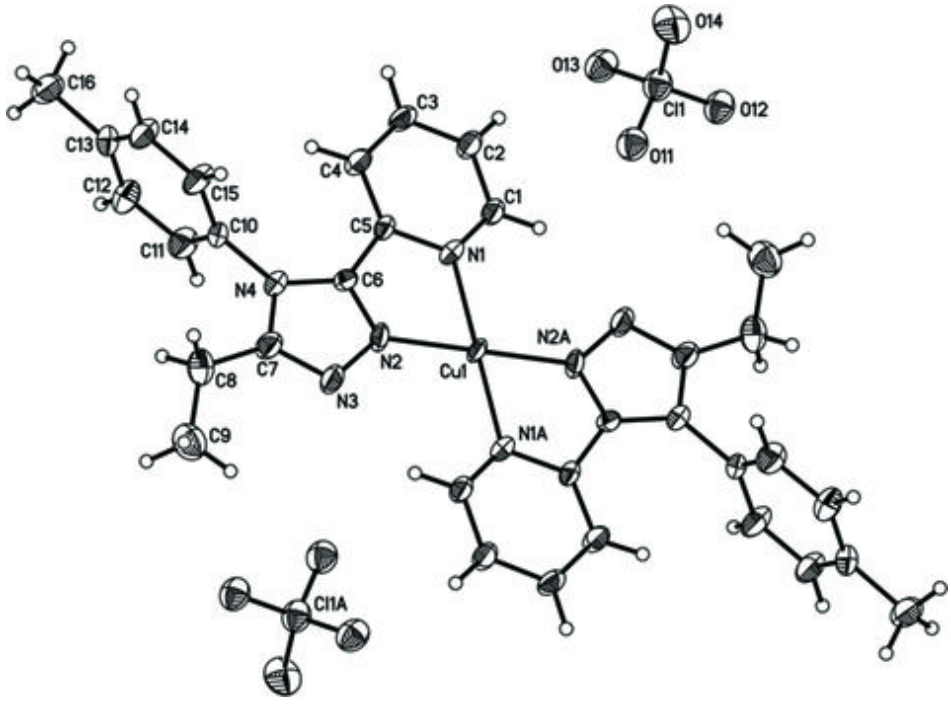
C1—N1	1.310 (5)	C10—N4	1.449 (4)
C1—C2	1.398 (5)	C11—C12	1.395 (5)
C1—H1	0.930	C11—H11	0.930
C2—C3	1.376 (5)	C12—C13	1.371 (6)
C2—H2	0.930	C12—H12	0.930
C3—C4	1.387 (5)	C13—C14	1.351 (6)
C3—H3	0.930	C13—C16	1.518 (5)

C4—C5	1.372 (4)	C14—C15	1.367 (5)
C4—H4	0.930	C14—H14	0.930
C5—N1	1.361 (4)	C15—H15	0.930
C5—C6	1.456 (4)	C16—H16A	0.960
C6—N2	1.312 (4)	C16—H16B	0.960
C6—N4	1.348 (4)	C16—H16C	0.960
C7—N3	1.325 (4)	Cl1—O12	1.398 (3)
C7—N4	1.356 (5)	Cl1—O14	1.407 (3)
C7—C8	1.464 (5)	Cl1—O13	1.422 (3)
C8—C9	1.474 (6)	Cl1—O11	1.426 (3)
C8—H8A	0.970	Cl1—Cu1	3.5736 (11)
C8—H8B	0.970	Cu1—N2	1.982 (3)
C9—H9A	0.960	Cu1—N2^{i}	1.982 (3)
C9—H9B	0.960	Cu1—N1^{i}	2.043 (3)
C9—H9C	0.960	Cu1—N1	2.043 (3)
C10—C11	1.353 (6)	N2—N3	1.374 (4)
C10—C15	1.394 (5)		
N1—C1—C2	121.6 (3)	C14—C13—C16	121.7 (4)
N1—C1—H1	119.2	C12—C13—C16	120.1 (4)
C2—C1—H1	119.2	C13—C14—C15	123.7 (4)
C3—C2—C1	119.6 (3)	C13—C14—H14	118.1
C3—C2—H2	120.2	C15—C14—H14	118.1
C1—C2—H2	120.2	C14—C15—C10	117.4 (4)
C2—C3—C4	118.8 (3)	C14—C15—H15	121.3
C2—C3—H3	120.6	C10—C15—H15	121.3
C4—C3—H3	120.6	C13—C16—H16A	109.5
C5—C4—C3	118.0 (3)	C13—C16—H16B	109.5
C5—C4—H4	121.0	H16A—C16—H16B	109.5
C3—C4—H4	121.0	C13—C16—H16C	109.5
N1—C5—C4	123.0 (3)	H16A—C16—H16C	109.5
N1—C5—C6	111.5 (3)	H16B—C16—H16C	109.5
C4—C5—C6	125.5 (3)	O12—Cl1—O14	112.3 (2)
N2—C6—N4	108.3 (3)	O12—Cl1—O13	110.27 (18)
N2—C6—C5	119.5 (3)	O14—Cl1—O13	108.0 (2)
N4—C6—C5	132.2 (3)	O12—Cl1—O11	108.75 (19)
N3—C7—N4	109.7 (3)	O14—Cl1—O11	110.0 (2)
N3—C7—C8	127.6 (4)	O13—Cl1—O11	107.42 (19)
N4—C7—C8	122.7 (3)	O12—Cl1—Cu1	90.71 (12)
C7—C8—C9	120.8 (4)	O14—Cl1—Cu1	138.86 (16)
C7—C8—H8A	107.1	O11—Cl1—Cu1	92.63 (13)
C9—C8—H8A	107.1	N2—Cu1—N2^{i}	180
C7—C8—H8B	107.1	N2—Cu1—N1^{i}	99.18 (12)
C9—C8—H8B	107.1	N2^{i}—Cu1—N1^{i}	80.82 (12)
H8A—C8—H8B	106.8	N2—Cu1—N1	80.82 (12)
C8—C9—H9A	109.5	N2^{i}—Cu1—N1	99.18 (12)
C8—C9—H9B	109.5	N1^{i}—Cu1—N1	180
H9A—C9—H9B	109.5	N2—Cu1—Cl1	101.05 (9)

C8—C9—H9C	109.5	$N2^{i}$—Cu1—Cl1	78.95 (9)
H9A—C9—H9C	109.5	$N1^{i}$—Cu1—Cl1	76.99 (8)
H9B—C9—H9C	109.5	N1—Cu1—Cl1	103.01 (8)
C11—C10—C15	120.4 (4)	C1—N1—C5	118.7 (3)
C11—C10—N4	120.6 (3)	C1—N1—Cu1	127.2 (2)
C15—C10—N4	119.0 (3)	C5—N1—Cu1	114.1 (2)
C10—C11—C12	120.1 (4)	C6—N2—N3	109.5 (3)
C10—C11—H11	120.0	C6—N2—Cu1	113.3 (2)
C12—C11—H11	120.0	N3—N2—Cu1	136.0 (2)
C13—C12—C11	120.1 (4)	C7—N3—N2	105.7 (3)
C13—C12—H12	120.0	C6—N4—C7	106.8 (3)
C11—C12—H12	120.0	C6—N4—C10	126.5 (3)
C14—C13—C12	118.2 (4)	C7—N4—C10	126.3 (3)

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

Fig. 1


O14
O13
Cl1
O12
O11
C16
C14
C13
C12
C15
C10
C11
C3
C4
C2
C1
C5
N1
N4
C6
N2A
C8
C7
N2
Cu1
N3
C9
N1A
Cl1A