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Bis(μ-5-phenyltetrazolate-κ^2N^2:N^3)bis[(2,2′-bipyridine-κ^2N,N')bis(5-phenyltetrazolate-κN^2)copper(II)]

Ze-Huai Shao, Jun Luo, Rui-Fang Cai, Xi-Geng Zhou,* Lin-Hong Weng and Zhen-Xia Chen

Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China

Correspondence e-mail: xgzhou@fudan.edu.cn

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The centrosymmetric title complex, $[Cu_2(C_7H_5N_4)_4(C_{10}H_8N_2)_2]$, comprises two Cu atoms, four 5-phenyltetrazolate ligands and two 2,2′-bipyridine ligands. The five-coordinated Cu atom adopts a distorted tetragonal–pyramidal geometry.

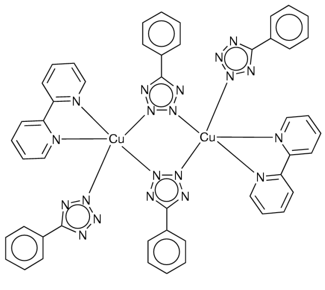
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.052
wR factor = 0.118
Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Owing to their fascinating properties, tetrazolate and substituted tetrazolate complexes have been extensively studied (Butler, 1996; Xiong *et al.*, 2002). The tetrazolate anion is not only isoelectronic with the cyclopentadienyl anion but is a potentially tetradentate ligand. Indeed, several coordination modes for tetrazolate exist in its coordination complexes (Moore & Robinson, 1988). Thus, research has shown that the tetrazolate anion can use different N atoms to bridge or chelate metal atoms (Carlucci *et al.*, 1999; Yélamos *et al.*, 2001; Zhou *et al.*, 1998). Although Cu complexes with neutral tetrazole and tetrazolate ligands have been well studied, only one Cu complex with tetrazolate has been structurally characterized until now. In that case, the Cu ion was univalent and the tetrazolate anion was monodentate (Gaughan *et al.*, 1972). To better understand the structural characteristics of copper(II) tetrazolate complexes, in this paper we report the crystal structure of a new 5-phenyltetrazolate copper(II) complex, namely $[Cu_2(bipy)_2(N_4CPh)_4]$, (I).



(I)

Complex (I) has a centrosymmetric dinuclear structure in which two Cu atoms are bridged by two 5-phenyltetrazolate ligands (Fig. 1). Each Cu^{II} ion is five-coordinated by five N atoms, derived from three different 5-phenyltetrazolate ligands and one bipy (bipy is 2,2′-bipyridine) ligand, to give a distorted tetragonal-pyramidal geometry. The basal plane is formed by atom N3 from a bridging 5-phenyltetrazolate, atom N7 (in the 2-position) of the monodentate 5-phenyltetrazolate, and two N atoms of the chelating bipyridine ligand. The apical site is occupied by the N2^{i} atom derived from the symmetry-related bridging 5-phenyltetrazolate [symmetry code: (i)

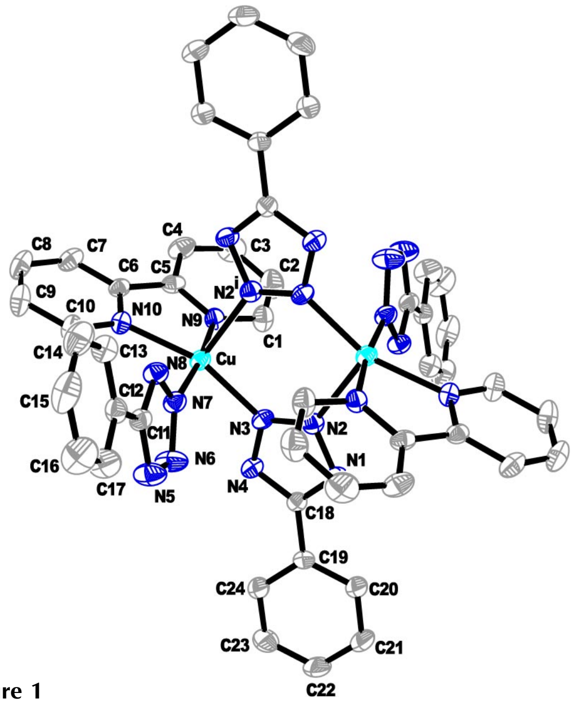


Figure 1

View of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

$1 - x, 1 - y, -z$]. The lengths of the four Cu—N bonds in the basal plane are almost equal and are considerably shorter than the apical Cu—N bond length (Table 1). In the basal plane, the *cis*-N—Cu—N angles lie in the range 80.07 (13)–94.35 (13)° and the N_{apical}—Cu—N_{basal} angles are in the range 89.59 (13)–103.66 (12)°. The deviations of these angles from the ideal value of 90° indicate that the geometry about the Cu atom is distorted tetragonal pyramidal. The Cu atom is 0.241 (4) Å above the basal plane. The distortion of the tetragonal pyramid can be described by the parameter τ, where values of 0 and 1 are indicative of ideal square pyramidal and trigonal bipyramidal geometries, respectively (Addison *et al.*, 1984; Nagle *et al.*, 1990). In (I), the calculated value is 0.3. The distance between the two Cu atoms is 3.987 (4) Å.

The two independent tetrazolate rings in the dimeric unit are planar within experimental error and there is substantial delocalization of π-electron density in the tetrazolate ring as evidenced by the approximately equal bond lengths within the ring (John *et al.*, 1989; Palazzi *et al.*, 2003). For the monodentate 5-phenyltetrazolate ligands, the dihedral angle between the phenyl ring and the tetrazolate ring is 4.1 (2)° (Yélamos *et al.*, 2001; Kreutzer *et al.*, 1972); the equivalent angle in the bridging 5-phenyltetrazolate ligand is 15.6 (2)°. The small dihedral angles may result from conjugation between the two rings. The short bond distances for C18—C19 [1.460 (5) Å] and C11—C12 [1.469 (6) Å] are consistent with this (Guilard *et al.*, 1991). The dihedral angle formed between the tetrazolate rings of the monodentate and bridging tetrazolates is 78.1 (1)°.

The bipyridine ligand is planar, with the largest deviation of any atom from the mean plane being 0.085 (1) Å. The bipyridine is almost perpendicular to planes through the bridging tetrazolate planes [the mean angle is 85.4 (1)°], and are inclined at 59.9 (1)° to the planes through the monodentate tetrazolate ligands.

Experimental

An ethanol (4 ml) solution of 2.2′-bipyridine (0.30 mmol, 46.9 mg) and an aqueous solution (4 ml) of copper acetate (0.30 mmol, 60.0 mg) were mixed and the resulting solution was stirred for 5 min; the mixed solution was deep blue. To the mixture was added an ethanol solution (2 ml) of 5-phenyl-1*H*-tetrazole (0.60 mmol, 87.6 mg). After another 5 min of stirring, the solution was filtered and the filtrate was slowly evaporated in air. After a month, green–blue plate-like crystals of (I) were isolated in 20% yield.

Crystal data

$[Cu_2(C_7H_5N_4)_4(C_{10}H_8N_2)_2]$
$M_r = 1020.05$
Triclinic, $P\overline{1}$
$a = 10.196$ (3) Å
$b = 10.410$ (4) Å
$c = 13.308$ (5) Å
$\alpha = 79.460$ (5)°
$\beta = 68.928$ (4)°
$\gamma = 61.010$ (4)°
$V = 1152.8$ (7) Å^3

$Z = 1$
$D_x = 1.469$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 785 reflections
$\theta = 2.2$–25.9°
$\mu = 0.98$ mm^{-1}
$T = 293$ (2) K
Plate, green–blue
0.10 × 0.05 × 0.02 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.908$, $T_{max} = 0.981$
4870 measured reflections

4003 independent reflections
3091 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 25.0°$
$h = -10 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.118$
$S = 1.04$
4003 reflections
316 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.823P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Cu—N7	1.971 (3)	N4—C18	1.331 (5)
Cu—N9	2.008 (3)	N5—C11	1.325 (5)
Cu—N3	2.010 (3)	N5—N6	1.342 (5)
Cu—N10	2.029 (3)	N6—N7	1.314 (5)
Cu—N2^i	2.196 (3)	N7—N8	1.335 (4)
N1—N2	1.331 (4)	N8—C11	1.331 (5)
N1—C18	1.343 (5)	C11—C12	1.469 (6)
N2—N3	1.324 (4)	C18—C19	1.460 (5)
N3—N4	1.331 (4)		
N7—Cu—N9	173.25 (13)	N2—N1—C18	105.0 (3)
N7—Cu—N3	90.60 (13)	N3—N2—N1	108.6 (3)
N9—Cu—N3	94.35 (13)	N2—N3—N4	110.5 (3)
N7—Cu—N10	93.53 (13)	N3—N4—C18	104.2 (3)
N9—Cu—N10	80.07 (13)	C11—N5—N6	106.0 (3)
N3—Cu—N10	155.32 (13)	N7—N6—N5	107.2 (3)
N7—Cu—N2^i	94.04 (13)	N6—N7—N8	111.4 (3)
N9—Cu—N2^i	89.59 (13)	C11—N8—N7	103.6 (3)
N3—Cu—N2^i	100.30 (12)	N5—C11—N8	111.7 (4)
N10—Cu—N2^i	103.66 (12)	N4—C18—N1	111.8 (3)

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

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H atoms were included in their idealized positions, with C—H distances of 0.93 Å, and refined using a riding model with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C) for all H atoms.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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References

Addison, A. W., Rao, T. N., Reedijk, J., Rijn, J. V. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Bruker (2000). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Butler, R. N. (1996). *Comprehensive Heterocyclic Chemistry* II, Vol. 4, edited by A. R. Katritzky, C. W. Rees and E. F. V. Scriven, pp. 621–677. Oxford: Pergamon Press.

Carlucci, L., Ciani, G. & Proserpio, D. M. (1999). *Angew. Chem. Int. Ed.* **38**, 3488–3492.

Gaughan, A. P., Bowman, K. S. & Dori, Z. (1972). *Inorg. Chem.* **11**, 601–608.

Guilard, R., Jagerovic, N., Tabard, A., Richard, P., Courthaudon, L., Louati, A., Lecomte, C. & Kadish, K. M. (1991). *Inorg. Chem.* **30**, 16–27.

John, E. O., Willett, R. D., Scott, B., Kirchmeier, R. L. & Shreeve, J. M. (1989). *Inorg. Chem.* **28**, 893–897.

Kreutzer, P., Weis, C., Boehme, H., Kemmerich, T., Beck, W., Spencer, C. & Mason, R. (1972). *Z. Naturforsch. Teil B*, **27**, 745–747.

Moore, D. S. & Robinson, S. D. (1988). *Adv. Inorg. Chem.* **32**, 171–239.

Nagle, P., O'Sullivan, E., Hathaway, B. J. & Muller, E. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3399–3406.

Palazzi, A., Stagni, S., Selva, S. & Monari, M. (2003). *J. Organomet. Chem.* **669**, 135–140.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (2000). *SHELXTL*. Version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Xiong, R.-G., Xue, X., Zhao, H., You, X.-Z., Abrahams, B. F. & Xue, Z. L. (2002). *Angew. Chem. Int. Ed.* **41**, 3800–3803.

Yélamos, C., Gust, K. R., Baboul, A. G., Heeg, M. J., Schlegel, H. B. & Winter, C. H. (2001). *Inorg. Chem.* **40**, 6451–6462.

Zhou, X.-G., Huang, Z.-E., Cai, R.-F., Zhang L.-X., Hou, X.-F., Feng, X.-J. & Huang X.-Y. (1998). *J. Organomet. Chem.* **563**, 101–112.

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