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Bis[4-(1-iminoethyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-olato-κ^2O,N^4]copper(II)

Hualing Zhu, Zhan Wang, Zhen Wei, Yanan Bai and Xiaoping Xv*

Department of Basic Science, Tianjin Agricultural College, Tianjin Jinjing Road No. 22, Tianjin 300384, People's Republic of China
Correspondence e-mail: zhuhualing2004@126.com

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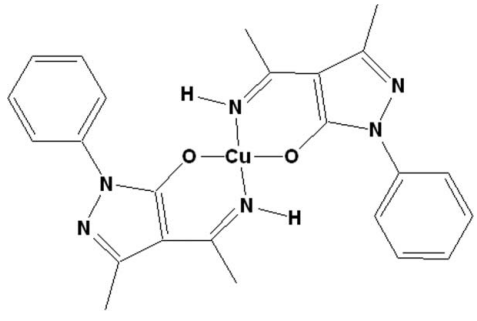
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.006 Å; R factor = 0.063; wR factor = 0.136; data-to-parameter ratio = 12.3.

In the title complex, $[Cu(C_{12}H_{12}N_3O)_2]$, the Cu^{II} ion is tetracoordinated by two N atoms and two O atoms from two bis-chelating 4-(1-iminoethyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-olate ligands in a square-planar geometry. The two N atoms and two O atoms around the Cu^{II} atom are *trans* to each other, as the Cu^{II} atom lies on an inversion centre. The six-membered ring composed of the Cu, an O, an N and three C atoms of the ligand and the pyrazole ring is nearly planar, the largest deviation being 0.037 (4) Å for an N atom. In the crystal, weak intermolecular C—H···N hydrogen-bonding interactions link the molecules into chains along the *c* axis.

Related literature

For our ongoing studies on pyrazolone derivatives, see: Zhu, Shi *et al.* (2010); Zhu, Wei *et al.* (2010). For related structures, see: Parsons *et al.* (2004); Shi *et al.* (2005).



Experimental

Crystal data

$[Cu(C_{12}H_{12}N_3O)_2]$ M_r = 492.03
Monoclinic, $P2_1/n$
a = 6.391 (6) Å
b = 9.010 (8) Å
c = 18.772 (17) Å
β = 98.701 (17)°
V = 1068.5 (16) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.06 mm^{-1}
T = 113 K
0.10 × 0.10 × 0.10 mm

Data collection

Rigaku Saturn724 CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2008)
T_{min} = 0.902, T_{max} = 0.902
8871 measured reflections
1888 independent reflections
1636 reflections with $I > 2\sigma(I)$
R_{int} = 0.130

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.136
S = 1.08
1888 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −1.64 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···N1^{i}	0.95	2.61	3.366 (6)	137

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

Data collection: *CrystalClear* (Rigaku/MSC, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *CrystalStructure* (Rigaku/MSC, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2436).

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Zhu, H., Shi, J., Wei, Z., Bai, Y. & Bu, L. (2010). *Acta Cryst.* E**66**, o1583.
Zhu, H., Wei, Z., Bu, L., Xu, X. & Shi, J. (2010). *Acta Cryst.* E**66**, m904.

supporting information

Acta Cryst. (2011). E**67**, m1208 [doi:10.1107/S1600536811030753]

Bis[4-(1-iminoethyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-olato-κ^2O,N^4]copper(II)

Hualing Zhu, Zhan Wang, Zhen Wei, Yanan Bai and Xiaoping Xv

S1. Comment

As a part of our onging studies on pyrazolone derivatives as potential ligands (Zhu, Shi *et al.*, 2010; Zhu, Wei *et al.*, 2010) we report the structure of the title complex in this article.

In the title complex (Fig. 1.), the central Cu^{II} ion is tetracoordinated by two N atoms and two O atoms from two bis-chelating 4-(2-methyl iminomethyl)-3-methyl- 1- phenyl-1*H*-pyrazol-5(4*H*)-onato ligands in a square-planar geometry. The two N atoms and two O atoms around the Cu^{II} atom are *trans* to each other, as the Cu^{II} atom lies on an inversion centre. The six membered chelate ring (Cu1/O1/N3/C1/C2/C5) / and the pyrazol ring are nearly coplannar with the largest deviation 0.037 (4)Å for N2 atom. In the crystal structure, weak intermolecular hydrogen bonding interactions (C11—H11···N1) link molecules into one-dimensional chains (Fig. 2).

S2. Experimental

The title compound was synthesized by dropping a copper acetate (15 mmol) ethanolic solution into an ethanolic solution of 4-[(3,4-dihydro-5-methyl-3-oxo-2-phenyl-2*H*-pyrazol-4–ylidene)(methyl) methylamino]-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one(30 mmol) and stirring for about 7 h at room temperature. The dark green blocks which were obtained were dried in air. The product was recrystallized from *N*,*N*-dimethylformamide which afforded crystals suitable for *X*–ray analysis.

S3. Refinement

The H atoms were geometrically positioned and refined using a riding model, with N—H = 0.88 Å and C—H = 0.95 or 0.98 Å for the aryl or methyl H atoms, respectively, and U_{iso}(H) = 1.2 U_{eq}(N/C-aryl) or 1.5U_{eq}(C-methyl).

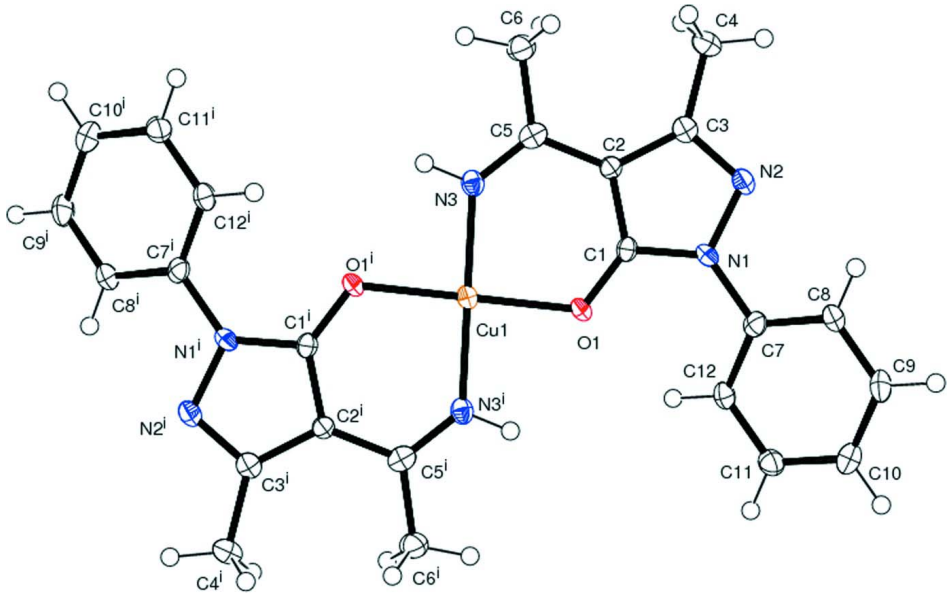

Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: ^{i}: -*x* + 1/2, -*y* + 1/2, -*z* + 1/2).

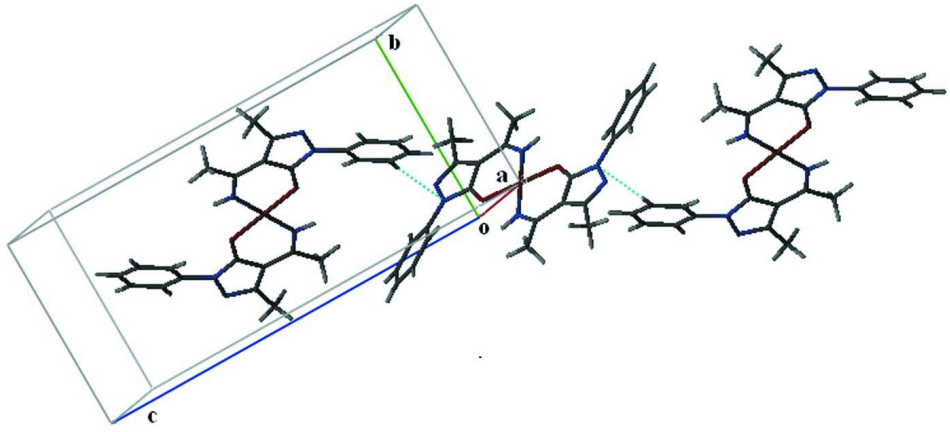

Figure 2

Part of the crystal structure showing intermolecular hydrogen bonding interactions (C—H···N) as dashed lines.

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Crystal data

$[Cu(C_{12}H_{12}N_3O)_2]$
M_r = 492.03
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 6.391 (6) Å
b = 9.010 (8) Å
c = 18.772 (17) Å
β = 98.701 (17)°
V = 1068.5 (16) Å^3
Z = 2
$F(000)$ = 510
D_x = 1.529 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3203 reflections
θ = 2.2–27.9°
μ = 1.06 mm^{-1}
T = 113 K
Block, dark green
0.10 × 0.10 × 0.10 mm

Data collection

Rigaku Saturn724 CCD diffractometer
Radiation source: rotating anode
Multilayer monochromator
Detector resolution: 14.22 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2008)
T_{min} = 0.902, T_{max} = 0.902
8871 measured reflections
1888 independent reflections
1636 reflections with $I > 2\sigma(I)$
R_{int} = 0.130
θ_{max} = 25.0°, θ_{min} = 2.2°
h = −7→7
k = −10→10
l = −22→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.136
S = 1.08
1888 reflections
154 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 2.9195P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −1.64 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.

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	1.0000	0.0000	0.0000	0.0168 (2)
O1	0.8267 (5)	0.0256 (3)	0.07637 (14)	0.0180 (6)
N1	0.5337 (5)	0.1293 (4)	0.11912 (17)	0.0175 (8)
N2	0.3649 (5)	0.2250 (4)	0.09578 (18)	0.0181 (8)
N3	0.8317 (5)	0.1373 (4)	−0.06383 (17)	0.0174 (8)
H3	0.8788	0.1521	−0.1049	0.018 (11)*
C1	0.6638 (6)	0.1120 (4)	0.0678 (2)	0.0149 (8)
C2	0.5770 (6)	0.2036 (4)	0.0094 (2)	0.0147 (8)
C3	0.3932 (6)	0.2692 (4)	0.0303 (2)	0.0172 (9)
C4	0.2369 (7)	0.3782 (5)	−0.0080 (2)	0.0226 (9)
H4A	0.1279	0.4000	0.0220	0.034*
H4B	0.1704	0.3356	−0.0540	0.034*
H4C	0.3105	0.4701	−0.0171	0.034*
C5	0.6613 (7)	0.2121 (4)	−0.0571 (2)	0.0186 (9)
C6	0.5517 (7)	0.3040 (5)	−0.1183 (2)	0.0248 (10)
H6A	0.6266	0.2943	−0.1599	0.037*

H6B	0.5513	0.4083	−0.1035	0.037*
H6C	0.4056	0.2694	−0.1314	0.037*
C7	0.5388 (7)	0.0532 (4)	0.1862 (2)	0.0171 (9)
C8	0.3507 (7)	0.0359 (5)	0.2136 (2)	0.0217 (9)
H8	0.2236	0.0788	0.1896	0.026*
C9	0.3505 (7)	−0.0449 (5)	0.2766 (2)	0.0242 (10)
H9	0.2219	−0.0586	0.2953	0.029*
C10	0.5372 (7)	−0.1061 (5)	0.3124 (2)	0.0239 (10)
H10	0.5354	−0.1621	0.3552	0.029*
C11	0.7253 (7)	−0.0854 (5)	0.2858 (2)	0.0220 (9)
H11	0.8529	−0.1265	0.3105	0.026*
C12	0.7277 (7)	−0.0043 (4)	0.2227 (2)	0.0182 (9)
H12	0.8570	0.0117	0.2046	0.022*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0155 (4)	0.0184 (4)	0.0171 (4)	0.0023 (3)	0.0047 (3)	−0.0003 (3)
O1	0.0137 (14)	0.0223 (15)	0.0186 (14)	0.0057 (12)	0.0044 (11)	0.0013 (12)
N1	0.0137 (17)	0.0185 (18)	0.0205 (17)	0.0046 (14)	0.0034 (14)	0.0012 (14)
N2	0.0151 (17)	0.0160 (17)	0.0240 (18)	0.0013 (14)	0.0057 (14)	−0.0006 (14)
N3	0.0184 (18)	0.0208 (18)	0.0140 (16)	−0.0009 (15)	0.0055 (14)	−0.0024 (14)
C1	0.0136 (19)	0.015 (2)	0.0166 (18)	−0.0032 (16)	0.0036 (16)	−0.0009 (15)
C2	0.015 (2)	0.0124 (19)	0.0170 (19)	−0.0017 (16)	0.0030 (16)	0.0006 (16)
C3	0.017 (2)	0.0125 (19)	0.022 (2)	−0.0026 (16)	0.0029 (17)	−0.0026 (16)
C4	0.020 (2)	0.020 (2)	0.027 (2)	0.0031 (18)	0.0017 (19)	0.0018 (18)
C5	0.021 (2)	0.016 (2)	0.018 (2)	−0.0043 (17)	0.0006 (17)	−0.0016 (17)
C6	0.030 (3)	0.024 (2)	0.020 (2)	0.004 (2)	0.0029 (19)	0.0001 (18)
C7	0.023 (2)	0.015 (2)	0.0138 (18)	0.0005 (17)	0.0044 (17)	−0.0034 (16)
C8	0.016 (2)	0.027 (2)	0.023 (2)	0.0053 (18)	0.0069 (18)	0.0012 (18)
C9	0.019 (2)	0.031 (2)	0.025 (2)	−0.0016 (19)	0.0104 (18)	−0.0015 (19)
C10	0.026 (2)	0.028 (2)	0.020 (2)	−0.004 (2)	0.0087 (19)	−0.0007 (18)
C11	0.020 (2)	0.026 (2)	0.019 (2)	0.0035 (19)	0.0014 (17)	−0.0021 (18)
C12	0.015 (2)	0.019 (2)	0.022 (2)	−0.0018 (17)	0.0058 (17)	−0.0016 (17)

Geometric parameters (Å, º)

Cu1—N3^{i}	1.932 (4)	C4—H4C	0.9800
Cu1—N3	1.932 (4)	C5—C6	1.502 (6)
Cu1—O1	1.953 (3)	C6—H6A	0.9800
Cu1—O1^{i}	1.953 (3)	C6—H6B	0.9800
O1—C1	1.290 (5)	C6—H6C	0.9800
N1—C1	1.373 (5)	C7—C8	1.385 (6)
N1—N2	1.399 (5)	C7—C12	1.395 (6)
N1—C7	1.430 (5)	C8—C9	1.389 (6)
N2—C3	1.330 (5)	C8—H8	0.9500
N3—C5	1.303 (5)	C9—C10	1.392 (6)
N3—H3	0.8800	C9—H9	0.9500

C1—C2	1.418 (5)	C10—C11	1.383 (6)
C2—C3	1.422 (6)	C10—H10	0.9500
C2—C5	1.435 (6)	C11—C12	1.395 (6)
C3—C4	1.505 (6)	C11—H11	0.9500
C4—H4A	0.9800	C12—H12	0.9500
C4—H4B	0.9800		

N3^{i}—Cu1—N3	180.0 (2)	H4B—C4—H4C	109.5
N3^{i}—Cu1—O1	86.83 (14)	N3—C5—C2	119.1 (4)
N3—Cu1—O1	93.17 (14)	N3—C5—C6	120.7 (4)
N3^{i}—Cu1—O1^{i}	93.17 (14)	C2—C5—C6	120.1 (4)
N3—Cu1—O1^{i}	86.83 (14)	C5—C6—H6A	109.5
O1—Cu1—O1^{i}	180.00 (14)	C5—C6—H6B	109.5
C1—O1—Cu1	121.1 (2)	H6A—C6—H6B	109.5
C1—N1—N2	111.8 (3)	C5—C6—H6C	109.5
C1—N1—C7	128.9 (3)	H6A—C6—H6C	109.5
N2—N1—C7	119.0 (3)	H6B—C6—H6C	109.5
C3—N2—N1	105.5 (3)	C8—C7—C12	120.7 (4)
C5—N3—Cu1	131.7 (3)	C8—C7—N1	118.4 (4)
C5—N3—H3	114.1	C12—C7—N1	120.9 (4)
Cu1—N3—H3	114.1	C7—C8—C9	119.2 (4)
O1—C1—N1	123.0 (3)	C7—C8—H8	120.4
O1—C1—C2	131.4 (4)	C9—C8—H8	120.4
N1—C1—C2	105.6 (3)	C8—C9—C10	120.5 (4)
C1—C2—C3	105.8 (3)	C8—C9—H9	119.7
C1—C2—C5	123.3 (4)	C10—C9—H9	119.7
C3—C2—C5	130.8 (4)	C11—C10—C9	120.0 (4)
N2—C3—C2	111.4 (4)	C11—C10—H10	120.0
N2—C3—C4	117.7 (4)	C9—C10—H10	120.0
C2—C3—C4	131.0 (4)	C10—C11—C12	120.0 (4)
C3—C4—H4A	109.5	C10—C11—H11	120.0
C3—C4—H4B	109.5	C12—C11—H11	120.0
H4A—C4—H4B	109.5	C11—C12—C7	119.5 (4)
C3—C4—H4C	109.5	C11—C12—H12	120.3
H4A—C4—H4C	109.5	C7—C12—H12	120.3

N3^{i}—Cu1—O1—C1	−178.9 (3)	C1—C2—C3—C4	178.8 (4)
N3—Cu1—O1—C1	1.1 (3)	C5—C2—C3—C4	−5.6 (7)
C1—N1—N2—C3	−1.2 (4)	Cu1—N3—C5—C2	3.6 (6)
C7—N1—N2—C3	−175.0 (3)	Cu1—N3—C5—C6	−175.4 (3)
O1—Cu1—N3—C5	−2.5 (4)	C1—C2—C5—N3	−3.1 (6)
O1^{i}—Cu1—N3—C5	177.5 (4)	C3—C2—C5—N3	−178.0 (4)
Cu1—O1—C1—N1	177.7 (3)	C1—C2—C5—C6	175.9 (4)
Cu1—O1—C1—C2	−1.4 (6)	C3—C2—C5—C6	0.9 (7)
N2—N1—C1—O1	−178.0 (3)	C1—N1—C7—C8	−151.2 (4)
C7—N1—C1—O1	−4.9 (6)	N2—N1—C7—C8	21.4 (5)
N2—N1—C1—C2	1.3 (4)	C1—N1—C7—C12	27.8 (6)
C7—N1—C1—C2	174.4 (4)	N2—N1—C7—C12	−159.6 (4)

O1—C1—C2—C3	178.3 (4)	C12—C7—C8—C9	−2.6 (6)
N1—C1—C2—C3	−1.0 (4)	N1—C7—C8—C9	176.4 (4)
O1—C1—C2—C5	2.3 (7)	C7—C8—C9—C10	0.9 (7)
N1—C1—C2—C5	−177.0 (4)	C8—C9—C10—C11	0.6 (7)
N1—N2—C3—C2	0.5 (4)	C9—C10—C11—C12	−0.5 (6)
N1—N2—C3—C4	−178.2 (3)	C10—C11—C12—C7	−1.1 (6)
C1—C2—C3—N2	0.3 (5)	C8—C7—C12—C11	2.7 (6)
C5—C2—C3—N2	175.9 (4)	N1—C7—C12—C11	−176.3 (4)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O1^{i}	0.88	2.47	2.670 (5)	94
C4—H4*B*···N3^{ii}	0.98	2.79	3.419 (6)	123
C9—H9···N2^{iii}	0.95	2.94	3.596 (6)	128
C11—H11···N1^{iv}	0.95	2.61	3.366 (6)	137
C11—H11···N2^{iv}	0.95	2.68	3.599 (6)	163
C12—H12···O1	0.95	2.39	2.923 (5)	115

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