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# Bis{2-[(2-pyridyl)iminomethyl]-phenolato}copper(II)

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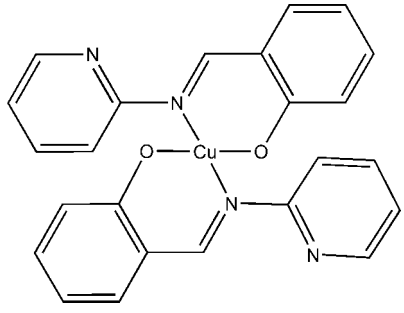
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.033; $wR$ factor = 0.077; data-to-parameter ratio = 11.9.

In the title compound, $[Cu(C_{12}H_9N_2O)_2]$, the $Cu^{II}$ atom lies on a crystallographic inversion center and has a nearly square-planar geometry. The $Cu^{II}$ center coordinates to the phenolic O and azomethine N atoms of the two symmetry-related 2-[(2-pyridyl)iminomethyl]phenolate ligands. The pyridyl N atoms do not coordinate to the $Cu^{II}$ atom but participate in intramolecular C—H···N hydrogen bonding. $\pi$–$\pi$ stacking between the benzene rings and between the pyridyl rings [centroid–centroid distances 3.8142 (5) and 3.8142 (5) Å, respectively] links the molecules into a chain propagating parallel to [100].

## Related literature

For the preparation of the title compound by an electrochemical method, see: Castineiras *et al.* (1989), and by a solution method, see: Parashar *et al.* (1988). For the crystal structures of related compounds, see: Castineiras *et al.* (1989).




## Experimental

### Crystal data

$[Cu(C_{12}H_9N_2O)_2]$
$M_r$ = 457.96
Triclinic, $P\overline{1}$
$a$ = 3.8142 (5) Å
$b$ = 11.217 (1) Å
$c$ = 11.9001 (12) Å
$\alpha$ = 106.884 (2)°
$\beta$ = 90.374 (1)°
$\gamma$ = 90.289 (1)°
$V$ = 487.16 (9) Å$^3$
$Z$ = 1
Mo $K\alpha$ radiation
$\mu$ = 1.15 mm$^{-1}$
$T$ = 298 K
0.41 × 0.17 × 0.15 mm

### Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min}$ = 0.650, $T_{max}$ = 0.846
2547 measured reflections
1695 independent reflections
1481 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.015

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.077
$S$ = 1.07
1695 reflections
142 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.29 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C1—H1···N1 | 0.93 | 2.29 | 2.684 (3) | 105 |

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; 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: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2176).

## References

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# supplementary materials

*Acta Cryst.* (2009). E**65**, m904 [ **doi:10.1107/S1600536809026051** ]

# Bis{2-[(2-pyridyl)iminomethyl]phenolato}copper(II)

**J. Miao, Z. Zhao, H. Chen, D. Wang and Y. Nie**

## Comment

The Schiff base, *N*-salicylidene 2-aminopyridine, has been widely studied as a potential tridentate ligand. The title compound has been prepared using an electrochemical method by Castineiras *et al.* (1989) starting from *N*-salicylidene 2-aminopyridine and copper. Parashar *et al.* (1988) reported that refluxing a mixture of $Cu(OAc)_2$ (OAc = acetato) and *N*-salicylidene 2-aminopyridine in a 1:2 molar ratio resulted in a green complex having the same formula but with an octahedral geometry deduced from spectroscopic properties. We have found that a simple method of solution diffusion produces the brown title compound.

As shown in Fig. 1, the copper atom lies on a crystallographic inversion center and has a square planar geometry. The copper center coordinates to the phenolic oxygen and the azomethine nitrogen atoms of the two symmetry related groups. The pyridyl nitrogen atoms do not coordinate to the copper. The Cu—O bond lengths are 1.9212 (17) Å, and the Cu—N bond lengths are 2.0216 (19) Å, respectively, all similar to those reported in the related structures (Castineiras *et al.*, 1989).

The interplane dihedral angles are found to be as follows: 31.60 (7)° between the $N_2O_2$ plane and the benzene ring, 54.28 (7)° between the $N_2O_2$ plane and the pyridyl ring, and 22.75 (9)° between the benzene and the pyridyl ring. The intramolecular hydrogen bond C1—H1···N1 (2.684 (3) Å, 105°, Table 1) further stabilizes the whole structure. The $\pi$-$\pi$ stacking between the benzene rings (centroid to centroid, 3.8142 (5) Å) and the pyridyl rings (centroid to centroid, 3.8142 (5) Å) links the molecules into a one-dimensional chain (Fig. 2).

## Experimental

To a green solution of salicylaldehyde (23 mg, 0.19 mmol) and $Cu(OAc)_2.H_2O$ (11 mg, 0.05 mmol) in ethanol (7 ml) was added slowly a solution of 2-aminopyridine (21 mg, 0.22 mmol) in ethanol (1 ml). The resulting mixture was allowed to stand still and brown crystalline needles were grown after 1 day. IR (KBr): $\nu$ = 3435, 1611, 1444, 1326, 1187 $cm^{-1}$.

## Refinement

All H-atoms were positioned geometrically and refined using a riding model with d(C—H) = 0.93 Å, $U_{iso}$=1.2$U_{eq}$ (C).

## Figures

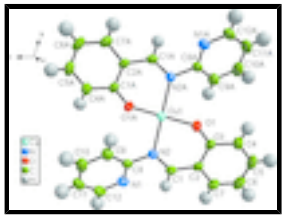

Fig. 1. The molecular structure, with atom labels and 25% probability thermal ellipsoids.

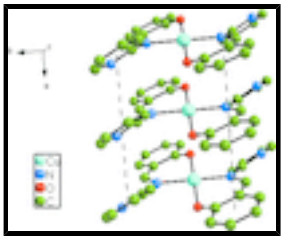

Fig. 2. The one-dimensional chain constructed by the $\pi$-$\pi$ stacking.

**Bis{2-[(2-pyridyl)iminomethyl]phenolato}copper(II)**

*Crystal data*

| | |
|---|---|
| $[Cu(C_{12}H_9N_2O)_2]$ | $Z = 1$ |
| $M_r = 457.96$ | $F_{000} = 235$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.561$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 3.8142$ (5) Å | Cell parameters from 1475 reflections |
| $b = 11.2170$ (10) Å | $\theta = 2.2$–$27.5^\circ$ |
| $c = 11.9001$ (12) Å | $\mu = 1.15$ mm$^{-1}$ |
| $\alpha = 106.884$ (2)° | $T = 298$ K |
| $\beta = 90.3740$ (10)° | Needle, brown |
| $\gamma = 90.2890$ (10)° | 0.41 × 0.17 × 0.15 mm |
| $V = 487.16$ (9) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART 1000 CCD area-detector diffractometer | 1695 independent reflections |
| Radiation source: fine-focus sealed tube | 1481 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.015$ |
| $T = 298$ K | $\theta_{max} = 25.0^\circ$ |
| φ and ω scans | $\theta_{min} = 1.8^\circ$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2001) | $h = -4 \rightarrow 4$ |
| $T_{min} = 0.650$, $T_{max} = 0.846$ | $k = -13 \rightarrow 13$ |
| 2547 measured reflections | $l = -9 \rightarrow 14$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.033$ | H-atom parameters constrained |
| $wR(F^2) = 0.077$ | $w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 0.355P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.07$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 1695 reflections | $\Delta\rho_{max} = 0.27$ e Å$^{-3}$ |

| | |
|---|---|
| 142 parameters | $\Delta\rho_{min} = -0.29$ e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0.5000 | 0.5000 | 0.5000 | 0.03882 (17) |
| N1 | 0.2225 (6) | 0.15806 (19) | 0.55001 (19) | 0.0400 (5) |
| N2 | 0.4891 (5) | 0.31537 (17) | 0.48298 (17) | 0.0305 (5) |
| O1 | 0.8250 (5) | 0.46999 (15) | 0.37229 (15) | 0.0413 (5) |
| C1 | 0.5395 (7) | 0.2344 (2) | 0.3821 (2) | 0.0331 (6) |
| H1 | 0.4927 | 0.1517 | 0.3774 | 0.040* |
| C2 | 0.6590 (7) | 0.2583 (2) | 0.2773 (2) | 0.0325 (6) |
| C3 | 0.7979 (7) | 0.3757 (2) | 0.2770 (2) | 0.0326 (6) |
| C4 | 0.9196 (7) | 0.3865 (3) | 0.1691 (2) | 0.0389 (6) |
| H4 | 1.0121 | 0.4623 | 0.1658 | 0.047* |
| C5 | 0.9057 (7) | 0.2886 (3) | 0.0689 (2) | 0.0459 (7) |
| H5 | 0.9870 | 0.2994 | −0.0010 | 0.055* |
| C6 | 0.7726 (8) | 0.1734 (3) | 0.0696 (2) | 0.0494 (7) |
| H6 | 0.7657 | 0.1072 | 0.0011 | 0.059* |
| C7 | 0.6524 (8) | 0.1595 (2) | 0.1727 (2) | 0.0427 (7) |
| H7 | 0.5635 | 0.0825 | 0.1738 | 0.051* |
| C8 | 0.4001 (6) | 0.2651 (2) | 0.5769 (2) | 0.0316 (6) |
| C9 | 0.5106 (7) | 0.3277 (3) | 0.6892 (2) | 0.0412 (6) |
| H9 | 0.6317 | 0.4030 | 0.7045 | 0.049* |
| C10 | 0.4374 (8) | 0.2761 (3) | 0.7780 (3) | 0.0494 (7) |
| H10 | 0.5085 | 0.3160 | 0.8547 | 0.059* |
| C11 | 0.2574 (8) | 0.1647 (3) | 0.7520 (3) | 0.0509 (8) |
| H11 | 0.2045 | 0.1278 | 0.8105 | 0.061* |
| C12 | 0.1583 (8) | 0.1094 (3) | 0.6381 (3) | 0.0491 (8) |
| H12 | 0.0394 | 0.0335 | 0.6208 | 0.059* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0584 (3) | 0.0241 (2) | 0.0318 (3) | −0.0022 (2) | 0.0154 (2) | 0.00443 (18) |
| N1 | 0.0457 (14) | 0.0298 (11) | 0.0452 (13) | −0.0023 (10) | 0.0071 (11) | 0.0116 (10) |
| N2 | 0.0343 (12) | 0.0261 (10) | 0.0306 (11) | −0.0019 (9) | 0.0037 (9) | 0.0073 (9) |
| O1 | 0.0597 (13) | 0.0304 (9) | 0.0301 (10) | −0.0079 (9) | 0.0143 (9) | 0.0029 (8) |
| C1 | 0.0363 (15) | 0.0233 (12) | 0.0375 (14) | 0.0001 (10) | 0.0005 (11) | 0.0054 (11) |
| C2 | 0.0341 (14) | 0.0286 (13) | 0.0312 (13) | 0.0052 (11) | 0.0027 (11) | 0.0030 (10) |
| C3 | 0.0335 (14) | 0.0330 (13) | 0.0290 (13) | 0.0046 (11) | 0.0036 (11) | 0.0051 (11) |
| C4 | 0.0384 (16) | 0.0444 (15) | 0.0339 (14) | −0.0010 (12) | 0.0047 (12) | 0.0112 (12) |
| C5 | 0.0437 (17) | 0.065 (2) | 0.0258 (14) | 0.0025 (14) | 0.0037 (12) | 0.0081 (13) |
| C6 | 0.0526 (19) | 0.0517 (18) | 0.0318 (15) | 0.0027 (14) | 0.0007 (13) | −0.0071 (13) |
| C7 | 0.0480 (17) | 0.0340 (14) | 0.0391 (15) | 0.0012 (12) | 0.0020 (13) | −0.0006 (12) |
| C8 | 0.0324 (14) | 0.0280 (12) | 0.0363 (14) | 0.0036 (10) | 0.0045 (11) | 0.0120 (11) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C9 | 0.0401 (16) | 0.0438 (16) | 0.0404 (16) | −0.0012 (12) | −0.0032 (12) | 0.0136 (13) |
| C10 | 0.0501 (18) | 0.064 (2) | 0.0370 (16) | 0.0118 (15) | 0.0021 (13) | 0.0186 (14) |
| C11 | 0.0545 (19) | 0.0555 (19) | 0.0544 (19) | 0.0185 (15) | 0.0182 (15) | 0.0336 (16) |
| C12 | 0.0541 (19) | 0.0367 (15) | 0.063 (2) | 0.0027 (13) | 0.0179 (15) | 0.0240 (14) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cu1—O1 | 1.9212 (17) | C4—H4 | 0.9300 |
| Cu1—O1$^{i}$ | 1.9212 (17) | C5—C6 | 1.388 (4) |
| Cu1—N2$^{i}$ | 2.0216 (19) | C5—H5 | 0.9300 |
| Cu1—N2 | 2.0216 (19) | C6—C7 | 1.363 (4) |
| N1—C8 | 1.330 (3) | C6—H6 | 0.9300 |
| N1—C12 | 1.339 (3) | C7—H7 | 0.9300 |
| N2—C1 | 1.294 (3) | C8—C9 | 1.379 (4) |
| N2—C8 | 1.433 (3) | C9—C10 | 1.373 (4) |
| O1—C3 | 1.310 (3) | C9—H9 | 0.9300 |
| C1—C2 | 1.426 (3) | C10—C11 | 1.376 (4) |
| C1—H1 | 0.9300 | C10—H10 | 0.9300 |
| C2—C7 | 1.406 (3) | C11—C12 | 1.366 (4) |
| C2—C3 | 1.419 (3) | C11—H11 | 0.9300 |
| C3—C4 | 1.406 (3) | C12—H12 | 0.9300 |
| C4—C5 | 1.366 (4) | | |
| O1—Cu1—O1$^{i}$ | 180.000 (1) | C4—C5—H5 | 119.4 |
| O1—Cu1—N2$^{i}$ | 90.50 (8) | C6—C5—H5 | 119.4 |
| O1$^{i}$—Cu1—N2$^{i}$ | 89.50 (7) | C7—C6—C5 | 118.6 (3) |
| O1—Cu1—N2 | 89.50 (7) | C7—C6—H6 | 120.7 |
| O1$^{i}$—Cu1—N2 | 90.50 (8) | C5—C6—H6 | 120.7 |
| N2$^{i}$—Cu1—N2 | 180.000 (1) | C6—C7—C2 | 121.8 (3) |
| C8—N1—C12 | 116.8 (2) | C6—C7—H7 | 119.1 |
| C1—N2—C8 | 115.7 (2) | C2—C7—H7 | 119.1 |
| C1—N2—Cu1 | 120.87 (16) | N1—C8—C9 | 123.6 (2) |
| C8—N2—Cu1 | 123.30 (15) | N1—C8—N2 | 117.7 (2) |
| C3—O1—Cu1 | 123.48 (16) | C9—C8—N2 | 118.7 (2) |
| N2—C1—C2 | 127.1 (2) | C10—C9—C8 | 118.3 (3) |
| N2—C1—H1 | 116.4 | C10—C9—H9 | 120.9 |
| C2—C1—H1 | 116.4 | C8—C9—H9 | 120.9 |
| C7—C2—C3 | 119.6 (2) | C9—C10—C11 | 119.2 (3) |
| C7—C2—C1 | 118.2 (2) | C9—C10—H10 | 120.4 |
| C3—C2—C1 | 122.1 (2) | C11—C10—H10 | 120.4 |
| O1—C3—C4 | 120.4 (2) | C12—C11—C10 | 118.4 (3) |
| O1—C3—C2 | 122.7 (2) | C12—C11—H11 | 120.8 |
| C4—C3—C2 | 116.9 (2) | C10—C11—H11 | 120.8 |
| C5—C4—C3 | 121.8 (3) | N1—C12—C11 | 123.8 (3) |
| C5—C4—H4 | 119.1 | N1—C12—H12 | 118.1 |
| C3—C4—H4 | 119.1 | C11—C12—H12 | 118.1 |
| C4—C5—C6 | 121.3 (3) | | |
| O1—Cu1—N2—C1 | −29.5 (2) | C3—C4—C5—C6 | −0.5 (4) |

| | | | |
|---|---|---|---|
| $O1^{i}$—Cu1—N2—C1 | 150.5 (2) | C4—C5—C6—C7 | 0.5 (4) |
| O1—Cu1—N2—C8 | 155.47 (19) | C5—C6—C7—C2 | 0.2 (4) |
| $O1^{i}$—Cu1—N2—C8 | −24.53 (19) | C3—C2—C7—C6 | −0.8 (4) |
| $N2^{i}$—Cu1—O1—C3 | −138.9 (2) | C1—C2—C7—C6 | −177.8 (3) |
| N2—Cu1—O1—C3 | 41.1 (2) | C12—N1—C8—C9 | −1.5 (4) |
| C8—N2—C1—C2 | −174.2 (2) | C12—N1—C8—N2 | 176.5 (2) |
| Cu1—N2—C1—C2 | 10.4 (4) | C1—N2—C8—N1 | −30.6 (3) |
| N2—C1—C2—C7 | −171.7 (3) | Cu1—N2—C8—N1 | 144.60 (19) |
| N2—C1—C2—C3 | 11.3 (4) | C1—N2—C8—C9 | 147.5 (2) |
| Cu1—O1—C3—C4 | 149.6 (2) | Cu1—N2—C8—C9 | −37.2 (3) |
| Cu1—O1—C3—C2 | −32.7 (3) | N1—C8—C9—C10 | 0.8 (4) |
| C7—C2—C3—O1 | −177.1 (2) | N2—C8—C9—C10 | −177.2 (2) |
| C1—C2—C3—O1 | −0.2 (4) | C8—C9—C10—C11 | −0.1 (4) |
| C7—C2—C3—C4 | 0.7 (4) | C9—C10—C11—C12 | 0.0 (4) |
| C1—C2—C3—C4 | 177.6 (2) | C8—N1—C12—C11 | 1.5 (4) |
| O1—C3—C4—C5 | 177.8 (2) | C10—C11—C12—N1 | −0.8 (5) |
| C2—C3—C4—C5 | −0.1 (4) | | |

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

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C1—H1···N1 | 0.93 | 2.29 | 2.684 (3) | 105 |

**Fig. 1**

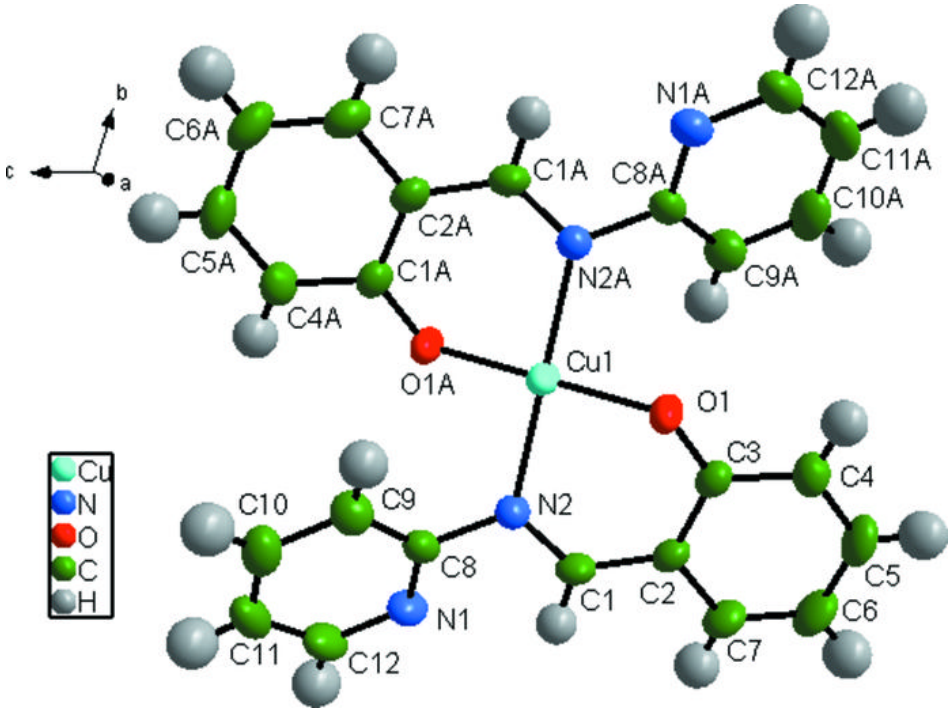
b
c
a
Cu
N
O
C
H
C6A
C7A
C1A
C8A
N1A
C12A
C11A
C10A
C2A
C5A
C1A
N2A
C9A
C4A
O1A
Cu1
O1
C3
C4
C10
C9
N2
C8
C5
C1
C2
N1
C6
C11
C12
C7

**Fig. 2**