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[1-Acetylacetone (2-hydroxybenzoyl)-hydrazonato]pyridinecopper(II)

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Key indicators

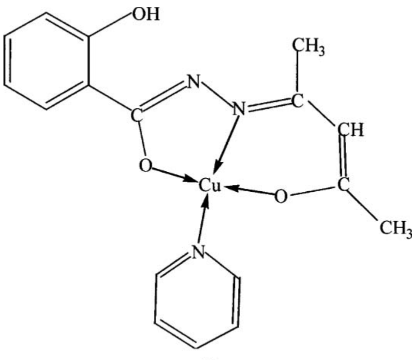
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.013 Å
R factor = 0.067
wR factor = 0.220
Data-to-parameter ratio = 13.5

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

In the title complex, [Cu($C_{12}H_{12}N_2O_3$)(C_5H_5N)], the Cu^{II} atom has a square-planar coordination geometry, formed by the tridentate hydrazone and the monodentate pyridine ligands. The distance of 3.706 (4) Å between the centroids of the nearly parallel [dihedral angle 4.9 (5)°] pyridine ring and the benzene ring of a neighbouring complex molecule suggests the existence of π–π stacking.

Comment

Metal–hydrazone complexes, especially copper complexes with acylhydrazone, continue to attract considerable attention as a result of their biological activities and structural versatility (Aruffo *et al.*, 1984; Ainscough *et al.*, 1995; Chan *et al.*, 1995; Ranford *et al.*, 1998). Abu-Ei-Wafa *et al.* (1990) synthesized copper–salicyloyl hydrazones derived from β-diketones, such as O—XC_6H_4C(O)NHN=C(Me)CH_2COR (X = H and OH, and R = Me and Ph), and found that the hydrazones behave as either monobasic or bidentate ligands. During research into the coordinating behaviour of salicyloyl hydrazones derived from β-diketones with Cu atoms in organic phases, the title complex, [Cu($C_{12}H_{12}N_2O_3$)(C_5H_5N)], (I), has been prepared. We present its crystal structure here.



(I)

The molecular structure of (I) is shown in Fig. 1. The Cu^{II} atom has a square-planar coordination geometry, formed by the tridentate hydrazone and monodentate pyridine ligands, with N atoms in a *trans* arrangement about the Cu atom. The Cu—N and Cu—O bond distances (Table 1) are consistent with the values of 1.930–2.062 and 1.900–1.975 Å found in other complexes with square-planar N_2O_2 coordination geometry (Astheimer *et al.*, 1985). Within the hydrazone group, the C1—O1 distance of 1.289 (8) Å is essentially within the range of 1.29–1.31 Å for enol forms of C—O (Sakarnoto *et al.*, 1989; Yan *et al.*, 1993), indicating that the hydrazone ligand displays the enol form in (I).

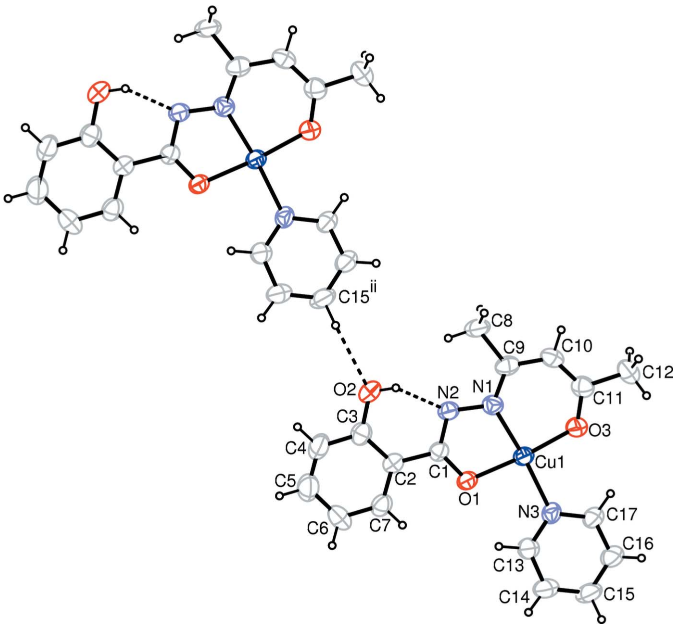


Figure 1
Two symmetry-related molecules of (I), with 30% probability displacement ellipsoids (arbitrary spheres for H atoms), showing the hydrogen bonding (dashed lines) [symmetry code: (ii) $-1 + x, y, z$].

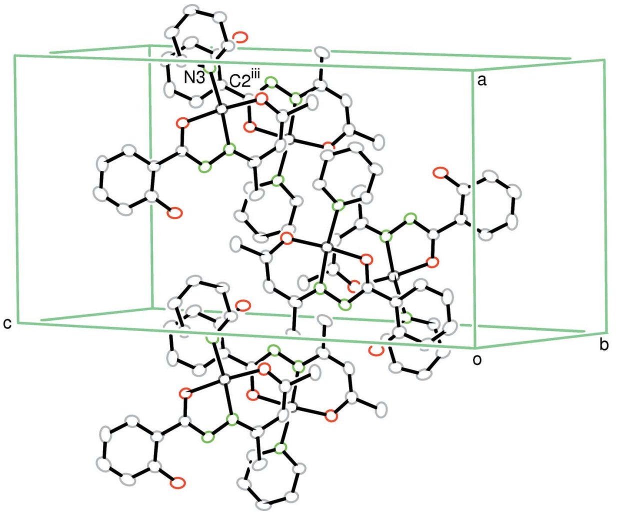


Figure 2
The packing in (I), showing π–π stacking between nearly parallel aromatic rings [symmetry code: (iii) $\frac{3}{2} - x, \frac{1}{2} + y, z$]. H atoms have been omitted.

Both intramolecular classical O—H···N hydrogen bonding and intermolecular weak C—H···O hydrogen bonding occur in the crystal structure of (I) (Table 2). As shown in Fig. 2, the pyridine ring is partially overlapped with the benzene ring of a neighbouring complex molecule, with a small dihedral angle of 4.9 (5)°. The distance of 3.706 (4) Å between the centroids suggests the existence of π–π stacking between these rings.

Experimental

A DMF solution (5 ml) of 2-hydroxynaphthaldehyde salicyloylhydrazone (0.25 mmol, 0.076 g) was mixed with a methanol solution (5 ml) of $Cu(OAc)_2 \cdot H_2O$ (0.25 mmol, 0.050 g). The mixture was stirred at 330 K for 4 h and then filtered. A green precipitate was produced after about 10 d. A pyridine/acetylacetone mixture (5 ml) (*v*/*v*, 1:1) was used to dissolve the precipitate at 330 K. Dark-green block-shaped crystals of (I) were obtained after one month (yield 30%, m.p. > 573 K). Analysis calculated for $C_{17}H_{17}CuN_3O_3$: C 54.42, H 4.57, N 11.24%; found: C 53.91, H 4.72, N 11.32%.

Crystal data

$[Cu(C_{12}H_{12}N_2O_3)(C_5H_5N)]$
$M_r = 374.88$
Orthorhombic, *Pbca*
$a = 12.503$ (5) Å
$b = 9.894$ (4) Å
$c = 26.88$ (1) Å
$V = 3325$ (2) Å^3
$Z = 8$
$D_x = 1.498$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1882 reflections
$\theta = 3.0$–19.7°
$\mu = 1.33$ mm^{-1}
$T = 298$ (2) K
Block, green
0.42 × 0.29 × 0.23 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.604$, $T_{max} = 0.749$
15733 measured reflections
2931 independent reflections
1494 reflections with $I > 2\sigma(I)$
$R_{int} = 0.125$
$\theta_{max} = 25.0°$
$h = -14 \rightarrow 13$
$k = -11 \rightarrow 11$
$l = -32 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.220$
$S = 1.06$
2931 reflections
217 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 10.1233P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.70$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Cu1—O1	1.925 (5)	N1—C9	1.310 (10)
Cu1—O3	1.900 (6)	N2—C1	1.320 (9)
Cu1—N1	1.902 (6)	O1—C1	1.289 (8)
Cu1—N3	1.998 (6)	O3—C11	1.292 (9)
N1—N2	1.394 (9)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···N2	0.82	1.82	2.547 (8)	148
C15—H15···O2^{i}	0.93	2.35	3.275 (11)	174

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

H atoms were placed in calculated positions with C—H = 0.93 or 0.96 Å and O—H = 0.82 Å, and were refined in riding mode, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C and O).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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m1664 Liu *et al.* • $[Cu(C_{12}H_{12}N_2O_3)(C_5H_5N)]$ *Acta Cryst.* (2005). E**61**, m1662–m1664