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(Morpholine-κN)(salicylaldehyde 4-nitrobenzoylhydrazonato-$\kappa^3 O,N,O'$)copper(II)

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Key indicators

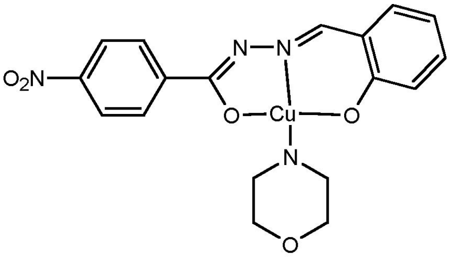
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.054
wR factor = 0.120
Data-to-parameter ratio = 14.3

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

In the structure of the title complex, $[Cu(C_{14}H_9N_3O_4)(C_4H_9NO)]$, the Cu atom is coordinated by two O atoms and one N atom from the N-salicylaldehyde p-nitrobenzoylhydrazone ligand and one N atom from a morpholine molecule, forming a square-planar Cu(ONO)(N) coordination. The g factors derived by an electron paramagnetic resonance study are typical for square-planar complexes.

Comment

Hydrazone compounds have been investigated for many years (Mitra *et al.*, 1996; Belicchi-Ferrari *et al.*, 1999). Recently, much attention has been focused on the study of aroylhydrazone derivatives with aryl, aroyl and heteroaroyl Schiff bases (Iskander *et al.*, 2001; Cariati *et al.*, 2002), because of their ability to form polynuclear complexes through the additional O-donor atom from the carbonyl group (Singh, 1992; Liu *et al.*, 2003). As part of our systematic research on new aroylhydrazone complexes, we report here the synthesis and characterization of the title copper(II) complex, (I), with the N-salicylaldehyde-p-nitrobenzoylhydrazone ligand (Wu & Liu, 2004).



(I)

The Cu^{II} atom in complex (I) (Fig. 1) has a square-planar coordination (Khandar & Nejati, 2000; Adams *et al.*, 1998; Lu *et al.*, 2003; Chan *et al.*, 1995). The tridentate ligand coordinates to the Cu^{II} atom *via* the enolate O, the imine N and the deprotonated amide O atoms, forming one five-membered chelate ring (Cu/N1/N2/C8/O2) and one six-membered chelate ring (Cu/N1/C7/C2/C1/O1) (Ruiz-Perez *et al.*, 1997). There is no significant deviation of the metal centre from the N_2O_2 coordination plane, which shows a small but significant tetrahedral distortion [maximum displacements from the least-squares plane are −0.066 (3) and 0.046 (3) Å for atoms N1 and O2, respectively], as indicated by the deviations of the bond angles around Cu from the values expected for a regular square-planar geometry (Table 1). Such distortion is often observed in Cu^{II} complexes of tridentate chelating agents (West *et al.*, 1993; Ali *et al.*, 1996, 2001). The Cu—O and Cu—

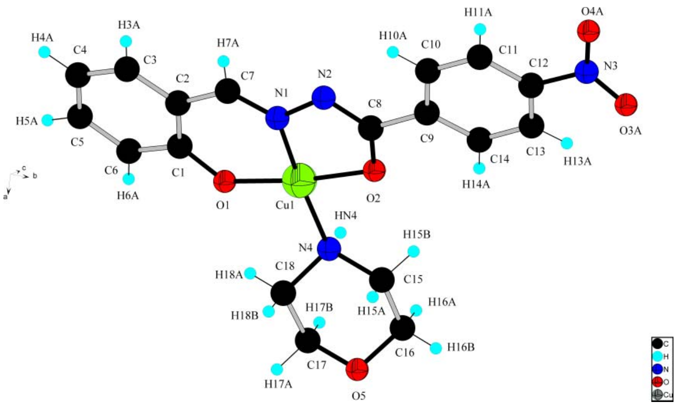


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Only one disorder component is shown.

N bond lengths (Table 1) are in agreement with those found in analogous aroylhydrazone copper complexes (Cheng *et al.*, 1996; Ruiz-Perez *et al.*, 1997; Cariati *et al.*, 2002).

The electron paramagnetic resonance spectrum of (I) is quasi-isotropic and asymmetric. The values of the *g* factors ($g_\perp$ = 2.180 and $g_\parallel$ = 2.047) are typical for square-planar compounds (David *et al.*, 2001; Sulekh & Rajiv, 2005).

Experimental

All reagents were of analytical grade, available commercially and used without further purification. *p*-Nitrobenzoic ethyl ester and *p*-nitrobenzoylhydrazine were prepared following the published procedure of Huang *et al.* (1997). The ligand was prepared by condensing 1 equivalent of salicylaldehyde and 1 equivalent of the corresponding *p*-nitrobenzoylhydrazine in ethanol (87.5% yield). The title compound was obtained by dissolving salicylaldehyde-*p*-nitrobenzoylhydrazone (0.0165 g, 0.05 mmol) in a mixture of dimethylformamide (2 ml) and methanol (6 ml), and adding a methanol solution (4 ml) containing $CuCl_2\cdot2H_2O$ (0.0170 g, 0.1 mmol) dropwise to the mixture. After 10 min, ten drops of morpholine were added. The mixture was then stirred at room temperature for 1 h and filtered. Blue block-shaped crystals of (I) formed upon slow evaporation of the filtrate over a period of two weeks.

Crystal data

$[Cu(C_{14}H_9N_3O_4)(C_4H_9NO)]$
$M_r = 433.90$
Monoclinic, $C2/c$
$a = 15.054\ (7)$ Å
$b = 6.538\ (3)$ Å
$c = 36.230\ (15)$ Å
$\beta = 95.800\ (6)^\circ$
$V = 3548\ (3)$ Å^3
$Z = 8$

$D_x = 1.625$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3892 reflections
$\theta = 2.3$–27.2°
$\mu = 1.27$ mm^{-1}
$T = 293\ (2)$ K
Block, blue
0.10 × 0.08 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.885$, $T_{max} = 0.938$
8552 measured reflections

3892 independent reflections
2581 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 27.2^\circ$
$h = -18 \rightarrow 19$
$k = -8 \rightarrow 8$
$l = -46 \rightarrow 34$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.120$
$S = 1.04$
3892 reflections
272 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 1.9541P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.886 (2)	O5—C16	1.414 (5)
Cu1—O2	1.923 (3)	N1—C7	1.279 (5)
Cu1—N1	1.924 (3)	N1—N2	1.406 (4)
Cu1—N4	2.019 (3)	N2—C8	1.294 (5)
O1—C1	1.312 (4)	N3—C12	1.456 (5)
O2—C8	1.296 (4)	N4—C15	1.470 (5)
O5—C17	1.414 (5)	N4—C18	1.477 (4)
O1—Cu1—O2	173.66 (10)	O4*B*—N3—C12	116.8 (11)
O1—Cu1—N1	93.38 (12)	C15—N4—C18	108.9 (3)
O2—Cu1—N1	81.24 (12)	C15—N4—Cu1	116.0 (2)
O1—Cu1—N4	92.24 (11)	C18—N4—Cu1	114.5 (2)
O2—Cu1—N4	93.30 (11)	O1—C1—C6	118.6 (3)
N1—Cu1—N4	173.77 (12)	O1—C1—C2	124.7 (3)
C1—O1—Cu1	127.1 (2)	N1—C7—C2	124.7 (3)
C8—O2—Cu1	110.3 (2)	N2—C8—O2	125.4 (4)
C17—O5—C16	110.1 (3)	N2—C8—C9	118.4 (3)
C7—N1—N2	117.8 (3)	O2—C8—C9	116.1 (3)
C7—N1—Cu1	127.4 (3)	C13—C12—N3	118.7 (4)
N2—N1—Cu1	114.6 (2)	C11—C12—N3	119.5 (3)
C8—N2—N1	108.4 (3)	N4—C15—C16	112.6 (3)
O3*B*—N3—O4*B*	124.3 (16)	O5—C16—C15	112.1 (4)
O3*B*—N3—C12	118.7 (12)	O5—C17—C18	111.6 (3)

All H atoms were placed in idealized positions (aromatic C—H = 0.93 Å, methine C—H = 0.93 Å, morpholine C—H = 0.97 Å and N—H = 0.91 Å) and refined using a riding model, with U_{iso} (H) = $1.5U_{eq}$(C); the isotropic displacement parameter of the H atom attached to N4 was allowed to vary freely. Atoms O3 and O4 of the nitro group are disordered over two positions; the final occupancy factors for the disordered atoms are both 0.5.

Data collection: *SMART* (Bruker, 1996); cell refinement: *SAINT* (Bruker, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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