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(Acetato-κO)[benzoylacetone (4-methoxybenzoyl)hydrazonato-$\kappa^3 O,N,O'$](pyridine-κN)zinc(II)

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Key indicators

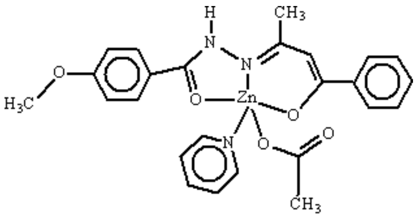
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.053
wR factor = 0.109
Data-to-parameter ratio = 17.3

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

The asymmetric unit of title complex, [Zn($C_{18}H_{17}N_2O_3$)($C_2H_3O_2$)(C_5H_5N)], consists of two independent Zn^{II} complex molecules, which are held together by N—H$\cdots$O hydrogen bonds, forming a dimer. Each Zn^{II} atom has a distorted trigonal–bipyramidal O_3N_2 configuration, defined by two O atoms and one N atom from the tridentate hydrazone ligand, one O atom from the acetate group and one N atom from pyridine molecule. The O atoms of the deprotonated hydrazone ligand occupy the axial sites.

Comment

Most hydrazone ligands are coordinated to the metal centre through their O/N atoms, which are similar to the coordination environments in biological system. Although a number of metal complexes with hydrazone ligands have been structurally characterized (Chen *et al.*, 1999; Gao *et al.*, 1998; Sangeetha *et al.*, 1999), there are few zinc hydrazonates in the list (Müller & Robson, 2000). The hydrazone ligands are readily synthesized by condensing thiosemicarbazone or its derivatives with, for example, acetylacetone (Toshev *et al.*, 1991) and salicylaldehyde (Gerbeleu *et al.*, 1990; Zelenin *et al.*, 1990; Cui & Hu, 1994). On the other hand, benzoylacetone (4-methoxybenzoyl)hydrazone (H_2L) is a potentially tridentate chelating agent. Recently, we have reported the structure of a Zn^{II} complex, *viz*. [Zn(HL)(OOCCH$_3$)(C_9H_7N)] (Gao *et al.*, 2004), with this ligand/zinc coordination mode. This coordination mode is also present in the title zinc complex, [Zn(HL)(OOCCH$_3$)(C_5H_5N)]$_2$, (I).



(I)

As shown in Fig. 1, the asymmetric unit of (I) contains two independent mononuclear complexes, which exist as a hydrogen-bonded dimer. The dimeric structure results from the interactions of the hydrazone N atoms (N2 and N5) with the free carbonyl O atoms (O10 and O5) of the actetate group [O$\cdots$N = 2.754 (3) and 2.787 (3) Å]. The Zn$\cdots$Zn separation is 7.116 (3) Å.

The hydrazone ligands are mono-deprotonated; the C11—O2 [1.248 (3) Å] and C36—O7 [1.257 (3) Å] distances are significantly shorter, indicating significant double-bond character. Both Zn1 and Zn2 possess distorted trigonal–bipyramidal geometry with N_2O_3 donor sets, defined by two O atoms and one N atom from the tridentate hydrazone ligand, one O atom from the acetate group and one N atom from pyridine molecule. The equatorial planes in the two molecules are defined by an imine N atom, an acetate O atom and a pyridine N atom; the apical positions are occupied by the O atoms of the hydrazone ligands [O1—Zn1—O2 = 162.62 (8)° and O6—Zn2—O7 = 155.27 (9)°].

The Zn—O and Zn—N bond distances (Table 1) are comparable with the corresponding bond distances observed in a related Zn^{II} hydrazone complex, *viz.* [Zn(H*L*)-(OOCCH$_3$)(C_9H_7N)] (Gao *et al.*, 2004). In one of the molecules of (I), that containing Zn1, the dihedral angle between two aromatic rings of the hydrazone ligand is 27.8 (2)°, whereas in the other (Zn2), the corresponding dihedral angle is 36.2 (2)°. The hydrazone ligands coordinated to the Zn^{II} cations in the tridentate coordination modes form six- and five-membered chelating rings, which are nearly planar.

Experimental

Benzoylacetone (4-methoxybenzoyl)hydrazone was synthesized by condensing benzoylacetone with an equimolar quantity of 4-methoxybenzoylhydrazine in ethanol. The title compound was prepared by the addition of zinc(II) acetate dihydrate (1 mmol) and pyridine (1 ml) to a methanol solution of benzoylacetone (4-methoxybenzoyl)hydrazone (1 mmol). The resulting mixture was refluxed with stirring for 30 min, then cooled slowly to room temperature and filtered. Yellow crystals separated from the solution after several days. Analysis calculated for $C_{25}H_{25}N_3O_5Zn$: C 58.55, H 4.91, N 8.19%; found: C 58.30, H 5.01, N 7.96%.

Crystal data

[Zn($C_{18}H_{17}N_2O_3$)($C_2H_3O_2$)\\-soft-return](C_5H_5N)]
$M_r = 512.87$
Triclinic, $P\overline{1}$
$a = 8.590$ (3) Å
$b = 11.631$ (3) Å
$c = 24.709$ (5) Å
$\alpha = 97.790$ (9)°
$\beta = 93.76$ (1)°
$\gamma = 103.828$ (9)°
$V = 2362.7$ (11) Å^3

$Z = 4$
$D_x = 1.442$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7440 reflections
$\theta = 3.2$–27.3°
$\mu = 1.08$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.38 × 0.26 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.684$, $T_{max} = 0.829$
22 995 measured reflections

10 723 independent reflections
6375 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 14$
$l = -27 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.109$
$S = 1.02$
10 723 reflections
619 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

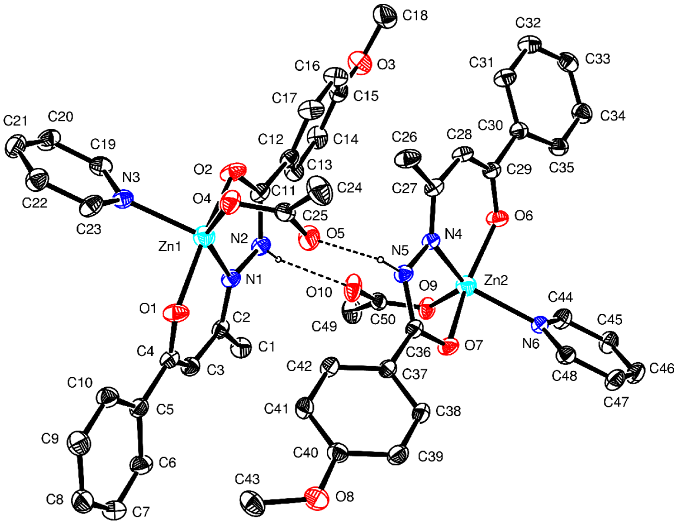


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I), with 30% probability displacement ellipsoids and N-bound H atoms represented by small spheres. The N—H···O hydrogen bonds forming the dimeric association are indicated by dashed lines. C-bound H atoms have been omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

Zn1—N1	2.048 (2)	N4—C27	1.315 (3)
Zn1—N3	2.094 (2)	O1—C4	1.288 (3)
Zn1—O1	2.025 (2)	O2—C11	1.248 (3)
Zn1—O2	2.173 (2)	O6—C29	1.284 (3)
Zn1—O4	2.015 (2)	O7—C36	1.257 (3)
Zn2—N4	2.043 (2)	C3—C4	1.387 (4)
Zn2—N6	2.100 (2)	C28—C29	1.378 (4)
Zn2—O6	2.012 (2)	N1—N2	1.395 (3)
Zn2—O7	2.162 (2)	N2—C11	1.338 (3)
Zn2—O9	1.966 (2)	N4—N5	1.391 (3)
N1—C2	1.320 (3)	N5—C36	1.339 (3)
N1—Zn1—N3	122.9 (1)	O4—Zn1—N3	93.10 (9)
N1—Zn1—O2	75.94 (8)	O4—Zn1—O1	96.91 (9)
N3—Zn1—O2	91.40 (9)	O4—Zn1—O2	99.56 (9)
N4—Zn2—N6	135.00 (9)	O6—Zn2—N4	88.92 (8)
N4—Zn2—O7	75.86 (8)	O6—Zn2—N6	90.05 (9)
N6—Zn2—O7	87.32 (8)	O6—Zn2—O7	155.27 (9)
O1—Zn1—N1	87.51 (9)	O9—Zn2—N4	122.66 (8)
O1—Zn1—N3	93.24 (9)	O9—Zn2—N6	101.90 (8)
O1—Zn1—O2	162.62 (8)	O9—Zn2—O6	99.12 (9)
O4—Zn1—N1	143.50 (9)	O9—Zn2—O7	105.49 (9)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H51···O10	0.86	2.06	2.754 (3)	138
N5—H52···O5	0.86	1.96	2.787 (3)	162

H atoms were placed in calculated positions, with C—H = 0.93 (aromatic) or 0.96 Å (methyl) and N—H = 0.86 Å (imino group), and with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}$(methyl), in the riding-model approximation.

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Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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