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(Acetato-κO)[butane-2,3-dione monooxime benzoylhydrazonato-$\kappa^3 O,N^2,O'$]bis(pyridine-κN)nickel(II)

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In the title complex, $[Ni(C_{11}H_{12}N_3O_2)(C_2H_3O_2)(C_5H_5N)_2]$, the Ni^{II} atom exhibits a distorted octahedral geometry, with two N atoms and one O atom of a tridentate butane-2,3-dione monooxime benzoylhydrazone ligand and one acetate O atom in the equatorial plane, and two pyridine N atoms in the axial sites. The uncoordinated acetate O atom forms an intramolecular hydrogen bond with the oxime O atom of the hydrazone ligand, with an O$\cdots$O distance and an O—H$\cdots$O angle of 2.541 (4) Å and 176 (5)°, respectively.

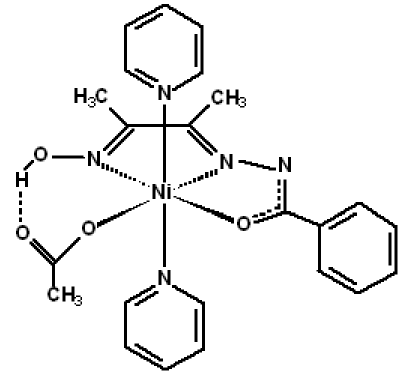
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.038
wR factor = 0.087
Data-to-parameter ratio = 16.1

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

Comment

Transition metal–hydrazone complexes, in which the hydrazone ligands are formed by condensing hydrazine with β-diketones, salicylaldehydes and their derivatives, have been studied extensively in the past few decades (Gao *et al.*, 1998; Liu & Gao, 1998). However, only one structure of a copper complex containing the butane-2,3-dione monooxime benzoylhydrazone ligand has been reported to date (Chumakov *et al.*, 1979). Recently, we have reported the structures of two zinc complexes, $[Zn(HL)(C_9H_7N)(OOCCH_3)]\cdot 0.5C_9H_7N$ and $[Zn(HL)(C_2H_3O_2)(C_3H_4N_2)]$ (H_2L is diacetyl monoxime benzoylhydrazone), in which the Zn atoms are in a geometry that is intermediate between square pyramidal and trigonal bipyramidal (Gao *et al.*, 2004; Huo *et al.*, 2004). In order to gain more insight into the metal-binding modes of this ligand, we synthesized the title compound, $[Ni(HL)(OOCCH_3)(C_5H_5N)_2]$, (I), by the reaction of nickel(II) acetate tetrahydrate, pyridine and diacetyl monooxime benzoylhydrazone in methanol solution; the crystal structure of (I) is reported here.



(I)

The molecular structure of (I) (Fig. 1) consists of a tridentate HL^- ligand, two pyridine molecules and one acetate group coordinated to Ni^{II}, which has a distorted octahedral

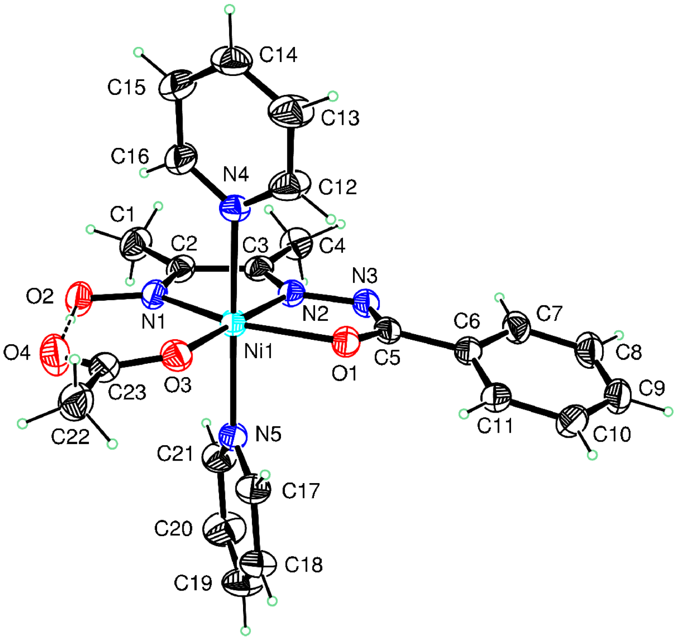


Figure 1

*ORTEP*II plot of the title complex, with 30% probability displacement ellipsoids. The O—H···O hydrogen bond is denoted by a dashed line.

coordination geometry. Its equatorial plane is defined by atoms N1, N2 and O1 of the tridentate hydrazone ligand and acetate atom O3 (the deviation from the mean plane being 0.02 Å), while the axial positions are occupied by two N atoms of pyridine molecules, the N4—Ni1—N5 angle being 174.5 (1)°. The Ni—N2 bond is significantly shorter than the other three Ni—N bond distances (Table 1), suggesting a much stronger Ni—N2 contact. The dihedral angle between the equatorial plane and the aromatic ring of the hydrazone ligand is 17.7 (1)°, while the pyridine rings are almost perpendicular to the benzene ring plane [89.3 (1) and 81.4 (1)°], and the dihedral angle between the two pyridine rings is 41.7 (2)°. The N2—N3 distance is intermediate between single- and double-bond lengths, indicating that the azo group is involved in resonance. The N1—C2, N2—C3, N3—C5, O1—C5 and C2—C3 bond lengths also suggest electron delocalization in the hydrazone ligand. Oxime atom O2 of the hydrazone ligand forms an intramolecular O—H···O hydrogen bond (Table 2) with the uncoordinated acetate O atom.

Experimental

The diacetyl monooxime benzoylhydrazone ligand was synthesized by condensing benzoylhydrazine (0.01 mol) with equimolar diacetyl monooxime (0.01 mol) in ethanol (50 ml) for 3.5 h, and the hydrazone ligand was isolated by crystallization form the resulting solution. A methanol solution containing nickel(II) acetate tetrahydrate (1 mmol) and pyridine (1 ml) was added dropwise to a 15 ml methanol solution of the hydrazone ligand (1 mmol). The resulting mixture was refluxed with stirring for 0.5 h, cooled slowly to room temperature and filtered. Green crystals were isolated from the solution after seven days. Analysis calculated for $C_{23}H_{25}N_5NiO_4$: C 55.90, H 5.10, N 14.17%; found: C 55.73, H 5.19, N 14.03%.

Crystal data

$[Ni(C_{11}H_{12}N_3O_2)(C_2H_3O_2)(C_5H_5N)_2]$
$M_r = 494.17$
Monoclinic, *Cc*
$a = 12.378$ (1) Å
$b = 14.770$ (1) Å
$c = 13.3291$ (7) Å
$\beta = 99.073$ (4)°
$V = 2406.4$ (3) Å^3
$Z = 4$
$D_x = 1.364$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 153 reflections
$\theta = 3.1$–27.5°
$\mu = 0.84$ mm^{-1}
$T = 293$ (2) K
Prism, green
0.38 × 0.25 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.739$, $T_{max} = 0.863$
11 139 measured reflections
4892 independent reflections
4039 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 27.5°$
$h = -14 \rightarrow 16$
$k = -19 \rightarrow 19$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.087$
$S = 1.06$
4892 reflections
304 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.1684P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Absolute structure: Flack (1983), 2313 Friedel pairs.
Flack parameter = 0.02 (1)

Table 1

Selected geometric parameters (Å, °).

Ni1—N1	2.102 (2)	N2—N3	1.380 (3)
Ni1—N2	1.982 (3)	C2—C3	1.469 (4)
Ni1—N5	2.130 (3)	N1—C2	1.294 (4)
Ni1—N4	2.165 (3)	N2—C3	1.288 (4)
Ni1—O1	2.106 (2)	N3—C5	1.328 (4)
Ni1—O3	2.020 (3)	O1—C5	1.286 (4)
N1—Ni1—N4	91.7 (1)	N5—Ni1—N4	174.5 (1)
N1—Ni1—N5	92.7 (1)	O1—Ni1—N4	91.04 (9)
N1—Ni1—O1	153.4 (1)	O1—Ni1—N5	86.51 (9)
N2—Ni1—N1	76.2 (1)	O3—Ni1—N1	107.5 (1)
N2—Ni1—N4	91.8 (1)	O3—Ni1—N4	87.2 (1)
N2—Ni1—N5	92.5 (1)	O3—Ni1—N5	88.3 (1)
N2—Ni1—O1	77.28 (9)	O3—Ni1—O1	99.06 (9)
N2—Ni1—O3	176.21 (9)		

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H24···O4	0.86 (4)	1.68 (3)	2.541 (4)	176 (5)

The H atoms on C atoms were placed in calculated positions and refined in the riding-model approximation, with C—H = 0.93 (aromatic) and 0.96 Å (methyl) and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$. The H atom on the oxime O atom was located in a difference Fourier map and refined with an O—H distance restraint of 0.85 (1) Å [$U_{iso}(H) = 1.5U_{eq}(O)$].

Data collection: *RAPID-AUTO* (Rigaku Corporation, 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

Acta Cryst. (2004). E**60**, m1450–m1452 Huo *et al.* • $[Ni(C_{11}H_{12}N_3O_2)(C_2H_3O_2)(C_5H_5N)_2]$ **m1451**

(Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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