Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

(Acetato-κ*O*)[diacetyl monooxime (4-methoxybenzoyl)hydrazonato-κ^3*O*,*N*,*N*′]bis(pyridine-κ*N*)nickel(II)

Shan Gao,* Li-Hua Huo, Zhao-Peng Deng and Hui Zhao

School of Chemistry and Materials Science, Heilongjiang University, Harbin, 150080, People's Republic of China

Correspondence e-mail: shangao67@yahoo.com

Received 10 December 2004
Accepted 16 December 2004
Online 24 December 2004

Key indicators

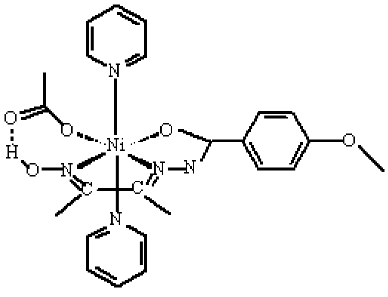
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
R factor = 0.041
wR factor = 0.104
Data-to-parameter ratio = 17.4

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

In the title complex, $[Ni(C_{12}H_{14}N_3O_3)(C_2H_3O_2)(C_5H_5N)_2]$, the Ni^{II} atom is six-coordinated by two N atoms and one O atom from a tridentate hydrazone ligand, two N atoms from two pyridine molecules, and one O atom from an acetate group, leading to a distorted octahedral geometry. The two N atoms of the pyridine molecules occupy the axial sites and the other four coordinated atoms define the equatorial plane. The uncoordinated acetate O atom forms an intramolecular hydrogen bond with the oxime O atom of the hydrazone ligand.

Comment

Transition-metal hydrazone complexes, in which the hydrazone ligands are formed by condensing hydrazine with β-diketones, salicylaldehydes and their derivatives, have been extensively studied in the past few decades (Aruffo *et al.*, 1982; Gao *et al.*, 1998; Gao, Liu *et al.*, 2004; Liu & Gao, 1998). However, there are few metal complexes containing hydrazone ligands formed by diacetyl monoxime (Chumakov *et al.*, 1979; Gao, Huo, Liu *et al.*, 2004; Huo, Gao *et al.*, 2004; Huo, Lu, Gao, Zhao & Ng, 2004). Recently, we have reported two mononuclear Ni^{II} complexes with the diacetyl monoxime benzoylhydrazone ligand, in which the Ni^{II} atoms have a distorted octahedral geometry and the diacetyl monoxime benzoylhydrazone ligand bears a formal charge of −1 or is a nuclear tridentate ligand (Gao, Huo, Zhao & Ng, 2004; Huo, Lu, Gao & Zhao, 2004). In order to obtain more information about metal-binding modes of this kind of hydrazone 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 *N*-(diacetyl monoxime)-*N*′-(4-methoxybenzoyl)hydrazone in methanol solution; the crystal structure is reported here.



(I)

As shown in Fig. 1, the uncoordinated oxime atom, O1, remains protonated, so that the organic hydrazone ligand (H_2L) bears a formal charge of −1. The Ni^{II} atom has a

doi:10.1107/S1600536804033495

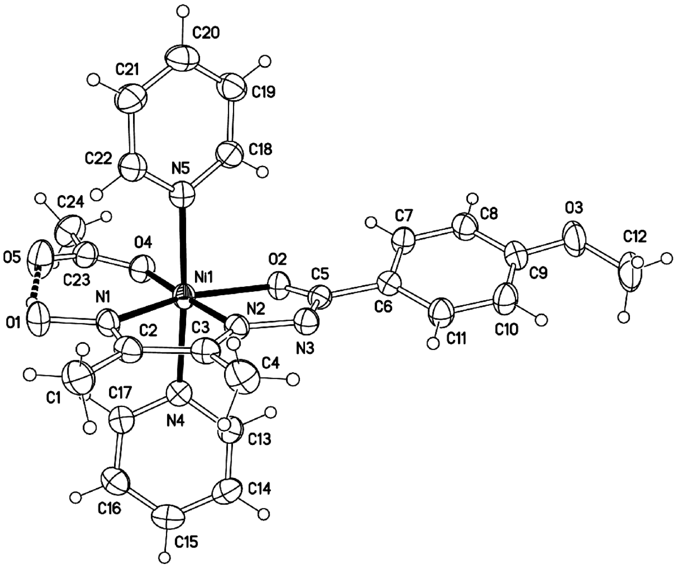


Figure 1

ORTEPII plot (Johnson, 1976) of the title complex, with displacement ellipsoids drawn at the 30% probability level. The hydrogen bond is shown as a dashed line.

distorted octahedral geometry, with an N_4O_2 donor set defined by two O atoms and one N atom from the tridentate hydrazone HL^- ligand, and two N atoms from two pyridine molecules and one acetate O atom. The equatorial plane is defined by atoms N1, N2 and O2 of the tridentate hydrazone ligand and acetate atom O4 [the deviation from the mean plane being 0.01 (3) Å and the displacement of the Ni^{II} atom from this plane being 0.015 (3) Å], while the axial positions are occupied by two N atoms of pyridine molecules, the N4—Ni1—N5 angle being 175.99 (7)°. The Ni—N2 bond is significantly shorter than the other Ni—N and Ni—O bond distances (Table 1). The coordination configuration of (I) is similar to that of the reported $[Ni(HL')(OOCCH_3)(C_5H_5N)_2]$ complex [where H_2L' is *N*-(diacetyl monoxime)-*N'*-(benzoyl)hydrazone; Huo, Lu, Gao & Zhao, 2004).

The two five-membered chelate rings, N1/C2/C3/N2/Ni1 and O2/C5/N3/N2/Ni1, are each essentially planar, with mean deviations of 0.02 (3) and 0.03 (3) Å, respectively. The aromatic ring (C6–C11) makes a dihedral angle of 21.5 (3)° with the N1/C2/C3/N2/N3/O2 fragment. The dihedral angle between the two pyridine rings is 35.7 (3)°. The N1—C2, N2—C3, N3—C5 and O2—C5 bond lengths suggest electron delocalization in the hydrazone ligand. Oxime atom O1 of the hydrazone ligand forms an intramolecular O—H···O hydrogen bond (Table 2) with the uncoordinated acetate O atom.

Experimental

The diacetyl monoxime (4-methoxybenzoyl)hydrazone ligand was synthesized by condensing (4-methoxybenzoyl)hydrazine (0.05 mol) with an equimolar quantity of diacetyl monoxime (0.05 mol) in ethanol (100 ml) for 2.5 h, and the hydrazone ligand was isolated as yellow crystals from the resulting solution. The title compound was prepared by the addition of nickel(II) acetate tetrahydrate (1 mmol) and pyridine (1 ml) to a methanol solution (15 ml) of the hydrazone ligand (1 mmol). The mixture was refluxed for 0.5 h, cooled slowly to room temperature and filtered. Red–brown crystals were isolated from the solution after five days. Analysis calculated for $C_{24}H_{27}N_5NiO_5$: C 54.99, H 5.19, N 13.35%; found: C 54.93, H 5.09, N 13.23%.

Crystal data

$[Ni(C_{12}H_{14}N_3O_3)(C_2H_3O_2)(C_5H_5N)_2]$
$M_r = 524.20$
Triclinic, $P\bar{1}$
$a = 8.1027$ (16) Å
$b = 12.668$ (3) Å
$c = 13.436$ (3) Å
$\alpha = 110.74$ (3)°
$\beta = 92.41$ (3)°
$\gamma = 103.37$ (3)°
$V = 1243.1$ (6) Å^3
$Z = 2$
$D_x = 1.400$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 312 reflections
$\theta = 3.0$–27.4°
$\mu = 0.82$ mm^{-1}
$T = 296$ (2) K
Prism, brown
0.34 × 0.25 × 0.13 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.767$, $T_{max} = 0.900$
12 322 measured reflections
5635 independent reflections
4089 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -16 \rightarrow 16$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.104$
$S = 1.05$
5635 reflections
323 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 0.0609P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Ni1—N2	1.988 (2)	N1—C2	1.294 (3)
Ni1—O4	2.0144 (18)	N2—C3	1.302 (3)
Ni1—O2	2.0794 (16)	N2—N3	1.379 (3)
Ni1—N1	2.107 (2)	N3—C5	1.347 (3)
Ni1—N4	2.140 (2)	O1—N1	1.381 (3)
Ni1—N5	2.154 (2)	O2—C5	1.271 (3)
N1—Ni1—N4	87.34 (8)	O2—Ni1—N1	153.30 (8)
N1—Ni1—N5	90.85 (8)	O2—Ni1—N4	92.89 (7)
N2—Ni1—N1	76.48 (8)	O2—Ni1—N5	90.34 (7)
N2—Ni1—N4	90.22 (8)	O4—Ni1—N1	108.63 (8)
N2—Ni1—N5	92.84 (8)	O4—Ni1—N4	88.55 (8)
N2—Ni1—O2	76.81 (7)	O4—Ni1—N5	88.64 (8)
N2—Ni1—O4	174.67 (7)	O4—Ni1—O2	98.06 (7)
N4—Ni1—N5	175.99 (7)		

Table 2

Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H25···O5	0.85 (3)	1.73 (3)	2.552 (3)	163 (3)

H atoms on C atoms were placed in calculated positions [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atom, C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms] and were included in the refinement in the riding-model approximation. The H atom on the oxime O atom was located in a difference Fourier map and refined with the O—H distance restrained to 0.85 (1) Å and 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: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors thank the National Natural Science Foundation of China (No. 20101003), the Scientific Fund of Remarkable Teachers of Heilongjiang Province (No. 1054 G036) and Heilongjiang University for supporting this study.

References

Aruffo, A. A., Murphy, T. B., Johnson, D. K., Rose, N. J. & Schomaker, V. (1982). *Inorg. Chim. Acta*, **67**, L25–L27.

Chumakov, Y. M., Mazus, M. D., Byushkin, V. N., Belichuk, N. I. & Malinovskii, T. I. (1979). *Izv. Akad. Nauk Mold. SSR Ser. Fiz. Tekh. Mater. Nauk*, **3**, 83–86.

Gao, S., Huo, L.-H., Liu, J.-W., Wang, C., Zhao, J.-G. & Ng, S. W. (2004). *Acta Cryst.* E**60**, m644–m646.

Gao, S., Huo, L.-H., Zhao, H. & Ng, S. W. (2004). *Acta Cryst.* E**60**, m1750–m1751.

Gao, S., Liu, J.-W., Huo, L.-H. & Zhao H. (2004). *Acta Cryst.* E**60**, m1722–m1724.

Gao, S., Weng, Z.-Q. & Liu, S.-X. (1998). *Polyhedron*, **17**, 3595–3606.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Huo, L.-H., Gao, S., Liu, J.-W., Wang, C. & Zhao, J.-G. (2004). *Acta Cryst.* E**60**, m696–m698.

Huo, L.-H., Lu, Z.-Z., Gao, S. & Zhao, H. (2004). *Acta Cryst.* E**60**, m1450–1452.

Huo, L.-H., Lu, Z.-Z., Gao, S., Zhao, H. & Ng, S. W. (2004). *Acta Cryst.* E**60**, m1611–m1613.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA.

Liu, S.-X. & Gao, S. (1998). *Polyhedron*, **17**, 81–84.

Rigaku Corporation (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.

Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.