

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: CR1174). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## {1-[(2-Hydroxybenzylidene)aminomethyl]-naphthalen-2-olato(2-)-N,O,O'}(piperidine-N)nickel(II)

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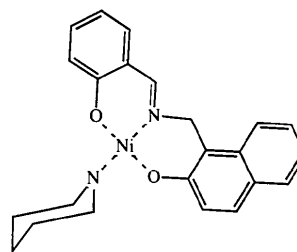
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## Abstract

The crystal structure of the title compound, [Ni(C<sub>18</sub>H<sub>13</sub>NO<sub>2</sub>)(C<sub>5</sub>H<sub>11</sub>N)], has been determined. The molecules have the *trans* form, as imposed by the geometry of the tridentate and monodentate ligands, and the Ni is in a slightly distorted square-planar environment.

## Comment

Schiff base complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety (Garnovskii, Nivorozhkin & Minkin, 1993). Recently, the structure of {1-[(2-hydroxyphenyl)aminomethyl]-naphthalen-2-olato-*O,O',N*}piperidinenickel(II) (Elerman, Paulus & Fuess, 1991) was reported in which the nickel(II) ion reacts with both the monodentate piperidine ligand and the tridentate ligand *N*-(2-hydroxyphenyl)-2-hydroxy-1-naphthaldimine. The purpose of this study is to examine the molecular configuration when the Ni atom reacts with both the tridentate ligand *N*-(2-hydroxy-1-naphthyl-methyl)salicylaldimine, instead of *N*-(2-hydroxyphenyl)-2-hydroxy-1-naphthaldimine in the previous work, and the monodentate piperidine ligand. Both coordinate to nickel(II), producing the title compound, (I).



(I)

In the previous work (Elerman *et al.*, 1991), the coordination of the ligands around the Ni atom was found to be almost planar and the angles between the planar organic groups were found to be smaller than 8°. In the title compound, (I), however, the methyl group plays a predominant role in the distortion of the molecule as a whole. The title molecule is twisted about the C1—O1 direction with torsion angles N1—C1—C2—C11 = -56.5 (6), C2—C11—O1—Ni = 55.1 (5), N1—C1—C2—C3 = 122.8 (5) and C10—C11—O1—Ni = -126.7 (4)°. The angle between the naphthaldimine ligand and the coordination plane of nickel(II) was found to be 49°, whereas the angle between the salicylaldimine and the coordination plane of nickel(II) is only 7°. The distortion can be seen in the crystal packing diagram (Fig. 2).

A strictly planar or slightly distorted *trans* configuration is characteristic for transition metal complexes of Ni<sup>II</sup> with an NiN<sub>2</sub>O<sub>2</sub> coordination sphere (Garnovskii *et al.*, 1993). In agreement with this, the Ni atom is in a slightly distorted *trans*-square-planar environment of two O atoms [1.829 (4) and 1.857 (4) Å] and two N atoms [1.859 (4) and 1.943 (4) Å] with O—Ni—N angles between 84.8 (2) and 95.2 (2)°. The Ni—O and Ni—N distances are longer than the values determined by the previous work.

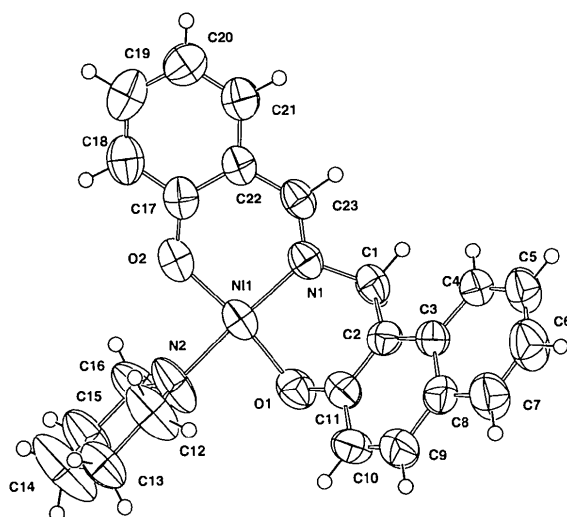


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are plotted at the 50% probability level.

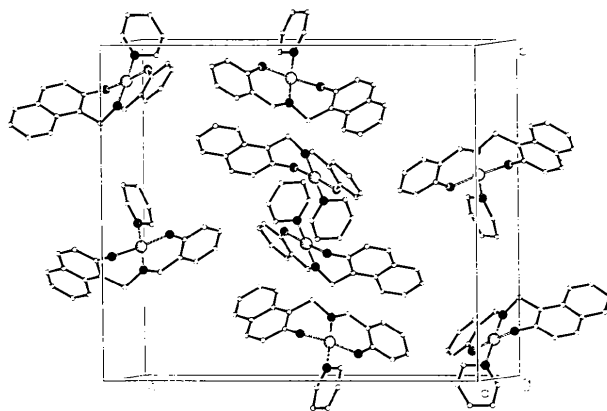


Fig. 2. Unit-cell packing diagram for the title compound.

## Experimental

A solution of 5 mmol of *N*-(2-hydroxy-1-naphthylmethyl)-salicylaldehyde in 50 ml of pure ethanol was prepared and 1.5 ml of piperidine was slowly added. 5 mmol of  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  was dissolved, by dropwise addition, in 30 ml of hot methanol. A mixture of the two solutions was then refluxed for 5 h. Red crystals were formed during the reflux operation and washed twice with ethanol. Elemental analysis was consistent with the formula  $\text{C}_{23}\text{H}_{24}\text{N}_2\text{NiO}_2$ .

### Crystal data

$[\text{Ni}(\text{C}_{18}\text{H}_{13}\text{NO}_2)(\text{C}_5\text{H}_{11}\text{N})]$   
 $M_r = 419.14$   
 Orthorhombic  
*Pbca*  
 $a = 9.313(1) \text{ \AA}$   
 $b = 19.202(3) \text{ \AA}$   
 $c = 22.330(3) \text{ \AA}$   
 $V = 3993.2(9) \text{ \AA}^3$

Mo  $K\alpha$  radiation  
 $\lambda = 0.7107 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 2.59\text{--}13.80^\circ$   
 $\mu = 0.992 \text{ mm}^{-1}$   
 $T = 297(2) \text{ K}$   
 Prism

$Z = 8$   
 $D_x = 1.394(3) \text{ Mg m}^{-3}$

$0.28 \times 0.28 \times 0.05 \text{ mm}$   
 Red

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  $\psi$  scan (North, Phillips & Mathews, 1968)  
 $T_{\min} = 0.879$ ,  $T_{\max} = 0.997$   
 3035 measured reflections  
 2774 independent reflections

1457 observed reflections [ $I > 2\sigma(I)$ ]  
 $R_{\text{int}} = 0.0607$   
 $\theta_{\max} = 22.98^\circ$   
 $h = -10 \rightarrow 1$   
 $k = 0 \rightarrow 21$   
 $l = 0 \rightarrow 24$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 1.9%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.0377$   
 $wR(F^2) = 0.0886$   
 $S = 1.063$   
 2774 reflections  
 253 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 3.3116P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$   
 $\Delta\rho_{\max} = 0.255 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.293 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Ni	0.09051 (7)	0.10721 (3)	0.05803 (3)	0.0607 (3)
N1	-0.0417 (5)	0.1790 (2)	0.0487 (2)	0.057 (1)
C1	-0.0152 (6)	0.2307 (2)	0.0008 (2)	0.061 (1)
C2	0.0095 (5)	0.1956 (2)	-0.0584 (3)	0.054 (1)
C3	-0.0714 (6)	0.2080 (2)	-0.1102 (2)	0.054 (1)
C4	-0.1886 (5)	0.2550 (3)	-0.1139 (3)	0.064 (1)
C5	-0.2621 (7)	0.2663 (3)	-0.1653 (3)	0.080 (2)
C6	-0.2238 (8)	0.2303 (4)	-0.2174 (3)	0.096 (2)
C7	-0.1118 (8)	0.1858 (3)	-0.2170 (3)	0.092 (2)
C8	-0.0335 (6)	0.1725 (3)	-0.1644 (3)	0.066 (2)
C9	0.0851 (7)	0.1269 (3)	-0.1637 (3)	0.080 (2)
C10	0.1582 (6)	0.1140 (3)	-0.1126 (3)	0.076 (2)
C11	0.1207 (5)	0.1476 (2)	-0.0586 (3)	0.059 (1)
O1	0.1950 (4)	0.1344 (2)	-0.0089 (2)	0.070 (1)
N2	0.2337 (6)	0.0341 (2)	0.0652 (2)	0.096 (2)
C12	0.2113 (7)	-0.0260 (3)	0.0353 (3)	0.104 (2)
C13	0.3204 (6)	-0.0830 (3)	0.0373 (3)	0.084 (2)
C14	0.4173 (9)	-0.0814 (4)	0.0878 (4)	0.159 (4)
C15	0.4370 (7)	-0.0198 (3)	0.1188 (3)	0.111 (3)
C16	0.3240 (7)	0.0354 (3)	0.1139 (3)	0.095 (2)
O2	0.0073 (4)	0.0715 (2)	0.1256 (2)	0.073 (1)
C17	-0.1163 (6)	0.0892 (3)	0.1493 (2)	0.062 (2)
C18	-0.1670 (7)	0.0521 (3)	0.1989 (3)	0.079 (2)
C19	-0.2968 (8)	0.0665 (4)	0.2250 (3)	0.084 (2)
C20	-0.3801 (7)	0.1205 (3)	0.2036 (3)	0.080 (2)
C21	-0.3335 (6)	0.1589 (3)	0.1562 (3)	0.074 (2)
C22	-0.2014 (6)	0.1444 (3)	0.1290 (2)	0.060 (1)
C23	-0.1562 (6)	0.1869 (3)	0.0802 (2)	0.059 (1)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Ni—O2	1.829 (4)	C10—C11	1.412 (7)
Ni—O1	1.857 (4)	C11—O1	1.334 (6)
Ni—N1	1.859 (4)	N2—C12	1.348 (7)
Ni—N2	1.943 (4)	N2—C16	1.376 (6)
N1—C23	1.287 (6)	C12—C13	1.494 (7)
N1—C1	1.479 (6)	C13—C14	1.444 (8)
C1—C2	1.502 (6)	C14—C15	1.383 (8)
C2—C11	1.386 (6)	C15—C16	1.497 (7)

C2—C3	1.400 (6)	O2—C17	1.312 (6)
C3—C4	1.418 (7)	C17—C18	1.398 (7)
C3—C8	1.435 (7)	C17—C22	1.399 (7)
C4—C5	1.354 (7)	C18—C19	1.371 (8)
C5—C6	1.400 (8)	C19—C20	1.381 (8)
C6—C7	1.348 (8)	C20—C21	1.359 (7)
C7—C8	1.405 (8)	C21—C22	1.400 (7)
C8—C9	1.409 (7)	C22—C23	1.426 (7)
C9—C10	1.351 (7)		
O2—Ni—O1	172.0 (2)	O1—C11—C10	119.8 (5)
O2—Ni—N1	95.2 (2)	C11—O1—Ni	116.9 (3)
O1—Ni—N1	92.8 (2)	C12—N2—C16	120.2 (5)
O2—Ni—N2	87.3 (2)	C12—N2—Ni	118.1 (4)
O1—Ni—N2	84.8 (2)	C16—N2—Ni	118.1 (4)
N1—Ni—N2	177.5 (2)	N2—C12—C13	120.4 (5)
C23—N1—C1	117.0 (4)	N2—C16—C15	118.3 (5)
C23—N1—Ni	125.1 (4)	C17—O2—Ni	127.4 (3)
C1—N1—Ni	117.9 (3)	O2—C17—C18	119.0 (5)
N1—C1—C2	111.1 (4)	O2—C17—C22	124.2 (5)
O1—C11—C2	120.7 (5)	N1—C23—C22	126.5 (5)

The structure was solved by direct phase determination. The parameters of the complete structure could be refined by full-matrix least squares. All phenyl rings were refined without any constraints. Values of distances and angles in the rings show no significant differences from those of an ideal benzene ring. The H atom on the piperidine N atom was not located; other H atoms were treated using a riding model with fixed isotropic *U*'s.

Data collection: *SDP* (Frenz, 1985). Cell refinement: *SDP*. Data reduction: *REDU4* (Stoe & Cie, 1988). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLUTON93* (Spek, 1993); *Xtal* (Hall, Flack & Stewart, 1992). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: J21023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## The Helical Packing of a Chiral Alkyl Cobaloxime in the Solid State

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### Abstract

Three units of the chiral title complex, (4-*tert*-butylpyridine-*N*)bis(dimethylglyoximate-*N,N'*)[(*R*)-6-hepten-2-yl]cobalt(III), [Co(C<sub>7</sub>H<sub>13</sub>)(C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>(C<sub>9</sub>H<sub>13</sub>N)], form one complete turn of a right-handed screw along the crystallographic *c* axis. The molecule shows a long C—Co bond [2.086 (7) Å] and a significant distortion in the hybridization of the Co-bound C atom from *sp*<sup>3</sup> towards *sp*<sup>2</sup> [C28—C27—C29 = 120.9 (6), Co—C27—C29—C30 = −172 (1) and C28—C27—C29—C30 = 41 (2)°].

### Comment

In the course of several mechanistic studies with alkylbis(dimethylglyoximate)(pyridine)cobalt(III) complexes [*i.e.* alkyl(pyridine)cobaloximes] (Branchaud, Meier & Malekzadeh, 1987; Giese & Hartung, 1992; Hartung, Hertel & Trach, 1993), primary alkylcobaloximes proved to be less prone to photolytic cleavage of the Co—C bond upon irradiation with incandescent light than the secondary derivatives. These findings were attributed to larger steric interactions between secondary alkyl and the two dimethylglyoxime ligands compared to the strain between a primary alkyl residue and the equatorial macrocycle (Halpern, 1985). In order to ob-

