C7	0.5838 (4)	0.5983 (6)	0.8669 (3)	0.0305 (8)
C8	0.5304 (5)	0.7934 (7)	0.8135 (4)	0.0529 (14)
C9	0.5370 (5)	0.8028 (7)	0.6967 (4)	0.0530 (14)
C10	0.5564 (3)	0.5902 (6)	0.6458 (3)	0.0277 (8)

Table 2. *Selected geometric parameters (Å, °)*

Rh1—O1	2.065 (2)	C3—C10	1.386 (5)
Rh1—O1^{i}	2.074 (2)	C3—C4	1.528 (6)
Rh1—C7	2.088 (4)	C4—C5	1.465 (6)
Rh1—C6	2.091 (4)	C5—C6	1.512 (6)
Rh1—C10	2.094 (4)	C6—C7	1.394 (6)
Rh1—C3	2.104 (4)	C7—C8	1.525 (6)
O1—C1	1.417 (4)	C8—C9	1.461 (7)
O1—Rh1^{i}	2.074 (2)	C9—C10	1.513 (5)
C1—C2	1.500 (6)		
O1—Rh1—O1^{i}	75.49 (11)	O1—C1—C2	111.7 (3)
C7—Rh1—C6	39.0 (2)	C10—C3—C4	123.1 (4)
C7—Rh1—C10	81.8 (2)	C5—C4—C3	113.8 (4)
C6—Rh1—C10	96.7 (2)	C4—C5—C6	115.6 (3)
C7—Rh1—C3	92.8 (2)	C7—C6—C5	124.2 (4)
C6—Rh1—C3	82.46 (15)	C6—C7—C8	122.4 (4)
C10—Rh1—C3	38.5 (2)	C9—C8—C7	113.8 (4)
C1—O1—Rh1	127.2 (2)	C8—C9—C10	113.8 (4)
C1—O1—Rh1^{i}	127.7 (2)	C3—C10—C9	126.3 (4)
Rh1—O1—Rh1^{i}	87.16 (9)		

Symmetry code: (i) $\frac{3}{2} - x, y, \frac{3}{2} - z$.

The C7—H7 bond length was restrained. All H-atom parameters were refined except for those of H41, H42, H51, H52, H81, H82, H91, H92 and H10, which were refined using a riding model.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971). Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[*N*-(2-Mercaptophenyl)-2-hydroxynaphthaldiminato](pyridine)nickel(II)

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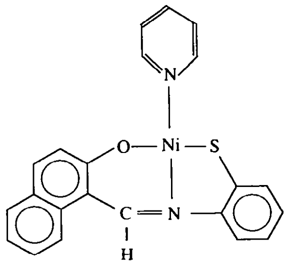
Abstract

The central Ni^{2+} ion in the title complex {systematic name: [1-(2-mercaptophenyliminomethyl)-2-naphtholato-*O*,*N*,*S*](pyridine-*N*)nickel(II); $[Ni(C_{17}H_{11}NOS)(C_5H_5N)]$} is in a slightly distorted square-planar environment of S, O and N atoms. The Ni^{2+} ion is 0.001 (1) Å out of the coordination plane.

Comment

Schiff base complexes have continued to be versatile stereochemical models in main group and transition metal coordination chemistry because of their facile preparation and structural variation (Garnovskii, Nivorozhkin & Minkin, 1993). The purpose of the present study is to elucidate what happens when the nickel(II) ion reacts with the monodentate pyridine ligand and the tridentate 2-mercaptophenyl-2-hydroxynaphthaldehyde ligand. The structure of the resulting complex, (I), has been determined.



(I)

The monodentate and tridentate ligands of (I) are coordinated to nickel(II) in a square-planar configuration (Fig. 1). The bond lengths of several complexes of *N*-substituted salicylaldimines are compared with the present results in Table 3.

The Ni—O and Ni—S distances are 1.843 (2) and 2.141 (2) Å, respectively. The Ni—N1 bond length of 1.862 (2) Å, however, is definitely shorter than Ni—N2 and other literature Ni—N distances. The reason for this

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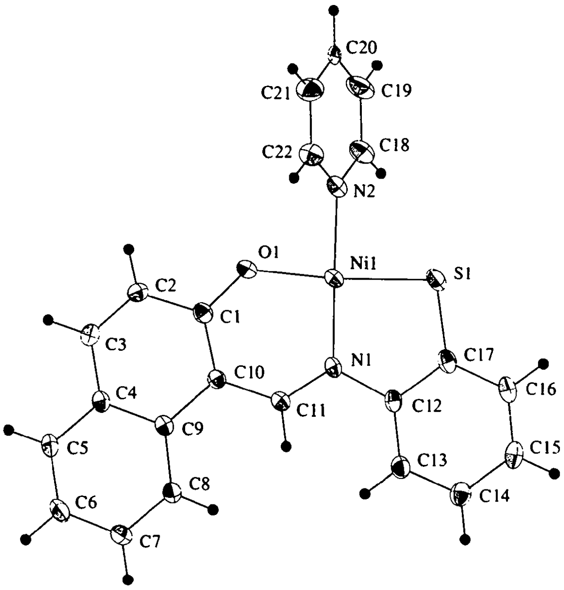

Fig. 1. The molecular structure and atomic labelling scheme of the title compound. Displacement ellipsoids are plotted at the 50% probability level.

is that the O and S atoms coordinated to the Ni atom draw the whole ligand, and therefore also the N atom, towards the Ni atom. This short length agrees with the Ni—N1 bond distances found in [1-(2-hydroxyphenyliminomethyl)-2-naphtholato-*N*,*O*,*O*′](piperidine)nickel(II) (Elerman, Paulus & Fuess, 1991) and (diethylamino)[1-(2-hydroxyphenyliminomethyl)-2-naphtholato-*N*,*O*,*O*′]-nickel(II) (Elerman, Fuess & Paulus, 1992).

A search of the Cambridge Structural Database (Allen & Kennard, 1993) for octahedrally coordinated nickel(II) ions resulted in 104 compounds with Ni—O and/or Ni—N bonds. The average Ni—O and Ni—N distances are 2.084 (7) and 2.110 (8) Å, respectively, which are significantly longer than those observed for square-planar complexes.

The coordination around the nickel(II) ion is planar, with an r.m.s. deviation of 0.002 Å from the least-squares plane through atoms Ni1, O1, S1, N1 and N2. The bonding angles of the ligands are between 85.71 (8) and 95.45 (8)°. The Ni—S bond length of 2.141 (2) Å agrees with the reported values of 2.139 (2)–2.204 (3) Å (Gyepes & Glowiak, 1989; Srdanov, Jacobson & Wudl, 1990).

Experimental

For the preparation of (I), solutions of *N*-(2-mercaptophenyl)-1-naphthaldimine (0.1 mmol) in 50 ml hot acetonitrile and [Ni(CH$_3$COO)$_2$].4H$_2$O (0.1 mmol) in 20 ml hot methanol were mixed. Pyridine (0.6 ml) was added slowly to the resulting solution which was then refluxed for 3 h during which time dark-red crystals were formed.

Crystal data

[Ni(C$_{17}$H$_{11}$NOS)(C$_5$H$_5$N)]
$M_r = 415.16$
Monoclinic
$C2/c$
$a = 39.326$ (5) Å
$b = 5.988$ (1) Å
$c = 15.109$ (3) Å
$\beta = 92.21$ (1)°
$V = 3555.3$ (10) Å^3
$Z = 8$
$D_x = 1.55$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2.84$–14.03°
$\mu = 1.22$ mm^{-1}
$T = 293$ (2) K
Prism
0.60 × 0.10 × 0.03 mm
Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.77$, $T_{\max} = 0.96$
4878 measured reflections
2473 independent reflections

1999 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.036$
$\theta_{\max} = 22.96°$
$h = -42 \rightarrow 42$
$k = 0 \rightarrow 6$
$l = -16 \rightarrow 14$
3 standard reflections frequency: 120 min intensity decay: 4.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.070$
$S = 1.029$
2473 reflections
249 parameters
Geometrically located H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0323P)^2 + 3.1806P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00004 (8)
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 (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
C1	0.13880 (6)	0.5272 (4)	0.4827 (2)	0.0344 (6)
C2	0.14784 (6)	0.7232 (5)	0.4355 (2)	0.0402 (6)
C3	0.12392 (6)	0.8519 (4)	0.3950 (2)	0.0392 (6)
C4	0.08904 (6)	0.7993 (4)	0.39630 (15)	0.0319 (6)
C5	0.06436 (7)	0.9428 (4)	0.3566 (2)	0.0394 (6)
C6	0.03070 (7)	0.8924 (5)	0.3566 (2)	0.0436 (7)
C7	0.02032 (7)	0.6938 (5)	0.3954 (2)	0.0425 (7)
C8	0.04369 (6)	0.5523 (4)	0.4352 (2)	0.0373 (6)
C9	0.07861 (6)	0.6005 (4)	0.43875 (15)	0.0295 (5)
C10	0.10443 (6)	0.4638 (4)	0.48428 (15)	0.0291 (5)
C11	0.09444 (6)	0.2744 (4)	0.5326 (2)	0.0316 (6)
C12	0.09770 (6)	−0.0459 (4)	0.62405 (15)	0.0320 (6)
C13	0.06334 (7)	−0.0962 (4)	0.6183 (2)	0.0388 (6)
C14	0.05097 (7)	−0.2826 (5)	0.6602 (2)	0.0429 (7)
C15	0.07287 (8)	−0.4207 (5)	0.7089 (2)	0.0440 (7)
C16	0.10684 (8)	−0.3708 (4)	0.7165 (2)	0.0428 (7)
C17	0.11980 (7)	−0.1816 (4)	0.6752 (2)	0.0362 (6)
C18	0.23039 (7)	0.0454 (5)	0.5878 (2)	0.0496 (7)
C19	0.26492 (8)	0.0717 (7)	0.5944 (2)	0.0619 (9)

C20	0.27849 (8)	0.2610 (7)	0.6310 (2)	0.0628 (9)
C21	0.25673 (8)	0.4226 (6)	0.6593 (2)	0.0609 (9)
C22	0.22212 (7)	0.3898 (5)	0.6490 (2)	0.0494 (7)
N1	0.11362 (5)	0.1400 (3)	0.58165 (12)	0.0303 (5)
N2	0.20882 (5)	0.2036 (4)	0.61384 (14)	0.0392 (5)
O1	0.16338 (4)	0.4178 (3)	0.52301 (11)	0.0409 (4)
S1	0.16238 (2)	−0.10773 (12)	0.68413 (4)	0.0445 (2)
Ni1	0.16055 (8)	0.17385 (5)	0.59674 (2)	0.0343 (2)

Table 2. *Selected geometric parameters (Å, °)*

C1—O1	1.299 (3)	C18—N2	1.341 (3)
C1—C10	1.405 (3)	C22—N2	1.333 (4)
C9—C10	1.456 (3)	N1—Ni1	1.862 (2)
C11—N1	1.313 (3)	N2—Ni1	1.914 (2)
C12—N1	1.439 (3)	O1—Ni1	1.843 (2)
C17—S1	1.732 (3)	S1—Ni1	2.141 (2)
C16—C17—S1	122.7 (2)	O1—Ni1—N1	95.45 (8)
C12—C17—S1	118.2 (2)	O1—Ni1—N2	85.71 (8)
C22—N2—Ni1	120.2 (2)	N1—Ni1—N2	178.84 (9)
C18—N2—Ni1	122.0 (2)	O1—Ni1—S1	174.59 (5)
C1—O1—Ni1	128.4 (2)	N1—Ni1—S1	89.96 (6)
C17—S1—Ni1	98.27 (9)	N2—Ni1—S1	88.88 (7)

Table 3. *Comparison of bond lengths (Å) in some similar nickel(II) complexes*

	Ni—S	Ni—N1	Ni—N2	Ni—O	S—C	C—O	C=N
(I)	2.141 (1)	1.862 (2)	1.914 (2)	1.843 (2)	1.732 (3)	1.299 (3)	1.313 (1)
(II)		1.848 (4)	1.947 (4)	1.817 (1)		1.315 (2)	1.292 (5)
(III)		1.849 (3)	1.955 (4)	1.831 (3)		1.322 (5)	1.303 (5)
(IV)		1.912 (3)		1.832 (2)		1.305 (4)	1.297 (4)
(V)		1.854 (4)	1.970 (4)	1.828 (4)		1.335 (8)	1.263 (5)
(VI)		1.898 (4)	1.936 (5)	1.848 (8)		1.322 (2)	1.285 (4)
(VII)	2.138 (2)	1.881 (2)	1.956 (2)	1.856 (3)	1.743 (3)	1.306 (4)	1.312 (5)
(VIII)	2.139 (2)	1.856 (4)	1.888 (4)	1.844 (4)	1.728 (5)	1.293 (6)	1.290 (7)
(IX)	2.142 (1)	1.890 (2)	1.950 (2)	1.850 (1)	1.748 (2)	1.322 (2)	1.289 (2)

Complexes: (I) [*N*-(2-mercaptophenyl)-2-hydroxynaphthaldiminato]-(pyridine)nickel(II) (present work); (II) [1-(2-hydroxyphenyliminomethyl)-2-naphtholato-*N*,*O*,*O*′](piperidine)nickel(II) (Elerman, Paulus & Fuess, 1991; CSD refcode: KIFYIH); (III) (diethylamino)[1-(2-hydroxyphenyliminomethyl)-2-naphtholato-*N*,*O*,*O*′]nickel(II) (Elerman, Fuess & Paulus, 1992; CSD refcode: VOKNOY); (IV) bis{*N*-[(1,3-dioxolan-2-yl)methyl]-2-hydroxy-1-naphthaldiminato}nickel(II) (Fernandez-G, Rosales-Hoz, Rubio-Arroyo, Salcedo, Toscano & Vela, 1987; CSD refcode: FEBWAK); (V) [*N*-(2-hydroxyphenyl)salicylaldiminato](ammine)nickel(II) (Elerman, Svoboda & Fuess, 1992; CSD refcode: VOPCIM); (VI) *N*-(2-hydroxyphenyl)salicylaldiminato-(diethylamine)nickel(II) (Elerman, Paulus & Svoboda, 1992; CSD refcode: VOPHUD); (VII) [*N*-(2-mercaptophenyl)salicylaldiminato]-(piperidine)nickel(II) (Kabak, Elerman & Ozbey, 1995); (VIII) ammine-(salicylaldehyde thiosemicarbazonato)nickel(II) (Gyepes & Glowiak, 1989; CSD refcode: AMSCNI11); (IX) [*N*-(2-mercaptophenyl)salicylaldiminato](diethylamino)nickel(II) (Elerman, Kabak & Svoboda, 1996).

Data collection: *SDP* (Frenz, 1985). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1375). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chloro(2,3,7,8,12,13,17,18-octaethylporphinato)gallium(III)

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Abstract

The crystal structure of $[Ga(C_{36}H_{44}N_4)Cl].1.45CH_2Cl_2$ has been determined. Examination of the crystal established a two-molecule triclinic unit cell with space group $P\bar{1}$. The asymmetric unit contains one porphyrin molecule and two solvate molecules, one as an approximate half molecule with required inversion symmetry. All measurements were made at 127 (2) K. The average Ga—N distance is 2.035 (4) Å and the axial Ga—Cl distance 2.240 (1) Å. The displacement of the Ga atom from the N_4 porphyrin plane is 0.40 Å.

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