N3	0.3252 (4)	0.0603 (6)	0.2127 (3)	0.0501 (13)
N4	0.1134 (3)	0.1615 (5)	0.0836 (3)	0.0376 (11)
N5	0.2750 (3)	0.3496 (5)	0.0746 (3)	0.0374 (11)
N6	0.4110 (3)	0.1356 (5)	0.0321 (3)	0.0353 (11)
C1	0.1727 (4)	−0.0728 (7)	−0.1133 (4)	0.0434 (14)
C2	0.2446 (4)	−0.1761 (7)	−0.0448 (4)	0.0428 (14)
C3	0.3263 (4)	−0.1895 (6)	0.1336 (4)	0.0431 (14)
C4	0.3244 (4)	−0.1054 (7)	0.2280 (4)	0.048 (2)
C5	0.1089 (4)	0.3244 (7)	0.1111 (4)	0.048 (2)
C6	0.1742 (4)	0.4166 (6)	0.0591 (4)	0.0458 (15)
C7	0.3433 (4)	0.3967 (7)	0.0129 (4)	0.049 (2)
C8	0.4366 (4)	0.3005 (7)	0.0348 (5)	0.053 (2)
C11	0.40654 (10)	0.4498 (2)	0.29790 (9)	0.0463 (4)
C12	0.03964 (10)	−0.2220 (2)	0.14121 (10)	0.0474 (4)
O1	0.1160 (4)	0.0396 (7)	0.2998 (4)	0.072 (2)

Table 2. *Selected geometric parameters ($\mathring{A}$, °)*

Ni1—N1	2.166 (4)	Ni1—N4	2.125 (4)
Ni1—N2	2.090 (4)	Ni1—N5	2.083 (4)
Ni1—N3	2.146 (4)	Ni1—N6	2.162 (4)
N1—Ni1—N3	161.9 (2)	N4—Ni1—N6	162.7 (2)
N2—Ni1—N5	177.5 (2)		
N1—C1—C2—N2	55.4 (6)	N4—C5—C6—N5	−51.8 (6)
N2—C3—C4—N3	−50.7 (6)	N5—C7—C8—N6	50.8 (7)

Table 3. *Hydrogen-bonding geometry ($\mathring{A}$, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···Cl2	0.76 (6)	2.50 (6)	3.195 (6)	153 (7)
O1—H2O···Cl2^i	0.87 (6)	2.33 (6)	3.187 (6)	171 (6)
N1—H1···Cl2^{ii}	0.90	2.59	3.419 (4)	154
N1—H1'···Cl1^{iii}	0.90	2.59	3.415 (4)	153
N2—H2···Cl2	0.91	2.47	3.365 (4)	169
N4—H4···Cl2^{ii}	0.90	2.59	3.418 (4)	153
N4—H4'···O1	0.90	2.38	3.195 (7)	151
N5—H5···Cl1	0.91	2.46	3.364 (4)	172
N6—H6···Cl1^{iv}	0.90	2.55	3.446 (4)	176
N6—H6'···Cl1^{iii}	0.90	2.46	3.344 (4)	167

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-x, -y, -z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL93*.

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{4-Methyl-2-[(2-oxidobenzylidene)amino]phenolato(2–)-N,O,O'}(piperidine-N)-nickel(II)

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Abstract

In the title compound, [Ni($C_{14}H_{11}NO_2$)($C_5H_{11}N$)], the coordination geometry at the Ni atom was found to be a slightly distorted square-planar polygon formed by the O, N and O' donor atoms of the tridentate ligand and the N donor atom of the monodentate ligand [O—Ni—N 86.6 (2)–95.9 (3)°, Ni—O 1.810 (5) and 1.833 (4), Ni—N 1.862 (6) and 1.933 (7) $\mathring{A}$]. The diamagnetic properties of the complex, determined by the Gouy method, are in agreement with the planar coordination.

Comment

Schiff bases and their biologically active complexes have been extensively studied over the last two decades. Several complexes of salicylaldimine (Stewart & Lin-

gafelter, 1959; Calligaris, Nardin & Randaccio, 1972; Bhatia, Bindlish, Saini & Jain, 1981; Kessissoglou, Raptopoulou, Bakalbassis, Terzis & Mrozinski, 1992) and the complexes formed between tridentate N-substituted phenylsalicylaldimines and divalent metal ions such as Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{2+} (Kato & Muto, 1988; Kurtz, 1990) have been characterized. In biological systems such as jack-bean urease and some hydrogenases, nickel is in the complexed form (Walsh & Orme-Johnson, 1987). Schiff-base complexes have also been used in electrochemical research and catalytic reactions (Araya, Vargas & Costamagna, 1986; Hamilton, Drago & Zombeck, 1987; Costamagna, Vargas, Latorre, Alvarado & Mena, 1992). The Ni^{2+}, Co^{2+}, Cu^{2+} and Fe^{3+} ions form similar complexes with Schiff-base ligands (Maggio, Pizzino & Romano, 1974). Among these ions, only Ni^{2+} forms a non-dimeric mononuclear square-planar diamagnetic complex when an amine is added (Maggio, Pizzino, Romano & Dia, 1976; Gunduz & Atakol, 1989). The structure of the title Ni^{2+} complex, (I), was determined in order to compare the geometrical features with those of related compounds using piperidine as the amine ligand.

Fig. 1. An *ORTEP* drawing (Johnson, 1965) displaying the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level for the non-H atoms.

(I)

Compound (I) is a diamagnetic square-planar nickel complex, as was obtained in previous cases (Elerman, Paulus & Fuess, 1991; Kabak, Elerman, Ozbey & Atakol, 1995). The coordination about Ni^{2+} is not completely regular; the bond angles are between 86.6 (2) and 176.8 (3)°. The average Ni—O and Ni—N distances are 1.821 (5) and 1.897 (7) Å, respectively. The bond lengths and angles are in agreement with values reported previously for Ni^{2+} complexes (Cariati, Ganadu, Zoroddu, Mansani & Quidacciolu, 1985; Fernández-G., Rosales, Toscano & Tapia T., 1986; Fernández-G., Rosales-Hoz, Rubio-Arroyo, Salcedo, Toscano & Vela, 1987; Hökelek, Gündüz, Hayvali & Kilic, 1995). The phenyl rings A (C1–C6) and B (C8–C13) are planar, while piperidine ring C (N2, C15–C19) is not. The latter group has the expected chair conformation. The dihedral angle between the best least-squares planes D (C15, N2, C19) and E (C15, C16, C18, C19) is 46.7 (6)°, and between E and F (C16, C17, C18) is 47.2 (7)°. The distances of the N2 and C17 chair atoms from the plane of the other four atoms of the six-membered piperidine ring are between 0.590 (6) and −0.615 (9) Å, far from the expected value of 0.726 Å.
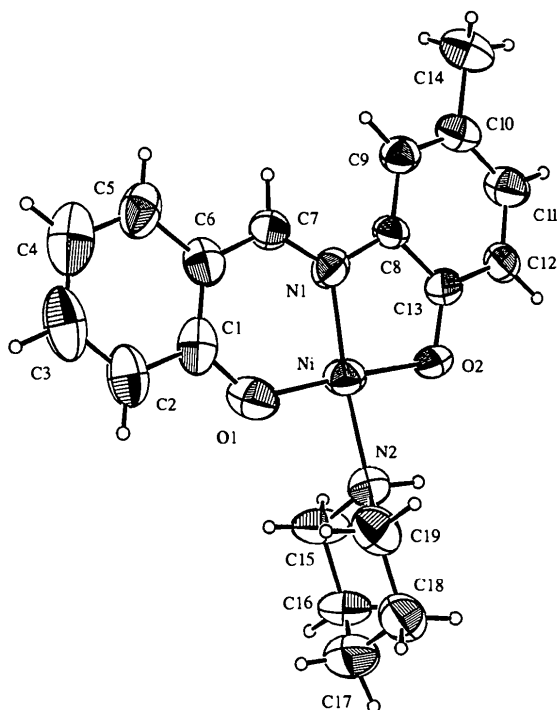
Experimental

A solution of N-(2-hydroxy-4-methylphenyl)salicylaldimine (1 mol) was dissolved in acetonitrile (50 ml) with heating. Piperidine (1.5 ml) was added slowly and the resulting solution mixed with $Ni(CH_3COO)_2.4H_2O$ (0.001 mol) dissolved in hot methanol. This final mixture was left to stand in air for 3 d. The red crystals that formed were filtered off and dried in air. Magnetic susceptibility was measured at 296 K using the Gouy method and the complex was found to be diamagnetic. The density D_m was measured pycnometrically.

Crystal data

[Ni(C₁₄H₁₁NO₂)(C₅H₁₁N)]	Mo $K\alpha$ radiation
$M_r = 369.11$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 15
$P2_1/c$	reflections
$a = 10.664 (3)$ Å	$\theta = 10-13°$
$b = 14.088 (5)$ Å	$\mu = 1.12$ mm⁻¹
$c = 12.494 (2)$ Å	$T = 296$ K
$\beta = 110.6 (1)°$	Prism
$V = 1757.0 (14)$ Å³	$0.40 \times 0.20 \times 0.08$ mm
$Z = 4$	Dark red
$D_x = 1.395$ Mg m⁻³	
$D_m = 1.358$ Mg m⁻³	

Data collection

Enraf–Nonius CAD-4	1414 observed reflections
diffractometer	$[I > 2\sigma(I)]$
$\omega/2\theta$ scans	$R_{int} = 0.01$

Absorption correction:
empirical *via* ψ scans
(*MolEN*; Fair, 1990)
$T_{min} = 0.978$, $T_{max} = 0.999$
3497 measured reflections
3173 independent reflections

$\theta_{max} = 25.3°$
$h = -12 \rightarrow 0$
$k = -16 \rightarrow 0$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F
$R = 0.059$
$wR = 0.060$
$S = 1.54$
1414 reflections
217 parameters
$w = 1/\sigma(F)^2$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.63$ e Å⁻³
$\Delta\rho_{min} = -0.21$ e Å⁻³
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

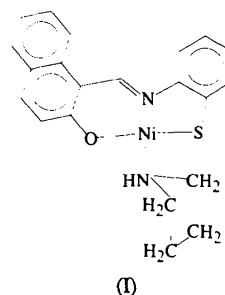$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ni	0.0576(1)	0.17291(8)	0.33844(8)	3.87(2)
O1	0.1839(5)	0.0919(4)	0.4260(4)	5.2(1)
O2	−0.0669(4)	0.2536(4)	0.2431(4)	4.0(1)
N1	−0.0330(5)	0.1859(4)	0.4406(4)	3.6(1)
N2	0.1360(5)	0.1671(5)	0.2207(5)	4.3(2)
C1	0.1963(7)	0.0592(6)	0.5274(6)	4.4(2)
C2	0.3017(8)	−0.0034(6)	0.5816(7)	5.8(3)
C3	0.3188(8)	−0.0417(7)	0.6854(8)	6.5(3)
C4	0.2318(9)	−0.0201(7)	0.7438(7)	6.6(3)
C5	0.1287(9)	0.0424(6)	0.6944(7)	5.3(2)
C6	0.1077(7)	0.0821(6)	0.5865(6)	4.2(2)
C7	−0.0042(7)	0.1422(5)	0.5372(6)	3.9(2)
C8	−0.1465(6)	0.2469(5)	0.3967(5)	3.0(2)
C9	−0.2370(7)	0.2736(6)	0.4474(6)	3.6(2)
C10	−0.3445(6)	0.3293(6)	0.3916(6)	4.0(2)
C11	−0.3630(7)	0.3581(6)	0.2807(6)	4.7(2)
C12	−0.2711(7)	0.3353(6)	0.2300(6)	4.5(2)
C13	−0.1611(7)	0.2784(6)	0.2866(5)	3.6(2)
C14	−0.4447(7)	0.3569(7)	0.4466(7)	6.0(3)
C15	0.2724(7)	0.1982(6)	0.2512(7)	5.6(3)
C16	0.3249(8)	0.1986(7)	0.1508(7)	6.8(3)
C17	0.3031(8)	0.1054(7)	0.0920(8)	7.0(3)
C18	0.1611(7)	0.0739(7)	0.0602(6)	5.7(2)
C19	0.1132(7)	0.0753(7)	0.1619(6)	5.8(2)

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

Ni—O1	1.810(5)	C4—C5	1.37(1)
Ni—O2	1.833(4)	C5—C6	1.40(1)
Ni—N1	1.862(6)	C6—C7	1.42(1)
Ni—N2	1.933(7)	C8—C9	1.38(1)
O1—C1	1.31(1)	C8—C13	1.40(1)
O2—C13	1.35(1)	C9—C10	1.36(1)
N1—C7	1.292(9)	C10—C11	1.39(1)
N1—C8	1.428(9)	C10—C14	1.51(1)
N2—C15	1.436(9)	C11—C12	1.38(1)
N2—C19	1.47(1)	C12—C13	1.39(1)
C1—C2	1.40(1)	C15—C16	1.54(1)
C1—C6	1.43(1)	C16—C17	1.48(1)
C2—C3	1.36(1)	C17—C18	1.49(1)
C3—C4	1.40(2)	C18—C19	1.53(1)
O1—Ni—O2	176.8(3)	C1—C6—C5	119.8(7)
O1—Ni—N1	95.9(3)	C1—C6—C7	121.5(7)
O1—Ni—N2	90.3(3)	C5—C6—C7	118.7(8)
O2—Ni—N1	87.2(2)	N1—C7—C6	125.3(8)
O2—Ni—N2	86.6(2)	N1—C8—C9	128.5(6)
N1—Ni—N2	173.8(2)	N1—C8—C13	110.7(6)
Ni—O1—C1	127.3(5)	C9—C8—C13	120.8(6)
Ni—O2—C13	111.8(4)	C8—C9—C10	121.3(7)
Ni—N1—C7	125.7(5)	C9—C10—C11	118.5(7)
Ni—N1—C8	111.8(4)	C9—C10—C14	121.2(7)
C7—N1—C8	122.4(7)	C11—C10—C14	120.2(6)
Ni—N2—C15	117.1(5)	C10—C11—C12	121.0(7)
Ni—N2—C19	112.3(5)	C11—C12—C13	120.6(7)
C15—N2—C19	112.1(6)	O2—C13—C8	118.3(6)
O1—C1—C2	118.6(8)	O2—C13—C12	124.1(7)
O1—C1—C6	124.1(7)	C8—C13—C12	117.6(7)
C2—C1—C6	117.2(8)	N2—C15—C16	114.2(6)
C1—C2—C3	121.8(9)	C15—C16—C17	111.1(8)
C2—C3—C4	121.4(8)	C16—C17—C18	111.3(8)
C3—C4—C5	118.5(9)	C17—C18—C19	112.4(6)
C4—C5—C6	121.3(9)	N2—C19—C18	112.5(7)
O2—Ni—O1—C1	−170(4)	C8—N1—C7—C6	−178.9(7)
O1—Ni—O2—C13	167(4)	N2—C15—C16—C17	−52.7(10)
N2—Ni—N1—C7	170(2)	C17—C18—C19—N2	52.8(9)

A riding model was used for all H atoms, with C—H and N—H = 0.95 Å, and displacement parameters 1.3 times those of the attached atoms. All non-H atoms were refined anisotropically. *CAD-4-Express Software* (Enraf–Nonius, 1993) was used for data collection. *MolEN* (Fair, 1990) was used for all calculations and preparation of the *ORTEP* (Johnson, 1965) plot.

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(Pyrrolidine-*N*)[1-(2-thiophenylimino-methyl)-2-naphtholato(2–)-*N,O,S*]nickel(II)

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Abstract

In the title compound, [Ni(C$_{17}$H$_{11}$NOS)(C$_4$H$_9$N)], the coordination around the Ni atom is slightly distorted from square planar. Bond angles within the coordination square have values between 85.0 (1) and 94.8 (1)°. The Ni—S, Ni—O and average Ni—N distances are 2.139 (1), 1.841 (3) and 1.908 (4) Å, respectively. The best plane through the pyrrolidine ring is approximately perpendicular to the planes of the other rings present in the molecule.

Comment

The title nickel(II) complex, (I), contains a monodentate (pyrrolidine) and a tridentate [1-(2-thiophenylimino-methyl)-2-naphtholate] ligand. Similar nickel complexes with O,N,S,N-planar coordination environments around the Ni atom (Soriano-García, Toscano, Valdés-Martínez & Fernández-G., 1985; Kabak, Elerman, Özbey &
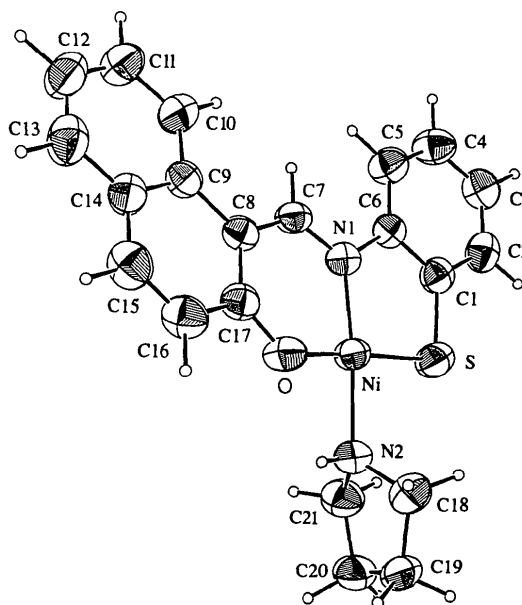
Atakol, 1995; Tahir, Ülkü, Atakol & Kenar, 1996) have been reported.

(I)

The Ni^{2+} ion has a slightly distorted square-planar coordination (Fig. 1). The O atom lies furthest from the best plane through the Ni, N1, N2, O and S atoms at a distance of 0.132 (3) Å. The bond lengths between the Ni atom and the donor S, N1, O and N2 atoms are 2.139 (1), 1.869 (3), 1.841 (3) and 1.948 (4) Å, respectively. Two inequivalent Ni—N distances have also been observed in similar complexes, an indication that these bonds are influenced by the nature of the N-donor atom and also by the number of atoms in the chelate rings (Curtis, 1979). The angles S—Ni—N1 [89.8 (1)°] and S—Ni—N2 [91.4 (1)°] are closer to 90° than the angles O—Ni—N1 [94.8 (1)°] and O—Ni—N2 [85.0 (1)°]. The pyrrolidine ring has an envelope confirmation, with the N2 atom lying 0.510 (4) Å from the C18–C21 plane. The phenyl rings are essentially coplanar with their respective chelate rings, the dihedral angles being less than 5°.

Fig. 1. An *ORTEP* (Johnson, 1965) drawing of (I) with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles with arbitrary displacement parameters.