

{4-Bromo-2-[2-(5-bromo-2-oxido-benzylideneaminomethyl)phenyl-iminomethyl]phenolato- κ^4 O,N,N',O'}-nickel(II)

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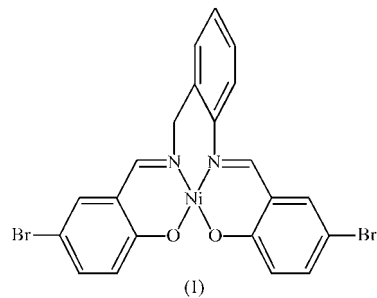
In the title complex, [Ni(C₂₁H₁₄Br₂N₂O₂)], the Ni^{II} atom is coordinated by the two imine N and two phenolate O atoms of the Schiff base ligand in a tetrahedrally distorted square-planar geometry. The Ni–N and Ni–O distances are within the ranges expected for Ni–Schiff base derivatives. Intermolecular C–H...O hydrogen bonds link the molecules into centrosymmetric dimers, forming R₂²(12) (A) and R₂²(10) (B) rings. These dimers combine to form a supramolecular ABAB... aggregate which propagates along the [100] direction.

Comment

Multidentate Schiff base ligands and their nickel(II) complexes have been studied extensively because of their preparative accessibility and structural variability (Garnovskii *et al.*, 1993). In addition to their diverse chelating ability, magnetic properties and applications in catalysis, Schiff base ligands derived from salicylaldehyde can serve as efficient models for biologically important systems (Long, 1995). In general, nickel(II) complexes of diamine Schiff bases display square-planar metal coordination (Elerman *et al.*, 1996; Sony *et al.*, 2004), but when the substituents in the imine bridge are bulky or the substitution is asymmetric, the metal coordination often exhibits tetrahedral distortion (Elmali *et al.*, 2000; de Castro *et al.*, 2001). As part of a systematic study of the characterization of tetradentate nickel(II)–diamine complexes (Datta *et al.*, 2003), and to build up a hierarchy for such systems, the synthesis, spectroscopy and X-ray structural studies of the title complex, (I), were undertaken.

The crystal structure of (I) (Fig. 1) is built from discrete NiL units (where L is the tetradentate Schiff base ligand) in which each Ni^{II} ion is coordinated by the two imine N and two phenolate O atoms. The coordination polyhedron around the metal centre is close to square planar, the N₂O₂ plane being

slightly tetrahedrally distorted [the maximum deviation is 0.104 (3) Å for atom N2]. The Ni atom [deviation 0.002 (1) Å] is well within the plane defined by atoms N1, N2, O1 and O2. The distortion of the metal coordination geometry from an ideal square-planar arrangement is revealed by the *cisoid* O–Ni–O angle of 82.64 (10)° (Table 1) and the dihedral angle of 8.2 (1)° between the two Ni/N/O planes. Similar distortions in the metal coordination geometry have been reported for tetradentate nickel(II)–Schiff base complexes (Arici *et al.*, 2001; Elmali *et al.*, 2000; de Castro *et al.*, 2001) where the substituents in the imine bridge are bulky.



The tetradentate ligand consists of three essentially planar parts, *viz.* two 5-bromosalicylideneimine groups [O1/N1/Br1/C1–C7 (L1) and O2/N2/Br2/C15–C21 (L2)] and the bridging benzyl moiety [C8–C14 (L3)]. The maximum deviation of an atom from least-squares planes L1, L2 and L3 is 0.085 (3) Å for atom C7 in L1; the corresponding deviations of the Ni atom from planes L1 and L2 are 0.467 (1) and 0.438 (1) Å, respectively. The dihedral angle between planes L1 and L2 is 8.8 (1)°, indicating a flat arrangement of the two bromosalicylideneimine groups in the molecule. This geometry is similar to that observed in the [Ni(salchd)] (de Castro *et al.*, 2001) and [Ni(–)(chxn)(sal)₂] (Wojtczak *et al.*, 1997) complexes [salchd is bis(salicylidene)cyclohexane-1,2-diamine, chxn is cyclohexylene and sal is salicylideneiminate] (see Table 3). The pronounced distortion of the planar geometry in the [Ni(salpd)] [salpd is bis(salicylidene)-2,2-dimethylpro-

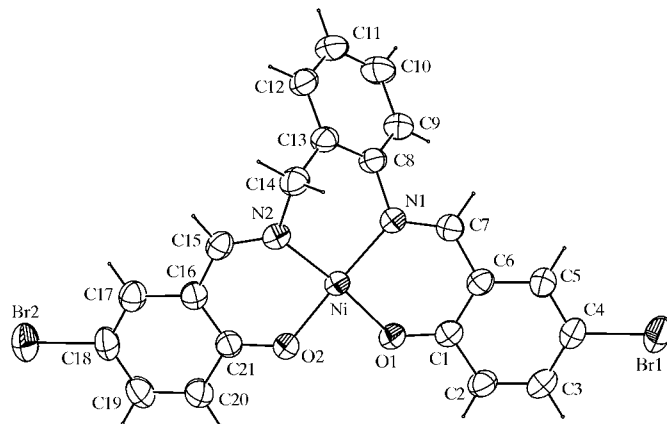


Figure 1
An ORTEP-3 (Farrugia, 1997) view (50% probability level) of the molecule of (I).

panediaminate; Arici *et al.*, 2001] and [Ni(–)(chxn)(hapi)₂] (hapi is hydroxyacetophenonylideneimine; Szlyk *et al.*, 1999) complexes (see Table 3), where the bridging moiety between the two imine N atoms has methyl substitution, is due to the steric requirements imposed by the interaction between the bulky methyl group and other H atoms of the ligand. The whole ligand in (I), however, is not planar; the bridging benzyl moiety (*L3*) is inclined to 5-bromosalicylideneimine planes *L1* and *L2* by 56.2 (1) and 60.7 (1)°, respectively. The bridging chelate ring composed of atoms Ni, N1, C8, C13, C14 and N2 has a distorted boat conformation, with ring puckering parameters (Cremer & Pople, 1975) $Q = 0.684$ (3) Å, $\theta = 97.5$ (3)° and $\varphi = 68.5$ (3)°. The distances of the two *para*-positioned boat atoms, N1 and C14, from the mean plane of the six atoms are 0.435 (2) and 0.715 (3) Å, respectively. The Ni–N and Ni–O bond distances (Table 1) are in good agreement with those observed in similar Ni^{II}–Schiff base complexes (Santos *et al.*, 2000; Szlyk *et al.*, 1999). The fact that the Ni–N bond distances are slightly longer in (I) may be attributed to the steric hindrance of the bulky benzyl group between the N atoms. Other bond distances and angles in (I) are within the ranges found for related structures (Elmali *et al.*, 2000; Elerman *et al.*, 1998).

Molecules of (I) are linked by two different C–H...O hydrogen bonds (Table 2) into centrosymmetric dimers, in which one of the phenolate O atoms acts as a double acceptor. Benzene atom C9 at (*x*, *y*, *z*) acts as a hydrogen-bond donor to atom O2 at (–*x*, –*y* + 1, –*z* + 1), thus forming a dimer characterized by an $R_2^2(12)$ motif (*A*) with an inversion centre at (0, $\frac{1}{2}$, $\frac{1}{2}$). Similarly, atom C14 at (*x*, *y*, *z*) acts as a donor to atom O2 at (–*x* + 1, –*y* + 1, –*z* + 1), generating an $R_2^2(10)$ ring (*B*) with an inversion centre at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). These two dimers combine to form a supramolecular *ABAB*... aggregate which propagates along [100] (Fig. 2). The observed Ni...Ni distance,

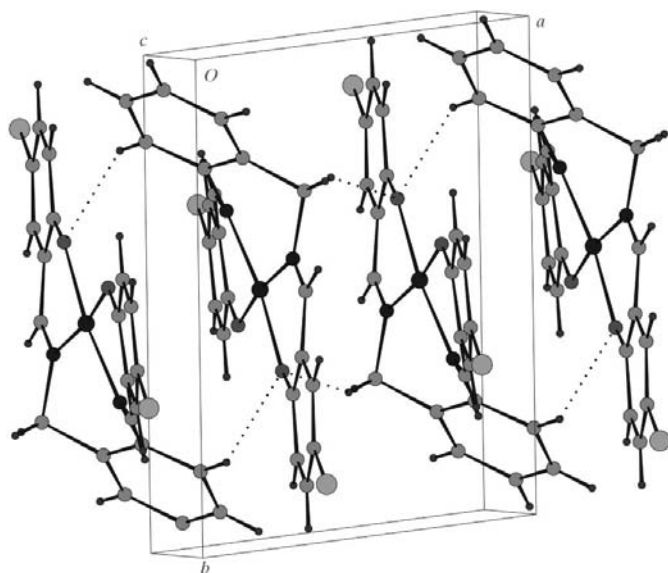


Figure 2

A view of the packing of the unit cell of (I) along the *c* axis, showing the formation of dimers.

3.480 (3) Å, in (I) is well within the values reported [3.201 (1)–3.582 (1) Å] for analogous Schiff base complexes (de Castro *et al.*, 2001; Ercan *et al.*, 1997; Wojtczak *et al.*, 1997) with Ni...Ni interactions.

Experimental

4-Bromo-2-[2-(5-bromo-2-hydroxybenzylideneaminomethyl)phenyl-iminomethyl]phenol (*H₂L*) was prepared by the condensation of 5-bromosalicylaldehyde (10 mmol, 2.01 g) and 2-aminobenzylamine (5 mmol, 0.61 g) in methanol (50 ml). The reaction mixture was stirred for 1 h and the resulting solution was used without further purification. Ni(ClO₄)₂·6H₂O (1 mmol, 0.366 g) was dissolved in methanol (20 ml) and a methanol solution of the ligand (*H₂L*, 1 mmol) was added dropwise. A brown compound, NiL, (I), was obtained on keeping the solution at room temperature (298 K) for three days. Recrystallization from dichloromethane yielded single crystals of (I), which were collected by filtration and dried in air (yield 65%). Analysis found: C 46.31, H 2.55, N 5.16%; calculated for C₂₁H₁₄Br₂N₂NiO₂: C 46.24, H 2.57, N 5.14%. IR (cm^{–1}): 1605 (C–N), 1320 (C–O), 2300–2840 (N–H), 535 (Ni–N), 405 (Ni–O). The broad band around 620 nm in the UV spectrum can be assigned to a *d–d* transition in the complex and suggests an approximate square-planar or tetrahedral metal coordination.

Crystal data

[Ni(C ₂₁ H ₁₄ Br ₂ N ₂ O ₂)]	<i>Z</i> = 2
<i>M_r</i> = 544.87	<i>D_x</i> = 1.873 Mg m ^{–3}
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 7.228 (5) Å	Cell parameters from 110 reflections
<i>b</i> = 10.834 (7) Å	θ = 1.2–26.0°
<i>c</i> = 12.831 (8) Å	μ = 5.16 mm ^{–1}
α = 100.09 (1)°	<i>T</i> = 293 (2) K
β = 99.83 (1)°	Needle, brown
γ = 95.63 (1)°	0.35 × 0.12 × 0.10 mm
<i>V</i> = 966.2 (11) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	3752 independent reflections
φ and ω scans	2981 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> _{int} = 0.024
<i>T</i> _{min} = 0.299, <i>T</i> _{max} = 0.597	θ _{max} = 26.0°
9936 measured reflections	<i>h</i> = –8 → 8
	<i>k</i> = –13 → 13
	<i>l</i> = –15 → 15

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 0.2635P]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.082$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.02	$\Delta\rho$ _{max} = 0.74 e Å ^{–3}
3752 reflections	$\Delta\rho$ _{min} = –0.39 e Å ^{–3}
253 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Br1–C4	1.904 (3)	Ni–N1	1.901 (3)
Br2–C18	1.905 (3)	O1–C1	1.299 (4)
Ni–O1	1.850 (2)	O2–C21	1.306 (4)
Ni–O2	1.859 (2)	N1–C7	1.299 (4)
Ni–N2	1.875 (3)	N2–C15	1.286 (4)
O1–Ni–O2	82.64 (10)	O1–Ni–N1	92.65 (10)
O1–Ni–N2	172.20 (10)	O2–Ni–N1	172.06 (10)
O2–Ni–N2	92.46 (10)	N2–Ni–N1	92.87 (11)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C9-H9\cdots O2^i$	0.93	2.68	3.484 (4)	145
$C14-H14A\cdots O2^{ii}$	0.97	2.51	3.403 (4)	152

 Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$.

Table 3

 Comparison of geometric parameters (Å, °) of similar Ni^{II}-Schiff base complexes.

	$D1^a$	$D2^b$	$A1^c$	$A2^d$	$A3^e$
(I) ^j	0.104 (3)	0.002 (1)	9.37 (7)	19.70 (5)	18.99 (6)
[Ni(salchd)] ⁱⁱ	0.044 (2)	0.002 (2)	6.1 (2)	9.9 (2)	4.0 (2)
[Ni(-)(chxn)(sal) ₂] ⁱⁱⁱ	0.08	0.06	8.9 (3)	4.0 (2)	4.9 (3)
[Ni(salpd)] ^{iv}	0.213 (4)	0.013 (3)	29.3 (3)	11.0 (3)	25.7 (3)
[Ni(-)(chxn)(hapi) ₂] ^v	0.004	0.029	43.5 (1)	24.9 (2)	19.0 (2)

 Notes: (a) the maximum deviation from the N₂O₂ plane; (b) the deviation of the Ni atom from the least-squares N₂O₂ plane; (c) the dihedral angle between the two chelating rings; (d) the angle between the N₂O₂ plane and the N1...O1 plane; (e) the angle between the N₂O₂ plane and the N2...O2 plane. References: (j) this work; (ii) de Castro *et al.* (2001); (iii) Wojtczak *et al.* (1997); (iv) Arici *et al.* (2001); (v) Szlyk *et al.* (1999).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SMART*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *SHELXL97* and *PARST95* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1022). Services for accessing these data are described at the back of the journal.

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