

NOTE

**Synthesis and Crystal Structure of
 Bis[2-((E)-(benzylimino)methyl)-6-bromo-4-chlorophenol]nickel(II)**

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A new nickel(II) complex, NiL₂ with the Schiff base ligand HL = 2-((E)-(benzylimino)methyl)-6-bromo-4-chlorophenol, has been synthesized and characterized on the basis of elemental analyses and single crystal X-ray diffraction. The complex crystallizes in the monoclinic space group P2(1)/c with the cell parameters a = 10.6405(8) Å, b = 6.01904(3) Å, c = 20.5986 (18) Å, β = 102.3620(10)°, V = 1288.65(17) Å³, Z = 2, D_c = 1.819 g/cm³, μ (MoK_α) = 7.024 mm⁻¹, F₍₀₀₀₎ = 700, S = 1.036, the final R = 0.0590 and wR = 0.1368 for 2269 unique reflections (R_{int} = 0.0428) with 5879 observed ones (I > 2σ(I)). The central nickel(II) is four coordinate and bonds to two nitrogen atoms and two oxygen atoms from two Schiff base ligands and the geometry around nickel(II) is a fairly square planar. The packing figure shows that there are no obvious interactions in the units of the complex.

Key Words: Nickel(II) Schiff base complexes, Crystal structure, Single crystal X-ray analysis.

For many years there have been continuous developments and extensive studies on Schiff base coordination compounds¹⁻³. Nevertheless, the chemistry of nickel complexes with multi-dentate Schiff base ligands has attracted huge attention because such complexes play an important role in bioinorganic chemistry and redox enzyme systems and may provide the basis of models for active sites of biological systems or act as catalysts^{4,5}. Thus, it is quite important to study the structure of such metal complexes. Recently, we studied the structure of a four coordinate Ni(II) complex of 2-[(E)-(benzylimino)methyl]-6-bromo-4-chlorophenol. In this structure, the Ni(II) ion is four-coordinate with two Schiff base ligands to form a fairly square planar configuration. The purpose of this study was to elucidate the differences in the crystal structures of four-coordinate Ni(II) complexes of this ligand.

Synthesis: To the vigorously stirred solution of 3-bromo-5-chlorosalicylaldehyde (0.2 mmol, 47.2 mg) in EtOH (5 mL), was added dropwise a colourless solution of phenylmethanamine (0.2 mmol, 31.4 mg) in solution of EtOH (5 mL) with stirring at room temperature for 1 h. To the resulting orange solution was added NiCl₂·6H₂O (0.1 mmol, 23.7 mg). The mixture was stirred for 1 h. Green block-shaped crystals of the complex **1** grew after 2 weeks (**Scheme-I**). The product was filtered, washed with EtOH and dried over anhydrous CaCl₂ *in vacuo* overnight. Yield: 75 %. Found (%) C, 49.3; H, 3.2; N, 3.5; C₂₆H₁₄N₂O₂Br₂Cl₄Cu caclcd. (%): C, 49.0; H, 3.6; N, 3.8.

Crystal structure determination: A crystal of NiL₂ was mounted on a glass fiber in a random orientation at room temperature. The data were collected by a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromated MoK_α radiation (λ = 0.71073 Å) in the range of 1.96 ≤ θ ≤ 25.02. The structure was solved by direct methods using program SHELXS-97⁶ and refined by full matrix least squares techniques on F² with SHELXL-97⁷. All the non-hydrogen atoms were refined anisotropically and hydrogen atoms were located at their idealized positions. The crystallographic data, experimental details and parameters of the structure solution and refinement for the complex are summarized in Table-1. The main bond distances and bond angles are listed in Table-2. The structural data for the complex was deposited in the Cambridge Crystallographic Data Center under the number CCDC 870017.

The centrosymmetric unit of the title complex (Fig. 1) is a mononuclear complex in which is four coordinate and bonds to two nitrogen atoms and two oxygen atoms from two ((E)-(benzylimino)methyl)-6-bromo-4-chlorophenol Schiff bases. In the crystal structure of the complex the atoms of the phenyl ring plane A (C(2)C(3)C(4)C(5)C(6)C(7)) and the chelate ring formed by the same ligand plane B ((O(1)/Ni(1)/N(1)/C(1)/C(2)/C(3)) are nearly coplanar with a dihedral angle of 5.4 (3)°. Because of the conjugation effects through the imino double bond N(1) = C(8), the phenyl ring A and the phenyl

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT PARAMETERS

Properties	Complex
Empirical formula	C ₂₈ H ₂₀ Br ₂ Cl ₂ NiN ₂ O ₂
Formula weight	705.89
Temperature/K	298 (2)
Radiation (MoK α) λ (Å)	0.71073
Crystal shape/colour	Block/green
Crystal size (mm ³)	0.45 mm × 0.40 mm × 0.15 mm
Crystal system	Monoclinic
Space group	P ₂ (1)/c
a (Å)	10.6405(8)
b (Å)	6.0190(4)
c (Å)	20.5986(18)
β (°)	102.3620(10)
V (Å ³)	1288.65(17)
Z	2
D _c (g/cm ³)	1.819
μ (mm ⁻¹)	4.092
F ₍₀₀₀₎	700
θ range (°)	1.96/25.02
Index range (h, k, l)	-12/9, -6/7, -24/23
Measured reflections	5897
Observed reflections [I \geq 2 σ (I)]	1345
Data/restraints/parameters	2269/0/169
Goodness-of-fit on F ²	1.036
R ₁ , wR ₂ [I \geq 2 σ (I)]	0.0590/0.1368
R ₁ , wR ₂ (all data)	0.1074/0.1549
Large diff. peak and hole (e Å ⁻³)	1.018 and -0.764

Note: $R_1 = \sum ||F_o| - |F_c||/|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0572P)^2 + 0.0000P]$, $P = (F_o^2 + 2F_c^2)/3$.

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond	(Å)	Angle	(°)
Ni(1)-O(1)	1.848(4)	O(1)-Ni(1)-O(1A)	180.0(2)
Ni(1)-O(1A)	1.848(4)	O(1)-Ni(1)-N(1A)	87.3(2)
Ni(1)-N(1A)	1.928(5)	O(1A)-Ni(1)-N(1A)	92.7(2)
Ni(1)-N(1)	1.928(5)	O(1)-Ni(1)-N(1)	92.7(2)
Br(1)-C(4)	1.898(7)	O(1A)-Ni(1)-N(1)	87.3(2)
Cl(1)-C(6)	1.737(7)	N(1)-Ni(1)-N(1A)	180.0(1)

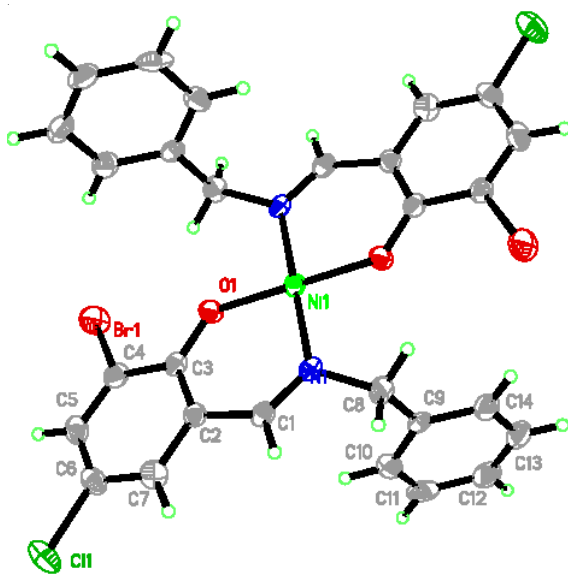
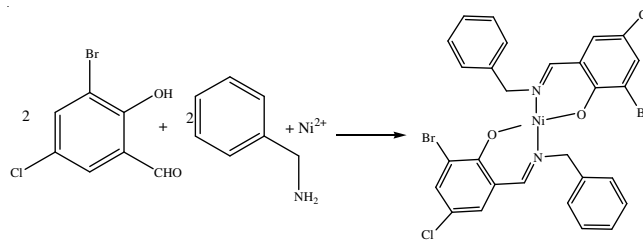


Fig. 1. A view of the complex, showing 30 % probability displacement ellipsoids (symmetry code: A -x + 1, -y + 1, -z + 1)



Scheme-I: Synthesis of the complex

ring B (C(9)C(10)C(11)C(12)C(13)C(14)) joined by the N(1) = C(8) bond, are non-coplanar (with the dihedral angle 89.8 (2)°), decreasing the steric effects between the two rings.

The Ni-N (amine) bond distances are 1.928(5) Å, which is significantly shorter than the normal distances. These bond shortenings presumably caused by the electron-withdrawing -Br and -Cl groups. The Ni-O (amine) distance (1.848(4) Å) is quite similar with other reported Ni-O distances, as in references^{8,9} mentioned. The values of bond angles around Ni(II) also indicate that the coordination is pseudo-square planar, with O(1A)-Ni(1)-N(1), O(1)-Ni(1)-N(1) and N(1A)-Ni(1)-N(1) angles of 87.3(2)°, 92.7(2)° and 180.0(1)°, respectively. (symmetry code: (A) -x + 1, -y + 1, -z + 1). From the packing figure (Fig. 2), we can see that there are no obvious interactions in the units of the complex.

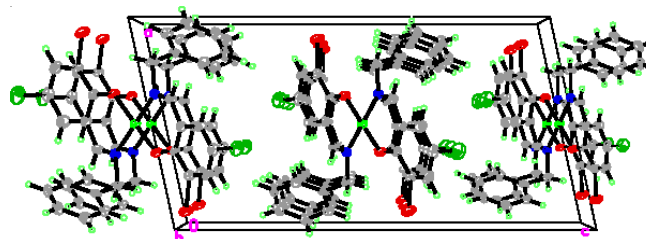


Fig. 2. Packing structure of the complex along the b-axis

In summary, a new asymmetric bidentate nickel(II) complex has been synthesized and characterized by elemental analyses and single-crystal X-ray diffraction.

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