

# Complexation behaviour of Schiff base derived from o-phenylenediamine and 5-bromosalicylaldehyde with some transition metals

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## Abstract

Interest in the synthesis and characterization of transition metal complexes of Schiff bases containing nitrogen and oxygen donor atoms has increased manifold in the recent past. The Schiff base ligands are considered to be good chelating agents especially when –OH functional group is close to the azomethine group. Schiff bases are a special class of ligands with a variety of donor atoms exhibiting interesting coordination modes towards transition metals. Transition metal complexes of Nickel (II) and Cobalt (II) with Schiff base, derived from the condensation of 5-bromosalicylaldehyde and o-phenylenediamine in 2:1 molar ratio were synthesized and characterized by IR, elemental analysis and some physical measurements. Comparison of the I.R spectra of Schiff base and the metal complex indicates that the Schiff base is a tetradentate and co-ordinates using N<sub>2</sub>O<sub>2</sub> chromophore. The binding sites are the nitrogen atoms of azomethine groups and oxygen atoms of the phenolic groups. Elemental analysis suggest the stoichiometry of the complex to be 1:1 [M: L] in all the complexes.

**Key Words:** Metal complexes, Schiff base, chelating agents, chromophore, stoichiometry.

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## INTRODUCTION

Schiff base ligands contain azomethine group (>C=N-) are easily prepared therefore are considered 'privileged ligands'<sup>1</sup>. Schiff bases are aldehyde or ketone like compounds in which the carbonyl group is replaced by an imine or azomethine group<sup>2</sup>. Schiff bases usually contain N, O and S donor atoms and may act as ligands. They are able to coordinate with many metals to stabilize their various oxidation states in such a way that a five or six

membered chelate ring can be formed. The chemistry of Schiff bases as a result of their potential applications is an area of increasing interest. Metal complexes with these bases have numerous applications, such as, in the treatment of cancer<sup>3</sup>, as antibacterial agents<sup>4</sup>, as antivirus agents<sup>5</sup>, as fungicide agents<sup>6</sup> and for other biological properties<sup>7</sup>. Schiff bases with N<sub>2</sub>O<sub>2</sub> donor atoms are well known to co-ordinate with various metal ions and have attracted a great deal of interest in recent years due to their rich co-ordination chemistry<sup>8</sup>. Schiff bases of o-phenylenediamine reported to have variety of applications including biological<sup>9</sup>, clinical<sup>10</sup> and analytical<sup>11</sup> fields. In the present paper we are discussing the synthesis of symmetrical Schiff base from o-phenylenediamine and 5-bromosalicylaldehyde and its complexation behavior with cobalt and nickel.

## MATERIALS AND METHODS

**Chemicals:** All the chemicals used were of AR/ GR grade. Pure sample of o-phenylenediamine and 5-bromo

salicylaldehyde were purchased from Sigma Aldrich; Nickel (II)chloride and Cobalt (II)chloride were from Himedia. Solvents used were ethanol, acetone, DMF and DMSO. All the chemicals were used as supplied without any further purification.

**Instrumentation Techniques:** Elemental analysis was performed on Perkin Elmer 240c model Elemental Analyzer at IIT Powai, Mumbai. The infra-red spectra of ligand and complexes were recorded with FT-IR spectrophotometer Model RZX (Perkin Elmer) using KBr pellets in the range of  $400\text{ cm}^{-1}$ -  $4000\text{ cm}^{-1}$  at SAIF, Punjab University Chandigarh. Electronic spectra were recorded on a UV-VIS-NIR-Spectrophotometer Model Synthesis Lambda 750 Perkin Elmer from SAIF, PU, Chandigarh. The magnetic susceptibility measurements were carried out on a Vibrating Sample Magnetometer (VSM) from IIT, Roorkee. The melting points of the ligand and the complexes were determined in open capillaries with electronic melting point apparatus and are uncorrected.

**Synthesis of Ligand:** 50ml Ethanolic solution of o-phenylenediamine (0.01 M) was added dropwise to 50ml ethanolic solution of 5-bromosalicylaldehyde (0.02 M) with continuous stirring. The resulting mixture was refluxed for 2 hours at  $75^{\circ}\text{C}$ . An orange colored solid product was obtained which was cooled to room

temperature, filtered, dried and recrystallized with ethanol.

**Synthesis of metal complexes:** The solid complexes were prepared by mixing equimolar ethanolic solution of ligand (0.002 mol) with M(II) Chloride (0.002 mol) separately where M stands for Ni(II) and Co(II) metal ions. The mixture was refluxed for 1.5 hours at  $60^{\circ}\text{C}$ . The product obtained was filtered, washed with ethanol and dried over  $\text{CaCl}_2$ .

## RESULTS AND DISCUSSIONS

The ligand and its metal complexes are colored and stable at room temperature. The ligand is soluble in common organic solvents, but the complexes are found to be soluble in DMSO and DMF. The elemental analyses data concur well with the planned formulae for the ligand and also recognized the M:L composition of the metal complexes. Based on elemental analysis, UV, the analytical data obtained for the new complexes agree well with the proposed molecular formula and presented in Table 1. It has been found that complexes are insoluble in water but fairly soluble in DMSO. It has also been found that complexes are non-hygroscopic which are stable at room temperature.

**Table 1:** Analytical data of ligand (L) and its metal complexes

Ligand /complex	Mol. Wt.	Color	M.Pt ( $^{\circ}\text{C}$ )	Elemental analysis calculated (found) %			
				C	H	N	M
HL $\text{C}_{20}\text{H}_{14}\text{Br}_2\text{N}_2\text{O}_2$	474	Orange	165	50.52 (50.64)	2.89 (2.98)	5.83 (5.93)	-
$[\text{Co}(\text{L})\text{Cl}_2]$ $[\text{C}_{20}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}_2\text{Cl}_2]$	602	Brown	265	39.12 (39.62)	2.40 (2.31)	5.10 (4.66)	12.06 (12.10)
$[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]$ $\text{C}_{20}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}_2(\text{H}_2\text{O})_2$	551	Brick red	282	45.23 (45.08)	2.18 (2.26)	5.35 (5.28)	10.06 (12.20)

**IR spectral studies:** IR spectra have proven to be the most suitable technique to give enough information to elucidate the nature of bonding of the ligand to the metal ion. The IR spectra of the free ligand and metal complexes were carried out in the range  $4000\text{--}200\text{ cm}^{-1}$ . Important IR spectral bands ( $\text{cm}^{-1}$ ) of the ligand and its complexes are presented in Table 2

**Table 2:** Important IR spectral bands ( $\text{cm}^{-1}$ ) of the ligand and its complexes

Ligand /Complex	$\nu(\text{OH})$ $\text{cm}^{-1}$	$\nu(\text{HC}=\text{N})$ $\text{cm}^{-1}$	$\nu(\text{C}=\text{O})$ $\text{cm}^{-1}$	$\nu(\text{M}-\text{N})$ $\text{cm}^{-1}$	$\nu(\text{M}-\text{O})$ $\text{cm}^{-1}$
HL $[\text{C}_{20}\text{H}_{14}\text{Br}_2\text{N}_2\text{O}_2]$	3215	1614	1383	-	-
$[\text{Co}(\text{L})\text{Cl}_2]$ $[\text{C}_{20}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}_2\text{Cl}_2]$	3340	1596	1452	625	451
$[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]$ $[\text{C}_{20}\text{H}_{12}\text{Br}_2\text{N}_2\text{O}_2(\text{H}_2\text{O})_2]$	3365	1601	1489	635	564

The IR spectra of the free ligands and the complexes exhibit various bands in the  $250\text{--}4000\text{ cm}^{-1}$  region. The O-H stretching frequency of the ligand is expected in the  $3300\text{--}3800\text{ cm}^{-1}$  region, however, this frequency is

displaced to the  $2960\text{--}3215\text{ cm}^{-1}$  region due to the internal hydrogen bridge  $\text{OH}\cdots\text{N}=\text{C}^{12,13}$ . As the hydrogen bond becomes stronger, the bandwidth increases, and this band sometimes is not detected. Hydrogen bonds in these

Schiff bases are usually very strong. The ligands are relatively planar with adequate intramolecular distance that favors intramolecular hydrogen bond formation<sup>14</sup>. For the metal (II) complexes, the disappearance of this band is expected due to the substitution of hydrogen for the metal on the complex formation. The  $\nu_{(C=N)}$  stretching frequencies are in the 1592–1640  $\text{cm}^{-1}$  region as reported for similar ligands<sup>15,16</sup>. The ligands exhibit the characteristic  $\nu_{(HC=N)}$  band in 1614  $\text{cm}^{-1}$  region, while in the complexes the  $\nu_{(HC=N)}$  were observed at 1596  $\text{cm}^{-1}$  and 1601  $\text{cm}^{-1}$  for Co (II) and Ni (II) complexes respectively. The  $\nu_{(HC=N)}$  stretching frequency is shifted to a lower frequency, indicating a decrease in the  $\nu_{(HC=N)}$  bond order due to the coordinate bond of the metal with the imine nitrogen lone pair<sup>17,18</sup>. In the 1500–1600  $\text{cm}^{-1}$  region, the observed bands were attributed to aromatic C=C vibrations. The C–O stretching frequency appears as a weak band within the 1270–1340  $\text{cm}^{-1}$  range as reported for similar ligands<sup>12,13</sup>. This band occurs in the 1274  $\text{cm}^{-1}$  region for the free ligands and in the 1330  $\text{cm}^{-1}$  region for the complexes. The C–O stretching frequency is shifted to a higher frequency, suggesting the coordination of phenolic oxygen with the metal ion<sup>19,20</sup>. In both the complexes a strong band is observed at 3340  $\text{cm}^{-1}$  and 3365  $\text{cm}^{-1}$  for Co (II) and Ni (II) complexes respectively suggesting the presence of coordinated water in these metal complexes which is further confirmed by the appearance of band at 820–840  $\text{cm}^{-1}$ . Further the bonding with the nitrogen and/or oxygen atom of the Schiff base is provided by the appearance of bands in at 625  $\text{cm}^{-1}$ , 635  $\text{cm}^{-1}$ , 451  $\text{cm}^{-1}$  and 564  $\text{cm}^{-1}$  for  $\nu_{(M-N)}$  and  $\nu_{(M-O)}$  respectively for Co(II) and Ni(II) complexes<sup>21</sup>.

**Electronic spectral studies:** The electronic spectrum of Co (II) complex showed absorption bands at 285 nm, 398 nm and 482 nm assigned to  ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$  ( $\nu_1$ ),  ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$  ( $\nu_2$ ) and  ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$  ( $\nu_3$ ), respectively suggesting octahedral geometry of Co(II) complex<sup>22</sup>. While that electronic spectrum of Ni (II) complex displays bands at 316 nm, 374 nm and 477 nm. These bands may be assigned to  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$  ( $\nu_1$ ),  ${}^3A(F) \rightarrow {}^3T_{1g}(F)$  ( $\nu_2$ ) and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  ( $\nu_3$ ) transitions, respectively suggest an octahedral geometry<sup>22</sup>. The Co (II) and Ni (II) complexes showed the magnetic moment 5.30 B.M. and 3.18 B.M. respectively at room temperature indicating octahedral environment around metal ion<sup>23</sup>.

## CONCLUSION

A symmetrical tetradentate Schiff base N, N'-bis(5-bromosalicylidene)-o-phenylenediamine containing  $N_2O_2$  donor and their corresponding Co(II) and Ni(II) complexes have been synthesized and spectrally characterized on the basis of elemental analysis, IR, UV and other physical measurements. The Schiff base ligand coordinates through azomethine N and phenolic O to the metal ion and acts as a tetradentate ligand. Octahedral geometries have been proposed for both the complexes.

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