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Synthesis and Characterization of Biologically Active Schiff base Complexes of Nickel and Cobalt compounds

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ABSTRACT

Some of the Schiff bases and their complexes and found to possess biological activities. The Schiff base was prepared from 2-hydroxynaphthaldehyde and 2-aminophenol and its complexes with nickel and cobalt chloride and nitrate were synthesized. They were characterized using elemental study IR and UV spectroscopy, Molar conductance in non aqueous solvents and Thermal studies. The complexes obtained were with the general formula ML_2, where M = Ni^{2+} /Co^{2+}. Here ligand is functioning as a uni negative tridentate ligand coordinating through azomethine nitrogen, phenolic oxygen and phenoxide oxygen. A coordination number of six may be assigned to the complexes. The complexes are found to show increased inhibition to the growth of bacterial stains of *Escherichia Coli* and *Bacillus Subtills* as evidenced from the presence of acidic hydrogen of the phenolic group.

Keywords: Schiff base, Complex, 2-hydroxynaphthaldehyde, 2-aminophenol

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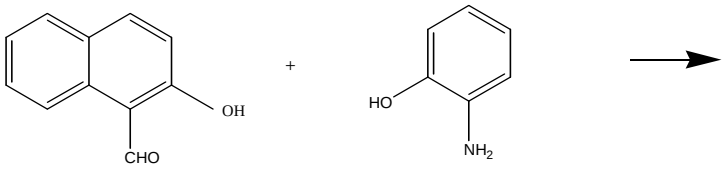
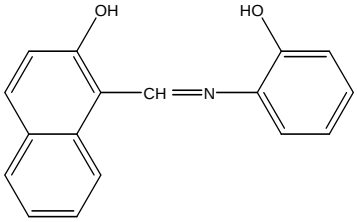
INTRODUCTION

The coordination chemistry of Schiff base complexes has gained importance in the biological studies including antibacterial, antifungal and anticancer activities[1]. Also Schiff bases and its complexes of both transition and inner transition metal ions are extensively used in the study of structure and bonding in coordination complexes. In continuation to our pharmacological studies of Schiff base complexes[2], we have synthesized a novel ligand(1c) from 2-hydroxynaphthaldehyde(1a) and 2-aminophenol(1b). Its complexes using nitrate and chloride salts of Ni(II) and Co(II) were prepared and characterized and tested for their antibacterial activities against bacterial stains of *Escherichia Coli* and *Bacillus Subtills*.



1a **1b**



1c

MATERIALS AND METHOD

All the chemicals used were of analytical reagent grade. Solvents used were purified by distillation and 2-hydroxynaphthaldehyde and 2-aminophenol were used as such supplied by Aldrich Chemical Company. The metal salts were prepared from their respective carbonates by action with 60% corresponding mineral acids and the crystallizing by evaporation over a water bath.

Synthesis of Schiff base: 2-hydroxynaphthylidene-2-aminophenol (L)(1c)

Equimolar quantity of 2-hydroxynaphthaldehyde (5 gm) and 2-aminophenol (3.2 gm) dissolved separately in methanol are mixed in an RB flask and heated under reflux for one hour over a water bath. The mixture is cooled and the orange colored compound separated was filtered and washed with small amount of methanol and dried. Melting point was noted and purity was ascertained by TLC method.

Synthesis of the complexes: From Ni(II) chloride and nitrate

The metal salt was dissolved in minimum quantity acetonitrile and added to the boiling acetonitrile solution of Schiff base kept over a water bath. These two are taken in 1:2 molar ratios and refluxed for 45 minutes. The mixture obtained was concentrated to reduce volume to quarter and cooled. The reddish brown precipitate obtained was further purified by solvent extraction using acetonitrile and finally recrystallized from ethanol. The complexes were dried under vacuum over P_2O_5.

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Synthesis of the complexes: From Co(II) chloride and nitrate

Dissolved 2 gm of cobalt salt in minimum quantity methanol and added to boiling solution of Schiff base (4.3 gm) in methanol kept under reflux over a water bath. The two solutions was mixed in 1:2 molar ratios and refluxed for one hour. The volume of the solution obtained was reduced to quarter and cooled to room temperature. The brown colored complexes obtained was purified by solvent extraction using acetonitrile and finally recrystallized from ethanol. The complexes were dried under vacuum over P_2O_5.

RESULT AND DISCUSSION

The ligand and complexes were characterized using elemental analyses, melting point determination, IR and UV Visible spectral studies, molar conductance, magnetic moment determination and thermal analyses. The CHN elemental analysis of Schiff base and all complexes were done on a Heracus CHN rapid analyzer and the metal analysis of complexes was done by gravimetric method as their oxides. The melting points Schiff base and complexes were carried out on a Thoshniwal melting point apparatus. The IR spectrum was recorded in the range 400 – 4000 cm^{-1} on a Schimadzu IR – 470 spectrophotometer in KBr discs. The electronic spectra in acetonitrile solution (10^{-3} M) were recorded in the range 200 – 900 nm on a Schimadzu UV – 160A spectrometer. TG and DTG analyses were done on a Perkin Elmer thermal analyzer in nitrogen atmosphere.

The antibacterial studies were conducted with bacterial stains of *Escherichia Coli* and *Bacillus Subtills* in cultural medium of nutrient Agar. This Agar medium was prepared in distilled water and inoculation was done in petry dishes using platinum wire. The compounds were dissolved in DMSO and 3mm diameter blotting paper disc are dipped in this solution and then dried in an incubator. This was applied on the bacteria and plates were kept in incubator at 37°C for 24hours. The zone of inhibition was measured in mm and its percentage is calculated.

Elemental Analysis

The observed data are given in the Table.1. All the complexes were having a general formula ML_2, where M = Ni(II) or Co(II). Both of the complexes have no anionic part and as a result the nature of nickel/ cobalt complexes formed from nitrate and chloride salts have identical properties. It is evidenced by melting points and elemental data.

Table.1 Elemental and melting point data

	Found (Calculated)				Melting Point(°C)
	Carbon%	Hydrogen%	Nitrogen%	Metal%	
Ligand	76.3(77.5)	4.8(4.94)	5.25(5.32)	-------	265
NiL_2 - 1	69.8(70)	3.9(4.12)	4.75(4.8)	10.8(10.1)	170
NiL_2 - 2	69.8(70)	3.9(4.12)	4.75(4.8)	10.8(10.1)	170
CoL_2 - 1	66.8(69.8)	4.1(4.12)	4.7(4.8)	10.1(10.11)	130
CoL_2 - 2	66.8(69.8)	4.1(4.12)	4.7(4.8)	10.1(10.11)	130

IR spectral Study

On comparison of the IR spectra of ligand with complexes, it is observed that the strong and intense peaks observed in the range 3200 – 3500 cm^{-1} which indicates the presence of O–H stretching frequency. The peak at 3400 cm^{-1} in the ligand and 3420 and 3410 cm^{-1} in the complexes corresponds to O–H stretching. The shift of frequency is due to the coordinate bonding of hydroxyl oxygen to the metal[3]. The azomethine peak in ligand at 1633 cm^{-1} is shifted to 1610 cm^{-1} in complexes suggesting the coordination[3]. A sharp band was observed around 1300 cm^{-1} is due to the bond bending vibration of –OH group. A weak peak at around 600 cm^{-1} in complexes is suggested due to M–N bonding[4], which was absent in the spectra of ligand. From the elemental analyses data

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and IR data it is concluded that the complexes are having the ML_2 structure[5]. Also three coordination through azomethine group, phenolic oxygen and phenoxide oxygen were suggested.

Electronic spectra

The electronic spectra of the complexes were recorded in acetonitrile medium. The cobalt complexes are showing three bands which is assigned due to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (at 9450 cm^{-1}), $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (at 17500cm^{-1}) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (at 19300 cm^{-1}) [6]. The spectrum of Ni(II) complexes show three transitions at 10400, 17000 and 24200 cm^{-1}, which is assigned respectively due to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$. The observed electronic spectral properties are due to weakly distorted octahedral geometry of the complex.

Molar conductance and magnetic study

Molar conductance in non aqueous solvents like DMF and acetonitrile shows (Table.2) non ionic nature, which is a confirmatory evidence for the above observations[7]. The observed magnetic moments also show decreased value than the spin only value.

Table.2: Molar conductance and magnetic moment data.

Complex	Molar conductance		Observed Magnetic Moment
	DMF	Acetonitrile	
NiL_2	83	78	2.53
CoL_2	72	66	3.75

Thermal studies

Thermal analyses were done in nitrogen atmosphere at heating rate of 10°C/min. The NI(II) complex showed three stage decomposition. The first decomposition starts at 170°C and ends at 210°C with a mass loss of 37.5%. The second plateau starts at 240 and goes up to 330°C with a loss of 10%. The final stage is between 330 and 510°C amounting to a loss of 9%. The decomposition of cobalt complex is beginning at 130°C and ends at 440°C with a loss of 47% and the final stage is between 500 and 630°C amounting to a loss of 22%. In both cases the final product obtained is considered to be the metal oxide.

Antibacterial Studies

The antibacterial studies were done both on complexes and Schiff base and the result is given in Table.3. They showed different activity towards bacterial stains of *Escherichia Coli* and *Bacillus Subtills*. The ligand was showing only moderate antibacterial activity, while complexes are showing intense activity. The reason for the increased activity can be explained due to the phenolic hydrogen[8,9], which can be easily removed as the oxygen containing hydrogen is bonded to the central metal ion.

Table.3 Antibacterial Activities

Compound	*E.Coli*		*B.Subtills*	
	Activity	Percentage	Activity	Percentage
DMSO	_	0	_	0
Ligand	+	11	+	9
NiL_2	+++	21	++	15
CoL_2	+++	24	+++	23
Standard Streptomycin	++++	56	++++	59

Percentage of Inhibition: Below 5mm = (_), 5mm – 10mm = (+), Active, 10mm – 15mm = (++), mildly active 15mm – 20mm = (+++), moderately active, (20 mm, up) = (++++), highly active

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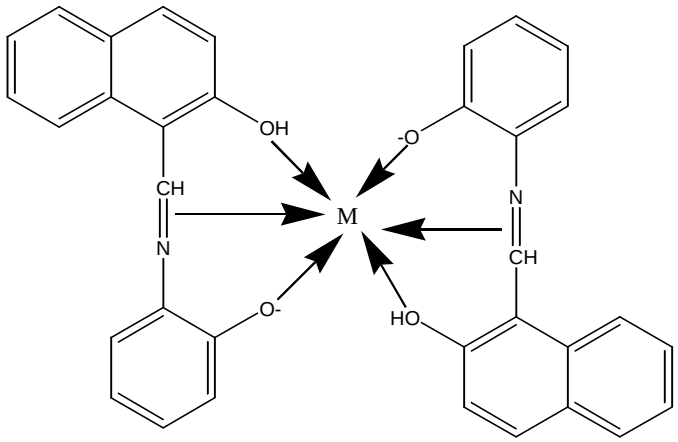
CONCLUSION

The elemental analyses data and spectral data proved the ML_2 type complex and the ligand is suggested to be uninegative tridentate ligand with six coordination. The tentative structure of the novel complexes is given in Fig.1. It is further confirmed by molar conductance data. The Ni(II) and Co(II) complexes formed are identical in all respect, even though they are prepared from corresponding chloride or nitrate salts. These two complexes showed increased antibacterial activity compared with the free ligand.



Where M = Ni(II) or Co(II)

Fig. 1. Tentative structure of the complex

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