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Synthesis, Characterization and Antimicrobial Activity of Schiff base Transition Metal Complexes Derived from 5-Chlorosalicyaldehyde

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ABSTRACT

The coordination complexes of Co(II), Ni(II) and Cu(II) were prepared from bidentate Schiff base. The Schiff base ligand synthesized by the condensation of 5-chloro-2-hydroxybenzaldehyde and 4-fluoro-2-methylaniline in an alcoholic medium. The ligand and its metal complexes were characterized by elemental analysis, molar conductance, electronic spectra, IR spectra, NMR spectra, electrical conductivity and magnetic susceptibility. The transition metal complexes are colored and stable in air. In the metal complexes the metal -ligand found to be 1:2. A sharp band at 1622 cm^{-1} is characteristics of the azomethine group present in the Schiff base ligand. This band was shifted to lower frequency (1598 – 1605 cm^{-}1) in all the metal complexes, which indicates the coordination of the azomethine nitrogen to metal ion in complexes. The IR spectra of the free ligand having phenolic (-OH) group showed a broad band at 3410 cm^{-1}, the disappearance of this band in metal complexes indicates the deprotonation of the hydroxyl group and coordinated through oxygen atom. The molar conductivity data of the complexes in DMSO solution indicates they are non-electrolytic nature. On the basis of magnetic susceptibility and electronic spectral data, geometry of complexes was proposed to be octahedral. The synthesized Schiff base complexes exhibit higher antimicrobial activity than the free Schiff base ligand due to chelation.

KEYWORDS:- 5-chlorosalicyaldehyde, 4-fluoro-2-methylaniline, metal complexes, biological activity.

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1. INTRODUCTION

Schiff bases are formed when condensation of primary amines with carbonyl compounds under specific conditions and were first synthesized by Hugo Schiff in 1864. Schiff bases are represented as $R – CH = N – R^1$ where R and R^1 may be alkyl, aryl or heterocyclic. Azomethine functional group present in Schiff bases. Due to effective conjugation Schiff bases of aromatic aldehydes are more stable than aliphatic aldehydes. Ketones react slower than aldehydes in condensation reaction due to steric hinderance. Schiff bases are generally unidentate, bidentate, tridentate, tetradentate and polydentate ligands to form stable complexes with transition metals. Schiff bases are effective ligands due to presence of azomethine group.[1,2] Schiff bases derived from aromatic carbonyl compounds and primary amines have more applications in the fields of biological, analytical, inorganic chemistry, catalysis and optical materials. Schiff base ligands have donor atoms may be nitrogen, oxygen or Sulphur which provided binding sites through non- bonding electrons. The presence of $-CH=N$ group in the transition metal complexes which contains donor nitrogen atom is responsible for stability, reactivity and biological activity of complexes. Transition metal Schiff base complexes are wide applications in medicinal chemistry, catalysis, polymerization reactions, dyes, corrosion, plant growth regulators and analytical chemistry.[3,4] Due to chelation transition metal Schiff base complexes are more stable and have wide applications in antibacterial, antifungal, antiviral, anticancer, and anti-inflammatory. Schiff base ligands acts as chelating ligands and their biological activity enhanced on coordination. The present aim of the work is to synthesize a Schiff base derived from 5-chlorosalicyaldehyde and 4-fluoro-2-methylaniline and to prepare its transition metal complexes, characterize them and study their antibacterial and antifungal activities.

2. EXPERIMENTAL

Chemicals and Reagents

The chemicals used in present work were of Anal-R grade and were used without purification. 5-chlorosalicyaldehyde and 4-fluoro-2-methylaniline used for the preparation of the Schiff bases were obtained from Sigma Aldrich. Metal salts were purchased from E.Merck.

Physical Measurements

The percentage (%) of Co, Ni and Cu were determined by EDTA complexometric titration. The elemental analysis (C, H and N) data was obtained using 2400 CHN Perkin-Elmer elemental analyzer. The molar conductivity of the complexes in DMSO solution (10^{-3}M) were measured by using DI-909 digital conductivity meter. The IR spectra of the ligand and metal complexes were recorded on Shimadzu FTIR spectrophotometer using KBr disc. The magnetic susceptibility data were measured by Gouy method using Hg $[Co(SCN)_4]$ as a calibrant. The electronic spectra of the complexes were recorded by using Shimadzu model UV-1601 spectrophotometer in DMSO solution.

Synthesis of Schiff base Ligand

The Schiff base ligand 4-chloro-2-{(E)-[(4-fluoro-2-methylphenyl) imino] methyl}phenol was prepared by adding 1.565g (0.01 mol) of 5-chlorosalicyaldehyde in 25 ml ethanol and 1.251g (0.01 mol) of 4-fluoro-2-methylaniline in 25 ml ethanol. The reaction mixture was refluxed for 4-5 h. On cooling the reaction mixture, the orange crystalline solid was formed. The precipitate is washed with cold ethanol and diethyl ether to obtain the required Schiff base.

Synthesis of Metal Complexes

The metal complexes were prepared by mixing (50 ml) ethanolic solution of $CoCl_2.6H_2O$ ⁄ $NiCl_2.6H_2O$ ⁄ $CuCl_2.2H_2O$ with the (50 ml) ethanolic solution of Schiff base in a metal-ligand ratio 1:2. The resulting mixture was refluxed on water bath for 5-6 h. The complex obtained in each time was cooled, filtered and washed with ether and recrystallized with ethanol and dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator

3. RESULTS AND DISCUSSION

The physical properties of ligand and its metal complexes are listed in Table 1. All the metal complexes are colored, solid and stable at room temperature. They decompose on heating at high temperature. The analytical data of the ligand and metal complexes are presented in Table 2.The metal ligand ratio in all the metal complexes have 1:2. Schiff base acts as bidentate ligand. The molar conductivities in DMSO solution show that all metal complexes are non-electrolytic nature.[5,6]

IR Spectra

The important infrared spectral bands of the Schiff base and its metal complexes are listed in Table 3. The coordination sites in chelate compounds are determined by the IR spectra of free ligand compared with that of complexes. The IR spectrum of the synthesized Schiff base ligand showed absorption band at 1622 $cm^{-1}$is characteristic of azomethine (>C=N) group present in the Schiff base ligand. This band was shifted to lower regions (1598-1605 cm^{-1}) in the metal complexes, which indicates the bonding of the metal to the azomethine nitrogen.[7,8] The spectra of metal complexes exhibit broad bands in the range of 3380 – 3400 cm^{-1} indicating the presence of coordinated water molecules. The IR spectra of the ligand having phenolic -OH group showed a broad band at 3410 cm^{-1}. The disappearance of this band in metal complexes suggests deprotonation of the phenolic – OH group after its chelation with the metal ion.[9,10] A medium intensity ligand band at 1286 cm^{-1} (phenolic ν(C-O)) which gets shifted to a lower frequency (1270 – 1238 cm^{-1}) in the complexes, which suggests the participation of phenolic oxygen in coordination with metal ion.[11-14] Two new bands appearing in the low frequency range 488-502 cm^{-1} and 526-532 cm^{-1} are indicate the formation of M-O and M-N bond in the complexes.

Electronic Spectra

The **g**eometry of these complexes has been deduced from electronic spectral data of the complexes. The electronic spectra of Schiff base ligand and its metal complexes were recorded at room temperature using DMSO solvent. In the spectra of ligand, the absorption band at 225 nm represents $\pi - \pi^*$ transition and the absorption bands at 268 nm and 343 nm are associated with $n - \pi^*$ transitions respectively. In the electronic spectrum of Co(II) complex , the absorption bands at 248 nm and 396 nm assigned to intraligand charge transfer and $^3T_{1g} \rightarrow {}^3T_{2g}$ transitions, which indicates the octahedral geometry. The electronic spectrum of Ni(II) complex showed three bands at 228 nm, 265.2 nm and 348.1 nm corresponds to intraligand transition, charge transfer and $^3A_{2g} \rightarrow {}^3T_{2g}$ transitions, which indicates the octahedral geometry. The Cu(II) complex showed three bands at 228 nm, 265.1 nm and 348 nm corresponds to intraligand, spin allowed and $^3T_{1g} \rightarrow {}^3T_{2g}$ transitions, which indicates the octahedral geometry around Cu(II) ion.[15,16]

Table: 1 Physical properties of ligand and metal complexes.

Compounds	color	yield(%)	molar conductivity (Ω^{-1} cm^2 mol^{-1})
L=$C_{14}H_{11}$Cl FNO	Orange	78	-
$[Co(L)_2(H_2O)_2]$	Dark brown	70	14.1
$[Ni(L)_2(H_2O)_2]$	Brown	65	11.4
$[Cu(L)_2(H_2O)_2]$	Pale brown	68	8.5

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Table: 2 Analytical data of ligand and its complexes

Compounds	% Analysis Found (Calc)			
	C	H	N	M
L=$C_{14}H_{11}ClFNO$	63.65 (63.71)	4.12 (4.17)	5.17 (5.30)	-
$[Co(L)_2(H_2O)_2]$	54.12 (54.19)	3.81 (3.87)	4.43 (4.51)	9.43 (9.51)
$[Ni(L)_2(H_2O)_2]$	54.14 (54.21)	3.76 (3.87)	4.45 (4.51)	9.41 (9.47)
$[Cu(L)_2(H_2O)_2]$	53.73 (53.80)	3.72 (3.84)	4.41 (4.48)	10.04 (10.16)

Table: 3 IR spectral data of ligands and its metal complexes

Compounds	ν (O-H) cm^{-1}	ν (C-O) cm^{-1}	ν (C=N) cm^{-1}	ν (H_2O) cm^{-1}	ν (M-N) cm^{-1}	ν (M-O) cm^{-1}
L= $C_{14}H_{11}ClFNO$	3410	1286	1622	-	-	-
$[Co(L)_2(H_2O)_2]$	-	1262	1605	3380	532	496
$[Ni(L)_2(H_2O)_2]$	-	1270	1600	3400	526	502
$[Cu(L)_2(H_2O)_2]$	-	1238	1598	3390	530	488

Table 4. Antimicrobial data of Schiff base ligand and its metal complexes.

S.No	Compound	Minimum inhibition concentration(mg /ml)			
		E. coli	S. aureus	A. niger	C. albicans
1.	Schiff base	5	7	10	13
2.	$[Co(L)_2(H_2O)_2]$	10	9	13	15
3.	$[Ni(L)_2(H_2O)_2]$	8	12	16	17
4.	$[Cu(L)_2(H_2O)_2]$	12	14	18	21

Antimicrobial Activity

The synthesized ligand and its complexes were screened for their in vitro antibacterial activity against Escherichia . coli and Staphylococcus aureus and antifungal activity against Aspergillus niger and Candida albicans by minimum inhibitory concentration method. The minimum inhibitory concentration profiles of all the compounds against bacteria and fungi are presented in Table 4. The MIC values indicated that all the complexes show more activity compared to the free ligand against microorganisms, and this activity is found to be enhanced on coordination with the metal ions. This also can be explained on the basis of Tweedy's chelation theory and the effect of the metal ion on the normal cell processes. It was further noted that the delocalization of electrons over the whole chelate ring enhanced the lipophilicity of the complexes. This increased lipophilicity enhanced the penetration of the complexes into lipid membrane and blocking the metal sites on enzymes of microorganisms.

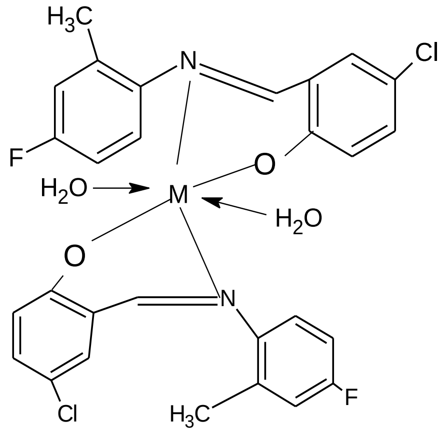

Fig 1. Proposed structure of metal complexes.

4. CONCLUSION

A new Schiff base has been prepared by the condensation of 5-chlorosalicyaldehyde and 4-fluoro-2-methylaniline. The metal complexes of Co(II), Ni(II) and Cu(II) were synthesized and characterized by analytical and spectroscopic techniques. The Schiff base acts as bidentate ligand and coordinating through azomethine nitrogen and deprotonated phenolic oxygen forming a six membered chelate. On the basis of electronic spectral data an octahedral geometry has been suggested for the metal (II) complexes. Antimicrobial activity showed that the metal complexes are more active than free Schiff base ligand.

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