

Synthesis, Characterization and Biological Relevance of O, N- Donor Schiff base ligand and its Iron(III), Cobalt(II), Nickel(II) and Zinc(II) complexes.

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Abstract- Iron(III), Cobalt(II), Nickel(II) and Zinc(II) complexes of Schiff base ligand derived from o-vanillin with o-toluidine were synthesized and characterized by microanalysis, melting points, molecular weight determinations, molar conductance measurements, UV-vis., IR and ¹H-NMR spectral studies. The Schiff base ligand and its complexes were screened for their antimicrobial activity against a number of fungal and bacterial strains. The activity data show that ligand and its metal complexes exhibited moderate to good activity against Gram-positive bacteria and fungi.

Keywords- Schiff base, o-vanillin, Transition metal complexes, Spectral studies, Anti-microbial activities.

I INTRODUCTION

The synthesis of a specific series of ligands was perhaps the most important way in the development of metal complexes which exhibit unique properties and novel reactivity. Schiff bases and their transition metal complexes have a crucial role in the field of biochemistry, pharmacy and medicine due to their excellent properties ranging from antimicrobial ¹⁻³ and catalysis ⁴. The Schiff base transition metal complexes have also been used as biological models to explain the structure of biomolecules and biological processes ⁵. Iron, cobalt, nickel and zinc are life essential metallic elements and exhibit greater biological activity when associated with certain metal protein complexes, participating in oxygen transport, electronic transfer reactions, or the storage of ions.

In view of the above all facts, We report herein the synthesis and characterization of O,N- donor Schiff base ligand (HL) and its four novel complexes of Iron(III), Cobalt (II), Nickel (II) and Zinc (II). Further, the antimicrobial activities of the Schiff base and its complexes have also been assessed against a number of microorganisms and a comparison of the potential has been made therefrom.

II EXPERIMENTAL

Materials and Methods-

All the reagents were purchased from E. Merck and all were of AR grade and used without further purification. They include: iron (III) chloride hexahydrate, cobalt (II) chloride hexahydrate, nickel (II) chloride hexahydrate, zinc(II) chloride and o-toluidine. O-vanillin was obtained from Hi-media and used as received.

Physical Measurements and Analytical data-

Microanalysis of carbon, hydrogen and nitrogen of the compounds were carried out on Carlo Erba 1108 elemental analyzer. Metal contents were analyzed by AAS technique. Chloride was determined by standard procedure reported in the literature ⁶ . IR spectra were recorded on a Perkin-Elmer infrared spectrophotometer in the range 4000-400 cm^{-1} using KBr palletes. Electronic spectra of the complexes were recorded on a Helios-alpha spectrophotometer. The $^1\text{H-NMR}$ spectra of the compounds were recorded on a Bruker Avance 300 MHz in CDCl_3 or DMSO-d_6 using TMS as an internal standard. Molar conductance was measured at room temperature in DMSO using a dip type cell electrode. The molecular weights were determined by Rast camphor method.

In- vitro antimicrobial assay-

The antibacterial activity of compounds were evaluated by paper disc diffusion method against two bacteria namely Escherichia coli and Staphylococcus aureus. Streptomycin was used as reference standard. The antifungal activity of the compounds were screened against two pathogenic fungi, Candida albicans and Aspergillus niger by the agar plate technique using Fluconazole as standard ⁷.

Synthesis of Schiff base ligand (HL)-

A mixture of o-vanillin (0.75 mol, 10 ml) and o-toluidine (0.75 mol, 10 ml) in ethanol was heated under refluxed for 2 hours at 60-65°C. The solution was cooled to room temperature to obtain the orange needle shaped crystals. These were washed with ethanol, dry ether and subsequently dried over anhydrous CaCl_2 in a desiccator.

Synthesis of metal complexes-

The complexes were synthesized by refluxing the reaction mixture of metal salts (ethanol and double distilled water) and respective ligand in 1:2 molar ratios in benzene for 3 to 4 hours. On cooling, the resulting coloured complexes precipitated out, which were filtered by suction, washed several times with ethanol and finally by ether and dried over anhydrous CaCl_2 in the desiccator. The purity of the compounds was checked by TLC using silica gel G.

III RESULTS AND DISCUSSION

Physical Properties-

The observed molar conductance (10.8 to $16.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) of all the complexes in 10^{-3} M dimethyl sulfoxide solutions indicate they are non-electrolytes and their monomeric nature has been confirmed by molecular weight determinations ⁸. The resulting complexes are non-hygroscopic, air stable and coloured solids. The analytical results of the ligand and its metal complexes are enlisted in Table-1.

Table-1 Analytical data of Schiff base ligand and its metal complexes

Compound	Color	M.P.(⁰ C)	Yield (%)	Molecular weight Found / (Calcd.)	Found / (Calcd.) %			
					C	H	N	M
LH (C ₁₅ H ₁₅ NO ₂)	Orange	81	82	238 (241)	73.317 (74.68)	5.85 (6.22)	5.467 (5.80)	-
[Fe(L) ₂ .Cl.H ₂ O]	Shining black	290	84	581 (589.34)	58.87 (61.08)	5.00 (5.09)	4.82 (4.75)	8.87 (9.46)
[Co(L) ₂ .(H ₂ O) ₂]	Dark blue	275	88	568 (574.93)	60.67 (62.62)	4.90 (5.56)	3.80 (4.87)	9.31 (10.23)
[Ni(L) ₂ .(H ₂ O) ₂]	Dark red	240	89	556 (574.69)	59.89 (62.64)	4.01 (5.56)	3.33 (4.87)	10.10 (10.21)
[Zn(L) ₂]	Pale yellow	202	83	540 (545.38)	64.82 (66.01)	4.86 (5.13)	5.11 (5.13)	10.89 (11.98)

Infrared spectra-

In order to study the binding mode of Schiff base to the central metal ion in complexes, the IR spectra of the free ligand is compared with the spectra of corresponding complexes. The important absorption frequencies of the ligand with its complexes and their assignments are enlisted in Table-2.

Table-2 IR absorption frequencies of Schiff base ligand and its metal complexes

Compounds	$\nu(\text{O-H})$ Phenolic	$\nu(\text{C=N})$ Azomethine	$\nu(\text{C-O})$	$\nu(\text{O-H})$ Coordinated water	$\nu(\text{M-O})$	$\nu(\text{M-N})$
LH (C ₁₅ H ₁₅ NO ₂)	3400 br	1628 s	1195 m	-	-	-
[Fe(L) ₂ .Cl.H ₂ O]	-	1605 s	1296 m	3510 br	592 w	480 w
[Co(L) ₂ .(H ₂ O) ₂]	-	1606 s	1310 m	3550 br	580 w	466 w
[Ni(L) ₂ .(H ₂ O) ₂]	-	1622 s	1300 m	3600 br	580 w	495 w
[Zn(L) ₂]	-	1610 s	1205 m	-	570 w	482 w

The IR spectra of the metal complexes show significant changes compared to the Schiff base ligand. A medium intensity band at 1628 cm⁻¹ due to the $\nu(\text{C=N})$ mode of azomethine group. This band shifts to lower wave numbers by 10-25 cm⁻¹ in all the complexes, suggesting the coordination of the azomethine nitrogen to the metal ion. This is further substantiated by the presence of a new band at 480-466 cm⁻¹ assignable to $\nu(\text{M-N})$. The characteristic phenolic $\nu(\text{O-H})$ mode due to the presence of hydroxyl group at ortho position in the free ligand was observed at 3400 cm⁻¹. A band at 1195 cm⁻¹ due to $\nu(\text{C-O})$ phenolic in the ligand spectrum has been shifted to the higher wave number in the spectra of the complexes. Such shift of $\nu(\text{C-O})$ band most probably supports the formation of M-O

bond. The complexes also showed medium intensity bands at appropriate positions in the far infrared region 580-592 cm^{-1} and 460-482 cm^{-1} due to $\sqrt{\nu}(\text{M-O})$ and $\sqrt{\nu}(\text{M-N})$ modes respectively. The presence of coordinated water molecules in Fe(III), Co(II) and Ni(II) complexes is revealed by appearance of a broad band around 3500-3600 cm^{-1} due to $\sqrt{\nu}(\text{O-H})$ mode⁹. The overall IR data suggests the monofunctional bidentate nature of the ligand in the complexes.

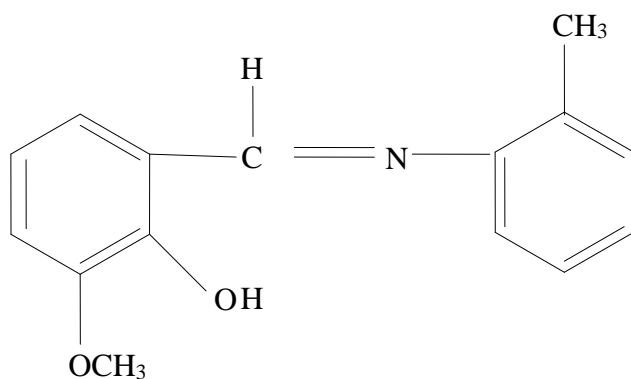
¹H NMR Spectra-

In the ¹H NMR spectrum of the Schiff base ligand was recorded in $\text{CDCl}_3\text{-d}_6$, using TMS as standard. A singlet was observed at 8.57 ppm which can be assigned for azomethine proton. This peak has shifted to the downfield region in the complexes indicating that the coordination of azomethine (>C=N-) to the metal ion. This ligand also show a signal for the phenolic (-OH) proton at 13.33 ppm. This signal shifted downfield in the spectra of complexes indicating the coordination of oxygen of the -OH group with metal ion. The multiplets between 6.90-7.60 ppm are assigned to the aromatic protons¹⁰.

Electronic spectra-

The electronic spectra of the complexes were measured in DMSO. The diffused reflectance spectra of Fe (III) complex exhibit a band at 21,497 cm^{-1} which may be assigned to the ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ transition suggested to octahedral geometry¹¹. The spectra also show a band at 25,400 cm^{-1} which may attribute to ligand-metal charge transfer. The Co (II) complex exhibits three characteristic bands at 12097, 18830 and 23675 cm^{-1} assignable to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ electronic transitions and thus the octahedral geometry can be attributed to it. The electronic spectra of Ni (II) complex display three absorption bands at 11450, 16600 and 25695 cm^{-1} . These have been assigned respectively to the transition ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{P}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ also corresponding to the octahedral geometry¹². The Zn (II) complex do not exhibits any characteristic d-d transitions and may have tetrahedral geometry.

Thus, on the basis of all above studies the expected structures of the Schiff base and its complexes may be represented as shown in Fig.-1



Schiff base (HL)

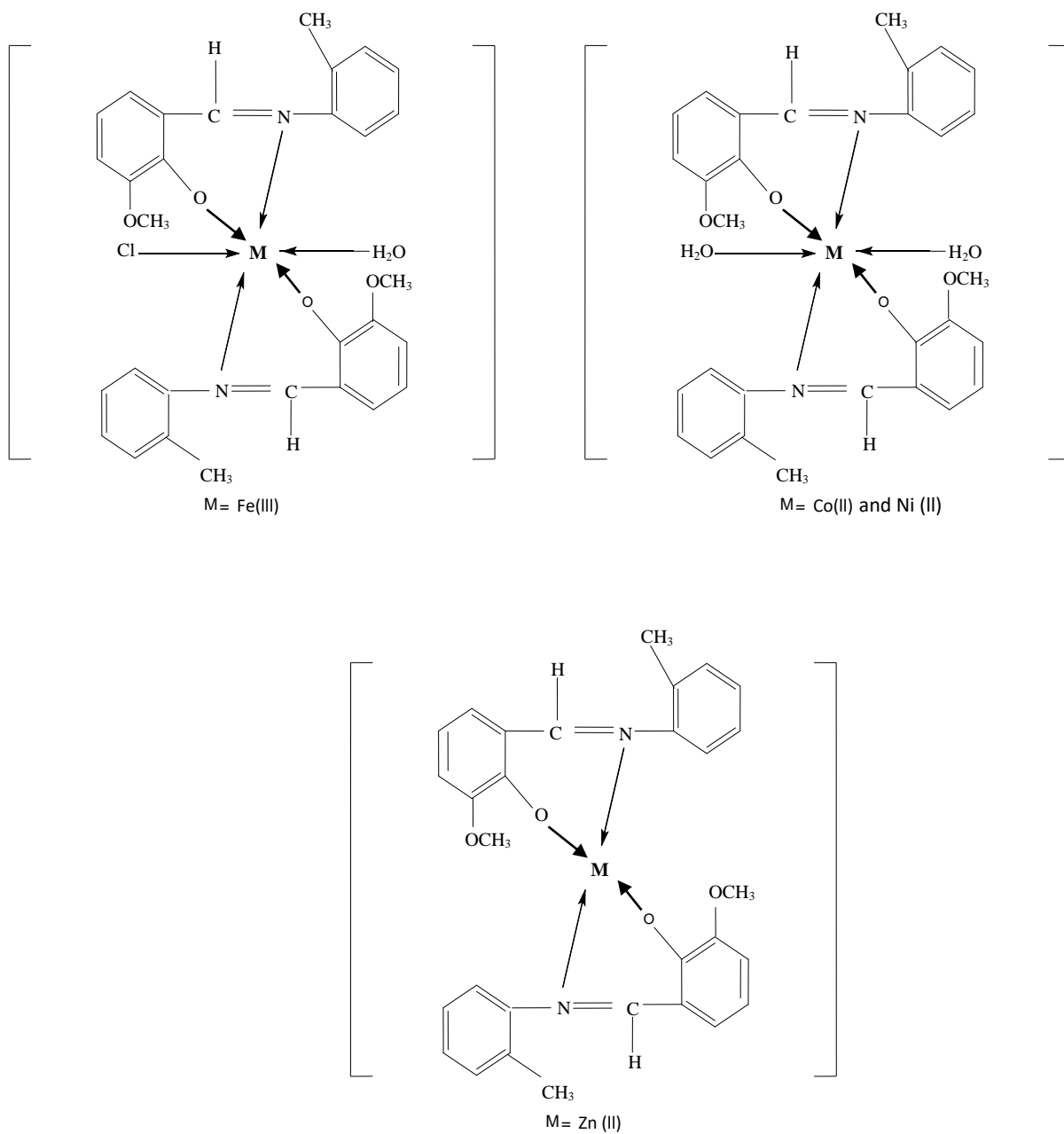


Fig.- 1: Proposed structure of the Schiff base ligand and its metal complexes

Antimicrobial activity-

The free ligand and its respective metal complexes were tested for their *in-vitro* growth inhibition against standard strains including two bacteria namely, Escherichia coli, Staphylococcus aureus and two fungi namely, Candida albicans, Aspergillus niger. The results were compared with those of the standard drug Streptomycin for bacteria and Fluconazole for fungi. The results are summarized in Table-2.

Table – 2 Antimicrobial data of Schiff base ligand and its metal complexes

Inhibition zones (mm)				
	Gram positive	Gram negative	Fungai	
Compound	Staphylococcus Aureus	Escherichia coli	Candida albicans	Aspergillus niger
LH (C ₁₅ H ₁₅ NO ₂)	16.5	16	12	10.5
[Fe(L) ₂ .Cl.H ₂ O]	18	16.5	19.5	10.5
[Co(L) ₂ .(H ₂ O) ₂]	22	21.5	23.5	11.5
[Ni(L) ₂ .(H ₂ O) ₂]	21	20	22	12
[Zn(L) ₂]	19.5	19	18.5	12
Straptomycin	28.5	25	–	–
Fluconazol	–	–	26	22

IV CONCLUSION

A series of Fe(III), Co(II), Ni(II) and Zn(II) complexes were synthesized with neutral bidentate O, N- donor Schiff base ligand (LH) derived from o-vanillin and o-toluidine which were characterized by various physical spectroscopic techniques. The results demonstrate that Fe(III), Co(II) and Ni(II) complexes have an octahedral geometry and Zn(II) complex has a tetrahedral geometry through the involvement of phenolic oxygen atom and azomethine nitrogen atom. The antimicrobial data of these compounds reveals that the complexes show remarkable activity than the parent ligand.

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