

Synthesis, Structural Characterization and Biological Aspects of O, N- Donar Schiff base ligand and its Fe(III), Co(II), Ni(II) and Zn(II) complexes

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Abstract

A mono-functional bidentate Schiff base derived from 2-hydroxy-1-naphthaldehyde with o-toluidine and its four novel complexes of Fe(III), Co(II), Ni(II) and Zn(II) have been synthesized. Schiff base ligand and its metal complexes have been characterized by elemental analysis, molecular weight determinations, molar conductance measurements, UV-vis., IR and ¹H-NMR spectral studies. The IR spectral data suggest the involvement of naphtholic oxygen after deprotonation and azomethine nitrogen in coordination to the central metal ion. The free ligand and its complexes have also been assessed in-vitro against a variety of fungal and bacterial strains.

Key words: Bidentate Schiff base, 2-hydroxy-1-naphthaldehyde, Metal complexes, Spectral studies, Anti-microbial activities.

Introduction

Despite the numerous attempts to develop new structural prototypes in the search for new effective antibacterial compounds, the Schiff bases still remain as one of the most versatile type of compounds against microbes and, therefore, are useful structures for further molecular exploration. The imine or azomethine (>C=N-) group present in such compounds has been shown to be critical to their biological activities. Schiff bases can stabilize different oxidation states of various metal ions, thereby offering the possibility to control the properties of transition metal complex in magnetism, catalysis, electronic spectra etc. 2-hydroxy-1-naphthaldehyde has been used widely to

synthesize a large number of Schiff ligands and their metal complexes. Transition metal complexes with Schiff base ligand not only display their intriguing chemical structures but also show many useful properties and applications in various fields.

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.

Experimental

Ferric chloride hexahydrate, Cobalt chloride hexahydrate, nickel chloride hexahydrate, zinc chloride and m-nitroaniline were purchased from E.Merck and used without further purification. 2-hydroxy-1-naphthaldehyde was obtained from Hi-media and used as received. All other chemicals and solvents used were of AR grade.

Synthesis of Schiff base ligand (HL)

A mixture of of 2-hydroxy-1-naphthaldehyde (0.5 mol,10 ml) and o-toluidine (0.5 mol,10 ml) in ethanol was heated under refluxed for 1.5 hours at 60-65°C. The solution was cooled to room temperature to obtained the yellow needle shaped crystals. These were washed with ethanol, dry ether and subsequently dried over anhydrous CaCl₂ in dasiccator.

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 5 hours. On cooling, the resulting coloured complex precipitated out, which was filtered by suction, washed several times with ethanol and finally by ether and dried over anhydrous CaCl₂ in the desiccator. The purity of the compounds was checked by TLC using silica gel G.

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. 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.

Antimicrobial studies

The antibacterial activity of compounds were evaluated by disc diffusion method against *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.

Results and discussion

The observed molar conductance (8.9 to $16.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) 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. The resulting complexes are non-hygroscopic, airstable 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.(°C)	Yield (%)	Molecular weight Found / (Calcd.)	Found / (Calcd.)%			
					C	H	N	M
LH(C ₁₈ H ₁₅ NO)	Yellow	120	89	229(261)	81.847 (82.75)	5.68 (5.74)	5.027 (5.36)	—
Fe(L) ₂ .Cl.H ₂ O	Yellowish Green	198	85	619(629.34)	65.00 (68.64)	4.25 (4.76)	3.69 (4.44)	8.86 (9.14)
Co(L) ₂ .2H ₂ O	Dirty Green	151	86	602(614.93)	65.58 (70.26)	5.01 (5.20)	3.80 (4.55)	8.69 (9.27)
Ni(L) ₂ .2H ₂ O	Light Green	320	89	599(614.69)	69.69 (70.27)	4.86 (5.20)	4.10 (4.55)	8.63 (8.00)
Zn(L) ₂	Red	208	82	550(585.38)	74.00 (73.79)	4.80 (4.78)	5.02 (4.78)	10.17 (10.90)

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	$\sqrt{\text{(O-H)}}$ Naphtholic	$\sqrt{\text{(C=N)}}$ Azomethine	$\sqrt{\text{(C-O)}}$	$\sqrt{\text{(O-H)}}$ Coordinated water	$\sqrt{\text{(M-O)}}$	$\sqrt{\text{(M-N)}}$
LH(C ₁₈ H ₁₅ NO)	3416 br	1638 s	1296 m	-	-	-
Fe(L) ₂ .Cl.H ₂ O	-	1616 s	1302 m	3460 br	585 w	482 w
Co(L) ₂ .2H ₂ O	-	1612 s	1310 m	3400 br	580 w	469 w
Ni(L) ₂ .2H ₂ O	-	1620 s	1301 m	3500 br	585 w	491 w
Zn(L) ₂	-	1610 s	1300 m	-	575 w	476 w

The IR spectra of the metal complexes show significant changes compared to the Schiff base ligand. A medium intensity band at 1638 cm⁻¹ due to the $\sqrt{\text{(C=N)}}$ mode of azomethine group. This band shifts to lower wave numbers by 10-28 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 482-469 cm⁻¹ assignable to $\sqrt{\text{(M-N)}}$. The characteristic naphtholic $\sqrt{\text{(O-H)}}$ mode due to the presence of hydroxyl group at ortho position in the free ligand was observed at 3416 cm⁻¹. A band at 1296 cm⁻¹ due to $\sqrt{\text{(C-O)}}$ phenolic in the ligand spectrum has been shifted to the higher wave number in the spectra of the complexes. Such shift of $\sqrt{\text{(CO)}}$ 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 580-596 cm⁻¹ and 492-469 cm⁻¹ due to $\sqrt{\text{(M-O)}}$ and $\sqrt{\text{(M-N)}}$ modes respectively 9-14. The presence of coordinated water molecules in Fe(III), Co(II) and Ni(II) complexes is revealed by appearance of a broad band around 3400-3500 cm⁻¹ due to $\sqrt{\text{(O-H)}}$ mode. The overall IR data suggests the monofunctional bidentate nature of the ligand in the complexes.

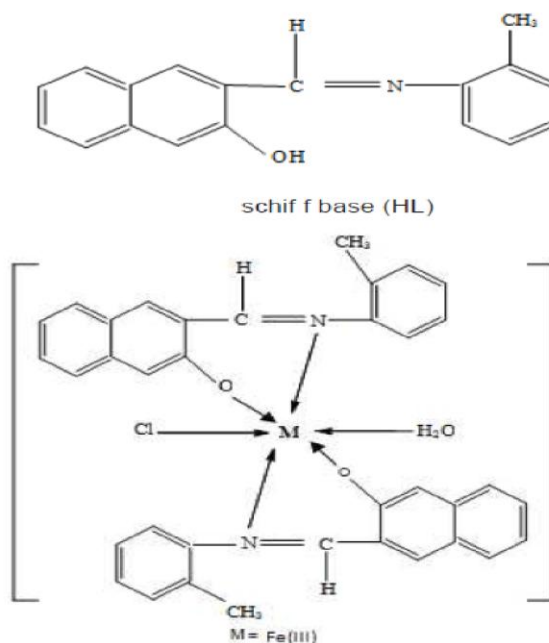
¹H NMR Spectra

In the ¹H NMR spectrum of the Schiff base ligand, a singlet was observed at 9.56 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 naphtholic (-OH) proton at 13.39

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 6.69-8.60 ppm are assigned to the naphthylidene aromatic protons.

Electronic spectra

The electronic spectra of the complexes were measured in DMSO. In the high spin Fe(III) complex, the 6S free ion ground term is the only sextuplet term arising from d^5 and it does split in the crystal field. All the electronic transitions are thus spin-forbidden, as well as Laporte forbidden, so that ligand field bands are very weak. The Co (II) complex exhibits three characteristic bands at 11096, 18630 and 23575 cm^{-1} assignable to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ electronic transitions and thus the octahedral geometry can be attributed to it. The electronic spectra of Ni (II) complex display three absorption bands at 10450, 16600 and 25695 cm^{-1} . These have been assigned respectively to the transition ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(P) \rightarrow {}^3T_{1g}(P)$ also corresponding to the octahedral geometry. 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



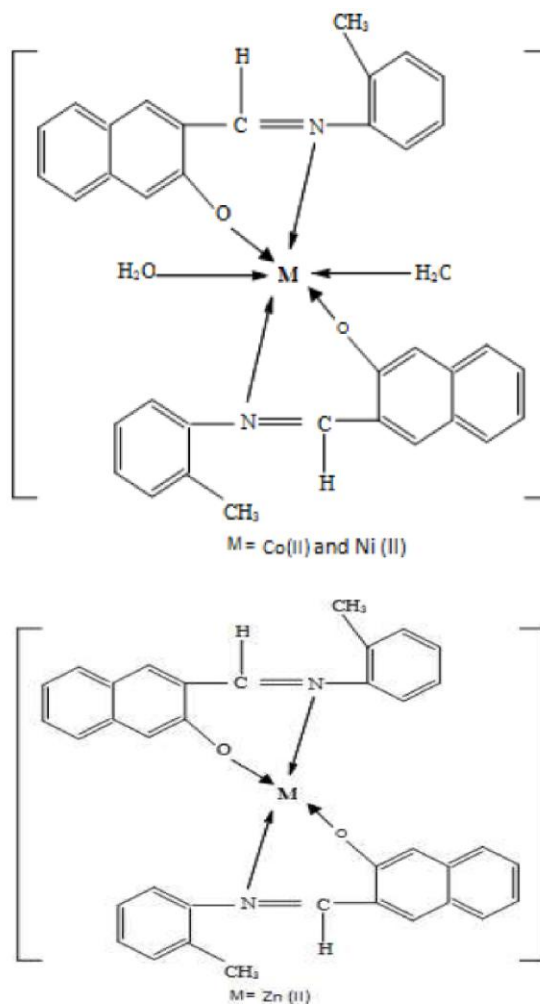


Fig.- 1: Proposed structure of the Schiff base ligand and its metal complexes

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-3.

Table – 3 : Antimicrobial data of Schiff base ligand and its metal complexes**Inhibition zones (mm)**

Compound	Gram positive	Gram negative	Fungai	
	StaphylococcusAureus	Escherichiacoli	Candida albicans	Aspergillusniger
LH(C ₁₈ H ₁₅ NO)	18.5	16	14	11.5
Fe(L) ₂ .Cl.H ₂ O	18	12	11.5	10
Co(L) ₂ .2H ₂ O	20	14.5	13	11.5
Ni(L) ₂ .2H ₂ O	20	21.5	17.5	12
Zn(L) ₂	19.5	16.5	15.5	12
Straptomycin	23	25	–	–
Fluconazol	–	–	20	22

Conclusion

A series of Fe(III), Co(II), Ni(II) and Zn(II) complexes were synthesized with neutral bidentate O, Ndonor Schiff base ligand (LH) derived from 2-hydroxy-1-naphthaldehyde and o-toluidine and 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 naphtho 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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