International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 9 Issue 01, January-2020

Synthesis, Characterization and Antimicrobial Studies of Metal Complexes from 2-Hydroxy-3-Methoxy Benzaldehyde and L-Serine

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***Abstract* -Transition metal complexes Cu(II), Ni(II) and Co(II) with Schiff base ligand (s)-2-(2-hydroxy-3-methoxybenzylideneamino)-3-hydroxypropanoic acid(HMA-HPA) were synthesized. The Schiff base ligand and the complexes were characterized by elemental analysis, spectral studies like FT-IR, UV-Vis, magnetic susceptibility and conductance studies. The prepared metal complexes and the free ligand were tested for their antimicrobial effectiveness against bacterial strains *Staphylococcus aureus ,Streptococcus mutans, Proteus Vulgaris, Klebsilla Pneumonie, Escherichia coli, Pseudomonas aeuroginosae, Bacillus* subtilis and antifungal activity against *Aspergillus niger, Aspegillus flavus, Saccharomyces cerevisiae* using disc-diffusion method.**

Key words:* *Transition metal, elemental analysis, conductance,disc-diffusion method.

I. I.INTRODUCTION

Transition metals are the metallic elements comprising incomplete d or f shells and they accept electrons from the ligand to form coordination complexes. Schiff bases prepared by the condensation process from amino acids and carbonyl compounds comes under the significant class of ligands comprising C=N linkage in their geometrical structure possessing important biological properties such as antibacterial, antifungal, antimalarial and anticancer activities [1]. Transition metal complexes find its major applications as antibacterial and antitumour agents for the bacterial infections and cancers.The use of Schiff bases in birth control, as oxygen detector and in food packages is also noted [2]. 2-hydroxy-3-methoxy benzaldehyde is a natural aldehyde mainly used for the treatment of belly aches and also used as spice products [3]. In this paper the Synthesis and spectral characterization of the Schiff base ligand(HMA-HPA) and the metal complexes Cu(II), Ni(II), Co(II) from 2-hydroxy-3-methoxybenzaldehyde and L- Serine, their antimicrobial activities were also discussed.

II. EXPERIMENTAL

The solvents and chemicals used in the present work were of analytical reagent grade. The metal (II) nitrate salts and the solvents DMSO, ethanol, diethyl ether were purchased from E.Merck. 2-hydroxy-3-methoxybenzaldehyde and L-serine were purchased from Sigma Aldrich. The FT- IR spectra were obtained from Thermo Nicolet, Avatar 370 in the frequency range 4000-400 cm^{-1}. The ultra violet visible spectral data were recorded in the range 200-800 nm using Varian, Cary 5000 spectrophotometer. The magnetic susceptibility data were calculated at room temperature using Gouy balance in DMSO solution . Conductivity measurements were carried out at room temperature using CM-82T Elico Conductivity bridge in DMSO solvent. The microorganisms used for antimicrobial studies were purchased from Microbial Type Culture Collection and Gene Bank (***MTCC***) Chandigarh.

A. Synthesis of Schiff base Ligand(HMA-HPA)

Aqueous solution of L-serine (0.1 mol,20 ml) was mixed with hot ethanolic solution of 2-hydroxy-3-methoxy benzaldehyde (0.1 mol, 20 ml) was heated under reflux for 5 h at 65°C. The completion of the reaction can be noted by TLC and the solution can be concentrated to half its volume at 65° C. This mixture is kept overnight without any disturbance. On mild heating yellow coloured flakes separates out which was filtered, repeatedly washed with diethyl ether and dried.

B. Preparation of metal complexes

To the hot ethanolic solution of the Schiff base ligand (0.1mol,20 ml) an aqueous solution of metal salts $Cu(NO_3)_2.3\ H_2O$, $Ni(NO_3)_2.6\ H_2O$ and $Co(NO_3)_2.\ 6\ H_2O$ were added separately drop by drop with continuous stirring at 65° C. The mixture was refluxed for 3 h. 5-6 drops of aqueous NaOH solution (0.1 mol) was added to this mixture until precipitates occurs. The resulting solution is heated for 1 h and the volume is reduced to half and allowed to stand overnight without any disturbance. The obtained precipitates were filtered, washed with diethyl ether and dried.

C. Antimicrobial Assay

The Schiff base Ligand and the metal complexes were screened for *invitro* antibacterial activity against *Staphylococcus aureus ,Streptococcus mutans, Proteus*

Vulgaris, Klebsilla Pneumonie, Escherichia coli, coli, Pseudomonas aeuroginosae, Bacillus subtilis and antifungal activity *against Aspergillus niger, Aspegillus flavus, Saccharomyces cerevisiae* using Kirby- Bayer's disc diffusion method [4] . Bacterial and Fungal strains were swabbed in nutrient agar plate and SDA agar plate (Disc 6mm, Whatman No.1 filter Paper).10 µ l and 40 µl concentration of the extract separately were introduced into the disc for bacterial and fungal and the plates were subjected to incubation at 37° C each for 24 and 48 h respectively. After the end of incubation their activity is measured in terms of diameter of zone of inhibition in mm with their control using DMSO. Streptomycin(S 25) is used as standard for antibacterial activity and Fluconazole as standard for antifungal activity.

III. RESULTS AND DISCUSSION

A. Elemental Analysis

The elemental analysis, analytical data of the Schiff base ligand and metal(II) complexes are given under Table.1 indicates the metal complexes followed 1:1 (metal : Ligand) Stoichiometry and the metal complexes were found to be soluble in DMSO and DMF.

Table 1.Physical Characterization and Analytical data of Schiff base Ligand and its Metal(II) complexes

Complex	Empirical Formula	Colour	M.W.	Yield	Elemental analysis, found(calculated)%			
				%	C	H	N	M
Ligand (HMA-HPA)	$C_{11}H_{13}NO_5$	Yellow	239	73	55.10 (55.23)	5.12 (5.48)	5.40 (5.86)	--
Cu(II)complex	$C_{11}H_{23}CuN_3O_{17}$	Dark green	533	68	24.90 (24.79)	4.14 (4.35)	7.60 (7.89)	11.72 (11.93)
Ni(II) complex	$C_{11}H_{23}N_3NiO_{17}$	brown	528	69	24.90 (25.02)	4.10 (4.39)	7.73 (7.96)	11.34 (11.12)
Co(II)complex	$C_{11}H_{17}CoN_3O_{14}$	brown	474	70	27.68 (27.86)	3.52 (3.61)	8.40 (8.86)	12.50 (12.43)

B. IR spectra

IR spectral data of the ligand and the metal compexes were tabulated under Table.2 . The Schiff base shown in the Fig. 1 has its characteristic IR bands at 3144 cm^{-1} ν (-OH), ν(-CH=N-) 1648 cm^{-1}, ν (C-O) 1245 cm^{-1}, ν_{asy}(COO^-) 1572 cm^{-1}, ν_{sym}(COO^-)1349 cm^{-1}.After the complexation process, the sharp band observed for the azomethine group ν (-CH=N-) at 1648 cm^{-1} [5] in the ligand spectra is shifted to lower frequency values 1621-1633 cm^{-1} in the case of metal complexes indicating the coordination of imino nitrogen with the metal ion [6]. The phenolic (C-O) stretching also underwent shift towards lower frequencies 1210-1234 cm^{-1} shows the coordination of phenolic oxygen with the metal ion [7]. The presence of broad bands in the metal complexes extended over the region from 3398-3450 cm^{-1} and a low frequency bands at 824-835 cm^{-1} corresponds to the –OH stretching and rocking vibrations of the coordinated water molecules [8]. The respective asymmetric ν_{asy}(COO^-) vibrations were shifted to their downward values 1560-1564 cm^{-1} simultaneously the symmetric vibrations ν_{sym}(COO^-) were shifted to their upward frequency 1356-1360 cm^{-1} from the ligand value and their difference Δ(COO^-) is greater than 200 cm^{-1} indicates the monodentate coordination with the metal ion [9]. The presence of new medium intensity bands appeared in the spectra of the metal complexes at about 505-585 cm^{-1} and 431-446 cm^{-1} due to ν (M-O) and ν (M-N) stretching vibrations formed after the complexation supports the coordination of imino nitrogen and phenolic oxygen with the metal ion [10]. The sharp bands noticed in all the metal complexes at 1382-1386cm^{-1} corresponds to the ν (NO_3^-) free nitrate anions.

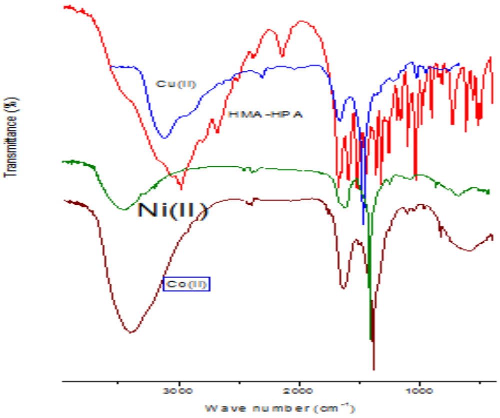


Fig.1. IR spectra of Ligand ,Cu(II),Ni(II) and Co(II) complexes

Table.2 Characteristic IR bands of ligand (HMA-HBA) and Metal (II) complexes in cm^{-1}

Compound	ν_{OH} (phenolic/H_2O)	ν (CH=N)	ν_{asy} (COO^-)	ν_{sym} (COO^-)	ν (C-O)	ν(M-O)	ν(M-N)	Others
(HMA-HPA)	3144	1648	1572	1349	1245	--	---	--
Cu(II) complex	3450 829	1631	1564	1360	1214	505	431	1382
Ni(II) complex	3422 835	1621	1560	1356	1210	585	435	1384
Co(II) complex	3398 824	1633	1562	1357	1234	568	446	1386

C. Electronic spectral studies

The electronic spectra of the ligand shown in the Fig. 2 exhibited two characteristic bands at 36363 and 28409 cm^{-1} with the assigned electronic transitions $\pi \rightarrow \pi^*$ of the aromatic ring and $n \rightarrow \pi^*$ transitions of the azomethine group. Copper complex showed a single band found at 16501 cm^{-1} with the assigned transition $^2B_{1g} \rightarrow {}^2A_{1g}$ support distorted square planar geometry[11,12]. The Ni(II) complex shows single d-d transition at 15847 cm^{-1} indicating $^3T_1(F) \rightarrow {}^3T_1(P)$ forming tetrahedral environment around the metal ion[13]. The electronic spectra of Co(II) complex shows bands at 24875cm^{-1} with the corresponding transitions $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ thereby supporting distorted square planar geometry [14,15] .

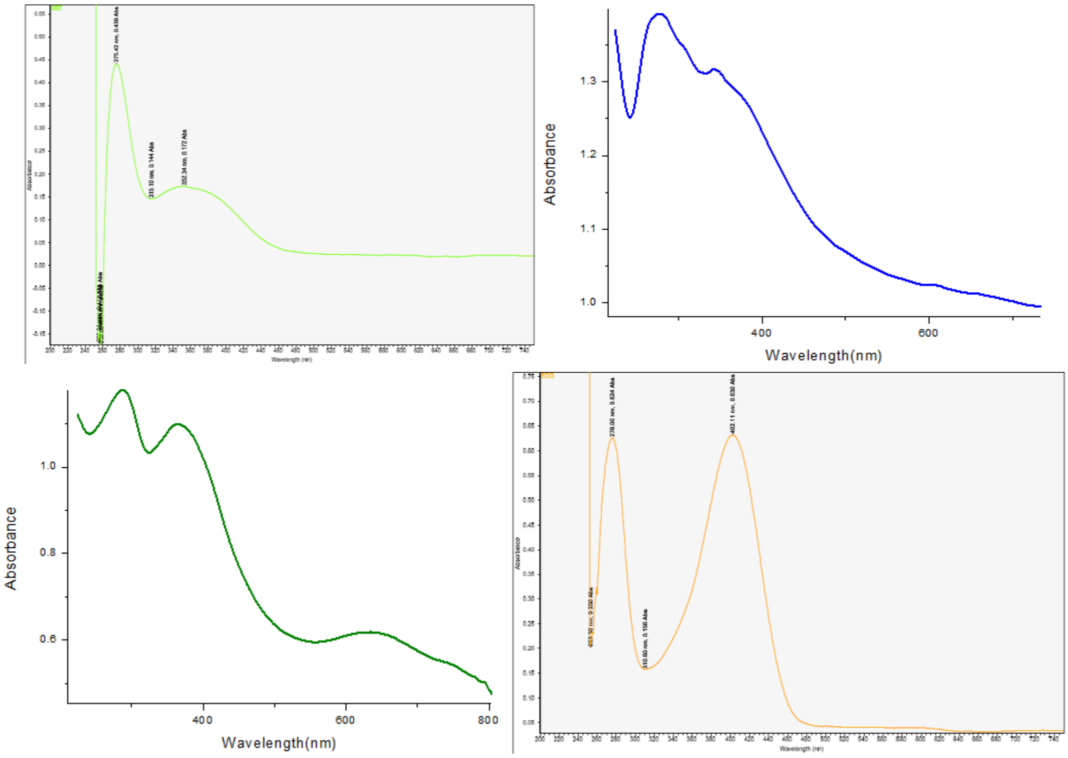


Fig. 2 Electronic spectra of Schiff base Ligand HMA-HPA,Cu(II), Ni(II), Co(II) complexes.

D. Magnetic susceptibility

The magnetic moment calculated for the d^{9}Cu(II) complex is 1.86 BM reported as distorted square planar geometry[16]. The magnetic moment observed for d^8 Ni(II) complex is 3.52 BM which is more compatible with the tetrahedral geometry[17]. The magnetic susceptibility measurement observed for the d^7 Co(II) complex is 2.31 BM which agrees with the distorted square planar geometry with the unpaired electron in the system[18].

E. Molar Conductivity

The Conductance measurements were carried out at room temperature of 10^{-3} M of their solutions in DMSO to confirm the charge type of metal complexes. The conductance values for the present metal complexes Cu(II), Ni(II) and Co(II) were found to be 87,70, 90 Ohm^{-1} cm^2 mol^{-1} respectively suggests the complexes are electrolytes [19] leaving nitrate anions outside the coordination sphere in solution and they dissociate very slowly in the solvent.

F. Antimicrobial Activity

The results obtained from the antibacterial studies were given under Table.3. The Ni(II) and Co(II) metal complexes exhibited more inhibition than the ligand but of course less than their standard against the growth of *bacteria S. aureus and S. mutans.* Cu(II) complex shows better inhibition against *Pseudomonas aeuroginosae*, possess moderate inhibition against *S.mutans* and *P.vulgaris* but shows zero activity towards *S.aureus.* Only the ligand shows some less inhibition against *E.coli* and *B.subtilis* and the complexes fail to show any activity. In the case of fungal microorganisms shown in Table.4 only Co(II) complex shows moderate inhibition towards *A. flavus* and *A.niger*. The increased inhibition activity of the metal complexes than the parent ligand in the Fig.3 can be well explained by Tweedy's Chelation theory [20] and this chelation causes the metal complexes to be more lipophillic. This increased lipophillicity allows the metal complexes enter into the lipid membranes of the cell [21] and thus destroys the respiration process of the cell thereby affecting the growth of the organism.

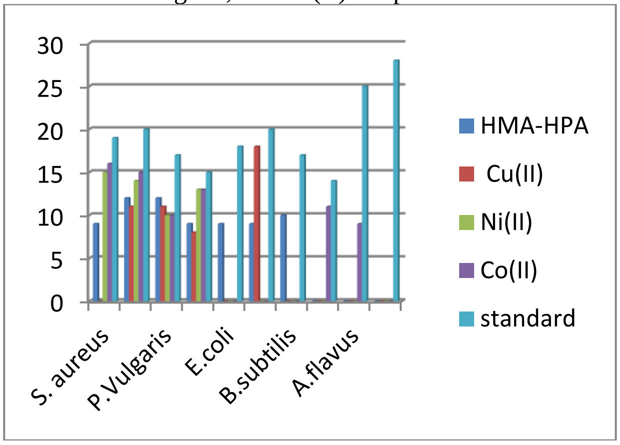
Table .3 Antibacterial activity of ligand HMA-HPA and metal(II) complexes

Compounds	Zone of inhibition (mm)						
	Bacteria						
Microorganisms	*S.aureus*	*S.mutans*	*P. vulgaris*	*K. pneumonie*	*E. coli*	*P. aeuroginosae*	*B. subtillis*
(HMA-HPA)	9	12	12	9	9	9	10
Cu(II) complex	--	11	11	8	--	18	--
Ni(II) complex	15	14	10	13	--	--	--
Co(II) complex	16	15	10	13	--	--	--
Streptomycin	19	20	17	15	18	20	17
Negative control	--	--	--	--	--	--	--

Table .4 Antifungal activity of ligand HMA-HPA and metal complexes

Compounds	Zone of inhibition (mm)		
	Fungi		
Microorganisms	*A. niger*	*A. flavus*	*S. cerevesiae*
(HMA-HPA)	--	--	--
Cu(II)complex	--	--	--
Ni(II) complex	--	--	--
Co(II) complex	11	9	--
Fluconazole	14	25	28
Negative control	--	--	--

Fig.3. Antimicrobial Activity of Schiff base ligand, metal (II)complexes



CONCLUSION

From the above spectral studies and determinations it is concluded that the Schiff base ligand (HMA-HPA) acts as tridentate by coordinating through azomethine nitrogen, phenolic oxygen, carboxylato oxygen. Electronic spectral and magnetic studies support Cu(II),Co(II) complexes posses distorted square planar geometry and Ni (II) complex adopts tetrahedral geometry around the corresponding metal ion. The antimicrobial studies carried by the ligand and the synthesised metal complexes presented better results against bacterial strains while comparing with fungal pathogens.

ACKNOWLEDGEMENTS

The authors recorded their thanks to SAIF, Cochin for spectral and analytical data, Inbiotics, Nagercoil for antimicrobial activity and S.T. Hindu College for providing necessary facilities.

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