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SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE METAL COMPLEXES DERIVED FROM 3-ETHOXYSALICYLALDEHYDE AND 2-AMINO-4-METHYL PHENOL.

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ABSTRACT

A new Schiff base, 2(E)-(5-hydroxy-2-methylphenylimino) methyl)-6-ethoxyphenol (EAP), has been synthesized from 3-ethoxysalicylaldehyde and 2-amino-4-methyl phenol. Metal complexes of the Schiff base were prepared from chloride salts of Ni(II), Co(II), Cu(II) and Zn(II) in alcoholic medium. Their structural data and antibacterial studies have been established on the basis of analytical, molar conductance, infrared electronic and magnetic studies, ^{1}H-NMR, ^{13}C- NMR, ESR and TGA. On the basis of color, magnetic moments and electronic spectral data, The geometries of Co(II), Ni(II), Cu(II), Zn(II) complexes have been assigned.

KEYWORDS: Schiff base, 3-ethoxysalicylaldehyde, 2-amino-4-methyl phenol, Metal complexes, ESR, Antibacterial activity.

INTRODUCTION

Schiff bases are considered as a very important class of organic compounds which have wide applications in many biological aspects.[1] They contains azomethine (C= N) as functional group and hence act as an effective ligand.[2] The azo group possesses excellent donor properties and is important in co-ordination chemistry,[3] and some azo compounds have shown to posses good antibacterial activity. Transition metal complexes of schiff bases are one of the most adaptable and thoroughly studied system. These complexes have also applications in clinical and analytical and industrial, in addition to their important roles in catalysis and organic synthesis.[4] The chemistry of transition metal complexes with schiff bases have played an important role in the development of co-ordination chemistry as a whole. Multidenate schiff bases have been widely used as ligands, because they can be easily attached to metal ions and they have been used to the formation of highly stable variety of catalytic, biological, antifungal, antitumor and anti HIV activities.[5-8] Vanilin and O-vanilin are such natural compounds which have both phenolic OH and aldehyde group. They are positional isomers, in which O-vanilin shows contradictory effects. There are several reports indicating that O-vanilin induces mutation and it has also been found to enhance chromosomal abreactions in in-vitro systems.[9-12] Morad *et.al* synthesized Ni(II) complex with schiff base ligand from salicylaldehyde of 2-amino benzoic acid and characterized them by various methods and also studied its antibacterial activity.[13] Matangi sunitha*et.al* synthesized Ni(II), Co(II), Cu(II), Zn(II) and VO(II) complex with 3-ethoxysalicylaldehyde and 2-(aminophenyl)1-H-benzimidazole and characterized it by various studies.[14]

MATERIAL AND METHODS

All chemicals like 3-ethoxysalicylaldehyde, 2-amino-4-methyl phenol, metal chloride salts and solvents used were reagent grade (Alfa aesar/Avra/spectrum) products and were used as such without further purifications. The percentage composition of C, H, N of complexes were measured Flash EA 112 series. Infrared spectra were measured using KBr pellets with Perkin Elmer RX1, Spectrophotometer in conventional range of 4000-400 cm^{-1}. The electronic absorption spectra of the complexes were recorded using a Perkin Elmer Lambda 35 Spectrophotometer in the range of 350 nm - 800 nm. Magnetic susceptibility measurements on powder samples were carried out by Gouy method. The diamagnetic correction were made by Pascal's constant and $Hg[Co(CNS)_4]$ was used as calibarant. The molar conductance measurements were carried out in DMSO (10^{-3} M) using Digisun Electronic digital conductivity meter DI-909 Having dip-type cell calibrated with KCl. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Mercury Plus 300 MHz NMR spectrometer by employing TMS as internal standard.

Synthesis of Schiff base (EAP)

The Schiff base was prepared by condensation of 3-ethoxysalicylaldehyde (0.01M) with 2-amino-4-methyl phenol (0.01M) in methanol and the resulting mixture were stirred for 2-3hrs during which a red colored solid product was obtained. The product were collected by filtration, washed several times with ethanol and recrystallized from hot ethanol and dried in a vacuum desiccator. The melting point of the ligand was found to be 179ºC. The yield of red colored product is 92٪.

Preparation of the complexes

The complexes of Co(II), Ni(II), Cu(II), Zn(II) were prepared by refluxing respective metal chloride in ethanolic medium of ligand (1:1). The resulting mixture was refluxed for 2-4 hrs at 70-80ºC. On cooling colored solid products were collected by filtration and then washed several times with diethyl ether until the washing become colorless. The product was dried in air and stored in desiccators over anhydrous $CaCl_2$ under vacuum.

RESULTS AND DISCUSSION

The reactions of appropriate metal (II) chloride with the Schiff base ligand derived from 3-ethoxysalicylaldehyde and 2-amino-4-methyl phenol acts as a bidentate ligand and the complexes were prepared in ethanol medium. The formulations were in accordance with data of elemental analysis and physic chemical measurements. The molar conductance of metal complexes are measured using 10^{-3} M DMSO solvent, the obtained values (Table 1) suggests that they are of non-electrolyte in nature.

Table 1: Analytical data and physical data of the ligand and its complexes.

Compound	Molecular formula	Mol. Weight	Color	Melting point	Elemental analysis Calculated/(Observed)			Ω cm^{-1}
					C	H	N	
Ligand	$C_{16}H_{17}NO_3$	271.31	Red	179	70.83 (69.20)	6.32 (5.80)	5.16 (4.82)	-
EAB.$CoCl_2$	$C_{16}H_{21}Cl_2CoNO_5$	436	Light Brown	>300	44.06 (43.58)	4.62 (4.28)	3.21 (3.05)	32.67
EAB.$NiCl_2$	$C_{16}H_{21}Cl_2NiNO_5$	437	Light yellow	>300	44.08 (43.78)	4.60 (4.46)	3.19 (3.02)	38.90
EAB.$CuCl_2$	$C_{16}H_{21}Cl_2CuNO_5$	440	Dark green	280	43.60 (42.78)	4.57 (4.28)	3.18 (2.99)	27.89
EAB.$ZnCl_2$	$C_{16}H_{21}Cl_2ZnNO_5$	442	Light Yellow	240	43.42 (42.88)	4.55 (4.35)	3.16 (2.78)	36.09

Infrared spectra of the Schiff base and its complexes

The infrared spectra provide valuable information regarding the nature of the functional group attached to the metal atom. In order to study the bonding mode of Schiff base to the metal complexes, IR spectrum of the free ligand was compared with the spectra of the complexes. The main infrared bands and their assignments are listed in (Table-2).

- The Infrared band assignment of all metal complexes exhibit broad band in the 3400 - 3350 cm^{-1} indicating the presence of co-ordinated water molecule in Cu, Ni, Co and Zn.[15]

- The spectrum of free Schiff base ligand show strong absorption at 1638 cm^{-1} assigned for the $\gamma(C = N)$ of azomethine group. In the spectra of analyzed complexes the absorbtion band have been shifted to lower region by 27 - 45 cm^{-1} which confirms the co-ordination of azomethine group through N-atom.[16]
- The stretching frequency γOH at 3062 cm^{-1} in free ligand which on complexation shifted to lower wave number at 3042 - 3029 cm^{-1} in all metal complexes which indicating –OH group involved in metal bonding.
- The New bands were observed region in complexes compared to the spectrum of ligand The bands in the range of 513-566 cm^{-1} and 408 – 463 cm^{-1} corresponding to γM-N[17,18] and γM-O.[19]
- The $\gamma_{C\text{-}O}$ (phenolic) stretching frequency of ligand is seen at 1376 cm^{-1} which gets shifted to a lower frequency region in the complexes in the range of 1372-1326 cm^{-1} and this is indicative of bonding through phenolic oxygen.[20]

Table 2: Infrared spectra of the Schiff base and its complexes.

Compound	γOH/H_2O	γC=N	γC-O	γM-N	γM-O
Ligand (EAP)	3068	1638	1398	-	-
EAP.$CoCl_2$	3038	1615	1377	541	410
EAP.$NiCl_2$	3029	1617	1377	565	418
EAP.$CuCl_2$	3042	1599	1385	541	458
EAP.$ZnCl_2$	3044	1613	1348	566	425

Electronic spectra

- The spectrum of Co(II) complex showed absorptions 22,222 cm^{-1} assigned to and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition. The cobalt(II) complex shows a magnetic moment of 4.82BM at room temperature. The magnetic moment and electronic transition suggest an octahedral geometry.[21]
- The electronic spectra of the Nickel(II) complex exhibit absorption bands at 21,834 cm^{-1} assigned to $^3A_{2g} \rightarrow {}^4T_{1g}(P)$ transition.[22] The magnetic moment of 3.1BM and electronic transition suggest an octahedral geometry of the complex.
- The electronic spectra of Copper(II) complex exhibit absorption band at 22,123 cm^{-1} mainly due to$^2E_g \longrightarrow {}^2T_{2g}$ transition. The magnetic moment of 1.74BM. Electronic spectrum and ESR studies suggests distorted octahedral geometry for the complex.

- The Zinc(II) complex shows no d-d transition and found to be diamagnetic in nature. On the basis of analytical, conductance and spectral data Zinc(II) complex was assigned to octahedral geometry.

Table 3: Electronic data of Schiff base and its complexes

Compound	**UV-Visible bands (cm^{-1})**	**μ eff (BM)**
Ligand (EAP)	-	-
Co(II) complex	22,222	4.52
Ni(II) complex	21,834	3.1
Cu(II) complex	22,123	1.74
Zn(II) complex	-	-

^{1}H-NMR and ^{13}C-NMR spectra

The ^{1}HNMR spectrum of the ligand in DMSO shows the following signals given in Table 4. The sharp singlet at 7.86 ppm attributed to azomethine proton confirming the formation of the ligand.[23,24]

Another singlet corresponding to one proton is observed in 14.02 ppm is due to phenolic proton. The signals in the region 6.54-7.42 ppm appear due to presence of aromatic protons were shown in figure.

The ^{13}CNMR spectrum of the ligand is recorded in $CDCl_3$. Azomethine carbon is observed at 152.81 ppm and phenolic carbon is observed at 169.48 ppm. Peak in the region 110-147 ppm were due to aromatic carbon.

Table 4: ^{1}H NMR of the Schiff base ligand

Chemical Shift,δ,ppm	**Functional Group assigned**
7.86(1H,s)	-CH=N-
14.02(1H,s)	-OH
6.54-7.42	Aromatic protons

ESR spectra of Cu(II) complexes

ESR spectral studies of Cu(II) complex provide information of the metal ion environment. The ESR spectrum of Cu(II) was recorded in DMSO at liquid nitrogen temperature. This complex in frozen state at 77K shows four slightly ressloved peaks of low intensities in the low field region and one intense peak in the high field region shown in figure.

The g values of the complex are $g_\parallel(2.2906) > g_\perp(2.087) > 2.0023$,indicating that the unpaired electron in the ground state of Cu(II) is predominantly in dx^2-y^2. The value of exchange interaction term G, estimated from the following expression is 3.3.
$G = g_\parallel-2.0023/g_\perp-2.0023$.

If G>4.0, the local tetragonal axes are aligned parallel. If G<4.0, significant exchange coupling is present and misalignment is appreciable. The observed value for the exchange interaction the term G suggests that the complex has distorted octahedral geometry.

Thermal analysis

A representative thermogram of Ni complex is given in figure. It is found from the figure that the heating rates were suitably controlled at 10ºC min^{-1} under nitrogen atomosphere and the weight loss was measured from the ambient temperature up to 1000ºC. Thermogram of Ni complex indicated a total weight loss of 42٪ up to 1000ºC which is observed in two steps i) Complexes lost co-ordinated H_2O molecules between 100-200ºC, from which the decomposition begins in the complex. ii) The formation of metal oxides above 600ºC for the Ni(II) complex.[25]

Antibacterial studies

The synthesized Schiff base and their corresponding metal complexes were screened against Bacillius subtillis, Staphylococcus, Escherischiacolli, Klebsillapneumonia to assess their potential as antimicrobial agent by diffusion method.[26]

The diffusion method requires filter paper disc, the medium used is muller-hinton agar and diameter of inhibition zone is visually read at 24hour after incubation at 37ºC. The compounds are added on to the filter paper containing this medium. The antimicrobial activity was estimated on the seeded agar plates. Chlorophenicol was used as standard. DMSO was used as solvent control. The zones of inhibition based upon zone size around the discs were measured. The measured zone of inhibition against the growth of various micro organism is listed in table 5. It is found that the metal complexes have higher antibacterial activity than the free ligand. Hence on complexation increases the microbial activity.[27][28]

Table 5: Growth inhibition zone of microbes in mm

Compound	E.coli	Kleb	B.subitils	S.aureus
Ligand	8	9	10	10
Co(II) complex	8	13	13	12
Ni(II) complex	9	10	8	8
Cu(II) complex	10	8	9	10
Zn(II) complex	10	9	11	10

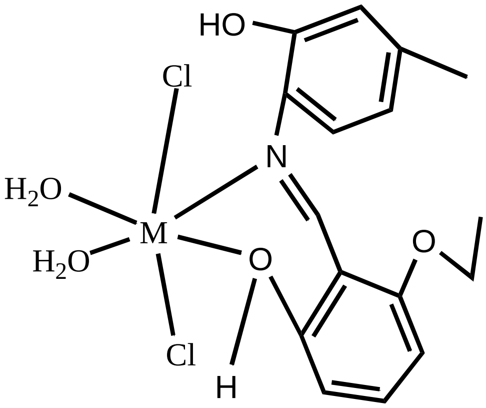

Figure 1: General structure of Complexes, M= Co(II), Ni(II), Cu(II), Zn (II).

CONCLUSION

The EAP ligand and its metal complexes of Ni(II), Co(II), Cu(II), Zn(II) have been structurally characterized. The analytical data show that the metal ligand stoichiometry in all these complexes 1:1. All these complexes are non-electrolyte in DMSO. The spectral data show that the ligand is bidenate which co-ordinates through the –OH group and –C=N- group of EAP. Based on analytical, conductance, magnetic, electronic spectral data, ESR and TGA analysis all these complexes are assigned to be in octahedral geometry. Biological studies of these complexes reveal that these complexes show better activity compared to the ligand.

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