Synthesis, Characterization and antimicrobial studies of Schiff base and its transition metal (II) complexes.

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ABSTRACT

Novel Co (II), Ni (II) and Cu (II) complexes of Schiff base lignad (L) derived form condensation of 3- ethoxy-2- hydroxybenzaldehydewith anthranilic acid were synthesized. The ligand and its complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, solubility, infrared and ESR.Thefree Schiff base ligand and its metal (II) complexes were screened for their antimicrobial activity against both Gram-positive and Gram-negative bacteria. It has been found that all the complexes are antimicrobially active and so higher activity than the free ligand. A very strong band at 1620 cm^{-1} is characteristics of the azomethine nitrogen present in the Schiff base ligand. This was shifted to 1590-1558 cm^{-1} in the complexes, which indicates the co-ordination of the metal to the azomethinenitrogen.The Phenolic stretching frequency of ligand is seen at 1382 cm^{-1} which gets shifted to a lower frequency region in the complexes in the range of 1370-1326 cm^{-1} which indicate the phenolic oxygen participate in bond formation with the metals. The molar conductivity data of the complexes in DMSO indicate they are non-electrolytes. On the basis of magnetic susceptibility and electronic spectral study, geometry of complexes were proposed to be octahedral.

Keywords:- Schiff base,3-ethoxy-2-hydroxybenzaldehyde, anthranilic acid, metal (II) complexes, antimicrobial studies.

1. INTRODUCATION :-

Schiff bases are one of the most prevalent and important of the mixed donar system in the field of co-ordination chemistry. Schiff bases are condensation products of primary amines with carbonyl compounds and they were first synthesized by Hugo Schiff in 1864. These compounds containing a general formula $RCH = N - R^1$ where R and R^1 are alkyl, aryl, cycloalkyl or hetrocyclic groups are also known as anils, imines or azomethines. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerisable, while those of aromatic aldehydes having effective conjugation are more stable in general, aldehydes react faster than ketones in condensation reactions, leading to the formation of Schiff bases as the reaction centre of aldehydes are less sterically hindered than that of ketones. The extra carbon of ketones donate electron density to the azomethine carbon and thus makes the ketone less electrophilic compared to aldehydes. Schiff bases are generally bidentate, tridentate, tetradentate and polydentate ligands capable of forming very stable complexes with transition metals. They can only act as coordinationg ligands if they bear a functional group, usually the hydroxyl, sufficiently near the site of condensation in such a way that a five or six memberedring can be formed when reaction with a metal ion. Schiff bases derived form aromatic amines and aromatic aldehydes have a wide variety of applications in many fields like biological, inorganic and analytical chemistry. Schiff bases are used in optical and electrochemical sensors, as well as in various chromatographic methods to enable detection of enhanced selectivity and sensitivity. Schiff bases are widely applicable in analytical determination using reactions of condensation of primary amines and carbonyl compounds in which the azomethinebond is formed. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial and anticancer applications. We report here the synthesis, characterization and antimicrobial studies of transition metal complexes of Co (II), Ni (II) and Cu (II) containing tridentate Schiff base, derived from the condensation of anthranilic acid and 3- ethoxy- 2- hydroxybenzaldehyde.

2. EXPERIMENTAL

2.1 Chemicals and Reagents :-

All the chemicals and reagents used were of analytical grade and were used without purification. They are 3-ethoxy-2- hydroxybenzaldehyde, anthranilic acid, $CoCl_2.6H_2O$,$Ni(NO_3)_2.6H_2O$,$CuCl_2.2H_2O$ and solvents.

2.2 Physical Measurements :-

The percentage (%) of Co, Ni and Cu were determined by EDTA complexometric titration. The elemental analysis of C, H and N was performed by using a perkin-Elmer elemental analyzer. The m.p of all compounds were determined using Griffin melting point apparatus. The solubility of the complexes was determined in some polar and non polar solvents like water, methamol, ethanol petroleum ether, chloroform, benzene,DMSO and acetone.The molar Conductivity were determined by using DMSO as a solvent in digital conductivity meter at 25^0c. The IRspectra of ligand and metal complexes were taken on perkin-Elmer model 577 spectophotometer using KBr disc. The magnetic susceptibility were determined on Gouy balance at room temperature using Hg $[Co(SCN)_4]$ as a calibrant. The electronic spectra of the complexes were recoreded on perkin-Elner UV/visspectrophotometer Lambda in DMF solution.

2.3 Synthesis of Schiff base ligand (L):-

The ligand N-(2^I- benzoic acid)- 3- ethoxy- 2- hydroxybenzalidinewas prepared by condensation of equimolar ratio of 3-ethoxy-2- hydroxybenzaldehyde (1.66g, 0.01 mol) with anthranilic acid (1.38 g, 0.01mol) in 25 ml ethanol. The reaction mixture was refluxed for 3hrs. A red precipitate was obtained. This precipitate was filtered and washed with ethanol and finally recrystallized from ethanol and ether and dried in air at room temperature and preserved in desiccator containg $CaCl_2$. The melting point of the Schiff base was found to be 148^OC.Yield: 94 %

2.4 Synthesis of the metal (II) complexes :-

The complexes of M(II) were synthesized by mixing 25 ml of ethanolic solution of Schiff base (0.01 mol) with 25ml of ethanolic solution of metal salt (0.01 mol) The reaction mixture was refluxed for 4 h on water bath. The precipitate formed was filtered and washed with ethanol and ether. Finally, the precipitate was dried in a vacuum over $CaCl_2$.

3.RESULTS AND DISCUSSION

The Co (II), Ni (II) and Cu (II) complexes were obtained with high yields (60-94%, Table-1). The complexes vary in colour depending on metal (II) ions and are soluble in DMSO but insoluble in water. The observed molar conductance of the complexes in DMSO at room temperature is consistent with the non- electrolytic nature of the complexes. The analytical data of the ligand and Itsmetal (II) complexes are presented in Table-2.

The m.p of the free ligand and its complexes was found to be the range of $148\text{-}310^0$c. Elemental analysis revealed the observed and calculated values for H, C and N compositions of the Schiff base and its metal complexes are in good agreement with the proposed structure.

IR Spectra of Schiff base ligand :-

The IR spectrum of free ligand was compared with that of complexes in order to determine the coordination site. (Table-3). A very strong band at $1620cm^{-1}$ is characteristics of the azomethine nitrogen (>C=N) present in the schiff base ligand. This was shifted to $1590\text{-}1558cm^{-1}$ in the complexes, which indicates the bonding of the metal to the azomethine nitrogen. The Phenolic stretching frequency of ligand is seen at 1382 cm^{-1} which gets shifted to a lower frequency region in the complexes in the range of 1370-1326 cm^{-1} which indicate the phenolic oxygen participate in bond formation with the metals. The IR band assignment of all metal complexes exhibit broad bands in the range of 3354 to $3425cm^{-1}$ indicating the presence of coordinated water molecules. A band at $1690cm^{-1}$ is assigned to ν (C=O) stretching frequency in the spectrum of free Schiff base which is also shifted to lower frequency $1650\text{-}1588cm^{-1}$ in the all metal complexes this indicates the involvement of oxygen atom of hydroxyl group of-COOH group in bonding with metal ions.The appearance of new band between $521\text{-}562cm^{-1}$ and $412\text{-}426cm^{-1}$ are indicate the formation of M-N and M-O bond in the complexes.

Electronic Spectra of Metal Complexes :-

The electronic absorption spectra of metal (II) complexes were recorded in the range of 200-1000 nm using DMF as a solvent are listed in Table-4. The electronic spectra of the Co(II) Complex shows three bands at 16285, 27026 and $32050cm^{-1}$ assigned for $4T_{1g}(F) \rightarrow 4T_2g(F), 4T_{1g}(F) \rightarrow 4A_{2g}(F) and\ 4T_{1g}(F) \rightarrow$

$4T_{1g}(P)$.These data and the magnetic moment value of 5.01 B.M, Which suggested the octahedral geometry of Co(II) complex.

The Ni (II) complex shows three bands at 16077,26178and 37730 cm^{-1} assigned to $3A_2g(F) \rightarrow 3T_{2g}$,$3A_{2g}(F) \rightarrow 3T_{1g}(F)$and $3A_{2g}(F) \rightarrow 3T_{1g}(P)$These data and the magnetic moment value of 3.31 B.M, which suggested octahedral geometry of NI (II) complex.The electronic spectra of Cu(II) complex exhibited low intensity band at 16580cm-1, which assigned$2E_g \rightarrow 2T_{2g}$ transition. Another high intensity band in region 24080 – 322260 cm^{-1} is due to symmetry for bidden LMCT and sharp band observed at 38460 cm^{-1}, which is due to ligand band. On the basis of electronic spectra and the magnetic moment value 1.61 B.M, which suggested distorted octahedral geometry.

Antimicrobial Activity :-

The Schiff base ligand and its metal (II) complexes (Table-5) were found with antimicrobial activity against E.coli, S.Typhi, K. Pneumonia, S. Aureus and B. Subtilis. It is obvious from the results that the ligand and its metal complexes show positive activity towards Gram-positive and Gram-negative bacteria. It is clear that the biological activity of the ligand gets enhanced appreciably in complexes. The activity of the ligand may be attributed to azomethine linkage in it. The increased activity of the metal complexes can be ascribed to the increase in lipophilic nature of complexes due to chelation.

Table :-1 Physical properties of Schiff base and its metal (II) complexes

Compounds	Mol.wt	colour	yield(%)	M.P(^{0}c)	molar conductivity (Scm^2 mol^{-1})
L=$C_{16}H_{15}NO_4$	285	Red	94	148	0
[$CoC_{16}H_{21}NO_8$]	415	Orange	62	305	6.8
[$NiC_{16}H_{21}NO_8$]	414	Green	74	308	5.7
[$CuC_{16}H_{21}NO_8$]	419	Green	82	310	10.2

Table:-2Analytical data of ligand and its metal complexes

Compounds	% Analysis Found (cal)		
	C	H	N
L=$C_{16}H_{15}NO_4$	67.24 (67.36)	5.53(5.26)	5.02(4.91)
[$CoC_{16}H_{21}NO_8$]	46.82 (46.26)	5.29 (5.06)	3.48 (3.37)
[$NiC_{16}H_{21}NO_8$]	46.68 (46.37)	5.18(5.07)	3.46 (3.38)
[$CuC_{16}H_{21}NO_8$]	46.04 (45.87)	5.12 (5.01)	3.63 (3.34)

Table :-3 IR Spectra data of Schiff base and its metal complexes.

Compounds	ν (OH/H_2O) cm^{-1}	ν (C-O) cm^{-1}	ν (C=O) cm^{-1}	ν (C=N) cm^{-1}	ν (M-N) cm^{-1}	ν (M-O) cm^{-1}
L=$C_{16}H_{15}NO_4$	3440	1382	1690	1620	-	-
[$CoC_{16}H_{21}NO_8$]	3354	1360	1650	1586	562	420
[$NiC_{16}H_{21}NO_8$]	3430	1370	1588	1558	521	426
[$CuC_{16}H_{21}NO_8$]	3425	1326	1615	1590	560	412

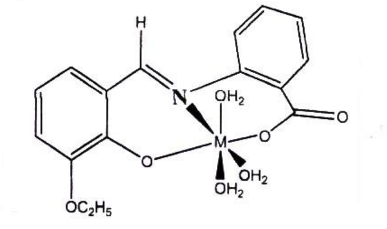
Table-4 :- Magnetic moment and electronic absorption spectral data of metal complexes

Compounds	Absorption (cm^{-1})	Assignments	Geometry	μ_{eff}(B.M)

[$CoC_{16}H_{21}NO_8$]	16285 27026 32050	$4T_{1g}(F) \rightarrow 4T_2g(F)$, $4T_{1g}(F) \rightarrow 4A_{2g}(F)$ $4T_{1g}(F) \rightarrow 4T_{1g}(P)$	Octahedral	5.01
[$NiC_{16}H_{21}NO_8$]	16077 26178 37730	$3A_2g(F) \rightarrow 3T_{2g}$ $3A_{2g}(F) \rightarrow 3T_{1g}(F)$ $3A_{2g}(F) \rightarrow 3T_{1g}(P)$	Octahedral	3.31
[$CuC_{16}H_{21}NO_8$]	16580	$2E_g \rightarrow 2T_{2g}$	Distorted Octahedral	1.61

Table-5 :- Antimicrobial activities of the synthesized Schiff base and its metal complexes

S. No.	Compound	Minimum inhibition concentration (mg/ml)				
		E.coli (mm)	S. typhi (mm)	K. Pneumonia (mm)	S. aureous (mm)	B. Subtilis (mm)
1.	L=$C_{16}H_{15}NO_4$	10	-	-	12	06
2.	[$CoC_{16}H_{21}NO_8$]	11	-	15	-	14
3.	[$NiC_{16}H_{21}NO_8$]	20	27	12	28	12
4.	[$CuC_{16}H_{21}NO_8$]	-	15	12	14	14



M=NI(II),Co(II) and Cu(II)

Proposed structure of metal complexes.

4. CONCLUSION

In the present work Co(II), Ni(II) and Cu(II) complexes were synathesized and characterized by various physicochemical and spectral analyses. The Schiff base acts as tridentate ligand. The M(II) Coordinated through the nitrogen atom of azomethine group and oxygen atom of oxygen atom of hydroxyl group of 3-ethoxy 2-hydroxybenzaldehyde beside the hydroxyl group of the carboxyl group of the anthranilic acid respectively. This is supported by infrared spectral data. The electronic spectral band observed are consistent with an octahedral geometry for Co(II), Ni(II) and Cu(II) complexes. The molar conductivity data of the complexes in DMSO indicated that they are non electrolytes. All the complexes are air stable.and soluble inDMSO. The biological activity of ligands gets enhanced after complexation with transition metal ion.

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