Synthesis, Characterization and antimicrobial activity of Schiff base complexes derived from vanillin and 2-amino-4-chlorobenzoic acid

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ABSTRACT

The coordination complexes of Co (II), Ni (II)) and Cu (II) were prepared from bidentate Schiff base. The Schiff base ligand were synthesized by the condensation of vanillin and 2-amino-4-chlorobenzoic acid in an alcoholic medium. The ligand and its complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, solubility, infrared and ESR.The free Schiff base ligand and its metal 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 1580 cm^{-1} is characteristics of the azomethine nitrogen present in the Schiff base ligand. This was shifted to 1545-1538 cm^{-1} in the complexes, which indicates the coordination of the metal to the azomethine nitrogen. The Phenolic stretching frequency of ligand does not undergo any change in the spectrum, hence the phenolic OH group does not participate in the bond formation with metals. A broad band at 2596 cm^{-1} (ν COOH) is found in the ligand. This broad band is absent in all the complexes, showing the participate of carboxylate anion group in chelation. The metal-ligand found to be 1 :2 in all the complexes. The magnetic susceptibility revealed that all the complexes are paramagnetic in nature. The infrared spectra suggested that the Schiff base behaves as bidentate ligand. 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 was proposed to be octahedral.

Keywords: - Vanillin,2-amino-4-chlorobenzoic acid, metal (II) complexes, antimicrobial activity.

1. INTRODUCATION

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 heterocyclic groups are also known as anils, imines or azomethines. Schiff bases are the condensation products of an amine and carbonyl compounds, and are important class of ligand that coordinates to metal ions via azomethine nitrogen (C=N). The carbonyl group of the aldehyde gives aldimines while that of ketone gives ketoimines, and these provided binding site for the metal ions through non-bonding electrons of the nitrogen. They also have many other hetro- elements like oxygen and sulphur which provided binding sites through non-bonding electrons. They are crystalline solids which are feebly basic, but at least some form insoluble salts with strong acids. They also offer a versatile and flexible

Series of ligand capable of binding with various metal ions to gives complexes with suitable properties for theoretical or practical applications. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable, 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 donates 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 coordinating 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 membered ring can be formed when reaction with a metal ion. Schiff bases derived from 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 azomethine bond is formed. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial and anticancer applications. Transition metal complexes of Schiff bases are one of the most adaptable and thoroughly studied systems. These complexes have also applications in clinical, analytical and industrial in addition to their important roles in catalysis and organic synthesis. Vanillin is both naturally occurring and synthetically produced. It is used in flavourings, foods, perfumes and pharmaceuticals. Vanillin is used as a chemical intermediate in the manufacture of several important drugs and other products. It also has medicinal uses as an anticlastogenic and antimicrobial agent. I report here the synthesis, characterization and antimicrobial studies of transition metal complexes of Co (II), Ni (II) and Cu (II) containing bidentate Schiff base, derived om the condensation of vanillin and 2-amino-4-chlorobenzoic acid.

2. MATERIALS AND METHODS

Chemicals and Reagents :-

All the starting materials vanillin, 4-Chloroanthranilic acid, metal salts and solvents used in this research were of analytical grade and were used in reaction as received without further purification. 2-amino-4-Chlorobenzoic acid and vanillin obtained from Sigma-Aldrich. Metal salts and solvents were obtained from Merck.

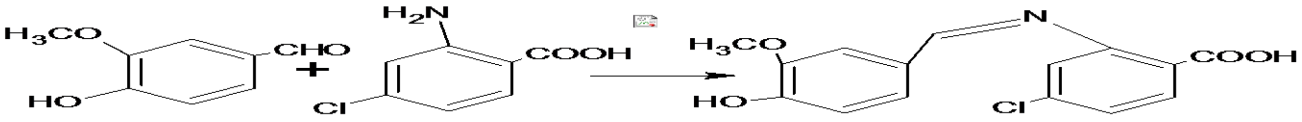
Physical Measurements: -

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 2400 elemental analyzer. The melting point of all compounds were determined using Griffin melting point apparatus. The molar Conductivity were determined by using DMSO as a solvent in digital conductivity meter at 25^0c. The IR spectra of the ligand and metal complexes were recorded on Shimadzu FTIR -8400 spectrophotometer using KBr disc. The magnetic susceptibility was determined on Gouy balance at room temperature using Hg [Co $(SCN)_4$] as a calibrant. The absorption spectra were recorded by using Shimadzu model UV-1601 spectrophotometer at room temperature in DMF solution.

Synthesis of Schiff base ligand (L): -

The Schiff base ligand was prepared by adding 1.52 g(0.01 mol) of vanillin in 25 ml ethanol and 1.72 g (0.01 mol) of 2-amino-4-chiorobenzoic acid in 25 ml ethanol. The resulting solution was refluxed for 3-4 h. On cooling the reaction mixture, the red crystalline solid was formed. The precipitate is washed with distilled water and ethanol several times and is then recrystallized with ethanol to obtain the required Schiff base.

Fig-1 Structure of Schiff base ligand.



Synthesis of the metal complexes:-

The metal complexes were prepared by refluxing 0.01 mol of metal salt of Co(II), Ni(II) and Cu(II) with 0.02 mol (6.12 g) of Schiff base in ethanolic medium for 3-4 h. A little of sodium hydroxide were added in drops to act as catalyst for the reaction. The solution was cooled at room temperature and was stirred for 20 min where by the precipitate of complexes appeared which was filtered on suction and washed with water and then with ethanol

3. RESULTS AND DISCUSSION

The reaction between 2-amino-4-chlorobenzoic acid and vanillin yielded Schiff base ligand which is red crystalline solid with the percentage yield of 78 % and melting point temperature of 160^{o}c (Table 1). All the metal complexes are coloured, solid, stable at room temperature and non- hygroscopic in nature. The complexes are insoluble in water but are soluble in some common organic solvents such as Dimethylsulphoxide (DMSO), Dimethylformamide (DMF), methanol, acetone, ethanol and chloroform. The observed molar conductance of the complexes in DMSO at room temperature is consistent with the non-electrolytic nature of the complexes, due to the low conductivity values. The analytical data of the ligand and Its metal (II) complexes are presented in Table 2. All the metal chelates have 1:2 (metal: ligand) stoichiometry. The melting point of the free ligand and its complexes was found to be the range of $160\text{-}320^{0}$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.

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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 are listed in Table 3. A very strong band at 1580 cm^{-1} is characteristics of the azomethine nitrogen (>C=N) present in the Schiff base ligand. This was shifted to 1545-1532 cm^{-1} in the complexes, which indicates the bonding of the metal to the azomethine nitrogen. The ν (OH) water is absent in the spectrum of the ligand but is present in the complexes. This shows the presence of hydration water in the complexes. The phenolic ν (OH) stretching does not undergo any change in the spectrum, hence, the phenolic OH group does not participate in the bond formation with metals. The carboxylate hydrogen ν (COOH) stretching is found to be broad on the region (2596 cm^{-1}) in the ligand. This broad band is absent in all the complexes, showing the participation of carboxylate anion group in chelation. A band at 1666 cm^{-1} is assigned to ν C=O stretching frequency in the spectrum of free Schiff base which is also shifted to lower frequency ranging from 1590 – 1598 cm^{-1} in all the metal complexes. The appearance of new band between 805 - 825cm^{-1} and 712-718 cm^{-1} are indicating 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 in DMF solution are listed in Table 4. The electronic spectra of the Co(II) Complex shows three bands at 16560, 28410 and 29310 cm^{-1} assigned to $4T_{1g}(F) \rightarrow 4T_{2g}(F)$, $4T_{1g}(F) \rightarrow 4A_{2g}(F)$ and $4T_{1g}(F) \rightarrow 4T_{1g}(P)$. These data and the magnetic moment value of 5.06 B.M, which suggested the octahedral geometry of Co(II) complex. The Ni (II) complex shows three bands at 15460, 28672 and 29610 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 3.32 B.M, which suggested octahedral geometry of Ni(II) complex. The electronic spectra of Cu(II) complex shows three bands at 13200, 18780 and 24112 cm^{-1} assigned to $^{2}A_1g \rightarrow 2B_1g$, $2B_2g \rightarrow 2B_1g$ and $2E_g \rightarrow 2B_1g$ transitions respectively. On the basis of electronic spectra and the magnetic moment value 1.86 B.M, which suggested distorted octahedral geometry.

Antimicrobial Activity: -

. The ligand as well as complexes were screened for their in vitro antibacterial activity against Gram- positive bacteria (B. subtilis, S. aureus) and Gram- negative bacteria (E. coli) using disc diffusion method by taking DMSO as solvent. The in vitro antifungal activities of the ligand and its metal complexes have been tested against the fungi Aspergillus Niger and Fusarium oxysporum by using disc diffusion method. The antimicrobial data of ligand and its metal complexes are presented in Table 5. A Comparative study of the growth inhibition zone values of Schiff base and its metal complexes indicate that metal complexes exhibit higher antibacterial and antifungal activity than the free Schiff base ligand. This is probably due to the greater lipophilic nature of the 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.

Fig. 2. Proposed structure of metal complexes M = Co^{+2}, $Ni^{+2}$and Cu $^{+2}$.

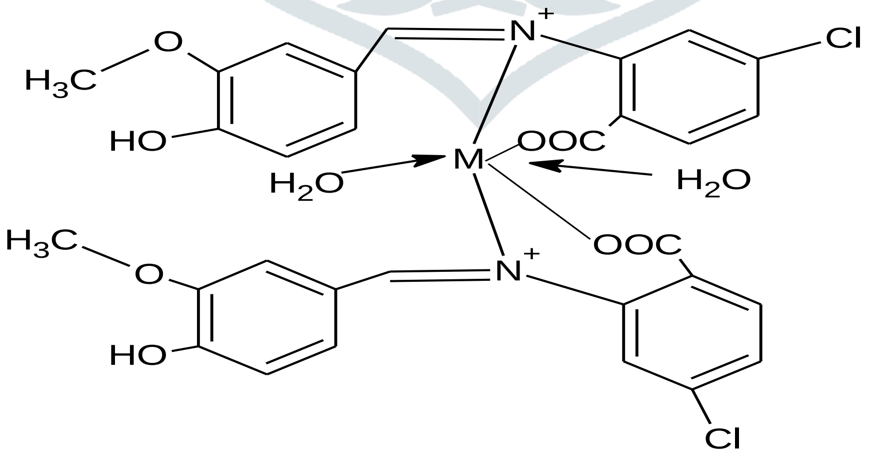

Table:-1 Physical properties of Schiff base and its metal complexes

Compounds	Mol.wt	color	yield(%)	M.P(^{0}c)	molar conductivity (S cm^2 mol^{-1})
L=$C_{15}H_{12}NO_4Cl$	305.5	Red	78	152	-
[$CoC_{30}H_{26}N_2O_{10}Cl_2$]	704	Orange	62	268	5. 7
[$NiC_{30}H_{26}N_2O_{10}Cl_2$]	703.7	Green	67	272	5. 9
[$CuC_{30}H_{26}N_2O_{10}Cl_2$]	708.5	Green	72	280	6.8

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

	Elemental analysis found (Calcd), %		
Compounds	C	H	N
L=$C_{15}H_{12}NO_4Cl$	58.83 (58.91)	4.01(3.92)	4.46(4. 58)
[Co $C_{30}H_{26}N_2O_{10}Cl_2$]	51.06 (51.13)	3.52 (3.69)	3.91 (3. 97)
[Ni $C_{30}H_{26}N_2O_{10}Cl_2$]	51.12 (51.15)	3.63(3.69)	3. 76 (3. 96)
[Cu $C_{30}H_{26}N_2O_{10}Cl_2$]	50.78 (50.81)	3.64 (3.66)	3. 75 (3. 95)

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

Compounds	ν (H_2O) cm^{-1}	ν (C=O) cm^{-1}	ν (C=N) cm^{-1}	ν(COOH) cm^{-1}	ν (M-N) cm^{-1}	ν (M-O) cm^{-1}
Schiff base	-	1666	1580	1490	-	-
Co - complex	3305	1590	1538	1460	825	718
Ni -complex	3301	1593	1532	1458	805	714
Cu - complex	3440	1598	1545	1462	821	712

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

Compounds	Absorption (cm^{-1})	Assignments	Geometry	μ$_{eff}$ (B.M)
[$CoC_{30}H_{26}N_2O_{10}Cl_2$]	16 560 2 8410 29310	$4T_{1g}(F) \to 4T_2g(F)$, $4T_{1g}(F) \to 4A_{2g}(F)$ $4T_{1g}(F) \to 4T_{1g}(P)$	Octahedral	5.0 6
[$NiC_{30}H_{26}N_2O_{10}Cl_2$]	1 5460 2 8672 29610	$3A_2g(F) \to 3T_{2g}$ $3A_{2g}(F) \to 3T_{1g}(F)$ $3A_{2g}(F) \to 3T_{1g}(P)$	Octahedral	3.3 2

10[$CuC_{30}H_{26}N_2O_{10}Cl_2$]	13200 18780 24112	$2A_1g \rightarrow 2B_1g$ $2B_2g \rightarrow 2B_1g$ $2E_g \rightarrow 2B_1g$	Distorted Octahedral	1. 86

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

S.N	Compound	Minimum inhibition concentration (mg/ml)				
		E.coli	S.aureus	B.subtilis	A.niger	F.Oxysporum
1.	Schiff base	6	5	4	1 0	12
2.	[Co $L_2(H_2O)_2$]	10	10	9	12	14
3.	[Ni $L_2(H_2O)_2$]	9	12	1 3	13	1 8
4.	[Cu $L_2(H_2O)_2$]	12	15	12	1 8	22

4. CONCLUSION

A new Schiff base has been prepared by the condensation of 2-amino-4-chlorobenzoic acid and vanillin. The coordination ability of Schiff base has been reported by physical characteristics, micro-analytical data, FTIR and UV spectral data confirm the ligand acts as bidentate and coordinating through azomethine nitrogen and deprotonated carboxylic acid oxygen forming a six membered chelate. It is concluded that metal complexes show coordinated octahedral geometry. The ligand as well as its metal complexes are active against Gram-positive and Gram-negative bacteria and also against both the fungi. The biological activity of ligand gets enhanced after complexation with transition metal ions.

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