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Synthesis and Characterization of bidentate Schiff base transition metal complexes of Co(II), Ni(II) and Cu(II).

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ABSTRACT

Vinillin which is a naturally ocuring. Food component Found in plants is used for the manufacture of Schiff base chelates. Schiff bases are versatile ligands which are synthesized from the condensation of an amino compound with carbonyl compounds. A novel series of transition metal complexes of Co(ll) , Ni(ll) and Cu(ll), with Schiff base ligand derived from condensation of vanillin with aniline were synthesized in alcolic medium. The ligand and its complexes were characterized on the basis of elemental analysis, conductivity, solubility, magnetic susceptibility measurements, IR and electronic spectral studies. The complexes were formed in moderate yields and they are various colours and have sharp melting points. The purity and composition of the Schiff base and the metal (ll) complexes were established by elemental analysis which suggests a metal: ligand ratio of 1:2 . The I.R spectra revealed that the complexes coordinatd through azomethine nitarogen and methoxy oxygen of the ligand. Further conclusive evidence of the coordination of the Schiff bases with the metal ions was shown by the appearance of new bands due to ν (M-N) and ν (M-O) in the metal complexes. Based on the electronic spectral transition, an octahedral structure has been assigned to all the metal (II) complexes.

KEYWORDS :- Schiff base, vanillin, aniline metal (II) complexes and synthesis.

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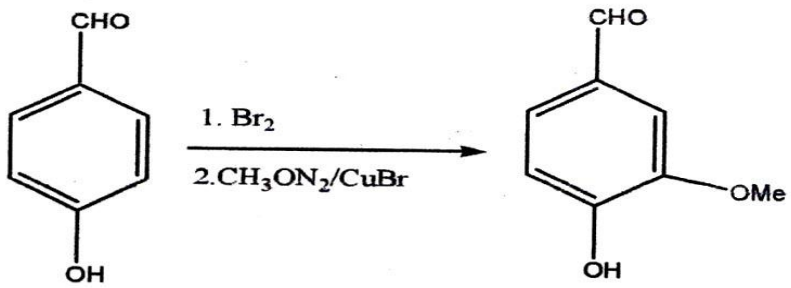
1. INTRODUCATION :-

Metal chelation is involved in many important biological processes where the coordinaton can occur between a veriety of the metal ions and a wide range of ligands. Schiff base metal complexes have been widely studied because they have industrial, antifungal and biological applications. They serve as models for biological catalytic reactions. Chelating ligands containing O and N donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. The synthesis of Schiff base ligands and their metal complexes have been extensively studied because of their interesting biological activities. Schiff bases have been reported to possess antimicrobial, antiviral, anticancer and anti-inflammatory activity. The imine functional functional group (HC=N) is believed to be responsible for the biological avtivity of Schiff base compounds. Vanillin is a phenolic aldehyde organic compound with the molecular formula $C_8H_8O_3$. 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 the of ketone. 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 azomethine bond is formed. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial and anticancer applications. Vanillin is the primary component of the extract of the vanilla bean Vanillin Schiff bases have been demonstrated to possess

polyvalent metal ions. Condensation product of vanillin with amines confers biological activity; as well as having good complexation ability with metal ions. I report here the synthesis and characterization of transition metal complexes of Co (II), Ni (II) and Cu (II) containing bidentate Schiff base, derived from the condensation of aniline and vanillin.

Vanillin synthesis from 4- hydroxybenzldehyd :- The developed a convenient two step synthesis of vanillin using electrophilic aromatic substitution, followed by an organometallic methoxylation procedure using copper bromide and sodium methoxide.



Vanilla Bean

Characteristic/Property Data Molecular Formula: C8H8O3 Common Synonyms 4-hydroxy-3-methoxybenzaldehyde; methyl-B Protocatechuic aldehyde; vanillic Aldehydes; 3- Methoxy-4-hydroxybenzaldehyde Chemical Structure (CH3O) C6H3 (OH) CHO Physical State white or slightly yellow nee Melting Point: 178-181 ° F Vapor Density: data unavailable Specific Gravity: 1.056 at 68.0 ° F. Boiling Point: 545.0 ° F at 760 mm Hg. Molar mass 152.15 g mol−1 Exact mass 152.047344122 g mol-1 Odor Floral, pleasant Acidity (pKa) 7.781 Basicity (pKb) 6.216 Crystal structure Monoclinic Water Solubility 1 g/100 ml Density 1.056 g/mL Vapor Density (air = 1) 5.2 KOC not found Log KOW not found Vapor Pressure 2.2 x 10-3 mm Hg Reactivity can react violently with bromine, potassium Tert-butoxide, tert-chlorobenzene + NaOH, Formic acid + Tl (NO3)3 and perchloric acid Flammability not found Flash Point not found Dissociation Constant pKa1 7.40, pKa2 11.4 (25°C)

2. EXPERIMENTAL

2.1 Chemicals and Reagents :-

All the chemicals and reagents used were of analytical grade and were used without purification. They are vanillin, aniline, $CoCl_2$. $6H_2O$, $NiCl_2.6H_2O$, Cu $(CH_3COO)_2.H_2O$ and solvents (methanol, ethanol, petroleum ether, Chloroform, benzene and acetone)

2.2 Physical Measurements :-

The percentage (%) of Co, Ni and Cu were determined by EDTA complexometric titration[16]. 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 and acetone, Molar Conductivity were determined by using DMF as a solvent in digital conductivity meter at 25^0c. The I.R. spectra of ligand and metal complexes were taken on perkin-Elmer model 577 spectophotometer using KBr disc. The magnetic susceptibility data were measured by Gouy method using Hg $[Co(NCS)_4]$ as a calibrant, Electronic spectra of the complexes were recorede in DMF on carry 2390 spectrophotometer.

2.3 Synthesis of Schiff base ligand (HL):-

The ligand 2-methoxy-4-(Phenyliminomethyl) phenol was prepared by condensation of equimolar ratio of vanillin (3.043 g, 20 mmol) with aniline (1.86 g, 20 m mol) in 40 ml ethanol (1:1 molar ratio). The reaction mixture was refluxed for 4h. A black precipitate was obtained. This precipitate was filtered and washed with distilled water, dried and preserved in desiccator containg $CaCl_2$.

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 (1.362 g, 6mmol) with 25ml of ethanolic solution of $CoCl_2.6H_2O$(0.714g, 3mmol) $Cu(CH_3COO)_2.H_2O$(0.59g, 3mmol and $NiCl_2.6H_2O$(0.713g, 3mmol). Keeping ligand-metal (II) ratio (2:1). The reaction mixture was refluxed for 4 h on water bath. The precipitate formed was filtered and washed with distilled water and ether. Finally, the precipitate was dried in a vacuum over $CaCl_2$.

$MX_2.nH_2O + 2L \rightarrow ML_2X_2 + nH_2O$

$M = Co(II), Ni(II) and\ Cu(II)$

$n = 1{,}6$

$x = Cl, CH_3COO$

$L = Schiff\ base\ ligand$

3. RESULTS AND DISCUSSION

The Co(II), Ni(II) and Cu(II) complexes were obtained with moderate yields (50-58%, table-1). The complexes vary in colour depending on metal (II) ions and are soluble in most organic solvents except water and petroleum ether. Cu(II) complexes were soluble in petroleum ether. The lower value of molar conductivity indicates non electrolytic nature of metal (II) complexes the analytical data of the ligands and their metal (II) complexes are presented in table-2.

The m.p of the free ligand and its complexes was found to be the range of 134-281^{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 1582cm^{-1} is characteristics of the azomethine nitrogen (>C=N) present in the schiff base ligand. This was shifted to 1580-1640cm^{-1} in the complexes, which indicates the bonding of the metal to the azomethine nitrogen. The metal complexes showed broad peaks at 3259-3381 cm^{-1}. This suggests that the oxygen atom of the phenolic –OH group does not participate in coordination. The IR Spectrum of free Schiff base ligand showed strong band at 1480cm^{-1} which is characteristics of ν(C-N) stretching vibration. This was shifted to 1488-1510cm^{-1} region in all the complexes. The spectral bands of the complexes at 1280-1305cm^{-1} were assigned to ν(C-O) which did not show shift from the region 1425cm^{-1} of the ligand. This suggests that oxygen atom of terminal methoxy and –OH group are not coordinated to the metal ions. The appearance of new band between 490-470cm^{-1} and 563-490cm^{-1} are indicate the formation of M-N and M-O bond in the complexes.

Electronic Spectra of Metal Complexes :-

The electronic absorption spectra (Table-4) of metal (II) complexes were recorded in the range of 300-700 nm using methanol as a solvent the electronic spectra of the Co(II) Complex shows three bands at 11275, 15085 and 24070cm^{-1} assigned for $4A_2g(F) \rightarrow 4T_1g(P), 4A_2g(F) \rightarrow 4T_1g(F) and\ 4A_2g(F) \rightarrow 4T_2g(F)$. Which suggest the octahedral geometry of Co(II) complex.

The Ni (II) complex show a band at 22885cm^{-1} assigned to $3A_2g(F) \rightarrow 3T_1g(P)$ suggest octahedral geometry.

The electronic spectra of Cu(II) complex exhibited band at 23755cm-1, which assigned $3A_2g \rightarrow 3T_2g$ for a low spin distorted octahedral geometry.

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

Compounds	colour	yield(%)	M.P(^{0}c)	molar conductivity (S cm^2 mol^{-1})
$L=C_{14}H_{13}NO_2$	Yelow	82	281	0
$[CoL_2]X_2$	Brown	58	134	$1.28x10^{-2}$
$[NiL_2]x_2$	Brown	52	143	$4.3x10^{-3}$
$[CuL_2]x_2$	Green	50	145	0

Table:-2 Analytical data of Systhesized ligands and their metal complexes

Compounds	% Analysis Found (cal)			
	C	H	N	M
$L=C_{14}H_{13}NO_2$	67.34 (69.21)	4.96(5.42)	6.63(5.81)	-
$Co(C_{14}H_{13}NO_2)_2$	62.46 (6231)	4.63 (4.81)	7.62 (5.81)	10.82 (10.73)
$Ni\ (C_{14}H_{13}NO_2)_2$	47.23 (61.53)	4.92(4.81)	7.46 (5.23)	11.06 (10.79)
$Cu(C_{14}H_{13}NO_2)_2$	49.12 (61.21)	4.65 (4.71)	8.62	11.53 (11.72)

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

Compounds	ν (O-H) cm^{-1}	ν (C-O) cm^{-1}	ν (C-N) cm^{-1}	ν (C=N) cm^{-1}	ν (O-CH_3) cm^{-1}	ν (M-N) cm^{-1}	ν (M-O) cm^{-1}
$L=C_{14}H_{13}NO_2$	3410	1425	1480	1582	2915	-	-
$Co(C_{14}H_{13}NO_2)_2$	3381	1282	1510	1580	3360	490	563
$Ni\ (C_{14}H_{13}NO_2)_2$	3308	1280	1488	1590	3250	481	505
$Cu(C_{14}H_{13}NO_2)_2$	3259	1305	1490	1640	3190	470	490

Table-4 :- Electronic absorption spectral data of metal complexes

Compounds	Absorption (cm^{-1})	Assignments	Geometry
$[CoL_2]X_2$	11275 15085 24070	$4A_2g(F) \rightarrow 4T_1g(P)$ $4A_2g(F) \rightarrow 4T_1g(F)]$ $4A_2g(F) \rightarrow 4T_2g(F)$	Octahedral
$[NiL_2]X_2$	22885	$3A_2g(F) \rightarrow 3T_1g(P)$	Octahedral
$[CuL_2]X_2$	23755	$3A_2g \rightarrow 3T_2g$	Octahedral

Table-5 :- ^{1}H NMR and ^{13}C NMR spectra data of Schiff base.

Position	**^{13}C NMR**	**^{1}H NMR (δ, ppm)**
1	152.43	9.95 (OH)
2	150.8	-
3	110.9	7.1 (d, J=1.2)
4	129.0	-
5	115.8	7.65 (dd, J=1.2, 8.0)
6	124.7	6.95 (d, J=8.0)
7	160.6	8.4 (-N=CH)-
2-OCH_3	56.0	3.8
1’	148.5	7.30
2’,6’	129.5	7.30
3’,5’	121.3	7.30
4’	128.7	7.30

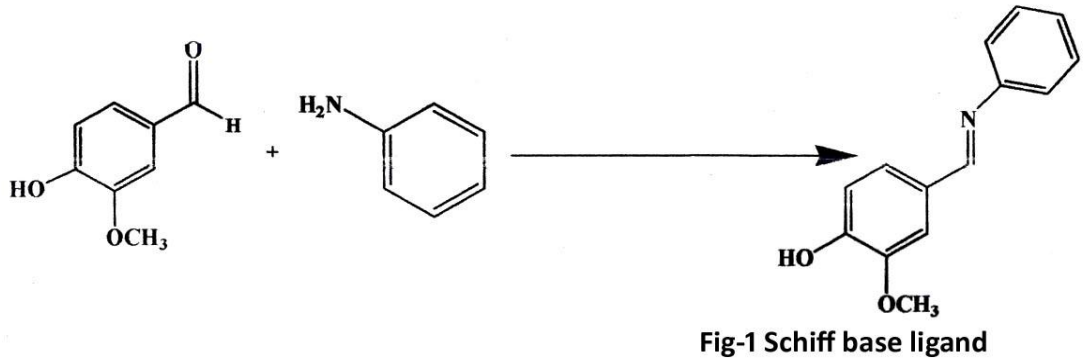


Fig-1 Schiff base ligand

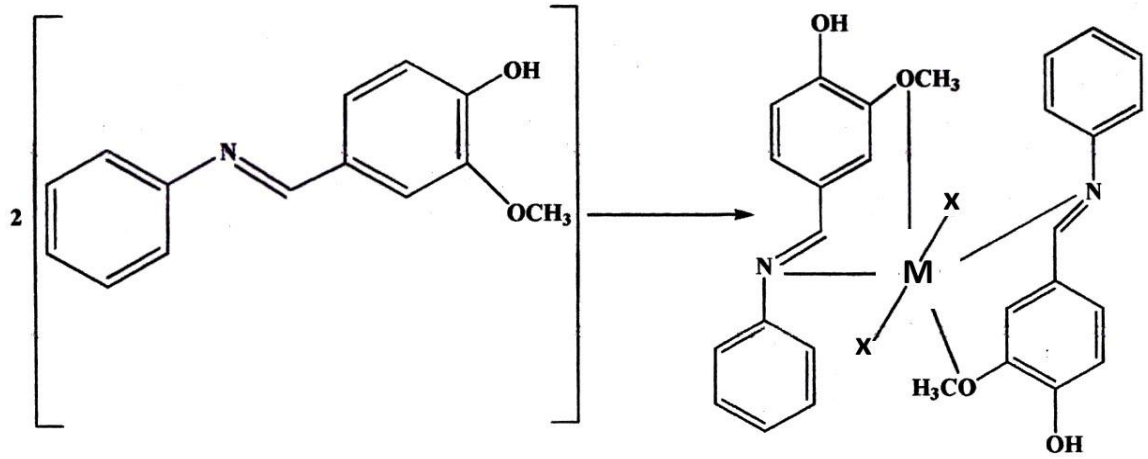


Fig. 2: Proposed structure of M(II) complexes M=Co, Ni & Cu

4. CONCLUSION

A novel Schiff base ligand was synthesized by the reaction of vanillin and aniline in equimolar ration with a molecular formula of $C_{14}H_{13}NO_2$. The complexes of Co(II), Ni(II) and Cu(II) were synthesized by direct reaction of the synthesized ligand with metal salt both in 2:1 ratio. In the present work Co(II), Ni(II) and Cu(II) complexes were synathesized and characterized by analytical and spectroscopic techniques. The Schiff base acts as bidentate ligand. The M(II) Coordinated through the nitrogen atom of azomethine group and oxygen atom of methoxy group of vanillin. 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 methanol indicated that they are non electrolytes. All the complexes are air stable and soluble in protic solvents like methanol and ethanol. They in vitro antimicrobial study shows that the complexes have higher activities compared to the free ligand.

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