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Synthesis and Characterization of new Schiff Bases Ligand and Their Complexes with Some Transition Metals

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Abstract : This study is concerned with the synthesis and coordination ligand(3-(2-(Z[(2-hydroxy phenyl)methylidene]amino)ethyl-endo)-7-ol . The ligand was characterized by FT-IR , proton NMR , Uv-Vis and elemental analysis studies. Complexes of Co(II) , Ni(II) and Cu(II) chloride were prepared ,these complexes were characterized by FT-IR , Uv-Vis , elemental analysis , conductance and magnetic susceptibility studies. FT-IR spectra and other studies showed that the ligand acting as bidentate and forms complexes through (-OH) and (-C=N- , Nitrogen atom of azomethen) groups so Suggest $[M(L)_2 Cl_2]$ (octahedral) composition of the coordination compounds.

Key words: Schiff base, Serotonin , 2-hydroxy benzaldehyde.

Introduction:-

Schiff base ligands are plays very important role in field of inorganic chemistry , and they are more effective as a chelating agent when they bear supporting and stabilizing group like -OH close -HC=N-group⁽¹⁻⁵⁾ . Schiff base are generally bi or tri -dentate ligands capable of forming very stable complexes with transition metals. development in the field of bioinorganic chemistry and pharmaceutical inorganic chemistry ,which is closely bound up with study of Schiff base ligand complex⁽⁶⁻¹⁰⁾. Schiff base ligand and their complexes have been found a number uses in medicine and pharmaceutical field, some of them have been showed to have antitumor activity, anticandidous , antihistaminic , antiinflammatory^(11,12). Also shown significant effect against cancer and antibacterial agent, another area of application of these Schiff bases is analytical and industrial chemistry and agricultures⁽¹³⁻¹⁶⁾.

In this paper we tried to synthesis of various a new Schiff bases derived from serotonin and 2-hydroxy benzaldehyde .Serotonin, 5-hydroxytryptamine (5-HT), is one of a ubiquitous monoamine that plays multiple roles as a neurotransmitter⁽¹⁷⁻¹⁹⁾, serotonin have a chemical template comprised of a basic amino group separated from an aromatic nucleus by a two carbon aliphatic chain. Serotonin, which is well known as a pineal hormone in mammals, plays a key role in conditions such as mood, eating disorders, and alcoholism⁽²⁰⁻²²⁾. In plants , although serotonin has been suggested to be involved in several physiological roles ,including flowering, morphogenesis, and adaptation to environmental changes, its regulation and functional roles are as yet not characterized at the molecular level. This has led to the suggestion a new drug to increased the level of serotonin in brain^(23,24), in this context, we Prepare a new Schiff base ligand and their complexes^(25,26) .

Experimental:-

All the chemical used in this work of highest purity available and used without further purification .All solution were prepared in doubly distilled deionized water.

Materials:-

Table -1- demonstrate the chemical substances being used in this research , the (%) age of purity and the companies supplied them.

Table-1- chemical substances used in this research

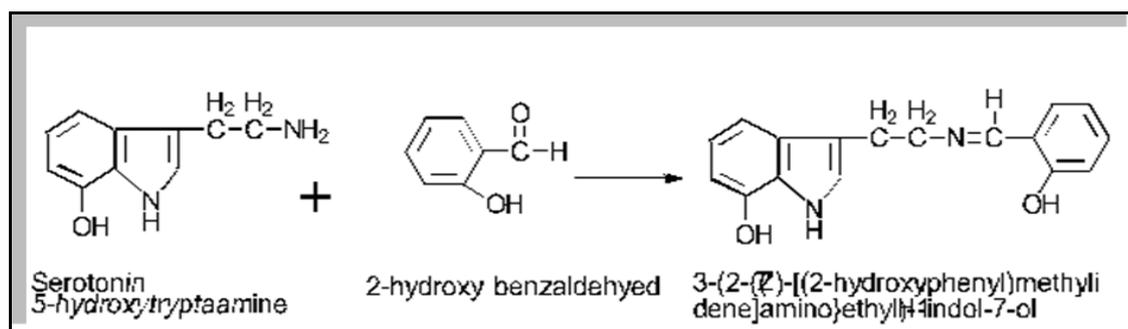
No.	Substance	Formula	Company	Purity%
1	Cobaltous chloride hexahydrate	CoCl ₂ .6H ₂ O	Merck	98.8
2	Nickel chloride hexahydrate	NiCl ₂ .6H ₂ O	Merck	99.9
3	Couper chloride hexahydrate	CuCl ₂ .6H ₂ O	Fluka	99.9
4	2-hydroxy benzaldehyde (Salicylaldehyde)	C ₇ H ₆ O ₂	Fluka	98
5	Serotonin hydrochloride (5-HT, 5-Hydroxytryptamine hydrochloride)	C ₁₀ H ₁₂ N ₂ O · HCl	Sigma Aldrich	99.9
6	Sulpheric acid	H ₂ SO ₄	B.D.H	98
7	Ethanol	C ₂ H ₅ OH	B.D.H	99.9
8	Methanol	CH ₃ OH	Fluka	99.9
9	Sodium nitrate	NaNO ₂	Merch	99
10	Tyramine[4-(2-Aminoethyl)phenol	C ₈ H ₁₁ NO	B.D.H	98.9
11	Dimethyl Formamide	(CH ₃) ₂ CONH	Merch	99
12	Dimethyl Sulfoxide	C ₂ H ₆ SO	G.C.C	99.55

Instrumentation :-

UV-Visible spectra were recorded on Shimadzu 1800 series spectrometer for ligand and complexes in DMSO solvent. FT-IR spectrum were recorded in KBr pellets with a 8400 FTIR Simadzu spectrometer, The Magnetic Moment Measurement was using Auto Magnetic Susceptibility Balance Sherwood scientific , The Molar Conductance Measurement in DMSO solvent using Digital conductivity meter alpha -800. The proton Nuclear Magnetic Resonance (NMR) spectra were recorded in DMSO were recorded on a Bruker Advance II 400 Spectrometer at room temperature the chemical shifts are reported in ppm relative to TMS (tri methyl silane). The metal ion contents in the complexes solutions were estimated on an atomic absorption spectrometer, 3410 Minitorch Soquential Inoductivly Coupled Plasma Spectrometer I.C.P. Carbon, hydrogen and nitrogen analyses were obtained from the microanalytical Euro EA Elemental Analyzer 3000 , Italy(C.H.N).Chloride analysis was carried out by Mohrs method.

Preparation of Schiff base ligand :-

The Schiff base was prepared by used general method^(27,28) , condensation of serotonin (0.01 mol) with 2-hydroxy benzadehyed (0.01 M) in ethanol (50 ml), and the mixture was refluxed for 14 hrs. The progress of reaction was monitored by TLC.The separated solid product was filtered and washed with cold saturated sodium bisulphate solution and recrystallized with ethanol. The reaction of the formation of Schiff base ligand is shown in scheme -1-

**scheme-1- Formation of the Ligand**

Preparation of Complexes:-

Complexes were prepared in a M:L ratio of 1:2 by dissolving (2mmol) of ligand respectively in minimum quantity of ethanol .The ligand solution was added gradually with stirring to the (1mmol) of metal salt solution dissolved in buffer solution with an appropriate pH. The mixture was stirred until deep colored precipitate was appeared. The solution mixture was filtered off and the precipitate was washed several times with a(1:1) (ethanol: water) mixture then washed by acetone and left to dry.

Results and Discussion:-

The physical data of Schiff base ligand and its complexes are given in table-2-.the complexes are fairly stable to heat and have been all found to melt above 360 °C. They are insoluble in water but highly soluble in most organic solvent such as ethanol, methanol ,acetone ,DMF and DMSO.

Table-2:- Characteristic physical data of Schiff base ligand and its complexes

Compound	Formula	Color	M.P(°C)	Yield (%)
L	C ₁₇ H ₁₆ N ₂ O ₂	Yellow	261	80
[CoL ₂ Cl ₂]	Co(C ₁₇ H ₁₆ N ₂ O ₂) ₂ Cl ₂	green	≥360	78
[NiL ₂ Cl ₂]	Ni(C ₁₇ H ₁₆ N ₂ O ₂) ₂ Cl ₂	Red	≥360	82
[CuL ₂ Cl ₂]	Cu(C ₁₇ H ₁₆ N ₂ O ₂) ₂ Cl ₂	Brown	≥360	85

Infrared spectra :-

The FT-IR Spectra of Schiff base ligand and their complexes were recorded at range of 4000-400 Cm⁻¹ . The IR spectrum of Schiff base ligand shows absorption bands at 1620 Cm⁻¹which attributed to the characteristic band of (-HC=N-) azomethine group , these bands shifted toward the lower wave number by 16-22 Cm⁻¹ in the spectra of complexes, suggested the coordination of Nitrogen atom of azomethine group to the metal in these complexes^(29,30). In the spectrum of free ligand abroad absorption band appeared at 3306 Cm⁻¹due to the presence two hydroxyl groups (-OH) These frequencies were shifted towards the lower wave number by 7-10 Cm⁻¹ in the spectra of metal complexes , this Indicates that only one the hydroxyl groups in the Schiff base ligand coordination with metal^(31,32) . Also shows aching in the absorption band of ν(C-O)stretching of the Schiff base ligand from 1257Cm⁻¹ to lower wave number by5-18 Cm⁻¹ indicating coordination through its (O) atom of hydroxyl group. The band ν(N-H) in region 3416 Cm⁻¹which remain in the same region in free Schiff base ligand and after complexation that means the Nitrogen atom in the (NH) group doesn't coordinate with metal in complexes .No new bands observed for M-Cl in the range 600-250Cm⁻¹ this is , in fact ,may due to the M-Cl band is always regarded as a weak band. Moreover the presence of many bands of the ligand in this region.Table-3- lists the most important FT-IR spectral bands of the Schiff base ligand and their complexes and typical FT-IR spectrum was shown in Fig(1-4).

Table-3- Characteristic FT- IR stretching bonds of Schiff base ligand and its metal complexes in Cm⁻¹

ν(C-O)	ν(OH)	ν(C=N)	ν(N-H)	Compound	NO.
1257	3306	1620	3416	L	1
1239	3299	1598	3415	[Co(L) ₂ Cl ₂]	2
1252	3300	1604	3416	[Ni(L) ₂ Cl ₂]	3
1248	3296	1601	3415	[Cu(L) ₂ Cl ₂]	4

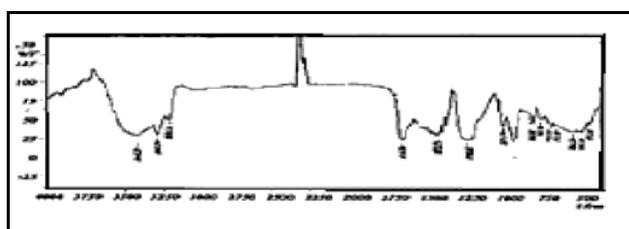


Fig.-1- FT-IR Spectrum of Free ligand

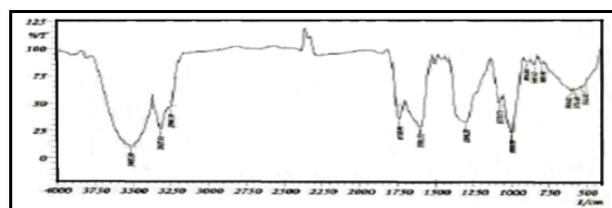


Fig. -2-FT-IR Spectrum of [Co(L)₂Cl₂]

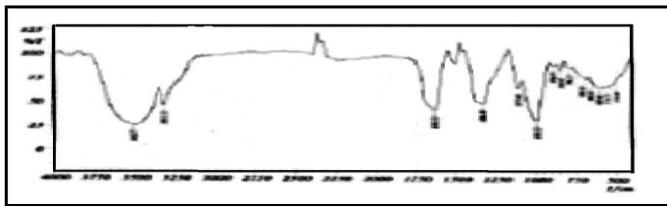


Fig. -3- FT-IR Spectrum of [Ni(L)₂Cl₂]

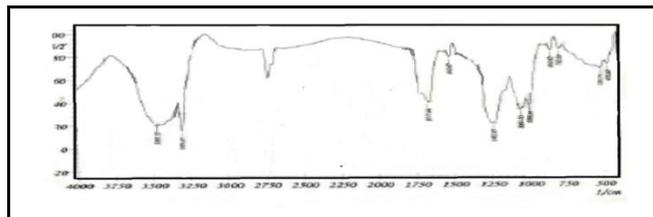


Fig. -4- FT-IR Spectrum of [Cu(L)₂Cl₂]

UV-vis spectrum of Schiff base metal complex:-

The UV-vis spectra of the Schiff base and its complexes were taken in ethanol (1×10^{-4} M). The UV-vis spectrum of free Schiff base ligand exhibit strong absorption bands at 245 nm and 327nm, the first band would be assigned to $\pi \rightarrow \pi^*$ transition within the aromatic rings , the second band would be due to $n \rightarrow \pi^*$ transition within the azomethine group (-HC=N-). Among these $\pi \rightarrow \pi^*$ transitions are not altered to a greater extent on complexation .The UV-Vis spectra of complexes appeared two intense broad band's at the region 400-700 nm due to d-d transition in metals ion. These results it is more agreement with the previous studies which showed withoctahedralgeometry⁽¹²⁾. The electronic absorption spectral data of freeSchiff base ligand and its transition metal complexes are given in table-4- and the absorption spectra are given in Figs(5-8).

Table-4-The absorption data

Compounds	Absorption band (nm)
L	245 , 327
[Co(L) ₂ Cl ₂]	246,375 449 , 552
[Ni (L) ₂ Cl ₂]	248 , 375 615
[Cu(L) ₂ Cl ₂]	247 , 361 475 , 582

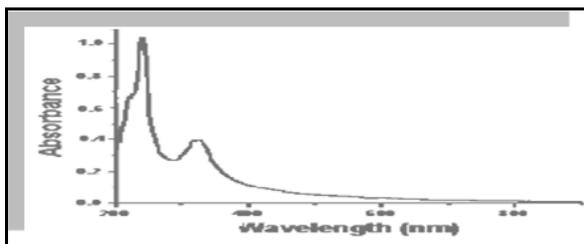


Fig-5- UV-Vis Spectrum of ligand

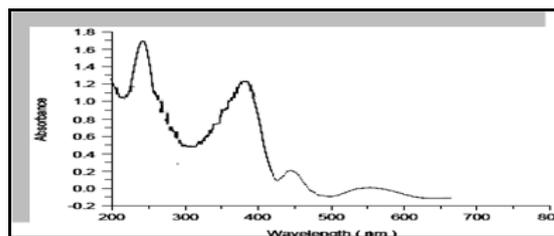


Fig-6- UV-Vis Spectrum of [Co(L)₂Cl₂]

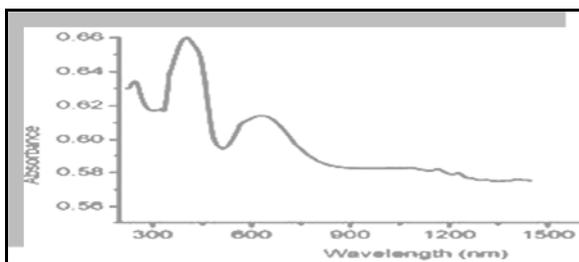


Fig-7- UV-Vis Spectrum of [Ni(L)₂Cl₂]

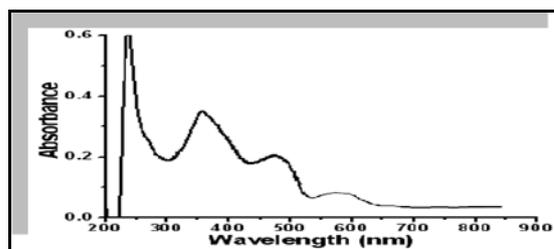


Fig-8- UV-Vis Spectrum of [Cu(L)₂Cl₂]

¹H-NMR spectra :-

The ¹H-NMR spectrum of the Schiff base ligand was recorded in DMSO-d⁶. In the ¹H-NMR spectra of Schiff base ligand, the multiplet peaks around 6.8-8.1 ppm represent the interaction between proton of(NH) group and aromatic protons While the singlet peak appeared at 8.8ppm was assigned to proton of azomethinegroup. A singlet peak appeared at 9.27 ppm represent the proton of (OH)group. The peak at 3.5ppm correspond to the protons attached to the neighboring alpha Carbon to the -C=N- group . The protons of solvent DMSO appeared in the range 1.5-2.6ppm .The ¹H-NMR spectra are given in Fig -9-

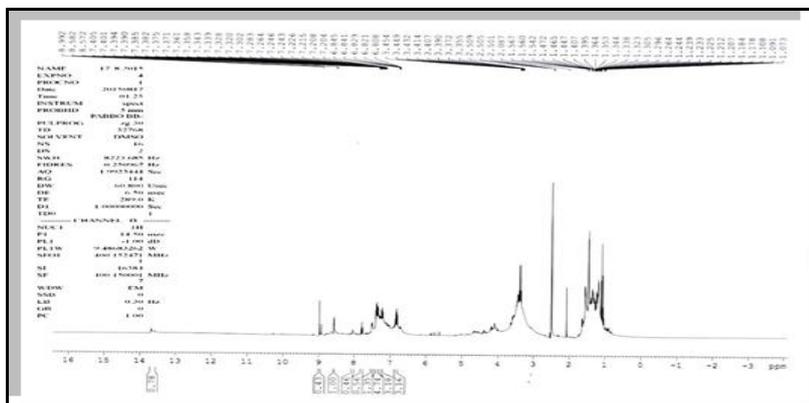


Fig-9-correspond the¹H-NMR spectra of free Schiff base ligand

Atomic absorption spectrum and Elemental analysis:-

The atomic absorption , elemental analyses and chloride ion percentage data of Schiff base ligand and its metal complexes presented in table-5-. The results are in a satisfactory agreement with the calculated values. The data shows that the ligand L forms a 1:2 (M: L) complexes with metal ions. The data clearly agree with the suggested molecular formula of these complexes.

Table -5- The atomic absorption and elemental analyses data

Compounds	M%		C%		H%		N%		Cl%	
	Cal.	Exe.	Cal.	Exe.	Cal.	Exe.	Cal.	Exe.	Cal.	Exe.
L	-----	-----	72.857	73.927	5.714	5.899	10.000	10.581	----	----
[CoL ₂ Cl ₂]	8.543	8.725	59.144	59.607	4.638	4.854	8.117	8.543	10.278	10.608
[Ni L ₂ Cl ₂]	8.511	8.659	59.164	59.859	4.640	4.905	8.120	8.565	10.282	10.598
[Cu L ₂ Cl ₂]	9.150	9.408	58.751	59.099	4.607	4.898	8.068	8.349	10.210	10.701

Magnetic susceptibility and conductivity:-

The magnetic moment value of the complexes is found to be in the range 1.75-3.98 B.M at room temperature. These value shows all the complexes are paramagnetic. While the molar conductivity of the complexes was recorded in ethanol solvent (1x10⁻³ M) appears the complexes are non-electrolytic nature. Supported with octahedral geometry for complexes. The magnetic susceptibility values and the molar conductivity values are given in Table -6- .

Table -6 The Magnetic Moments and Molar Conductance data

Complexes	Magnetic Moments		Molar Conductance (ohm ⁻¹ Cm ² Mole ⁻¹)
	Theoretical μs=√4s(s+1)	Experimental μeff(B.M)	
[CoL ₂ Cl ₂]	3.708	3.986	4.89
[Ni L ₂ Cl ₂]	2.828	3.113	3.35
[Cu L ₂ Cl ₂]	1.732	1.752	2.04

Conclusion:-

New schiff base ligand (3-(2-(Z[{(2-hydroxy phenyl)methyl idene] amino} ethyl -indo)-7-ol and its complexes with Co(II) ,Ni(II) and Cu(II) metal ion have been synthesized in 1:2 molar ratio of metal ion to ligand. They have been characterized by FT-IR ,Uv-Vis ,¹H-NMR , elemental analysis , The results of these investigations support the suggested structure of the metal complexes. Molar conductance values and magnetic susceptibility data suggests. The Schiff base acts as neutral bidentate ligand and forms complexes through its Oxygen atom of one hydroxyl group(-OH) and Nitrogen atom of azomethen group (-C=N-).Chloride ion was presented in complexes as coordinated ion this will give rise to the metal ion to displays the coordination number 6 in these complexes .So suggest [M(L)₂ Cl₂] (octahedral) composition of the coordination compounds. The octahedral geometry of metal complex given in fig. -10.

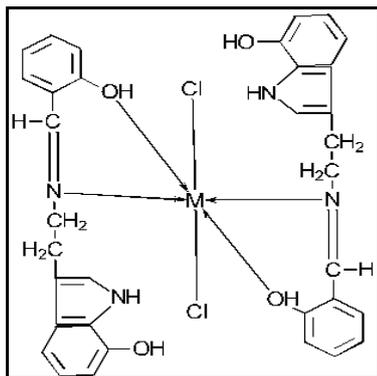


Fig -10- The octahedral geometry of metal complex

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