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# Novel Based Schiff Base Metal Complexes from Natural sources: Characterization and Biological screening

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**ABSTRACT:** Cardanol is a renewable natural agro- based resource and a product of cashew nut shell liquid (CSNL). Cardanol was obtained by the vacuum distillation of roasted cashew nut shell liquid. It contains a phenolic moiety with unsaturated 15 carbon side chain. CSNL belongs to family of long chain hydrocarbon phenols, which are phenolic liquid present in leaves of yemenian plant Rhusthysia *flora* of family *Anacardiacae*. αformylmethoxy bis(3-pentadecenylphenyl)methane under go condensation with L- tryptophan to form Schiff base ligand, which on treated with metal nitrates to form Schiff base complexes

**KEYWORDS:** Cardanol, αformylmethoxy bis(3-pentadecenylphenyl)methane, L- tryptophan, Schiff base

### I. INTRODUCTION

Schiff base metal complexes are key chemical players in photosynthesis, metabolism, oxygen transport, and a host of other processes. The unique electronic and structural characteristics and their complexes endow them with a wide range of functions and properties. Schiff base metal complexes of transition element with heterocyclic ligands, containing nitrogen and sulphur have diverse applications in various fields including biology and ant herbicidal activities. Many developments in the field of biochemistry promote inorganic chemist to court in the new specialized area of "Bioinorganic chemistry". Principal idea of bioinorganic chemistry is the synthesis of metal complexes having the mimic functional properties of natural metalloprotein <sup>(1-3)</sup>. Synthesis of ligand , synthesis of metal complexes and estimation of metal ion intake, elemental analysis, molar conductivity, UV-visible spectra, IR Spectra, XRD, SEM, analysis, and anti-bacterial, anti-fungal, larvacidal, ant-cancerus and anti-inflamatory were studied <sup>(4-6)</sup>.

### Synthesis of Schiff base ligand with DFMPM and L-tryptophan

The Schiff base ligand was prepared by the reported methods. Equimolar ethanolic solution of DFMPM and L-tryptophan were mixed in 1:2 and refluxed for about an hour. Pour the reaction product in ice, (1+2) Schiff base ligand was obtained <sup>(7)</sup>. The precipitated yellow compound was filtered washed with water and dried over anhydrous calcium chloride. The crude sample was recrystalised from 50% absolute alcohol yield = 64%. Melting point =  $223^{\circ}$ C. Fig.1 Structure of ligand.



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#### Fig.1 Structure of ligand

#### Synthesis of Cu(II), Co(II) and Ni(II) Schiff base metal complexes

All the metal complexes were prepared by mixing ethanolic solution of Schiff base ligand with the corresponding aqueous metal salt solution of Co(II), Cu(II) and Ni(II) nitrates in 2:1 molar ratio. The resulting mixture was refluxed for about twelve hours at 70-80<sup>o</sup>C. A coloured solution appeared on standing. The complexes were filtered, washed with ethanol, diethyl ether, acetone and hot water and finally dried under vaccum at 90<sup>o</sup>C. yield = 59%. Fig.2 Structure of Schiff base complexes, M=Cu(II), Co(II) and Ni(II)<sup>(7)</sup>. The filtrates obtained in the above method were collected and it is used for the estimation of Co(II), Cu(II) and Ni(II) intake for complexation using standard methods.



Fig.2 Structure of Schiff base complexes, M=Cu(II), Co(II) and Ni(II)



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#### **II. RESULT AND DISCUSSION**

Physical and Analytical data of ligand and Metal complexes are mention in Table.1. The complexes are in  $ML_2$  composition in which the metal complexes of Co(II), Cu(II) and Ni(II) are coloured solids, stable towards air and have high melting points above (250°C). The complexes are insoluble in water and common organic solvents but are soluble in DMF, CDCl<sub>3</sub>, and DMSO. All the complexes are mononuclear with the ligand coordinated to the central metal atom and the metal to ligand ratio in all complexes was 1:2. Complexes with conductance below 50 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> are non electrolyte in nature. For non-electrolytes conductivity was slightly higher it may be due to partial solvolysis of the complexes in DMSO medium<sup>(8)</sup>.

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Compound	Yield	Colour	Mol. formula	Mol.wt	Mel. point	Elemental found (cal	l  cd) %	Analysis,	Molar conductance
· · · · · · · · · · · · · · · · · · ·	%				°C	С	н	N	ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
Ligand L	65	ash	$C_{69}H_{104}N_4O_6$	1084	234	72.67 (76.38)	9.06 (9.59)	2.41 (3.189)	
[CuL <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	58	grey	$C_{138}H_{208}N_{10}O_{14}$	2291	>250	73.11 (75.20)	8.16 (11.21)	1.52 (3.07)	16
[CoL <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	62	Grey	$C_{138}H_{208}N_{10}O_{14}$	2286.93	>250	73.41 (75.37)	8.11 (11.23)	1.27 (3.08)	19
[NiL <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	61	Brown	$C_{138}H_{208}N_{10}O_{14}$	2286.69	>250	72.44	8.75	1.97 (3.08)	14

#### Table 6.1 Physical and Analytical data of ligand and Metal complexes

#### FT-IR Spectrum Analysis

The IR spectrum of the ligand shows broad band at 1654 cm<sup>-1</sup>, which was assigned due to vC=N stretching of azomethine group . In complexes this band was shifted to lower regions, 1620cm<sup>-1</sup>, 1633cm<sup>-1</sup>, 1631cm<sup>-1</sup> for Cu(II), Co(II) and Ni(II) complexes respectively, suggesting the coordination of azomethine nitrogen to metal atom in complexation <sup>(8)</sup>. This was due to the donation of electron density from nitrogen to metal. v(-OH) group for the complexes are at 3525-3371cm<sup>-1</sup>. Moreover, the strong band at 2854cm<sup>-1</sup> due to v (C-O) (phenolic) in the ligand has been shifted to the 2886-2333cm-1 in the spectra of complexes. The strong absorption band at 2924cm-1 due to v (C-H) for ligand and has shifted to 2924-2900 cm<sup>-1</sup> in the complexes exhibit a broad and strong absorption band in the region 1450-1382cm<sup>-1</sup> and 1651-1620 cm<sup>-1</sup> it confirms the presence of free-COOH and v (N-O) respectively.



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Table 5 T T-IN in equencies and 0 v speech and of the ngana and complexes	Table 3	FT-IR	frequencies	and UV	spectrum	of the li	igand and	complexes
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Ligand/ Complexes	$v_{O-H}$ cm <sup>-1</sup>	ν <sub>O-C</sub> cm <sup>-1</sup>	ν <sub>C-H</sub> cm <sup>-1</sup>	v <sub>C=N</sub> cm <sup>-1</sup>	$v_{C=0}$ cm <sup>-1</sup>	free – COOH cm <sup>-1</sup>	v <sub>M-N</sub> cm <sup>-1</sup>	$v_{M-0}$ cm <sup>-1</sup>	λ max(nm)
Ligand L	-	2854	2924	1654	1581	1449	-	-	-
[CuL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	3525	2888	2924	1620	1490	1450	513	401	320,400,650
[CoL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	3371	2850	2900	1633	1400	1382	567	401	320, 450,650
[NiL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	3371	2850	2900	1631	1490	1394	565	401	320,390,650



Fig. 3 FTIR Spectrum of ligand (L)



Fig.4 FTIR Spectrum of Cu(II) complex



Fig.5 FTIR Spectrum of Co(II) complex



Fig. 6 FTIR Spectrum of Ni(II)complex



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#### UV-Vsible specrum analysis

The transitions of uv-visible spectrum are connected with the electronic energy levels of the compound under observation. Cu(II) complex shows absorption bands at 320nm, 340nm. The multiple bands have been assigned  ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ transition. The nature of band suggests distorted octahedral geometry. The UV spectrum of Co(II) shows bands at 325nm, 350nm Which are assigned to  ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g(P)}$ ,  ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}$ ,  ${}^{4}T_{1g} \rightarrow {}^{4}T_{2g}$  transitions respectively and supports octahedral geometry. In the Spectrum of Ni(II) complex, bands are observed at 400nm, 470nm. Which are assigned to  ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ ,  ${}^{3}A_{2g} \rightarrow {}^{3}A_{1g(F)}$ ,  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ 

#### SEM analysis of the complexes

The surface morphology of the complexes has been examined using scanning electron microscope. Fig 7, Cu(II) shows microscopic template coarse surface and core shell structure and are nano crystalline in nature <sup>(16)</sup>.



Fig.7 SEM images of Cu(II) complex at 1µm, 2µm, 5µm, 10µm X-Ray Diffraction Analysis

The diffracto-gram is in fig.8 and grain size of complexes is shown in table. 4. It is evident that the strong and broad peaks confirm that the complex formation and the appearance of large feeble peaks indicate micro crystalline. The grain size of the complexes was calculated using Scherrer's formula. The calculated grain size of the  $[NiL_2(NO_3)_2]$  complex is in the range of 10.645nm value suggested that the complexes are in nano crystalline size <sup>(17)</sup>.



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#### **Table 4 Grain size of complexes**

Complex	Grain size(nm)
[NiL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	10.645



Fig.8 XRD structure of Ni(II) complex

#### 6.3.8 Metal ion intake

The complexation behaviour of cardanol based Schiff base was affected by structural parameters. This study indicates that the metal ion intake decreased Cu(11),Co(11), and Ni(11) at their natural pH<sup>(18)</sup>. The data of metal ion intake are given in table 5. This can be explained by Pearson's proposal. Nature of the ligand and the chelate effect were the factors involved in the environmental chemistry and technological interest. It can also be used for the removal of Cu(II),Co(II) and Ni(II) ions from water.

#### Table.5 Metal Ion intake

Complexes	Metal Ion intake meq/g
$[CuL_2(No_3)_2]$	0.5689
[CoL <sub>2</sub> (No <sub>3</sub> ) <sub>2</sub> ]	0.4463
[NiL <sub>2</sub> (No <sub>3</sub> ) <sub>2</sub> ]	0.4164



#### Antibacterial activity

The antibacterial activities of the metal complexes have been screened against E. coli, S. aureus and S.typhi. It includes gram +ve (standard drug) and gram -ve (DMSO) pathogens namely *streptomycin and fluconozole*. The stock solution (T1=4mg and T2=8mg) of the test solution was prepared in DMSO solution. Cu(II), Co(II) and Ni(II)



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showed significantly antibacterial activity. Biological activity of metal chelates could be explained on the basis of overtones concept and chelation theory  $^{(19-20)}$ . Table. 6 show antibacterial activity of complexes.

	Positive	33	34	36
	Negative	-	-	-
E.coli	T <sub>1</sub>	9	19	12
	$T_2$	14	23	20
	Positive	32	30	31
	Negative	-	-	-
S.typhi	T <sub>1</sub>	24	20	22
	$T_2$	27	22	29
	Positive	16	35	20
	Negative	-	-	-
S.aureus	T <sub>1</sub>	25	20	25
	$T_2$	28	26	29

### Table. 6 Antibacterial activity of Cu(II), Co(II) asnd Ni(II) complexes

Gram + ve streptomycin and gram -ve fluconozole and stock solution (T1 = 4mg and T2 = 8mg)

#### **Antifungal Activity**

Cu(II), Co(II) and Ni(II) complexes are studied against Aspergillus niger and Aspergillus flavus. It is found that the activity increases upon coordination. The increased activity of the metal chelates can be explained on the basis of chelation theory. Cu(II) and Co(II) complex show more activity towards Aspergillus niger <sup>(21)</sup>. These results may be due to higher stability of complexes noted n table.7

#### Table. 7 Anti-fungal data of complexes

FUNGAI	FUNGAI Cu(II )		Ni(II)	
Aspergillus niger	18	13	6	
Aspergillus flavus	9	8	6	

#### Anti-inflammatory activity

Table 8 Anti-inflammatory activity of Ni(II) complex

Anti-inflammatory activity of Ni(II) complex has been
done using HRBC membrane stabilization method.
Diclofenac sodium was used as standard and distilled
water was used as control. Table.8 pointed the
percentage inhibition of haemolysis by Diclofenac
sodium and Ni(II) complex by HRBC membrane
stabilization method which decreases with increase in
concentration <sup>(22-23)</sup> . The percentage inhibition of
haemolysis by Ni(II) complex is not showing
concentration dependent manner. It may be due to very
low or no anti-inflammatory activity.

Drug	Concentration [µg]	% Inhibition of haemolysis
	100	83.03
[NiL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	300	81.86
	500	82.74



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#### Larvacidal activity

#### Table .12 Larvacidal activity data of Ni(II) complex

Concentration (µg/ml)	50 μg	200 μg	400 μg	600 μg	control	-ve control
Number of brine shrimp per test sample	10	10	10	10	10	10
Average number of survivors	0	0	0	0	10	10
Average number of deaths	10	10	10	10	0	0
Percentage mortality	100	100	100	100	0	0

Brine shrimp cytotoxic assay was used to evaluate cytotoxic activity of  $[NiL_2(NO_3)_2]$  complex , it show enhanced larvacidal activity. The result obtained is presented in table.12 . 100% mortality was observed in all concentrations  $^{(25)}$ .

#### Anticancer activity

Determination of Invitro Antiproliferative effect of  $[NiL_2(NO_3)_2]$  extracts on cultured hela cells and it is done in 6,12 and 24(µl) concentrations. From fig.12 and in table.13, When concentration increases the viability decreases that mean the cytotoxicity of the cells decreases there by the cells are not cytotoxic cells increases and the complex is potential due to less number of live cells <sup>(25-26)</sup>

#### Table.13 Anticancer activity data of complex

Sample volume Different concentrations (µl)	Average Absorbance @ 540nm	Percentage Viability
6	0.2822	61.42
12	0.2515	48.84
24	0.1905	36.99

Control = 0.5149



Fig.12 MTT assay of Ni (II) Complex at control6 µM, 12 µM, 24 µM

Conclusion

In this contribution, starting from Schiff base metal complexes of Cu(II), Ni(II) and Co(II) we have identified and explored a new class of complexes to investigate the influence of FTIR spectrum, UV-vis spectrum, XRD powder analysis, SEM analysis, Elemental analysis, Molar conductance and Metal ion intake . The XRD and



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SEM studies reveal that the complexes are nano crystalline. complexes showed significantly antibacterial activity. Co(II) complex exhibit statically significant activity in invitro and invivivo percentage inhibition From invitro and invivo analysis the percentage inhibition of  $[NiL_2(NO_3)_2]$  complex increases with increase in concentration and exhibit statistically significant proteinase inhibitory activity. Cu(II) shows anticancerus property. It can be inferred that the and T2 shows significant larvacidal activity. The samples T1 and T3 also show the larvacidal activity and in every sample the morality occurs in higher concentrations. In larvacidal activity 100% morality was observed in all concentrations with in 12 hr for  $[NiL_2(NO_3)_2]$ .

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