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Invitro Biological Studies and Characterisation of Schiff Base Complexes of Co(Ii), Cu(Ii), Ni(Ii) and Zr(Iv) Using Dfmpm and 2,2-Diphenylethanamine

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ABSTRACT

This article evokes that cardanol, the important component obtained from cashewnut shell liquid (CNSL), plays a pivotal role in the synthesis and enactment of variety of novel compounds of futuristic application .Cardanol transfigures into an aldehyde, di - α- formylmethoxybis(3-pentadecenylphenol) methane (DFMPM) as per earlier methods . The synthesised aldehyde was used to prepare Schiff base ligand by using 2,2-diphenylethanamine, which on treatment with Co(II), Ni(II), Cu(II) and Zr(IV) metal salt solutions forming complexes. The prepared complexes were characterised by UV- visible, IR and NMR spectroscopy. The surface morphology of the crystals were studied by SEM and XRD. The studies such as elemental analysis, melting point, conductivity, metalion intake, antibacterial, antifungal, anticancer, DNA cleavage, larvicidal, anti-inflammatory and insecticidal were conducted. The studies confirmed hexacoordination in the Co(II), Ni(II) and Cu(II) complexes and octacoordination inZr(IV) complex. Other studies indicated that the complexes were good biological agents and they showed a ray of hope in their usage as pharmaceutical agents.

Keywords: Cardanol, DFMPM, Biological agents, Spectroscopy, Anticancer agent.

INTRODUCTION

Schiff's bases and their complexes possess versatile properties as catalysts in various biological systems, and are used as polymers, dyes, antimicrobial agents, antifungal agents and have antitumor and cytotoxic activities, plant growth regulating, enzymatic activity and pharmaceutical properties.[1]Cardanol is the main component obtained by vacuum distillation of roasted cashew nut shell liquid (CNSL) and was used for the preparation of bioactive transition Schiff base metal complexes using standard methods.[2,3,4]The ligand and complexes were characterised by UV-visible, FTIR,^{1}HNMR, SEM, XRD and elemental analysis, melting point, conductivity, metal ion intake, anti bacterial, anti fungal, anti cancer, DNA cleavage, larvicidal,anti-inflammatory and insecticidal activity were studied. The result indicated that the complexes of Cu(II), Co(II) Ni(II) and Zr(IV) were bioactive and also used for the removal of such ions from water and the nano crystalline nature of complexes were confirmed by SEM and XRD studies.[5,6.7]

EXPERIMENTAL

Synthesis of Schiff base ligand with DFMPM and 2,2-diphenylethanamine

The Schiff base ligand was prepared by the reported methods[8,9]Equimolarethanolic solution of DFMPM and 2,2 diphenylethanamine were mixed and refluxed for about an hour. Poured the reaction product in ice, (1+2) Schiff base ligand was obtained.[1] The precipitated yellow compound was filtered washed with water and dried over anhydrous calcium chloride. The crude sample was recrystalised from 60% absolute alcohol

Synthesis of 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 Cu(II) nitrate, Co(II) nitrate, Ni(II) nitrate and Zr(IV) nitrate in 2:1 molar ratio. The resulting mixture was refluxed for about twelve hours at 70-80^{o}C,[10,11,12] a coloured solution appeared on standing. The complexes were filtered, washed with ethanol, diethyl ether, acetone and hot water and finally dried under vacuum at 90^{o}C.

Estimation of metal ion intake

The filtrates obtained in the above method were collected. The collections were used for the estimation of Cu(II), Co(II) , Ni(II) and Zr(IV) intake for complexation using standard methods. [13]

RESULT AND DISCUSSION

The analytical data of the complexes, together with their physical properties are mentioned in Table 1. The data suggested that the complexes were in ML_2 composition. The metal complexes of Cu(II), Co(II) ,Ni(II) and Zr(IV) were coloured solids, stable towards air and had high melting points above (250^oC). The complexes were insoluble in water and common organic solvents but soluble in DMF, $CDCl_3$ and DMSO. Analytical data suggested the metal to ligand ratio in all the complexes to be 1:2.[15] Conductivities of solutions of the complexes showed as non electrolytes because their conductivity value were in the range 14-18 ohm^{-1}cm^2 mol^{-1}.

Elemental Analysis

The analytical data suggested that all the complexes were mononuclear with the ligand coordinated to the central metal atom and the metal to ligand ratio in all complexes was 1:2, and their empirical formulae have been computed and are given in Table 1.[15]

TABLE -1
PHYSICAL CHARACTERISTICS AND ANALYTICAL DATA OF COMPLEXES

Complexes /Ligand	Yield	Colour	Molecular formula	Mol.weight	Meltingpoint	Elemental Analysis (found)		
						C	H	N
Ligand L	56	brown	$C_{75}H_{98}N_2O_2$	1058	217	85.07 (84.94)	9.26 (9.42)	2.65 (2.87)
[CuL_2 $(NO_3)_2$]	60	brown	$C_{150}H_{196}N_6O_{10}$ Cu	2303.55	>250	78.14 (77.91)	8.51 (9.0)	3.65 (3.52)
[CoL_2 $(NO_3)_2$]	58	brown	$C_{150}H_{196}N_6O_{10}$ Co	2298.93	>250	78.30 (78.1)	8.53 (8.91)	3.65 (3.50)
[NiL_2 $(NO_3)_2$]	62	grey	$C_{150}H_{196}N_6O_{10}$ Ni	2298.69	>250	78.31 (79.1)	8.53 (9.1)	3.65 (3.82)
[ZrL_2 $(NO_3)_4$]	61	Light brown	$C_{150}H_{200}N_8O_{18}$ Zr	2491.22	>250	72.25 (72.48)	8.02 (7.98)	4.49 (4.20)

Conductivity Measurements

The molar conductivity values are given in Table 2. The conductivity was in the range 14-18 ohm^{-1} cm^2 mol^{-1}. Complexes with conductance below 18 ohm^{-1} cm^2 mol^{-1} are non electrolyte in nature. The slightly higher conductance values may be due to partial solvolysis of the complexes in DMSO medium.[15]

TABLE -2
MOLAR CONDUCTANCE DATA OF THE COMPLEXES

Compounds	Molar conductance Ohm^{-1} cm^2 mol^{-1}
[CuL_2 $(NO_3)_2$]	15
[CoL_2 $(NO_3)_2$]	14
[NiL_2 $(NO_3)_2$]	14

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$[ZrL_2(NO_3)_4]$	18

FT-IR spectrum analysis

The IR spectral data of the ligand and complexes are shown in the Table 3. Coordination of the ligand to the metal causes shift of infrared bands to higher or lower frequencies with different intensities.The mode of coordination has been assigned by comparing the spectra of the metal complexes with that of the ligand. The IR spectrum of the ligand (L) showed characteristic bands at 2850 cm^{-1}, 2900 cm^{-1},1600 cm^{-1} due to the ν_{O-C}, ν_{C-H}, $\nu_{C=N}$ respectively.[16] ‘The IR spectra of the complexes exhibited bands with the appropriate shifts due to complex formation. The IR broad bands of metal complexes in the range of 3350 cm^{-1} to 3250cm^{-1}indicate the presence of co-ordinated or lattice water molecule.[17,18] The absorption of phenyl groups is seen in the region 1700 cm^{-1}-1550cm^{-1}. The γ_{C-O} phenolic stretching frequency is observed around 2340 cm^{-1} to 2000cm^{-1} which get shifted to lower or higher frequency region indicating co-ordination of phenolic oxygen. The band at 2900 cm^{-1} to 2780cm^{-1} and 1681 cm^{-1} to 1620 cm^{-1} were assigned to C-H and respectively.[19,20] The imine peaks in the metal complexes showed changes in the ligand indicating co-ordination of the imine nitrogen atom to the metal ion. Another absorption band at 800 cm^{-1} to 700 cm^{-1} is assigned to M-N bond and bands at 730cm^{1} to 700 cm^{-1} is assigned to M-O bond.[21,22] Fig1- 5 show the IR spectrum of ligand and metal complexes.[23]

TABLE --3
FT-IR FREQUENCIES (CM^{-1}) OF THE LIGAND AND COMPLEXES

Ligand/ Complexes	ν_{O-H} cm^{-1}	ν_{O-C} cm^{-1}	ν_{C-H} cm^{-1}	$\nu_{C=N}$ cm^{-1}	$\nu_{C=O}$ cm^{-1}	free - C_6H_5	ν_{M-N} cm^{-1}	ν_{M-0} cm^{-1}
Ligand L	3350	2850	2900	1600	1630	1700	760	710
$[CuL_2(NO_3)_2]$	3350	2350	2905	1634	1490	1650	780	700
$[CoL_2(NO_3)_2]$	3300	2200	2900	1623	1480	1500	750	720
$[NiL_2(NO_3)_2]$	3250	2265	2900	1651	1501	1600	740	700
$[ZrL_2(NO_3)_4]$	3300	2000	2792	1681	1500	1550	800	730

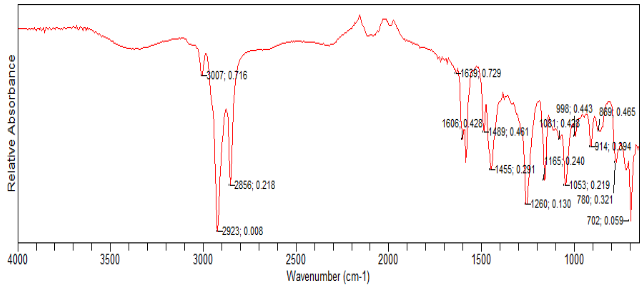

Fig. 1. FTIR Spectrum of ligand (L)

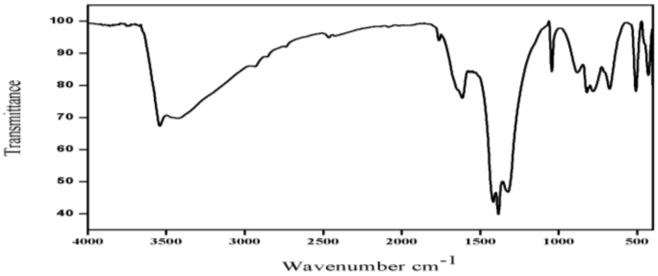

Fig. 2. FTIR Spectrum of Cu(II) complex

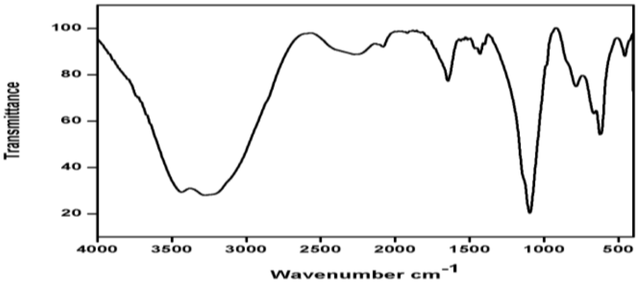

Fig.3. FTIR Spectrum of Co(II) complex

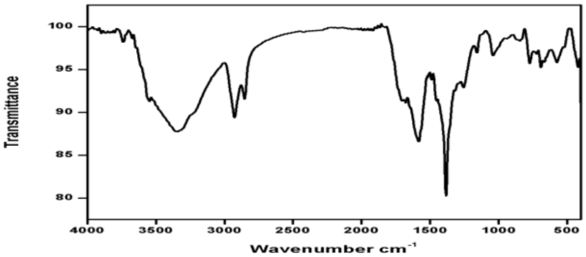

Fig. 4. FTIR Spectrum of Ni(II) complex

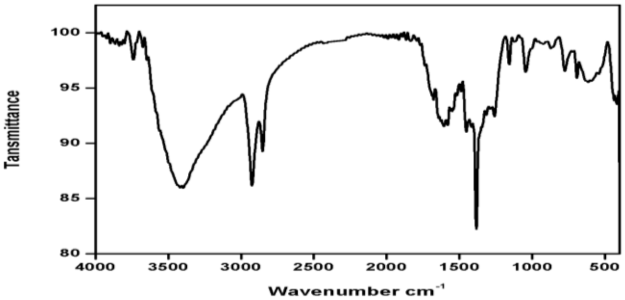

Fig. 5. FTIR Spectrum of Zr(IV) complex

UV-visible spectrum analysis

The UV-visible spectra are often very helpful for structural identification. The ligand showed a broad band at 480 nm which is assigned to π-π* transition of the >C=N chromophore. This band was shifted to lower wave length suggesting the co-ordination of imine nitrogen with central metal ion. The UV-visible spectrum of Cu(II) complex showed three absorption bands at 398, 580 and 588nm giving an octahedral geometry with field transition $^2B_1g\text{->}^2A_1g$, $^2B_1g\text{->}^2B_2g$ and $^2B_1g\text{->}^2E_2g$ respectively.[24] Co(II) and Ni(II) complexes, showed absorption bands at 598 to 398 nm and 598 to 395 nm respectively and suggested octahedral geometry.[25] The spectrum of Zr(IV) complexes showed three absorption bands at 398, 568 and 606 nm respectively suggesting octacoordination, table 4 shows the UV-visible spectral data of complexes.[26]

TABLE - 4:
UV-VISIBLE SPECTRAL DATA OF COMPLEXES

Ligand/Complexes	$\lambda_{max(nm)}$
Ligand L	360, 480, 520
$[CuL_2(NO_3)_2]$	398, 580, 588
$[CoL_2(NO_3)_2]$	398, 512, 598
$[NiL_2(NO_3)_2]$	395, 572, 598
$[ZrL_2(NO_3)_4]$	398, 568, 606

^{1}H NMR Spectrum analysis

The ^{1}HNMR spectrum of ligands and metal complexes in $CDCl_3$ vividly gave high presence of – CH, ,–C_6H_5, – O – CH_2 groups. On examining the ^{1}HNMR spectrum of ligand (Fig.6) it exhibited a multiplet signal at δ=7.002 ppm –7.020 ppm is due to substituted aromatic ring protons. The presence of H – C = N- group is indicated by the singlet at δ = 7.022ppm. The multiplet at δ 6.537 ppm □ δ = 6.639 ppm and δ = 5.168 ppm – δ = 5.691 ppm were due to the olifinic protons of the side chain and – O-CH_2 -group of the ligand respectively.[12,27]

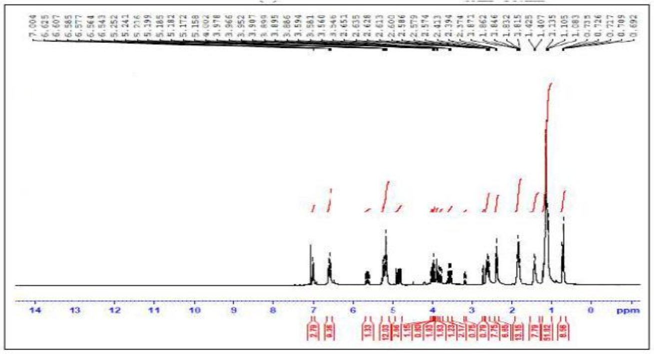

Fig. 6. ^{1}H NMR spectrum of ligand

In the ^{1}H NMR spectrum of the Cu(II) complex (Fig.7), the presence of H – C = N- group is indicated by the singlet at δ = 7.120 ppm. A singlet at δ = 2.15 ppm is due to the substituted – CH_2 -group. The signal at 2.736 is due to the presence of O – CH_2 group. The signals at δ = 2.27 and 2.6 gave light on the presence of C_6H_5 - CH - group.[28]

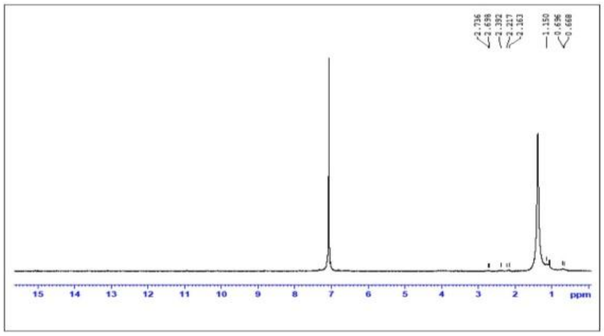

Fig. 7.^{1}H NMR spectrum of Cu(II) complex

In the ^{1}HNMR spectrum of the Co(II) complex (Fig.8), the presence of H – C = N- group is indicated by the singlet at δ = 7.250 ppm. This also gave signals of– O-CH_2 group at δ =2.56 ppm δ =1.238 ppm for □ CH_2 groups and δ =2.27 for C_6H_5-CH group.[28,29]

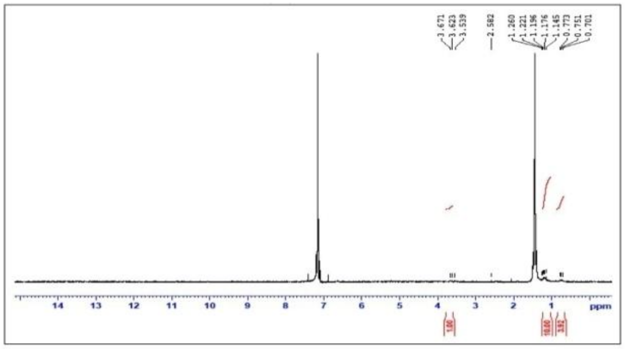

Fig.8. ^{1}H NMR spectrum of Co(II)complex

In the ^{1}H NMR spectrum of the Ni(II) complex (Fig.9), the presence of H – C = N- group is indicated by the singlet at δ = 7.220ppm. The spectrum gave signals for – O-CH_2 -group at δ =2.582ppm and δ =1.26 ppm for -CH_2 group.[28,29]

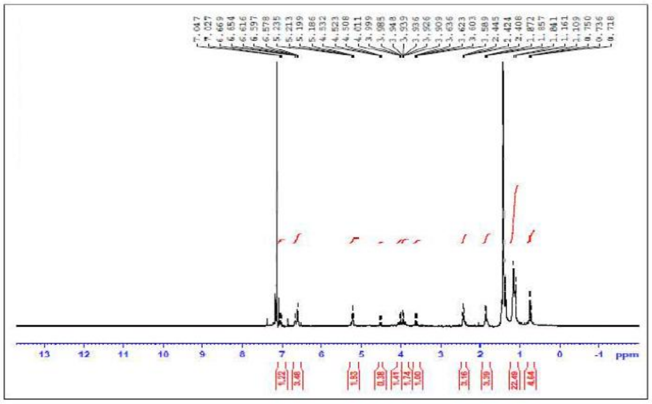

Fig.9 . ^{1}H NMR spectrum of Ni(II) complex

In the ^{1}H NMR spectrum of the Zr(IV) complex (Fig.10), the presence of H – C = N- group is indicated by the singlet at δ = 7.800ppm it is due to the olifinic protons of the side chain and a singlet at δ = 7.213 ppm is due to – O-CH_2 -group. A singlet at δ =2.810 ppm is due to substituted H-C-C=O-group and a singlet at δ = 1.994ppm is due to substituted -CH_2-NH group.[28,29]

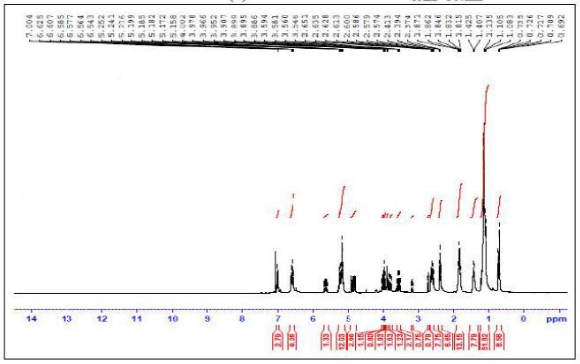

Fig.10. ^{1}H NMR spectrum of Zr(IV) complex

Based on the observations in elemental analysis, FT-IR, electronic and ^{1}H NMR spectral studies, the proposed structure of ligand (L) and its metal complexes are given in Fig.11 - 13.

Fig.11.Structure of ligand

Fig.12. Structure of Schiff base complexes, M = Cu(II),Co(II) and Ni(II)

Fig.13. Structure of Schiff base complex, M=Zr(IV)

SEM analysis

The surface morphology of the complexes has been examined using scanning electron microscope. The SEM image of Ni(II) and Zr(IV) complexes are given in fig 14 and 15. The SEM image ofNi(II) complex showed sand grain like and rock piece like appearances. Also the SEM image ofZr(IV) complex showed crystal like appearance. Careful examination of the SEM images clearly indicate the nano scale size of the complexes.[10]

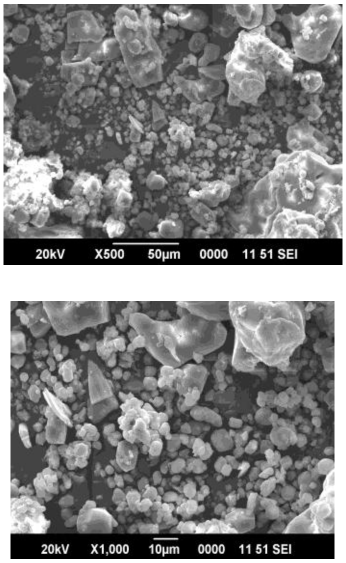

Fig.14.SEM images of Ni(II) complex

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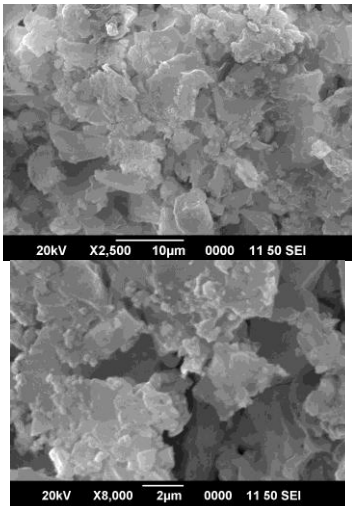

Fig. 15. SEM images of Zr(IV) complex

X-Ray Diffraction Analysis

The X-ray diffractogram of Cu(II) and Zr(IV) complexes are given in Fig.16 and 17and the grain size of the complexes are shown in table 5. The maximum peak recorded was at 3.504nm and 7.760 nm for $[CuL_2(NO_3)_2]$ and $[ZrL_2(NO_3)_4]$ respectively.[30] It is evident that the strong and broad peaks confirm the complex formation and the appearance of large feeble peaks indicate micro crystalline nature. The grain size of the complexes was calculated using Scherrer`s formula. These values suggested that the complexes are in nano crystalline size.[31,32]

TABLE – 5: GRAIN SIZE OF THE COMPLEXES

Complex	Grain size (nm)
$[CuL_2(NO_3)_2]$	3.5
$[ZrL_2(NO_3)_4]$	7.7

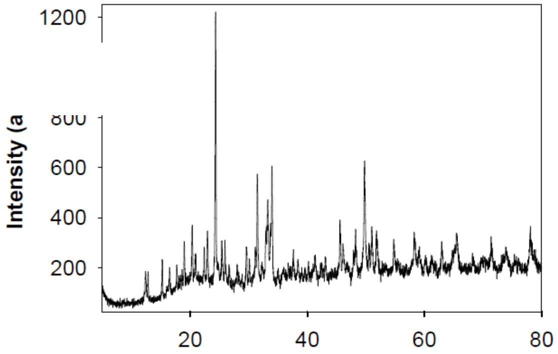

Fig.16. X-Ray Diffraction analysis of Cu(II) complex

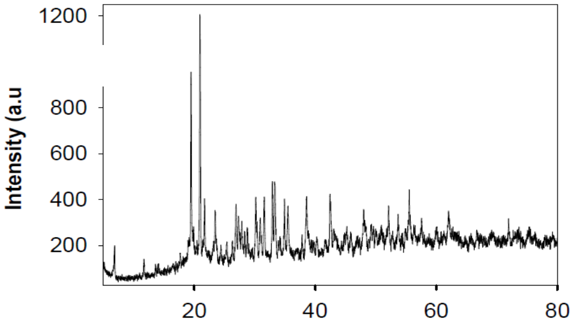

Fig.17. X-Ray Diffraction analysis ofZr(IV) complex

Metal ion intake

The structural parameters play pivotal role in complex formation.[33]It can be understood by noting in the metal ion intake and is decreased in the order Ni(II), Co(II)>Zr(IV) > Cu(II) at their natural pH.According to Pearson, hard acid preferred to combine with hard base and soft acid preferred to combine with soft base. In the present study the interaction of Ni(II) is more intense than other divalent metal ions with the Schiff base ligand.Nature of the ligand and the chelate effect were other factors involved in the complex formation.[34]

TABLE - 6
METAL ION INTAKE MEQ/G OF COMPLEXES

Complexes	Metal Ion intake meq/g
$[CuL_2(NO_3)_2]$	0.3890
$[CoL_2(NO_3)_2]$	0.4942
$[NiL_2(NO_3)_2]$	0.6012
$[ZrL_2(NO_3)_4]$	0.4520

BIOLOGICAL SCREENING

Antibacterial activity

Ligand and metal complexes were screened against bacteria in order to determine their antibacterial property. The result obtained showed that the activity of Schiff bases are more pronounced when coordinated with the metal ion. Schiff bases are characterized by an imine group –N=CH-, which helps to clarify the mechanism of transamination and racemization reaction in biological system. The mode of action of the compounds may involve formation of a hydrogen bond through the azomethine group (>C=N–) with the active centres of various cellular constituents, resulting in interference with normal cellular processes.[34]

TABLE. -7
ANTIBACTERIAL ACTIVITY DATA OF METAL COMPLEXES

Organisms	Diameter of zone of inhibition (mm)				
	Name of the sample				
	Identity	H1	H2	H3	H4
E.coli	**Positive**	33	33	33	36
	F_1	9	6	13	4
	F_2	12	8	18	10
V.cholerae	**Positive**	35	35	33	32
	F_1	12	8	13	11
	F_2	14	12	16	11
S.typhi	**Positive**	35	36	36	39
	F_1	11	4	12	7
	F_2	12	6	16	8
S.aureus	**Positive**	39	37	39	38
	F_1	10	5	11	9
	F_2	11	9	10	9

H1 =$[CuL_2(NO_3)_2]$, H2 = $[CoL_2(NO_3)_2]$,
H3 =$[NiL_2(NO_3)_2]$,H4 = $[ZrL_2(NO_3)_4]$

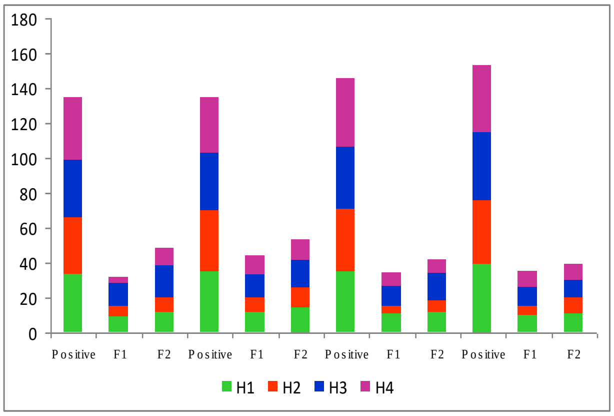

Fig.18. Graphical representation of antibacterial activity in metal complexes

Antifungal Activity

Cu(II), Co(II), Ni(II) and Zr(IV) complexes are studied against Aspergillusniger and Aspergillusflavus. Antifungal activity data are shown in table 8 and graphical representation in fig.20. It is found that the activity increased upon coordination. The increased activity of the metal chelates can be explained on the basis of chelation theory. The orbital of each metal ion is made so as tooverlap with the ligand orbital. Increased activity enhances the lipophilicity of complexes due to delocalization of pi-electrons in the chelate ring. In some cases increased lipophilicity leads to break down of the permeability barrier of the cell. Ni(II) complex showed more activity towards Aspergillusniger. These results may be due to the higher stability of complexes.[35]

TABLE -8
ANTI-FUNGAL ACTIVITY DATA OF SCHIFF BASE COMPLEXES

FUNGAI	$[CuL_2(NO_3)_2]$ (mm)	$[CoL_2(NO_3)_2]$ (mm)	$[NiL_2(NO_3)_2]$ (mm)	$[ZrL_2(NO_3)_4]$ (mm)
Aspergillusniger	19	7	12	10
Aspergillusflavus	7	9	8	7

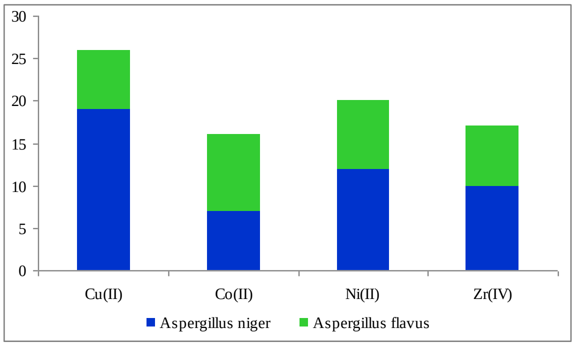

Fig. 19. Graphical representation of antifungal activity of complexes

Anti-inflammatory activity

In vitro anti-inflammatory study, $[NiL_2(NO_3)_2]$ was performed to evaluate the effect of HRBC membrane stabilization. Diclofenac sodium was used as standard and distilled water was used as control. The percentage inhibition of haemolysis by Diclofenac sodium and $[NiL_2(NO_3)_2]$ samples increased with increase in concentration. Diclofenac sodium and [$NiL_2(NO_3)_2$] samples exhibited statistically significant anti-inflammatory activity (NCCLS- 1993). Table.9 depicts the anti inflammatory activity data of Ni(II) complex.[34]

TABLE- 9
ANTI-INFLAMMATORY ACTIVITY OF Ni(II) COMPLEX

Sl No.	Drug	Concentration [µg]	% Inhibition of haemolysis
1	Diclofenac	100	80
		300	97
		500	98
2	[$NiL_2(NO_3)_2$]	100	88.04
		300	90.02
		500	92.01

Larvicidal activity

The metal complex [$NiL_2(NO_3)_2$] showed enhanced larvicidal activity. The result obtained is presented in table.10. The action of larvicides upset the normal behaviour and action of target organism. Chelation increases the lipophilic nature of central metal atom, which in turn favours the molecule in crossing the cell membrane of the microorganism and enhancing larvacidal activity of complexes. Brine shrimp cytotoxic assay of [$NiL_2(NO_3)_2$] was performed to evaluate its cytotoxic activity. Sample exhibited very high cytotoxic activity, at 50µg, 200µg, 400µg and 600µg it showed 60%,70%,90% and 100% mortality respectively.[36]

TABLE --10
LARVICIDAL 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	4	3	1	0	10	10
Average number of deaths	6	7	9	10	0	0
Percentage mortality	60	70	90	100	0	0

Anticancer activity

Determination of invitroantiproliferative effect of Ni(II) complex was done. The extracts developed were culturedin hela cells and it was done in 6,12 and 24(µl) volume. When concentration increased the number of dead cells increased and the complex is potential due to less number of live cells. Anticancer activity of the complex is shown in table.11 and in fig.20. From this it was found that as thevolume of the samples increases the percentage viability of the assay decreases. Reduction of MTT can only occur in metabolically active cells and the level of activity is a measure of the viability of the cells.[37]

TABLE - 11
ANTICANCER ACTIVITY DATA OF Ni(II) COMPLEX

	Sample volume (µl)	Average Absorbance @ 540nm	Percentage Viability
CONTROL		0.5149	_
$[NiL_2(NO_3)_2]$	6	0.4703	91.33812
$[NiL_2(NO_3)_2]$	12	0.3163	57.05962
$[NiL_2(NO_3)_2]$	24	0.2938	54.80676

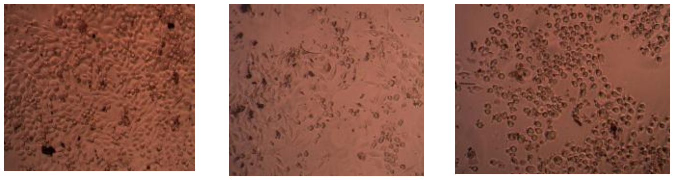

Fig. 20.MTT assay of Ni(II) Complex

Nuclease Activity

The nuclease activities of metal complexes of ligand were studied using gel electrophoresis and the respective photograph is shown in Fig.21. The cleavage efficiency of the complexes were compared with the control DNA to study the binding ability. The presence of smear in the gel diagram indicates the radical cleavageby the abstraction of hydrogen from sugar units of DNA. The metal complexes were able to convert super coiled DNA into opencircular DNA (Yano, S, Inoue, S 1998). The reaction is modulated by the metallo complexes bound hydroxyl or peroxide radical generated from the oxidant H_2O_2. Complexes of Zr(IV) showed enhanced nuclease activity.[38]

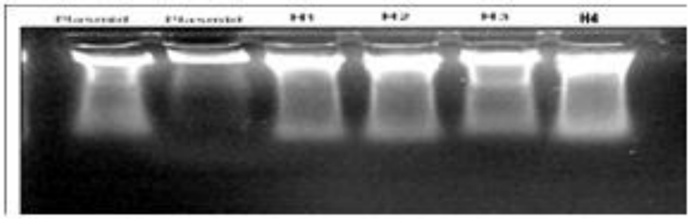

Fig.21. Gel electrophoresis diagram of complexes

Lane 1-Control DNA
Lane 2-DNA treated with H_2O_2
Lane3-DNA+Cu(II) complex + H_2O_2
Lane4-DNA + Co(II) complex + H_2O_2
Lane5-DNA+Ni(II) complex + H_2O_2
Lane6-DNA+Zr (IV) complex + H_2O_2

Insecticidal activity

The eggs of *C. cephalonica* were collected and these eggs were inoculated in clean and sterile plastic tubs (35 x 10 cm; 5 L capacity), which contained mixture of partially ground Bajra grains (2.5 kg) and groundnut powder (100 g) in the laboratory at 28±2° C. This was kept as the mother colony and sub cultured for further generations. The complexes were found to be inactive towards the medium and reaction did not occur**.**

CONCLUSION

The Schiff base metal complexes were synthesized from cardanol using 2,2-diphenylethanamine. The ligands and complexes were insoluble in water and common organic solvents, but soluble in DMF, $CDCl_3$, acetone and DMSO. The ligands and their complexes were characterized using spectral and analytical data. From the spectral and stoichiometric analysis, a hexacoordinated nature was assigned for the Cu(II),Ni(II) and Co(II) complexesand octacoordinated nature for the Zr(IV) complex. FT-IR, UV-visible and NMR studies showed the presence of nitrate group inside the coordination sphere. Careful examination of XRD and SEM studies clearly indicated that the complexes were nano crystalline and lower magnification showed grain like appearance. Metal ion intake explained that the ligand can be effectively used for extraction of metal ions from waters. All complexes were found to be more potent towards E.coli and V.choleraebacteria.Ni(II) complex showed more activity towards Aspergillusniger. Anticancer and larvicidal activity has been done in $[NiL_2(NO_3)_2]$ complex. $[ZrL_2(NO_3)_4]$ complex showed enhanced nuclease activity.Compounds show bright path towards pharmaceutical as well as chemical sciences.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interestsregarding the publication of this article.

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