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Synthesis And Characterization Of Schiff Base Metal Complexes Of Zr(IV) And Th(IV) Using (DFMPM) And L-Alanine

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Abstract: *Schiff base nano complexes of Zirconium(IV) and Thorium(IV) of general composition ML2 have been synthesized using DFMPM and L-alanine. The complexes were prepared by standared methods.The melting point, elemental analysis, molar conductance, magnetic moment studies were conducted and the complexes were characterized by IR, UV–Vis, ^{1}H NMR, SEM, and XRD. Based on the above studies the ligand was bidentate and the complexes were hexa coordinated proposing octahedral geometry to the complexes and are nano crystalline in size. Biological studies such as antibacterial, antifungal and DNA cleavage studies of the complexes indicated that the complex have better antibacterial, antifungal and DNA cleavage properties. The XRD and SEM studies revealed the nano crystalline nature of the complexes. The conductance measurements indicated the non-electrolytic nature of the complexes and are used for the removal of these metals from water.*

Keywords: *DFMPM, L-alanine, Schiff base, nano crystalline, DNA cleavage.*

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I. Introduction

Transition metal complexes with Schiff base ligands have been extensively investigated of as physical and chemical properties and their antimicrobial and anticancer agents. Schiff base complexes derived from aminoacids are important due to their ability to posses unusual configurations and biological importance [1-8]. DFMPM is prepared from cardanol which formed Schiff base ligand (L) with L-alanine. The present investigation involved the synthesis and characterization of the Schiff base Ligands (L) and the complexes of Zr(IV) and Th(IV) ions. The above complexes were characterized by elemental analysis, conductance measurements, magnetic susceptibility, uv-visible, IR, powder XRD, SEM , antimicrobial activity, DNA cleavage and anticancer activity.

II. Materials And Physical Measurements

Cardanol was obtained from M/S Satya Cashew, Chennai, India. Formaldehyde (37% solution) hydrochloric acid, epichlorohydrin, sodium hydroxide and other chemicals used were of AR grade quality obtained from Merk Chemicals. All the solvent used was purified by standard methods[9]. The micro analytical data (C, H, N) were collected using Perkin Elmer 2400 instrument. The metal ion intake were estimated by standard methods[1,2]

IR spectra were obtained using PE IR spectrum instrument model : system 2000. 1 HNMR spectra were obtained using AMX–300 MHz, FT NMR Spectrometer. Conductance measurements were obtained using systronics–305 conductivity meter. Electronic spectra of the ligands and its complexes was obtained using Perkins Elmer Lamda–25 UV-visible spectrometer in the range of 200-1100 nm. Surface morphological studies was obtained using JSM–5610 scanning electron microscope.

2.1 Preparation of Schiff base Ligand (L) with DFMPM and L-alanine

The Schiff base Ligand (L)were prepared by mixing equimolar ethanolic solution of DFMPM and L-alanine in ethanol and refluxed for 2 hour and then cooled the mixture and the Schiff base was separated and recrystallized from ethanol and washed thoroughly with diethyl ether. (fig1)

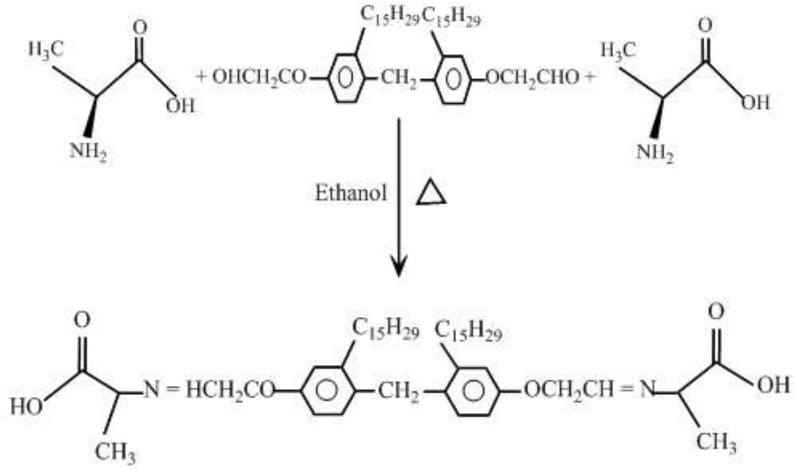


Fig 1 Schiff base Ligand (L_1)

2.2 Preparation of the metal complexes

Schiff base complexes of Ligand(L) were prepared by the addition of hot ethanolic solution (60°c) of Ligand(L) and aqueous solution nitrates of Zr(IV) and Th(IV) ions in drop by drop in 2:1 molar ratio. The mixture was stirred for 12 hours at 65°c. The precipitated solids were washed thoroughly by ethanol and then by diethyl ether. The solid complexes were dried in vaccum desicator.

III. Results And Discussion

All the metal complexes pepared above are coloured while Zr(IV) and Th(IV) complex is colourless and are stable towards air and have high melting point. The complexes are insoluble in water and common organic solvents but are soluble in DFM and DMSO.

3.1 Elemental analysis

The analytical data suggested that all complexes are mono nuclear with ligand coordinatedTo the central metal atom. The metal to ligand ratio in all the complexes was 1:2 [3-4]. The details are given in Table. 1 .

Table.I Physical characteristics and analytical data of the complexes

Ligand/ Complexes	Yield %	colour	Molecular formula	Molecular wt	Melting point	Elemental analysis		
						C	H	N
Ligand (L)	62	Brown	$C_{47}H_{84}O_2N_2$	826	228	76.99 (76.86)	11.86 (11.12)	3.35 (3.34)
$[Zr(L)(NO_3)_2.2H_2O]$	55	Light Brown	$ZrC_{106}H_{200}O_{12}N_6$	1887.22	>250	67.40 (67.33)	10.59 (9.98)	4.45 (4.42)
$[Th(L)(NO_3)_2.2H_2O]$	56	Grey	$ThC_{106}H_{200}O_{12}N_6$	2028.03	>250	62.72 (62.68)	9.86 (9.78)	4.54 (4.50)

3.2 Molar Conductivity

The molar conductivity values are given in table 2 . The molar conductivity value were in the range of 18-22 ohm^{-1} cm^2 mol^{-1} it showed that all the complexes are non-electrolytes because their conductivity value were low.

Table II. Molar conductance data of ligand and its complexes

Ligand/complexes	**Molar conductance Ohm^{-1} cm^2 mol^{-1}**	**nature**
Ligand(L)	21	non-electrolyte
$[Zr(L)(NO_3)_2.2H_2O]$	18	non-electrolyte
$[Th(L)(NO_3)_2.2H_2O]$	22	non-electrolyte

3.3 IR Spectra studies of ligand and complexes

Selected IR Spectra data for the ligand and its complexes are given in Table 3.The IR Spectrum of the free ligand (fig 2) is characterized mainly the strong bands of $2924cm^{-1}$, $2854.65cm^{-1}$,$1604.77cm^{-1}$ and $1381cm^{-1}$ which are attributed to the stretching frequencies of ϑ_{C-H}, ϑ_{C-O}, $\vartheta_{C=N}$ ϑ- CH_3 respectively[4]

The FT-IR Spectrum of the ligand is compared with the spectra of the complexes. The Characterization of absorption bands $3410.15cm^{-1}$ – $337.57cm^{-1}$ range were attributed to –OH group of the lattice water or the coordinated water. In the IR spectrum of the complexes (Fig 3,4) the absorption bands in the range 2924.09cm^{-1} – 2399.45cm^{-1} were assigned to ϑ_{C-H} stretching frequencies. The absorption bands in the range 2854.65cm^{-1} – 2059.98cm^{-1} were assigned to ϑ_{C-O} stretching frequencies. The $\vartheta_{C=N}$ bands for the free ligand in the spectra of the complexes 1604.77cm^{-1} – 1627.92 cm^{-1} suggesting coordination of both the nitrogen atoms of metal . The absorption bands at 1381cm^{-1} -1311.59 cm^{-1} is assigned to free CH_3 group. It shows that the terminal CH_3 is not involved in bonding. The imine peak in the metal complexed showed change in Schiffs compared to the ligand indicating coordination of the imine nitrogen atom to the metal ion due to coordination.The assigned to the coordinate nitro group with the central metal atom 748cm^{-1} -763 cm^{-1} is assigned to ϑ_{M-N} bond and 563cm^{-1} -686 cm^{-1} is assigned to ϑ_{M-O} band [5,6] .

Table III Selected FTIR frequencies (cm^{-1}) of the ligand and complexes

Ligand/Complexes	ϑ_{O-H}	ϑ_{C-H}	ϑ_{C-O}	$\vartheta_{C=N}$	ϑ CH_3	ϑ_{M-N}	ϑ_{M-O}	λmax(nm)
Ligand (L)	_	2924.09	2854.65	1604.77	1381	_	_	281, 274, 270
$[Zr(L)(NO_3)_2.2H_2O]$	3410.15	2924.09	2376.3	1627.92	1381.03	763.81	686.60	279, 273,264
$Th(L)(NO_3)_2.2H_2O]$	3371.57	2399.45	2059.98	1627.92	1311.59	748.38	563.21	278, 271, 264

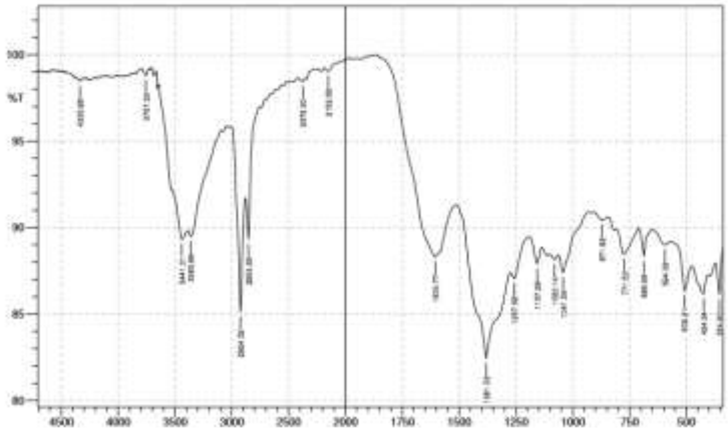


Fig.2 FTIR spectrum of Schiff base ligand (L)

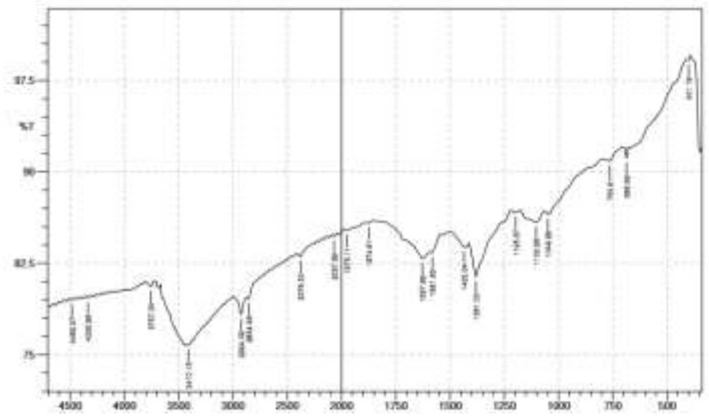


Fig 3 FTIR spectrum of Zr(IV) complex of ligand(L)

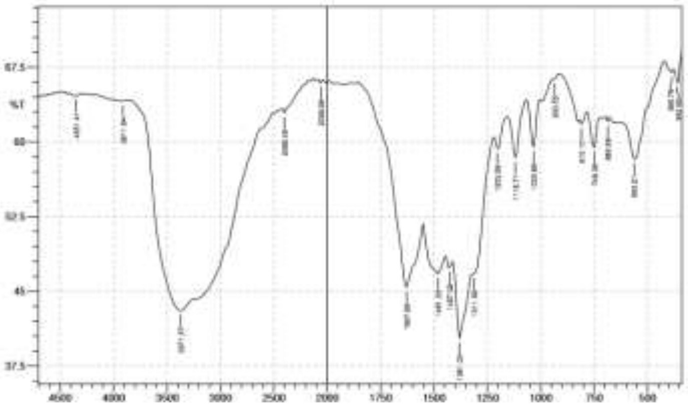


Fig 4 FTIR spectrum of Th(IV) complex of ligand(L)

3.4 Electronic Spectra

The electronic spectral data are given Table 4 .The nature of the ligand field around the metal ions has been derived from uv-visible spectra. The uv-visible spectra of ligand(L) shows the peak around at 274nm which are assigned to π-π* transition of the C-N chromophere respectively [7,8].

The uv absorption spectra of the Zr(IV) and Th(IV) complexes exhibited a absorption band at 279nm, 273nm, 264nm, 278nm, 271nm and 264nm respectively due to the charge transfer band transition.Earlier researches indicated that Zr(IV) and Th(IV) has the coordination number of 4, 6, 7 and 8. The coordination number of Th(IV) is also 6, 8 and 10. The Zr(IV) and Th(IV) formed 1:2 complexes. Hence the complexes of Zr(IV) and Th(IV) are believed to have the coordination number of 8 . The $–NO_3$ group is present in the coordination sphere conductance data showed that the complexes are non-electolytes.

3.5 ^{1}HNMR Spectra

The ^{1}HNMR spectrum of schiff base ligand (L) (Fig 8) exhibit a multiplet signal at (δ=7.031ppm - 7.021ppm) is due to substituted aromatic ring protons [22]. The multiplet at (δ=6.63ppm-6.608ppm) and (δ=5.70ppm- 5.425ppm) were due to olefinic protons of the side chain and $–O-CH_2$ group of the ligand respectively [9]

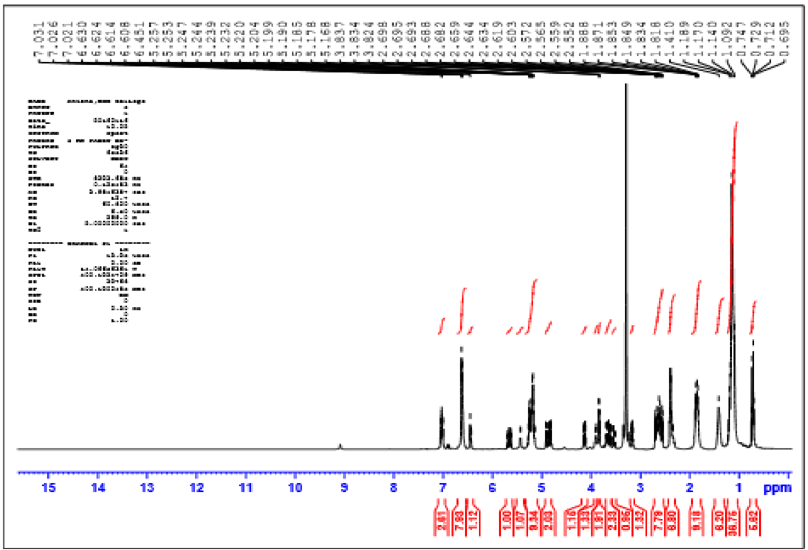


Fig 5 : The ^{1}HNMR spectrum of schiff base Ligand(L)

The ^{1}HNMR spectrum of the Th(IV) complex fig(9) gave the signal for aromatic protons (δ=7.146 - 7.176 ppm), olefinic protons of the side chain (δ=6.723-6.742 ppm), $O-CH_2$ protons (δ=3.629-3.947 ppm) and H-C=N proton (δ=8.3ppm) of the complex. The ^{1}HNMR study also conformed both functional groups and other structural information both ligand and complexes

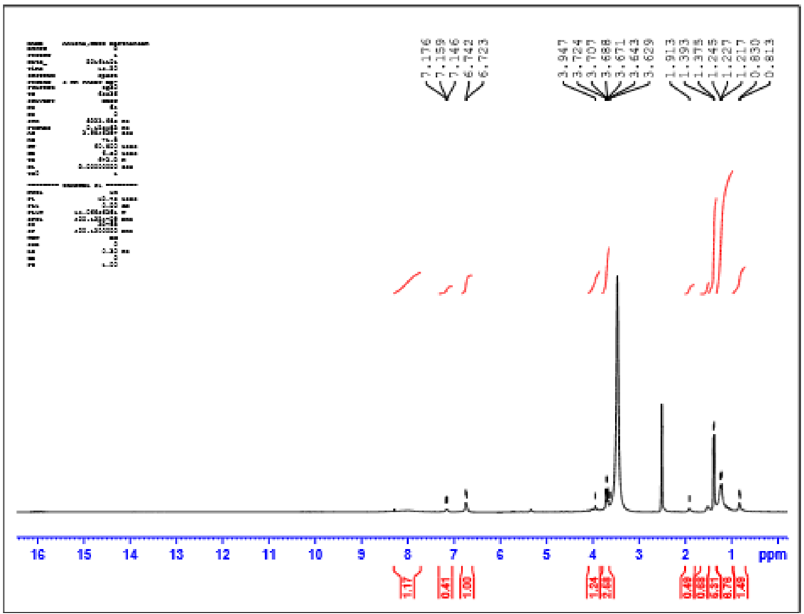


Fig 6: ^{1}HNMR spectrum of Th(IV) complex of Ligand (L)

Based on the observations in elemental analysis, IR spectra, uv-visible spectra and ^{1}HNMR spectral studies, the proposed structure of metal Schiff base Ligand and complexes[$M(L)(NO_3)_2(H_2O)_2$] are given in(Fig 7)

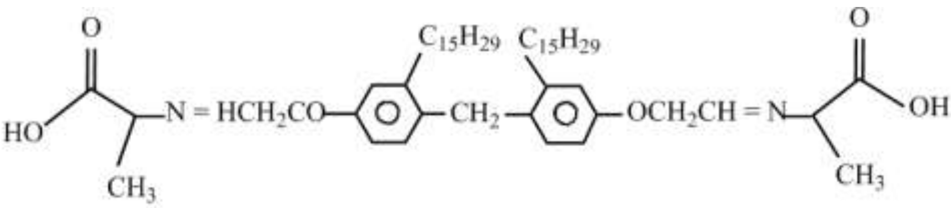


Fig 7 : Structure of Schiff base Ligand(L)

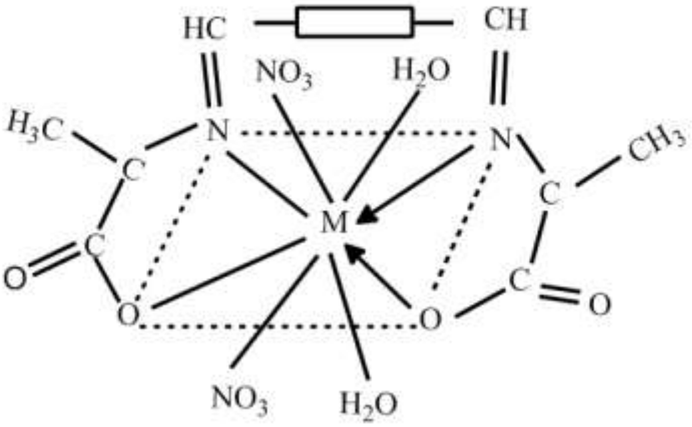


Fig 8 : General structure of Schiff base complexes of Zr(IV) and Th(IV)
M = Zr(IV) and Th(IV)

3.6 XRD Analysis

The powder XRD for the (Zr(IV) and Th(IV) complexes were performed . The diffractogram for the complexes are given in (Fig 9).The grain size of the complexes was calculate using scherre's formula . The strong broad peaks confirm the complexes formation and appearance of large feebile peaks indictes the complex to be microcrystalline. The calculated grain size 5.37nm this values suggested the crystals of the (Zr(IV) and Th(IV) compexes is nano size [10,12]

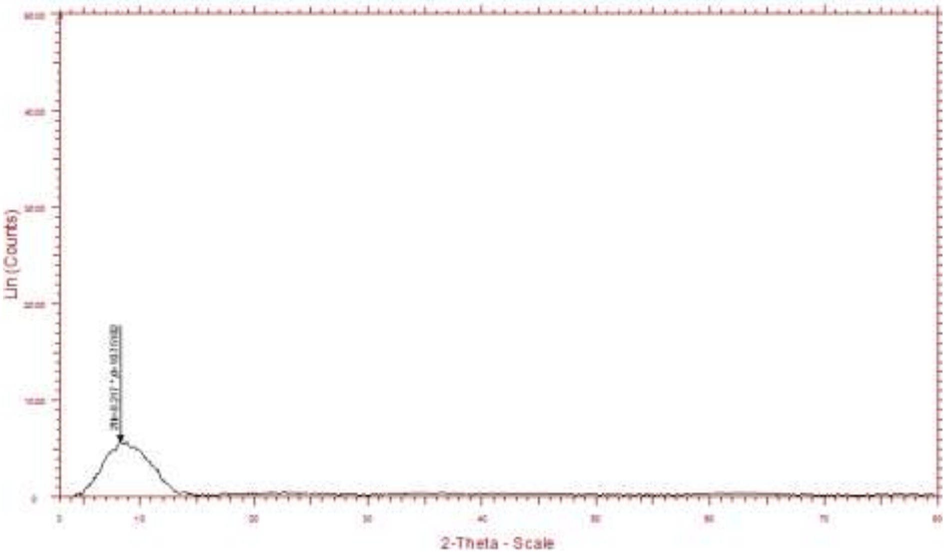


Fig 9: XRD spectrum of Th(IV) complex of (L)

3.7 SEM Analysis

The surface morphology of the complexes was studied using JSM 5610 scanning electron microscope. The SEM images of and Zr(IV) and Th(IV) complex is given fig (10,11). The SEM image showed that the complexes is nanocrystalline in nature.Careful examination of the single crystal clearly indicated the nano scale size of the single crystal of the complexes. The SEM images showed that all the complexes are nanocrystalline in nature showed rough, granular and pitted surface [13]

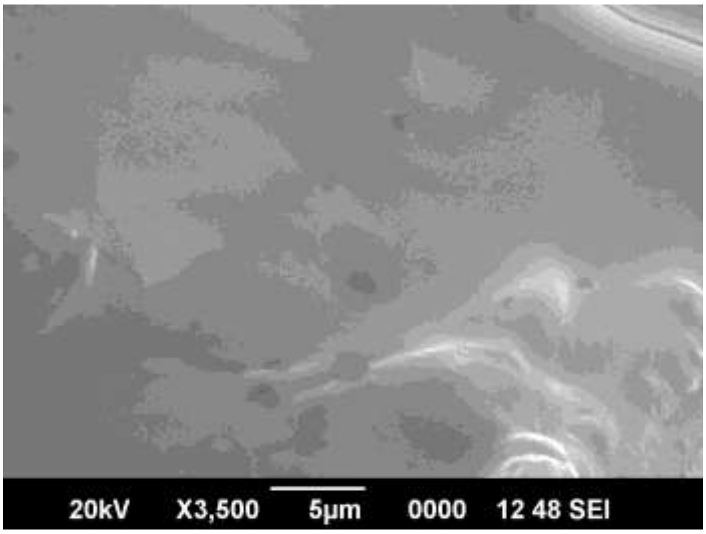


Fig 10: (a) SEM image of Th(IV) complex of LIgand (L)

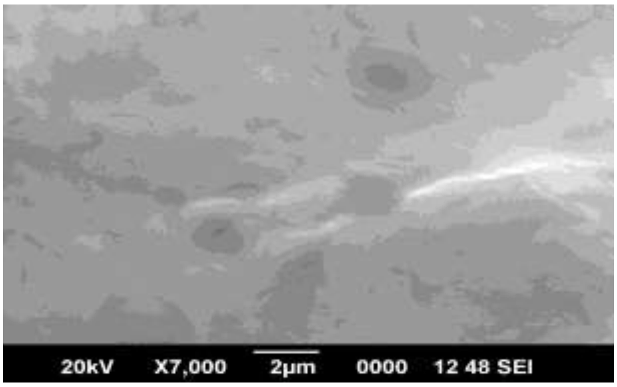


Fig 11: (b) SEM image of Th(IV) complex of Ligand (L)

IV. Biological Screening

4.1 Antbacterial activity.

The antibacterial activity of the ligand and complexes are presented in Table 4.The antibacterial activity were estimated based on the size of inhibition zone in the discs under identical conditions the Schiff base complexes of Zr(IV) and Th(IV) have moderate antibacterial activities against bacteria.The test drug solution of (100g) of each compound was prepared by dissolving 1mg of each compound separately in 1ml of DMSO. Staphylococus aureus,Streptococus mutans, E.Coli, Klebsilla pneumonia. The antibacterial activity was estimated based on the size of inhibition zone in the discs[14].

The results of antibacterial activity substanticate the findings of earlier researchers. That biologically inactive compounds become active and less biologically active compounds become more active upon coordination. Such enhancement in biological activity of metal complexes can be explained on the basis of overtones concept and chelation theory according to overtones concept of cell permeability, the lipid membrane that surrounds the cell favours the passage as only lipid soluble materials due to which liposolubilty is an important factor that controls antimicrobial activity. On chelation, the polarity of the metal ion is reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further it increases the delocalization of π – electron over the whole chelated ring end enhanced lipophilicity of the complex. This enhanced the lipophilicity in turn enhances the penetration of the complexes in to lipid membranes and blocking of metal binding sites on the enzymes of the microorganisms.

The results were also expressed by means of activity index.

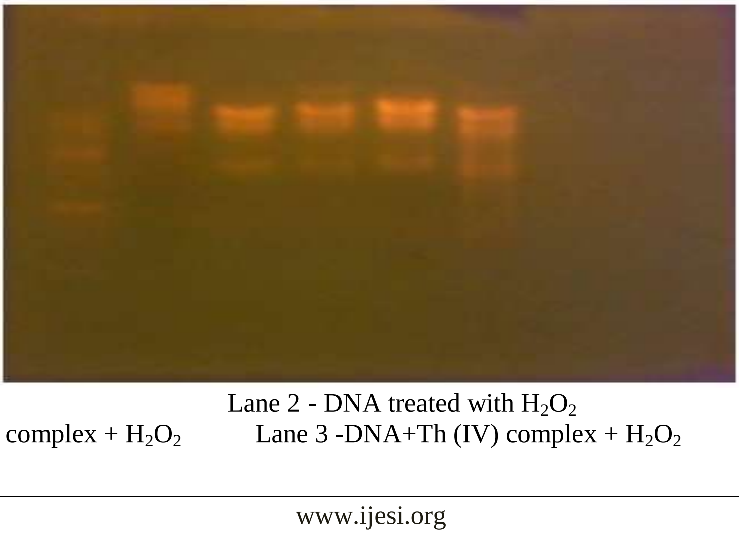
$$\text{Activity index (AI)} = \frac{\text{Inhibition zone of the sample}}{\text{Inhibition zone of the standard}}$$

Table: IV Antimicrobial activity data of ligand and its complexes

Ligand/ complexes	Media	Antibacterial activity			
		Staphylococ us aureus	Streptococus mutans	E-Coli	KIlebsilla Pneumonia
Ligand(L) $C_{47}H_{84}N_2O_2$	Muller Hinton Agar Bacteria	7	7	7	7
$[Zr(L)(NO_3)_2 2H_2O]$		13	10	9	7
$[Th(L)(NO_3)_2 2H_2O]$		10	9	8	13
PC		22	17	14	21

4.2 DNA Cleavage studies

The DNA cleavage activities of Schiff base ligand and its metal complexes at a 1µM concentration were studied using pUC18 DNA (2µg) in H_2O_2 (10µL) in 30 mm Tris Buffer (pH 7.4) and upon radiation with uv light. The reaction is modulated by metallo complexes bound hydroxyl radical or a peroxo species generated from the co-reactant H_2O_2. It is evident from Fig 10, that the Ni(II) complex cleave DNA more efficiently in the presence of an oxidant than the ligand and Ni(II) complex. This may be hydroxyl free radicals,which can be produced by metal ions reacting with H_2O_2 to produce the diffusible hydroxyl radical or molecular oxygen, which may damage DNA through Fenton type chemistry. This hydroxyl radical participates in the oxidation of the deoxyribose moiety, followed by hydrolytic cleavage of sugar- phosphate back bone Further, the presence of a smear in the gel diagram indicated the presence of radical cleavage[15].



Lane 1-Control DNA Lane 2 - DNA treated with H_2O_2
Lane2-DNA+Zr (IV) complex + H_2O_2 Lane 3 -DNA+Th (IV) complex + H_2O_2

V. Conclusion

Schiff base metal complexes of Cu(II), Co(II), Ni(II), Zr(IV) and Th(IV) were synthesized from DFMPM using L-alanine were clearly described and characterized on the basis of analytical and spectral data. The XRD, SEM analysis indicate that the crystals of Schiff base metal complexes of nanocrystalline in nature. . Antibacterial study showed that the complexes of Cu(II), Co(II), Ni(II), Zr(IV) and Th(IV). The more active than the complex of Zr(IV) complexes. Antifungal activity showed that the complexes of Cu(II), Co(II), Ni(II), Zr(IV) and Th(IV). The more active than the complex of Co(II) when compared to other complexes and DNA Cleavage study.

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