

Anti-microbial, Anti-insecticidal and Anti-inflammatory screening of Zr(IV) and Th(IV) complexes derived from di- α -formyl methoxybis(3-pentadecenylphenyl) methane and L-tryptophan

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Abstract : Cardanol, a naturally occurring aliphatic side chain substituted phenol derived from cashew nut shell liquid (CNSL) was used for the preparation of bis(3-pentadecenylphenol)methane (BPPM). BPPM when treated with epichlorohydrin followed by the action of sodium periodate, di- α -formylmethoxy bis(3-pentadecenylphenyl)methane (DFMPM) was obtained. DFMPM was the starting material for the present study.

Index terms: Cardanol, Formaldehyde, Epichlorohydrin, L-Valine, Schiff base

I. INTRODUCTION

The study of coordination compounds has emerged as one of the major centres of attraction for chemists. Coordination chemistry covers a comprehensive range of fascinating and theoretical applications. They are essential in many life processes such as oxygen transfer and metal ion control. Moreover, the study of coordination compounds has enabled the chemists to make significant progress in the various properties of the compounds. Synthesis of ligand, synthesis of metal complexes and estimation of metal ion intake, elemental analysis, molar conductivity, UV-visible spectra, IR Spectra, ¹H NMR spectra, SEM, analysis, and antimicrobial activity, anti-insecticidal, anti-inflammatory and DNA cleavage were discussed and characterized.

1. Preparation 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. The precipitated yellow compound was filtered washed with water and dried over anhydrous calcium chloride [8]. The crude sample was recrystallised from 50% absolute alcohol yield = 62%. Melting point = 223°C.

2. Preparation of Schiff base metal complexes

The metal complexes were prepared by adding aqueous solution of Zirconium (IV) nitrate and Thorium (IV) nitrate, to the ligand in ethanol in 1:1 molar ratio and refluxed for about twelve hours at 80°C. The resulting product was collected by filtration, washed with ethanol, diethyl ether and hot water, and finally dried under vacuum at 90°C. Yield = 57-62%.

3. Estimation of metal ion intake

The filtrates obtained in the above method were collected and it is used for the estimation of Zr(IV) and Th(IV) intake for complexation using standard methods.

II. RESULT AND DISCUSSION

The analytical data of the complexes, together with their physical properties are mentioned in Table 6.1. The data suggested that the complexes are in ML₂ composition in which the metal complexes of Zr(IV) and Th(IV) 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, CDCl₃, and DMSO. Analytical data suggest that the ligand to metal ratio in all the complexes to be 2:1⁽⁵⁻⁶⁾. Conductivities of solutions of the complexes are non electrolytes because their conductivity value were in the range 14-19 ohm⁻¹cm² mol⁻¹. However the conductivity value is higher than expected for non electrolytes probably due to partial solvolysis of the complexes in DMF medium⁽⁸⁻¹⁰⁾.

1. Elemental Analysis

The analytical data suggest that 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, and their empirical formulae have been computed and are given in Table.1.

Table 1 Physical and Analytical data of ligand and Metal complexes

Complexes / Ligand	Yield	Colour	Molecular formula	Mol. weight	Melting point	Elemental Analysis		
						C	H	N
Ligand L	65	ash	C ₆₉ H ₁₀₄ N ₄ O ₆	1084	234	72.67 (76.38)	9.06 (9.59)	2.41 (3.189)
[ZrL ₂ (NO ₃) ₂] 2H ₂ O	55	Brown	C ₁₃₈ H ₂₁₂ N ₁₀ O ₁₆	2355.22	>250	68.64 (72.65)	8.97 (11.04)	1.73 (2.97)
[ThL ₂ (NO ₃) ₂] 2H ₂ O	60	Brown	C ₁₃₈ H ₂₁₂ N ₁₀ O ₁₆	2496	>250	64.83 (67.58)	8.17 (10.27)	1.58 (2.76)

2. Conductivity Measurements

The molar conductivity values are given in Table. 2. The conductivity was in the range 17-18 ohm⁻¹ cm² mol⁻¹. Complexes with conductance below 50 ohm⁻¹ cm² mol⁻¹ 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⁽¹¹⁾.

Table. 2 Molar Conductance data of the complexes

Compounds	Molar conductance Ohm ⁻¹ cm ² mol ⁻¹
[ZrL ₂ (NO ₃) ₂]2H ₂ O	18
[ThL ₂ (NO ₃) ₂]2H ₂ O	17

3. FT-IR Spectrum analysis

The presence of important functional groups in the compound can be identified using- FTIR Spectrometer. The Infrared spectrum of the ligand was compared with the spectra of Zr(IV) and Th(IV) complexes. The FT-IR spectral data are shown in table.3 and the spectrum are shown in fig.1-3.

The IR spectrum of the ligand shows broad band at 1654 cm⁻¹, which was assigned due to νC=N stretching of azomethine group. Band at 1637cm⁻¹ and 1651cm⁻¹for Zr(IV) and Th(IV) complexes suggesting the coordination of azomethine nitrogen to metal atom in complexation. This was due to the donation of electron density from nitrogen to metal. Complexes shows band at 3441-3415cm⁻¹ due to ν(-OH) group. Band at 2854cm⁻¹ due to ν (C-O) (phenolic) and 2886-2850cm⁻¹ in the spectra of complexes. The strong absorption band at 2924cm⁻¹ due to ν (C-H) for ligand and has shifted to 2918-2900 cm⁻¹ in the complexes. The ligand exhibit band at 1449 cm⁻¹ and 1654cm⁻¹ due to free-COOH and ν (C=N) group; metal complexes exhibit a broad and strong absorption band in the region 1384-1381cm⁻¹ and 1651-1637cm⁻¹ it confirms the presence of free-COOH and ν (>C=N) group. The bands between 694-501cm⁻¹ was assigned to stretching frequencies of ν (M -N) the band between 401-399cm⁻¹ have been assigned to the stretching frequencies ν (M- O) respectively ⁽¹²⁻¹⁶⁾.

Table 3 FT-IR frequencies and UV spectrum of the ligand and complexes

Ligand/ Complexes	ν _{O-H} cm ⁻¹	ν _{O-C} cm ⁻¹	ν _{C-H} cm ⁻¹	ν _{C=N} cm ⁻¹	ν _{C=O} cm ⁻¹	free - COOH cm ⁻¹	ν _{M-N} cm ⁻¹	ν _{M-O} cm ⁻¹	λ max(nm)
Ligand L	-	2854	2924	1654	1581	1449	-	-	-
[ZrL ₂ (NO ₃) ₂] 2H ₂ O	3441	2886	2918	1637	1490	1384	694	399	330,460,650
[ThL ₂ (NO ₃) ₂] 2H ₂ O	3415	2850	2900	1651	1509	1381	501	401	320,450,660

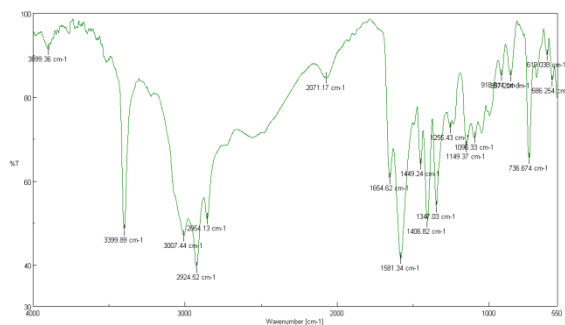


Fig. 1 FTIR Spectrum of ligand (L)

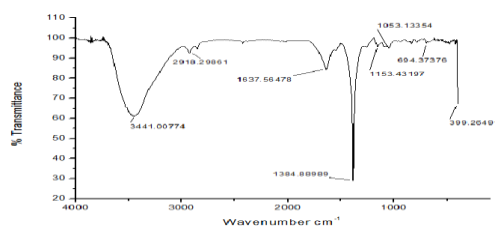


Fig.2 FTIR Spectrum of Zr(IV) complex

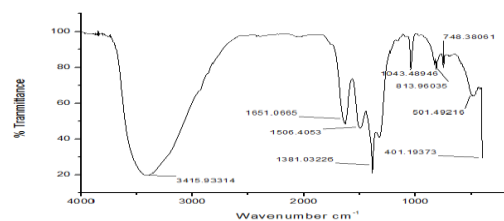


Fig. 3 FTIR Spectrum of Th(IV) complex

4. UV-VISIBLE Spectrum analysis

The transitions of uv-visible spectrum are connected with the electronic energy levels of the compound under observation. The transition metal ions occur in a multiplicity of anatomical conditions and its electronic structures are extremely varied. The structures can be analyzed with UV-visible spectroscopy. The nature of metal ions and the geometry of complexes has been figure out from the electronic spectra. The Zr(IV) and Th(IV) complexes display band at 405nm, 570nm and 420nm, 450nm which mate assigned to ${}^2T_{2g} \rightarrow {}^4T_{2g}$ transition⁽¹⁶⁾. The nitrate group is present inside the coordination sphere, the conductance data sight the complexes are non-electrolytes.

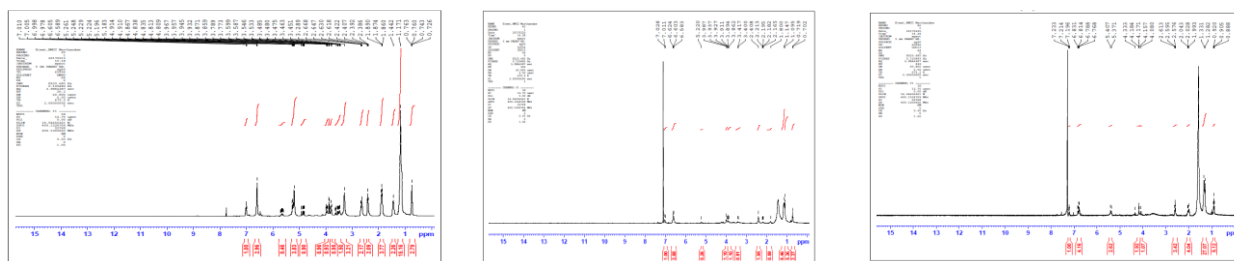
5. ${}^1\text{H}$ NMR Spectrum analysis

NMR spectroscopy is need of subsidizing the nature and structure of Schiff base and their complexes. The NMR spectra of Schiff base were recorded in DMSO solution, using tetramethylsilane (TMS) as internal standard. The NMR spectra specify the chemical shifts of the protons in Schiff base and their metal complexes.

From Fig.4, the ligand shows a single signal at 7.80ppm due to the presence of H – C = N- group .A broad band at $\delta = 7.010\text{ppm} - \delta = 7.005\text{ppm}$, due to – O-CH₂ -group. The doublet at $\delta = 6.998\text{ ppm} - \delta = 6.589\text{ ppm}$ and $\delta = 5.261\text{ ppm} - \delta = 5.183\text{ ppm}$ were due to the olifinic protons of the side chain and – O-CH₂ -group of the ligand. Multiplet at $\delta = 2.647\text{ ppm} - \delta = 2.386\text{ ppm}$ is due to substituted H-C-C=O- group and band at $\delta = 1.890\text{ppm} - \delta = 1.171\text{ppm}$ due to substituted -CH₂-NH group⁽¹⁶⁾.

Fig.5, reveals the ${}^1\text{H}$ NMR spectrum of Zr(IV) complex, a single band at $\delta = 7.10\text{ppm}$ exhibit the presence of H – C = N- group . Doublet at $\delta = 7.028\text{ppm} - \delta = 7.011\text{ppm}$, due to – O-CH₂ -group. Singlet at $\delta = 5.220\text{ ppm}$ due to – O-CH₂ -group. Multiplet at $\delta = 2.613\text{ ppm} - \delta = 2.028\text{ ppm}$ due to substituted H-C-C=O- group and band at $\delta = 1.993\text{ppm} - \delta = 1.095\text{ppm}$ due to substituted -CH₂-NH group.

Fig.6, point out the ${}^1\text{H}$ NMR spectrum of Th(IV) complex, a single band at 7.500ppm due to the presence of H – C = N- group .A broad band at $\delta = 7.233\text{ppm} - \delta = 7.196\text{ppm}$, due to – O-CH₂ -group. The doublet at $\delta = 6.831 - \text{ppm} - \delta = 6.768\text{ppm}$ and $\delta = 5.407\text{ppm} - \delta = 5.317\text{ppm}$ were due to the olifinic protons of the side chain and – O-CH₂ -group of the ligand. Multiplet at $\delta = 2.613\text{ppm} - \delta = 2.023\text{ ppm}$ is due to substituted H-C-C=O- group and band at $\delta = 1.993\text{ppm} - \delta = 1.282\text{ppm}$ due to substituted -CH₂-NH group

Fig.4,5,6 ${}^1\text{H}$ NMR spectrum of ligand, Zr(IV) complex & Th(IV) complex

Based on the observations in elemental analysis, FT-IR, electronic and ^1H NMR spectral studies, the proposed structure of Ligand (L) and metal Schiff base complexes were given in Fig.7-8

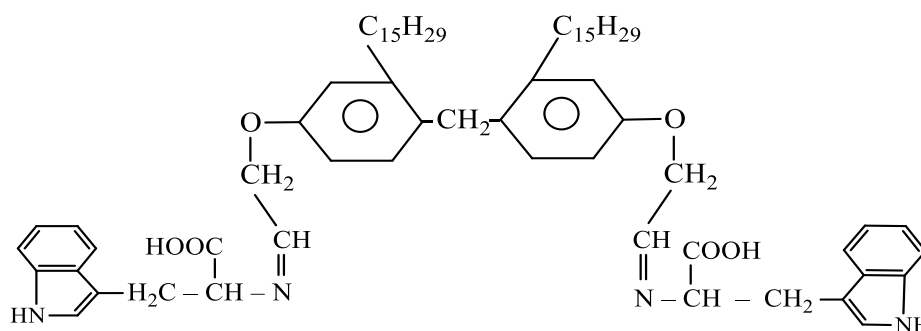


Fig.7 Structure of ligand

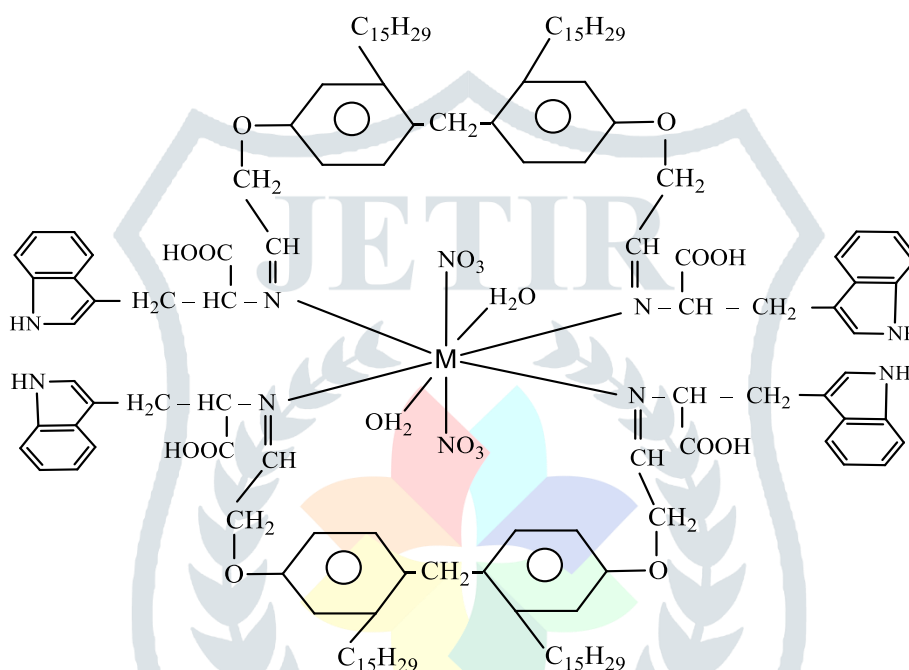
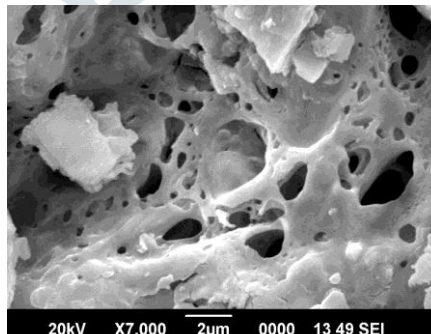
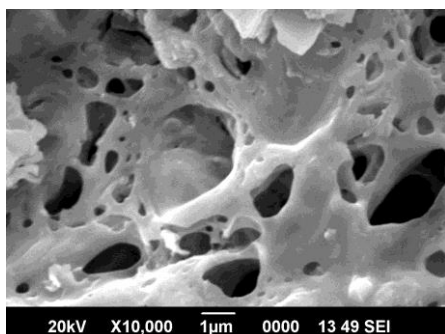


Fig.8 Structure of Schiff base complexes, M=Zr(IV) and Th(IV)

6. SEM ANALYSIS

The surface morphology of the complexes has been examined using scanning electron microscope. As shown in fig .9 microsphere template has coarse surface and core shell structure. The SEM Th(IV) complex showed that they are nano crystalline in nature. Careful examination of single crystal, clearly indicate the nano scale size of the single crystal of the complexes⁽¹⁷⁾. The SEM observation promotes a better understanding of the role of organic additives in crystal growth.



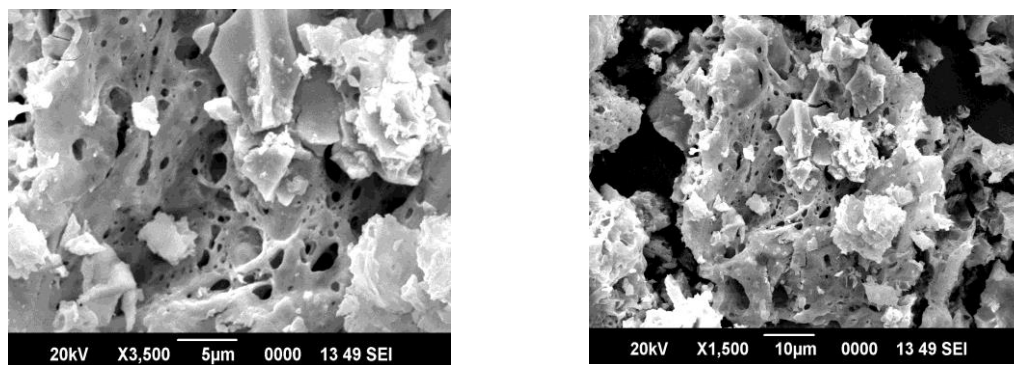


Fig.9 SEM images of Th(IV) complex at 1µm, 2µm, 5µm 10µm,

III. ANTI-MICROBIAL STUDIES

1. 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 *fluconazole*. The stock solution (T1=4mg and T2=8mg) of the test solution was prepared in DMSO solution. The results of antibacterial activity substantiate the findings of earlier researchers that biologically active 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 Overtone's concept and chelation theory⁽¹⁸⁻¹⁹⁾. The antimicrobial activity significantly increased on coordination. From table 5. Zr(IV) complex showed significantly antibacterial activity.

Table.5 Antibacterial activity of complexes

	Positive	[ZrL ₂ (NO ₃) ₂] H ₂ O	[ThL ₂ (NO ₃) ₂] H ₂ O
E.coli	Negative	33	32
	T ₁	-	-
	T ₂	13	-
	Positive	15	-
S.typhi	Negative	32	30
	T ₁	-	-
	T ₂	11	-
	Positive	16	-
S.aureus	Negative	15	35
	T ₁	-	-
	T ₂	11	9
	Positive	13	11

Gram + ve *streptomycin* and gram –ve *fluconazole* and stock solution (T1 = 4mg and T2 = 8mg)

2. Antifungal Activity

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 to overlap 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. From fig Th(IV) complex show more activity towards *Aspergillus niger*.

Table. 6 Anti-fungal data of complexes

FUNGAI	[ZrL ₂ (NO ₃) ₂]]2H ₂ O mm	[ThL ₂ (NO ₃) ₂]]2H ₂ O mm
<i>Aspergillus niger</i>	9	11
<i>Aspergillus flavus</i>	9	7

3. Anti-inflammatory activity

The anti-inflammatory activity of Zr(IV) and Th(IV) were performed to evaluate the effect of the invivo and invitro stabilization. Bovine serum albumin and dichlorofenac sodium solution was used as the standard and distilled water as control. From table.7 shows the percentage inhibition increases with increase in concentration ⁽²⁰⁾. In the case of Invivo when concentration increases, there is a gradual increase in percentage inhibition for complexes Zr(IV). Here Zr(IV) complex exhibit statically significant activity in invitro and invivivo percentage inhibition.

Table 7 Anti inflammatory activity data of complexes

Sample code	Concentration	Invivo Percentage Inhibition	Invitro Percentage Inhibition
Zr(IV)	25	61.13	13.89
	50	63.172	31.31
	100	73.504	57.07
Th(IV)	25	62.40	26.02
	50	66.89	38.41
	100	68.96	40.03

4. Insecticidal activity

The eggs of *Corcyra cephalonica* were collected from the Department of Entomology, Tamil Nadu Agricultural University, Coimbatore, India. These eggs were inoculated in clean and sterile plastic tubs (35 x 10 cm; 5 L capacity), which contains 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. Different concentrations (62.5, 125, 250, 500 and 1000 ppm) of T1, T2, T3, T4 and T5 were mixed with 10 g of feed in separate containers (500 mL capacity). Third instar larvae (4 Nos. per container) were introduced and maintained in the laboratory at RT. Controls consisted of the same conditions except for absence of T1, T2, T3, T4 and T5 and observed for its effect on the larval stages. Table.9, and fig. 10-11, shows Insecticidal activity of complexes ⁽²¹⁾. From the statistical analysis, it can be inferred that the Th(IV), Zr(IV) and Co(II) shows significant insecticidal activity.

Table.9 Insecticidal activity of Zr(IV) Complex

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean	
					Lower Bound	Upper Bound
Dead	1	.3333	.57735	.33333	-1.1009	1.7676
	2	.0000	.00000	.00000	.0000	.0000
	3	2.3333	.57735	.33333	.8991	3.7676
	4	4.0000	.00000	.00000	4.0000	4.0000
	5	4.0000	.00000	.00000	4.0000	4.0000
	Total	15	2.1333	1.80739	.46667	1.1324
Live	1	3.6667	.57735	.33333	2.2324	5.1009
	2	4.0000	.00000	.00000	4.0000	4.0000
	3	1.6667	.57735	.33333	.2324	3.1009
	4	.0000	.00000	.00000	.0000	.0000
	5	.0000	.00000	.00000	.0000	.0000
	Total	15	1.8667	1.80739	.46667	.8658

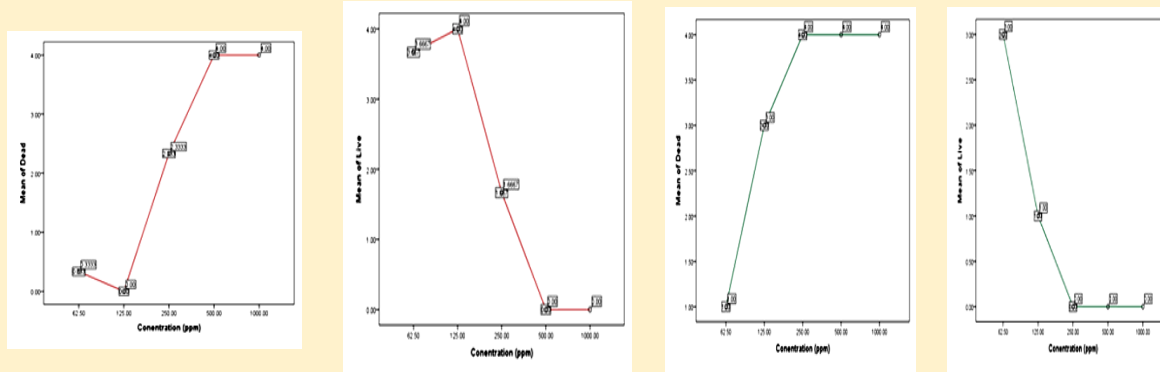


Fig.10 Graphical representation of insecticidal activity of Zr(IV) & Th(IV) complex

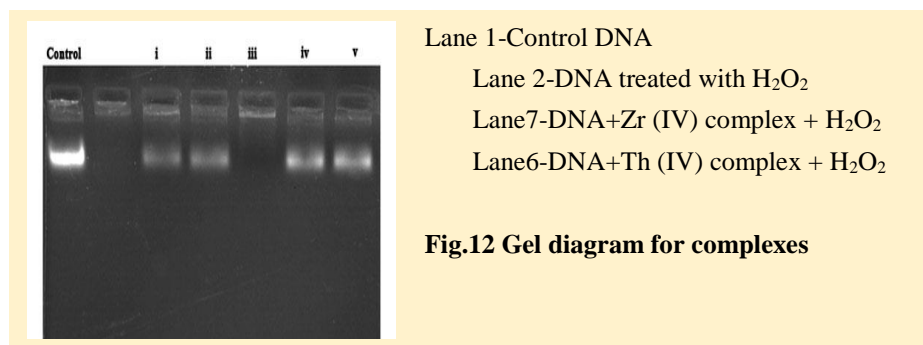
Table.10 Insecticidal activity of Th(IV) Complex

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean	
					Lower Bound	Upper Bound
Dead	1	3.0000	.00000	.00000	3.0000	3.0000
	2	1.0000	1.73205	1.00000	-1.3027	7.3027
	3	4.0000	.00000	.00000	4.0000	4.0000
	4	4.0000	.00000	.00000	4.0000	4.0000
	5	4.0000	.00000	.00000	4.0000	4.0000
Total	15	3.2000	1.37321	.35456	2.4395	3.9605
Live	1	3.0000	.00000	.00000	3.0000	3.0000
	2	1.0000	1.73205	1.00000	-3.3027	5.3027
	3	.0000	.00000	.00000	.0000	.0000
	4	.0000	.00000	.00000	.0000	.0000
	5	.0000	.00000	.00000	.0000	.0000
Total	15	.8000	1.37321	.35456	.0395	1.5605

6. Nuclease activity

The DNA binding is crucial for understanding biochemical processes as replication, repair, recombination and expression of genes. The possible binding mechanisms of ligands to double stranded DNA can be divided into specific binding and binding modes that lack sequence specificity. Specific binding between ligand and receptor often termed as molecular recognition is the basis for the interaction of many transcription factors with DNA. Small agents that bind with lower sequence specificity to DNA are often capable of influencing or inhibiting these processes and intrinsically exhibit magnetic properties. Consequently these molecules find applications as pharmaceuticals mainly in the treatment of cancer. Others are employed as staining agents⁽²²⁾.

In the present study, DNA cleavage experiment was conducted using plasmid DNA by gel electrophoresis in the presence of H₂O₂ as an oxidant photo induced DNA cleavage experiment have been carried out in UV light. The results of the experiments are in fig.12, DNA alone is inactive and these results indicate the importance of metal in the complex for observing the chemical nuclease activity. Higher DNA cleaving efficiency indicating the presence of free radicals cleavage. Zr(IV) and Th(IV) shows cleavage. Meta complexes were able to convert super coiled into open circular DNA.



7. Anticancer activity

Determination of In vitro Antiproliferative effect of Zr(IV) extracts on cultured hela cells and it is done in 6, 12 and 24 (μ l) concentrations. When concentration increases the number of dead cells increases and the complex is potential due to less number of live cells, it's shown in fig.6.13 and listed in table.11 From this it is cleared that when concentration increases the viability decreases that means the cytotoxicity of the cells decreases there by the cells are not cytotoxic⁽²³⁾.

Table.11 Anticancer activity data of complex

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

Control = 0.5149

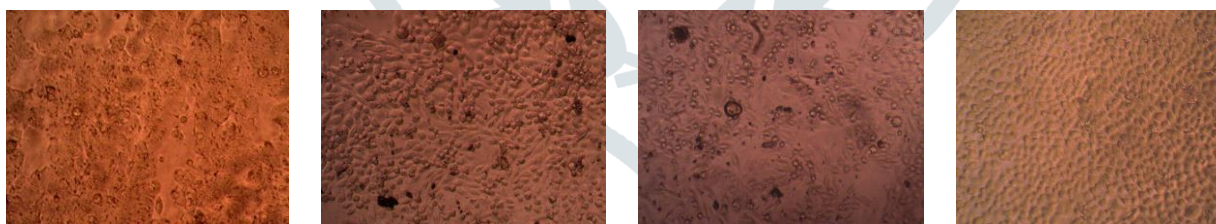


Fig.13 MTT assay of complex Zr(IV) Complex at control, 6 μ M , 12 μ M & 24 μ M

IV. CONCLUSION

In this contribution, starting from Schiff base metal complexes of CuZr(IV) and Th(IV) we have identified and explored a new class of complexes to investigate the influence of FTIR spectrum, UV-vis spectrum, SEM analysis, Elemental analysis, Molar conductance, Metal ion intake, ¹HNMR Spectral studies reveals that the metal binds the ligand through pyridine nitrogen, azomethine nitrogen and nitrate moiety of the metal salt used in the preparation of complex. The SEM study reveals that the complexes are nano crystalline. Zr(IV) complexes were showed significantly antibacterial activity. DNA cleavage was studied by gel electrophoresis and certain complexes showed enhanced nuclease activity. From invitro and invivo analysis the percentage inhibition of Zr(IV) complex increases with increase in concentration and exhibit statistically significant proteinase inhibitory activity. Zr(IV) shows anticancerus property.

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