



## Synthesis, Characterization and Biological evaluation of bidentate ligand with metal ions of Zr(IV) & Th(IV)

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### ABSTRACT

The Schiff base complexes of Zr(IV) and Th(IV) with bidentate ligand of di- $\alpha$ -formylmethoxybis(3-pentadecenylphenyl) methane (DFMPM) and n-propylamine were synthesized and characterized by elemental analysis, conductivity measurements, electronic, IR, <sup>1</sup>HNMR spectral measurements, Powder XRD and SEM. The conductance measurements indicate that all the complexes are non electrolytes. Infrared spectra indicate the coordination of imino nitrogen, M-N and M-O bonds. The electronic <sup>1</sup>HNMR spectral results indicate that both Zr(IV) and Th(IV) ions are octacoordinated. The Zr(IV) and Th(IV) complexes have better antimicrobial activity, DNA cleavage ability and anticancer activity.

**Key words:** DFMPM, n- propylamine, antimicrobial activity, anticancer activity, DNA cleavage.

### INTRODUCTION

The metal-based anticancer complexes have attracted many bioinorganic chemist's interest since the success of platinum complexes as anticancer agents[1-3]. Various metal complexes have been intensively investigated due to their more physiological activities and lower toxicities after coordination with ligand. People have paid great interest to synthesis, DNA cleavage and anticancer activity of Schiff base metal complexes in recent years [4-7]. In this work, we synthesized and characterized a novel Zr(IV) and Th(IV) complex with Schiff base ligand derived from DFMPM and n-propyl amine and focused our attention on comparative studies of DNA cleavage and invitro anti cancer activities of Schiff base ligand L and its Zr (IV) and Th (IV) complexes.

### EXPERIMENTAL SECTION

Cardanol was obtained from M/S Satya Cashew, Chennai, India. Formaldehyde (37% solution) hydrochloric acid, epichlorohydrin, n-propylamine, sodium hydroxide and other chemicals used were of AR grade quality obtained from Merk Chemicals. All the solvent used was purified by standard methods[8, 9]. The micro analytical data (C, H, N) were collected using Perkin Elmer 2400 instrument. The metal ion intake were estimated by standard methods[8]. IR spectra were obtained using PE IR spectrum instrument model: system 2000. <sup>1</sup>HNMR spectra were obtained using AMX-300 MHz, FT NMR Spectrometer. Conductance measurements were obtained using systronics-305 conductivity metre. 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. HT-29(colon cancer) cell line was initially procured from National Centre for cell sciences, Pune

### 2.1 Synthesis

Synthesis of bis(3-pentadecenyl)phenylmethane (BPPM), diglycidylether of bis(3-pentadecenylphenyl) methane (DEBPPM), di- $\alpha$ formylmethoxybis(3-pentadecenyl) methane (DFMPM) were prepared as per the earlier methods[13]

### 2.2 Synthesis of Schiff base ligands with DFMPM and n-propyl amine :

The synthesis of Schiff base ligand was carried out by reported methods[13]. Ethanolic solution of DFMPM and n-propylamine were taken in RB flask in 1:2 molar ratios and refluxed for an hour. The reaction mixture was poured in ice, an yellow compound of Schiff base ligands was obtained[13]. The precipitated yellow compound was filtered, washed with water and dried over anhydrous calcium chloride. The crude sample was recrystallised from 50% absolute alcohol. Yield = 60% Melting point = 228°C.

### 2.3 Preparation of Schiff base metal complexes.

The metal complexes were prepared by adding aqueous solution of Cu(II) nitrate, Ni(II) nitrate, Co (II) nitrate to the ligand in ethanol in 1:2 molar ratio and refluxed for about twelve hours at 80°C[10]. The precipitated solids were filtered, washed with ethanol, diethyl ether and hot water and finally dried under vacuum at 90°C. Yield = 57 – 61%.

## RESULTS AND DISCUSSION

All the metal complexes 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,  $\text{CDCl}_3$  and DMSO.

### 3.1 Elemental Analysis

The analytical data suggest that all the complexes are mono nuclear with the ligands coordinated to the central metal atom. The metal to ligand ratio in all complexes was 1 : 2 and their formulae have been computed and given in table 1. Molar conductivities of solution of the complexes in DMF are shown in Table 1. All the complexes are non - electrolytes because their conductivity values were low. However, the conductivity value is higher than expected for non- electrolytes probably due to partial solvolysis of complexes in DMF medium.

Table 1 : Physical characteristics and analytical data of the complexes

Compound	Yield %	Colour	Mol. formula	Mol.wt	Melting point °C	Elemental Analysis			Molar conductance $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
						C	H	N	
Ligand L $\text{C}_{53}\text{H}_{86}\text{N}_2\text{O}_2$	60	Brown	$\text{C}_{53}\text{H}_{86}\text{N}_2\text{O}_2$	782	220	81.76 (81.33)	10.57 (10.9)	3.25 (3.58)	-
$[\text{ZrL}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$	57	Brown	$\text{C}_{106}\text{H}_{176}\text{N}_6\text{O}_8\text{Zr}$	1907.22	>250°C	66.18 (66.18)	9.51 (9.22)	4.90 (4.4)	13
$[\text{ThL}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$	61	Brown	$\text{C}_{106}\text{H}_{176}\text{N}_8\text{O}_8\text{Th}$	1975.52	>250°C	64.23 (64.4)	8.91 (8.91)	3.44 (3.64)	15

### 3.2 IR Spectra

Selected IR spectral bands for the ligand and its complexes are given in table 2. The IR spectrum of the free ligand is characterized mainly by the strong bands at  $2856\text{cm}^{-1}$ ,  $2923\text{cm}^{-1}$  and  $1606\text{cm}^{-1}$  which are attributed to the stretching frequencies of O – C, C – H and C = N (azomethine) respectively[9] Fig. 1. Hence the probable structure of the ligand is given in fig 6. The IR spectrum of free ligands was compared with the spectra of metal complexes. The characterization absorption band at  $3051\text{cm}^{-1}$  and  $3700\text{cm}^{-1}$  were attributed to –OH group of the coordinated water[10]. The absorption bands in the range  $2760\text{cm}^{-1}$  and  $2740\text{cm}^{-1}$ ,  $2912\text{cm}^{-1}$  and  $2781\text{cm}^{-1}$ ,  $1562\text{cm}^{-1}$  and  $1519\text{cm}^{-1}$  were assigned to O – C, C – H and C = N respectively[11, 12]. The imine peak in the metal complex showed change in Shifts compared to the ligand indicating coordination of the imine nitrogen atom to the metal ion due to coordination. The absorption at  $759\text{cm}^{-1}$  and  $750\text{cm}^{-1}$  were due to the coordination of –  $\text{NO}_3$  group with central metal atom. (Fig 2 & 3).

Table 2 : Selected UV and FTIR frequencies ( $\text{cm}^{-1}$ ) of the ligand and complexes

Ligand/ Complex	$\nu_{\text{O-H}}(\text{H}_2\text{O})$	$\nu_{\text{O-C}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	$\lambda_{\text{max}}(\text{nm})$		
Ligand L $\text{C}_{53}\text{H}_{86}\text{N}_2\text{O}_2$	-	2856	2923	1606	-	-	-	272	354
$[\text{ZrL}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$	3051	2760	2912	1562	759	500	266	333	366
$[\text{ThL}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$	3700	2740	2781	1519	750	492	251	317	317

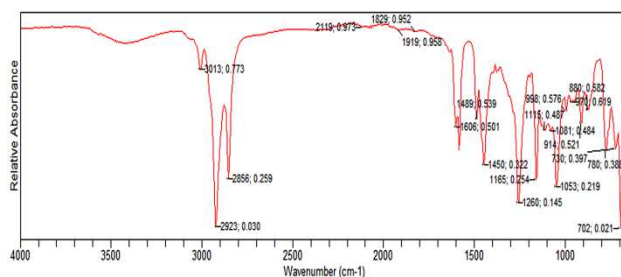


Figure 1 : FTIR Spectrum of Schiff base ligand

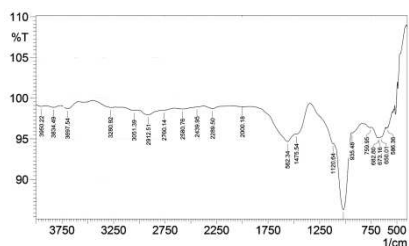


Figure 2 :FTIR Spectrum of Zr (IV) complex

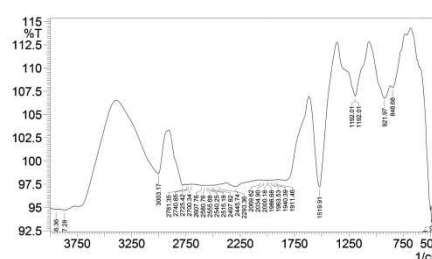
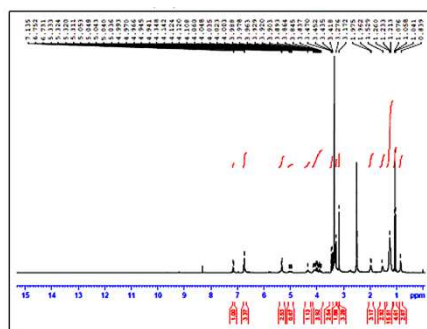
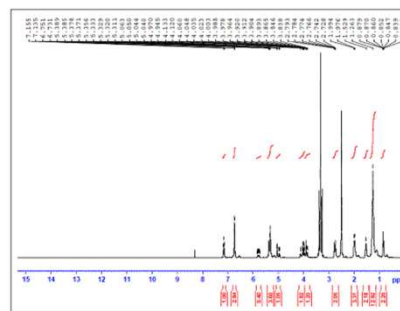


Figure 3: FTIR Spectrum of Th(IV) complex

### 3.3 $^1\text{H}$ NMR Spectra

On examining the  $^1\text{H}$ NMR spectrum of ligand fig. 4, it exhibited a multiplet signal at  $\delta = 7.135 \text{ ppm} - 7.174 \text{ ppm}$  is due to substituted aromatic ring protons. The presence of  $\text{H} - \text{C} = \text{N}$  group is indicated by the singlet at  $\delta = 8.3 \text{ ppm}$ . A signal at  $\delta = 1.263 \text{ ppm} - 1.529 \text{ ppm}$  indicate the presence of  $-\text{CH}_2-$  protons. The multiplet at  $\delta = 6.731 \text{ ppm} - 6.751 \text{ ppm}$  and  $\delta = 3.838 \text{ ppm} - 3.988 \text{ ppm}$  were due to the olefinic protons of the side chain and  $\text{O} - \text{CH}_2$  group of the ligand respectively.

Figure 4 :  $^1\text{H}$ NMR Spectrum of LigandFigure 5 :  $^1\text{H}$  NMR Spectrum of Th(IV) Complex

The  $^1\text{H}$ NMR of the Th (IV) complex fig.5 gave the signals for aromatic protons ( $\delta = 7.135 - 7.176 \text{ ppm}$ )  $\text{O} - \text{CH}_2$  protons ( $\delta = 3.837 - 3.988 \text{ ppm}$ ), Olefinic proton of the side chain ( $\delta = 6.71 - 6.752 \text{ ppm}$ ) and  $\text{H} - \text{C} = \text{N}$  proton ( $\delta = 8.34 \text{ ppm}$ ). There is a downfield shift of imine proton after complex formation than in the ligand. Thus  $^1\text{H}$  NMR study also confirmed the structural informations of both ligand and its complexes[13].

### 3.4 UV - visible spectra

The UV - visible spectra, are often very helpful in the evaluation of results furnished by other methods of structural investigation. The ligands showed a broad band at 272 nm which is assigned to  $\pi \rightarrow \pi^*$  transition of the  $\text{C} = \text{N}$  chromophore[16]. On complexation this band was shifted to the lower wavelength suggesting the coordination of imine nitrogen with central metal ion. The UV absorption spectra of the Zr(IV) and Th(IV) exhibit only one extra highly intensive band in the region on 366 nm & 317 nm which may be due to charge transfer band besides ligand bands. However UV- visible spectra could not provide structural details of these complexes[14 -17]. Zr(IV) has the coordination number of 4, 6, 7 and 8. Earlier researchers are indicated the coordination number of Th(IV) is also 6, 8 or 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  $-\text{NO}_3$  group is present in the coordination sphere because conductance data showed that the complexes are non - electrolytes and  $\text{NO}_3$

groups were coordinated with the central Zr(IV) or Th(IV) ion. On the basis of forgoing observation the probable structure of ligand and Zr(IV) and Th(IV) complexes may be presented as follows[18]. Fig 6 & 7 Earlier researcher also reported the octacoordination of Zr(IV) and Th(IV) Schiff base complexes[19 - 21].

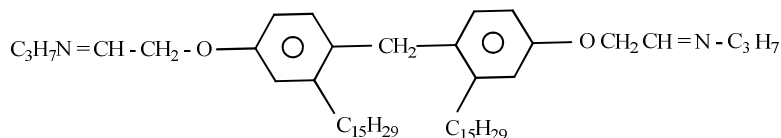


Figure 6 : Structure of Schiff base

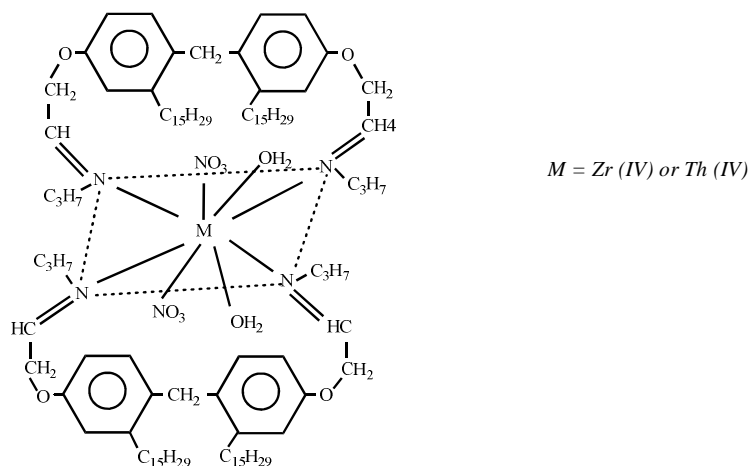


Figure 7 : Structure of Schiff base complexes

### 3.5 SEM Analysis

Surface morphology of the Th(IV) complex in this study is shown in fig. 8. From the fig 8 pitted and rough surface is observed in the complex. The particle size of the Th(IV) complex was in the diameter range of few microns. Careful examination of the single crystal, clearly indicated the nano scale size of the single crystal of the complex[27].

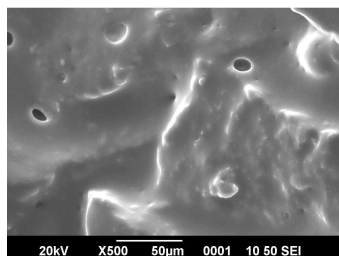


Figure 8 SEM image of Schiff base complex of Th(IV)

### 3.6 Powder XRD

Powder XRD patterns of Th(IV) complex recorded in the range ( $2\theta = 0 - 180^\circ$ ) was shown in Fig 9. XRD patterns of the metal complexes show the sharp crystalline peaks indicating their crystallite phase. The average crystalline size ( $d_{XRD}$ ) of the complexes was calculated using Scherrer's formula[22]. The Th(IV) complex has an average crystallite size of 12.94nm.

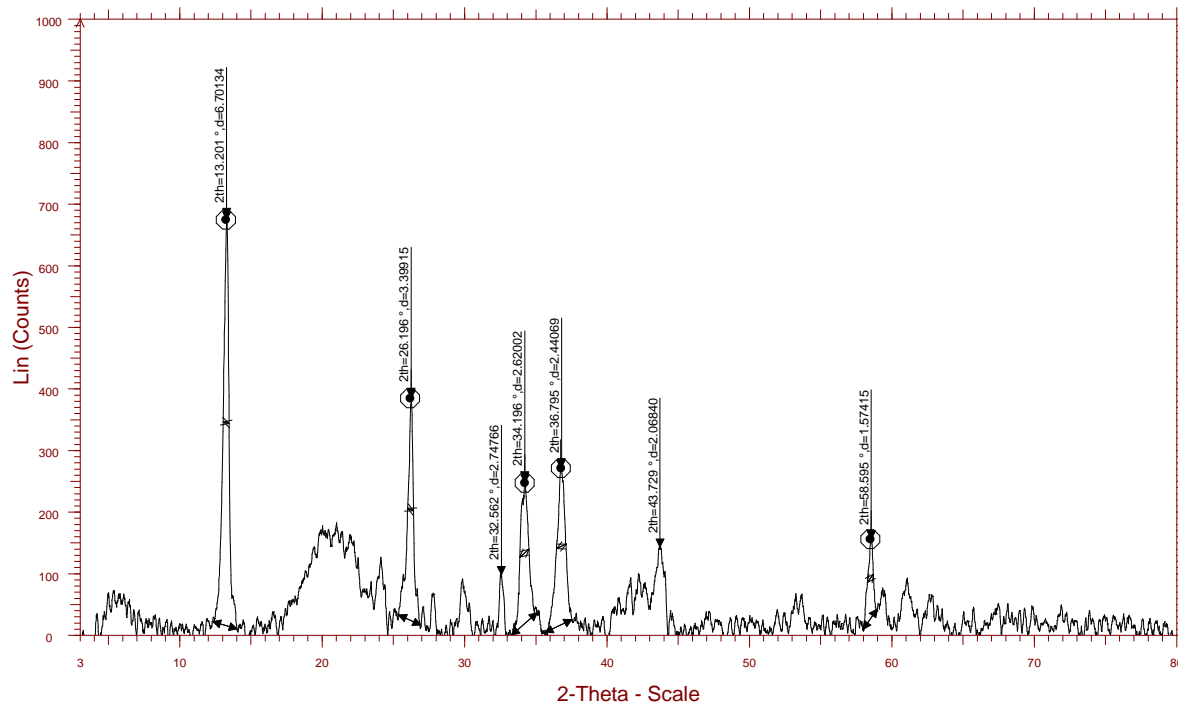


Figure 9: XRD Spectrum of Th (IV) Complex

### 3.7 Antimicrobial Activity

In the present investigation, biological activity of the ligands and their complexes with Zr(IV) and Th (IV), have been screened for antimicrobial activity against bacteria (*Klebsiella* sps, *E.coli*, *P.aeruginosa* and *S. aureus*) and fungi (*Candida* sps and *Aspergillus* sps) by disc diffusion method. The concentration for these samples was maintained as 1mg/mL in DMSO. The results thus obtained were explained on the basis of Overton's concept and Chelation theory[23, 24]. The mode of action of the compounds may involve formation of a hydrogen bond through the azomethine group with the active centers of cell constituents, resulting in a interference with the normal cell process[25].

The variation in the activity of different complexes against different organisms depends either on impermeability of the cells of the microbes or difference in ribosome of microbial cell. A composition of the biological activity of the synthesized compounds with some known antibiotics (Chloramphenicol and Nystatin) is presented in Table.3 & 4. It is observed that the some of Schiff base metal complexes exhibit better activity than the corresponding ligand.

Table 3. Antimicrobial activity for Bacteria

S.No	Samples	Media	Zone of Inhibition (mm)			
			<i>Klebsiella</i>	<i>E.coli</i>	<i>aeruginosa</i>	<i>S.aureus</i>
1	Ligand	Muller Hinton Agar	6.0	6.0	6.0	6.0
2	[ZrL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]		6.0	6.0	12.0	6.0
3	[ThL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]		10.0	15.0	14.0	13.0
4	PC (Chloramphenicol)		25.0	26.0	24.0	25.0
5	NC		6.0	6.0	6.0	6.0

Table. 4 Antimicrobial Activity for fungi

S.No	Samples	Media	Zone of Inhibition (mm)	
			<i>Candida</i> sps	<i>Aspergillus</i> sps
1	Ligand	Muller Hinton Agar	6.0	6.0
2	[ZrL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]		6.0	6.0
3	[ThL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]		6.0	12.0
4	PC (Nystatin)		25.0	26.0
5	NC		6.0	6.0

### 3.8 DNA Cleavage Studies

The DNA cleavage activities of Schiff base ligand and its metal complexes at a 1  $\mu$ M concentration were studied using pUC18 DNA (2  $\mu$ g) in H<sub>2</sub>O<sub>2</sub> (10  $\mu$ L) in 30 mM Tris Buffer (pH-7.4) and upon irradiation with UV light. The reaction is modulated by metallo complexes bound hydroxyl radical or a peroxy species generated from the co-reactant H<sub>2</sub>O<sub>2</sub>.

In the control experiment using DNA alone (lane 1), no significant cleavage of DNA was observed even on longer exposure time. It is evident from Fig. 10, that the Zr(IV) and Th(IV) complex cleave DNA more efficiently in the presence of an oxidant than the ligand. This may be hydroxyl free radicals, which can be produced by metal ions reacting with H<sub>2</sub>O<sub>2</sub> 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 [26-28]. Further, the presence of a smear in the gel diagram indicated the presence of radical cleavage.

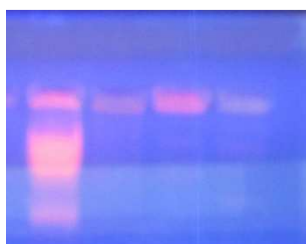


Figure 10 : Gel electrophoresis diagram of the Schiff base metal complexes

Lane 1: Control DNA ;  
Lane 2 : DNA + L + H<sub>2</sub>O<sub>2</sub>

Lane 3 : DNA + [Zr L<sub>2</sub> (NO<sub>3</sub>)<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] + H<sub>2</sub>O<sub>2</sub>  
Lane 4 : DNA + [Th L<sub>2</sub> (NO<sub>3</sub>)<sub>2</sub> (H<sub>2</sub>O)<sub>2</sub>] + H<sub>2</sub>O<sub>2</sub>

### 3.9 Anticancer Activity

The result of anticancer activities are presented in table 5 & 6. The colon carcinoma (HT-29) cells, were sensitive to the Zr (IV) complex with an IC<sub>50</sub> value of 23.82  $\mu$ M. The Th (IV) complex had the better activity with an IC<sub>50</sub> value of 11.5  $\mu$ M. The enhancement of cytotoxic activity may be assigned to that the positive charge of the metal increased the acidity of coordinated ligand that bears protons, leading to stronger hydrogen bonds which enhanced the biological activity [29-33]. It seems that changing the anion, coordination sites, and the nature of the metal ion has a pronounced effect on the biological behavior by altering the binding ability of DNA. Gaetke and Chow had reported that metal has been suggested to facilitate oxidative tissue injury through a free radical mediated pathway analogous to the Fenton reaction. (fig 11, a and Fig.12 : a & b)



Fig 11a) Zr(IV) complex at 25  $\mu$ M

Table : 5 Percentage viability of Zr(IV) complex

Sample volume ( $\mu$ l)	Average OD at 540nm	Percentage Viability
Control	2.2297	
6.25	1.7297	77.57546
12.5	1.0964	49.17253
25	0.8767	39.31919
50	0.6564	29.43894
100	0.2997	13.44127

IC<sub>50</sub> value = 23.82  $\mu$ g/ml

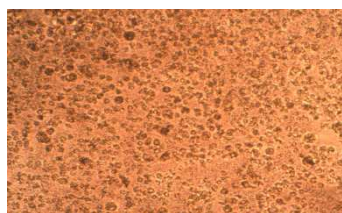
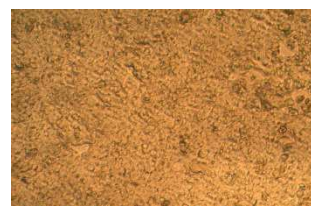
Fig. 12 a) Th (IV) complex at 6.25  $\mu\text{M}$ b) Th (IV) complex at 12.5  $\mu\text{M}$ 

Table: 6 Percentage viability of Th(IV) complex

Sample volume ( $\mu\text{l}$ )	Average OD at 540nm	Percentage Viability
Control	0.8039	
6.25	0.4564	56.77323
12.5	0.3982	49.53352
25	0.348	43.28897
50	0.2992	37.21856
100	0.2706	33.6609

IC<sub>50</sub> value=11.5  $\mu\text{M}$ 

### CONCLUSION

Schiff base complexes of Zr(IV) and Th(IV) were synthesized from DFMPM using n-propyl amine were clearly described and characterized on the basis of analytical and spectral data. The SEM & XRD analysis indicate that the crystals of Schiff base metal complexes are nano crystalline in nature. Anti microbial study showed that the complex of Th(IV) have higher anti microbial activity than Zr(IV). The DNA cleavage studies show that the Zr (IV) and Th (IV) complexes cleave DNA more efficiently. The in-vitro anti cancer studies reveal that the Th(IV) complex had better anticancer activity against HT-29(colon carcinoma) cell with IC<sub>50</sub> value of 11.5  $\mu\text{M}$

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