

## Synthesis, Characterization of Zirconium and Thorium Schiff Base Complex and its spectral and biological Nature

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**ABSTRACT** : A novel series of transition metal complexes of Zr(IV) and Th(IV) have been synthesized from the Schiff base derived from DFMPM and L-Valine.. These complexes have been characterized from their elemental analysis, melting point, molar conductance, UV-Vis, FT- IR, <sup>1</sup>H-NMR, SEM and XRD. The data show that the complexes have composition of the ML<sub>2</sub> type. The UV-Vis, FT-IR data of the complexes suggest a tetrahedral geometry around the central metal ion. The Schiff's base ligand and its complexes have been screened for antibacterial, antifungal anti cancerus, anti inflammatory and DNA cleavage. The conductance measurements indicate that all the complexes are non-electrolytes. The SEM, and XRD result indicate that the complexes are nano crystalline. The hexa co-ordinated complexes have moderate antibacterial, antifungal, anti cancerus, anti inflammatory and DNA cleavage. The metal ion intake can be used for the removal of these metals from water.

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### I. INTRODUCTION

Complexes of Schiff bases are of having great importance due to their attractive chemical and physical properties and wide range of application in numerous scientific areas. The design and synthesis of macrocyclic Schiff base complexes are currently attracting considerable attention since they can be used as supra molecular devices, sensors and contrast agents in magnetic resonance imaging<sup>[1-2]</sup>. Schiff bases are characterized by -CH=N- (imine) group which is important in elucidating the mechanism of transimination and racemisation reactions in biological systems<sup>[3]</sup>. DFMPM is prepared from cardanol using formaldehyde, epichlorohydrin and sodium periodate in three stages. DFMPM formed Schiff base ligand with l-valine. The results indicate that both Zr(IV) and Th(IV) complexes are octa coordinated having moderate antibacterial activity. The metal ion intake indicates the ligand can be used for the removal of these metals from water. XRD and SEM analysis indicates the complexes are nano crystalline in nature<sup>[4-5]</sup>.

### II. MATERIALS AND METHODS

Cardanol was obtained from M/S Sathya Cashew Chennai India, formaldehyde (37% solution), hydrochloric acid, epichlorohydrin, L-valine sodium hydroxide and other chemicals were used of GR/AR grade quality obtained from Merck chemicals. All the solvents used were purified by standard methods<sup>[6]</sup>. Elemental analyses (C,H,N) were performed by using Elementar Vario EL III and NMR by using Bruker Avance III 400MHz at STIC, CUSAT, Cochin. The IR spectra were recorded in KBr pellets using Shimadzu FTIR spectrometer (4000 – 400 cm<sup>-1</sup>). The UV-Vis electronic spectra (200 – 800 nm) were recorded using Lab India 3000+ double beam spectrophotometer. The micro analytical data were collected using Perkin Elmer 2400 instrument. The nano crystalline nature were performed by SEM and XRD by using JEOL Model JSM-6390LV and Bruker AXS D8 Advance at STIC, CUSAT, Cochin. The metal ion intake were estimated by standard methods<sup>[7]</sup>.

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

The Schiff base ligand was prepared by the reported methods<sup>[8-9]</sup>. Equimolar ethanolic solution of DFMPM and L-valine 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>[10]</sup>. 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=63%. Melting point =223<sup>o</sup>C.

#### Synthesis of Zr(IV) and Th(IV) 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 Zr(IV) and Th(IV) nitrates in 2:1 molar ratio. The resulting mixture was refluxed for about twelve hours at 70-80<sup>0</sup>c<sup>[11,12]</sup>. 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>0</sup>C. yield=59%

#### Estimation of metal ion intake

The filtrates obtained in the above method were collected. The collections were used for the estimation of Zr(IV) and Th(IV) intake for complexation using standard methods<sup>[7]</sup>.

### III. 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 are in ML<sub>2</sub> 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<sup>0</sup>C). The complexes are insoluble in water and common organic solvents but are soluble in DMF,CDCl<sub>3</sub>, DMSO. Analytical data suggest that the metal to ligand ratio in all the complexes to be 2:1<sup>[13]</sup> (Table 1). Conductivities of solutions of the complexes are non electrolytes because their conductivity value were in the range 13-21 ohm<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>. However the conductivity value is higher than expected for non electrolytes probably due to partial solvolysis of the complexes in DMF medium.

#### 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 characteristics and analytical data of complexes**

Complex / Ligand	Yield	Colour	Molecular formula	Mol. weight	Melting point	Elemental Analysis C	H	N
Ligand L	63	brown	C <sub>57</sub> H <sub>102</sub> N <sub>2</sub> O <sub>4</sub>	878	234	73.67 (77.90)	9.06 (11.61)	2.41 (3.189)
[ZrL(NO <sub>3</sub> ) <sub>2</sub> ] 2H <sub>2</sub> O	56	brown	C <sub>114</sub> H <sub>208</sub> N <sub>4</sub> O <sub>10</sub> Zr	1883	>250	68.64 (72.650)	8.97 (11.04)	1.73 (2.97)
[ThL(NO <sub>3</sub> ) <sub>2</sub> ] 2H <sub>2</sub> O	59	brown	C <sub>114</sub> H <sub>208</sub> N <sub>4</sub> O <sub>10</sub> Th	2024	>250	64.83 (67.58)	8.17 (10.27)	1.58 (2.76)

#### Conductivity Measurements

The molar conductivity values are given in Table.2 and fig.1. The conductivity were in the range 13-21 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. The low conductivity of complexes poses the nitrate moiety of the metal salt used in the preparation and in coordination. For non-electrolytes conductivity were slightly higher it may be due to partial solvolysis of the complexes in DMSO medium.

**Table 2. Molar Conductance data of the ligand and complexes**

Compounds	Molar conductance Ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>
Ligand L	19
[NiL(NO <sub>3</sub> ) <sub>2</sub> ] H <sub>2</sub> O	13
[ZrL(NO <sub>3</sub> ) <sub>2</sub> ]2H <sub>2</sub> O	21
[ThL(NO <sub>3</sub> ) <sub>2</sub> ]2H <sub>2</sub> O	18

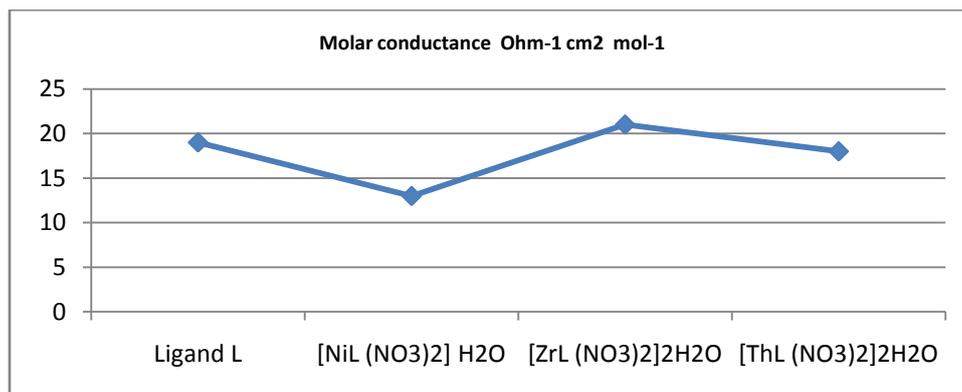


Fig. 1 Molar Conductance of the ligand and complexes

### IR Spectra

The diagnostic IR frequencies of the ligand and its complexes are compiled in Table 3. The IR spectrum of free ligand is compared with that of complexes in order to determine the co-ordination sites that may have involved in chelation. Characteristic peaks in the spectra of the ligand and complexes were considered and compared. The selected IR spectral data are given in (Table3).The IR spectrum of the ligand (L) shows characteristic bands at 2856 cm<sup>-1</sup>, 2923 cm<sup>-1</sup>, 1601 cm<sup>-1</sup> due to the  $\nu_{\text{O-C}}$ ,  $\nu_{\text{C-H}}$ ,  $\nu_{\text{C=N}}$  respectively<sup>[14]</sup>. The IR spectra of the complexes exhibited ligand bands with the appropriate shifts due to complex formation. The IR broad bands of metal complexes in the range of 3000cm<sup>-1</sup> indicate the presence of co-ordinated or lattice water molecule<sup>[15]</sup>. The  $\nu_{\text{C-O}}$  phenolic stretching frequency is observed around 2856-2850cm<sup>-1</sup> which get shifted to lower or higher frequency region indicating co-ordination of phenolic oxygen. Band at 2934-2923cm<sup>-1</sup> and 1628-1584 cm<sup>-1</sup> were assigned to C-H and C=N respectively<sup>[16-17]</sup>. The imine peaks in the metal complexes showed changes in the ligand indicating co-ordination of the imine nitrogen atom to the metal ion due to co-ordination. Another absorption bands at 810-808cm<sup>-1</sup> is assigned to M-N bond and 780-763cm<sup>-1</sup> is assigned to M-O bond<sup>[18-19]</sup>.

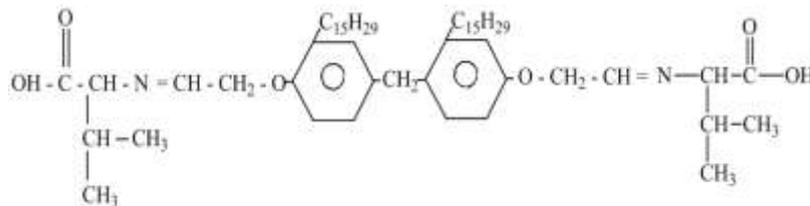


Figure 2: structure of ligand

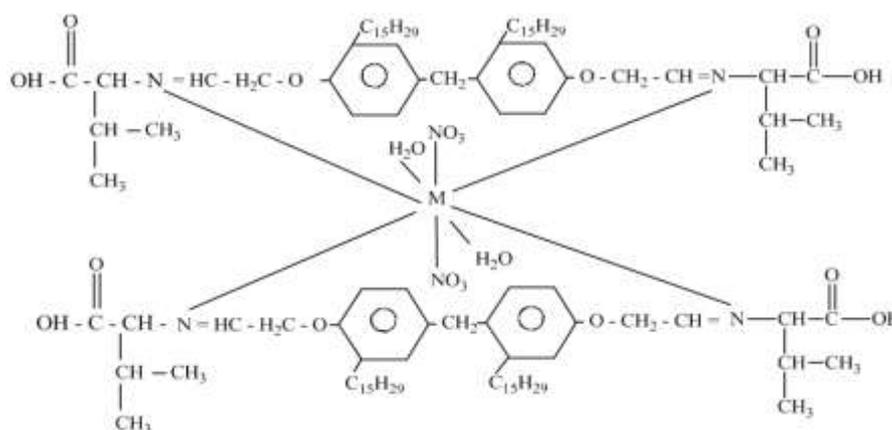
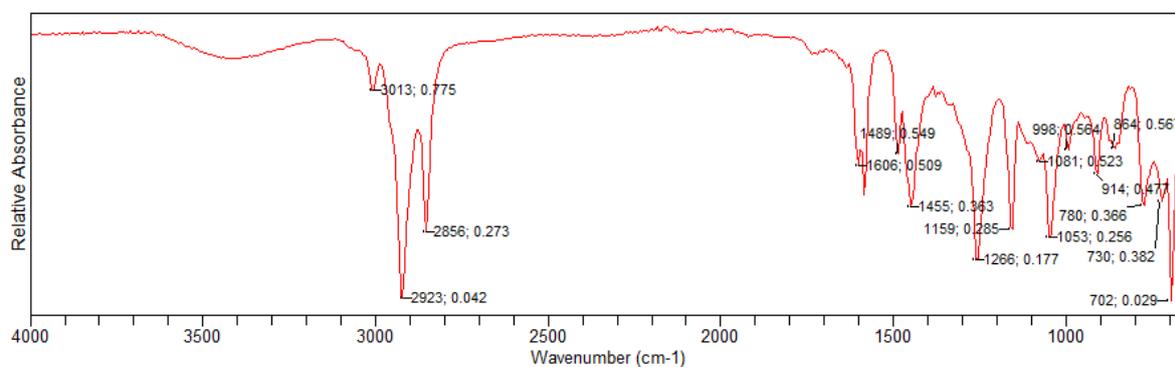


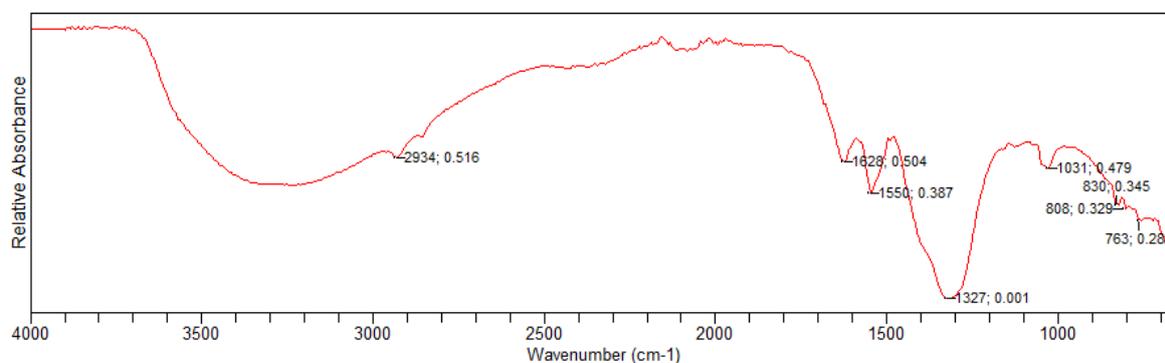
Figure 3: structure of Schiff base complexes, M=Zr(IV) and T(IV)

**Table 3: Selected FT-IR frequencies (cm<sup>-1</sup>) and UV of the ligand and complexes**

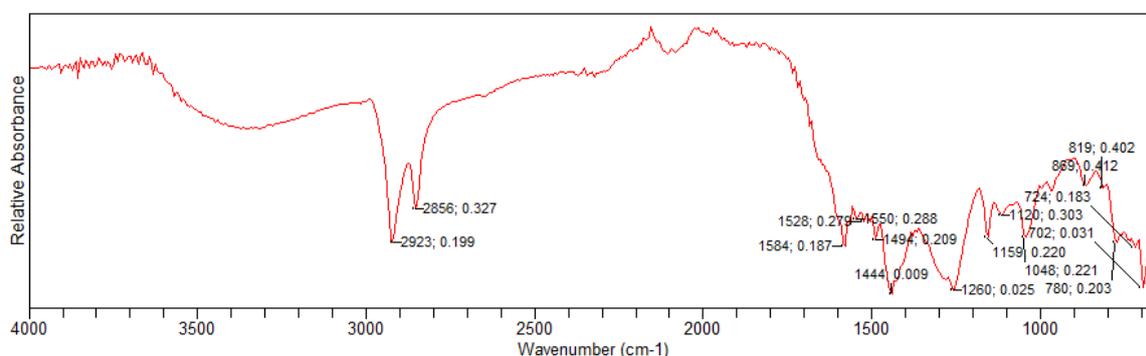
Ligand/ Complexes	$\nu_{\text{O-H}}$	$\nu_{\text{O-C}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}}$	free - COOH	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	$\lambda$ max(nm)
Ligand L	3013	2856	2923	1601	1489	1455	730	702	-
[ZrL(NO <sub>3</sub> ) <sub>2</sub> ] 2H <sub>2</sub> O	3000	2850	2934	1628	1492	1444	763	-	330,460.650
[ThL(NO <sub>3</sub> ) <sub>2</sub> ] 2H <sub>2</sub> O	3000	2856	2923	1584	1490	1416	724	702	320,450,660



**Fig. 4: FTIR Spectrum of ligand (L)**



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



**Fig66: FTIR Spectrum of Th(IV) complex**

#### UV visible spectra

The UV visible spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The ligand showed a broad band at 360nm which is assigned to  $\pi\text{-}\pi^*$  transition of the C=N chromophore<sup>[18]</sup>. On complexation this band was shifted to lower wave length suggesting the co-ordination of imine nitrogen with central metal ion. The UV spectrum of Zr(IV) complex showed three absorption bands at 330,460 and 650nm giving an octahedral geometry with field transition  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2B_{1g}$



5.290 ppm were due to the olefinic protons of the side chain and – O-CH<sub>2</sub> -group of the ligand. A multiplet at  $\delta$  =2.455 ppm - $\delta$  =2.623 ppm is due to substituted H-C-C=O- group and a singlet at  $\delta$  = 1.918ppm due to substituted -CH<sub>2</sub>-NH group respectively<sup>[21-22]</sup>.

### SEM analysis

The surface morphology of the complexes has been examined using scanning electron microscope. The SEM image of Th(IV) complex is given below. The SEM images showed that the complex is micro crystalline in nature. Careful examination of the single crystal, clearly indicated the nano scale size of the single crystal of the complex. In ethanol solvent they showed crystal like appearance but the powdered samples showed rough and amorphous nature. The SEM images showed that the complex is nano crystalline in nature. Careful examination of single crystal, clearly indicate the nano scale size of the single crystal of the complexes<sup>[23]</sup>.

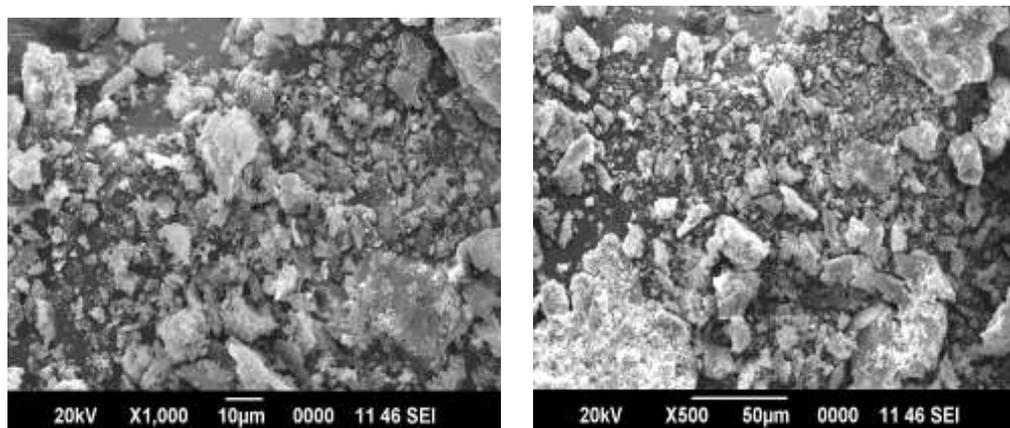


Fig.10 SEM image of Th(IV)

### X-Ray Diffraction Analysis

The powder XRD for the Zr(IV) was performed. The diffractogram is given in Fig.11. It is evident that the strong and broad peaks confirm 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 complexes is in the range of 8.2849nm. These values suggested that the complexes are in nano crystalline size<sup>[24]</sup>.

Table:3 Grain size of the Zr(IV) complexes

Complex	Grain size(nm)
[ZrL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ] 2H <sub>2</sub> O	8.2849

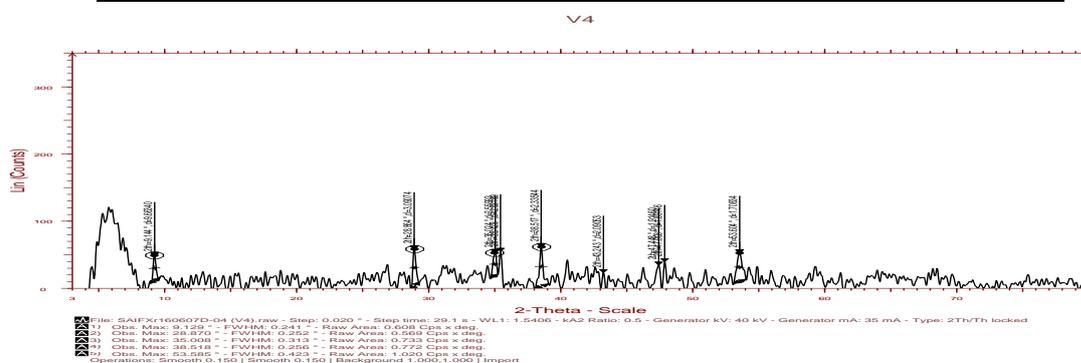


Fig.11: XRD of Zr(IV) complex

### 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 Zr(IV) and Th(IV) (Table.4 ).This order can be explained by Pearson's proposal hard acid preferred to combine with hard base and soft acid preferred to combine with soft base. It was found that the interaction of Th(IV) is normally more intense than other divalent metal ion with Schiff base ligand. Nature of the ligand and the chelate effect were the the factors involved in the environmental

chemistry and technological interest. The complexes also be used for the removal of Zr(IV) and Th(IV) ions from water.

**Table:4.** Metal ion intake

Complexes	Metal ion intake Meq/g
ZrL(NO <sub>3</sub> ) <sub>2</sub> ] 2H <sub>2</sub> O	0.6783
[ThL(NO <sub>3</sub> ) <sub>2</sub> ] 2H <sub>2</sub> O	0.9360

**Antibacterial activity**

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 centers of various cellular constituents, resulting in interference with normal cellular processes. Heterocyclic compounds play important role in regulating biological activities. This is further evidenced when valine based Schiff base metal complexes shows good antibacterial activity as they contains heterocyclic group<sup>[30-31]</sup>. The antibacterial activity of *S.aureus* shows activity only in *Th(IV)* complexes. Ager well diffusion method is used for antifungal activity and Th(IV) have fungal activity.

**Table 4 Antibacterial activity data of complexes**

Organisms	ZrL(NO <sub>3</sub> ) <sub>2</sub> ] 2H <sub>2</sub> O	[ThL(NO <sub>3</sub> ) <sub>2</sub> ] 2H <sub>2</sub> O
<i>E.coli</i>	Positive =36 T <sub>1</sub> ..0 T <sub>2</sub> -0	Positive =36 T <sub>1</sub> ..0 T <sub>2</sub> -0
<i>S.typhi</i>	Positive =30 T <sub>1</sub> ..0 F <sub>2</sub> -0	Positive =30 T <sub>1</sub> ..0 T <sub>2</sub> -0
<i>S.aureus</i>	Positive =32 T <sub>1</sub> ..0 F <sub>2</sub> -0	Positive =32 T <sub>1</sub> ..0 T <sub>2</sub> -14

**Invitro Antiproliferative effect determination by MTT assay**

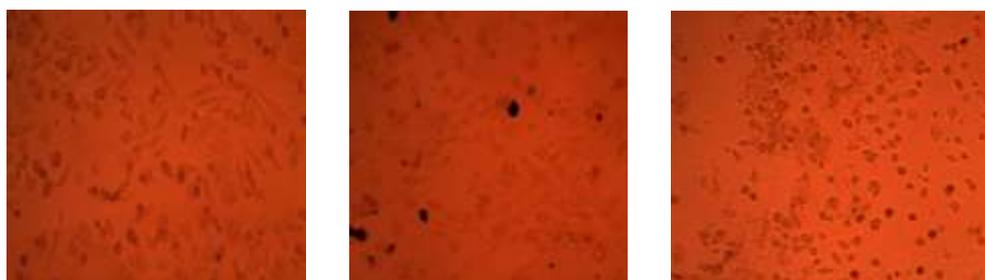
HeLa (cervical cancer) cell line was initially procured from National Centre for Cell Sciences (NCCS), Pune, India and maintained Dulbecos modified Eagles medium ( Gibco, Invitrogen). The cell lines were cultured in 25 cm<sup>2</sup> tissue culture flask with DMEM supplemented with 10% FBS, L-glutamine, sodium bicarbonate and antibiotic solution containing: Penicillin (100U/ml), Streptomycin (100µg/ml), and Amphotericin B (2.5µg/ml). Cultured cell lines were kept at 37°C in a humidified 5% CO<sub>2</sub> incubator (NBS Eppendorf, Germany). Entire plate was observed at an interval of each 24 hours; up to 72 hours in an inverted phase contrast tissue culture microscope (Olympus CKX41 with Optika Pro5 CCD camera) and microscopic observation were recorded as images. Any detectable changes in the morphology of the cells, such as rounding or shrinking of cells, granulation and vacuolization in the cytoplasm of the cells were considered as indicators of cytotoxicity. Concentration increases viability decreases, result shows that Zr(IV) and Tr(IV) were not cytotoxic<sup>[32]</sup>.

**Table 5 MTT assay data of complexes**

Sample Concentration (µg/ml)	Average OD at 540nm	Percentage Viability
Sample - V4		
6.25	0.5481	68.06159195
12.5	0.4384	54.43933938
25	0.4161	51.67018502
50	0.3542	43.98360859
100	0.1746	21.68136098
Sample - V5		
6.25	0.5405	67.11784428
12.5	0.491	60.97106668
25	0.3963	49.21147398
50	0.2898	35.98658885
100	0.1812	22.50093133



**Fig.12** MTT assay of Zr(IV) complex with concentration : 25,50,100



**Fig.13** MTT assay of Th(IV) complex with concentration : 25,50,100

#### **Antiinflammatory activity**

Proteinase inhibitory activity was performed according to the modified method. Concentration increases with increase in % inhibition, then the complex show more inflammation and it is more active. From Invivo and Invitro analysis the percentage inhibition of Zr(IV) increases with increase in concentration and exhibit statistically significant Proteinase inhibitory activity<sup>[33-34]</sup>.

**Table 6 Antiinflammatory activity data of complexes**

Sample	Concentration	Invitro % inhibition	Invivo % inhibition
ZrL(NO <sub>3</sub> ) <sub>2</sub> ]2H <sub>2</sub> O	6.25	64.20	45.91
	12.5	77.60	50.58
	25	88.39	55.51
		94.25	63.03
[ThL(NO <sub>3</sub> ) <sub>2</sub> ]2H <sub>2</sub> O	6.25	50.93	33.59
	12.5	55.80	35.79
	25	61.43	48.24
	50	72.45	61.41

#### **Nuclease Activity**

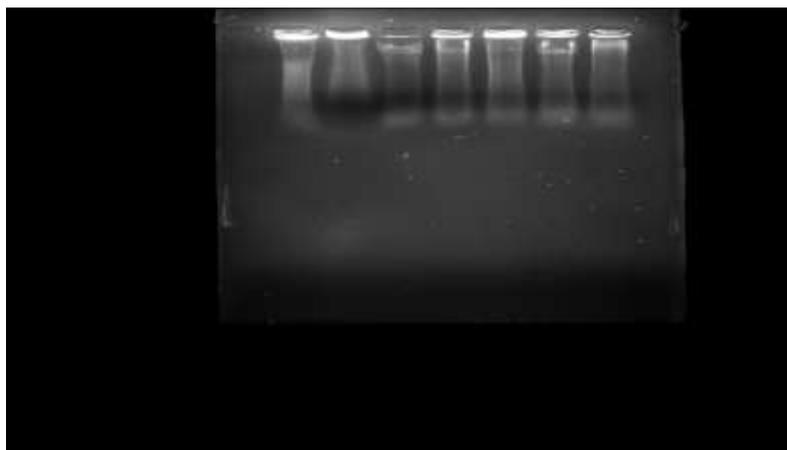
The nuclease activity of Zr(IV) and Th(IV) complexes of ligand were studied using gel electrophoresis and the respective photograph is shown in Fig . The cleavage efficiency of the complexes is compared with the control DNA to study the binding ability. The presence of smear in the gel diagram indicates the radical cleavage<sup>[35]</sup> by the abstraction of hydrogen from sugar units of DNA. The metal complexes were able to convert super coiled DNA into open circular DNA<sup>[36]</sup>. The reaction is modulated by the metallo complexes bound hydroxyl or peroxy radical generated from the oxidant H<sub>2</sub>O<sub>2</sub>. All the complexes of ligand L<sub>3</sub> showed enhanced nuclease activity.

Lane 1-Control DNA

Lane 2-DNA treated with H<sub>2</sub>O<sub>2</sub>

Lane6-DNA+Zr (IV) complex + H<sub>2</sub>O<sub>2</sub>

Lane7-DNA+Th (IV) complex + H<sub>2</sub>O<sub>2</sub>



**Fig.14 Gel diagram for Zr(IV) and Th(IV) complexes**

#### **IV. CONCLUSION**

The Schiff base of Zr(IV) and Th(IV) were synthesized from cardanol using L-valine. The ligands and complexes are insoluble in water and common organic solvents, but are soluble in ethanol, acetone and DMSO. The ligands and their complexes were characterized using spectral and analytical data. From the spectral and stoichiometric analysis, a hexa coordinated nature was assigned for the metal complexes. The nitrate group is present inside the coordination sphere. The XRD and SEM studies reveal that the complexes are nano crystalline. Antimicrobial activity and nuclease activity were studied. The antimicrobial study showed that Th(IV) only have antibacterial and antifungal activity. Zr(IV) and Th(IV) are non cytotoxic. Zr(IV) shows activation in vivo and in vitro % inhibition for anti inflammatory studies. Nuclease activity studies of complexes showed greater cleavage.

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