

Zr(IV) And Th(IV) Complexes with Schiff Base Ligands : Synthesis, Characterization, Antimicrobial Studies

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Abstract: Schiff base nano complexes of Zirconium(IV) and Thorium(IV) of general composition ML_2 have been synthesized using DFMPM and Histidine. The complexes were prepared by standard methods. The melting point, elemental analysis, molar conductance, magnetic moment studies were conducted and the complexes were characterized by IR, UV-Vis, ¹H 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, Histidine, Schiff base, nano crystalline, DNA cleavage.

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I. INTRODUCTION

Metal complexes have received a great attention because the complexes possess remarkable properties^[1]. The design, synthesis and characterization of complexes with Schiff base ligands play a relevant role in the coordination chemistry. Cardanol, the main component obtained by vacuum distillation of cashew nut shell liquid (CNSL) and was used for the preparation of bioactive transition Schiff base metal complexes. The preparation involves conversion of cardanol into bis(3-pentadecenyl phenol)methane (BPPM) using formaldehyde thus formed DFMPM on treat with epichlorohydrin, followed by the action of sodium periodate, then it under go condensation with histidine to form Schiff base ligand^[2-3] and finally formed the Schiff base complex with metal salts. The ligand and complexes were studied and characterized by UV-visible, FTIR, ¹H NMR, elemental analysis, melting point, conductivity, metal ion intake and bacterial and fungal activity and DNA cleavage were studied^[4-6]. The result indicate that the complexes were bioactive and also used for the removal of such ions from water the nano crystalline nature of complexes were confirmed by SEM and XRD studies.

II. MATERIALS AND METHODS

Cardanol was obtained from M/S Sathya Cashew Chennai India, formaldehyde (37% solution), hydrochloric acid, epichlorohydrin, L-histidine, sodium hydroxide and other chemicals were used of GR/AR grade quality obtained from Merk chemicals. All the solvents used were purified by standard methods^[6]. 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⁻¹). 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^[7].

Synthesis of Schiff base ligand with DFMPM and L-histidine

The Schiff base ligand was prepared by the reported methods^[8-9]. Equimolar ethanolic solution of DFMPM and L-histidine were mixed in 1:2 and refluxed for about an hour. Pour the reaction product in ice, (1+2) Schiff base ligand was obtained^[10]. 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 =229⁰C.

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 70-80⁰C^[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 90⁰C. yield=56%

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^[7].

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 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 (250⁰C). The complexes are insoluble in water and common organic solvents but are soluble in DMF, CCl₄, DMSO. Analytical data suggest that the metal to ligand ratio in all the complexes to be 2:1^[13] (Table 1). Conductivities of solutions of the complexes are non electrolytes because their conductivity value were in the range 14-26 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.

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	60	brown	C ₅₉ H ₉₈ N ₆ O ₄	954	229	72.52 (74.213)	8.94 (10.27)	7.11 (8.80)
[ZrL(NO ₃) ₂] 2H ₂ O	57	green	C ₁₁₈ H ₂₀₀ N ₁₄ O ₁₆	2156	>250	64.14 (65.677)	7.82 (9.276)	7.73 (9.090)
[ThL(NO ₃) ₂] 2H ₂ O	56	black	C ₁₁₈ H ₂₀₀ N ₁₄ O ₁₆ Th	2300	>250	60.29 (61.565)	7.43 (8.695)	7.05 (8.521)

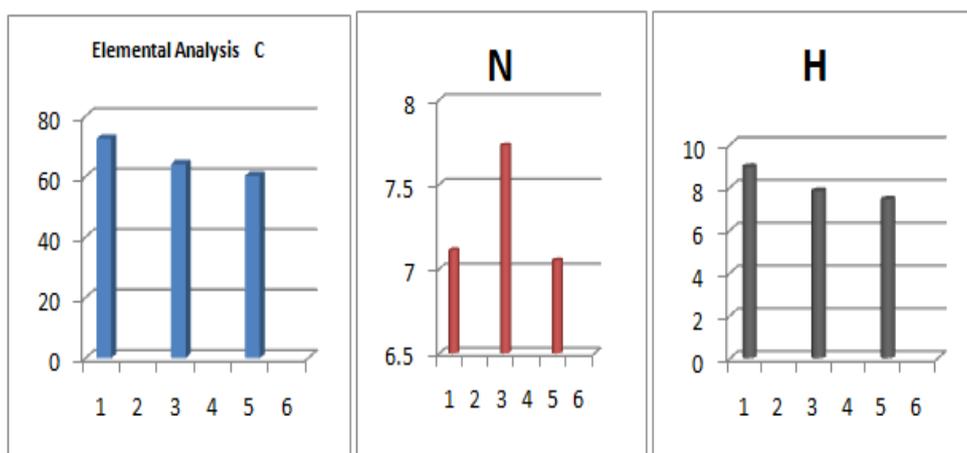


Fig.1 Elemental analysis

Conductivity Measurements

The molar conductivity values are given in Table.2. The conductivity were in the range 14-26 ohm⁻¹ cm² mol⁻¹. 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 complexes

Compounds	Molar conductance Ohm ⁻¹ cm ² mol ⁻¹
Ligand L	8
[NiL (NO ₃) ₂] H ₂ O	14
[ZrL (NO ₃) ₂]2H ₂ O	19
[ThL (NO ₃) ₂]2H ₂ O	26

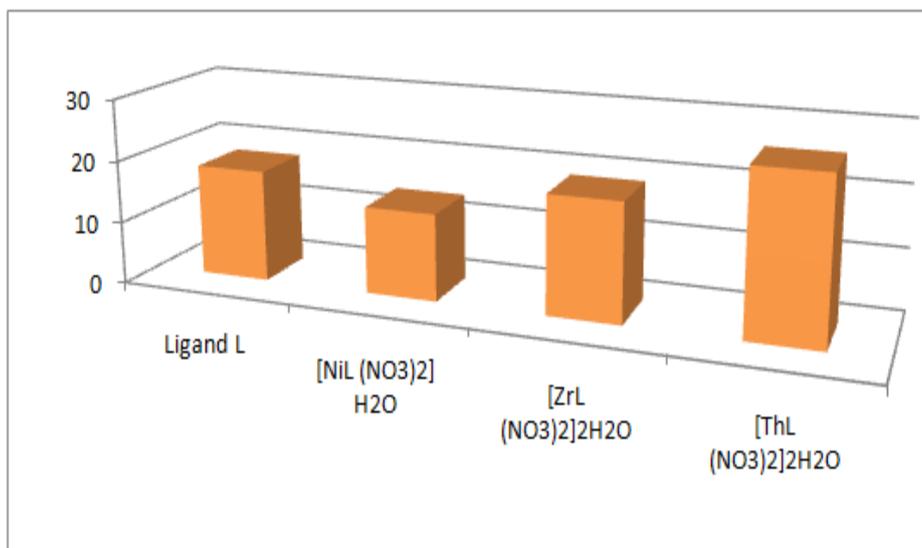


Fig. 1 Molar Conductance data of the complexes

IR Spectra

The diagnostic IR frequencies of the ligand and its complexes are compiled in Table 2. 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 (Table2) and fig: 4,5,6. The IR spectrum of the ligand (L) shows characteristic bands at 3350 cm⁻¹, 1606 cm⁻¹, 2700 cm⁻¹, 1690 cm⁻¹, 1489 cm⁻¹, 1455 cm⁻¹, 3007 cm⁻¹ due to the ν_{O-H}, ν_{O-C}, ν_{C-H}, ν_{C=N}, ν_{C=O}, ν_{COOH}, free N-H respectively^[14]. 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 3253-3197 cm⁻¹, 1546-1544 cm⁻¹, 2792-2790 cm⁻¹, 1681-1680 cm⁻¹, 1357-1355 cm⁻¹, 1436 cm⁻¹, 3496-3361 cm⁻¹ to the ν_{O-H}, ν_{O-C}, ν_{C-H}, ν_{C=N}, ν_{C=O}, ν_{COOH}, free N-H respectively^[14-17]. 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 480-478cm⁻¹ is assigned to M-N bond and 601-510cm⁻¹ is assigned to M-O bond^[18-19].

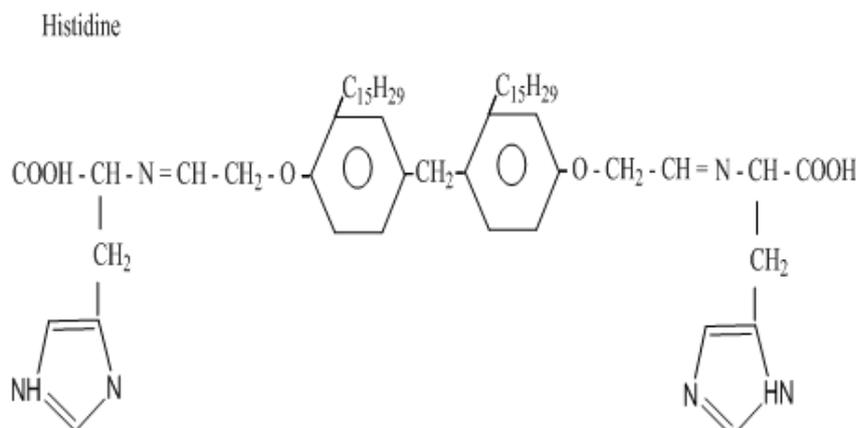


Figure 2: structure of ligand

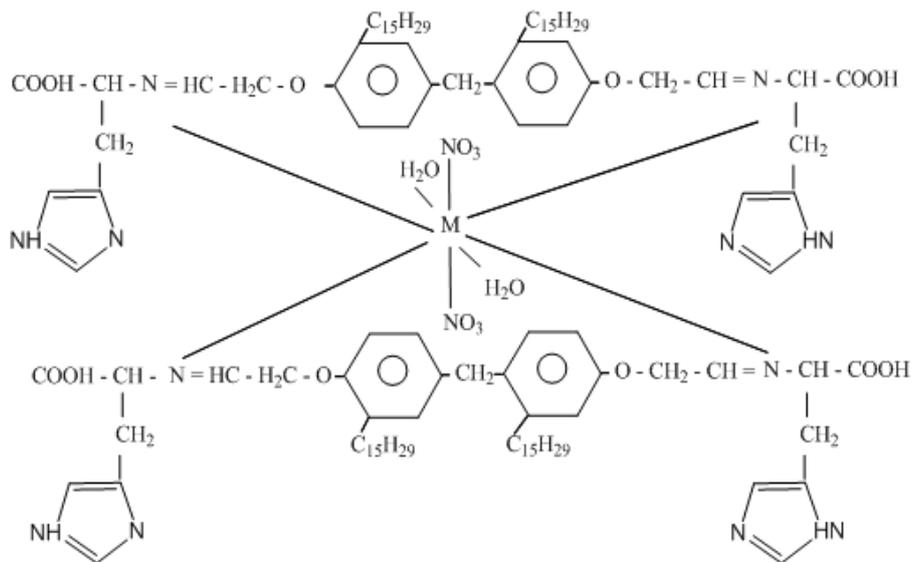


Figure 3: structure of Schiff base complexes, M=Zr(IV) and T(IV)

Table 2 Selected FT-IR frequencies (cm⁻¹) and UV of the ligand and complexes

Ligand/Complexes	ν_{O-H}	ν_{O-C}	ν_{C-H}	ν_{C-N}	ν_{C-O}	free COOH	free -NH	ν_{M-N}	ν_{M-O}	λ max(nm)
Ligand L	3350	1606	2700	1690	1489	1455	3007	780	702	-
[ZrL(NO ₃) ₂] 2H ₂ O	3197	1546	2792	1681	1357	1436	3361	478	516	401,587,612
[ThL(NO ₃) ₂] 2H ₂ O	3253	1544	2790	1680	1355	1436	3496	480	601	404,586,605

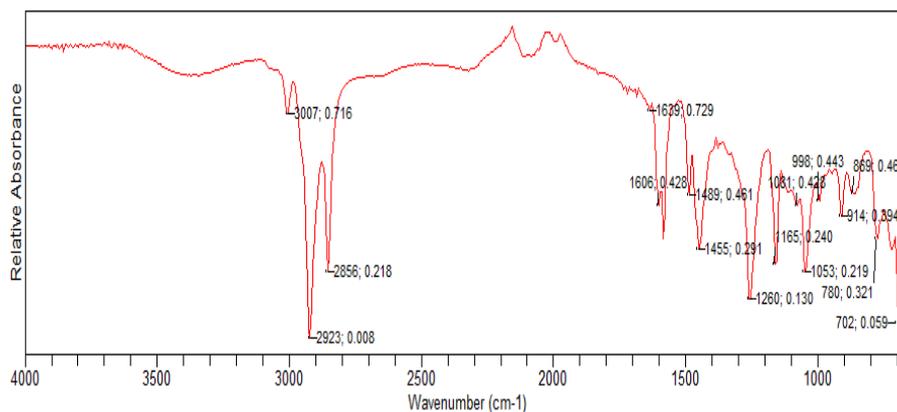


Fig. 4: FTIR Spectrum of ligand (L)

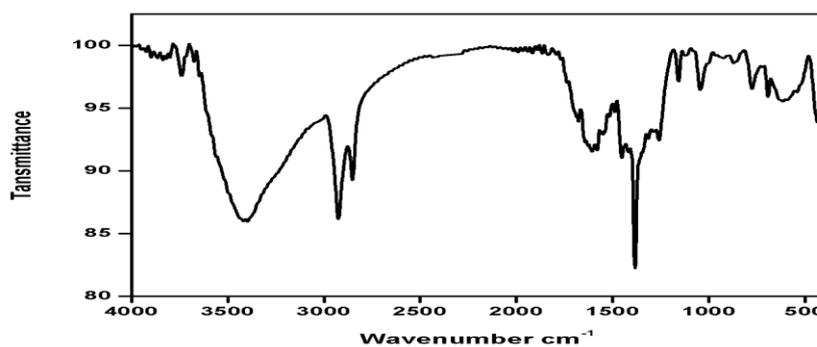


Fig.5: FTIR Spectrum of Zr(IV) complex

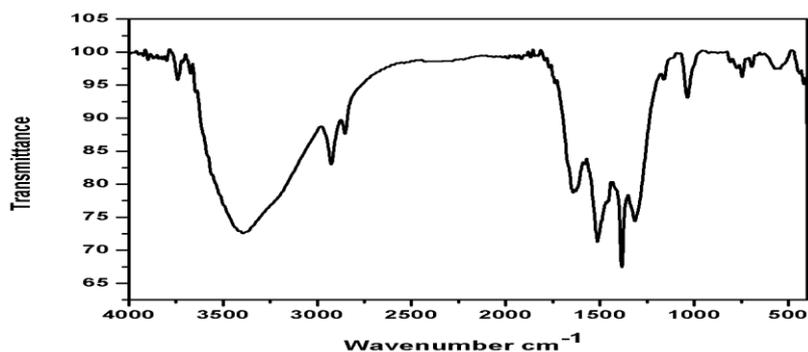


Fig6: FTIR Spectrum of Th(IV) complex

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 $\pi-\pi^*$ transition of the C=N chromophore^[18]. 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 401, 587 and 612nm giving an octahedral geometry with field transition ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_{2g}$, respectively^[19-20] in fig;7. The UV spectrum of Th(IV) complexes showed absorption bands at 404, 586 and 605nm respectively suggesting octahedral geometry in fig; 8.

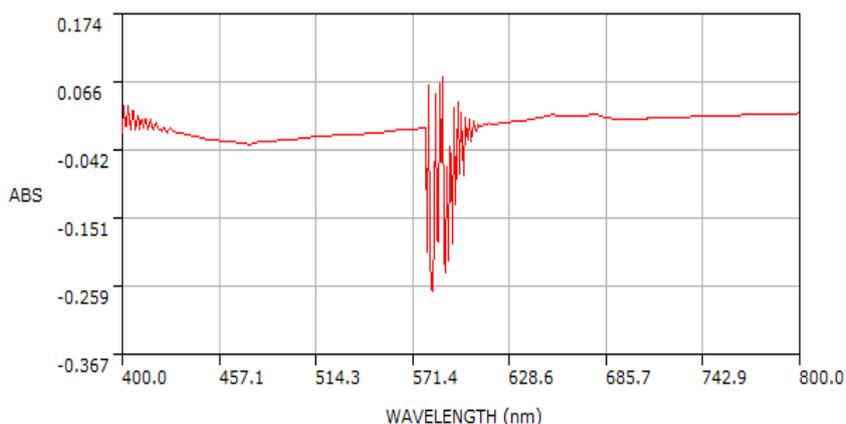


Fig .7 UV visible spectra of Zr(IV)

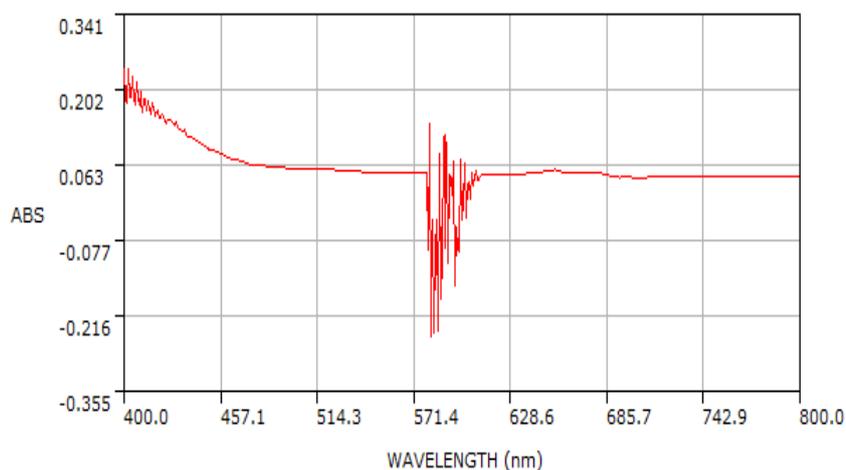


Fig.8 UV visible spectra of Th(IV)

The ¹HNMR spectrum of the Th(IV) complex (Figure 11), the presence of H – C = N- group is indicated by the singlet at δ = 7.800ppm it is due to the olefinic protons of the side chain and a singlet at δ = 7.213ppm due to – O-CH₂ -group. A singlet at δ =2.810 ppm is due to substituted H-C-C=O- group and a singlet at δ = 1.994ppm due to substituted –CH₂-NH group.. Thus ¹HNMR study also confirms the binding of metal with Schiff base ligand through pyridine nitrogen and azo methane nitrogen.

SEM analysis

The surface morphology of the complexes has been examined using scanning electron microscope. The SEM image of Zr(IV) complex is given below. 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^[23]. Lower magnification showed grain like appearance.

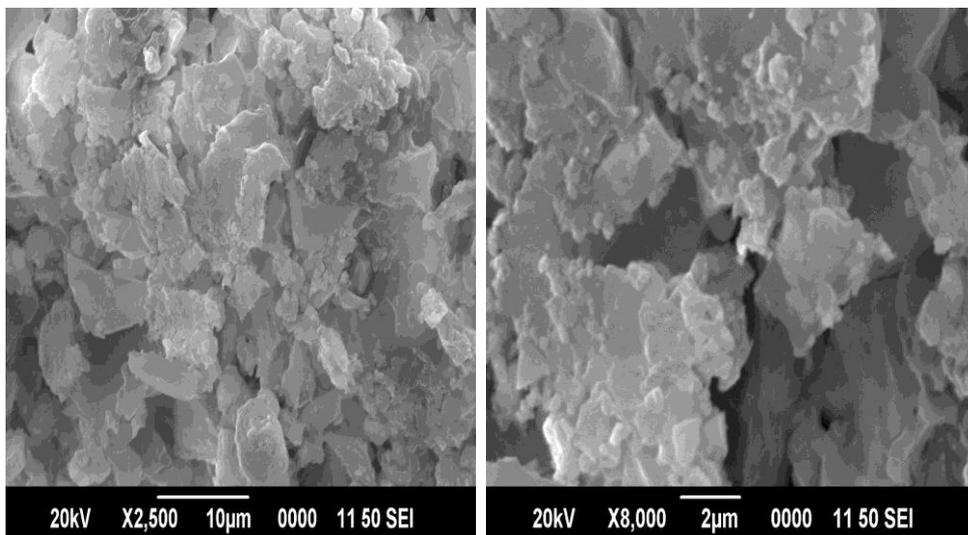


Fig.12 SEM image of Zr(IV)

X-Ray Diffraction Analysis

The powder XRD for the Th(IV) was performed. The diffractogram is given in Fig.13. 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 0.1352nm. These values suggested that the complexes are in nano crystalline size^[24].

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

Complex	Grain size(nm)
[ThL ₂ (NO ₃) ₂] 2H ₂ O	0.1352

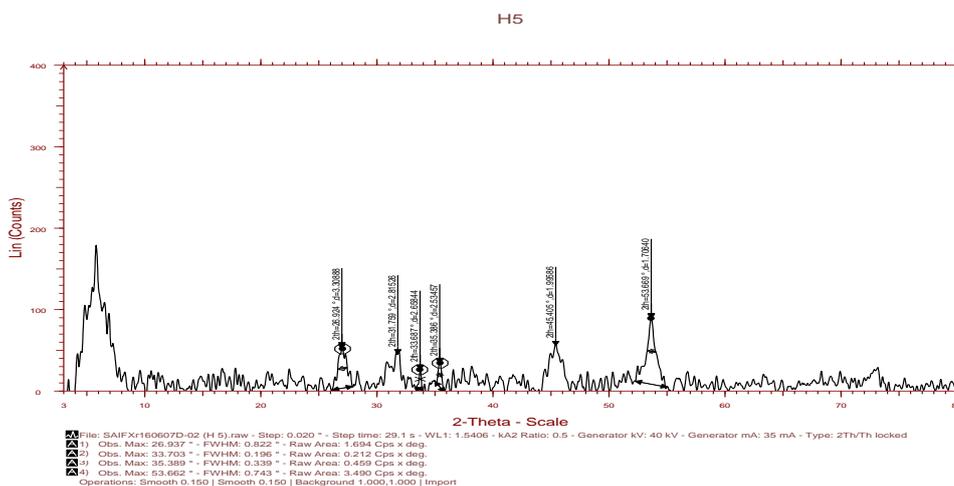


Fig.13: XRD of Th(IV) complex

Metal ion intake

The complexation behaviour of cardanol based Schiff base was affected by structural parameters [25]. This study indicates that the metal ion intake decreased Zr(IV) and Th(IV) [26] (Table.4).This order can be explained by Pearson’s proposal [27], 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 [28]. Nature of the ligand and the chelate effect were the the factors involved in the environmental chemistry and technological interest [29]. 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 ₃) ₂] 2H ₂ O	0.8348
[ThL(NO ₃) ₂] 2H ₂ O	0.9214

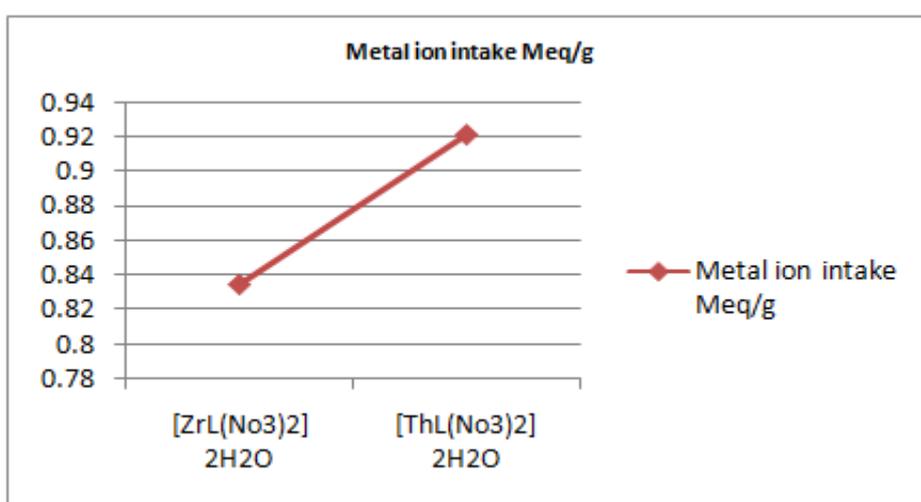


Fig.14 Metal ion intake

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 histidine based Schiff base metal complexes shows good antibacterial activity as they contains heterocyclic group [30]. The antibacterial activity of *S.aureus* shows activity in Zr(IV) and Th(IV) complexes. Ager well diffusion method is used for antifungal activity and it shows that zr(IV) is more active in green fungi.

Table 4 Antibacterial activity data of complexes

Organisms	ZrL(NO ₃) ₂] 2H ₂ O	[ThL(NO ₃) ₂] 2H ₂ O
E.coli	Positive =36 F ₁ ..0 F ₂ ..9	Positive =34 F ₁ ..7 F ₂ ..9
V.cholerae	Positive =32 F ₁ ..8 F ₂ ..9	Positive =33 F ₁ ..7 F ₂ ..9
S.typhi	Positive =39 F ₁ ..0 F ₂ ..0	Positive =39 F ₁ ..0 F ₂ ..0
S.aureus	Positive =38 F ₁ ..7 F ₂ ..9	Positive =38 F ₁ ..7 F ₂ ..10

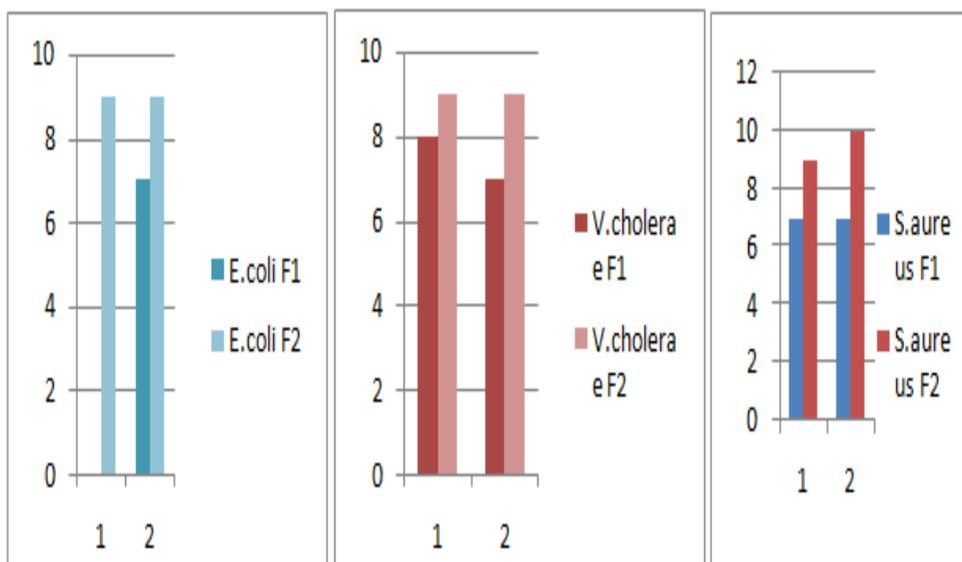


Fig. 15 Antibacterial data of complexes

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 4.35-4.36. 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^[31] by the abstraction of hydrogen from sugar units of DNA. The metal complexes were able to convert super coiled DNA into open circular DNA^[32]. The reaction is modulated by the metallo complexes bound hydroxyl or peroxy radical generated from the oxidant H₂O₂. Complexes of Zr(IV) showed enhanced nuclease activity.

Lane 1-Control DNA Lane 2-DNA treated with H₂O₂
 Lane6-DNA+Zr (IV) complex + H₂O₂ Lane7-DNA+Th (IV) complex + H₂O₂

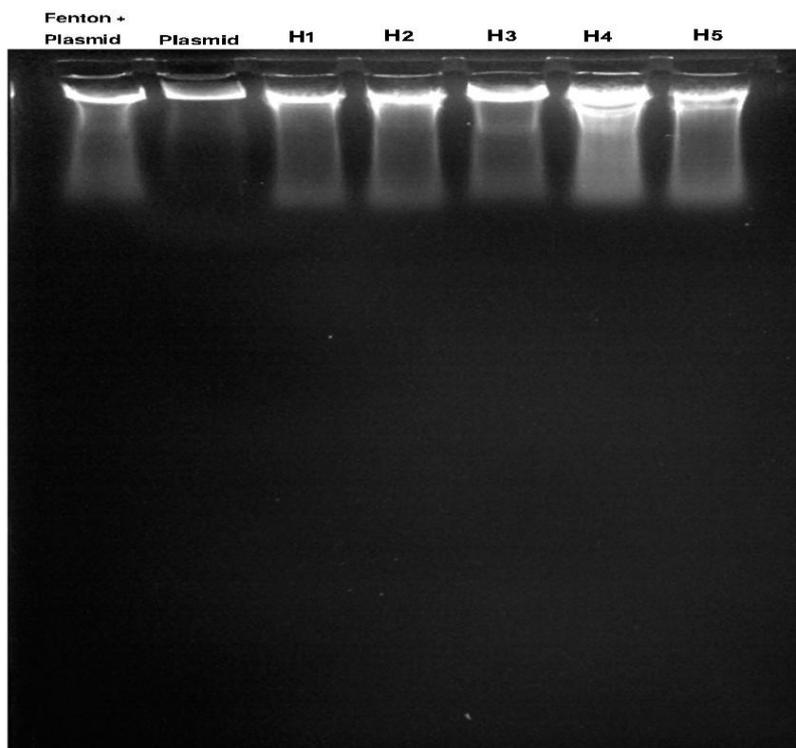


Fig.16 Gel diagram for Zr(IV) and Th(IV) complexes of Ligand

IV. CONCLUSION

The Schiff base of Zr(IV) and Th(IV) were synthesized from cardanol using L-histidine. 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 Zr(IV) have more antibacterial activity than Th(IV) complexes. The antifungal study revealed that Zr(IV) complexes have more antifungal activity than other complexes. Nuclease activity of Zr(IV) complexes showed greater cleavage.

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