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Research Paper

Synthesis and Characterization of Bio active Transition Metal Complexes of Zr(IV) and Th(IV) using natural sources

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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 Schiff base ligand using Glutamine. The ligand formed Schiff base complexes with Zr(IV) and Th(IV) ions. The ligand and complexes were characterized by UV-visible, IR, and the elemental analysis, melting point, metal ion intake, SEM, XRD antibacterial,antifungal,anti-inflamatory and DNA clevage were studied. The result indicate that the complexes of Zr(IV) nd Th(IV)) are hexaco-ordinated and have moderate antibacterial and antifungal activity. The metal ion intake indicated the ligand can be used for the removal of these metals from water. The SEM and XRD studies revealed the nano crystalline nature of the complexes.*

Keywords: Cardanol, Formaldehyde, Epichlorohydrin, Glutamine, Schiff base.

Introduction

Schiff base complexes of transition metals are highly useful due to their structure and physico-chemical properties. Cardanol is the main component obtained by vacuum distillation of roasted cashew nut shell liquid (CNSL) and was used for the preparation of bioactive transition Schiff base metal complexs. The preparation involves (i) conversion of cardanol into bis(3-pentadecenyl phenol)methane (BPPM) (ii) conversion of BPPM to DFMPM (iii) condensation of DFMPM with glutamine to give Schiff base ligand and finally (iv) Schiff base complexes with transition metal salts. The ligand and complexes were characterised by UV-visible, FTIR and the elemental analysis, melting point, conductivity, metal ion intake, anti bacterial, anti fungal,anti inflammatory and DNA cleavage activity were studied[1-3].The result indicate that the complexes of Zr(IV) and Th(IV) 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. Antibacterial, antifungal, anti inflammatory and DNA cleavage study indicates the complexes are potential agents.

Material and Methods

Cardanol was obtained from M/S Sathya Cashew Chennai India, formaldehyde (37% solution), hydrochloric acid, epichlorohydrin, L-glutamine, 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[4] . The micro analytical data (C, H, N) were collected using Perkin Elmer 2400 instrument. The metal ion intake were estimated by standard methods[5] IR spectra were obtained by using PEIR spectrum instrument Model : 2000. SEM, XRD, anti bacteria, anti fungal, anti inflammatory and DNA cleavage were studied by standard methods.

Synthesis of Schiff base ligand with DFMPM and L-glutamine

The Schiff base ligand was prepared by the reported methods[6-7]. Equimolar ethanolic solution of DFMPM and L-glutamine were mixed and refluxed for about an hour. Pour the reaction product in ice, (1+2) Schiff base ligand was obtained[8]. The precipated yellow compound was filtered washed with water and dried over anhydrous calcium chloride. The crude sample was recrystalised from 50% absolute alcohol yield=62%. Melting point =223^{0}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) nitrate, and Th(IV) nitrate in 2:1 molar ratio. The resulting mixture was refluxed for about twelve hours at 70-80^{0}C[9]. The complexes were filtered, washed with ethanol, diethyl ether, acetone and hot water and finally dried under vaccum at 90^{0}C.yield=60%

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[10].

Results and Discussion

The metal complexes of Zr(IV) and Th(IV) are coloured solids, stable towards air and have high melting points above (250^{o}C). The complexes are insoluble in water and common organic solvents but are soluble in DMF, $CDCl_3$ and DMSO. Analytical data (Table 1) suggest that the metal to ligand ratio in all the complexes to be 1:2[11]. Conductivities of solutions of the complexes are non electrolytes because their conductivity value were in the range 12-15 ohm^{-1}cm^2 mol^{-1}.However the conductivity value is higher than expected for non electrolytes probably due to partial solvolysis of the complexes in DMF medium.

Table 1: Physical characteristics and analytical data of complexes

Compounds	yield	Colour	molecular formula	Molecular Weight	Melting point	Elemental Analysis		
						C	H	N
Ligand(L)	60	Brown	$C_{57}H_{100}N_4O_8$	968	229	70.01 (70.66)	10.05 (10.33)	5.07 (5.78)
[ZrL $(NO_3)_2$] $2H_2O$	57	Light green	$C_{114}H_{204}N_6O_{24}$ Zr	2131	>250	63.89 (64.16)	9.11 (9.57)	3.21 (3.94)
[ThL $(NO_3)_2$] $2H_2O$	56	Grey	$C_{114}H_{204}N_6O_{24}$Th	2272	>250	59.29 (60.21)	7.84 (8.97)	3.19 (3.69)

IR Spectra

IR spectra of the complexes were compared with the free ligand in order to determine the involvement of co-ordination sites 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).The IR spectrum of the ligand (Fig.1) showed characteristic bands at 2856 cm^{-1} ,2923 cm^{-1},1606 cm^{-1} ,1489 cm^{-1},1455.02 cm^{-1},3013 cm^{-1},780 cm^{-1} , 702 cm^{-1} , due to the ν_{O-C}, ν_{C-H}, $\nu_{C=N}$, $\nu_{C=O}$, ν_{COOH}, ν_{NH2}, ν_{M-N}, ν_{M-O}, respectively[12]. The IR spectra of the complexes (Figure 2-4) exhibited ligand bands with the appropriate shifts due to complex formation. The IR broad bands of metal complexes in the range of 3505-3486cm^{-1}indicate the presence of co-ordinated or lattice water molecule[13]. The ν_{C-O} phenolic stretching frequency is observed around 2854-2852cm^{-1} which get shifted to lower or higher frequency region indicating co-ordination of phenolic oxygen. Bands at 2923-2922 cm^{-1} and 1610-1590cm^{-1} were assigned to C-H and C=N respectively[14-15]. 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.

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}	$\nu_{C=N}$	$\nu_{C=O}$	free -COOH	free $-NH_2$	ν_{M-N}	ν_{M-0}	λ max(nm)
Ligand(L)	-	2856	2923	1606	1489	1455.02	3013	780	702	-
[ZrL $(NO_3)_2$]$2H_2O$	3486	2854	2923	1610	1590	1447	3853	772	687	368 231
[ThL $(NO_3)_2$]$2H_2O$	3505	2852	2922	1590	1588	1445	3786	770	695	372 228.8 324.8

Another absorption bands at 772-770cm^{-1} is assigned to M-N bond and 695-687cm^{-1} is assigned to M-O bond[16-17]. The absorption bands at 3853-3786 cm^{-1} is assigned to free NH_2 group and 1447-1445 cm^{-1} is assigned to free COOH group and 1590-1588cm^{-1}is assigned to C=O group. It shows that the terminal NH_2 group is not involved in bonding,

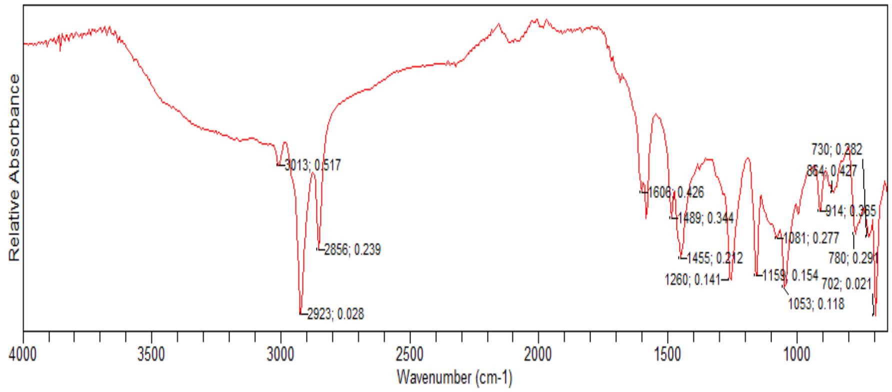

Figure 1: FTIR Spectrum of ligand (L)

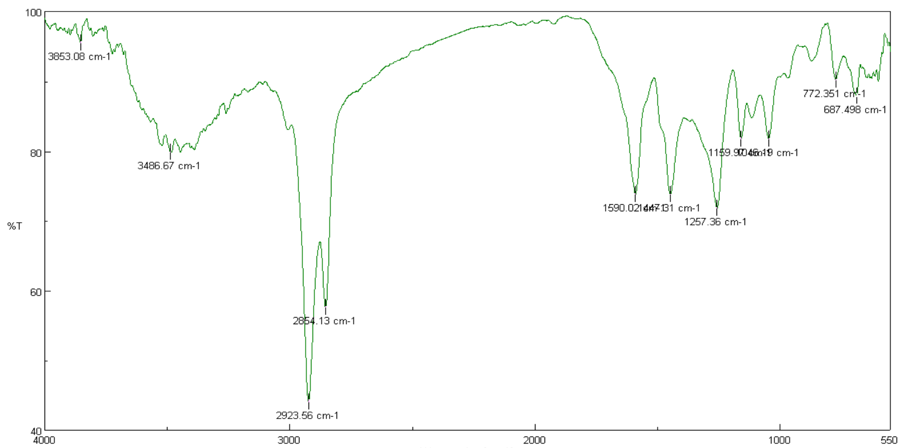

Figure 2: FTIR Spectrum of Zr(IV) complex

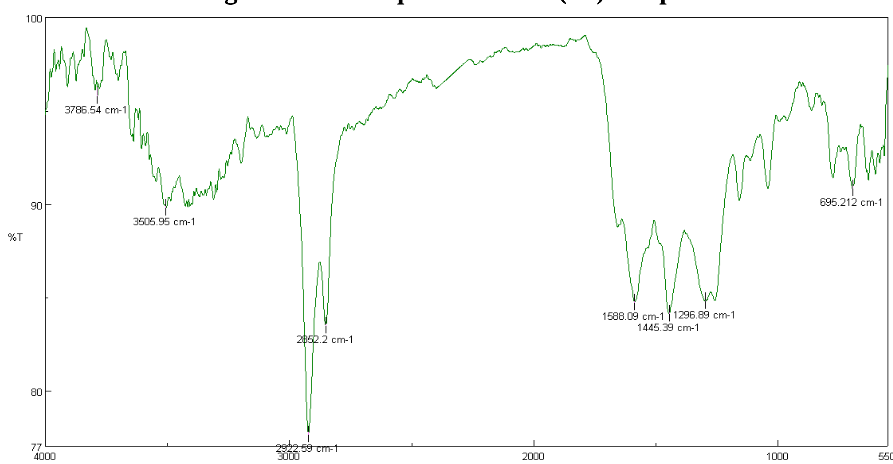

Figure 3: FTIR Spectrum of Th(IV)) complex

^{1}H NMR Spectra

On examining the ^{1}H NMR spectrum of ligand (Figure 4), it exhibited a multiplet signed at δ=7.004 ppm – 7.032 ppm is due to substituted aromatic ring protons[16]. The presence of H – C = N- group is indicated by the singlet at δ = 7.024ppm. The multiplet at δ 6.539 ppm - δ = 6.640 ppm and δ = 5.158 ppm – δ = 5.676 ppm were due to the olifinic protons of the side chain and – O-CH_2 -group of the ligand respectively.

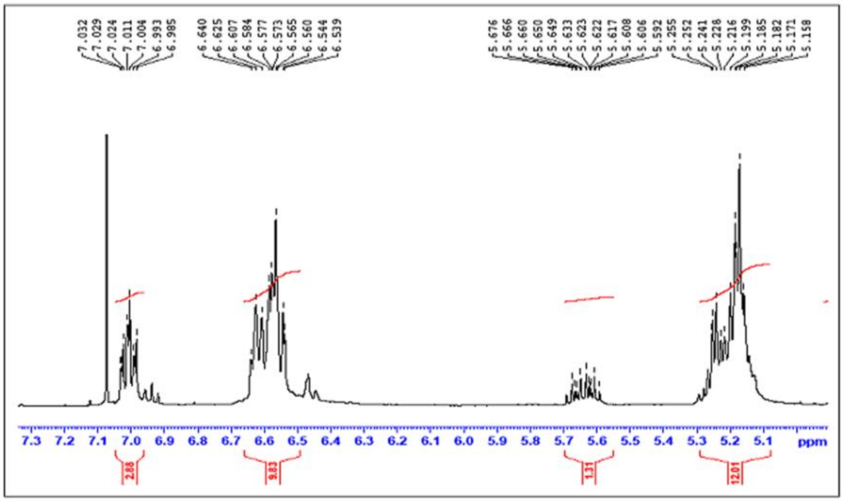

Figure 4: The ^{1}H NMR Spectrum of Ligand

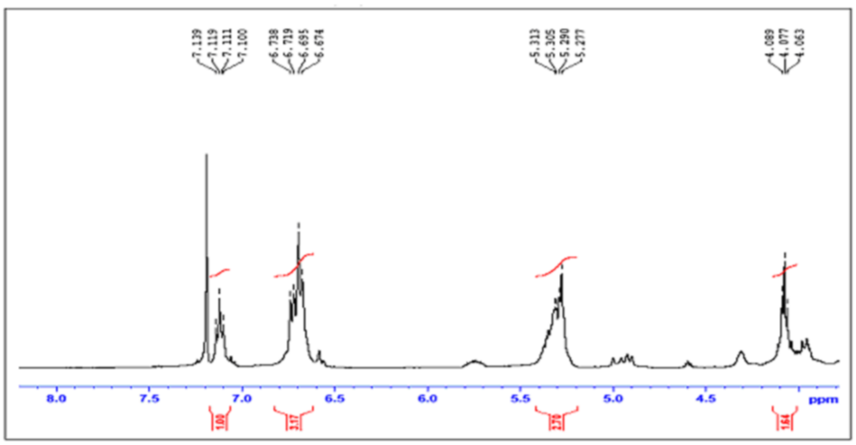

Figure 5: The ^{1}H NMR Spectrum of Zr(IV) Complex

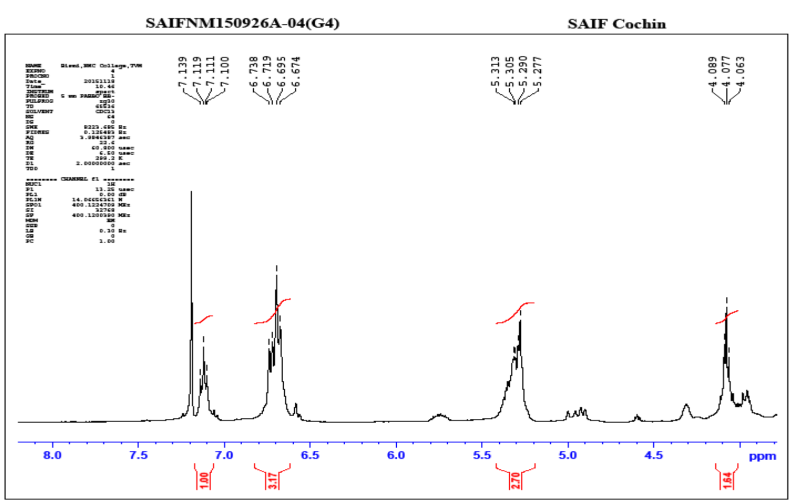

Figure 6: The ^{1}H NMR Spectrum of Th(IV) Complex

The ^{1}H NMR spectrum of the Zr(IV) complex (Figure 5) it exhibited a multiplet signed at δ=7.100 ppm – 7.139 ppm is due to substituted aromatic ring protons. The presence of H – C = N- group is indicated by the singlet at δ = 7.119 ppm. δ = 5.277 ppm – δ = 5.313 ppm were due to the olifinic protons of the side chain and – O-CH_2 -group. A multiplet at =4.063 – 4.089 ppm is due to substituted NH-C=O- proton. Thus ^1H NMR study also confirms the binding of metal with Schiff base ligand through pyridine nitrogen and azomethine nitrogen.

The ^1H NMR spectrum of the Th(IV) complex (Figure 6) gave a multiplet signed at δ=7.098ppm –7.140 ppm is due to substituted aromatic ring protons. The presence of H – C = N- group is indicated by the singlet at δ = 7.117ppm. δ = 5.274 ppm due to the olifinic protons of the side chain and – O-CH_2 -group. A multiplet at =4.061 – 4.086 ppm is due to substituted NH-C=O- proton. Thus ^1H NMR study also confirms the binding of metal with Schiff base ligand through pyridine nitrogen and azomethine nitrogen.

UV-visible spectra

The UV visible spectra (Figure 5-7) 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 π-π* transition of the C=N chromophore[18].On complexation this bond 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 two absorption bands at 368 and 231.2 nm giving an octahedral geometry with field transition ^2B_1g->^2A_1g,^2B_1g->^2B_2g and ^2B_1g->^2E_2g,respectively[19-20]. The UV spectrum of Th(IV) complexes showed absorption bands at 372.8nm and 228.8nm and 324.8 nm respectively suggesting octahedral geometry.

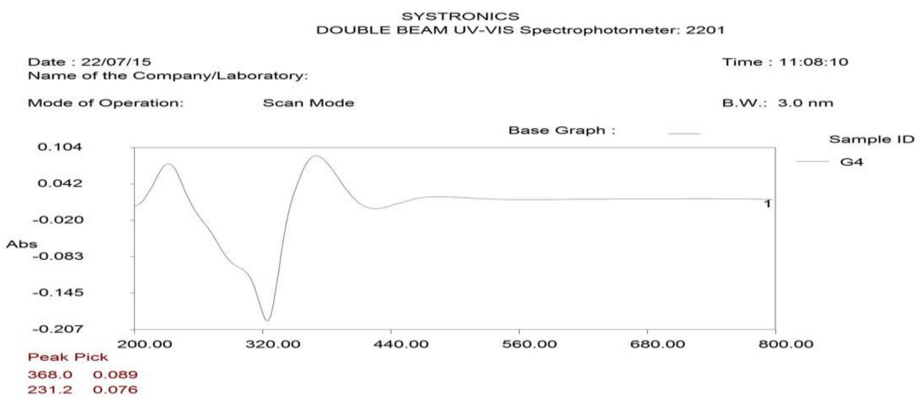

Figure 4: UV-Visible Spectrum Zr(IV) complex of ligand

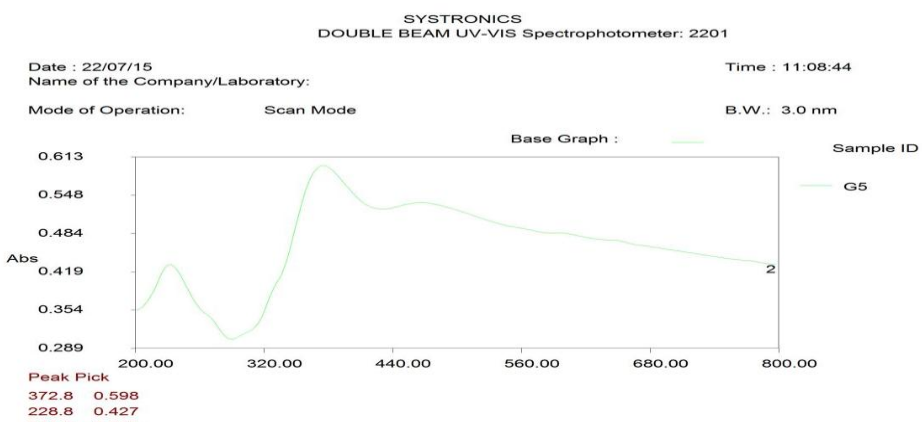

Figure 5: UV-Visible Spectrum Th(IV) complex of ligand

However UV – visible spectra could not provide structural details of these complexes[15-18]. 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 1:1 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 because conductance data showed the complexes are non-electrolytes and the NO_3 groups were coordinated with the central Zr(IV) or Th(IV) ion. On the basis of foregoing observation the probable structure of Zr(IV) and Th (IV) complexes may be presented as in (Figure 4,5). Earlier researchers also reported the octacoordination of Zr(IV) and Th (IV) Schiff base complexes[20-22].

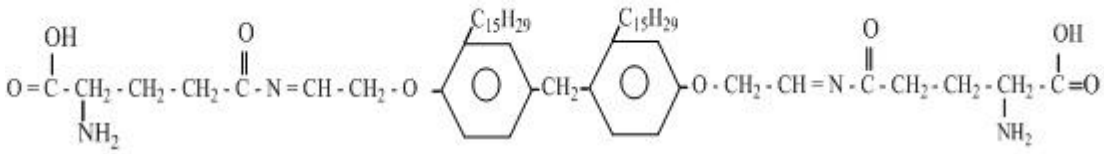

Figure 6: Structure of ligand

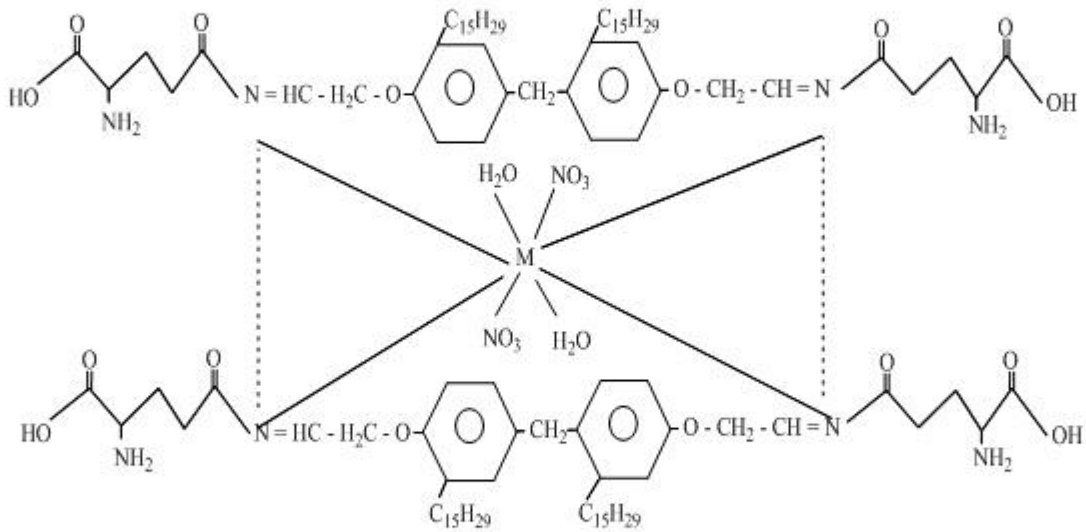

Figure 7: Structure of Schiff base complexes, M=Zr(IV), Th(IV)

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 micro crystalline in nature. Careful examination of single crystal, clearly indicate the nanoscale size of the single crystal of the complexes[23]. Lower magnification showed grain like appearance.

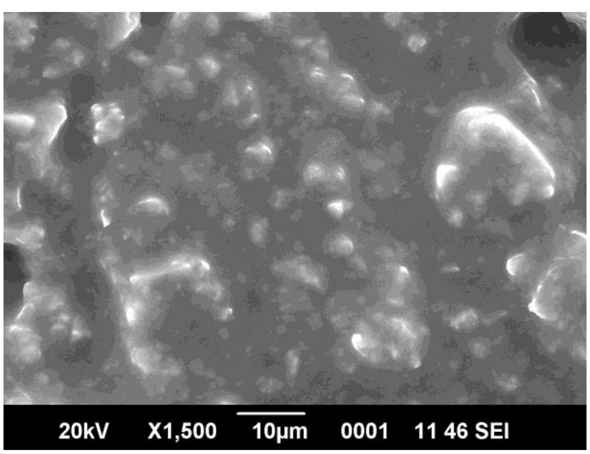

Figure 8: SEM image of Schiff base of Zr(IV) in ethanol

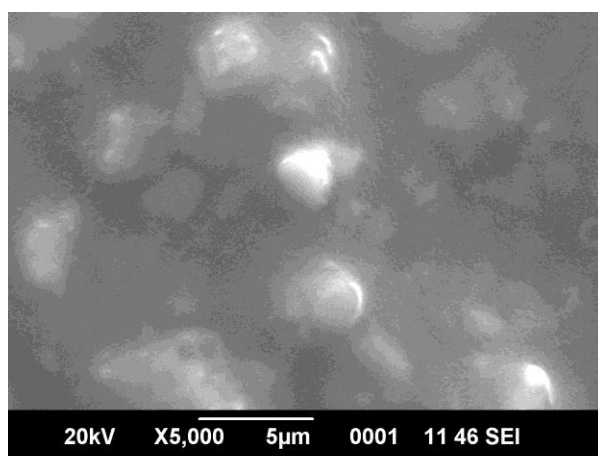

Figure 9: SEM image of powder sample of Zr(IV)

X-Ray Diffraction Analysis

The powder XRD for the Th(IV) was performed. The diffractogram is given in Figure 12. 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 1.6544nm. These values suggested that the complexes are in nano crystalline size[24].

Table 3: Grain size of the Cu(II) complexes

Complex	Grain size(nm)
[ThL $(NO_3)_2$] $2H_2O$	1.6544

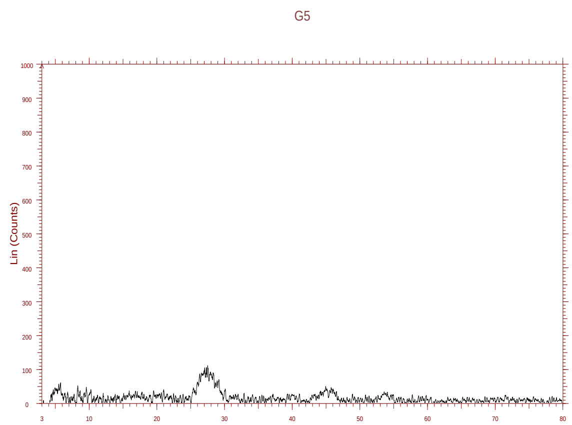

Figure 10: XRD spectrum of Th(IV)of ligand

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 from Zr toTh[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 factors involved[29].

Antibacterial activity

Antibacterial activity of the ligand complexes and standard drugs were screened by the disc diffusion method in ethanol as solvent. The result of antibacterial study is given in table 3[30]. Under identical conditions the Schiff base complexes of Zr and Th have moderate antibacterial activities against these bacteria[31]. The results of antibacterial activity substantiate the findings of earlier research[32] the biological inactive compound become active and less biologically active compounds become more active upon coordination[33].

Table 4: Antibacterial and Anti fungal activity data of complexes

Ligand / Complex	*E. coli*	*P. aeruginosa*	*Klebsiella pneumoniae*	*Staphylococcus aureus*	*Candida albicans*	PC	NC	Metal Ion intake meq/g
[ZrL $(NO_3)_2$] $2H_2O$	6.0	15.0	6.0	19.0	16.0	23.00	6.0	0.4532
[ThL $(NO_3)_2$] $2H_2O$	6.0	17.0	6.0	10.0	6.0	25.00	6.0	0.6201

*Media: Mueller Hinton Agar for bacteria * PC - Chloramphenicol*

Such enhancement in biological activity of metal complexes can be explained on the basis of Overtone's concept of cell permeability, the lipid membrane that surrounds the cell flavours the passage as only lipid soluble materials due to which lipho solubility is an important factor that controls antimicrobial activity[34]. Also other factors such as solubility, conductivity and dipole moment may also be among the possible reason causing enhancement of bactericidal activity of the metal complexes as compared to the uncomplexed Schiff base compound. Under identical conditions the Schiff base complex of Zr (IV) shows maximum antibacterial activity than Th(IV) against these bacteria[35].

Proteinase Inhibitory 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 analysis the percentage inhibition of [ThL$(NO_3)_2$]$2H_2O$ increases with increase in concentration and exhibit statistically significant Proteinase inhibitory activity[36]. From Invitro analysis the percentage inhibition of [ZrL$(NO_3)_2$]$2H_2O$ and [ThL$(NO_3)_2$]$2H_2O$ increases with increase in concentration and exhibit statistically significant Proteinase inhibitory activity. In Invitro more inflamation is shown by [ThL$(NO_3)_2$]$2H_2O$[37].

Table 5: Invivo Antiarthritic Activity by inhibition of protein denaturation method

Sample Code	Concentration	% of Inhibition
[ZrL $(NO_3)_2$]$2H_2O$	25	91.27
	50	86.13
	100	86.665
[ThL $(NO_3)_2$]$2H_2O$	25	56.42
	50	61.319
	100	77.08

Table 6: Invitro Antiarthritic Activity by inhibition of protein denaturation method

Sample Code	Concentration (µg/ml)	% of Inhibition
$[ZrL (NO_3)_2]2H_2O$	25	10.77
	50	23.46
	100	26.51
$[ThL (NO_3)_2]2H_2O$	25	10.58
	50	25.61
	100	52.49

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 Figure 11. 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[38] by the abstraction of hydrogen from sugar units of DNA. The metal complexes were able to convert super coiled DNA into open circular DNA[39]. The reaction is modulated by the metallo complexes bound hydroxyl or peroxo radical generated from the oxidant H_2O_2. All the complexes of ligand L_3 showed enhanced nuclease activity.

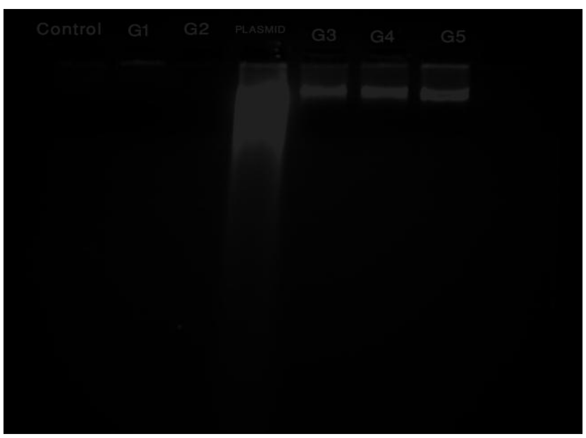

Figure 11: Gel diagram of Zr(IV) and Th(IV)

Lane 1-Control DNA
Lane 2-DNA treated with H_2O_2
Lane6-DNA+Zr (IV) complex + H_2O_2
Lane7-DNA+Th (IV) complex + H_2O_2

Conclusion

The Schiff base of Zr(IV) and Th(IV) were synthesized from cardanol using L-glutamine. The ligands and complexes are insoluble in water, 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 complexe. 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 Th (IV) complexes have more antifungal activity than other complexes. In proteinase inhibitory activity of Th(IV) show more inflammatory activity Nuclease activity studies of complexe showed greater cleavage .

References

1. Jaszberenyi Z., Banyai I., Brucher E., obertKiraly R., Hideg K. and Kalai T. Equilibrium and NMR studies on GdIII, YIII, CuII and ZnII complexes of various DTPA–N,N″-bis(amide) ligands. Kinetic stabilities of the gadolinium(III) complexes, *Dalton Trans*., **48,** 1082-1091 **(2006)**

2. Sessler J.L., Moody T.D., Hemmi G.W., Lyneh V., Young S.W. and Miller R.A., Gadolinium(III) texaphyrin: a novel MRI contrast agent, *J. Am. Chem. Soc*., **115**, 10368 **(1993)**

3. Oude Wolbers M.P., Van VeggelFCJM.,Snellick-Ru BHM., Hofstraat J.W., Guerts FAJ. and Reinhoudt DNJ. Novel Preorganized Hemispherands To Encapsulate Rare Earth Ions: a Shielding and Ligand Deuteration for Prolonged Lifetimes of Excited Eu^{3+}Ions, *J. Am. Chem. Soc*., **119**, 138 **(1997)**

4. Nair M.S. and David S.T., Studies on the solution equilibria involved in some Co(II) and Zn(II) Schiff base complexes systems, *Ind. J. Chem Soc*., 77, 220-222 **(2000)**

5. Vogel A.I., A text book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis, Longman, London **(1978)**

6. Borisova N.E., Reshetova M.D., Ustynyuk Y.A., Metal free methods in synthesis of macrocyclic Schiff base, *Chemical Reviews*, **107**, 46-79 **(2007)**

7. Lakshmi B., Shivananda K.N., Prakash G.A., Rama K.R.K. and Mahendra K.N., Synthesis of Co(II), Ni(II) and Cu(II) complexes from Schiff base ligand and reactivity studies with thermosetting epoxy Resin, *Bull. Korean Chem. Soc*., **32 (5),** 1613-1619 **(2011)**

8. IsacSobana Raj C., Christudhas M., and Allen Gnana Raj G., Synthesis, Characterization, Metal ion intake and Antibacterial Activity of Cardanol based Polymeric Schiff base Transition Metal Complexes using Ethylenediamine, *J. Chem. Pharm. Res*., **3(6),** 127-135 **(2011)**

9. Bismi S. Prakash., Isac Sobana Raj C., and Allen Gnana Raj G., Synthesis and, Characterization of bio active transition Metal complexes of Co(II),Cu(II) and Ni(II) using natural sources, *Asian J. Res. in chem*., **8(12)**,726-732**(2015)**

10. Vogel A.I., Text book of quantitative inorganic analysis including Elementary Instrumental Analysis 4th Edn., Longman London, 3, **(1978)**

11. Hermansen Ralph D. and Lau Steren E., Adhesive of epoxy resine, amine-terminated ban and conductive filler, US. Patent 5929141 A, 08/9011, 153 **(2004)**

12. Ramazan Gup, Bülent Kirkan, Emrah Giziroğlu, Synthesis and Characterization of Complexes of Copper(II), Nickel(II) and Cobalt(II) with vic-Dioximes Bearing *N′-p*-Aminobenzoyl Benzaldehyde Hydrazone, *Chinese Journal of Chemistry*, **24**, 2 **(2006)**

13. Liu J., BBo-wan Wu, Bing Zang, Yong C.L., Synthesis andCharacterization of Metal Complexes of Cu(II), Ni(II), Zn(II), Co(II),Mn(II) and Cd(II) with Tetradentate Schiff Bases, *Turk J. Chem*., **30**, 41-4 **(2006)**

14. Raman N., Ravichandran S. and Thangaraja C., Copper(II), Cobalt(II), Nickel(II), and zinc(II) complexes of Schif base derived from benzil-2,4-dinitrophenylhydrazone with aniline, *J. Chem. Sci*. **116(4)**, 215 **(2004)**

15. Y. Harinath, D. Harikishore Kumar Reddy, B. Nareshkumar, K. Lakshmi and K. Seshaiah, Copper(II), Nickel(II) complexes of N-heteroaromatic hydrazone: L Synthesis, Characterization and in vitro antimicrobial evaluation, *J. Chem. Pharm. Res.*, **3(1)**, 698 **(2011)**

16. Tuncel M., Ozbulbul A. and Serin S., Synthesis and Characterization of the thermally stable Schiff base polymers and their Copper(II),Cobalt(II) and Nickel(II) complexes, *Reactive and functional Polymers*, **68**, 292 **(2008)**

17. Gopalakrishnan S. and Sujatha R., Synthesis and thermal properties of polyurethrane from cardanol of furfural resin *J. Chem. Pharm. Res.*, **2(3)**, 193-205 **(2010)**

18. Mukerreem K., Esin I., Synthesis, Characterization and Biological Evaluation of Cobalt(II), Nickel(II) and Copper(II) Complexes of Schiff Base, *Asian J. Chem.*, **19(2)**, 1239-1245 **(2007)**

19. Agarwal R.K., Garg R. and Sindhu S.K., Synthesis spectral and thermal properties of some high coordinated complexes of Th(IV) and dioxouranium(VI) derived from 4[N - (2□ – hydroxyl – 1□ -Naphthalidene) amino] antipyrinethiosemi carbozone, *Bull. Chem. Soc. Ethiop*., **19(2),** 185 **(2005)**

20. Day V.W. and Fay R.C., Stereochemistry of eight-coordinate mixed-ligand complexes of zirconium. I. Characterization and the crystal and molecular structure of dinitratobis (acetylacetonato) zirconium(IV), *J. Amer. Chem Soc.*, **97**, 5136 **(1975)**

21. Muller E.G., Day V.W. and Fay R.C., Stereochemistry of eight-coordinate mixed-ligand complexes of zirconium. II. Characterization and the crystal and molecular structure of nitratotris (acetylacetonato) Zirconium(IV), *J. Amer. Chem. Soc*., **98,** 2165 **(1976)**

22. Peterson E.J., Von Dreele R.B., Brown T.M., Crystal and molecular structure of tetraisothiocyanatobis(2,2'-bipyridine)niobium(IV) and -zirconium(IV), *Inorg. Chem.*, **15(2)**, 309–315 **(1976)**

23. Isac Sobana Raj C., Christudhas M., and Allen Gnana Raj G., Synthesis, Characterization, Metal ion Schiff base complexes of Zr(IV) and Th(IV) derived from Di-□-formyl methoxybis(3-pentadecenylphenyl) methane [DEMPM] and ethylenediamine, *Asian J. Res. in chem.*, **4(11)**,1765-1770 **(2011)**

24. Destri S., Pasini M., Pelizzi C., Porzio W., Predieri G., Vignali C., Synthesis and Characterization of Conjugated Polyazines and Polyazomethines Containing the Thienylene Moiety and Flexible Hydrocarbon Side Chains, *Macro Molecules*, **32**, 353 **(1999)**

25. Pearson R.G., *Coordination Chemistry Rev*., **100**, 403 **(1990)**

26. Nejo A.A., Kolawole G.A., and Nejo A.O., Synthesis, characterization, antibacterial, and thermal studies of unsymmetrical Schiff-base complexes of cobalt(II), *Journal of Coordination Chemistry*, **63(24)**, 4398–4410 **(2010)**

27. San Miguel V., Fernando Catalina A. and Carmen Peinado, Self assembly of physically crosslinked micelles of poly(2-acylamido-2methyl-1-propane sulphonic acid-co-isodecyl methacrylate)- copper(II) complexes, *European Polymer Journal*, **44**, 1368-1377 **(2008)**

28. Mohapatra R.K. and Chandran Dash D., Synthesis and characterization of UO_2(VI), Th(IV), ZrO(IV) and VO(IV) complexes with Schiff base actaazamacrocyclic ligands, *J. Korean Chem. Soc.*, **54(4),** 395 **(2010)**

29. Cherutoi J.K., Cheruiyot L.L. and Kiprono C.P., Synthesis and Characterization of zinc(ii) and copper(ii) complexes of embelin, *Chem. Soc. Ethiop.*, **19(2)**, 295-299 **(2005**)

30. Kaya I., Vilayetoglu A.R. and H., Mart, The synthesis and properties of oligosalicylaldehyde and its Schiff base poligomers, *Polymer*, **42**, 4859 **(2001)**

31. Clarke P.A., Poele R., Wooster R., Workman P., Gene expression microarray analysis in cancer biology, pharmacology, and drug development: progress and potential, *Biochem. Pharmacol.*, 15, **62(10)**,1311-36 **(2001)**

32. British Pharmacopoeia-II, Biological assay and Tests, the Stationary Office Ltd., London, **A-205**, (**1998)**

33. June M.Li., Structure and Function of metallo antibiotics, *Med Resear. Rev*., **23**, 697 **(2003)**

34. Kandaswamy N., Nanth, Synthesis, characterization, in vitro antimicrobial and anticancer evaluation of random copolyesters bearing biscoumarin units in the main chains, *Research on Chemical Intermediates*, **41(10)**, 7189-7206 **(2015)**

35. Thamizharasi S., Vasantha J., Reddy B.S.R., Synthesis, characterization and pharmacologically active sulfamethoxazole polymers, *Eur. Polym. J.*, **38**, 551 **(2002)**

36. Luf, Zarkesh R.A, A Redox-Active Ligand as reserviour for protons and electrons, O_2 Reductional Zr(IV), *Eur. J. Inorg. Chem.*, **3**, 4670, **(2012**)

37. Anilkumar M. Ethanomedical plants as Anti-inflamatory and Analgesics agents, Ethanomedicine, A source of Complementary Therapeutis, Research signpost Kerala India. 267-293**(2010)**

38. Mishra L. and Singh V.K., *Ind. J. Chem.*, **32(4)**, 446, **(1997)**

39. Zhang C.X. and Lippard S.J., New metal complexes as potential therapeutics, *Curr. Opin. Chem. Biol.*, 7, 481, **(2003).**