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Synthesis and characterization of transition metal complexes of Zr(IV) and Th(IV) using cardanol and 4-aminoantipyridine

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ABSTRACT

Cardanol, a naturally occurring aliphatic chain substituted phenol derived from cashew nut shell liquid (CNSL) was used for the preparation of Schiff base ligand using 4-aminoantipyridine. The Schiff base complexes of Zr(IV) and Th(IV) of di- α -formyl methoxybis(3-pentadecenylphenyl)methane (DFMPPM) and 4-aminoantipyridine were synthesized in three stages. The ligand and complexes were characterized by UV-visible, IR Spectroscopy. The elemental analysis, melting point, metal ion intake, SEM, XRD, antibacterial and antifungal activity were also studied. The conductance measurements indicate that all the complexes of non-electrolytes. The result indicated that the complexes of Zr(IV) and Th(IV) are hexacoordinated 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, 4-aminoantipyridine, Schiff base.

INTRODUCTION

Schiff bases of azomethine nitrogen donor heterocyclic ligands are well known due to their wide range of applications in pharmaceutical and industrial fields and have been found to act as antibacterial and antifungal agents[1-7]. Schiff base can accommodate different metal centres involving various coordination methods there by allowing successful synthesis of homo and hetero metallic complexes with varied stereochemistry[8,9]. Metal complexes of nitrogen-oxygen chelating agents derived from 4-aminoantipyridine have been studied[10,11]. The present of study deals with the synthesis, characterization and biological studies of the Schiff base complexes of Zr(IV) and Th(IV) derived from DFMPPM and 4-aminoantipyridine.

MATERIALS AND METHODS

Cardanol was obtained from M/S Satya Cashew, Chennai India, formaldehyde (37% solution) hydrochloric acid, epichlorohydrin, 4-aminoantipyridine and other chemicals used were of GR/AR grade quality obtained from Merck chemicals. All the solvent used was purified by standard methods[12]. The micro analytical data (C,H,N) were collected using Perkin Elmer 2400 instrument. IR spectra were obtained using PE IR spectrum instrument model: system 2000.

Synthesis of Schiff base ligand with DFMPPM and 4-aminoantipyridine

The synthesis of Schiff base ligand was carried out by reported methods (14) ethanolic solution of DFMPPM and 4-aminoantipyridine were taken in RB flask in 1:2 molar ratios and refluxed for an hour. The reaction

mixture was poured in ice, a yellow compound of Schiff base ligand was obtained[15]. 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%.

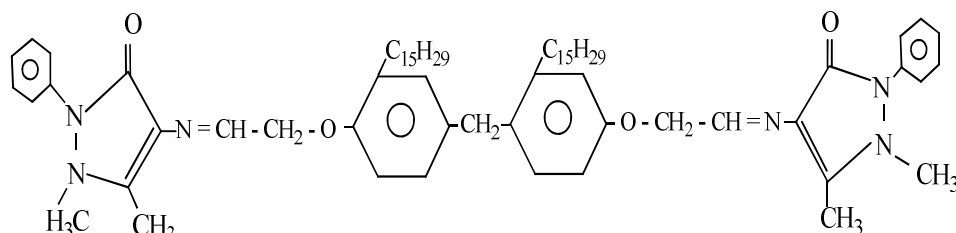


Figure 1 : Formation of Schiff base Ligand

Synthesis of Zr(IV) and Th(IV) Schiff base complexes :

The metal complexes of the ligand were prepared by adding aqueous solution of Zr(IV) nitrate and Th(IV) nitrate to the ligand in 1:2 ratio and refluxed for about twelve hours at 65°C- 70°C. The final product was filtered washed with ethanol, diethyl ether and hot water, and finally dried under vacuum at 90°C yield = 58%

Estimation metal ion intake :

The filtrates obtained in the above methods were collected. The collection was used for the estimation of Zr(IV) and Th(IV) intake for complexation using standard methods[16].

Table-1 Physical characteristics and analytical data of the complexes

Compound	Yield %	Colour	Mol. formula	Mol.wt	Melting point °C	Elemental Analysis		
						C	H	N
Ligand (L)	60	brown	C ₆₉ H ₁₃₆ N ₆ O ₄	1112	228	74.52 (74.46)	12.03 (12.23)	7.03 (7.55)
[ZrL(NO ₃) ₂].2H ₂ O	57	Light green	C ₁₃₈ H ₂₇₆ N ₁₄ O ₁₀ Zr	2379	>250	69.60 (69.53)	11.60 (11.74)	8.23 (8.46)
[ThL(NO ₃) ₂].2H ₂ O	59	brown	C ₁₃₈ H ₂₇₆ N ₁₄ O ₁₀ Th	2520	>250	65.71 (65.68)	10.95 (10.77)	7.77 (7.48)

Table2:..Metal ion intake of the complexes

Compound	Metal ion intake meq/g
[ZrL(NO ₃) ₂].2H ₂ O	0.9730
[ThL(NO ₃) ₂].2H ₂ O	1.0214

RESULTS AND DISCUSSION

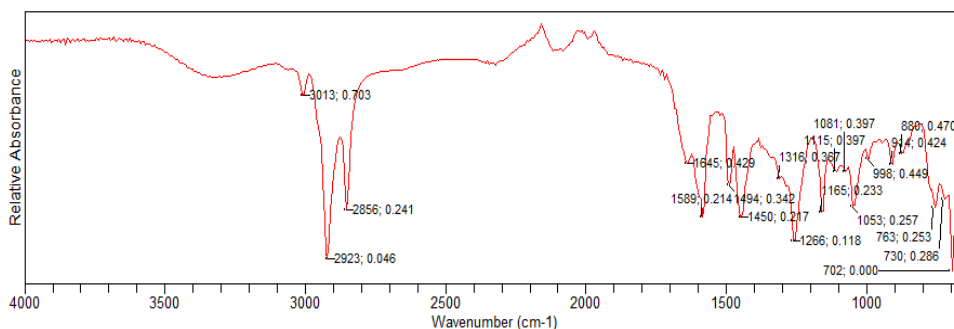
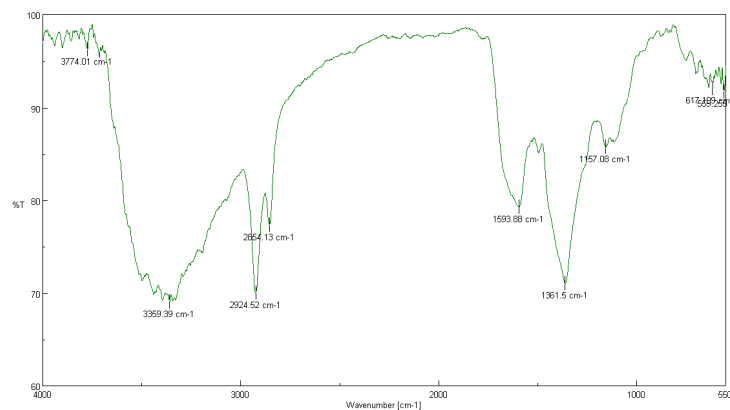
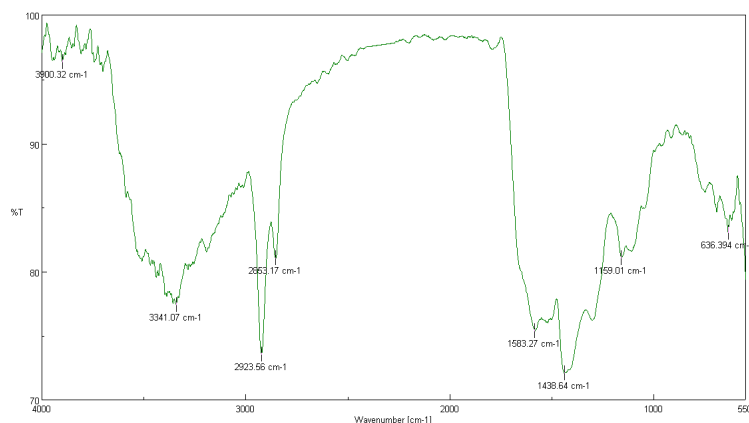
The metal complexes of Zr(IV) and Th(IV) coloured solids, stable towards air and have high melting points (above 250°C). The complexes are soluble in DMF, CDCl₃ and DMSO. Analytical data suggest that the metal to ligand ratio (1:2) in all the complexes to be conductivities of solutions of the complexes in DMF are shown in table 1. All the complexes are non-electrolytes because their conductivity values were in the range 12-15 ohm⁻¹cm⁻²mol⁻¹. However, the conductivity value is higher than expected for non-electrolytes probably due to partial solvolysis of the complexes in DMF medium.

IR spectra:

Selected IR spectral bands for the ligand and its complexes are given in table. The IR spectrum of the free ligand is characterized mainly by the strong bands at 3013cm⁻¹, 2856cm⁻¹ and 2923cm⁻¹. Which are attributed to the stretching frequencies of O-C, C-H and C=N (azomethine) respectively^[17]. The IR spectrum of the free ligand was compared with the spectra of metal complexes. The characteristic absorption bands 3359.39-3341.07cm⁻¹ range were attributed to ν-OH group of the coordinated or lattice water. The absorption bands in the range 2924-2923cm⁻¹, 2854.15-2853.17cm⁻¹ and 1593.88-1583.37cm⁻¹ were assigned to ν_{O-C}, ν_{C-H}, and ν_{C=N} respectively. The imine peak in the metal complexes showed change in Schiff's compared to the ligand indicating coordination of the imine nitrogen atom to the metal ion due to coordination. Another absorption bands at 1157.08cm⁻¹ and 1159.01cm⁻¹ is assigned to the coordinated nitro group with the central metal atom 636-617cm⁻¹ is assigned to M-N bond and 559-394cm⁻¹ is assigned to M-O bond. The absorption band at 1438.64-1361.5cm⁻¹ is assigned to free CH₃ group. It shows that the terminal CH₃ is not involved in bonding.^[18]

Table 3: selected FT-IR frequencies (cm⁻¹) of the ligand complexes

Ligand/ Complexes	$\nu_{\text{O-H(H}_2\text{O)}}$	$\nu_{\text{O-C}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{-CH}_3}$
ligand		2856	2923	1589			1450
[ZrL[NO ₃] ₂ 2H ₂ O]	3359.39	2924	2854.13	1593.88	617	559	1361.5
[ThL[NO ₃] ₂ 2H ₂ O]	3341.07	2923	2853.17	1583.27	636	394	1438.64

**Figure :2 FTIR Spectrum of Ligand****Fig 3 : FTIR Spectrum of Zr(IV) complex of Ligand****Fig 4 : FTIR Spectrum of Th(IV) complex of Ligand****UV visible spectra :**

The absorption region assignment and geometry of the ligand and complexes are given in Table 4. The ligand showed a broad band at 360 nm which is assigned to π - π^* transition of the C = N chromophore^[19]. On complexation this band was shifted to lower wave length suggesting the coordination of imine nitrogen with central metal ion. The UV and visible spectra of the Zr(IV) complex showed three absorption bands at 318nm, 307 nm and 300 nm giving an octahedral geometry with field transitions. $2B_{1g} \rightarrow 2A_{1g}$, $2B_{1g} \rightarrow 2B_2$ and $2B_{1g} \rightarrow 2E_2g$ respectively. The broadness and position of the band favours distorted octahedral geometry for complex due to Jahn-Teller effect. The electronic spectra of Th(IV) complexes showed absorption bands at 329nm, 319 nm and 312 nm respectively suggesting octahedral geometry for the complexes.

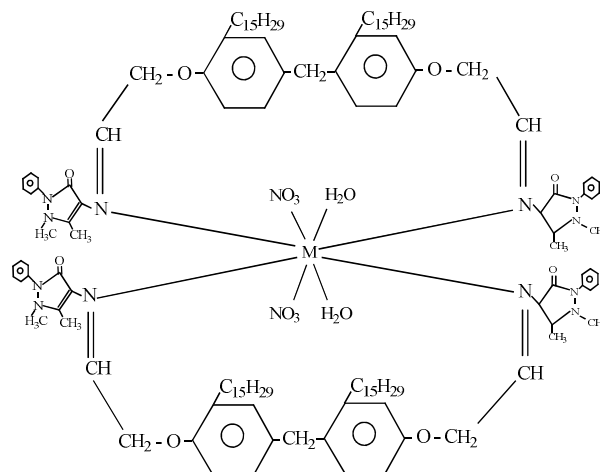


Fig 5 : Structure of Schiff base complexes M=Zr(IV) and Th(IV)

Table 4 UV Visible spectra of the ligand and its complexes

Ligand/ Complex	$\lambda_{\max}(\text{nm})$
$\text{C}_{68}\text{H}_{136}\text{N}_8\text{O}_4$	
$[\text{ZrL}(\text{NO}_3)_2]2\text{H}_2\text{O}$	318, 307, 300
$[\text{ThL}(\text{NO}_3)_2]2\text{H}_2\text{O}$	329, 319, 312

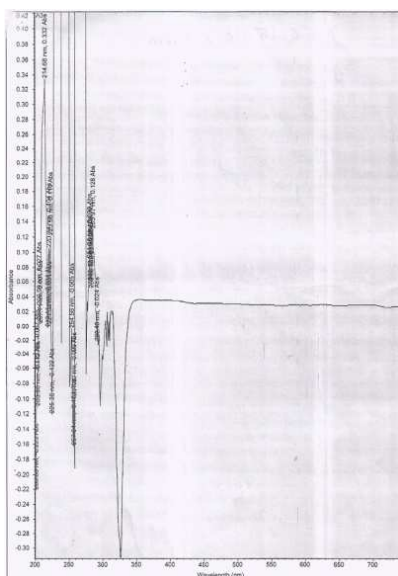


Fig: 6 UV spectrum of Zr(IV) complex

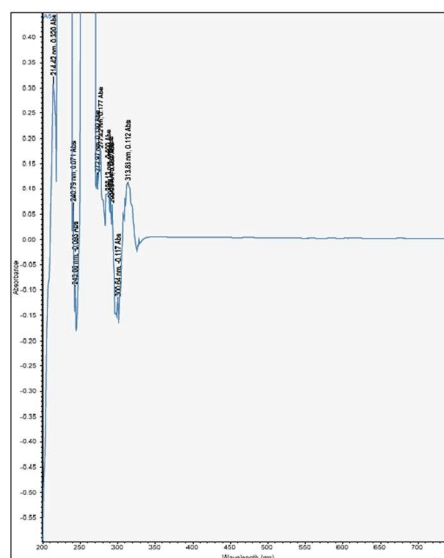


Fig : 7 UV spectrum of Th(IV) complex

^1H NMR Spectrum:

^1H NMR Spectrum of the Th(IV) complex (figure:8) it exhibited a multiplet signed at $\delta = 4.025\text{ppm}$ - 3.958 ppm is due to substituted aromatic ring protons. The presence of $\text{H}-\text{C}=\text{N}$ - group is indicated by the singlet at $\delta = 7.162\text{ppm}$. A signal at $\delta = 1.98\text{ppm}$ - 1.53ppm indicated the presence of $-\text{CH}_2-$ protons. The multiplet at $\delta = 6.545\text{ppm}$ - $\delta = 6.758\text{ppm}$ and $\delta = 3.43\text{ppm}$ - $\delta = 3.99\text{ppm}$ were due to the olefinic protons of the side chain- $\text{O}-\text{CH}_2-$ group. Thus ^1H NMR study also confirmed the structural information of both ligand and its complexes

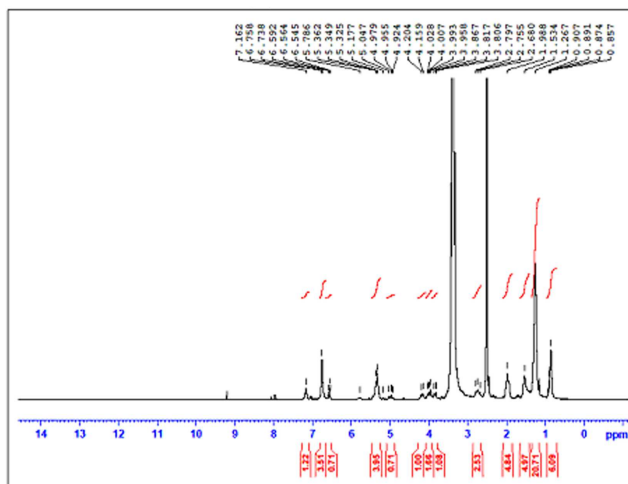


Figure:8 ¹H NMR spectrum of Th(IV) Complex of Ligand

SEM analysis:

The surface morphology of the complexes was studied using JSM 5610 scanning electron microscope. The SEM images 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 nanoscale size of the single crystal of the complexes. The SEM images showed that all the complexes are nano crystalline in nature showed rough, granular and pitted surface^[20].

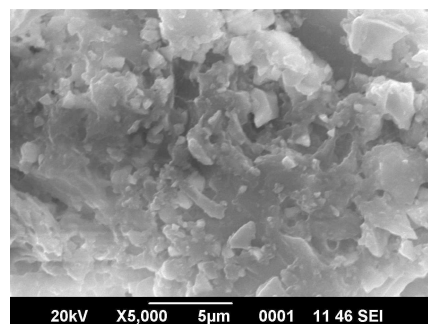
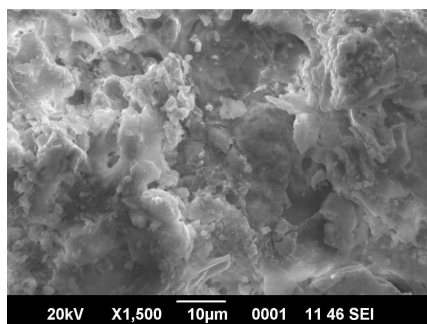


Fig 9 : SEM image of Schiff base complex of Th(IV) in ethanol Fig :10 SEM image of powder sample of Th(IV) complex

X-ray Diffraction Analysis:

The powder XRD of Zr(IV) complex was performed. The diffractogram is given in Figure(11) . The grain size of the complex was calculated using Scherrer’s formula. The calculated grain size is 1.69 nm. This values suggested the crystals of the Zr(IV) complex is in nano size^[21]. This value is closely in agreement with SEM images of the above complex.

Table 5. Grain size of the Complexes

Complex	Grain size(nm)
[Zr(NO ₃) ₂].2H ₂ O	1.690

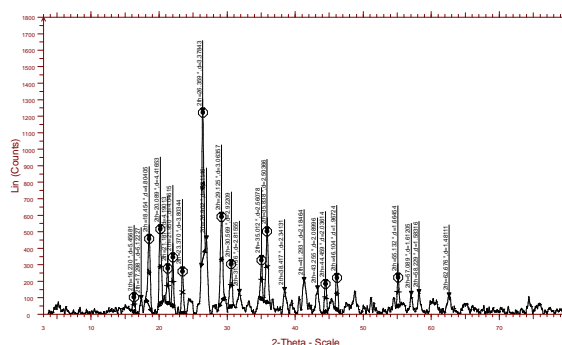


Figure : 11 XRD Structure of Zr(IV) complexes

Antibacterial activity:

Antibacterial activities of the ligand complexes and standard drugs were screened by the disc diffusion method in DMSO as solvent explained. The results of antibacterial study is given in table. The antibacterial activity was estimated based on the size of inhibition zone in the discs. Under identical conditions the Schiff base complexes have moderate anti bacterial activities against these bacteria. The results of antibacterial activity substantiate the findings of earlier researcher^[22] The biologically inactive compounds become active and less biologically active compounds become more active upon coordination^[23] such enhancement in biological activity of metal complexes can be explained on the basis of overtones concept of cell permeability, the lipid membrane that surrounds the cell favours the passage as only lipid soluble materials due to which lipophilicity is an important factor that controls antimicrobial activity. On chelation, the polarity of the metal ion is reduced to a greater extent due to overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π -electron over the whole chelate ring and enhanced lipophilicity of the complex^[24]. This enhanced the lipophilicity in turn enhances the penetration of the complex in to lipid membranes and blocking of metal binding sites on the enzymes of the micro organisms. The metal complex may also be a vehicle for activation of the ligand as the cytotoxic agent. More over, coordination may lead to significant reduction of drug resistance. Also other factors such as solubility, conductivity and dipole moment may also be among the possible reasons causing enhancement of bactericidal activity of the metal complexes as compared to the uncomplexed Schiff base compound.

Table :6 Antibacterial activity data of complexes

Complex	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>Klebsiella pneumoniae</i>	<i>Staphylococcus aureus</i>	Chloramphenicol
[ZrL(NO ₃) ₂]2H ₂ O	7.5	6.0	8.0	6.0	25
[ThL(NO ₃) ₂]2H ₂ O	6.0	6.5	6.0	9.2	22

1-6.0 less active

Antifungal activity

Schiff bases possess effective antifungal activity. Presence of methoxy, halogen and naphthyl groups enhance fungicidal activity towards *Candida albicans* pyranone Schiff bases show physiological activity against *A. niger*. Some Schiff bases of quinazolinones show antifungal activity against *Candida albicans*, *Trichophyton rubrum*, *A. niger*^[25].

Table 7 Antifungal activity data of complexes

Complex	<i>Candida albicans</i>	Nystatin
[ZrL(NO ₃) ₂]2H ₂ O	6.0	6.0
[ThL(NO ₃) ₂]2H ₂ O	16.0	6.0

CONCLUSION

Schiff base metal complexes of Zr(IV) and Th(IV) were synthesized from cardanol using 4-aminoantipyridine were clearly described and characterized on the basis of analytical and spectral data of which the UV-Visible and IR spectral studies indicated the geometry of complexes. Based on the study all the complexes are hexacoordinated. Metal ion intake explained that they can be effectively used for extraction of metal ion from water. The SEM, XRD, studies revealed the complexes are nano crystalline in nature. The SEM studies also confirmed the nano crystalline nature of the complexes. The antibacterial activity revealed that Zr(IV) complex have more antibacterial activity than other complex. The antifungal activity revealed that Th(IV) complex have more antifungal activity than other complex.

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