

# Synthesis, characterization and biological activity of Cardanol bridging ligands with Schiff base metal complex Zirconium (IV) and Thorium (IV)

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## Abstract

The Schiff base ligands (L1) and (L2) were prepared from the Cardanol 'C15' aliphatic unsaturated compound that naturally contains substituted phenol derived from CNSL (Cashew Nut Shell Liquid) and P-toluidine. Moreover, the ligands were characterized by SEM elemental analysis, IR, UV spectra. The Zr(IV) and Th(IV) complexes of the ligands L1 and L2 were prepared and characterized by the analytical and spectroscopic methods. Spectral report from UV-visible provides structural information of these complexes. The IR spectra specify the location of the nitro imino group and M-N bonds. The SEM analysis revealed the nanocrystalline nature of the complexes. The findings from antimicrobial activity presented that the Zr(IV) and Th(IV) complexes involve moderate activity. The ion metal intake displays that the ligand can be expressed for the separation of these ions metals from water molecules.

**Keywords:** Cardanol, Cashew Nut Shell Liquid (CNSL), P-toluidine

## 1. Introduction

DFMPM is derived from the natural source of Anacardium Occidentale (L) plant nut shell oil. It is otherwise known as cardanol which is a distinctive by-product of the cashew nut small and large scale industry prepared or manufactured from the CNSL obtained by vacuum distillation process [1]. Cardanol, a distillate of CNSL varies in its reactivity with formaldehyde and is used for the improvement of substituted phenolic resins and numerous other valuable industrial products. Bis(3-pentadecenylphenol) methane (BPPM) was prepared by the reaction between cardanol and formaldehyde in the equimolar ratio in the presence of 3% hydrochloric acid solution at 90-95°C for 2hours. The phenolic group of BPPM was converted to

diglycidylether with epichlorohydrin, which on therapy with DFMPM (di- $\alpha$ -formylmethoxy bis(3-pentadecenylphenyl) methane) and sodium periodate was obtained [2].

The CNSL derived cardanol based Schiff complexes can accommodate the various metal orientations including multiple coordination techniques, thereby allowing effectively synthesized along with hetero and homo metallic complexes based on its stereochemistry. Characterization and synthesis of Schiff base metal complexes are much familiar throughout the field of coordination Chemistry [1]. While Schiff base ligand plays a significant role as tetradentate Schiff base ligand, have a maximum potential of coordination with various metal ions for forming stable compounds [3]. With the preparative accessibility and potential biological properties, it is the Schiff bases with O and N donor that attracted substantial attention towards the coordination Chemistry [4]. Schiff base ligand formed Schiff base metal complexes with transition metal salts at their natural pH. The formation of a Schiff base intermediate in reactions of biological significance is well documented [2]. The present investigation involves the synthesis, characterization and biological activity of cardanol bridging ligands with Schiff base metal complexes of Zirconium(IV) and Thorium(IV).

Anusha et al. [5] investigated that the 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 antifungal and antibacterial agents. Schiff base can accommodate different metal centres involving various coordination methods thereby allowing successful synthesis of homo and hetro metallic complexes with various stereochemistry. Metal complexes of nitrogen-oxygen chelating

agents derived from 4-aminoantipyridine have been studied.

Borisova et al. [6] had been examined the Schiff bases of cardanol based metal complexes of N-O<sub>2</sub> chelating agents are derived from the natural source of CNSL and its diverse spectrum activity towards the biological studies. Since the development and discovery of antibiotics are considered as the most influential and positive achievements of modern medical science especially as a prominent use for controlling fungal along with bacterial infections, the probable for further improvement of Schiff base complexes as antimicrobial agent for the treatment for enormous epidemic diseases. Tracing out the importance of Schiff base complexes as a part of our continuing study, the synthesis, characterization and biological investigation of Schiff base tetradentate ligand (DFMPMNA) derived from 2nitroaniline with di- $\alpha$ -formylmethoxybis (3pentadecenylphenyl) methane, i.e. (DFMPPM) is done to analyze the anticancer and its capability for DNA cleavage. Still, there is a little amount of work has been analyzed about this complex of ligand. Hence the current investigation designed the following objectives, initially synthesized and characterization of Cardanol bridging ligand and metal complexes Zr (IV) and Th(IV) by spectroscopic investigation of Electronic, UV-visible, <sup>1</sup>H NMR, IR and XRD techniques. Analyzed the metal complex product possessed biological activities like antifungal and antibacterial activity.

## 2. MATERIALS AND METHODS

### 2.1 Chemicals

All chemicals used were of the analytical grade (AR), and the purity of chemicals was checked by traditional tests like melting point, boiling point, thin layer chromatography, etc. They included Zirconium(IV), Thorium (IV), formaldehyde (Aldrich), Phenylhydrazine (Aldrich), L-valine (Aldrich),  $\alpha$ -naphthyl ammine (Aldrich), 3,3'-diaminobenzidine (Aldrich), L-phenylalanine (Aldrich) and Cardanol (Aldrich). The microanalytical data (C,H,N) were collected using a Perkin Elmer 2400 instrument. IR spectra were attained utilizing PE IR spectrum, Instrument model: System 2000. <sup>1</sup>H NMR spectrum was attained utilizing AMX-300MHz, FT NMR spectrometer. Conductance measurements were obtained utilizing systronics-305 conductivity meter. Electronic spectra of the ligands and its complexes were attained utilizing Perkins Elmer Lamda-25 UV-Visible spectrometer in the range of 200-1100 nm. Surface morphological investigations were attained utilizing JSM-5610 SEM.

### 2.2 Synthesis of DFMPM

Synthesis of bis (3-pentadecenylphenyl) methane (BPPM), diglycidylether of bis (3-pentadecenylphenyl) methane (DEBPPM), di- $\alpha$ -formylmethoxybis (3pentadecenylphenyl) methane (DFMPPM) was prepared as per the earlier method [7].

### 2.3 Synthesis of Schiff base ligand with DFMPM

The Schiff base ligand was prepared by the described methods [8, 9]. An equimolar ethanolic solution of DFMPM and P-touline were mixed and refluxed for about an hour. Pour the reaction product in ice, (1+2) Schiff base ligand was attained [10]. The precipitated yellow compound was filtered, washed with water and dried over unhydrous CaCl<sub>2</sub>. The crude sample was recrystallised from 50% absolute alcohol yield=62%. Melting point =223°C.

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

All the metal complexes were prepared by mixing an ethanolic solution of Schiff base ligands (L<sup>1</sup>-L<sup>5</sup>) with the corresponding aqueous metal salt solution of Zr(IV) and Th(IV) nitrate in 1:2 molar ratios. The following mixture was refluxed for about 12hr at 70-80°C [11], 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 90°C yield=60%.

#### Antibacterial activity

The in-vitro growth inhibitory activity of the complexes was tested against bacteria by disc diffusion technique using agar as nutrient [9]. The standard drug Gentamycin was dissolved in DMSO which acts as control was also tested at the same concentration under similar conditions to that of complexes. The liquid medium containing the bacterial subcultures were autoclaved for 20 minutes at 121°C at 15 lb pressure before incubation. The bacteria were incubated in nutrient broth at 37°C for 24hrs. The bacteria were injected into Petri dishes (100 mm x 70 mm) in the amount of 0.01 cm<sup>3</sup>; 15 ml of potato dextrose agar were homogeneously distributed into the sterilized Petri dishes. All the complexes were injected into an empty sterilized antibiotic disc having the diameter of 6mm in the amount of 30 ml. The complexes were dissolved in DMSO to a final concentration of 2000 ppm and soaked in filter paper. The Petri dishes were kept at 4°C for 2hrs and incubated at 25°C for 24hrs. The width of the growth inhibition zone around the disc was measured after 24 hours incubation, and the activity of each treatment was made in duplicate.

## 2.5 Characterization of Ligands

The structures of ligands will be predicted with the help of elemental analysis, electronic absorption spectra, NMR spectra, infrared spectra (IF).

<sup>1</sup>H-NMR spectra of the precursor were recorded on a Varian Gemini 2000 NMR with a proton frequency of 300 MHz, and deuterated chloroform was utilized as a solvent. FTIR spectra were attained on a Bomem Michelson MB100 FTIR spectrometer, with a deuterated triglycine sulfate detector. Thin films of precursors and polymerized sample composed of 50% wood flour were cast on a KBr plate and purged with dry air. At a spectral resolution of 4 cm<sup>-1</sup>, spectra of 64 scans of the films were collected.

To observe the polymerization of the precursor and samples after and before the heating, differential scanning calorimetry, TA Instruments DSC model 2920, was utilized. Samples, which were enclosed in hermetic aluminum pans with lids, were heated from 25-300°C at a heating rate of 10°C/min under N-purge at a constant flow rate of 62 mL/min.

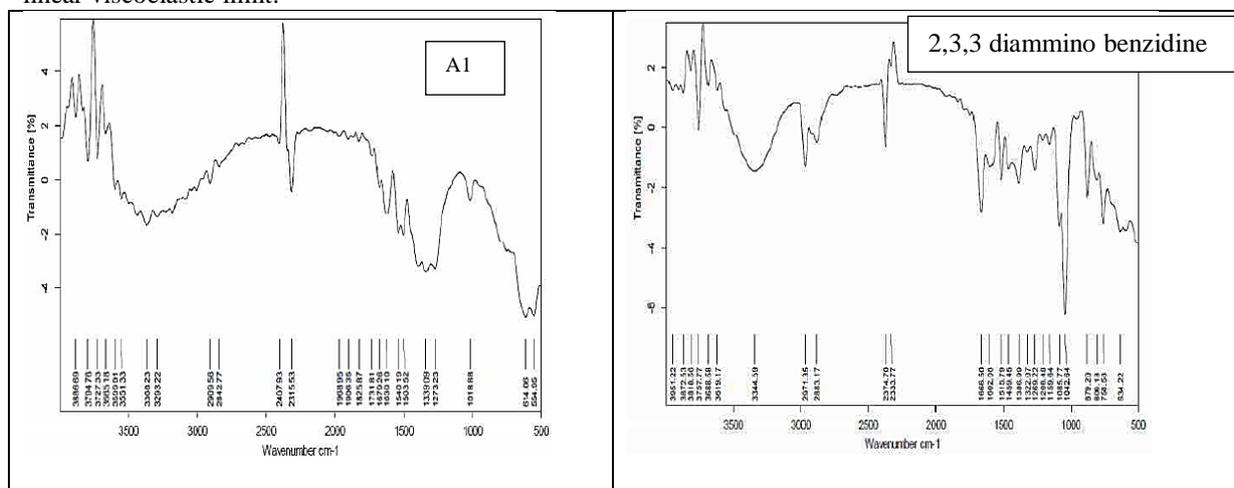
A TA Instruments Q500 Thermo Gravimetric Analysis (TGA) was utilized to examine the degradation temperatures. Samples were placed in an open platinum crucible and heated from 25-850°C at a heating rate of 10°C/min under a nitrogen purge at a constant flow rate of 32 mL/min.

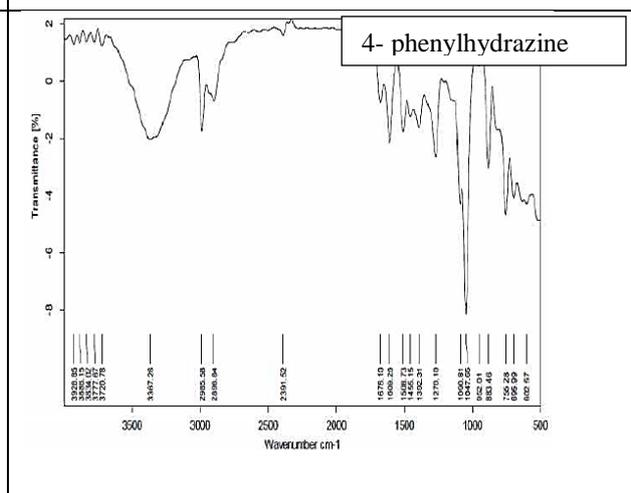
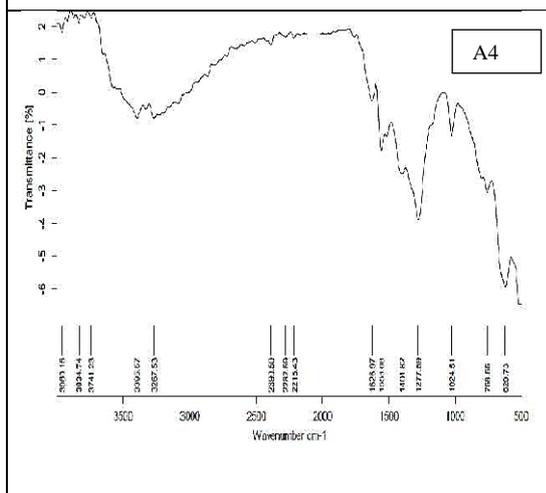
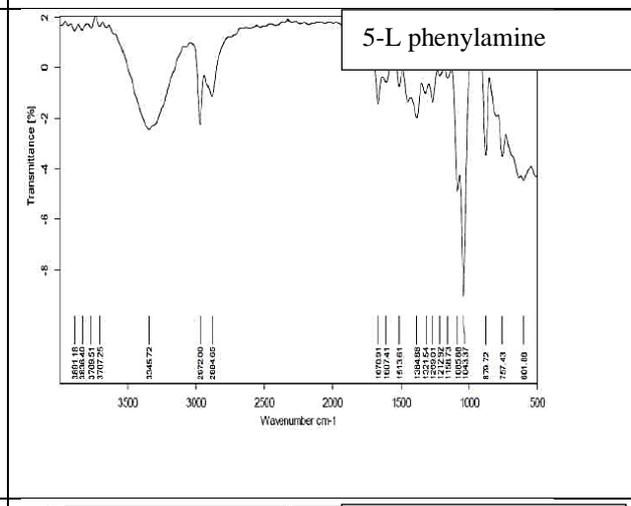
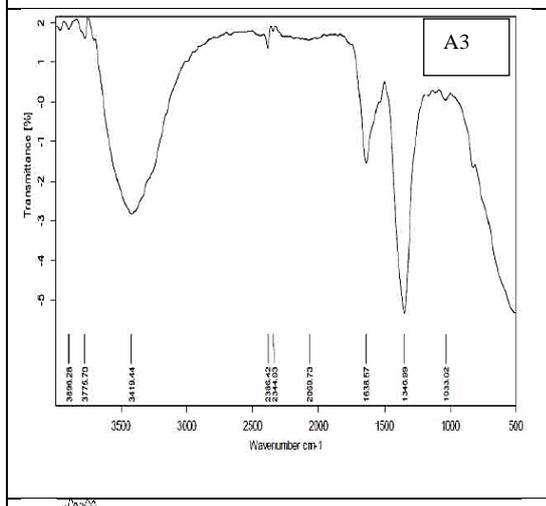
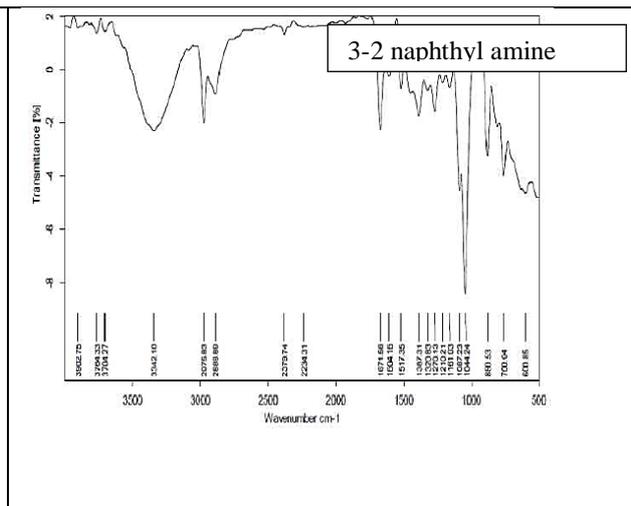
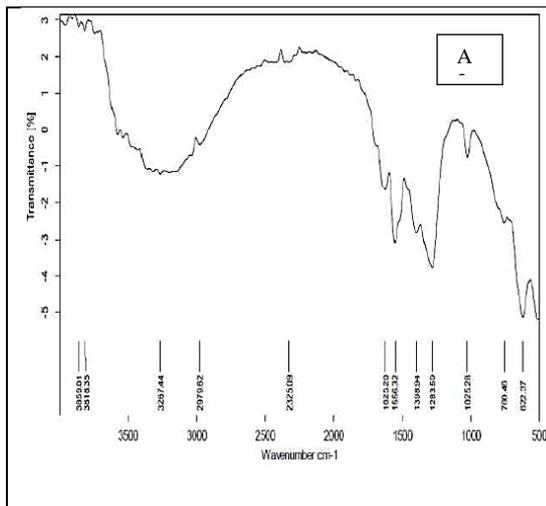
Dynamic mechanical analysis (DMA) was conducted on a TA instruments Q800 DMA with a heating rate of 3°C/min from 100 to 100°C at an operating frequency of 1 Hz. The deformation was within the linear viscoelastic limit.

## 3. RESULTS AND DISCUSSION

### 3.1 FTIR

Bands of IR spectra for selected ligand and its ion metal complexes are represented in Figure 1 (A1 to A5). The IR spectrum of free ligand is likened with that of complexes to determine the coordination sites that may have involved in chelation. Characteristic peaks in the spectra of the metal and ligand complexes were measured and compared. The IR spectrum of the ligand (L) shows characteristic bands at 2842 cm<sup>-1</sup>, 2909 cm<sup>-1</sup>, 1968 cm<sup>-1</sup> due to the  $\nu$ O-C,  $\nu$ C-H,  $\nu$ C=N respectively [12]. The IR spectra of the complexes exhibited ligand bands with suitable shifts because of their complex formation. The IR broad bands of metal complexes in the range of 2407 cm<sup>-1</sup> indicate the presence of co-ordinated or lattice water molecule [13]. The  $\nu$ C-O phenolic stretching frequency is observed around 2407-2379 cm<sup>-1</sup> which get shifted to lower or higher frequency region indicating co-ordination of phenolic oxygen. The band at 2315-2234 cm<sup>-1</sup> and 1679-1671 cm<sup>-1</sup> were assigned to C-H and C=N respectively [14]. The imine peaks in the metal complexes exhibited alterations in the ligand indicating coordination of the imine nitrogen atom to the metal ion due to coordination. Another absorption band at 880-768 cm<sup>-1</sup> are assigned to M-N bond, and 614-600cm<sup>-1</sup> is assigned to M-O bond [15].





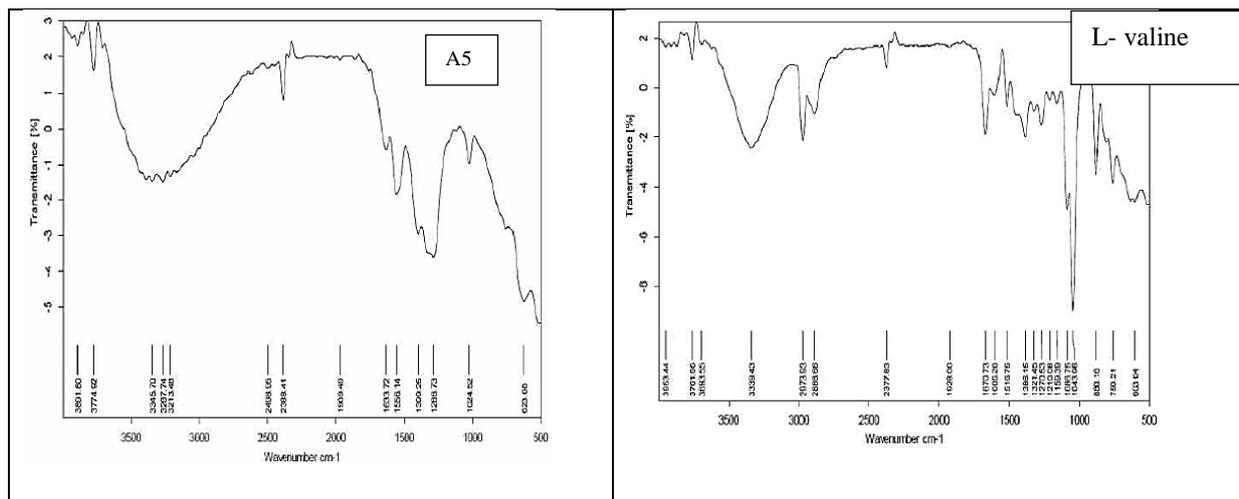
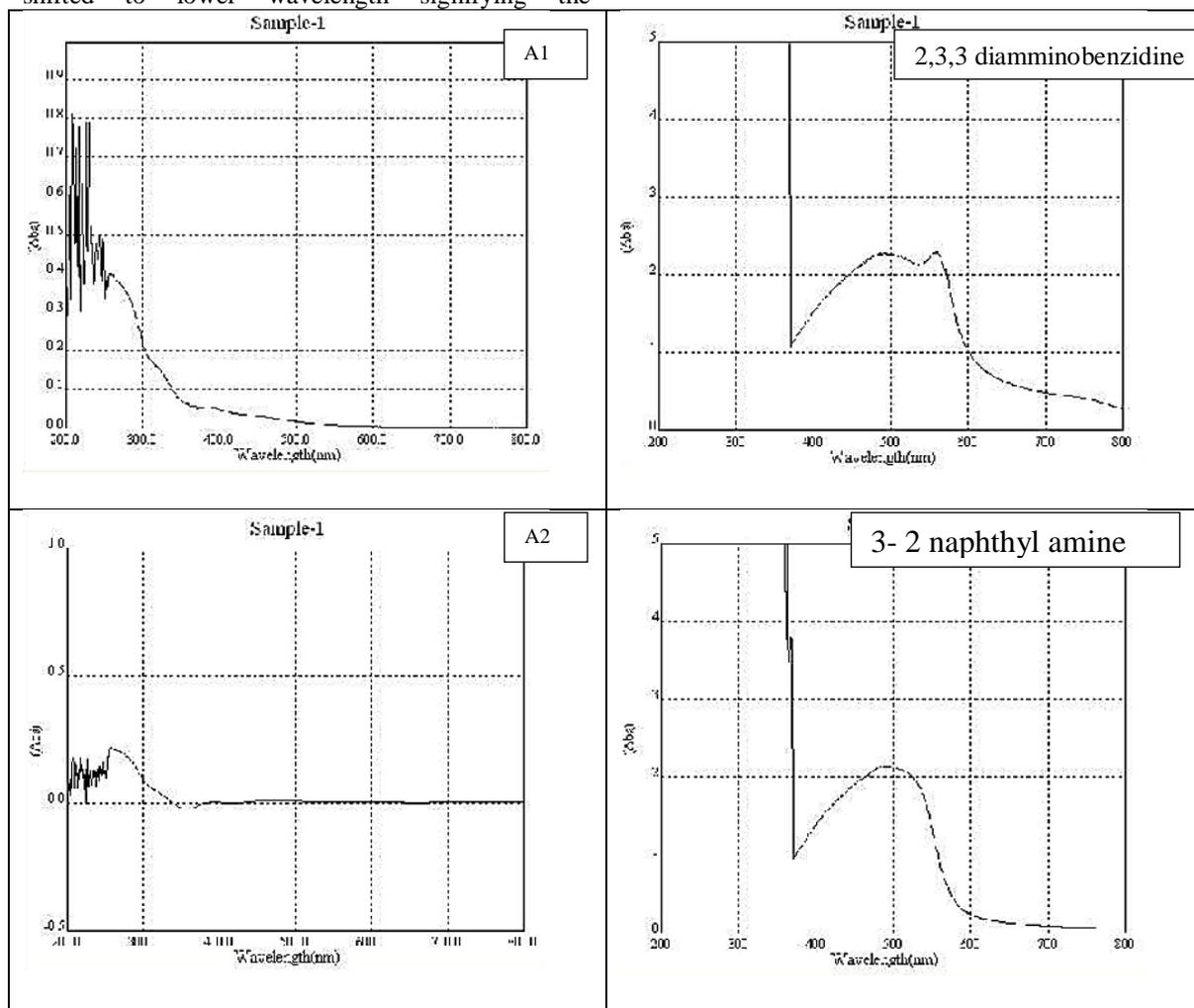


Figure 1: (A1-A5) FT IR frequencies ( $\text{cm}^{-1}$ ) of the ligand and its Zr (IV) complexes UV - Visible Spectra

The UV-visible spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation, and it is presented in Figure 2(A1 to A5). The ligand displayed broadband at 360 nm which is assigned to  $\pi-\pi^*$  transition of the C=N chromophore [16]. On complexation, this bond is shifted to lower wavelength signifying the

coordination of imine nitrogen with a central metal ion. The UV and visible spectra of the Zr(IV) complex displayed five absorption bands at 210nm, 219 nm, 230nm, 237nm and 276nm giving an octahedral geometry with field transitions.  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2B_{1g} \rightarrow {}^2E_{2g}$ , respectively.



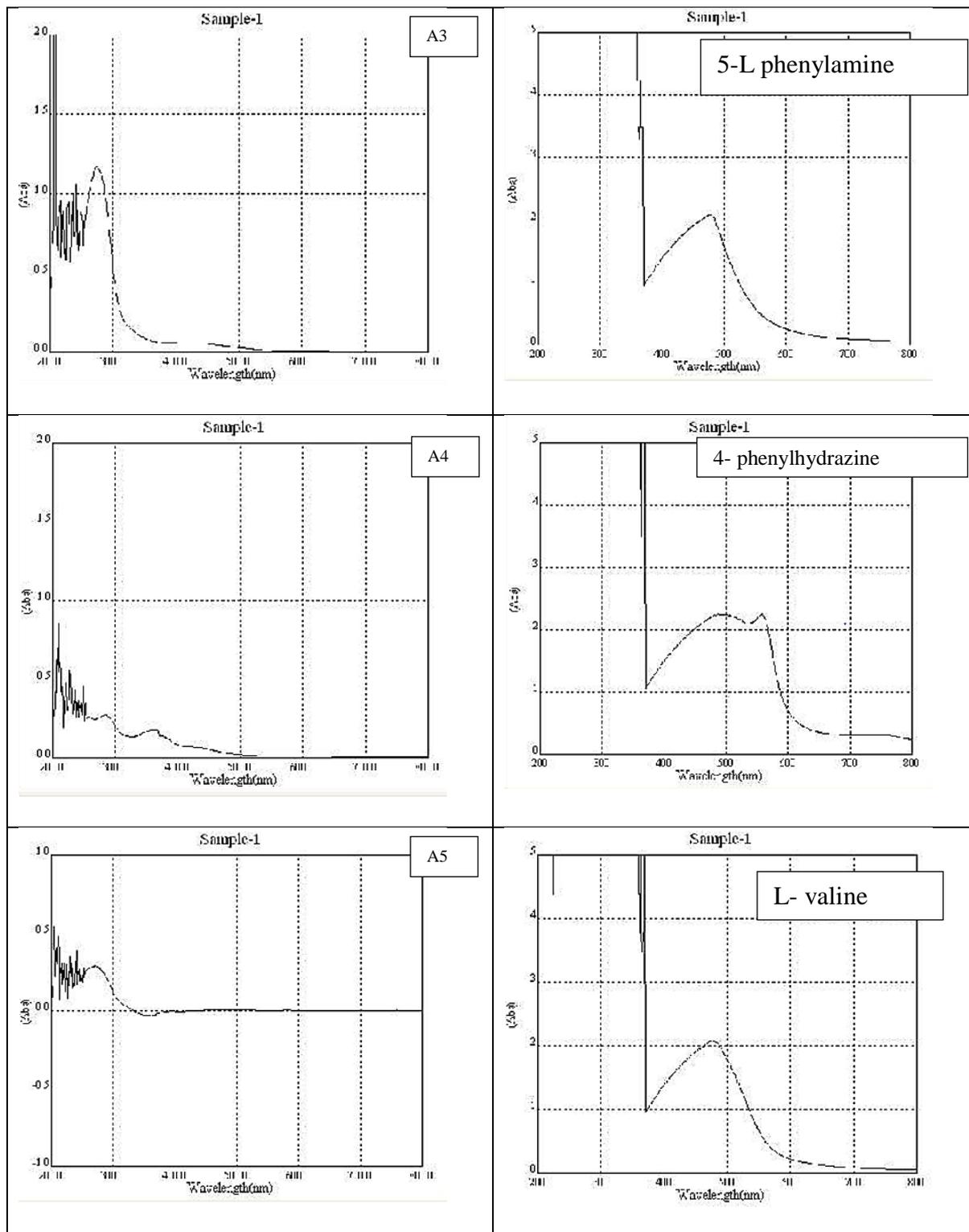
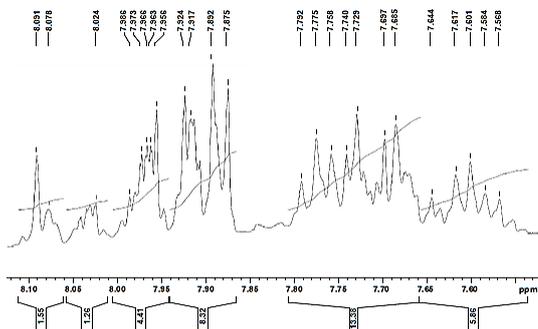
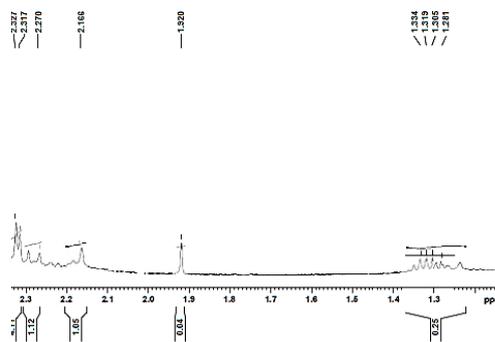


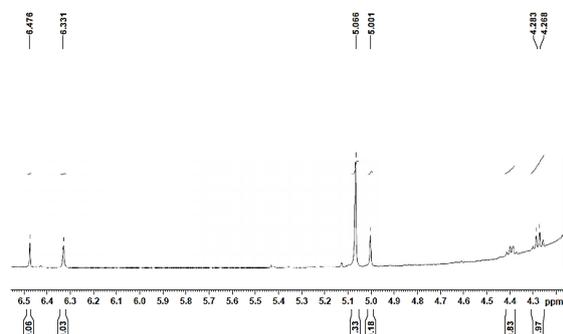
Figure 2: (A1-A5) Uv visible of the ligand and its Zr (IV) complexes NMR



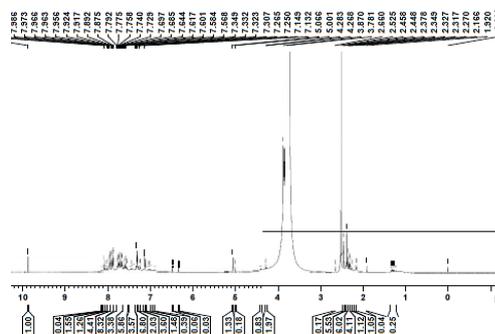
**Figure 3a: NMR spectra of the Zr (IV) ligand complexes**  
 On examining the <sup>1</sup>H NMR spectrum of ligand (Figure 3a), it exhibited a multiplet signed at  $\delta=8.091$ -  $\delta=8.078$  ppm which is due to substituted aromatic ring protons [17]. The presence of H - C = N- group is indicated by the singlet at  $\delta = 7.986$ ppm. The multiplet at  $\delta 7.792$  ppm -  $\delta= 7.729$  ppm and  $\delta = 7.617$  ppm -  $\delta = 7.568$  ppm were due to the olefinic protons of the side chain and - O-CH<sub>2</sub> -group of the ligand respectively [18].



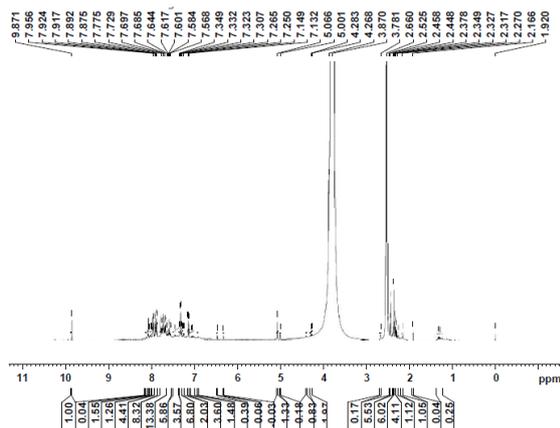
**Figure 3c: NMR spectra of the Zr (IV) ligand complexes**  
 The <sup>1</sup>H NMR spectrum of the Zr(IV) complex (Figure 3c), a singlet at  $\delta =2.456$  ppm-  $\delta = 2.166$  is due to substituted H-C-C=O- group and a singlet at  $\delta = 1.926$  ppm -  $\delta = 1.281$  due to substituted -CH<sub>2</sub>-NH group. Thus <sup>1</sup>H NMR investigation also confirms the binding of metal with Schiff base ligand through pyridine nitrogen and azo methane-nitrogen.



**Figure 3b: NMR spectra of the Zr (IV) ligand complexes**  
 The <sup>1</sup>H NMR spectrum of the Zr(IV) complex (Figure 3b), the presence of the H - C = N- group is indicated by the singlet at  $\delta = 6.476$  ppm which is due to the olefinic protons of the side chain and multiplet signed at  $\delta =4.283$  ppm- $\delta =4.268$  ppm is due to substituted aromatic ring protons. Thus <sup>1</sup>H NMR study also confirms the structural information of both ligand and its complexes.



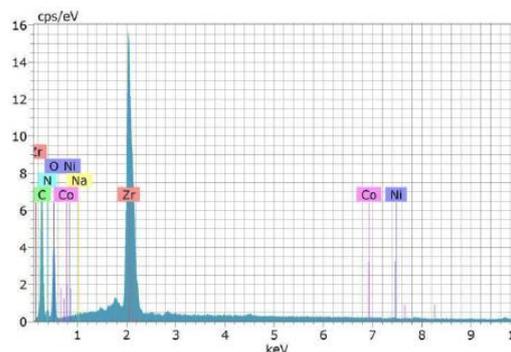
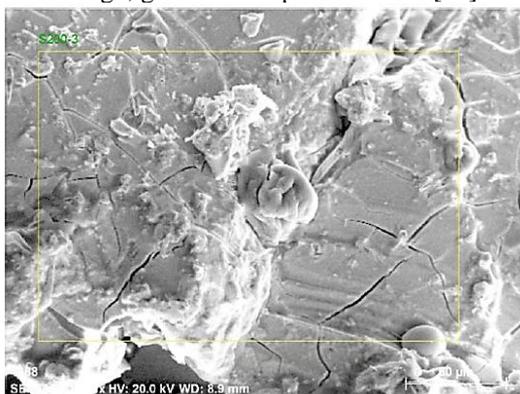
**Figure 3d: NMR spectra of the Zr (IV) ligand complexes**  
 The <sup>1</sup>H NMR spectrum of the Zr(IV) complex (Figure 3d), the presence of the H - C = N- group is indicated by the singlet at  $\delta = 7.568$  ppm it is due to the olefinic protons of the side chain and multiplet at  $\delta = 7.149$  -  $\delta =7.132$  ppm due to - O-CH<sub>2</sub> -group. A multiplet at  $\delta =2.458$ -  $\delta =2.448$ ppm is due to substituted H-C-C=O- group and a singlet at  $\delta = 1.920$ ppm due to substituted -CH<sub>2</sub>-NH group.



**Figure 3e: NMR spectra of the Zr (IV) ligand complexes**  
 The <sup>1</sup>H NMR spectrum of the Zr(IV) complex (Figure 3e), the presence of H – C = N- group is indicated by the singlet at  $\delta = 7.875$  ppm it is due to the olefinic protons of the side chain and a singlet at  $\delta = 7.214$  ppm due to O-CH<sub>2</sub> -group. A singlet at  $\delta = 2.660$  ppm is due to substituted H-C-C=O- group and a singlet at  $\delta = 1.920$  ppm due to substituted -CH<sub>2</sub>-NH group.

### 3.2 SEM Analysis

The surface morphology of the complexes was examined utilizing a JSM 5610 SEM. The SEM images of Zr(IV) complex are presented in figure 4. The SEM images displayed that the complex is microcrystalline in nature. Careful investigation of the single crystal specified the nanoscale size of the single crystal of the complexes. The SEM images showed that all the complexes are nanocrystalline showed rough, granular and pitted surface [19].



**Figure 4: SEM image of Powder Sample of Zr (IV) elemental**

Microanalysis of carbon and nitrogen contents present in the samples were recorded. By using SEM primary electron beam that is responsible for the release of an electron from the elements that creates up the specimen upper layers. The emitted electrons are gathered, and the amplified motion is exhibited on a tubular cathode ray. By scanning the primary electron beam across the specimen's surface in synchronization with the cathode ray tube, it is probably to convert the emitted electrons into an image of the specimen for display in the Figures.4.

### 4. CONCLUSION

Schiff base metal complexes of Zr(IV) and Th(IV) were synthesized from cardanol using 4 P-toluidine were clearly defined and characterized from spectral and analytical data of which the UV-Visible and IR spectral studies specified the geometry of complexes. Elemental analysis displays the metal to ligand ratio is 1:2. Conductivity measurements show that all complexes are non-electrolytes. Based on the study all the complexes are hexa-coordinated. Metal ion intake explained that could be efficiently utilized for the extraction of metal ion from water. The SEM, revealed the complexes are nano-crystalline in nature. The SEM studies also confirmed the nanocrystalline nature of the complexes. The antibacterial activity revealed that Zr(IV) complex have more antibacterial activity than other complexes. The antifungal activity revealed that Th(IV) complex have more antifungal activity than other complexes.

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