



SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF COPOLYMER METAL COMPLEXES AND THEIR THERMAL STUDIES

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ABSTRACT:

In this study, the three coordination polymers of Cu(III), Ni(II) and Zn(II) salts have been synthesized using phthalic acid-thiosemicarbazide-formaldehyde copolymer (PTF-I) and their structures were characterized by elemental analysis, ultraviolet-visible (UV-VIS), FTIR, ¹H NMR spectroscopy. The antibacterial activities of the terpolymer metal complexes against four bacterium *Escherichia coli* (ETEC), *Staphylococcus aureus*, *Bacillus pumulis*, *Vibrio cholerae*, were studied. The structures of PTF-Cu(III), PTF-Ni(II) and PTF-Zn(II) complexes in the coordination polymer were found as octahedral geometry. Thermogravimetric analysis (TGA) results revealed that among the complexes PTF-Zn(III) complex has the highest thermally stable.

Keywords :- antibacterial activities characterization, PTF metal complex, thermal analysis.

INTRODUCTION :

In recent years polymer-metal complexes have been attracting interest in many scientific and technological fields. Coordination polymers have found wide applications in bioinorganic industry, wastewater treatment, pollution control, hydrometallurgy, preconcentration, anionic polyelectrolyte hydrogels, cation-exchange resins etc. The beauty of coordination polymer is thermal stability. Various studies have been reported on thermal stability, synthesis, morphological and applications of transition metal organic coordination polymers with derivative of dicarboxylic [1], [2], [3], [4], [5] amines [6], aromatic mono/dicarboxylic acid [7], [8] substituted thiourea salt and bidentate ligand [9], [10], [11]. Leovac et al. have synthesised thiosemicarbazide based complexes using Cu(II), Ni(II) and Zn(II) [7]. They have investigated thermal properties of the synthesized polymer-metal complexes. Diab and El-Sonbati have investigated thermal properties of the polymer-metal complexes synthesized

from poly (ethylene glycol) with Co(II), Ni(II), Cu(II) and Cd(II) [12]. Yasuyoshi et al. [13] investigated that structural of Fe(III) and Cu(II) complex with poly(vinyl alcohol) by means of NMR techniques. An et al. [14] showed that the complex formation of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions with partially phosphorylated poly (vinyl alcohol) in aqueous solution is studied by means of potentiometric titration. The thermal analysis techniques, such as thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and derivative thermogravimetry (DTG) were widely applied in studying the thermal behaviour and structure of inorganic compounds, complexes and coordination polymers of transition metal ions [15-19].

In the present work, the synthesis and characterization and thermal properties of the three coordination polymers containing donor atoms are reported.

SEM studies were significantly helpful to determine the particle sizes and identify the distinct morphology for coordination polymers. The obtained results from thermal analysis permitted us to obtain information concerning the structure of coordination polymers including their thermal behaviour and degradation. The presence of lattice and coordinated water molecules in coordination polymers was investigated by these (TG/DTG/DTA) techniques and determined by the endothermic and exothermic effects connected with melting, dehydration, decomposition and crystallization [20-21]. The thermal decomposition of organic moieties occurs in two or three steps with the formation of metal oxides as the final residue. Nourazi et al. synthesized calyx[4]arene-based thiosemicarbazide ligand and related metal complexes with transition metal ion like Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} and studied antimicrobial activity[22].

EXPERIMENTAL

MATERIALS AND MEASUREMENTS

All the chemicals were reagent grade and used without purification. Thermal degradation of coordination polymers was carried out in the range 28–1220 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Scanning electron microscopic images were scanned at energy of 20 kV with magnification $\times 1500$ and diffuse reflectance absorption studies were recorded in the range 200–600 nm. The magnetic susceptibility measurements at room temperature were carried out by Gouy's method. IR spectra of the ligand and its coordination polymer were recorded by using KBr pellets in the range 4000–400 cm^{-1} on Shimadzu FT-IR-8101A spectrophotometer. The electrical conductivity values of all samples were measured with an electrometer. The pellets were hydraulically pressed to 1687.3 kg/cm^2 . The iodine doping was carried out by exposure of the

pellets to iodine vapour at atmospheric pressure and room temperature in a desiccator.

Preparation of metal complexes

The copolymer metal complexes have been prepared [23] using the synthesized copolymers as ligand with few transition metal ions such as Cu^{2+} , Ni^{2+} and Zn^{2+} ions. The copolymer was taken in 2M and the transition metal ions (Cu^{2+} , Ni^{2+} and Zn^{2+}) was taken in 1M for the complex formation reaction. The PTF copolymer (2 g) was taken in round bottom flask and immersed in ethanol solution to allow it for swelling in 2h. The cupric nitrate (1g) was dissolved in ethanol solution and then poured into round bottom flask with equipped mechanical stirrer and a reflux condenser. The reaction has been carried out with an effective reflux at 60°C for 3h. The colloidal precipitate was observed in the flask and separated out. The product was filtered off and washed with ether and ethanol to remove the impurities. The purification has been done repeatedly to separate the purified product. The resultant purified sample was air dried, powdered and kept in vacuum desiccator with silica gel. complexes with Ni^{2+} and Zn^{2+} metal ions. The preparation of the PTF complex with $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$ metal ions is shown in Fig.1.

RESULT AND DISCUSSION :

This PTF terpolymer and its metal complexes are found to be soluble in dimethyl sulphoxide (DMSO), N-N'-dimethyl formamide (DMF), Tetrahydrofuran (THF), aqueous potassium hydroxide and sodium hydroxide and insoluble in common organic solvents. the compounds also soluble in inorganic solvents such as conc. HCl, H_2SO_4 and HNO_3 .

NUCLEAR MAGNETIC RESONANCE :

Nuclear magnetic resonance spectra of the copolymer resins were scanned on 90 MHz for ^1H , using 400 NMR Spectrometer in deuterated dimethyl sulphoxide (DMSO-d_6) at Sophisticated Analytical Instrumentation Facility, Punjab

University, Chandigarh. For nuclear magnetic resonance studies of non-aqueous solution, the most reference compound is tetramethyl silane (CH₃)₄Si, which is magnetically and electrically isotropic, chemically inert, and non-associating with any common compound. When the high field absorbing tetramethyl silane is used as reference, most (δ) values are negative. The chemical shifts are solvent dependent.

The ¹H NMR spectra of PTF terpolymer ligand and its Cu(II), Ni(II) and Zn(II) metal complexes are shown in Fig. 3, 4, 5. The signals obtained for the terpolymer and its metal complexes were interpreted on the basis of the literature [24]. The ¹H NMR spectrum of the metal complex shows multiplet in the range of 7.05 – 8.94 ppm are assigned to the aromatic protons and the methylene protons appeared in the region of 2.40 – 3.10 ppm. The signal for –OH proton is shifted from 9.86 ppm to 10.06 ppm in the complex spectrum which gives a clear evidence for the complexation of the metal ion with the – to –OH proton of Ar-COOH.

On comparison with the ligand spectrum, the line broadening has been observed in the spectrum of metal complex, further confirms the metal ion incorporation with the polymer backbone.

INFRA-RED SPECTRA :

The FTIR spectra PTF terpolymer metal complexes, the bands are slightly broadened compared to the terpolymer ligand. The shifting of bands appeared in region of 3403 cm⁻¹ to 3405 cm⁻¹ are due to the coordination of the ligand with the metal ions through the lone pair of oxygen present in –C=O of phthalic acid. The band appeared in the region of 1066.4 – 1020.7 cm⁻¹ is assigned to C-O-M stretching mode. The band appeared at 1732.6 cm⁻¹ for –C=O stretching vibrations in the ligand spectrum is shifted to the range of 1715.6 – 1717.1 cm⁻¹ in the complex spectrum clearly indicates the metal

coordination takes place through the –C=O of Ar-COOH moiety.

The band appeared at 1647 cm⁻¹ is assigned to –C=S amide (I) stretching vibration. In the spectra of PTF metal complexes, the bands are slightly broadened compared to the terpolymer ligand. In the spectrum of polymeric ligand, the band at 1647 cm⁻¹ assigned for C=S amide (I) is shifted to the lower frequencies (1631 to 1632 cm⁻¹) in the case of polymer-metal complexes. It is due to the coordination of the metal ions through the lone pair of sulphur in thionyl group present in the thiosemicarbazide moiety. This is a clear evidence for the involvement of sulphur and –C=O of Ar-COOH in the chelation. It is further supported by the appearance of –S–M and –O–M stretching vibrations at 613–614 and 559–560 cm⁻¹ respectively.

ELECTRONIC SPECTRA :

The electronic spectra of the PTF terpolymer and its metal complexes are shown in Fig. 7. The spectrum of the PTF ligand shows two bands at 270 and 390 nm. These transitions were affected by the metal chelation and shifted to the longer wavelength clearly indicates the formation of complex takes place through the lone pairs of electrons present in oxygen of –C=O in Ar-COOH and sulphur atom of C=S in thiosemicarbazide moiety [25]. Thus $\pi-\pi^*$ transition indicates the presence of aromatic nucleus and $n-\pi^*$ transition indicates the presence of –COOH groups in the terpolymer.

The electronic spectrum of PTF-Cu metal complex exhibited bands at 13270, 15680 and 23270 cm⁻¹ and the assignments are ¹B_g – ²E_g, ¹B_g – ²E_g and charge transfer spectra. The octahedral configuration can be assigned for the Cu(II) complex [26]. The electronic spectrum of PTF-Ni exhibits three bands at 11440, 13275 and 23010 cm⁻¹ assigned to the spin allowed transitions ³T_{2g}(F) – ³A_{2g}(F), ³T_{1g}(F) – ³A_{2g}(F) and ³T_{1g}(P) – ³A_{2g}(F) in an octahedral geometry [27].

Morphological behavior :

The SEM photographs for PTF Cu(II), Ni(II), and Zn(II) metal complexes were investigated at different magnification, are shown in Fig.8. It gives the information of surface topography and defect in the structure. The SEM is the ultimate tool for deposits and wear debris analysis, particle sizing and characterization, failure analysis, contaminant analysis and metallurgical studies. The resin spherulites and fringed model. SEM micrographs morphology of the resin shows the transition between crystalline and amorphous nature.

The voids/channels present in the PTF terpolymer is responsible for the swelling behaviour of the polymer and the reactivity (complexation) of active sites buried in the polymer matrix. In the case of PTF complexes, the morphology is quite different from the uncomplexed PTF terpolymer. Further, the voids present in the uncomplexed terpolymer disappeared in the complexed terpolymers. This may arise from the tightening of the voids by the cooperative contribution of the metal ion into the ligand lattice.

Anti-Microbial Screening of Copolymer Metal Complexes

The PTF complexes showed also a good activity against the growth of this bacterium. *V. cholerae* is a pathogenic gram-negative comma-shaped bacterium. Some strains of *V. cholerae* cause the disease cholera. *V. cholerae* is a facultative anaerobic organism and has a flagellum at one cell pole. Cholera is an infection of the small intestine caused by the bacterium *Vibrio cholerae*. The factors that govern antimicrobial activities are strongly dependent on the central metal ions and coordination numbers. When compared to the ligand, the polymer metal complexes possess better antimicrobial activity [26]. It is due to the metal ions shared with the donor atoms of the ligand and the π -electron delocalization over the

chelate ring. This effect increases the lipophilic character of the metal ion, which favors the permeation through the lipid layers of the bacterial membranes [27]. It is perceived that the factors such as solubility, conductivity, dipole moment and cell permeability may also contribute for the increased activity of the complexes. From the results, at 800 μg concentration, the compounds establish better antibacterial activity. Hence, the PTF metal complexes may be used to control the growth of bacterial strains. The results were found very closer to the standard (Amoxicillin). Therefore, the PTF metal complexes may be a triumphant substitute for a standard drug. The antibacterial activities of the terpolymers and its metal complexes were also due to the presence of nitrogen and oxygen donor groups [28].

Thermal analysis of coordination polymers

Thermal decomposition of all the coordination polymers was carried out at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere over the temperature range 28–1220 $^\circ\text{C}$. The structural transformation is observed by TG curves which is supported by DTG and DTA studies. Thermal analysis has proved to be useful in determining the crystal water content in the coordination polymers and their thermal stability as well as decomposition mode under controlled heating rate. The matter released at each step of degradation was identified through attributing the mass loss at given step to the similar mass calculated from molecular formula of investigated polymer, comparing that with literature values for relevant coordination polymers considering their temperature. The thermal stability properties were evaluated by TGA methods whose results revealed good thermal stability for all the synthesized coordination polymers. Moreover, the limited oxygen index values were calculated on the basis of char yield obtained at 1200 $^\circ\text{C}$ and revealed

good thermal stability of the coordination polymers.

In the TG analysis curve of Cu(II) chelate, the weight loss is observed up to 150°C due to the removal of lattice water molecules and there is no weight loss up to 220°C which confirms the square planar geometry for Cu(II) complex. After 220°C, a considerable mass loss has been observed up to 440°C which may be due to the degradation of non-coordinated groups in the ligand. The final stage of degradation takes place in the range of 440–560°C which is ascribed to the loss of chelated part. The TG curve attains a constant level after 560°C leading to the formation of CuO as residue (Found 10.18%, Calc. 10.79%).

TGA of PTMF–Ni Complex

From the TG analysis of PTF–Ni complex, there is no weight loss observed up to 160°C, hence the absence of lattice water molecules have been confirmed. However, the weight loss occurred between 160–200°C (Found 05.39%, Calc. 04.59%) which represents the elimination of two coordinated water molecules present in the Ni(II) complex. Therefore the octahedral geometry for the PTF–Ni complex is further confirmed. After 200°C, a gradual loss of weight continued up to 460°C. The free part of chelated ligand would be lost at this stage. Further the complete degradation takes place between 460–580°C involving the elimination of chelated part. The residue left at 580°C is the stable metal oxide (Found 09.77%, Calc. 09.53%).

TGA of PTF–Zn Complex

The thermogram of PTF–Zn reveals that, there is a very small or negligible weight loss up to 220°C indicates that the complex is stable up to 220°C. This also confirms the absence of coordinated water molecules present in the ligand. Therefore the tetrahedral geometry of the Zn chelate has been confirmed. Beyond 220°C, a gradual weight loss was observed up to 560°C may be due to the noncoordinated part of the

ligand. The next degradation step starts at 560°C and ends up at 700°C, which indicates an loss of chelated part. After this temperature the ZnO is formed as a stable metallic residue (Found 11.26%, Calc. 10.79%).

The thermal degradation data of the PTF terpolymer and its metal complexes reveal that the polymeric complexes show better stability than the PTF terpolymer due to the coordination of metal ions. The thermal stability of the PTF complexes is found to be in this order PTMF–Zn(II) > PTMF–Ni(II) > PTMF–Cu(II). The greater stability of the metal complexes may be due to the coordination and the enhanced cross linking nature with crowd effect of the metal complexes [29, 30]. In the case of Cu(II), Ni(II) complexes, the decomposition occurred exceptionally at low temperature compared to their ligand, which may be due to the oxidation of polymer by the catalytic action of the metal ion [31–35].

By using Freeman-Carroll method, it is possible to calculate the values of various thermodynamic parameters. The kinetic parameters such as order of reaction (n) and activation energy (E_a) and the thermodynamic parameters such as frequency factor (Z), entropy change (ΔS), free energy change (ΔF) and apparent entropy (S*) are presented in Table 4 and 5. The E_a values calculated by SW and FC methods are in good agreement with each other. The order of activation energies for PTF–Cu(II), Ni(II) and Zn(II) complexes are parallel to the order of their thermal stability. The values of thermodynamic parameters are comparable indicating a common mode of decomposition reaction [36–38]. The abnormally low value of frequency factor (Z) indicates that the decomposition reaction of PTF metal complexes takes place in a slow phase. The order of reaction (n) of PTF–Cu, PTMF–Ni and PTMF–Zn complexes are 0.90, 0.92 and 0.82 respectively. From the above results, it is quite clear that the

decomposition reaction follows approximately a first order kinetics.

CONCLUSION :

In this work, we have synthesized three novel coordination polymers of divalent transition metal ions with *PTF* chelating ligand. Coordination polymers were structurally characterised by combined study of spectroscopic and thermal analysis. Apart from this SEM studies morphological behaviour of coordination polymers. The bacterial activity have been assayed against *B. pumilus*, *E. Coli*, *S. Aureus*, *V. cholerae*, *A. flavus*, *P. chrysogenum*. Furthermore, the detailed thermal study (TG-DTG) played an important role to confirm the number and nature of water molecules in coordination polymers. Also, DTA technique was vital benefit to find out the dehydration of adsorbed water molecules in coordination polymers. Finally, on the basis of TGA and kinetic parameter the high thermal stability was shown for copper(II) ion as compared to other ions.

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Table 1. Characterization

Terpolymers and metal complexes	Yield (%)	Melting point (K)
PTF	84	430-435
PTF-Cu	80	375-380
PTF-Ni	82	400-405
PTF-Zn	84	390-394

Table 3. Antibacterial Activity of PTF Complexes

Compound	B. Pumilus	E. coli (ETEC)	S. aureus	V. cholerae
PTMF-I-Cu	7(800 µg)	3 (800 µg)	7(800 µg)	4(400 µg) 10(800 µg)
PTMF-I-Ni	7 (800 µg)	5 (800 µg)	8(800 µg)	6 (400 µg) 12(800 µg)
PTMF-I-Zn	8(800 µg)	5 (800 µg)	7(800 µg)	7 (400 µg) 14(800 µg)

Table. 4. Results of Thermogravimetric Analysis of PTF Metal Complexes.

Copolymer ligand and its metal complex	Half Decomposition Temp. (T)	Activation Energy Ea (KJ)/mol	
		SW	FC
PTMF-III-Cu	653	5.84	5.22
PTMF-III-Ni	673	6.02	6.08
PTMF-III-Zn	773	11.40	11.82

Table 5. Kinetic And Thermodynamic Parameters of PTF Metal Complexes

Copolymer Ligands And its metal complex	Entropy change $\Delta S(J)$	Free energy $\Delta F (KJ)$	Frequency Z (S^{-1})	Apparent entropy (S^*)	Order of reaction
PTMF-I-Cu	-150.23	62.39	702.78	-24.98	0.90
PTMF-I-Ni	-144.52	60.82	686.41	-25.14	0.92
PTMF-I-Zn	-156.24	80.21	643.24	-26.32	0.82

Fig. 1: Reaction of the PTF Terpolymer Metal Complex.

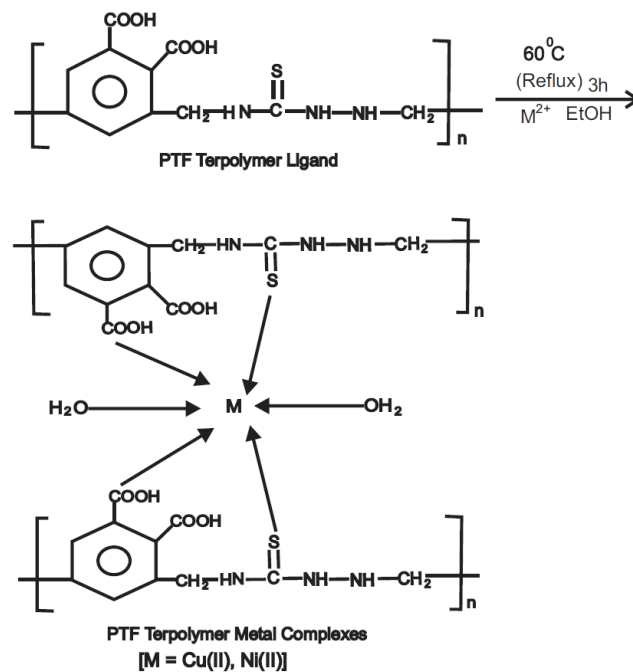


Fig. 2: ^1H NMR spectra of the PTF-Zn Metal Complex.

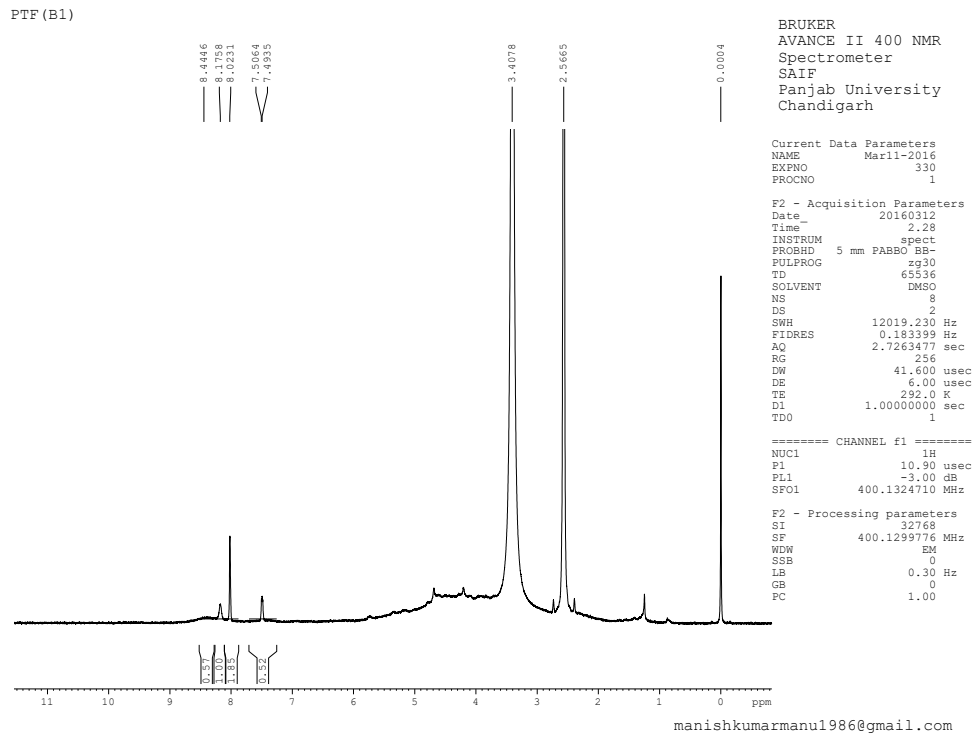


Fig. 3: ^1H NMR spectra of the PTF-Cu Metal Complex.

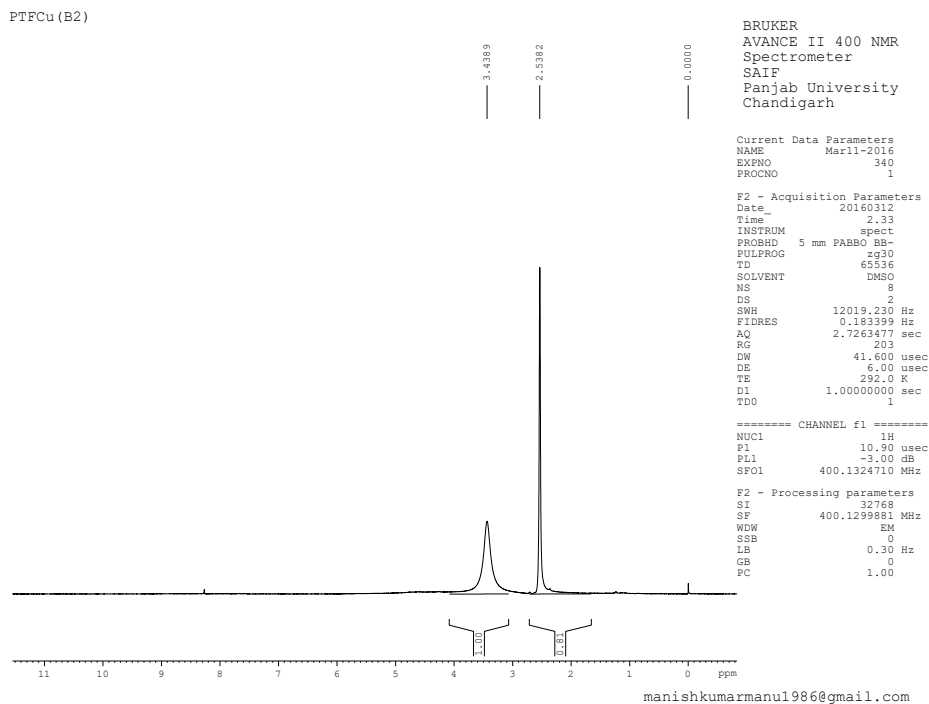


Fig. 4: H¹ NMR spectra of the PTF-Ni Metal Complex.

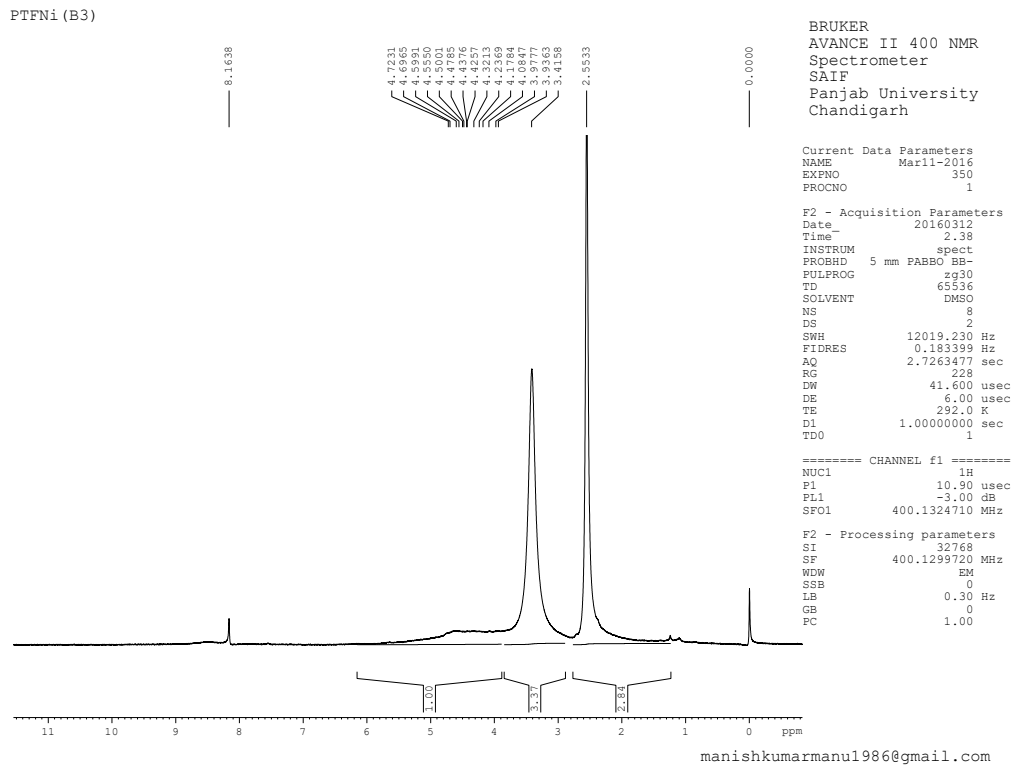


Fig. 5: FTIR Spectra of PTF-Cu Ligand

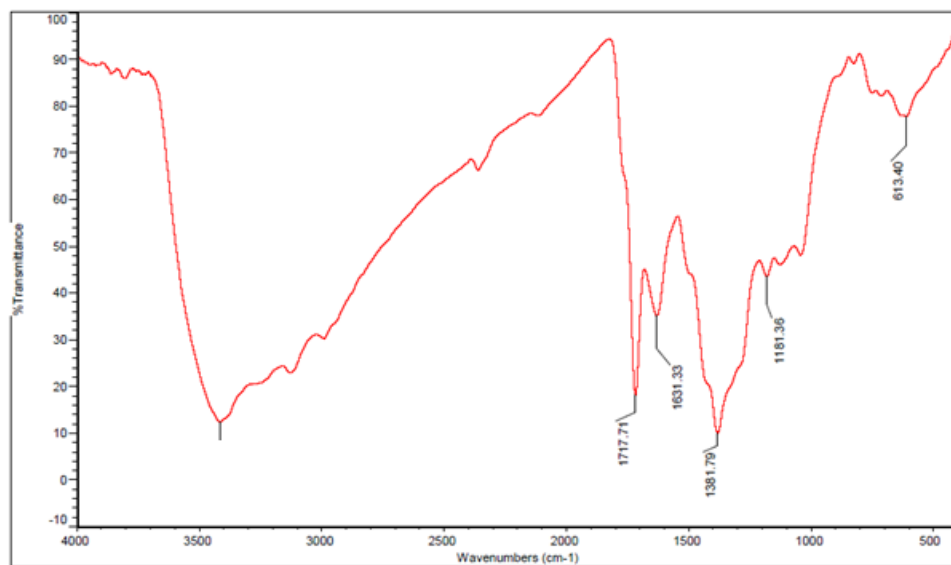


Fig. 6: FTIR Spectra of PTF-Ni Ligand

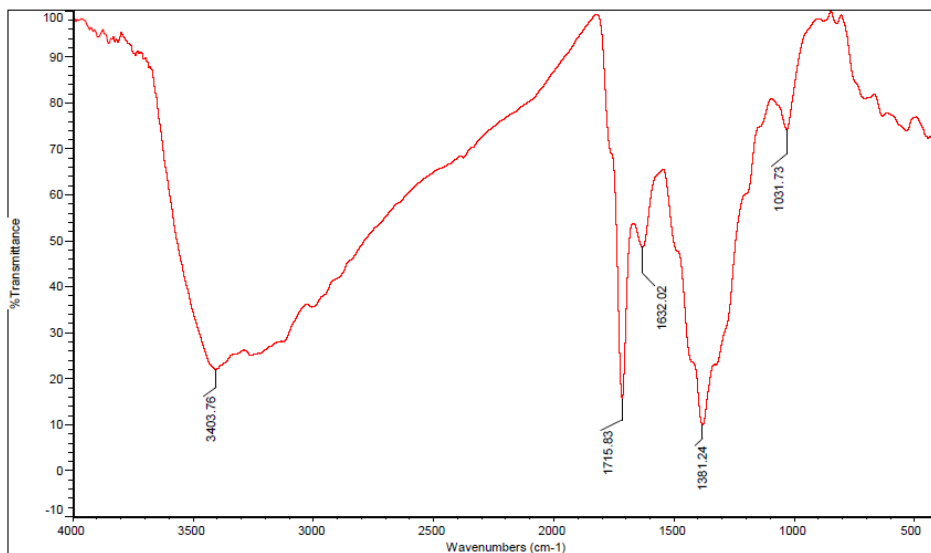


Fig. 7. UV-Visible Spectra of (b) PTF -Cu, (c) PTF-Ni and (d) PTF-Zn

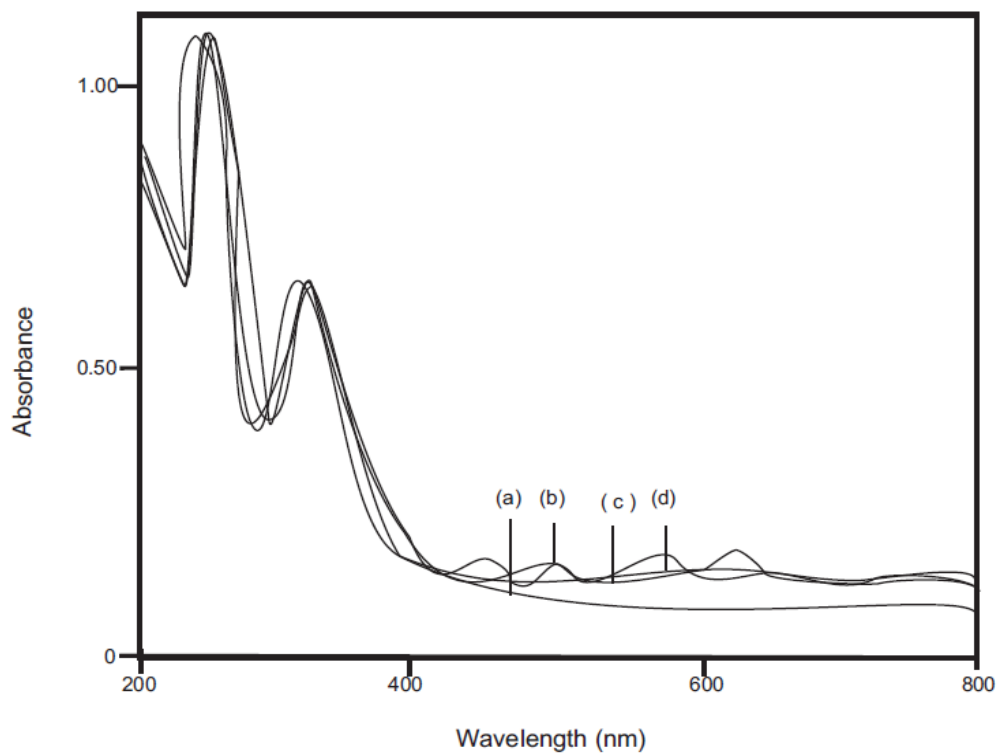


Fig. 8. SEM Images of (a) PTF-Cu, (b) PTF -Ni and (c) PTF -Zn

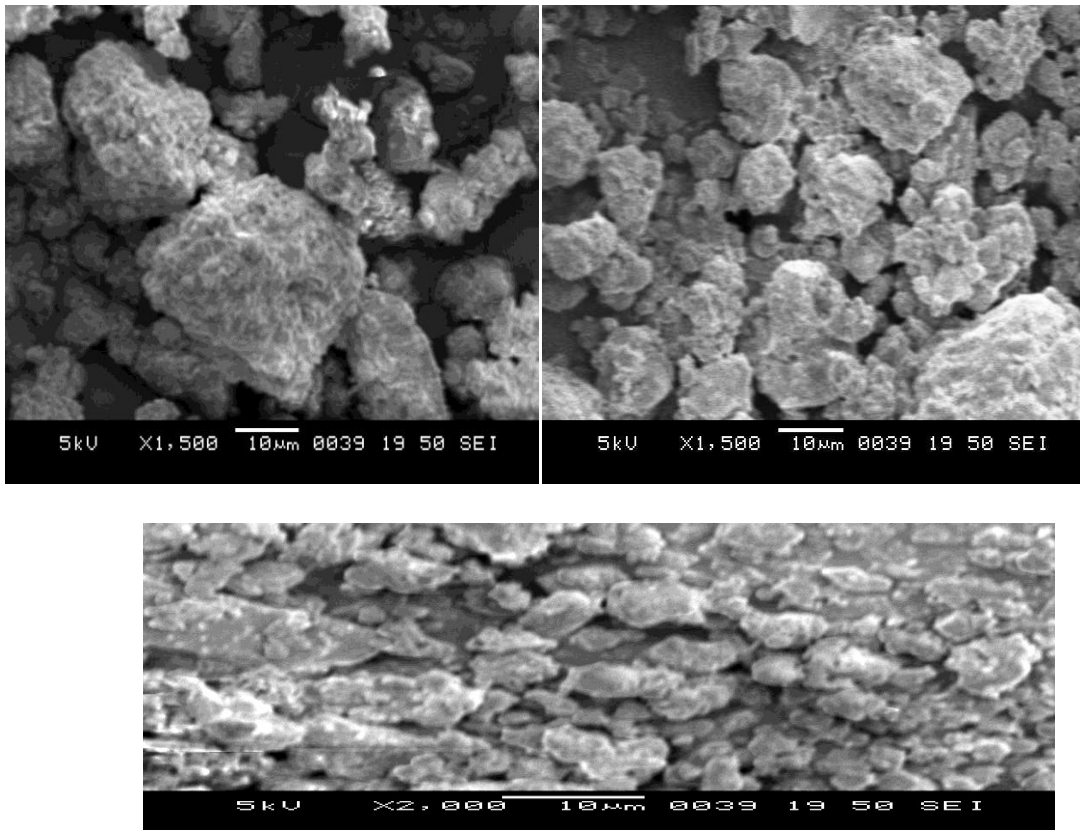


Fig.4.22. Thermogram of PTF-Cu, Ni, Zn.

