Synthesis, Characterization and Thermal degradation study of transition Metal Complexes Derived from Novel Terpolymer Ligand 2-Hydroxy, 4-Methoxy, Benzophenone - Melamine -Formaldehyde (2H,4-M,Bphn-M-F)

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Abstract

In this studies metal complexes have been synthesized by the buildup of 2-Hydroxy, 4-Methoxy, Benzophenone, melamine and formaldehyde with 2 M acetic acid is required as a catalyst for polymerization in (1:1:3) ratio of monomers. The structure of three coordination polymer were characterized by NMR, FTIR and elemental analysis. Thermogravimetric analysis was used for the investigation of thermal stability of the terpolymer ligand metal complexes. Additionally, Freeman-Carroll method was utilized for the calculation of activation energy with the help of TGA data. The structures of Cu(II), Ni(II) and Zn(II) complexes in the all coordination polymers were found as octahedral geometry. TGA results revealed that among the complexes 2-H,4-M-B-M-F-Cu(II) complexe has the highest thermally stable than the Ni and Zn.

Keyword: synthesis, characterization, structure, thermal studies.

1. Introduction

The excessive usage of heavy metals in industries are affecting with toxic effects on life of organism. Therefore it must be removed from environment. Recently copolymer-metal complexes have been more attracting in scientific and technological fields. In many areas have found that coordination polymers have vast applications in wastewater treatment, bioinorganic industry, pollution control , superconducting materials, ultra high strength material, anionic polyelectrolyte hydrogels , cation-exchange resins, etc. Due to its features as high thermal stability and antimicrobial behavior, the synthesis of polymer-metal complexes attracted researchers . The synthesize and characterization of several polymer-metal complexes have been

reported in literature survey [1-4]. Shedmake et al. have synthesized metal complexes using Cu(II), Ni(II) and Zn(II) and characterized by different spectral and physical technique. They have studied thermal and antimicrobial properties of the synthesized copolymer-metal complexes [30].

Azarudeen et al. synthesized new terpolymer ligand and metal chelates derived from anthranilic acid, phenyl hydrazine and formaldehyde with Cu(II), Ni(II), Zn(II), Co(II). The complexes were studied for thermal stability and antibacterial screening [26-27]. The results reveals that all the complexes are highly thermally stable and more potent antibacterial agents than their corresponding ligands [5-7]. Some divalent transition metal complexes of 8-hydroxquinoline were prepared and described for their warm air stability and antibacterial activities [8-9].

In present research work, synthesis of new terpolymer metal complexes. Further, Structure of the copolymer metal complexes were confirmed by different spectroscopic and physical methods.

2. Materials and Methods

2.1. Materials

Entire starting materials utilized were of AR grade. The 2-Hydroxy,4-Methoxy,Benzophenone-. (Fisher India), Melamine (S.D. Fine Chemicals) and formaldehyde (Sigma Aldrich) were procured from the market. Synthesized 2-H,4-M, Bph-M-F terpolymer ligand in 1:1:2 ratio.

2.2. Method of Synthesis of 2-H, 4-M, Bph-M-F-Cu, Ni, Zn complexes:

The terpolymer metal complexes have been prepared [10] using the synthesized terpolymers as ligand with few transition metal ions such as Cu2+, Ni2+ and Zn2+ ions. The terpolymer was taken in 2 M and the transition metal ions (Cu^{2+}, Ni^{2+} and Zn^{2+}) was taken in 1 M for the complex formation reaction. The 2-Hydroxy,4-Methoxy-Benzophenone-Melamine-Formaldehydeterpolymer (2g) was taken in round bottom (RB) flask and immersed in ethanol solution to allow it for swelling in 2 h. The cupric nitrate (1 g) 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 3 h. 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. The same procedure was also followed for the preparation of 2-H,4-M,Bphn-M-F complexes with Ni^{2+} and Zn^{2+} metal ions. The scheme of preparation of the 2-H,4M,Bphn-M-F complex with Cu(II), Ni(II) and Zn(II) meal ions is shown in fig.1.
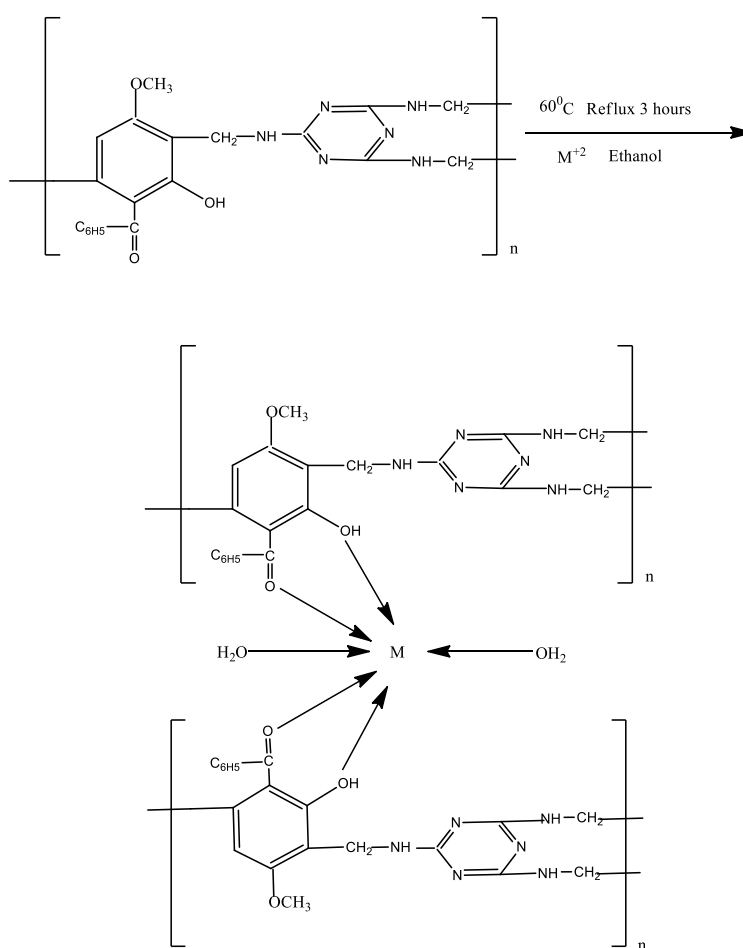

Fig. 1. Synthesis of copolymer meatal complexes [M= Cu, Ni, Zn]

Elemental analysis

The synthesized 2-H, 4-M, Bph-M-F –Cu, 2-H, 4-M, Bph-M-F –Ni and 2H, 4-M, Bph-M-F –Zn complexes were analysed for carbon, hydrogen, nitrogen and sulphur from Sophisticated Analytical Instrumentation Facility, STIC, Punjab university, Chandigarh.

Table-1: Elemental analysis and empirical formula of copolymer resin

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Compound	Elemental Analysis (%)				Empirical Formula of Repeating Unit	Empirical Mass
	Found (Calc.)					
	C	H	N	M		
2-H, 4-M,Bph-M-F-Cu	54.44 (54.32)	4.55 (4.97)	1.65 (1.35)	7.23 (7.19)	$C_{40}H_{40}O_6N_{12}Cu.2H_2O$	883.54
2-H,4-M,Bph-M-F-Ni	54.34 (54.62)	5.24 (5.00)	19.01 (19.12)	6.23 (6.68)	$C_{40}H_{40}O_6N_{12}Ni.2H_2O$	878.693
2-H,4-M,Bph-M-F-Zn	54.43 (54.21)	4.56 (4.96)	18.78 (18.97)	7.55 (7.38)	$C_{40}H_{40}O_6N_{12}Zn.2H_2O$	885.38

Electronic Spectra

The electronic spectra of 2-H,4-M,Bphn-M-F terpolymer ligand and its metal complexes in pure DMSO was recorded in the region 200-850 nm at a scanning rate of 100 nm min^{-1} and a chart speed of 5 cm min^{-1} and its metal complexes are shown in Fig.2. Copolymer samples displayed two characteristic broad bands at 270 and 360 nm. The observed positions of the absorption bands with different intensities indicate the more intense band 260 nm is due to $(\pi \rightarrow \pi^*)$ allowed transition which readily attains coplanarity and shoulder merging (loss of fine structure) and also due to chromophore groups like >C=C, >C=N and >C=O groups are in conjugation with an aromatic nucleus (Biphenyl ring) and the less intense band at 320 nm may be due to $(n \rightarrow \pi^*)$ forbidden transition in >C=N, OCH_3 and –OH groups [10]. the presence of aromatic nuclei and n$\rightarrow \pi^*$ transition indicates the presence of –NH and –OH group. The bathochromic shift from the basic value viz. 250 nm and 320 nm may be due to combined effect of conjugation

(due to chromophore) and phenolic hydroxyl groups as well as –NH groups (auxochrome). The hyperchromic effect is due to the presence of –OH and –NH groups, which act as auxochrome [11]. These transitions were affected by the metal chelation and shifted to longer wavelength which clearly indicates that the complex formation takes place through the lone pair of oxygen atom of carbonyl COC_6H_5 and hydroxyl group which is in conjugation with the aromatic nucleus. The electronic spectra of the 2-H, 4-M, Bphn-M-F-Ni terpolymer metal complex in DMSO was recorded and displayed two characteristic broad bands at 210-340 nm and Zn complex has 220-360 nm. and –OH group [12]. The electronic spectrum of 2-H,4-M,Bphn-M-F–Cu metal complex exhibited bands at 14460, 16500 and 24430 cm-1 and the assignments are $^1Bg \rightarrow {}^2Eg$, $^1Bg \rightarrow {}^2Eg$ and charge transfer spectra. The octahedral configuration can be assigned for the Cu(II) complex [75]. The electronic spectrum of 2-H,4-M,Bphn-M-F –Ni exhibits three bands at 12620, 14600 and 24200 cm−1 assigned to the spin allowed transitions $^3T_{2g}(F) \rightarrow {}^3A_{2g}(F)$, $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$ and $^3T_{1g}(P) \rightarrow {}^3A_{2g}(F)$ in a octahedral environment [76]. The 2-H,4-M,Bphn-M-F–Zn is diamagnetic in nature with tetrahedral geometry. Thus the electronic spectra further supports the structure proposed for the polymer–metal complexes.
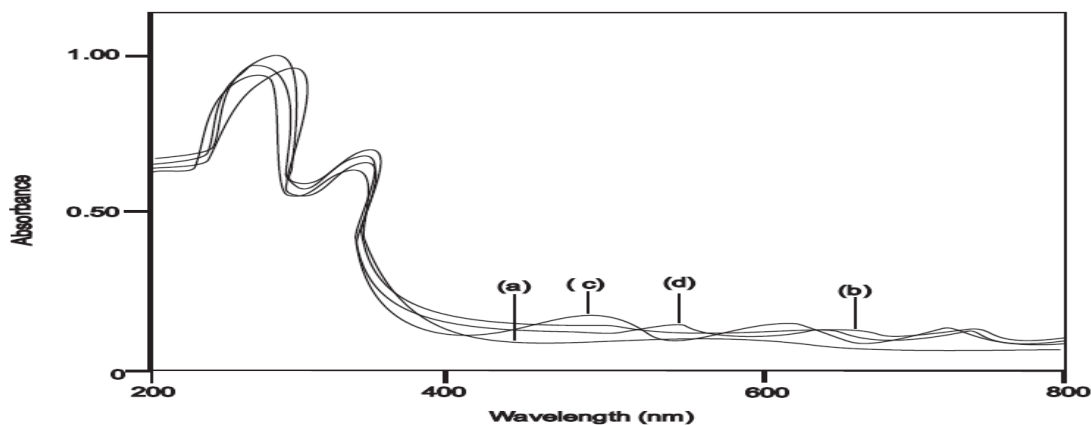

Fig. 2. UV–Visible Spectra of (a) 2-H, 4-M, Bphn-M-F -I ligand, (b) 2-H, 4-M, Bphn-M-F –Cu, (c) 2-H, 4-M, Bphn-M-F –Ni and (d) 2-H, 4-M, Bphn-M-F – Zn

Fourier transform infrared spectra

The terpolymer metal complexes FTIR spectrum is portrayed in the Fig. 3 to Fig.5. In the spectrum of ligand an expansive band. The FTIR spectra of 2-H,4-M,Bphn-M-F-Cu terpolymer metal complexes are presented in Fig. 4. The band frequencies and the groups

assigned for both the terpolymer metal complexes are based on the earlier literature [13-14].In the spectra of 2-H, 4-M, Bphn-M-F-Cu (M=Ni,Zn) metal complexes, the bands are slightly broadened compared to the terpolymer ligand. In the spectrum of polymeric ligand, the band at 1810 cm−1 assigned for C=O is shifted to the lower frequencies (1788.8 cm−1) in the case of polymer–metal complexes. It is due to the coordination of the metal ions through the lone pair of oxygen in carboxyl group and the terminal oxygen of –OH present in the benzophenone moiety. A broad absorption band appeared in the region 3330.9 cm-1may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding[15-16]. Broad and medium band which appeared at 2971.6 cm-1 may be assigned due to >NH stretching vibration of secondary amine [17-18]. Aromatic C-H group represent weak band for stretching vibration at 2844.2 cm-1.

This is a clear evidence for the involvement of oxygen of carboxyl and oxygen of hydroxyl atoms in the chelation. The presence of >NH bending of secondary amine may be ascribed as sharp band at 1620 cm-1. Stretching mode and strong bond at 1557.2cm^{-1} is attributed to C=N stretching of quinolone ring. The presenceof −CH2 bending vibration in –CH2–N bridge in the spectrum is confirmed by the absorption band appeared at 1384-1347.9cm−1. The band appearing in the region 1508.3cm-1 might appear from a C=C stretch which is a characteristic feature of the aromatic region. Itis further supported by the appearance of C-O-M(Cu) and –O-M(Cu) stretching vibrations at 1165.8-1121.7cm^{-1} and 700-684.5 cm−1 respectively.
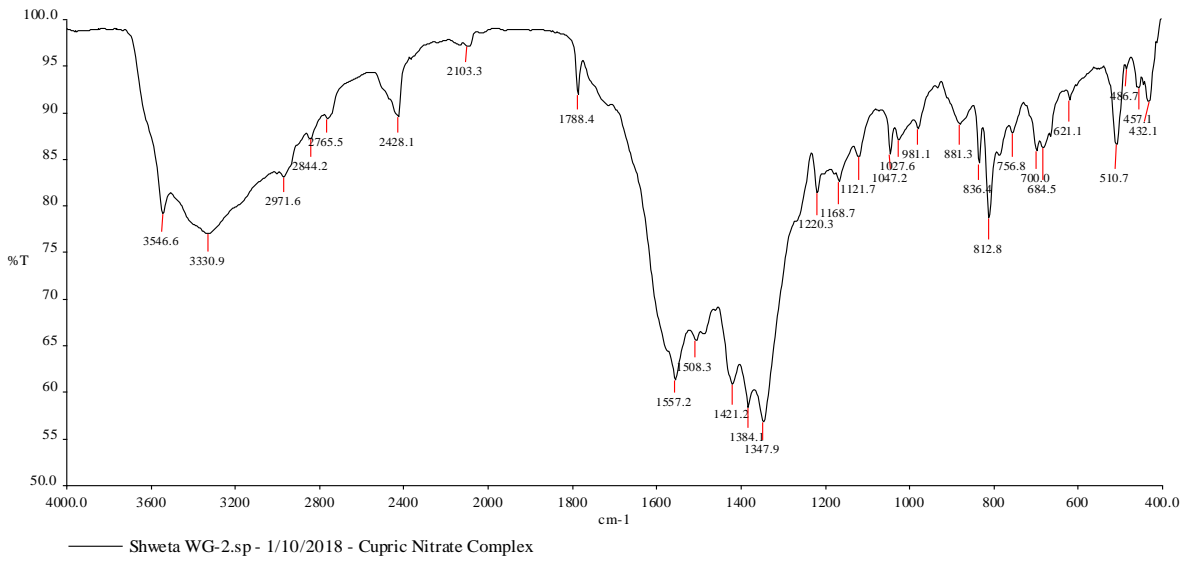
Fig.3. FTIR Spectra of 2-H, 4-M, Bphn-M-F –Cu
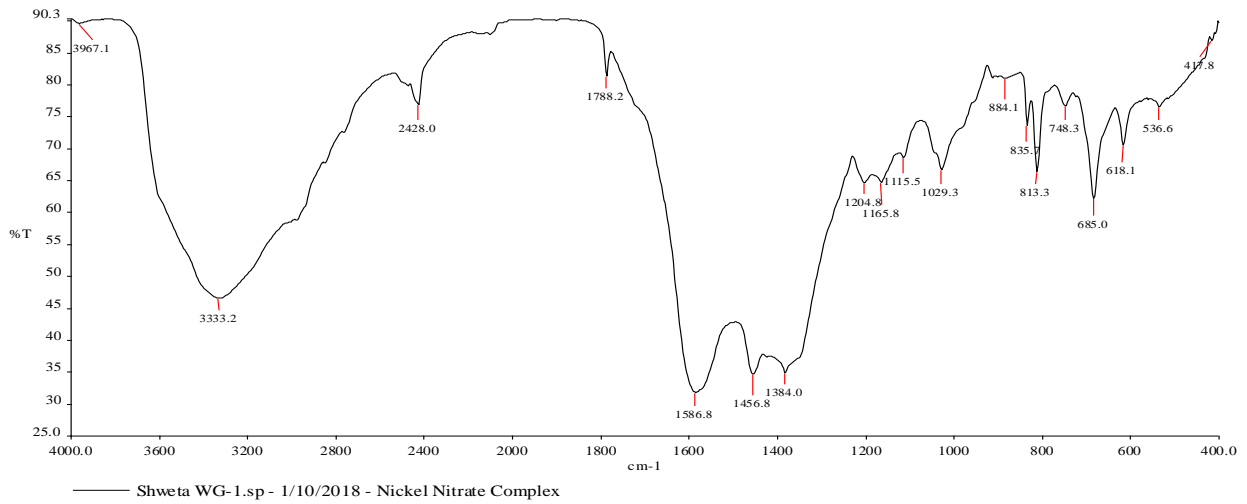
Fig.4. FTIR Spectra of 2-H, 4-M, Bphn-M-F –Ni

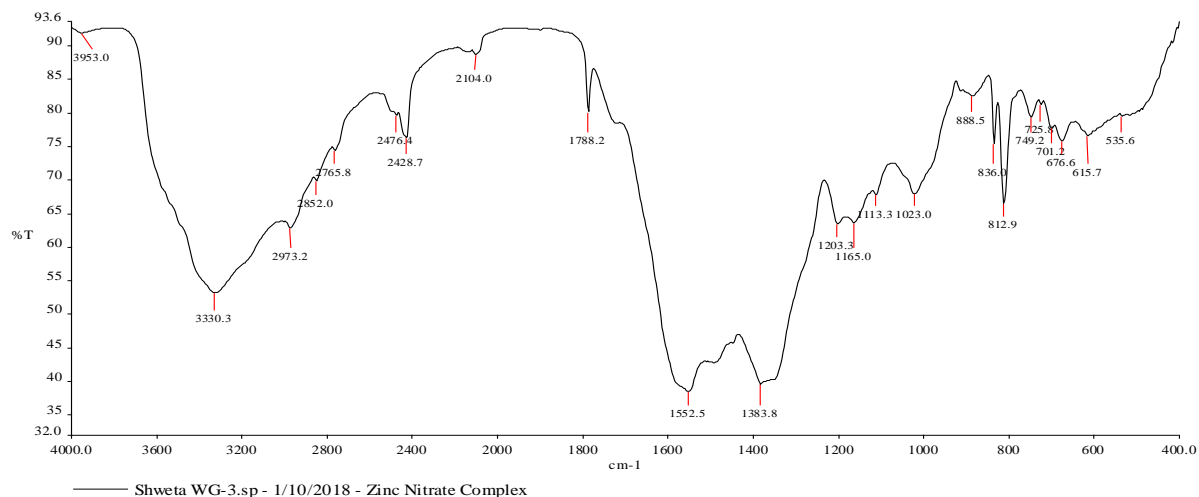Shweta WG-3.sp - 1/10/2018 - Zinc Nitrate Complex

Fig.5. FTIR Spectra of 2-H, 4-M, Bphn-M-F –Zn

Nuclear Magnetic Resonance

The NMR ^{1}H spectra of 2-H,4-M,Bph-M-F-Metal ion (Cu, Ni, Zn) terpolymer metal complexes was recorded to substantiate the linkages of the proposed structure. The nuclear magnetic resonance study has been carried out using Bruker Avance-II, 400 NMR spectrometer DMSO-d_6 as a solvent were carried out at Sophisticated Analytical Instrumentation Facility (SAIF) Punjab University, Chandigarh . For nuclear magnetic resonance studies of non-aqueous solution, the most reference compound is tetramethyl silane $(CH_3)_4Si$, which is magnetically and electrically isotropic, chemically inert, and non- associating with any common compound. The chemical shift are solvent dependent [19-21]. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature.

The NMR spectra for Cu and Ni metal complexes are complicated. The ^{1}H-NMR spectra of Cu(II) metal complex shows in figure 6-8 which was scan by using solvent DMSO-d_6 this complex shows multiplate in the region of 7.61 ppm are assigned to the aromatic protons and the methylene protons appeared in the region of 2.504 ppm and the signal appeared for –NH bridge appeared in the region 6.038 ppm. The signal for –OH proton is shifted from 8.23 ppm to 10.42 ppm in the complex spectrum which gives a clear evidence for the complexation of the metal

ions with the –OH of benzophenone on comparison with ligand spectrum, the line broadening has been observed in the spectrum of metal complex. The signal present in the region 3.38 ppm is attributed to the Ar-CH$_2$-N moiety, further confirm thr metal ion incorporation with the polymer backbone.
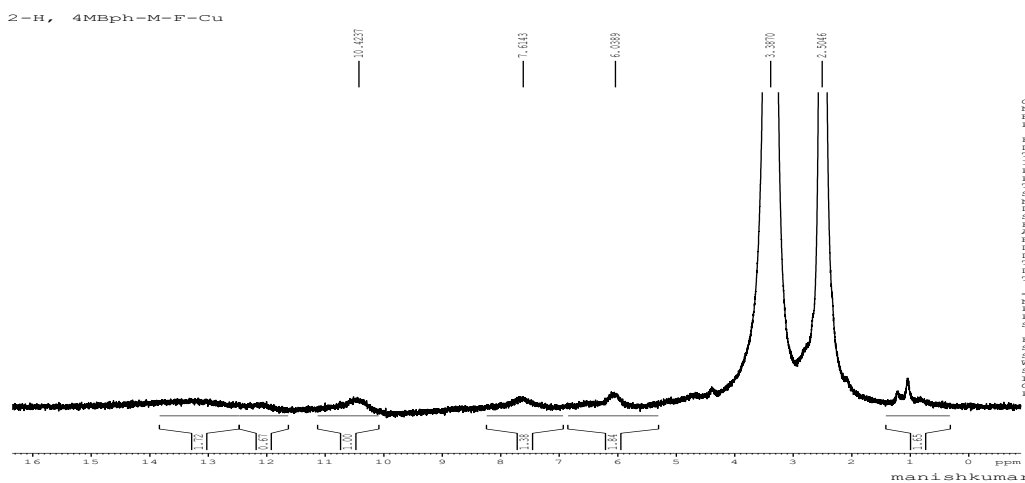

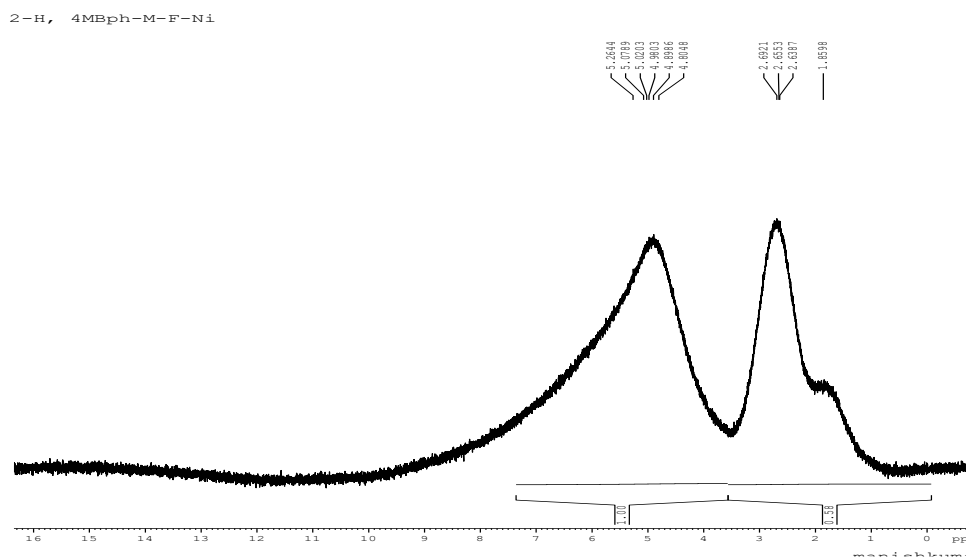**Fig.6. NMR Spectra of 2-H,4-M,Bph-M-F-Cu**

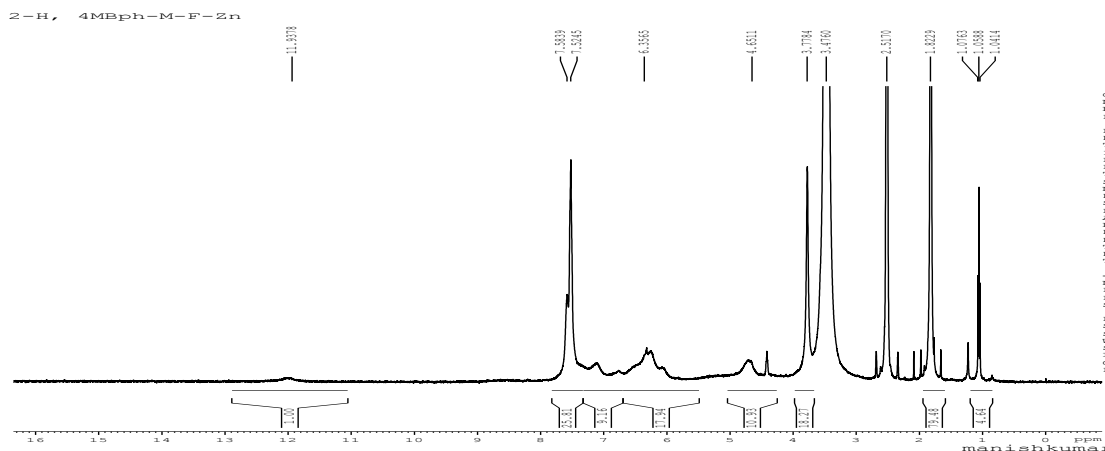**Fig.7. Fig.5. NMR Spectra of 2-H,4-M,Bph-M-F-Ni**

Fig.8. NMR Spectra of 2-H,4-M,Bph-M-F-Zn

Thermal Stability

The non-isothermal thermogravimetric analysis was performed in air atmosphere with heating rate of 20^oc min^{-1} for temperature range of 40^0C to 700^0C. the thermogram were recorded at Sophisticated Instrumentation Centre for applied Capital research and Testing, Cochin. Stability of the 2-H,4-M,Bph-M-F-Cu (Cu=Ni,Zn) terpolymer metal complexes has been analyzed by thermogravimetric analysis (TGA). To obtain the relative thermal stability of terpolymer metal complexes, the method described by Sharp-Wentworth adopted [22-24]. Thermoanalytical data and the decomposition temperatures were determined for different stages.
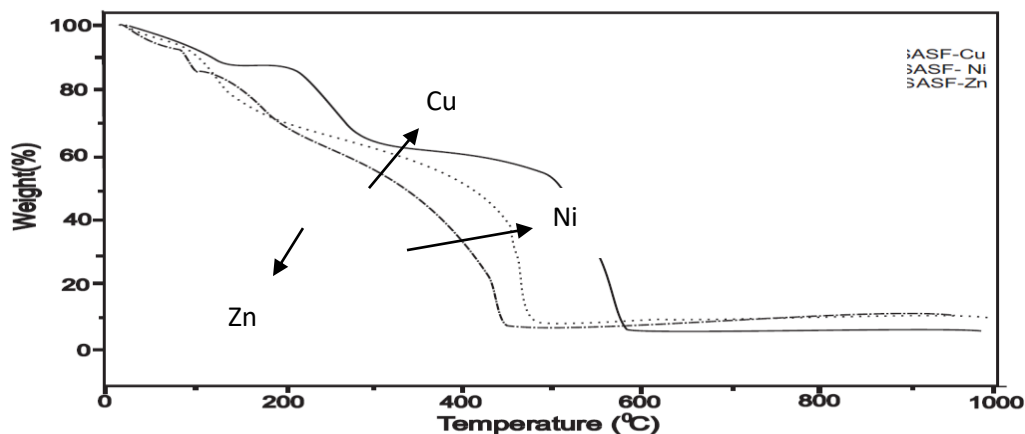

Fig.8. Thermogram of 2-H, 4-M, Bph-M-F -Cu, Ni, Zn.

TGA of 2-H, 4-M, Bph-M-F–M Complex   (Cu, Ni, Zn)

From the weight loss curve of the 2-H,4-M,Bph-M-F–Cu complex, the initial weight loss is observed up to 120°C due to the elimination of lattice water molecules and then the weight loss is continued up to 228°C (Weight loss in found–4.10% and calc.–4.07%) represents the release of two coordinated water molecules from the Cu(II) complex [22-23]. This also confirms the octahedral geometry of the 2-H,4-M,Bph-M-F–Cu complex. The first stage degradation was observed in the range of 228^0C and 370^0C. Beyond gradual weight loss was observed up to 370°C, which may be due to the degradation of unchelated part of the polymeric ligand. Above 370°C again a rapid weight loss up to 440°C has been observed which is attributed to the loss of chelated part. The TG curve attains a constant after 430°C leading to the formation of CuO as residue (Residue in found–10.44%, and calc.–9.00%). The analysis of 2-H,4-M,Bph-M-F–Ni thermogram reveals that, there is a weight loss at 230 - 420°C (Weight loss found–4.13% and calc.–4.09%) indicates the release of two coordinated water molecules. This also confirms the octahedral geometry for the nickel complex. Beyond 230°C, a gradual weight loss is observed up to 420°C, whichmay be due to the loss of non-coordinated part of the ligand. The next degradationstage starts at 420°C and ends up at 590°C which involves an elimination of chelatedpart. After this temperature the NiO is formed as a stable metallic residue (Residuein found–8.46% and calc.–8.50%). In the TG analysis of 2-H,4-M,Bph-M-F–Zn complex, there is no weight loss observed up to 120°C, which confirm the absence of lattice water molecules. However, the weight loss occurred between 200–250°C (Weight loss in found–4.08% and calc.–4.06%). This may be due to the elimination of two coordinated water molecules from the complex. Therefore the octahedral geometry for the 2-H,4-M,Bph-M-F–Zn complex is further confirmed. Similar to the other metal complexes, the 2-H,4-M,Bph-M-F-Zn exhibited two stage of thermal degradation i.e. 250 - 430^0C and beyond 250^0C, a gradual loss of weight continued up to 430°C. This may be due to the degradation of the free part of chelated ligand. Further the complete degradationtakes place between 430 - 550°C which is attributed to the removal of chelated part. The residue left at 550°C may be considered as the stable metal oxide (ZnO)formation (Residue in found–9.14% and calc.–9.19%) [25-28].

In all the thermogram of the metal complexes, the rate of second stage thermal degradation was very fast as compare to the first stage. This is due to the degradation of unchelated part of the terpolymer ligand. Further the low thermal stability of the metal complexes is also due to the oxidation of terpolymer by the catalytic action of metal ions. The order of thermal stability of the terpolymer metal complexes are in the following order:-

2-H,4-M,Bph-M-F-Ni > 2-H,4-M,Bph-M-F-Zn > 2-H,4-M,Bph-M-F-Cu

By using an analytical technique suggested by Sharp-Wentworth and Freeman-Carroll [29-30], we developed the TG curves to give further proof about the degradation mechanism of the examined substances.

Table. 2. Thermogravimetric Analysis of 2-H,4-M,Bph-M-F Terpolymer Metal Complexes.

Copolymer	Half Decomposition Temp. (T)	Activation Energy Ea (KJ)/mol	
		SW	FC
2-H,4-M,Bph-M-F -Cu	320	3.54	3.74
2-H,4-M,Bph-M-F -Ni	440	8.98	9.26
2-H,4-M,Bph-M-F -Zn	380	7.24	7.45

Table 3. Kinetic and Thermodynamic Parameters of 2-H,4-M,Bph-M-F Ligand and its Metal Complexes

Copolymer Ligands and its metal complexes	Entropy Change ΔS(J)	Free Energy Change ΔF (KJ)	Frequency factor Z (S^{-1})	Apparent Entropy Change (S*)	Order reaction
2-H,4-M,Bph-M-F -I	-135.12	88.22	507.92	-38.35	0.98
2-H,4-M,Bph-M-F-Cu	128.34	41.54	430.34	-38.02	1.30
2-H,4-M,Bph-M-F-Ni	124.42	68.46	523.42	-38.17	1.24
2-H,4-M,Bph-M-F-Zn	124.12	56.24	565.30	-38.06	1.11

Conclusions

2-H,4-M-B-M-F-M (M=Cu,Ni,Zn) metal complexes were prepared by using 2-Hydroxy 4-methoxy benzophenone- melamine- formaldehyde copolymer as ligand. The structure of both the metal complexes and terpolymer was confirmed on the basis of spectral and physico-chemical investigation. The thermal stability of the metal complexes is less compared to its terpolymer ligand. In TGA, the kinetic parameters derived using the Freeman-Carroll approach are found to be comparable, and the energy of activation assessed using the Sharp-Wentworth and Freeman-Carroll methods are found to be substantially equivalent, suggesting the same reaction mechanism. It is challenging to get any original conclusions on the breakdown process. According to thermogravimetric research, this copolymer is thermally stable at high temperatures.

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