

Synthesis, Characterization, and Preliminary Antimicrobial Evaluation of Bisphenol-A Formaldehyde Resin Coordinated with Transition Metal Complexes of Ethylenediamine

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ABSTRACT: Coordination polymers containing bisphenol-A, formaldehyde, and transition metal complexes of ethylenediamine [M(en)₂] were synthesized by the reaction of bisphenol-A, formaldehyde, and M(en)₂ complex in alkaline medium, using M for Fe⁺³, Co⁺², Ni⁺², Cu⁺², and Zn⁺². The materials were characterized by elemental analysis, FTIR, UV-Vis, ¹H-NMR spectra, TGA, and magnetic susceptibility measurement. The geometry of the central metal ions was determined by electronic spectral studies and magnetic moment measurement. The M–N and C–N bonds were confirmed by the IR spectra of the polychelates. The ¹H-NMR spectra of the chelating resins con-

firmed polycondensation with well-defined peaks for bridging methylene functions. Complexation studies with transition metal ions revealed effective coordination of the bisphenol-A formaldehyde resin. The antimicrobial activities of these chelated resins were screened against *E. coli*, *S. dysantraea* (bacteria), and *C. albicans*, *A. niger* (fungi) by using agar well diffusion method. All the polymeric chelates show promising antimicrobial activities. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1251–1258, 2011

Key words: bisphenol-A; formaldehyde; polychelates; agar well diffusion method

INTRODUCTION

Most of the current interest in inorganic polymers has been brought about by the demands of modern technology.¹ The coordination polymer has great advantage over organic polymer and is widely used in many specified application such as catalysis, chirality, conductivity, luminescence, magnetism, non-linear optics, thermal insulation, coating material, and wood industry.^{2–8} Polymeric coordinating reagents are novel type of substances possessing a combination of the physical properties of polymers and chemical properties of the attached reagent. The synthesis of coordination polymers is achieved by combining the appropriate metal salt and ligand in a suitable solvent under mild or at the most hydrothermal conditions.⁹ Coordination polymer containing N,O,S,P donor atom and their transition metal complexes has been the subject of many studies mainly because of their interesting physicochemical and potentially beneficial biological activities.¹⁰

Formaldehyde is an extremely reactive substance that interacts with proteins,^{11,12} DNA, and RNA¹³ *in vitro*. It is a bactericidal, sporicidal, and virucidal agent. It has long been considered a sporicide by virtue of its ability to penetrate into the interior of bacterial spores.¹⁴ The interaction and crosslinking properties of formaldehyde must play a considerable role in this activity. Recently, there have been a number of reports highlighting the use of transition metal complexes as anticancer agents.¹⁵ A number of *in vivo* studies have indicated that biologically active compounds become more bacteriostatic and carcinostatic upon chelation.^{16,17} Polymer-bound chelating ligands have the ability to remove and concentrate metal ions, particularly those that have an impact on the environment.¹⁸ These chelates are an active part of metalloenzymes¹⁹ and biomimic model compounds,²⁰ and resemble with natural proteins like hemerythrin. Useful synthetic methods have been developed by Fujita et al. to prepare coordination polymer by changing the length and flexibility of the spacer bridges connecting the donor groups.²¹ Polychelates of phenol formaldehyde with transition metals show better heat and mechanical resistance properties than common phenol-formaldehyde resins.²² Moreover, chelates of phenols possess interesting microbial activities like growth inhibition and acceleration. This article reports the synthesis by

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TABLE I
Analytical Data of BPF-Metal Polychelates

Compound	C cal./obs.	H cal./obs.	N cal./obs.	M cal./obs.	Color	Yield (%)
BPF-Fe(III)	50.71/50.65	6.88/6.67	11.25/11.20	11.22/11.10	Red brown	60
BPF-Co(II)	54.19/54.21	7.36/7.02	12.04/12.14	12.66/12.58	Green	62
BPF-Ni(II)	54.22/54.16	7.37/7.29	12.04/12.01	12.62/12.65	Dark brown	65
BPF-Cu(II)	58.11/58.30	6.97/6.89	12.91/12.85	14.64/14.60	Green	60
BPF-Zn(II)	57.87/57.82	6.94/6.91	12.85/12.84	15.00/14.94	Cream	65

condensation and characterization of bisphenol-A formaldehyde resin (BPF) having transition metal ethylenediamine complexes with Fe(III), Co(II), Ni(II), Cu(II), Zn(II). The goal of this study is to investigate the biocidal properties of these coordination polymers. The compounds are characterized by electronic, FTIR, $^1\text{H-NMR}$, and magnetic susceptibility measurements. The thermal stability of these compounds has also been determined by using thermogravimetric analysis (TGA). The antimicrobial activity of these chelates were tested against *E. coli*, *S. dysantraea*, *C. albicans*, and *A. niger* by using agar well diffusion method.

EXPERIMENTAL

Materials

The following starting materials were used as received: bisphenol-A (G.S. Chemicals, Coimbatore, India) Formaldehyde 37–41% ethylenediamine (S.D. fine chemical, Mumbai, India), Sodium hydroxide pellets (Merck, Mumbai, India), and dimethyl Sulfoxide (DMSO) (Merck, Mumbai, India) were of analytical grade. Metal(II) chlorides and metal(III) chlorides (Merck, Mumbai, India) were used as received. All the antimicrobial tests were carried out by the Department of Microbiology, All India Institute of Medical Sciences (AIIMS), New Delhi. The metal complexes of ethylenediamine, $[\text{M}(\text{en})_2]$ were synthesized by reported methods.²³

Synthesis of $[\text{M}(\text{en})_2]$ complexes

The preparation of $[\text{Cu}(\text{en})_2]$ complex was carried out by adding copper chloride (1.70 g dissolved in 10 mL of water) in the ethylenediamine (1.34 mL) in 1 : 2 molar ratios, with continuous stirring. Violet-colored crystals were obtained, which were filtered, washed with ethanol and diethyl ether, and dried in desiccator. The same procedure was adopted for the synthesis of other metal complexes.

Synthesis of metal polychelates

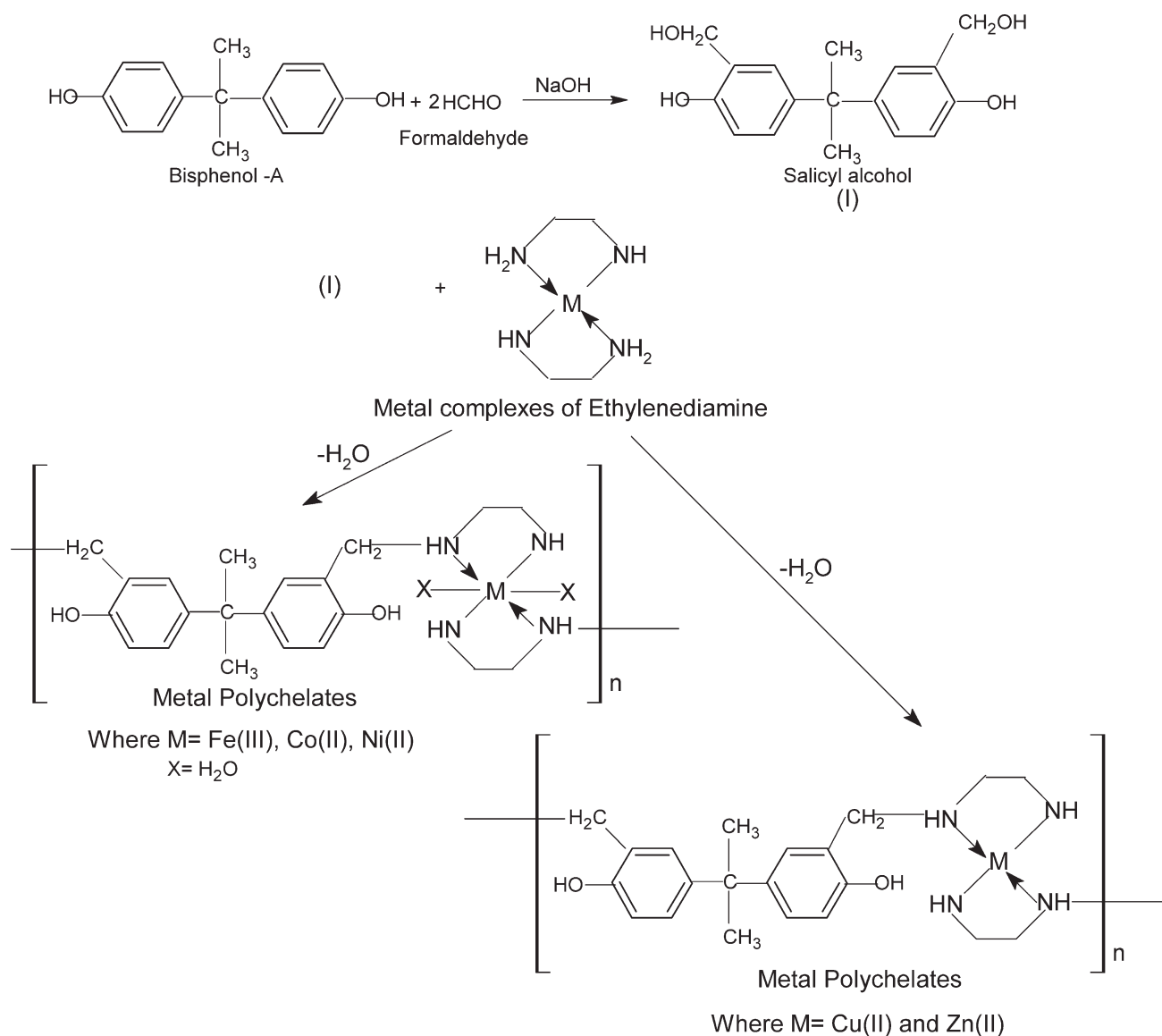
The polychelates were synthesized by polycondensation of bisphenol-A, formaldehyde, and metal complexes of ethylenediamine in alkaline medium. In a

250-mL three-necked round bottom flask, bisphenol-A (2.28 g, 0.01 mol) and DMSO (5–7 mL) was heated until the bisphenol-A was completely dissolved. Then, formaldehyde (1.5 mL, 0.02 mol, 37% aqueous solution) was added, and the pH was adjusted to 8 with sodium hydroxide. The mixture was then stirred magnetically, and the temperature was increased and maintained at 60°C for 4 h. The resulting mixture obtained was colorless. A metal complex of ethylenediamine (e.g. 0.91 g of $[\text{Cu}(\text{en})_2]$ in 5 mL of DMSO) was added drop wise. The reaction mixture was refluxed for 3 h with continuous stirring, and temperature of the reaction increased up to 70°C. A dark brown-colored liquid was formed that was digested at 35°C for 6 h. The final product, BPF-Cu(en)₂ polychelate, a viscous green-colored, was obtained, which was washed several times with ethanol and then with diethyl ether. The product was filtered and reprecipitated by solvent–nonsolvent method and dried in desiccator. A similar procedure was adopted for the preparation of BPF-Fe(en)₂, BPF-Co(en)₂, BPF-Ni(en)₂, and BPF-Zn(en)₂ polychelate. Different colored viscous solutions were obtained for different metals (see Table I). The color and the solubility of the metal ions changed on complexation. All the polychelates were soluble in polar solvents, namely DMSO and DMF, and insoluble in water, ethanol, methanol, chloroform, and carbontetrachloride.

Measurements

The infrared (IR) spectra were recorded on a Perkin Elmer IR spectrophotometer (Waltham, USA, Model 621) using KBr discs in the range 4000–500 cm^{-1} . The Ultra violet–visible

(UV–vis.) spectra were taken on a Perkin Elmer Lambda (Waltham, USA EZ –201) spectrophotometer in solution form, and $^1\text{H NMR}$ spectra were recorded on a Bruker spectropin DPX-30 MHz (Ontario, Canada) Elemental analysis of C, H, and N of the metal polychelate was obtained by a elemental analyzer system GmbH Vario ELIII (Hanau, Germany). The percentage of metals in the metal polychelates was determined by complexometric titration with ethylenediaminetetraacetic acid after decomposition with fuming HNO_3 . Magnetic susceptibility of the powder samples was measured on a vibrating



Scheme 1 Synthesis of BPF-metal polychelates.

sample magnetometer (Newjersy, US, model 155). The thermal behavior of the metal polychelates were recorded with TGA analyzer Perkin Elmer Pyris Diamond (Waltham, USA) at a heating rate of 10°C/min in a nitrogen atmosphere.

Preparation of microbial culture

The antimicrobial activities of the metal polychelates were tested against various microorganisms in DMSO as the solvent. The concentration of sample tested was 50 µg mL⁻¹ for antibacterial and antifungal studies, respectively. Bacterial strains were nourished in a nutrient broth (peptone, 5 g/L; beef extract, 3.0 g/L; PH 6.8) and yeasts in a malt-extract broth and incubated for 24 and 48 h, respectively. According to the agar-diffusion method, bacteria

were incubated on Muller–Hinton agar and yeast on Sabouraud dextrose agar. The wells were dug in the media with the help of a sterile steel borer and then 0.1 mL of each sample was introduced in the corresponding well. Other wells were supplemented with solvent (DMSO) for positive control and standard drug, viz. kanamycin (antibacterial) and miconazole (antifungal), for negative control. The resulting zones of inhibition on the plates were measured in millimeters.

RESULTS AND DISCUSSION

Metal polychelates having the bisphenol-A formaldehyde moiety were obtained in a good yield by reacting bisphenol-A, formaldehyde, and metal (II)- and metal (III)- complex of ethylenediamine in an

TABLE II
Important IR Spectral Assignments of BPF-Metal Polychelates

Assignments	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)	M(en) ₂
$\nu(\text{OH} + \text{NH})$	3250 –3450(br)	3250 –3450(br)	3250 –3450(br)	3250 –3450(br)	3250 –3450(br)	–
def. NH ₂	–	–	–	–	–	1583(s)
δNH	1610(s)	1610(s)	1611(s)	1600(s)	1610(s)	1620(s)
δCH_2	1442(w)	1432(w)	1435(w)	1440(w)	1435(w)	1436(w)
HOH	1650(w)	1650(w)	1652(w)	1652(w)	1650(w)	–
Isopropyl group (Doublet)	1385(s) 1375(s)	1385(s) 1375(s)	1384(s) 1370(s)	1385(s) 1370(s)	1384(s) 1370(s)	–
$\nu\text{C}-\text{N}$	1230(w)	1225(w)	1228(w)	1230(w)	1228(w)	1226(w)
$\nu\text{C}-\text{O}$ (Phenols)	1013(s)	1010(s)	1013(s)	1010(s)	1013(s)	–
def. CH	761(s)	760(s)	761(s)	760(s)	755(s)	–
Aromatic ring	1510(s)	1511(s)	1511(s)	1515(s)	1520(s)	–
$\nu\text{M}-\text{N}$	567(s)	564(s)	567(s)	564(s)	565(s)	566(s)

w-weak, s-strong, br-broad.

alkaline medium (Scheme 1). The analytical data and color of the BPF-[M(en)₂] resin are given in Table I. All the polychelates were colored, insoluble in water and common organic solvents, such as ethanol, methanol, benzene, chloroform, and soluble in DMSO and DMF. The molecular weight of the coordination polymers could not be determined by GPC because of their insoluble nature in common organic solvents.

FTIR analysis

The important bands and their assignments based on IR studies on metal polychelates are listed in Table II. In the FTIR spectra of metal polychelate, the region with a maximum broadness around 3250–3450 cm⁻¹ can be attributed to stretching vibration of the both hydroxyl and NH group. Furthermore, the broadening in this region suggests intermolecular hydrogen bonding, which is possible between the hydrogen of the phenolic group and the nitrogen of the amine group. A comparison of the IR spectra of [M(en)₂] with those of their coordination polymers indicate that the band at 1583 cm⁻¹ in [M(en)₂] is due to the presence of NH₂ group which shifts to the higher frequency by 10–20 cm⁻¹ in metal polychelate which is attributed to NH group. This is strong evidence for the polymerization.²⁴ The band in the region 1010–1170 cm⁻¹ is attributed to C–H in plane bending and the band at 1432–1442 cm⁻¹ was assigned to the CH₂ bending. The presence of coordinated water molecules in the complexes was confirmed by the appearance of a strong band in the region 1650–1652 cm⁻¹ for deformation mode of coordinated water.²⁵ The isopropyl group of bisphenol-A shows a strong doublet, with peaks of almost equal intensity at 1384–1385 and 1370–1375 cm⁻¹.²⁶ The

spectra of metal polychelate showed a band of C–N stretching in the region of 1225–1230 cm⁻¹.²⁷ The C–O stretching vibration of phenols produces a strong band in the 1010–1013 cm⁻¹ region of the spectrum. The IR spectra show absorption bands in the region of 755–761 cm⁻¹ corresponding to out of plane deformation vibrations of aromatic C–H bonds. The presence of a sharp band in the region 564–567 cm⁻¹ for all the coordination polymers can be assigned to ν (M–N), which supports the involvement of nitrogen in coordination.²⁸

¹H-NMR spectra

The ¹H-NMR spectra of Zn(II) metal polychelate shown in Figure 1 reveals peaks for protons of dimethyl groups of bisphenol-A and the protons of aromatic rings at $\delta = 1.5$ ppm²⁹ and $\delta = 7.98$ –7.11 ppm, respectively. The methylene groups present in polychelate exhibited signals at 3.12, 3.54 and 3.65 ppm due to CH₂–CH₂–NH,³⁰ Ar–CH₂–NH and Ar–CH₂–OH, respectively. The appearance of peaks at $\delta = 4.45$ ppm is due to the hydroxyl proton of

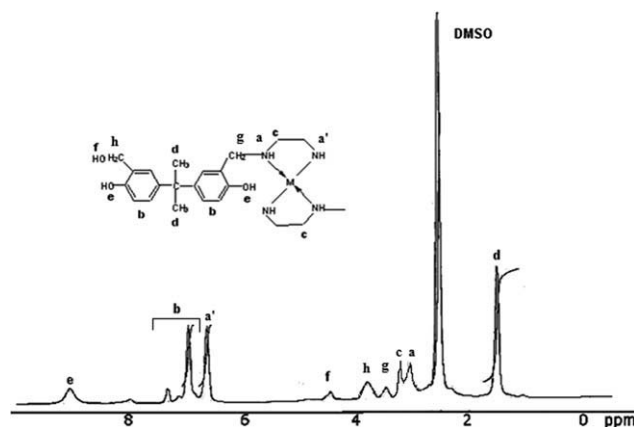


Figure 1 ¹H-NMR spectra of BPF-Zn polychelate.

TABLE III
Electronic Spectra and Ligand Field Parameters of the $[M(en)_2]$ Complexes

Complex	Frequency (cm^{-1})	Assignment	10Dq (cm^{-1})	B (cm^{-1})	β (cm^{-1})	β^0	Geometry (%)
$[\text{Fe}(en)_2 \cdot 2\text{H}_2\text{O}] \cdot \text{Cl}$	14233	${}^4\text{T}_{1g}(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$	11420	985	0.87	13	Octahedral
	20748	${}^4\text{T}_{2g}(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$					
	24776	${}^4\text{E}_g(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$					
$[\text{Co}(en)_2 \cdot 2\text{H}_2\text{O}]$	9850	${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$	10860	869	0.89	11	Octahedral
	15540	${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$					
	21739	${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$					
$[\text{Ni}(en)_2 \cdot 2\text{H}_2\text{O}]$	10500	${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$	13803	642	0.59	41	Octahedral
	18000	${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$					
	23653	${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\text{F})$					
$[\text{Cu}(en)_2 \cdot 2\text{H}_2\text{O}]$	15600	${}^2\text{A}_{1g} \leftarrow {}^2\text{B}_{1g}(\text{F})$	-	-	-		Square planar
	18315	${}^2\text{E}_g \leftarrow {}^2\text{B}_{1g}(\text{F})$					
$[\text{Zn}(en)_2]$		-	-	-	-		

terminal CH_2OH group³¹ confirms the reaction of bisphenol-A with formaldehyde as well as the chelate shows a signal at $\delta = 6.62$ ppm due to the $-\text{NH}$ protons which had actually shifted from its original position at $\delta = 7.25$ ppm because of the hydrogen bonding between the NH and OH group of resin.³² A peak for proton of another $-\text{NH}$ group at 2.56 ppm provide the evidence of reaction between $[M(en)_2]$ complex, bisphenol-A and formaldehyde.

Electronic spectra and magnetic measurement studies

The electronic spectra of ethylenediamine complexes of Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) and their polychelates were recorded in DMSO solution. The various Crystal field parameter (10 Dq), Racah inter-electronic repulsion parameter (B), Nephelauxetic ratio (β), and Covalency parameter (β^0) were calculated using known equations, and the values were given in Tables III and IV. The magnetic moment of the Fe(III) polychelate was 5.6 B.M. corresponding to five unpaired electrons. Three bands at 11,220, 21,725, and 27,765 cm^{-1} related to the ${}^4\text{T}_{1g}(\text{G}) \leftarrow$

${}^6\text{A}_{1g}(\text{F})$ (ν_1), ${}^4\text{T}_{2g}(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$ (ν_2), and ${}^4\text{E}_g(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$ (ν_3). These transitions predicted for an octahedral geometry.³³ The previous data were used to calculate Crystal field parameter (Dq), Racah parameter (B), Nephelauxetic effect (β), and Covalency parameter (β^0). The value of 10 Dq was found to be 11,400 cm^{-1} and B was 980 cm^{-1} . The β value was reduced to about 85% of the free ion value for Fe(III), and the β^0 value of 15% indicated the covalent nature of the compound. The Co(II) polychelate had a magnetic moment of 4.98 B.M. due to four unpaired electrons, and the spectra display three bands at 9810, 14,070, and 20,350 cm^{-1} due to ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ (ν_1), ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ (ν_2), and ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ (ν_3) transitions, respectively. The $\nu_3 : \nu_1$ value for the compound was 2.07, which falls within the useful range (2.0–2.8) reported for the majority of Co(II) octahedral compounds. The spectral parameters were 10Dq = 9998 cm^{-1} , B = 768 cm^{-1} , $\beta = 0.79$, and β^0 value was 21%. The reduction of the Racah parameter from the free ion value and the value of β indicate the presence of covalence in the compound.³⁴ Ni(II) polychelate had a magnetic moment of 2.71 B.M. The electronic spectrum pattern

TABLE IV
Electronic Spectra, Magnetic Moments, and Ligand Field Parameters of the Metal Polychelates

Compound	Magnetic moment (μ_B)	Frequency (cm^{-1})	Assignment	10Dq (cm^{-1})	B (cm^{-1})	β (cm^{-1})	β^0 (%)
$(\text{C}_{21}\text{H}_{30}\text{N}_4\text{O}_2\text{Fe} \cdot 2\text{H}_2\text{O})_n \cdot n\text{Cl}$	5.6	11220	${}^4\text{T}_{1g}(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$	11400	980	0.85	15
		21725	${}^4\text{T}_{2g}(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$				
		27765	${}^4\text{E}_g(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$				
$(\text{C}_{21}\text{H}_{30}\text{N}_4\text{O}_2\text{Co} \cdot 2\text{H}_2\text{O})_n$	4.98	9810	${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$	9998	768	0.79	21
		14070	${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$				
		20350	${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$				
$(\text{C}_{21}\text{H}_{30}\text{N}_4\text{O}_2\text{Ni} \cdot 2\text{H}_2\text{O})_n$	2.71	10520	${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$	10610	583	0.54	46
		18020	${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$				
		24500	${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\text{F})$				
$(\text{C}_{21}\text{H}_{30}\text{N}_4\text{O}_2\text{Cu})_n$	1.78	15610	${}^2\text{A}_{1g} \leftarrow {}^2\text{B}_{1g}(\text{F})$				
$(\text{C}_{21}\text{H}_{30}\text{N}_4\text{O}_2\text{Zn})_n$	Diamagnetic	25373	Charge transfer				

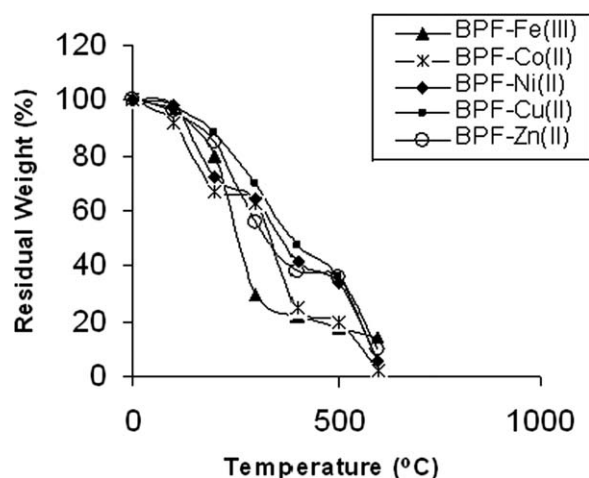


Figure 2 Thermogram of BPF-Metal(II) and BPF-Metal(III) polychelates.

is satisfactorily interpreted in terms of octahedral symmetry, and the bands are then assigned as follows: 10,520, (ν_1), ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$; 18,020, (ν_2), ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$; 24,500, (ν_3), ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$. The spectral parameters were $10Dq = 10610 \text{ cm}^{-1}$, $B = 583 \text{ cm}^{-1}$, $\beta = 0.54$, and β^0 value was 46%. The reduction in the Racah parameter from the free ion value of 1080 cm^{-1} to 583 cm^{-1} , and the β value of 0.54 indicate the covalent nature of the compound.³⁵ The above discussion very strongly indicates an octahedral geometry around the central metal ion in all polychelates. It accounts for the occupation of two coordinating sites by H_2O out of six in making the octahedral environment. In another study, the electronic spectra of Cu(II) polychelate exhibit bands at 15,610 and $25,373 \text{ cm}^{-1}$ due to ${}^2A_{1g} \leftarrow {}^2B_{1g}(F)$ and charge transfer spectra and 1.78 B.M. magnetic moment of polychelate point out that Cu(II) chelate possess square planer geometry.³⁶ In the case of dia-

magnetic Zn(II) polychelate, there is no d-d transition occurred. The slight change in the λ_{max} indicates that the geometry remains same after polymerization, but the formation of new covalent bonds is observed in polychelates, which is confirmed by the increase in covalency parameter (β^0).

Thermal analysis

The TGA thermograms of BPF-M(II) and BPF-M(III) polychelates are depicted in Figure 2, and their corresponding data are summarized in Table V. The TGA curves of all the chelate polymers decompose at 100°C with 2–8% weight loss because of elimination of water/ solvent molecules. In case of Fe(III), Co(II), and Ni(II) polychelates, the curve showed a 10–23% weight loss corresponding to two coordinating water molecules in the temperature range of $100\text{--}150^\circ\text{C}$, whereas the Cu(II) and Zn(II) polychelate did not show any weight loss in this temperature range which indicates the absence of coordinated water molecules, thus favoring four coordinated geometry for the Cu(II) and Zn(II) polychelate. Above 200°C , a gradual mass loss was observed, but the rate of decomposition was quite rapid between 300 and 600°C , which can be attributed to the decomposition of the chelate polymer followed by the formation of metal oxides (Fe_2O_3 , CoO, NiO, CuO, and ZnO). These results reveal that all the polychelates show good heat resistant characteristics due to the coordination of metal ions. The thermal stability of polymeric chelates was found to be in the order $\text{Cu} > \text{Ni} > \text{Zn} > \text{Co} > \text{Fe}$. The greater stability of BPF-Cu(II) compared with the other polychelates is in agreement with the spectrochemical series, where Cu(II) complexes are always more stable than other complexes.

TABLE V
Thermal Behavior of the Coordination Polymers

Compound	% loss in weight found	Temperature	Assignment of mass loss % Char	Residue at 750°C
BPF-Fe(III)	4	Up to 100°C	Loss of lattice/absorbed water/Solvent molecules	3.2
	23.5	$100\text{--}150^\circ\text{C}$	Loss of two coordinated water molecules	
	76.8	$200\text{--}750^\circ\text{C}$	Decomposition of polymer and formation of Fe_2O_3	
BPF-Co(II)	8	Up to 100°C	Loss of lattice/absorbed water/Solvent molecules	1.4
	20.3	$100\text{--}150^\circ\text{C}$	Loss of two coordinated water molecules	
	65.6	$200\text{--}750^\circ\text{C}$	Decomposition of polymer and formation of CoO	
BPF-Ni(II)	2	Up to 100°C	Loss of lattice/absorbed water/Solvent molecules	3.5
	10.5	$100\text{--}150^\circ\text{C}$	Loss of two coordinated water molecules	
	68.5	$200\text{--}750^\circ\text{C}$	Decomposition of polymer and formation of NiO	
BPF-Cu(II)	2	Up to 100°C	Loss of lattice/absorbed water/Solvent molecules	4.2
	–	$100\text{--}150^\circ\text{C}$	–	
	83.8	$200\text{--}750^\circ\text{C}$	Decomposition of polymer and formation of CuO	
BPF-Zn(II)	4	Up to 100°C	Loss of lattice/absorbed water/Solvent molecules	3.0
	–	$100\text{--}150^\circ\text{C}$	–	
	82	$200\text{--}750^\circ\text{C}$	Decomposition of polymer and formation of ZnO	

TABLE VI
Antimicrobial Activities of $[M(en)_2]$ Complexes and BPF-Metal Polychelates

Microorganism	Fe(III) Com./Poly. ^a	Co(II) Com./Poly. ^a	Ni(II) Com./Poly. ^a	Cu(II) Com./Poly. ^a	Zn(II) Com./Poly. ^a	BPA- HCHO	DMSO	X ^b	Y ^b
<i>E. coli</i>	10/16	9/14	8/12	11/15	11/16	5	–	29	–
<i>S. dysantraea</i>	9/12	9/15	10/17	12/18	11/14	8	–	27	–
<i>C. albicans</i>	8/11	7/10	12/19	10/14	10/17	7	–	–	22
<i>A. niger</i>	13/18	11/16	8/10	10/15	12/18	5	–	–	25

X = Kanamycin, Y = Miconazole. Kanamycin and Miconazole were used as standard drug.

DMSO was used as a control.

^a Value of zone of inhibition (in mm) at 50 µg/ml concentration of $[M(en)_2]$ complexes and BPF-Metal polychelates.

^b Including disc diameter, 0–5 = inactive, 5–10 = mildly active, 10–15 = moderately active.

Antimicrobial evaluation

The antibacterial and antifungal activities of $[M(en)_2]$ complexes and their corresponding chelated resins were shown Table VI. The agar well diffusion method was used for the bacteria and fungi with respect to Kanamycin and Miconazole as negative control. The growth was compared with DMSO as the control and expressed as zone of inhibition. It has also been observed from the antimicrobial screening studies that the metal chelated resins have higher activity than the corresponding $[M(en)_2]$ complex and BPA-HCHO compound under the same conditions (Table VI). This enhancement in the activity can be rationalized on the basis of the structure of BPA-HCHO compound, $[M(en)_2]$ complexes, and metal chelated resins, possessing an additional donor groups like N, O as well as the presence of hydroxyl groups. It is well known that bacterial cell surfaces are negatively charged. Hence, adsorption onto the negatively charged cell surface is expected to be enhanced with increasing charge density of the cationic biocides. The adsorption onto the bacterial cell surface is much more enhanced for polymers, compared with that for modal compounds (monomers).^{37,38} Polymers are more capable of disrupting and disintegrating cell membrane than small biocides due to the enhancement of interactions through polyvalency. With the combination of the functional groups and the increased permeability due to the structure of the polymers, they become more effective than metal complexes. The variation in the effectiveness of different compounds against different organisms can be correlated to the impermeability of the cells of the microbes or differences in ribosome of microbial cells.³⁹

CONCLUSIONS

It can be concluded that the synthesized polymer chelate complexes have practically the same structure with octahedral co-ordination in case of Fe(III), Co(II), Ni(II) and square planar coordination in Cu(II) and Zn(II) around the metal atoms. The stabil-

ity of these species as found to increase according to the order Cu(II) > Ni(II) > Zn(II) > Fe(III) > Co(II). All the polymers were found to be soluble in DMF and DMSO, but insoluble in water, ethanol, benzene, xylene, and chloroform. It was observed that the polymeric backbone having metal ions show good thermal stability and antimicrobial activity. These metal polychelates may be used as antifouling and antifungal coatings. The protective application of these polychelates is under consideration.

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