

Synthetic, Spectroscopic, Magnetic, Thermal, and Antimicrobial Approach Towards New Biocidal Coordination Polymers

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ABSTRACT: O-aminophenol was reacted with glutaraldehyde to obtain Schiff base, which was then reacted with formaldehyde in slight acidic medium to generate phenolic groups. Now the substituted Schiff base was reacted with the transition metal acetates of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) to get polymeric metal complexes. Their structures have been elucidated on the basis of elemental analyses, ^1H NMR spectra, ^{13}C NMR spectra, magnetic measurements, thermogravimetric analyses, electronic spectra, and infrared spectra. The results are in accordance with an octahedral environment around the central metal ion. The polychelates of Mn(II), Co(II), Ni(II), and Cu(II) are paramagnetic while Zn(II) polychelate was found to be diamagnetic. The synthesized Schiff base acted as a unine-

gative bidentate ligand and bonding occurs through the hydroxyl oxygen and nitrogen atoms. The thermal behavior of these coordinating polymers was studied by TGA in nitrogen atmosphere up to the temperature range of 800°C. All the synthesized polychelates were also screened for their biocidal activity against *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis* (bacteria), *Candida albicans*, and *Muller species* (yeast) by using agar well diffusion method. All the metal polychelates show promising antimicrobial activities. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3971–3979, 2012

Key words: coordination polymers; Schiff base; spectroscopic; thermal and antimicrobial studies

INTRODUCTION

Although Schiff base and the transition metal complexes has been studied extensively, but this subject is still found to be of great interest in coordination chemistry.^{1–3} Schiff base complexes are known to show antifungal activity, which is increased by the presence of azomethine or sulfur groups in the ligand.⁴ Schiff base complexes have played a significant role in analytical chemistry, biochemistry and agricultural chemistry. In addition to the above discussion, the coordination polymers, derived from Schiff base are also the center of interest. They are defined as materials in which metal ions are linked together with diol polyfunctional ligands. Much attention has been paid to porous high-dimensional coordination polymers, because of their potential zeolite applications.⁵ Metal-containing polymers on the other hand are thermally stable and impart high flexibility owing

to the presence of organic moiety, as well as high thermal stability due to presence of inorganic functional groups in the same polymeric backbone.⁶ The association of these properties makes them highly useful for industrial and scientific applications. The incorporation of metal ions in the polymeric backbone is not only affecting their physical properties but also alters chemical properties of the polymer.⁷ Previously a number of metal-chelated polymers with Schiff base complexes,⁸ crown ether complexes,⁹ and ferrocene complexes¹⁰ have been prepared and reported. These polymers are widely being used in semiconductor devices¹¹ and in the field of nanotechnology.¹² The metal-chelated polymers also have biological significance since they can also act as antimicrobial agents; these polymers are reported to show superior antimicrobial activity than do organic polymers.¹³ The present article reports on the synthesis and characterization of newly developed coordination polymers along with their antimicrobial activity against several bacteria and fungi by using agar disk diffusion method.¹⁴

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EXPERIMENTAL

Material

2-aminophenol (S.D. Fine), 25% glutaraldehyde (Merck), 35% hydrochloric acid (Merck), 37% aqueous

solution of formaldehyde (Merck). Transition metal(II) acetates (Qualigens): Manganese(II) acetate tetrahydrate, $[\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$, Copper(II) acetate monohydrate $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$, Nickel(II) acetate tetrahydrate $[\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$, Cobalt(II) acetate tetrahydrate $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$, Zinc(II) acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ were used without further purification. Solvents like dimethylformamide (DMF), dimethylsulphoxide (DMSO), ethanol, methanol, and acetone (Qualigens) were distilled before use. The microorganisms such as *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis* (bacteria) and *Candida albicans*, *Muller species* (yeast) were provided by the culture collection of microbiology laboratory, department of microbiology (A.M.U. Aligarh).

Analytical procedures

Nitrogen, hydrogen and carbon were analyzed with an Elemental analyzer system VarioEL CHNS (IIT Roorkee). The FT-IR Spectra were recorded over the (4000–500 cm^{-1}) range on a Perkin–Elmer infrared spectrophotometer model 621 by using KBr pellets. The polymers were analyzed for the metal content by complexometric titration against EDTA after decomposing with a mixture of perchloric acid, sulfuric acid and concentrated nitric acid (HNO_3) [1 : 1.5 : 2.5]. The electronic spectra were measured on a Perkin–Elmer Lambda EZ-201 spectrophotometer by using DMSO as a solvent and the magnetic susceptibility measurements of these polymers were carried out on a Gouy balance by using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a celebrant. Proton-1 and Carbon-13 nuclear magnetic resonance spectra (^1H -NMR and ^{13}C -NMR) were recorded on a JEOL-GSX 300-MHz FX-1000 FT-NMR spectrometer using DMSO as a solvent and tetramethylsilane (TMS) as an internal standard. Thermal behaviors of these polymers were carried out on a TGA analyzer Perkin–Elmer (Pyris Diamond) in nitrogen atmosphere at a heating rate of 10 $^\circ\text{C}/\text{min}$ (IIT Roorkee). The solubility of the polymers was tested in various solvents at room temperature. All the synthesized polychelates were screened against some bacteria and fungi for their antimicrobial activity in the department of microbiology, A.M.U. (Aligarh).

Synthesis of the polymeric Schiff Base [PSBG]

Schiff base of 2-aminophenol and glutaraldehyde was synthesized by slightly modified method of literature.¹⁵ 2-aminophenol (2.18 g, 0.02 mol) was dissolved in 30 mL ethanol, then glutaraldehyde (3.78 mL, 0.01 mol) was added drop wise to this solution with continuous stirring. The mixture was heated on a water bath for 1 h at 70 $^\circ\text{C}$ and left over night at room temperature to obtain a yellow crystal-

line solid Schiff base, it was now washed successively with water and ethanol and dried in vacuum.

The above prepared Schiff base (2.80 g, 0.01 mol) dissolved in 30 mL DMF and formaldehyde (0.56 mL) were mixed in presence of 2-3 drops of hydrochloric acid. The resulting mixture was refluxed for 1 h at 70–80 $^\circ\text{C}$. After that the solution was made viscous by vaporizing around 15 mL of solvent. It was now precipitated by adding excess amount of cold water. Dark orange solid was collected by filtration, washed several times with acetone and diethyl ether to remove excess solvent and water it was then dried in vacuum, yield 79%.

Ana. $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$ Calcd (%): C-73.44, H-6.16, N-9.51 Found (%): C-72.89, H-6.40, N-9.45.

^1H NMR (DMSO- d_6 , δ , ppm) 9.70 (Ar-OH), 8.27 (HC = N), 5.6 (CH_2 -Ar), 6.41-7.0 (Ar-H), 1.0-2.95 ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$).

FT-IR (KBr pellets) $\nu_{(\text{max})}$ cm^{-1} : 3200-3600 $\nu(\text{OH})$, 1620 $\nu(\text{HC} = \text{N})$, 2850-2940 ($-\text{CH}_2$ (asym-sym)), 1276 (C-O).

Synthesis of the coordination polymer

A series of coordination polymers of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) was prepared from the above prepared Schiff base. A typical procedure for the preparation of the nickel polychelates is as follows:

The prepared Schiff base (2.94 g, 0.01 mol) was dissolved in 30 ML DMSO then nickel(II) acetate tetrahydrate (2.48 g, 0.01 mol) was added to it. This reaction mixture was heated at 70 $^\circ\text{C}$ with continuous stirring upto 9 h. The solution was reduced on water bath, till it become viscous and sticky. This sticky product was precipitated in distilled water. The obtained brown precipitate was filtered and washed several times with acetone and diethyl ether. The product was dried in a desiccator over anhydrous calcium chloride, yield 68%.

Similar method was applied for the synthesis of other polymer metal complexes.

Preparation of microbial cultures

The antimicrobial activity of metal-chelated polymers was carried out against *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis* (bacteria), and *Candida albicans*, *Muller species* (yeast). Bacterial strains were nourished in nutrient broth (Difco, Sparks, MD) and yeast in malt extract broth (Difco) and incubated for 24 and 48 h, respectively. According to agar disk diffusion method bacteria were inoculated on Muller Hinton Agar and yeast on sabouraud dextrose agar. A circular well was made at the center of each petri plate with a sterilized steel borer. Metal-chelated polymer samples were prepared using DMSO as a solvent at a concentration of 25 g/mL. Then 0.1 mL

TABLE I
Elemental Analysis of the Metal Polychelates

Compound abbreviation		Elemental analysis			
		Carbon	Hydrogen	Nitrogen	Metal
[PSBG-Mn(II).2H ₂ O] _n	[(C ₁₈ H ₂₀ N ₂ O ₄ -Mn(II)]	56.40 (56.92)	5.26 (5.22)	7.30 (6.37)	14.33 (13.80)
[PSBG-Co(II).2H ₂ O] _n	[(C ₁₈ H ₂₀ N ₂ O ₄ -Co(II)]	55.82 (55.70)	5.20 (5.60)	7.23 (6.45)	15.21 (14.30)
[PSBG-Ni(II).2H ₂ O] _n	[(C ₁₈ H ₂₀ N ₂ O ₄ -Ni(II)]	55.85 (55.97)	5.21 (5.03)	7.23 (6.50)	15.16 (15.19)
[PSBG-Cu(II)] _n	[(C ₁₈ H ₁₆ N ₂ O ₂ -Cu(II)]	60.74 (60.11)	4.53 (5.02)	7.87 (6.30)	17.85 (16.87)
[PSBG-Zn(II)] _n	[(C ₁₈ H ₁₆ N ₂ O ₂ -Zn(II)]	60.43 (61.51)	4.50 (4.82)	7.83 (7.67)	18.27 (17.98)

of each test solution was added to the well and incubated at about 36°C for 24 h and the yeast sample were incubated at 25°C for 72 h. DMSO-absorbed disks were used for control only. The resulting inhibition zones on the palates were measured in mm by using Imipenem as a standard drug for the bacteria and Miconazol for fungi.

RESULTS AND DISCUSSION

Chemistry

The polymeric Schiff base PSBG and their metal polychelates were formed in good yield by the condensation of glutaraldehyde, *o*-aminophenol, and formaldehyde. The compounds were insoluble in common organic solvents. The elemental analytical data of the compounds (Table I) indicate that the Schiff base formation has occurred in the 1 : 1 ratio as in Scheme 1. The observed electronic, FTIR, ¹H NMR data of the complexes are fully consistent with the proposed structure. Structural analysis of these compounds may provide some explanation for the structure activity relationships. Such an analysis might be helpful in the design of better inhibitors. The biological activity of a particular substance depends on a complex sum of individual properties including compound structure, affinity for the target site and survival in the medium of application, survival within the biological system, transport properties, and state of the target organism.¹⁶ These compounds are stable at room temperature and are non hygroscopic.

FTIR spectra

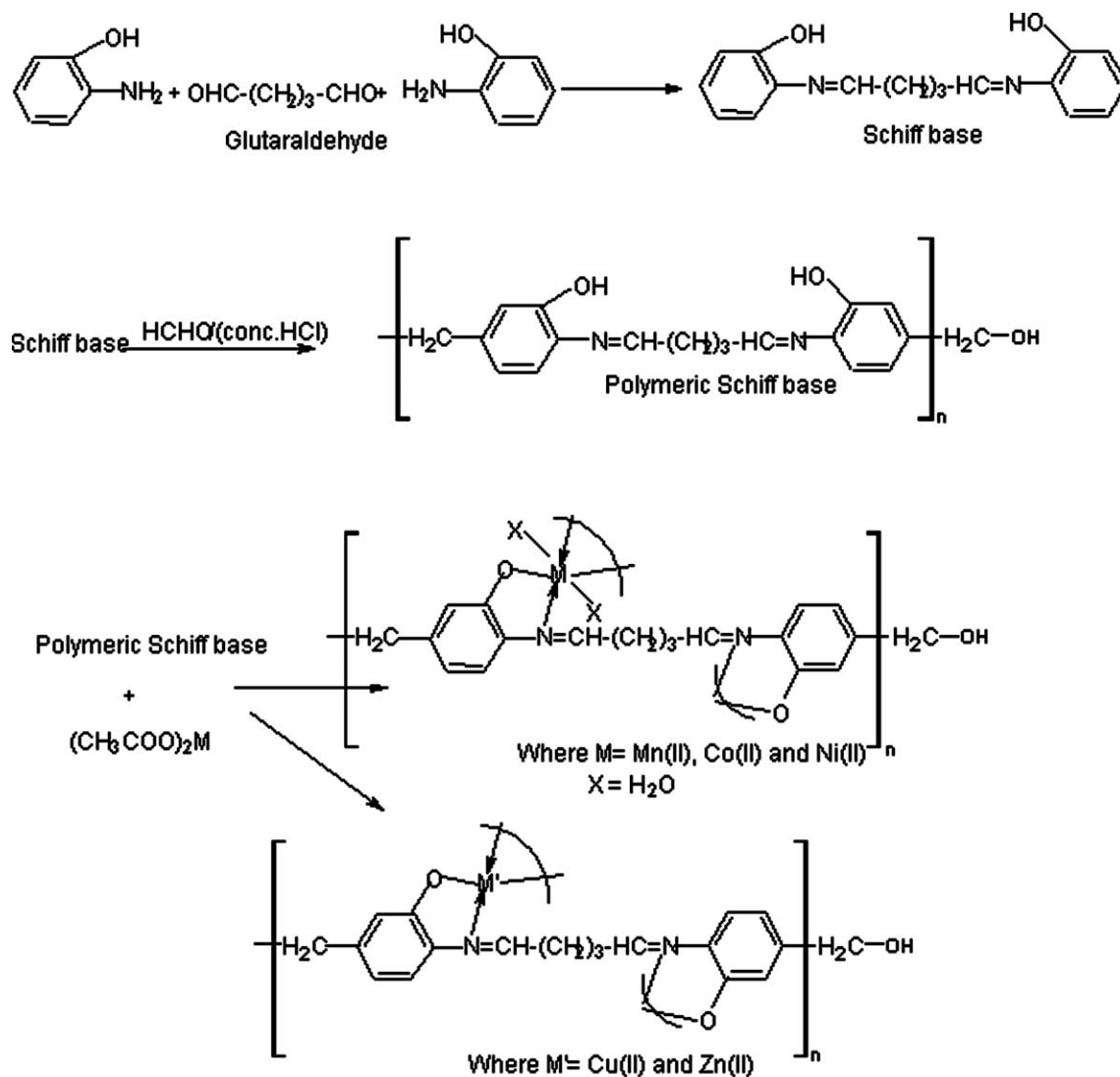
To study the binding mode of Schiff base to the metal ion in the coordination polymers, FTIR spectrum of the free ligand was compared with the spectra of the corresponding coordination polymers. The important infrared spectra of the chelates and their assignments are presented in Table II, Figure 1(a,b). The spectra of PSBG show a medium intense band at 2700 cm⁻¹ due to intramolecular hydrogen bonded -OH group.¹⁷ While its absence in the metal polychelates indicates deprotonation.

The infrared spectra of the Schiff base show a weak band at 3200–3600 cm⁻¹ which is assigned to hydrogen bonded O–H stretching. This band becomes broader on chelation. The spectra of the chelates exhibit a broad band in the region of 3300–3400 cm⁻¹ suggesting the presence of water molecule.^{18,19} The weak bands around 860 and 792 cm⁻¹ are assigned as OH rocking and wagging vibrations, respectively.²⁰ The presence of coordinated water molecules is also confirmed by elemental analysis and thermogravimetric analyses. The Schiff base exhibits a medium strong band at 1620 and 1276 cm⁻¹ due to azomethine ν(C=N) mode and C–O band respectively. When the FTIR spectral data of azomethine and C–O was compared, it was found that the band shifted to lower frequency by 8–17 cm⁻¹ showing the coordination of the azomethine nitrogen and ortho position of hydroxyl oxygen atoms to metal ions. The bands appearing in between 495 and 509 cm⁻¹ is for ν(M–O)²¹ while the band in between 450 and 465 cm⁻¹ is for ν(M–N).²²

¹H NMR and ¹³C NMR spectra

The ¹H NMR and ¹³C NMR spectra of the prepared polymers were studied and spectra of Zn(II) polychelate is given in Figures 2 and 3. The phenolic OH protons in the Schiff base at 9.7 ppm, were not present in the Zn(II) polychelate, indicating that the OH proton is removed by chelation with the Zn(II) ion. It confirms the bonding of phenolic oxygen to the metal ion.²³ Peak observed at 6.41–7.0 ppm is due to the protons of phenyl ring (8H, Ar-H). The resonance signals appeared at 9.28 ppm is due the azomethine protons. These signals were shifted downfield in the polymer metal complexes, suggesting deshielding of azomethine group due to the coordination of polymer with the metal ion.²⁴ Methylene protons of Ar-CH₂-O show signals at 5.6 ppm while signals at 2.95 ppm are assigned to the other methylene protons.

In the ¹³C NMR spectrum, the peaks observed at 165 ppm is due to the azomethine carbon for PSBG-Zn(II). The chemical shift of benzyl carbon of Ar-CH₂-O was observed at 57.8 ppm in PSBG-



Scheme 1

Zn(II). The signals due to the aromatic ring carbons were observed in 110.3–134.08 ppm. Carbon of different $-\text{CH}_2$ groups show the resonance signals at 42.14 ppm in PSBG-Zn(II) while the peak observed at 179.46 ppm were assigned to aromatic carbon.

Magnetic moments and electronic spectra

The information regarding geometry of the coordination polymers is obtained from the electronic spectral data and magnetic moments which are tabulated in Table III. Mn(II) coordination polymer exhibited

TABLE II
FTIR Spectral Bands and Assignments of Metal Polychelates

Compounds	Assignments						
	$\nu(\text{H}_2\text{O})$	(HOH) (ρ & ω)	$\nu(\text{C}-\text{O})$	$-\text{CH}_2$ (asym-sym)	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
PSBG-Mn(II)	3337	792(s)	1265	2940–2850 (m)	1605 (s)	504 (s)	455 (s)
PSBG-Co(II)	3400	700(s)	1262	2940–2850 (m)	1608 (s)	498 (m)	460 (s)
PSBG-Ni(II)	3300	860(s)	1264	2940–2850 (m)	1609 (s)	509 (s)	465 (s)
PSBG-Cu(II)	–	–	1268	2940–2850 (m)	1604 (s)	500 (s)	450 (m)
PSBG-Zn(II)	–	–	1263	2940–2850 (m)	1603 (s)	495 (m)	465 (s)

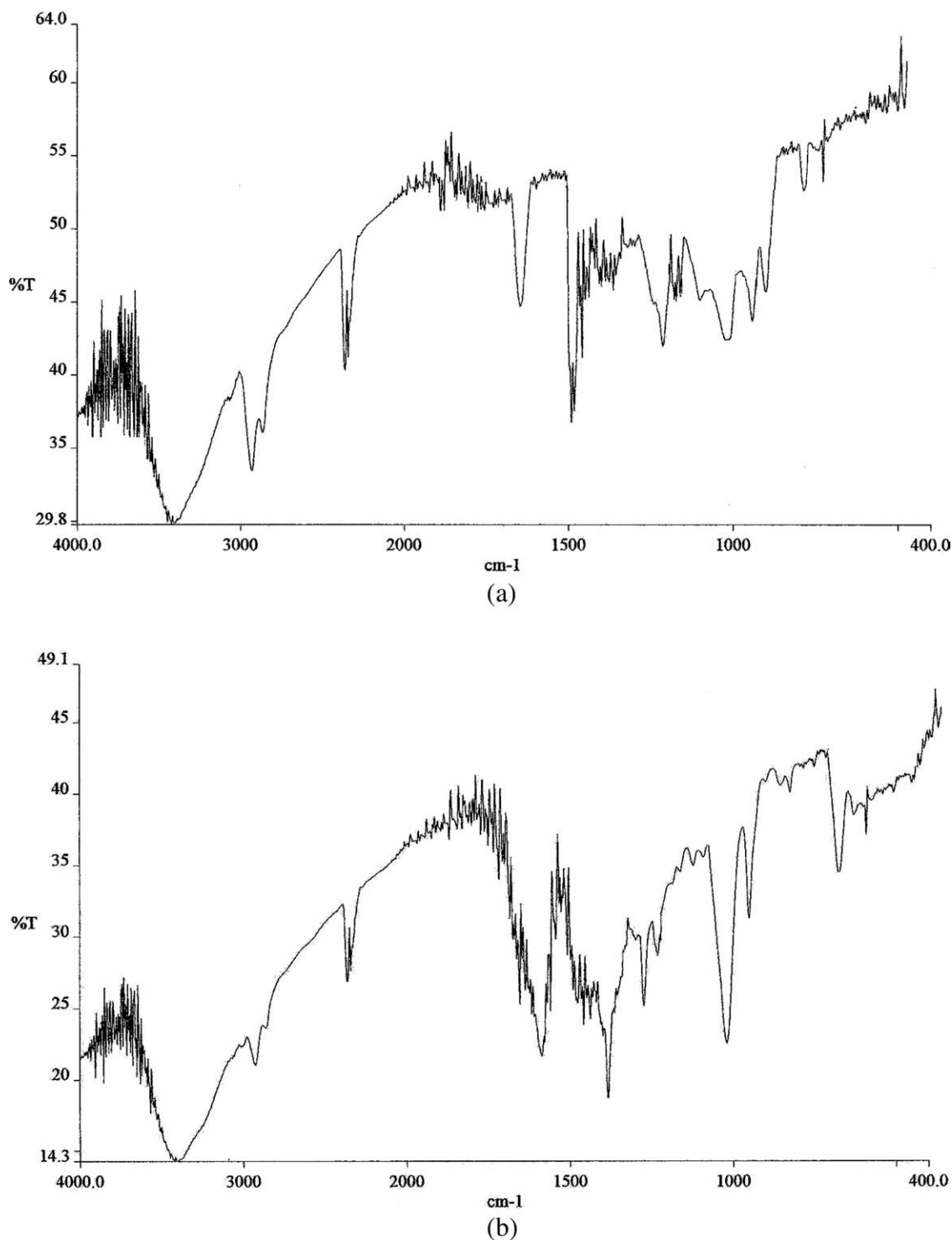


Figure 1 (a) FTIR spectra of PSBG; (b) FTIR spectra of PSBG-Ni(II).

three weak absorption bands at $18,260\text{ cm}^{-1}$, $20,500\text{ cm}^{-1}$ and $24,000\text{ cm}^{-1}$, which have been assigned to the transitions ${}^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)(\nu_1)$, ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)(\nu_2)$ and ${}^4A_{1g}(G) \leftarrow {}^6A_{1g}(F)(\nu_3)$, respectively, in an octahedral field.²⁵ The magnetic moment value of the Mn(II) coordination polymer is 6.01 B.M., which is within the limits of the spin-free value for five unpaired electrons, indicating that the coordination polymers are high-spin d^5

system with an octahedral geometry.²⁶ For the Co(II) coordination polymer, the reflectance spectra exhibits the bands of medium intensity at 8200, 18,000, and $19,500\text{ cm}^{-1}$, which are assigned to the ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)(\nu_1)$, ${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)(\nu_2)$ and ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)(\nu_3)$, respectively, for an octahedral cobalt (II) coordination polymer²⁷ with a magnetic moment value of 4.08 B.M.²⁸ The electronic spectra of the Ni(II)

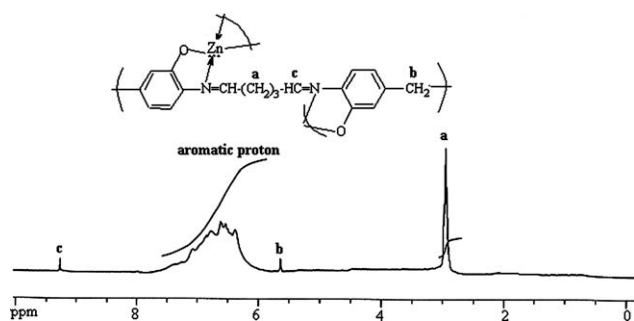


Figure 2 ^1H NMR of PSBG-Zn(II).

coordination polymer exhibits absorption bands at 10,500, 14,165, and 24,100 cm^{-1} attributed to $^3\text{T}_{2g}(\text{F}) \leftarrow ^3\text{A}_{2g}(\text{F})(\nu_1)$, $^3\text{T}_{1g}(\text{F}) \leftarrow ^3\text{A}_{2g}(\text{F})(\nu_2)$ and $^3\text{T}_{1g}(\text{P}) \leftarrow ^3\text{A}_{2g}(\text{F})(\nu_3)$, respectively, in an octahedral geometry,²⁹ having magnetic moment of 2.92 B.M., which can be taken as an additional evidence for their octahedral structure.³⁰ Cu(II) coordination polymers display a broad band at 15,365 cm^{-1} due to the $^2\text{A}_{1g} \leftarrow ^2\text{B}_{1g}$ and 25,050 cm^{-1} due to the charge transfer spectra. Its magnetic moment value is 1.75 B.M., which offers the possibility of square planer geometry.³¹ The values of the electronic parameters such as the ligand field splitting energy (10 Dq), Racah inter electronic repulsion parameter (B) and nephelauxetic ratio (β) is presented in Table III. Zn(II) coordination polymer is diamagnetic in nature as expected for d^{10} systems.

ESR spectra

The ESR spectrum of PSBG-Cu(II) recorded in DMSO at 300°C and 77°C are shown in Figure 4(a,b). The ESR spectrum provides the information of importance in studying the metal ion environment. The ESR spectrum of PSBG-Cu(II) polychelate is anisotropic with resolved hyperfine structure. This anisotropic spectrum shows a $g_{\parallel} > g_{\perp}$ with the following values $g_{\parallel} = 2.308$, $g_{\perp} = 2.0721$ in which $g_{\parallel} > g_{\perp}$. These values indicate that the ground state of Cu(II) is predominately dx^2-y^2 , which supports a

square planar structure. From the above results, it is found that the bonds between the polymer ligand and metal ion have an ionic character more than the covalent character. The covalent character of a bond becomes more pronounced when the parameters g_{\parallel} and g_{\perp} are decreased.

The most sensitive parameter is the g_{\parallel} , the variation in the g_{\parallel} value is the best indication about the covalent character. According to Kivelson and Neimen, for ionic environment the g_{\parallel} value is normally > 2.3 and for the covalent character the value is less than 2.3. The g -values can be used to calculate the G value, with this factor indicating that the ligand is a weak field or strong field ligand. The equation used is as follows:

$$G = (g_{\parallel} - 2.002)/(g_{\perp} - 2.002)$$

Where G is less than 4.0, the ligand forming Cu^{2+} complex is regarded as a strong field ligand.³² In these resins, the G value is 5.397, indicating that the resin forms a weak field ligand.³³

Thermogravimetric studies

The thermogravimetric analysis for the polymer metal complexes was carried out within a temperature range of 0–800°C in nitrogen atmosphere to establish their compositional differences as well as to ascertain the nature of associated water molecules.³⁴ Thermogravimetric curve of the polymer metal complexes is shown in Figure 5. The determined temperature range, percent weight loss and thermal effects accompanying the changes in the polymer metal complexes on heating are given in Table IV, which revealed some important findings. The TG curves of the Mn(II), Co(II), and Ni(II) except Cu(II) and Zn(II) coordination polymers show a two-decomposition steps within the temperature ranges of 150–180°C and 180–800°C. The first estimated weight loss (%) for PSBG-M(II) complexes are of 9.81, 9.74, and 9.79 in the temperature range of 150–180°C, which may

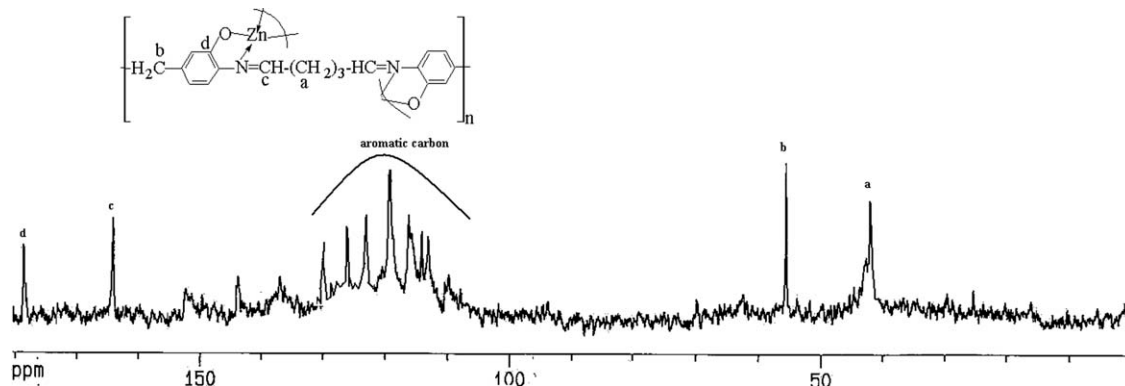


Figure 3 ^{13}C NMR of PSBG-Zn(II).

TABLE III
Magnetic Susceptibility and Electronic Spectral Parameters of Metal Polychelates

Abbreviation	Magnetic moment ^a (B.M.)	Electronic		Spectral data		Geometry	10Dq	B	β	$\beta\%$
		Transition (cm ⁻¹)	Assignment	Assignment	Assignment					
PSBG-Mn(II)	6.01	18,260 20,500 24,000	${}^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$ ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$ ${}^4A_{1g}(G) \leftarrow {}^6A_{1g}(F)$	Octahedral	8360	760	0.79	0.21		
PSBG-Co(II)	4.08	8,200 18,000 19,500	${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ ${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	Octahedral	7450	745	0.76	0.24		
PSBG-Ni(II)	2.92	10,500 14,165 24,100	${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$ ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$	Octahedral	8870	944	0.87	0.13		
PSBG-Cu(II)	1.75	15,365 25,050	${}^2A_{1g} \leftarrow {}^2B_{1g}$ Charge transfer	Square Planar						

^aBohr Magneton.

be attributed to the loss of two coordinated water molecules³⁵ of the Mn(II), Co(II), and Ni(II) polymer metal complexes, respectively. The second estimated mass loss (%) for PSBG-M(II) complexes are of 80.53, 77.59, 79.76, 78.74, and 78.36 within the temperature range of 180–800°C, attributed to the loss of ligand molecule and formation of metal oxide of the Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) polymer metal complexes, respectively.

Antimicrobial effect

The antimicrobial effects of the polymer metal complexes were determined against three bacteria and two yeasts as described in experimental section. The agar disc diffusion method was employed by using *Imipenem* and *Miconazole* as standard drugs against

bacteria and yeast respectively. The results of activity showed that polychelates are very effective in comparison to Schiff base on some of the microorganisms as summarized in Table V, Figure 6. The PSBG-Cu(II) exhibited highest antibacterial and antifungal activities against *E. coli*, *S. aureus*, *C. albicans*, and *M. species* (22, 20, 23, and 22 mm), respectively. PSBG-Ni(II) polychelate displayed promising activity (15 and 16 mm) against *B. subtilis* (bacteria), *C. albicans* (yeast) and high activity 22 mm against *E. coli*. PSBG-Co(II) showed high activity (24 and 22 mm) against *E. coli* and *B. subtilis*, respectively. PSBG-Mn(II) exhibited 20, 21 mm against *B. subtilis*, *M. species* and inactive against *S. aureus*. The PSBG-Zn(II) polychelate was found to be inactive against *C. albicans* and *B. subtilis*. The results reveal that the antimicrobial activity of these metal-chelated polymers

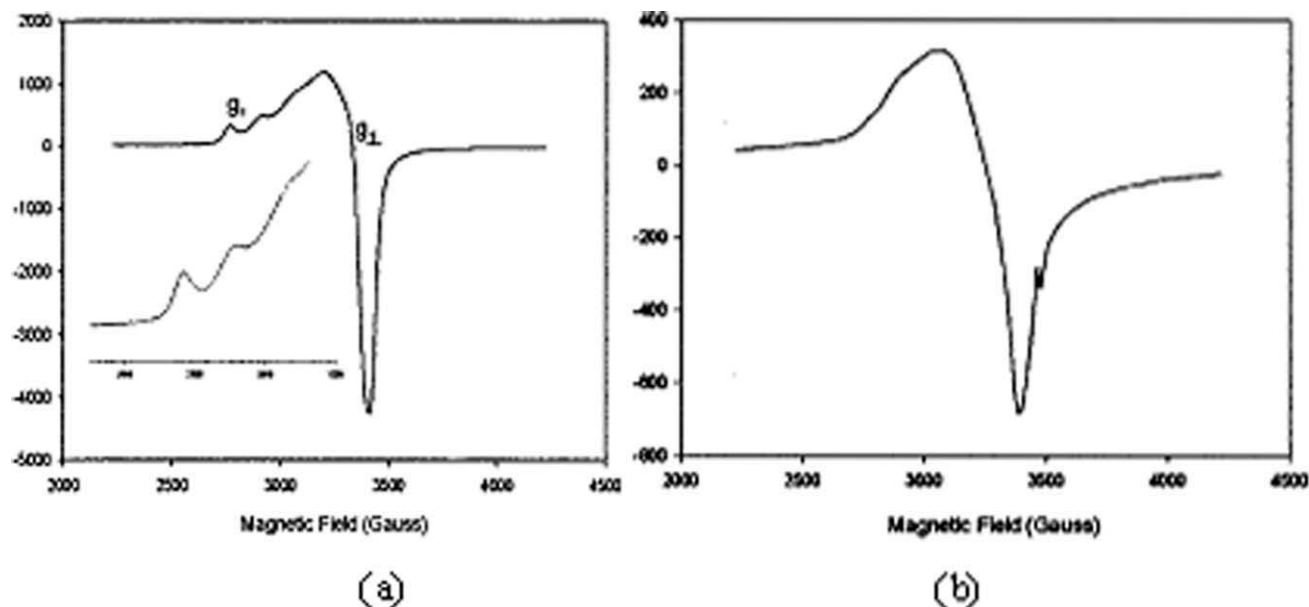


Figure 4 (a) and (b) ESR of PSBG-Cu(II).

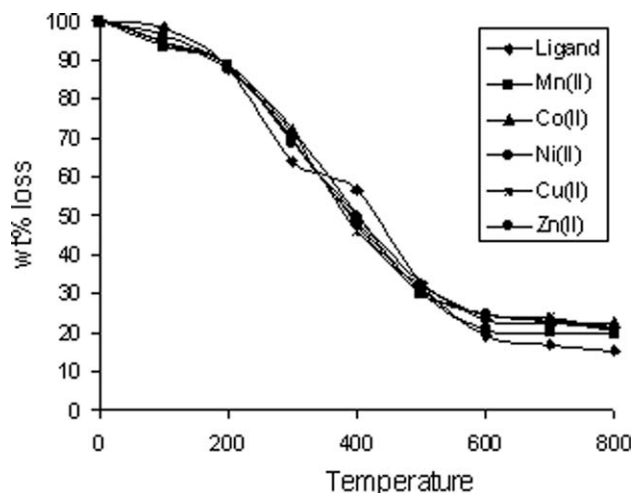


Figure 5 TGA of PSBG and PSBG-M(II).

is due to the presence of nitrogen and oxygen donor groups. It has been suggested that the compound with the N and O donor system might have inhibited enzyme production because enzymes that require a free hydroxyl group for their activity appear to be especially susceptible to deactivation by the ions of the complexes.³⁶ Since chelation reduces the polarity of the metal ion, mainly because of the partial sharing of its positive charge with the donor groups and possibly the π electron delocalization within the whole chelate ring thus formed during coordination. This process of chelation thus increases the lipophilic nature of the metal atom, which in turn favors its permeation through the lipid layer of the membrane. The lethal action of formaldehyde biocides is an outcome of their ability

TABLE IV
Thermogravimetric Data of Metal Polychelates

Coordination polymers	TG range (°C)	Mass loss (%)	Assignment
PSBG-Mn(II)	150–180	9.81	loss of two coordinated water molecules
	180–800	80.53	decomp. of ligand and formation of metal oxide
PSBG-Co(II)	150–180	9.74	loss of two coordinated water molecules
	180–800	77.59	decomp. of ligand and formation of metal oxide
PSBG-Ni(II)	150–180	9.79	loss of two coordinated water molecules
	180–800	79.76	decomp. of ligand and formation of metal oxide
PSBG-Cu(II)	150–180	–	no loss
	180–800	78.74	decomp. of ligand and formation of metal oxide
PSBG-Zn(II)	150–180	–	no loss
	180–800	78.36	decomp. of ligand and formation of metal oxide

TABLE V
Antimicrobial Activity of Metal Polychelates

Abbreviation	Zone of Inhibition (mm) 50 μ g/disk				
	<i>E. coli</i>	<i>S. aureus</i>	<i>B. subtilis</i>	<i>C. albicans</i>	<i>M. species</i>
PSBG	7	11	9	6	8
PSBG-Mn(II)	18	8	20	14	21
PSBG-Co(II)	24	13	22	10	16
PSBG-Ni(II)	22	9	15	16	10
PSBG-Cu(II)	22	20	14	23	22
PSBG-Zn(II)	19	15	19	–	17
DMSO	–	–	–	–	–
Miconazole ^a	–	–	–	15	20
Imipenem ^b	19	15	18	–	–

to inhibit the microbes. Formaldehyde is an extremely reactive chemical that interacts with protein, DNA, and RNA resulting from a combination with the primary amide as well as with the amino groups, although phenol groups bind little with formaldehyde. Low concentrations of formaldehyde are sporostatic and inhibit germination.³⁷ It is difficult to pinpoint accurately the mechanism(s) responsible for formaldehyde-induced microbial inactivation. Clearly, its interactive, and crosslinking properties must play a considerable role in this activity. Most of other aldehydes: glutaraldehyde, glyoxal, succinaldehyde, and *o*-phthalaldehyde [OPA] have sporicidal activity but glyoxal and succinaldehyde are less active. The distance between the two aldehyde groups in glutaraldehyde (and possibly in OPA) may be optimal for interaction of these -CHO groups in nucleic acids and especially in proteins and enzymes.³⁸

CONCLUSIONS

Newly developed metal-chelated compounds were prepared in good yield and characterized by various instrumental techniques. As it is well established now that inclusion of metal ion into a polymeric Schiff base enhances its activity, whether it is

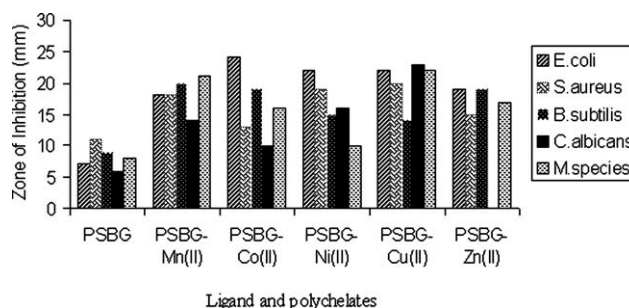


Figure 6 Inhibition growth of PSBG and PSBG-M(II).

biocidal or thermal, the newly synthesized polymeric ligands were synthesized from the easily available reactants which have low cost and can be easily synthesized in a short span of time. Synthesized Schiff base show less toxic and thermal activity as compared to the metal polychelates and in metal included Schiff base the highest activity was observed by PSBG-Cu(II), therefore these polychelates can be further utilized as antifungal and anti-fouling material in various processes.

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