Synthesis, Characterization, and Thermal and Antimicrobial Studies of Newly Developed Transition Metal–Polychelates Derived from Polymeric Schiff Base

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ABSTRACT: Monomeric Schiff base derived from salicylaldehyde and 1,3-diaminopropane was subjected to polycondensation reaction with formaldehyde and piperazine in basic medium. The resin was found to form polychelates readily with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) metal ions. The materials were characterized by elemental analysis, spectral studies (IR, ^{1}H-NMR, ^{13}C-NMR, and UV–visible), magnetic moment measurements, and thermal analysis. The electronic spectra and magnetic moment measurements of the synthesized polychelates confirmed the geometry of the central metal ion. Metal–resin bonds were registered in the IR spectra of the polychelates. The thermogravimetric analysis data indicated that the polychelates were more stable than the corresponding polymeric Schiff base. All the synthesized metal–polychelates showed excellent antibacterial activities against the selected bacteria. The antimicrobial activities were determined by using the shaking flask method, where 25 mg/mL concentrations of each compound were tested against 10^5 CFU/mL bacteria solutions. The number of viable bacteria was calculated by using the spread-plate method, where 100 μL of the incubated antimicrobial agent in bacteria solutions were spread on agar plates, and the number of bacteria was counted after 24 h of incubation period at 37°C. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1671–1679, 2009

Key words: Schiff base; 1,3-diaminopropane; polycondensation; thermogravimetric analysis; spread-plate method; antimicrobial activity

INTRODUCTION

A significant amount of research has been dedicated to the study of organic polymers, but the major drawbacks of these polymers are their low thermal stability and microorganisms such as bacteria and fungi that can infect them.[1] This has created an impetus for the development of new, thermally stable inorganic polymeric chelates with unique combinations of properties that have not been encountered in organic polymers.[2] Recently, a wide variety of coordination polymers have been developed that constitute a very important field in chemistry because of their application in organic synthesis, waste water treatment, hydrometallurgy, polymer drug grafts, nuclear chemistry,[3–5] as catalysts,[6] surface coatings,[7] and heat-resistant materials.[8] Transition metal–polychelates with Schiff base, in particular, are intensively studied because of their analytical and biological applications.[9,10] Application of many new analytical devices requires the presence of organic reagents as essential compounds of the measuring system. They are used in optical and electrochemical sensors as well as in various chromatographic methods to enable the detection of enhanced selectivity and sensitivity.[11,12]

Coordination polymers may be classified into different groups according to the metal's position on the chain, which is determined by the preparation techniques. A polymeric Schiff base (PSB) is an important class of coordination polymers, which have multidentate donor sites or groups and known to form polychelates with transition metal ions readily.[13] The basic properties of Schiff base polymers are due to the linkage of azomethine group (C=N) in the polymeric backbone.[14] In general, these polymers are insoluble in common organic solvents and infusible or melted at high temperature,[15] which impede their use in certain domains. Their insolubility is explained by the formation of coordination networks.[16]

A wide variety of investigations such as preconcentration and separation of metal ions, semiconductivity, redox reactions, biomedical applications, and so forth have been carried out using polymers with metal-chelated groups. The incorporation of metal ion into the polymeric chain not only affects their physical characteristics, like strength, but also their

chemical behavior and biological properties.[17,18] Previously in our laboratory, a number of articles based on the synthesis and studies of a series of coordination polymers and their metal–polychelates have been reported[19,20] and they are expected to show good affinity and selectivity toward the metal ions at an appropriate pH. This led us to synthesize the PSB by condensing several diamines with aldehydes. In the reaction conditions set for condensation, the azomethine bonds (C=N) of the Schiff base did not undergo hydrolytic cleavage. As a part of our ongoing research, this article deals with the synthesis of formaldehyde-based piperazine containing PSB and characterized using various spectral (IR, ^{1}H-NMR, ^{13}C-NMR, and UV–visible) and physicochemical techniques. The elemental analysis, magnetic moment measurements, thermal property, the type of chelation of ligand, and the geometry of the central metal ion are discussed. In addition, the antimicrobial activity was carried out against several bacteria and fungi by using the spread-plate method. The PSB had varied antimicrobial as well as thermal properties, which were enhanced after chelation.

EXPERIMENTAL

Reagents and strains

The solvents salicylaldehyde, 1,3-diaminopropane, piperazine, ethanol, formaldehyde (37% aqueous solution) S. D. Fine, Ltd. (Mumbai, India), *N*,*N*′-dimethylformamide (DMF), dimethylsulfoxide (DMSO), acetone, NaOH, transition metal acetates (Qualinges, India) were all used as received. Transition metal acetates (Qualinges) were obtained commercially. Tryptic soy agar (TSA) was purchased from Difco Laboratories (Lawrence, KS). It contained 15.0 g of pancreatic digest of casein, 5.0 g of enzymatic digest of soybean meal, 5.0 g of sodium chloride, and 15.0 g of agar. Tryptic soy broth (TSB) was also purchased from Difco Laboratories. It contained 17.0 g of pancreatic digest of casein, 3.0 g of enzymatic digest of soybean meal, 2.5 g of dextrose, 5.0 g of sodium chloride, and 2.5 g of dipotassium phosphate. Bacterial strains used for the antibacterial activity tests included *S. aureus*, IFO 3060, *B. subtilis*, IFO 3037, and *E. coli*, *S. typhi*, IFO 3080 strain. The strains were kept at −80°C in a freezer.

Preparation of monomeric Schiff base

Monomeric Schiff base was synthesized from salicylaldehyde and 1,3-diaminopropane in 2 : 1 molar ratio. In a 250-mL round-bottomed flask, a solution of salicylaldehyde (0.02 mol) in ethanol (100 mL) was added dropwise to a solution of 1,3-diaminopropane (0.01 mol) in ethanol (50 mL). The reaction

mixture was acidified with conc. hydrochloric acid (0.5 mL) and refluxed with constant stirring at 70°C temperature for 2 h. It was then placed into ice–cold water and allowed to stand for 30 min, which produced yellow-colored precipitate. The precipitate was filtered off and purified by washing repeatedly with ethanol, distilled water, and acetone, and then dried in a vacuum desiccator on calcium chloride; the monomeric Schiff base was obtained in yield 70% and soluble in DMF and DMSO at room temperature.

Preparation of polymeric Schiff base

The PSB was synthesized in DMF solution in the molar ratio 1 : 2 : 1 (monomeric Schiff base : formaldehyde : piperazine). 2.84 g (0.01 mol) of monomeric Schiff base and 1.5 mL (0.02 mol) of formaldehyde were dissolved in 100 mL DMF in a three-necked round-bottomed flask equipped with a water-cooled condenser, thermometer, and a magnetic stirrer, and two or three drops of 40% aqueous NaOH was added to this solution. The temperature was raised upto 70°C and stirred magnetically for 30 min. To this solution, 0.86 g (0.01 mol) of piperazine dissolved in 25 mL DMF was added. After the addition, the reaction mixture was stirred continuously at 80°C for 2 h. The progress of the reaction was monitored by thin layer chromatography. The reaction mixture was cooled and precipitated into 50/50 (v/v) water/acetone mixture. The solid brown product was filtered and then reprecipitated from DMF in ethanol. The brown solid product of SPFP was filtered and washed thoroughly with distilled water and acetone. Finally, the product was dried in vacuum oven and gave polymeric ligand in 75% yield.

Preparation of the metal–polychelates

Polychelates of PSB were prepared by using equimolar ratio (1 : 1) of PSB and metal salts. A typical procedure for the preparation of the Cu(II)–polychelate is carried out as follows: 0.01 mmol of PSB was dissolved in a minimum quantity (∼ 20 mL) of hot DMF and 0.01 mmol of Cu(II) salt was dissolved in hot DMF (∼ 10 mL) separately. Both the solutions were filtered and mixed in hot condition with constant stirring. Then the reaction mixture was refluxed at 60°C under stirring for 3–4 h. A dark-green-colored product was obtained, which was reprecipitated in distilled water. Finally, the product was filtered and washed with distilled water and alcohol with acetone, and then dried in a vacuum desiccator on calcium chloride, yield 80%.

A similar procedure was adopted for the synthesis of the other metal–polychelates such as PSB–Mn (II), PSB–Co (II), PSB–Ni (II), and PSB–Zn (II) in 1 : 1

TABLE I
Elemental Analysis of PSB and Its Metal–Polychelates

Compounds	Yield (%)	Elemental analysis			
		%C	%H	%N	%M
$C_{23}H_{28}N_4O_2$	75	68.40 (69.98)	6.80 (7.72)	13.23 (14.20)	– –
$C_{23}H_{30}N_4O_4$-Mn(II)	80	56.20 (57.10)	5.30 (6.71)	11.01 (11.60)	11.03 (11.35)
$C_{23}H_{30}N_4O_4$-Co(II)	73	55.40 (56.63)	5.07 (6.70)	10.20 (11.48)	11.85 (12.10)
$C_{23}H_{30}N_4O_4$-Ni(II)	85	55.50 (56.63)	5.23 (6.69)	11.12 (11.49)	12.05 (12.80)
$C_{23}H_{26}N_4O_2$-Cu(II)	70	60.09 (60.57)	5.42 (6.20)	11.30 (12.28)	13.17 (13.93)
$C_{23}H_{26}N_4O_2$-Zn(II)	75	60.10 (60.32)	5.20 (6.18)	12.10 (12.23)	11.72 (12.28)

Found (calculated).

resin to metal molar ratio, and their yield is given in Table I.

Measurements

The infrared (IR) spectra were recorded on a Perkin-Elmer infrared spectrometer model 621 by using KBr pellets. The ^{1}H-NMR spectra were recorded on a JOEL-FX-100 FT NMR instrument in DMSO solution and tetramethyl silane as an internal standard. The elemental analysis of carbon, hydrogen, and nitrogen was carried out on a Perkin-Elmer model-2400 elemental analyzer (CDRI, Lucknow, India). The percentage of metals was determined by complexometric titration against EDTA after decomposing with concentrated nitric acid (HNO_3). The solubility of polymeric ligand and its metal–polychelates were checked at room temperature in different solvents. The thermal stability of PSB and its metal–polychelates have been evaluated for recording thermograms by TA analyzer 2000 at a heating rate of 20°C/min under nitrogen atmosphere. The electronic spectra of the metal–polychelates were recorded on a Perkin-Elmer Lambda-201, and the magnetic moment measurements were done with vibrating sample magnetometer. The solubility of the polymers was tested in various solvents at room temperature. Antibacterial assays were incubated in a Gyromax 737 shaker at 30°C with a gyration speed of 300 rpm.

Antimicrobial assessments

The antimicrobial activity of the synthesized polymers was performed using the shaking-flask method, and the number of viable cell was counted using the spread-plate method. S. aureus, B. subtilis, E. coli, and S. typhi were streaked out on TSA plates and incubated at 37°C for 24 h. A representative colony was lifted off with a wire loop and placed in 6 mL of TSB, which was then incubated with shaking at 37°C for 24 h. At this stage, the cultures contained ∼ 10^9 colony-forming units (CFU) per mL. Cultures of S. aureus, B. subtilis, E. coli, and S. typhi containing 10^7 CFU/mL were prepared by dilution with TSB, which were used for antibacterial tests. The antibacterial activities were determined by testing 25 mg/mL concentrations of the PSB and its metal–polychelates against S. aureus, B. subtilis, E. coli, and S. typhi using the aforementioned methods. The PSB was mixed with TSB and formed a suspension. The suspension containing polychelates was mixed with 10^5 CFU of the test organism in a 10-mL culture tube. The test tube was stirred at 300 rpm at 30°C for 24 h, at the end of this period; an amount (0.5 mL) of the mixture from each test tube was pulled out and diluted with TSB. From these dilutions, surviving bacteria were counted on agar plates by spread-plates methods. These plates were incubated at 37°C, and the colonies were counted after 24 h, except for the case of E. coli, whose colonies were counted after 42 h. The number of bacterial cells was calculated by multiplying the number of colonies with the dilution factors.

RESULTS AND DISCUSSION

The PSB was prepared in three stage process as shown in Scheme 1. The structure of resin was identified by elemental analysis, IR, ^{1}H-NMR, and ^{13}C-NMR spectra, and thermogravimetric analysis (TGA). The UV–visible spectra and magnetic moment measurement were carried out to find the geometry of central metal ion in the case of metal–polychelates. The elemental analysis of the resin and its metal–polychelates are in good agreement with theoretical expectations. The analytical and physical data show that the reaction of resin with metals
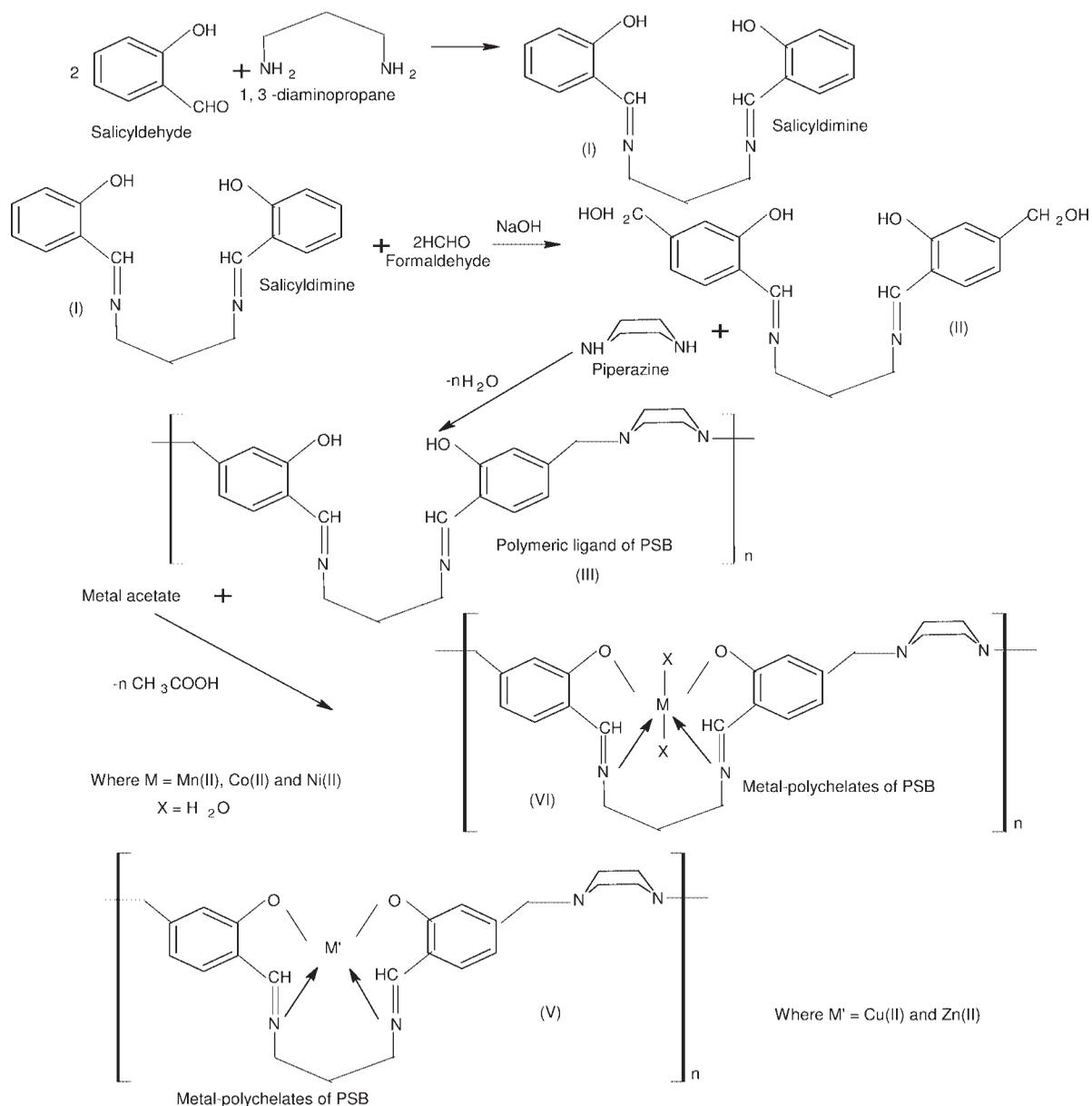
Scheme 1 Synthetic route of the polymeric ligand and its meta-polychelates.

gives the product with 1 : 1 metal to resin molar ratio. The results of elemental analysis of the synthesized compounds are given in Table I. It was also observed through the analytical data that Mn(II), Co(II), and Ni(II) polychelates were coordinated with two water molecules, but that Cu(II) and Zn(II) polychelates did not have coordinated water, which was further supported by the TGA results. All the metal–polychelates were soluble in DMF and DMSO but insoluble in water, methanol, ethanol, and other common organic solvents.

IR spectra

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The ligand and metal–polychelates were mainly characterized using the azomethine and Ar—OH bands. Infrared spectrum of ligand and the metal–polychelates were taken by using KBr pellets in the region of 5000–400 cm^{-1}. The main infrared bands and their assignments are listed in Table II. The appearance of a broad strong band in the IR spectra of the ligand in 3450–3400 cm^{-1} is assigned to Ar—OH stretching vibrations. In the metal–polychelates, this band disappeared, indicating that the ligand was coordinated to metal ions through the oxygen atom of Ar—OH. It is seen that PSB exhibits a band at 1630 cm^{-1}, which can be assigned to the azomethine (C=N) linkage of Schiff base.[21] This band is observed to show a negative shift by 20–40 cm^{-1} in the polychelates, indicating the coordination

TABLE II
Important IR Spectral Bands and Their Assignments of Polymeric Ligand (PSB) Resin and Its Metal–Polychelates

Assignments	Poly–PSB	PSB–Mn(II)	PSB–Co(II)	PSB–Ni(II)	PSB–Cu(II)	PSB–Zn(II)
Azomithine group (C=N)	1630	1610	1620	1590	1600	1610
Ar—OH/coordinated water	3450–3400	3450	3450	3450	–	–
C=C	1550	1565	1560	1570	1555	1550
C—H Asym–sym	2930	2900	2920	2930	2910	2858
M—N	–	565	550	554	560	565
M—O	–	650	643	630	640	638

of this nitrogen to the metal ion.[22,23] The C—H asymmetric and symmetric stretching due to the methylene group observed in the range 2930–2858 cm^{-1}. The peak at 770–765 cm^{-1} is due to the C—H out-of-plane bending vibrations of aromatic system. All the polymeric compounds display a strong band in the frequency range 1570–1550 cm^{-1}, which ascribed to C=C aromatic ring stretching. The appearance of two well-defined absorption in the range 650–630 cm^{-1} and 565–550 cm^{-1} were assigned to M—O and M—N modes, respectively.[24,25] Polychelates of Mn(II), Co(II), and Ni(II) ion show one common absorption band at 3350 cm^{-1}, which assigned to the water molecules with in the coordination sphere as well as lattice water.[9] This band is not found in the spectra of Cu(II) and Zn(II) polychelates, which was also supported by electronic spectra and TGA analysis.

Electronic spectra and magnetic moment measurements

The electronic spectra of metal–polychelates were recorded in DMSO. The electronic spectral bands and their magnetic properties are depicted in Table III. The magnetic moment of the Mn(II)–polychelate was 5.65 B.M., which suggested the presence of five unpaired electrons. The electronic spectrum of Mn(II)–polychelate exhibited three bands at 18,770, 22,980, and 24,900 cm^{-1}, which may reasonably correspond to $^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$, $^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$, and $^4A_{1g}(G) \leftarrow {}^6A_{1g}(F)$ transitions, respectively. These data were used to calculate the Dq, B, and β values. The value of crystal field parameter (10 Dq) was found to be 8810 cm^{-1} and the Racah parameter (B) was 725 cm^{-1}. The nephelauxetic effect (β) value was reduced to about 75% of the free ion value for Mn^{2+} (960), and the covalency parameter (β^0) value of 25% indicated the covalent nature of the compound.[26] The Co(II)–polychelate has a magnetic moment of 3.99 B.M. corresponding to four unpaired electrons and showed three bands at 9800, 14,070, and 20,300 cm^{-1}, which were assigned to $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$, $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$, and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transition, respectively, which indicates an octahedral environment around the Co(II) ion.[27] The crystal field parameter of the compound were 10 Dq = 11,000 cm^{-1}, B = 787 cm^{-1}, β = 81%, and β^0 = 19%. The reduction of the Racah parameter from the free ion values of 971–787 cm^{-1} and the value of β indicate the presence of covalence nature of the compound. The octahedral Ni(II)–polychelate was expected to be paramagnetic because of the two unpaired d-electrons, and the experimental

TABLE III
Magnetic Susceptibility and Electronic Spectra of Polymeric Ligand (PSB) and Its Metal–Polychelates

Abbreviation	Magnetic moment (B.M.[a])	Electronic transition (cm^{-1})	Assignment transition (cm^{-1})	10 Dq	B'	β	β^0
			Electronic spectral data				
FPS-Mn(II)	5.65	24900	$^4A_{1g}(G) \leftarrow {}^6A_{1g}(F)$	5286	881	0.92	8
		20980	$^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$				
		16770	$^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$				
FPS-Co(II)	3.99	20300	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	10997	780	0.80	20
		14070	$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$				
		9800	$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$				
FPS-Ni(II)	2.33	25230	$^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$	9820	829	0.77	23
		16667	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$				
		9820	$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$				
FPS-Cu(II)	2.14	25885	Charge transfer				
		15860	$^2A_{1g} \leftarrow {}^2B_{1g}$				

[a] Bohr magneton.
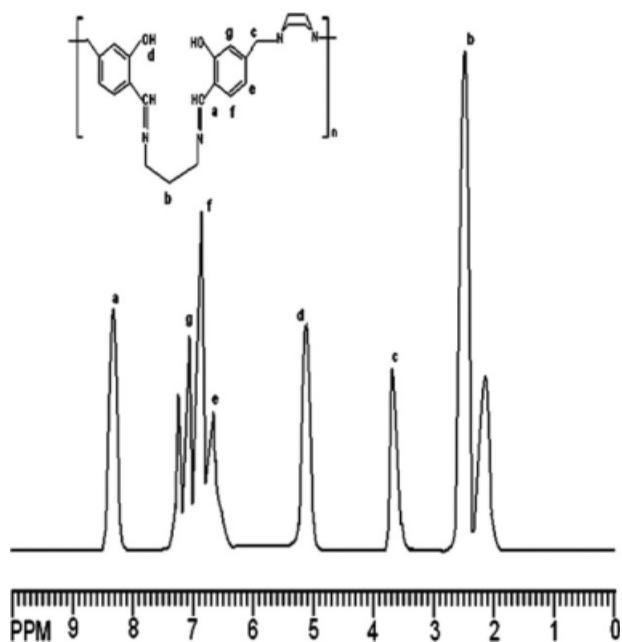
Figure 1 ^{1}H-NMR spectra of polymeric resin.

Figure 2 ^{1}H-NMR spectra of Zn(II)–polychelate.

magnetic moment was found to be 2.33 B.M. The electronic spectra showed three bands at 9820, 16,667, and 25,230 cm^{-1}, which assigned to $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$, and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ transition, respectively. The crystal field parameter were 10 Dq = 9830 cm^{-1}, B = 767 cm^{-1}, β = 71%, and β^0 value 29%, which is in the favor of octahedral geometry for Ni(II)–polychelate.[28] The reduction in the free ion value of 1080–767 cm^{-1} and the β value indicate the covalent nature of the compound.

The discussion strongly indicates an octahedral geometry around the central metal ion in all polychelates. It accounts for the occupation of two coordinating sites by H$_2$O out of six in making the octahedral environment.

In another study, the electronic spectra of the Cu(II)–polychelate exhibited two bands, at 15,860 and 25,885 cm^{-1} due to $^2A_{1g} \leftarrow {}^2B_{1g}(F)$ and charge transfer, respectively, which indicate square-planar geometry. In this study, the magnetic moment value of Cu(II)–polychelate was found to be 2.14 B.M., which is in accordance with square-planar geometry.

^{1}H-NMR spectra

The ^{1}H-NMR spectra of PSB and of its polychelate with Zn(II) metal ion are shown in Figures 1 and 2. The ligand spectrum showed a signal at 8.2 ppm for the CH=N protons of the azomithine group.[29] A set of multiples in the range 6.51–7.4 ppm was due to aromatic protons.[30] The multiple resonance signals observed at 3.5 and 2.5 ppm are due to Ar—CH$_2$—N

and N—CH$_2$—CH$_2$—CH$_2$—N protons, respectively. The PSB showed a signal at 5 ppm due to Ar—OH group. In the ^{1}H-NMR spectra of the Zn(II) polychelate, a significant shift in the azomithine (CH=N) proton is observed when compared with the free ligands. This is indicative of the azomithine nitrogen lone pairs coordinating to the metal center and the signal of Ar—OH group completely disappeared, suggesting that the bond formation takes place through the Ar—OH with metal ion.

Thermogravimetric analysis

The thermal decomposition of all the synthesized compounds was studied by the thermogravimetric method. The TGA traces are shown in Figure 3, and
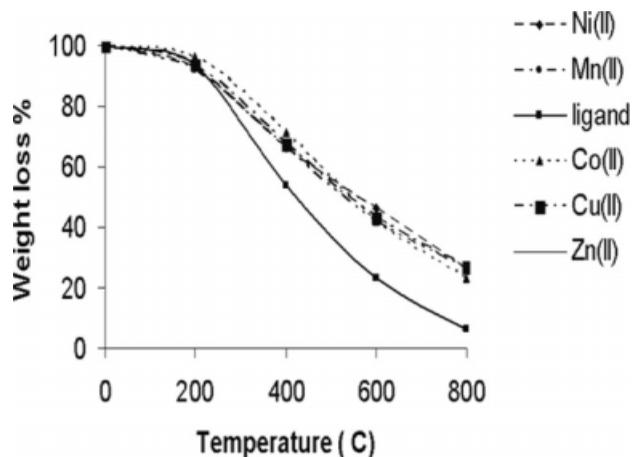
Figure 3 Thermogravimetric analysis of polymeric resin and its metal–polychelates.

TABLE IV
Thermal Properties of Polymeric Ligand (PSB) and Its Metal–Polychelates

Empirical formula	Weight loss (%) at the indicated temperature in °C			Characteristic weight left (%) at 800°C
	200	400	600	
$C_{23}H_{28}N_4O_2$	6	46.5	77	3
$C_{23}H_{30}N_4O_4$-Mn(II)	7.5	33.5	54	26.5
$C_{23}H_{30}N_4O_4$-Co(II)	4	29	58	23
$C_{23}H_{30}N_4O_4$-Ni(II)	8	34	58	26
$C_{23}H_{26}N_4O_2$-Cu(II)	3	28	44.5	30
$C_{23}H_{26}N_4O_2$-Zn(II)	6.5	32.5	57	27

thermal analytical data are presented in Table IV. These data revealed that the thermal stability of all the polychelates is higher than that of the parent resin and did not decompose easily even at high temperature. The thermogravimatric curves confirmed the presence of water molecules in all the polychelates, except that of Cu(II) and Zn(II) according to the literature.[31] The water molecules eliminated upto 160°C may have been due to its coordination with the metal atoms in the polychelates. In this study, the removal of water from Mn(II), Co(II), and Ni(II) polychelates was completed upto 130°C, which was probably considered as crystalline or coordinated water. Most of the polychelates started to decompose with weight losses from 4–8 wt % at 200°C, which was due to the elimination of the water molecules. The thermogram in Figure 3 indicated that the decomposition of the polychelates was very slow in the initial state, but above 350°C, the weight loss became fast. The thermal data indicated that the thermal and binding affinity in the polychelates were in the order Cu(II) > Zn(II) > Mn(II) > Ni(II) > Co(II), this showed that Cu(II) ion has more binding affinity to the resin better than the other metal ions. The decomposition in all of the coordination polymers was completed at 800°C. The polychelates were thermally stable upto 350°C. The char yield at 800°C for the polychelates was 23–30%, mostly due to the nonvolatile metal oxide.

Antimicrobial activity

The antibacterial activity of the synthesized PSB was determined according to the experimental procedure mentioned earlier. The minimum bacterial concentration (MBC) values of the polychelates were obtained from spread-plate tests, and these results are summarized in Table V. The best antibacterial activity was obtained for the Cu(II)–polychelate, which had MBC values of 160 and 180 μg/mL against B. subtilis and S. aureus, respectively. The Mn(II)–polychelate had MBC values of 215 and 210 μg/mL against these bacteria. The agar plates showing the MBC results of Zn(II)–polychelate against E. coli and S. typhi and found >220 and >270 μg/mL. Considering that Cu(II) ion has higher stability constant than other transition metals used in this study, Cu(II)–polychelate show very good antibacterial activities. No growth was observed for the negative control, which is just the TSB (20 μg/mL), whereas the bacterial growth was observed for the positive control, which is the TSB (20 μg/mL) mixture inoculated with bacteria.

Figure 4 shows log(survivors) versus exposure time plots for the metal [Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)] polychelates against these bacteria. Exposure of the polymers to bacterial cells was carried as aforementioned method in "Experimental" section. The concentration of the polymers was 25 μg/mL and mixed with certain number of bacteria (5×10^{-5} CFU/mL). Figure 4(a) shows the plots for E. coli at 25 μg/mL with (5×10^{-5} CFU/mL), in which the bacterial cells were killed within 20 h when exposed to Cu(II)–polychelate. Figure 4(c) indicates the same plots for the S. typhi, exposure of the S. typhi cell to these polymers at the similar concentration exerted little effect on reducing the number of survivors. Figure 4(b) shows the log(survivors) versus exposure time plots for the synthesized polymers against B. subtilis at 25 μg/mL with (5×10^{-5} CFU/mL) of bacteria. In this case, the bacterial cells were killed within 20 h when exposed to Cu(II) and Zn(II) polychelates. Similarly, antibacterial activity of the polychelates was screened against S. aureus, and the exposures are given in Figure 4(d). In this case,

TABLE V
Antibacterial Activity (MBC)[a] Data for the Metal–Polychelates of PSB

Bacteria	PSB–Mn(II)	PSB–Co(II)	PSB–Ni(II)	PSB–Cu(II)	PSB–Zn(II)
E. coli (−ve)	250	240	230	200	>220
S. aureus (+ve)	210	230	225	180	225
B. subtilis (+ve)	215	240	235	160	240
S. typhi (−ve)	140	225	210	180	>270

−ve, Gram negative; +ve, Gram positive.
[a] Minimum bacterial concentration.
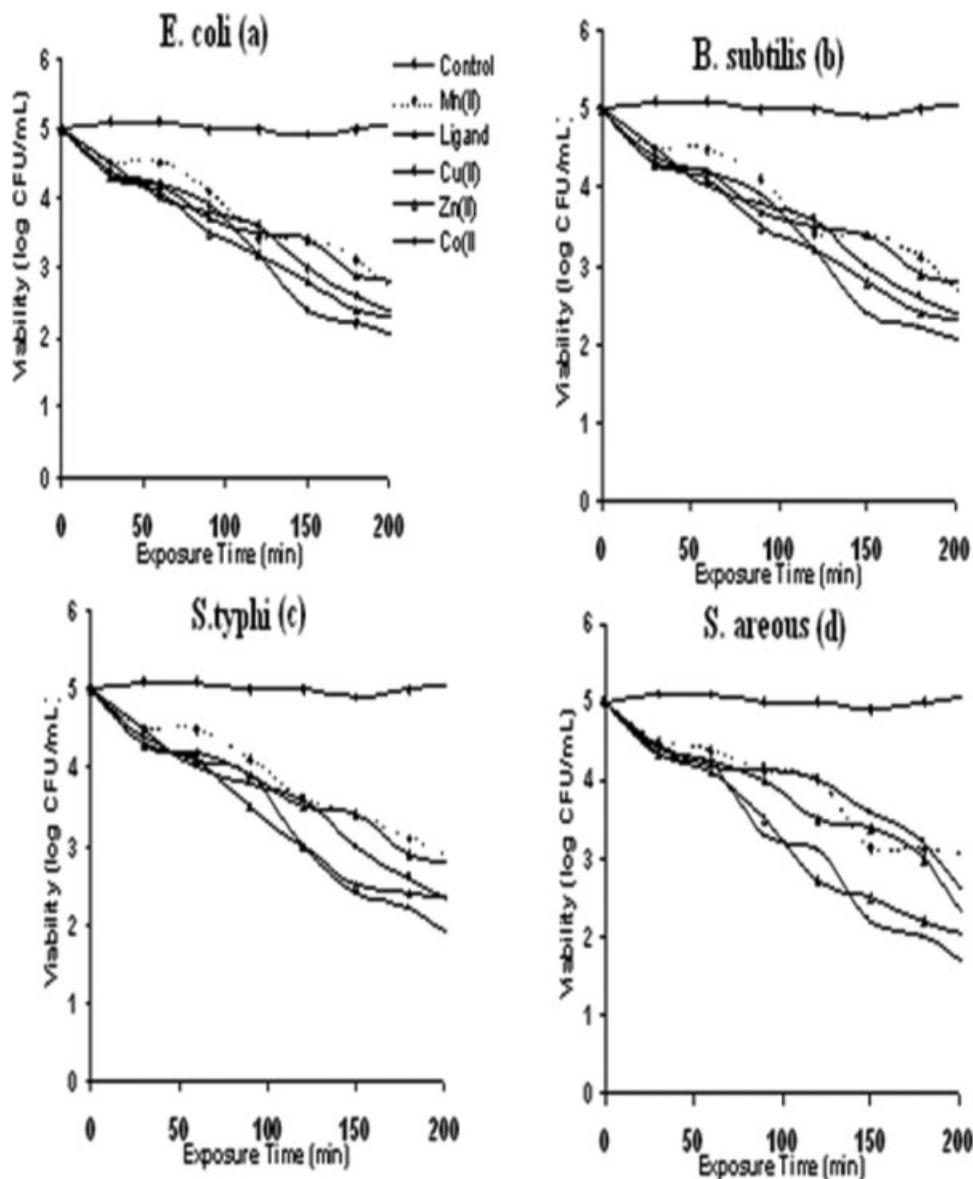
Figure 4 Antimicrobial activity of polymeric resin and its metal–polychelates.

the bacterial cells were killed within 16 and 20 h when exposed to Cu(II) and Zn(II), respectively. From Figure 4(a–d), it is evident that the polycheletes [Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)] are moderately active against all the microorganism used in this study. It is clear that Cu(II)–polychelates is more active than other polymers against all the bacteria because of the higher stability constant of Cu(II) ion. The most probable explanation for the higher activity of the Cu(II) ion may be given by considering their contribution with the cell membrane. The bacterial cell surface is negatively charged as evidenced by electrophoretic mobility. Absorption of copper cations onto the negatively charged cell surface is supposed to be much more favored than that of other metal cations. Thus, the antibacterial activity is expected to be more enhanced for Cu(II) cations when compared with that for other cations.

CONCLUSION

Newly developed metal-chelated polymers were prepared in good yield and characterized by various instrumental techniques. It has been observed that the attachment of metal ion in the polymeric backbone enhances thermal as well as antmicrobial activity. Because of their more toxic behaviors, Cu(II)–polychelate may be used as antifungal and antifouling coating for various projects. The synthesized polychelates could be used as solvent-resistant coating materials because of their insolubility nature.

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