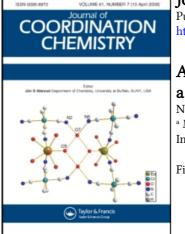
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# Antimicrobial agents: synthesis, spectral, thermal, and biological aspects of a polymeric Schiff base and its polymer metal(II) complexes

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## Antimicrobial agents: synthesis, spectral, thermal, and biological aspects of a polymeric Schiff base and its polymer metal(II) complexes

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Some new coordination polymers of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) obtained by the interaction of metal acetates with polymeric Schiff base containing formaldehyde and piperazine have been investigated. Structural and spectroscopic properties have been studied by elemental, spectral (FT-IR, <sup>1</sup>H-NMR, and UV-Vis), and thermogravimetric analysis. UV-Vis spectra and magnetic moments indicate that Mn(II), Co(II), and Ni(II) polymer metal complexes are octahedral, while Cu(II) and Zn(II) polymer metal complexes are square planar and tetrahedral, respectively. All compounds were screened for their antimicrobial activities against *Escherichia coli, Bacillus subtillis, Staphylococcus aureus, Pseudomonas aeruginosa, Salmonella typhi, Candida albicans, Agelastes niger*, and *Microsporum canis* using the Agar well diffusion method with 100 µg mL<sup>-1</sup> of each compound.

Keywords: Polymeric Schiff base; Piperazine; Thermal decomposition; Antimicrobial activity

#### 1. Introduction

The development of coordination polymers by linking transition metal ions with polydentate ligands has been constantly growing [1–7]. Coordination polymers (polymeric chelates) are defined as materials in which metal ions are linked together with di- or polyfunctional ligands and known for their thermal stability [8, 9]. Important applications have been reported, such as their use as solar energy converters [10] and the ability to remove  $SO_x$  and  $NO_x$  from the environment [11]. The choice of the metal ions, the ligand design, the counter ions, and the solvents can have a considerable effect on the final architecture of the coordination polymers and particularly its dimensionality [12].

Preparation and study of coordination polymers containing biologically important ligands are made easier because certain metal ions are active in many biological processes; species of low molecular weight are sought that reproduce, as far as possible,

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the structural properties and the reactivity of naturally occurring complexes of these ions.

In the field of coordination polymers, polymer metal complexes of Schiff bases have played a central role and have a curious history. Considerable interest attached with the chemistry of Schiff bases derived from aldehydes, amine Schiff bases having oxygens, nitrogens, and sulfurs has been reported and applications of Schiff bases and their metal complexes in pharmacological and non-pharmacological fields have received increased attention.

Schiff bases are an important class of ligands due to their synthetic flexibility and sensitivity toward the central metal ion, structural similarities with natural biological substances, and also the presence of imine (N=CH-) which assists in elucidating the mechanism of transformation and racemization in biological systems.

By incorporating metal ion into the polymeric backbone, the physical and chemical properties are modified. Polymer metal complexes of Schiff base have been applied as polymer catalysts [13, 14], metallomesogens [15], supramolecular metal complexes [16], dendritic polymers [17], and in the construction of supramolecular systems [18].

Herein, we describe the synthesis of a polymeric Schiff base (PSB), which is capable of being tetradentate and which should form linear polymer when allowed to react with suitable metal ions like Mn(II), Co(II), Ni(II), Cu(II), and Zn(II). All the synthesized polymeric compounds were characterized by using various spectral (IR, <sup>1</sup>H-NMR, and UV-Vis) and physico-chemical techniques. The elemental analysis, magnetic moment measurements, thermal behavior, type of chelation of ligand, and the geometry of the metal are discussed. In addition, the antimicrobial activities were determined using the agar well diffusion method, where  $100 \,\mu g \,m L^{-1}$  concentration of each compound was tested against these microbes. The PSB had varied antimicrobial as well as the thermal properties, which were enhanced after chelation.

#### 2. Experimental

#### 2.1. Materials and strains

In this study, o-tolidine, 2-hydroxyacetophenone, formaldehyde (37% aqueous soluacetic acid, sodium hydroxide, manganese(II) tion), acetate tetrahydrate tetrahydrate  $Mn(CH_3COO)_2 \cdot 4H_2O$ , cobalt(II) acetate  $Co(CH_3COO)_2 \cdot 4H_2O$ , nickel(II) acetate tetrahydrate Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, copper(II) acetate monohydrate  $Cu(CH_3COO)_2 \cdot H_2O$ , and zinc(II) acetate dihydrate  $Zn(CH_3COO)_2 \cdot 2H_2O$  were used without purification. Solvents such as acetone, methanol, ethanol, diethyl ether, dimethylformamide (DMF), and dimethylsulfoxide (DMSO) were purified by standard procedures before use. All microorganisms were provided by the Microbiological Laboratory AMU.

#### 2.2. Synthesis

**2.2.1.** Synthesis of monomeric Schiff base. Monomeric Schiff base was prepared by a known procedure [19]. In a 250 mL round bottom flask, a solution of

2-hydroxyacetophenone (0.02 mol) in ethanol (100 mL) was added dropwise to a solution of *o*-tolidine (0.01 mol) in ethanol (50 mL). The reaction mixture was acidified with concentrated hydrochloric acid (0.05 mol) then refluxed with constant stirring for 2 h and then the reaction mixture was allowed to stand for 30 min. Pale yellow precipitate was obtained which was filtered and purified by washing repeatedly with ethanol, distilled water, and acetone, then dried in a vacuum desiccator over calcium chloride to remove the trapped solvent (ethanol); the monomeric Schiff base was obtained in 65% yield and is soluble in DMF and DMSO at room temperature.

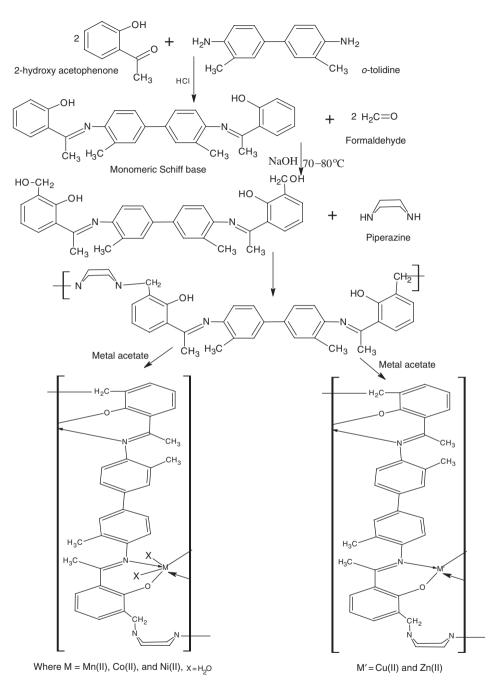
**2.2.2.** Synthesis of PSB. A mixture of monomeric Schiff base (0.01 mol) and formaldehyde (0.02 mol) in a molar ratio of 1:2 was taken into a 250 mL threenecked round bottom flask equipped with thermometer condenser and magnetic stirrer. DMSO ( $\sim$ 50 mL) was used as a solvent. In this reaction mixture, one or two drops of 40% aqueous NaOH were added and the temperature increased to 70–80°C for 3 h with continuous stirring. After that (0.01 mol) piperazine solution in 25 mL ethanol was added to this system and stirred again for 1 h at 90–100°C. The reaction progress was monitored by thin-layer chromatography (TLC). The reaction mixture was cooled and precipitated into 50/50 (v/v) water/acetone mixture. The solid brown product was filtered, and reprecipitated from DMSO in ethanol, the brown solid product of PSB was filtered and washed repeatedly with distilled water and acetone, and dried in a vacuum oven to remove the trapped solvent (DMSO and ethanol), giving polymeric resin at 75% yield.

**2.2.3.** Synthesis of polymer metal complexes. All polymer metal complexes were prepared by using equimolar ratio (1:1) of PSB and metal salts. The synthetic route for preparation of polymer metal complex of Mn(II) is as follows: a hot solution of manganese(II) acetate tetrahydrate (2.45 g, 0.01 mol in 10 mL DMF) was added to a solution of PSB (5.31 g, 0.01 mol in 20 mL DMF). The mixture was refluxed at 80°C for 3h with constant stirring. It turned brown and was precipitated in distilled water. Finally, the product was filtered, washed with distilled water, alcohol, and acetone and dried in a vacuum desiccator on calcium chloride (yield 68%).

A similar procedure was adopted for the synthesis of other polymer metal complexes, PSB–Co(II), PSB–Ni(II) PSB–Cu(II), and PSB–Zn(II), in yields between 71% and 78%. The products were soluble in DMF and DMSO and insoluble in other common solvents. The synthetic route for the preparation of all polymer metal complexes has been given in scheme 1.

#### 2.3. Preparation of microbial culture

The microorganisms used in this study were provided by the culture collection of the Microbiological Laboratory of AMU. *Escherichia coli, Bacillus subtillis, Staphylococcus aureus, Pseudomonas aeruginosa, Salmonella typhi, Candida albicans, Agelastes niger,* and *Microsporum canis* were used to investigate the bacteriological and antifungal activities of the PSB and its polymer metal complexes. Bacterial strains were nourished in nutrient broth (Difco) and yeast in malt extract broth (Difco) and incubated for 24 and 28 h, respectively.



Scheme 1. Synthetic route for the preparation of PSB and its polymer metal complexes.

According to the agar well diffusion method bacteria were incubated in Muller Hinton agar (Difco) and yeast in Saburoud dextrose agar (Difco). The PSB and its polymer metal complexes  $(100 \,\mu g \, m L^{-1})$  were dissolved in DMSO. A circular well was made at the center of each Petri dish with a sterilized steel borer. Then, 0.1 mL of each

test solution was added to the well and incubated at  $37^{\circ}$ C for 24 h; yeast samples were incubated at  $30^{\circ}$ C for 72 h. The experiment was repeated three times simultaneously under the same conditions for each compound and the mean value obtained from the three wells was used to calculate the zone of growth inhibition of each sample. DMSO was used for positive control. The resulting inhibition zones on the dish were measured in millimeters and compared with Kanamycine as a standard drug for antibacterial activity and Miconazole for antifungal activity. The data are given in tables 5 and 6.

#### 2.4. Measurements

The elemental analyses of metal coordination polymers were carried out on a Perkin Elmer Model-2400 elemental analysis [IIT, Roorkee]. The metal contents were determined by complexometric titration against EDTA after decomposing with concentrated nitric acid. The FT-IR spectra were recorded (4000–400 cm<sup>-1</sup>) on a Perkin Elmer infrared spectrophotometer model 621 using KBr pellets. The UV-Vis spectra were carried out on a Perkin Elmer Lambda EZ-201 spectrophotometer using DMSO. Proton and carbon-13 nuclear magnetic resonance spectra 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 (thermogravimetric analysis (TGA)) of all the synthesized polymeric compounds were determined on a TA analyzer 2000 in nitrogen atmosphere at a heating rate of 20°C and 10°C min<sup>-1</sup>. The solubility of the polymer was tested in various solvents at room temperature. Antimicrobial activities of all the polymeric compounds were determined against various selected microorganisms from the Microbiological Laboratory of AMU.

#### 3. Results and discussion

Analytical data of the PSB and its polymer metal complexes and some physical properties are given in table 1. The PSB was prepared in two steps by polycondensation. In the first step monomeric Schiff base was prepared by the reaction of 2hydroxyacetophenone with o-tolidine in 2:1 molar ratio. In the second step monomeric Schiff base was polymerized with formaldehyde and piperazine in 1:2:1 molar ratio. The PSB was soluble in DMF and DMSO and insoluble in common organic solvents and water. The polymer metal complexes were obtained by the reaction of PSB with metal acetates in DMSO in 1:1 molar ratio. The polymer metal complexes were insoluble in common organic solvents but soluble in DMSO and DMF. The polymer metal complexes were colored and obtained in good yield. The high thermal stability, metal to PSB ratio (1:1), and insolubility of the polymer metal complexes in common organic solvents suggest their polymeric nature [20]. The insolubility of the polymer metal complexes in common organic solvents does not permit the determination of molecular weight, but indicates the polymeric nature. Elemental analyses, physical properties, and IR data provide good evidence that the compounds are polymeric in nature [21]. The elemental analyses (table 1) show that PSB to metal ratio in all the polymer metal complexes was 1:1 and in agreement with the calculated values.

		Calculated (found) (%)				
Polymeric compounds	Color (yield %)	С	Н	Ν	М	
PSB	Dark yellow (75)	77.38	6.85	10.02	_	
		(78.02)	(7.03)	(10.55)	_	
PSB-Mn(II)	Brown (68)	66.76	6.22	8.65	8.48	
		(67.10)	(6.55)	(9.00)	(8.75)	
PSB-Co(II)	Light brown (74)	66.35	6.18	8.59	9.04	
	e ()	(66.70)	(6.41)	(8.68)	(9.29)	
PSB-Ni(II)	Light green (71)	66.37	6.18	8.60	9.00	
	8 8 ( )	(66.50)	(6.23)	(8.79)	(9.21)	
PSB-Cu(II)	Light brown (72)	69.71	5.85	9.03	10.24	
	e ()	(69.92)	(5.99)	(9.20)	(10.44)	
PSB–Zn(II)	Yellow (78)	69.50	5.83	9.00	10.51	
		(69.70)	(6.01)	(9.25)	(10.65)	

Table 1. Analytical and physical data of polymeric ligand (PSB) and its polymer metal complexes.

The structure of PSB and its metal complexes was also confirmed by IR, proton NMR, UV-Vis, and magnetic susceptibility measurements.

#### 3.1. FT-IR spectra

In order to study the bonding of PSB to the metal, the IR spectrum of PSB was compared with spectra of the corresponding polymer metal complexes (table 2). In the spectra of PSB, a strong band at  $1650 \text{ cm}^{-1}$  is attributed to C=N (azomethine). On coordination, due to shift of lone pair density toward the metal, this band is expected to shift to lower frequency indicating coordination of azomethine nitrogen to metal [21]. IR spectra of PSB exhibit a broad band at  $3400-3250 \text{ cm}^{-1}$  due to phenolic -OH [22]. The phenolic -OH stretch disappears in spectra of polymer metal complexes indicating that the ligand coordinates with metal through oxygen of Ar–OH. The vC–H out-ofplane bending vibration of the aromatic system is at  $775-740 \text{ cm}^{-1}$  and the C–N band appears at 1020 cm<sup>-1</sup>. A comparison between IR spectra of PSB and PSB-M(II) also show that a band, characteristic of v(C-O) at 1310 cm<sup>-1</sup>, is shifted to 1350–1330 cm<sup>-1</sup>, due to C-O-M bond formation [23]. Bands at 2920-2850 cm<sup>-1</sup> are assigned to CH<sub>2</sub> asymmetric and symmetric stretching vibrations. The PSB showed a band at 1534 cm<sup>-</sup> for  $\nu$ C=C of aromatic rings while its polymer metal complexes shift to 1555–1540 cm<sup>-1</sup>. In addition to these, all polymer metal complexes show two new bands at 537-520 and 470-430 cm<sup>-1</sup> due to formation of M-O and M-N bonds [24, 25] further confirming the formation of coordination polymer. Spectra of the polymer metal complexes of Mn(II), Co(II), and Ni(II) exhibited a broad band  $(3350-3200 \text{ cm}^{-1})$  suggesting the presence of water [26, 27]. This band is not found in spectra of polymer complexes of Cu(II) and Zn(II) which is also supported by electronic spectra and TGA.

#### 3.2. <sup>1</sup>H-NMR spectra

<sup>1</sup>H-NMR spectra of PSB and its Zn(II) complex are shown in "Supplementary material". The aromatic protons show multiple resonance signals between 6.92 and

			Assignme	ents			
Compounds	Ar–OH/H <sub>2</sub> O	CH (asym-sym)	vC=N	vC=C	νС–О	vM–О	vM–N
PSB	3400-3250	2920-2850	1650	1534	1310	_	_
PSB-Mn(II)	3350-3200	2920-2850	1635	1540	1350	525	463
PSB-Co(II)	3350-3200	2920-2850	1629	1550	1346	537	449
PSB-Ni(II)	3350-3200	2920-2850	1622	1555	1330	520	470
PSB-Cu(II)	-	2920-2850	1630	1550	1350	530	430
PSB-Zn(II)	-	2920-2850	1640	1554	1339	520	435

Table 2. IR spectral bands and their assignments for polymeric ligand (PSB) and its polymer metal complexes.

8.1 ppm [28]. The methyl proton attached to the carbonyl carbon of acetophenone was observed at 2.02 ppm. Resonance at 4.87 ppm is due to the proton of phenolic–OH and resonances at 2.74–2.88 ppm indicate the presence of  $-CH_2-CH_2$ — of piperazine and a resonance at 1.70 is due to proton of benzylic methylene. The <sup>1</sup>H-NMR spectra reveal that the piperazine moieties are attached to the Schiff base with methylene groups of formaldehyde. In the <sup>1</sup>H-NMR spectra of Zn(II) polymer complex, the signal for the protons of phenolic–OH disappear suggesting formation of Ar–O–M and a significant shifting in all the peaks was observed confirming formation of polymer metal complexes. The peak of benzylic methylene proton was at 2.08 ppm. Aromatic protons became broad due to the intermolecular interaction towards the metal ion.

#### 3.3. Electronic spectra and magnetic properties

The electronic spectra and magnetic properties of polymer metal complexes of PSB were recorded at room temperature using  $DMSO-d_6$  as a solvent; transitions with their assignment are given in table 3. The electronic spectrum of PSB-Mn(II) exhibited bands at 13,465, 18,574, and 22,445 cm<sup>-1</sup> due to  ${}^{4}T_{1g}(G) \leftarrow {}^{6}A_{1g}(F)$ ,  ${}^{4}T_{2g}(G) \leftarrow {}^{6}A_{1g}(F)$ , and  ${}^{4}A_{1g}(G) \leftarrow {}^{6}A_{1g}$  transitions, respectively, and suggest octahedral environment around Mn(II) [29]. The magnetic moment of PSB-Mn(II) was 5.83 BM Ligand field parameters  $10 D_{\rm q}$ , B and  $\beta$  are 5020, 837, and  $0.87 \,{\rm cm}^{-1}$ , respectively. The magnetic moment value of PSB-Co(II) was 3.95 BM [30, 31] and it shows three bands at 16,584, 23,310, and 29,412 cm<sup>-1</sup> due to  ${}^{4}T_{2g}(F) \leftarrow {}^{4}T_{1g}(F)$ ,  ${}^{4}A_{2g}(F) \leftarrow {}^{4}T_{1g}(F)$  and  ${}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}(F)$  transitions. The value of  $10 D_{g}$ , B and  $\beta$  are 8650, 1081, and 0.97 cm<sup>-1</sup>. All these observations suggest an octahedral environment for Co(II). PSB-Ni(II) showed three bands at 16,583, 25,510, and 29,762 cm<sup>-1</sup> due to  ${}^{3}T_{2g}(F) \leftarrow {}^{3}A_{2g}(F)$ ,  ${}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}(F)$ , and  ${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}(F)$ , respectively, with ligand field parameters  $10 D_{q}$ , *B*, and  $\beta$  as 13,600, 850, and 0.79 cm<sup>-1</sup>, respectively. The  $\mu_{eff}$  value 2.79 BM is in the range expected for the spin only value for two unpaired electrons in an octahedral or distorted octahedral geometry [32]. Electronic spectra of the copper(II) complex show broad bands centered at 25,000 and 16,556 cm<sup>-1</sup>, which may be due to square planar configuration [33, 34]; the magnetic moment value of PSB-Cu(II) at 1.70 BM is in accord with square planar geometry.

		Electronic spectral data	al data						
Abbreviation	Magnetic moment (BM)	Electronic transition (cm <sup>-1</sup> )	Assignment	$10  D_{ m q}$	В	β	$\beta\%$	е <sup>а</sup>	Geometry
PSB-Mn(II)	5.83	22,445 18,574	$\stackrel{4}{\overset{4}{}} A_{1g}(G) \leftarrow \stackrel{6}{\overset{6}{}} A_{1g}(F)$ $\stackrel{4}{\overset{4}{}} T_{2g}(G) \leftarrow \stackrel{6}{\overset{6}{}} A_{1g}(F)$	5020	837	0.87	13	11 10	Octahedral
PSB-Co(II)	3.95	29,412 29,412 23,310	$\begin{array}{c} 1_{1g}(\mathbf{U}) \leftarrow \mathbf{A}_{1g}(\mathbf{F}) \\ {}^{4}\mathrm{T}_{1g}(\mathbf{P}) \leftarrow {}^{4}\mathrm{T}_{1g}(\mathbf{F}) \\ {}^{4}\mathrm{A}_{2g}(\mathbf{F}) \leftarrow {}^{4}\mathrm{T}_{1g}(\mathbf{F}) \end{array}$	8650	1081	0.97	б	13 113 16	Octahedral
PSB-Ni(II)	2.79	16,584 29,762 25,510	$\begin{array}{c} {}^{4}\mathrm{T}_{2g}(\mathrm{F}) \leftarrow {}^{4}\mathrm{T}_{1g}(\mathrm{F}) \\ {}^{3}\mathrm{T}_{1g}(\mathrm{P}) \leftarrow {}^{3}\mathrm{A}_{2g}(\mathrm{F}) \\ {}^{3}\mathrm{T}_{1g}(\mathrm{F}) \leftarrow {}^{3}\mathrm{A}_{2g}(\mathrm{F}) \end{array}$	13,600	850	0.79	21	17 11 41	Octahedral
PSB-Cu(II)	1.70	16,583 25,000 16,555	${}^{5}T_{2g}(F) \leftarrow {}^{5}A_{2g}(F)$ Charge-transfer ${}^{2}A$ ${}^{2}D$	I	I	I	I	16 17	Square planar
PSB-Zn(II)	Diamagnetic	0000,01 -	$\mathbf{A}_{\mathrm{lg}} \leftarrow \mathbf{D}_{\mathrm{lg}}$	I	I	I	I	I - ا	Tetrahedral
$\mu_{\rm eff}$ , effective mag	$\mu_{\rm eff}$ effective magnetic moment in BM and $\varepsilon^{\rm a},$ extin	$\varepsilon^{a}$ , extinction coefficient in dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> .							

Table 3. Magnetic susceptibility and electronic spectra of PSB and its metal complexes.

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		Weight le	~					
Compounds	100	200	300	400	500	600	700	Characteristic weight left (%) at 800°C
PSB	90	72	65	50	43	30	23	5
PSB-Mn(II)	92	76	70	61	56	46	30	10
PSB-Co(II)	95	83	72	59	47	36	27	13
PSB-Ni(II)	92	88	75	69	57	49	33	18
PSB-Cu(II)	98	95	82	70	63	51	37	25
PSB-Zn(II)	94	90	77	68	58	47	32	19

Table 4. Thermal properties of PSB and its metal complexes.

The above discussion very strongly indicates octahedral geometry around the Mn(II), Co(II), and Ni(II), requiring two coordination sites by  $H_2O$  making the octahedral environment.

#### 3.4. Thermogravimetric analysis

Thermal decompositions of PSB and its polymer metal complexes are depicted in "Supplementary material"; data are given in table 4. All the compounds were highly heat resistant and they do not decompose easily, even at high temperature. No sharp weight loss was observed in the TGA curves of the polymer metal complexes, consistent with their polymeric nature. The thermograms show two step decomposition with the first, faster than the second step. This may be due to the non-coordinated part of the ligand decomposing first, while the coordinated part decomposes later [35]. In Mn(II), Co(II), and Ni(II) polymer metal complexes, the curve showed 8–15% weight loss corresponding to two water molecules up to 150°C. The presence of water in these polymer metal complexes was also supported by IR studies. In the case of Cu(II) and Zn(II) polymers, this weight loss corresponds to lost solvent or absorbed water up to  $150^{\circ}$ C. For thePSB, a steady and regular loss of weight was observed, and at  $300^{\circ}$ C the weight loss was about 35%. The temperature of maximum rate of decomposition for the ligand was  $700^{\circ}$ C and almost the entire ligand was lost by  $800^{\circ}$ C, whereas the polymer metal complexes lost only 75–90%. This suggests that all the polymer metal complexes have higher thermal stability than the PSB due to chelation. Another factor responsible for increased thermal stability of the polymer metal complexes is increase in molecular weight due to joining of two different polymer chains. The thermal stability of the polymeric compounds was in the order Cu(II) > Zn(II) > Ni(II) >Co(II) > Mn(II) > PSB. The greater stability of Cu(II) polymer metal complex compared with other polymer metal complexes is in agreement with the spectrochemical series, according to which Cu(II) polymer metal complex is always more stable than other polymer metal complexes.

#### 3.5. Antimicrobial activity

PSB and its metal complexes exhibited varying degrees of inhibitory effects on the growth of the bacterial and fungal strains. These results, given in tables 5 and 6, show that the newly synthesized PSB and its manganese(II), cobalt(II), nickel(II), copper(II),

	Zones diameter showing complete growth inhibition <sup>a</sup> (mm)					
Compound	E. coli	P. aeruginosa	B. subtillis	S. aureus	S. typhi	
PSB	$10 \pm 1$	$12 \pm 1$	$11 \pm 2$	$11 \pm 1$	$10 \pm 1$	
PSB-Mn(II)	$11 \pm 1$	$12 \pm 1$	$12 \pm 1$	$13 \pm 3$	$11 \pm 1$	
PSB-Co(II)	$12 \pm 2$	$10 \pm 1$	$11 \pm 1$	$10 \pm 1$	$11 \pm 1$	
PSB-Ni(II)	$10 \pm 1$	$12 \pm 1$	$12 \pm 2$	$10 \pm 2$	$13 \pm 1$	
PSB-Cu(II)	$14 \pm 2$	$13 \pm 1$	$14 \pm 1$	$15 \pm 1$	$13 \pm 1$	
PSB-Zn(II)	$12 \pm 2$	$11 \pm 2$	$11 \pm 3$	$12 \pm 1$	$12 \pm 2$	
Kanamycine <sup>b</sup>	$20 \pm 1$	$18 \pm 1$	$18\pm 2$	$20 \pm 1$	$18 \pm 1$	

Table 5. Antibacterial activities of polymeric ligand and its polymer metal complexes.

<sup>a</sup>14–15 mm: significant activity and 7–13 mm: moderate activity. <sup>b</sup>Standard drug.

	Zones diameter showing complete growth inhibition <sup>a</sup> (mm)					
Compound	C. albicans	M. canis	A. niger			
PSB PSB–Mn(II)	$13 \pm 1$ $18 \pm 1$	$15 \pm 2$ $14 \pm 3$	$16 \pm 2$ $18 \pm 1$			
PSB-Co(II)	$17 \pm 1$	$19 \pm 1$	$16 \pm 1$			
PSB–Ni(II) PSB–Cu(II)	$\begin{array}{c} 20 \pm 2 \\ 21 \pm 1 \end{array}$	$21 \pm 3$ $22 \pm 2$	$19 \pm 1$ $22 \pm 1$			
PSB–Zn(II) Miconazole <sup>b</sup>	$\begin{array}{c} 19 \pm 1 \\ 20 \pm 1 \end{array}$	$\begin{array}{c} 20\pm1\\ 25\pm1 \end{array}$	$\begin{array}{c} 19\pm3\\ 25\pm2\end{array}$			

Table 6. Antifungal activity of PSB and its metal complexes.

<sup>a</sup>14–22 mm: significant activity and 7–13 mm: moderate activity.

<sup>b</sup>Standard drug.

and zinc(II) complexes possess good biological activity. The compounds were screened for their antibacterial activity against *E. coli*, *B. subtillis*, *S. aureus*, *P. aeruginosa*, and *S. typhi* and for their antifungal activity against *C. albicans*, *A. niger*, and *M. canis*. All complexes show moderate to high biocidal action as compared to the ligand, but the activity was less than that of standard drugs while more significant antifungal activity was observed against most strains. The results as described by Nishat *et al.* [36] show comparatively high activities, while the microbial action of Kumaraguru *et al.* [37] was in correlation with our results. A marked enhancement of activity was exhibited in all the polymer metal complexes against all the bacterial/fungal strains. It was evident from the data that the antimicrobial activity of all the polymeric compounds was increased on coordination.

This enhancement in the activity can be rationalized on the basis of their structures possessing an additional C=N bond and chelation. It has also been observed [38–41] that solubility, conductivity, and dipole moment are influenced by the presence of metal ions and could be significant factors responsible for increasing the hydrophobic character and liposolubility of the molecule, hence enhancing biological activity. The results of antifungal and antibacterial screening indicate that polymer complexes of Cu(II) show more activity than the other polymer metal complexes, perhaps from higher stability. Cu(II) has stronger interaction with N and O donors by which lipophilic nature is increased.

#### 4. Conclusion

Newly developed polymer metal complexes were prepared in good yield and characterized by various instrumental techniques. All the polymeric compounds were soluble in DMF and DMSO, but insoluble in common organic solvents, allowing the possibility of use as solvent resistant coating materials. The attachment of metal ion in the polymeric backbone enhances thermal as well as antimicrobial activity. Due to stability at high temperatures, they can be used for medical and biomaterial applications requiring thermal sterilization. Owing to effective toxic behaviors, PSB–Cu(II) may be used as antifungal and antifouling coating for various projects.

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