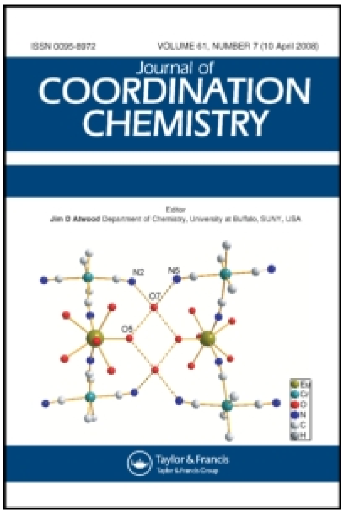

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Synthesis, characterization and anti-microbial studies of a newly developed polymeric Schiff base and its metal-polychelates

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A new polymeric Schiff base containing formaldehyde and piperazine moieties has been synthesized by condensation of salicylaldimine, formaldehyde and piperazine in alkaline medium; its metal polychelates have also been synthesized with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) acetate. The synthesized Schiff base and its metal polychelates were characterized by elemental, spectral (IR, ^{1}H NMR, UV-visible) and thermogravimetric analysis (TGA). Electronic spectra and magnetic moments indicate that Mn(II), Co(II) and Ni(II) polychelates show octahedral geometry, while Cu(II) and Zn(II) polychelates show square planar and tetrahedral geometry, respectively. All compounds show excellent anti-bacterial as well as anti-fungal activity against three bacteria and two fungi. The anti-microbial activities were determined by using agar well diffusion method, with $50\,\mu g\,mL^{-1}$ and $100\,\mu g\,mL^{-1}$ concentration of each compound tested against the microbes.

Keywords: Piperazine; Condensation; Thermogravimetric analysis; Agar well diffusion method

1. Introduction

Syntheses of new polymers containing metal complexes with applications such as high thermally resistant and biologically active polymers, is a demand of polymer chemistry and technology. Polymeric Schiff base has attractive physico-mechanical, chemical and biological properties which make it highly processible [1]. Polymeric Schiff bases are an important class of coordination polymer with multidentate donor sites, known to readily form polychelates with transition metal ions. The basic properties of Schiff base polymers are due to the azomethine linkages (C=N) in the polymeric backbone [2]. Schiff base polymers have high thermal stability [3] as well as antimicrobial activities. These polymers are widely used in the surface coating [4], semiconductor devices [5], in hydrometallurgy, environmental protection [6, 7] and in the field of nanotechnology [8]. Polymeric Schiff bases have practical importance in biology due to the presence of N, S, O and P donor groups which inhibit the growth of bacteria. Polymeric Schiff bases are

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highly useful for industrial, medical and scientific applications [9]. The incorporation of a metal ion in the polymeric backbone affects the physical and chemical characteristics and also biological properties [10, 11]. The resulting metal polychelates have wide application, such as aqueous thickeners, impregnates, textile seizers, adhesives, additives, resins and catalysts [12–16].

In our laboratory a number of metal polychelates with polymeric Schiff bases have been synthesized [17]. In continuation of our research we report herein the synthesis, characterization, thermal and antimicrobial activities of salicylaldimine containing formaldehyde and piperazine moieties (SDFP) and its metal polychelates. Monomeric Schiff base (salicylaldimine) is prepared by reaction of salicylaldehyde and ethylenediamine; then salicylaldimine on interaction with formaldehyde and piperazine in alkaline medium forms polymeric ligand which can form metal polychelates with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) acetate. All the synthesized polymers were characterized by using various spectral techniques such as IR, ^{1}H-NMR and UV-visible, and are expected to have applications in adhesives, coatings and biomedical fields. Electronic spectra and magnetic properties indicate the proposed geometry around the metal. The antibacterial and antifungal activity of the resin and its polychelates were screened against *Escherichia coli, Staphylococcus aureus*, *Salmonella typhi* (bacteria) and *Candida albicans* and *Aspergillus niger* (yeast) by using the agar well-diffusion method [18].

2. Experimental

2.1. *Materials and strains*

Salicylaldehyde, ethylenediamine, piperazine, ethanol, formaldehyde (37% aqueous solution) (s.d. Fine), DMF, DMSO, acetone, NaOH and transition metal acetates (Qualinges India) were purchased. All the solvents were distilled before use. The agars were purchased from Difco Laboratories. Microorganisms such *as Escherichia coli*, *Staphylococcus aureus*, *Salmonella typhi* (bacteria) and *Candida albicans*, *Aspergillus niger* (yeast) were obtained from the culture collection of Microbiological Laboratory of J.N.U. The strains were kept at −80°C in a freezer.

2.2. *Synthesis*

2.2.1. Synthesis of monomeric Schiff base. The salicylaldimine was prepared by a known procedure [19]. In a 100 mL round bottom flask a solution of salicylaldehyde 2.44 g (0.02 mol) in ethanol (25 mL) was added dropwise to ethylenediamine 0.67 g (0.01 mol) in ethanol (25 mL). The reaction mixture was acidified with concentrated hydrochloric acid (0.5 mL) then refluxed with constant stirring at room temperature for 2 h, producing yellow crystals of salicylaldimine. The reaction mixture was cooled and the crystals were separated by filtration and purified by washing repeatedly with ethanol, distilled water and acetone. A solid yellow product was dried in a vacuum desiccator on calcium chloride to remove trapped solvent; the monomeric Schiff base was obtained in 75% yield.

2.2.2. Synthesis of polymeric ligand. A mixture of monomeric Schiff base (salicylaldimine) (5.36 g, 0.01 mol) and formaldehyde (1.5 mL, 0.02 mol) in the molar ratio of (1 : 2) were taken in a 250 mL three necked round bottom flask equipped with a thermometer, condenser and a magnetic stirrer. In this reaction mixture 2 mL of 40% aqueous NaOH was added and the temperature was raised to 70–80°C for 1 h with continuous stirring. After that 1.72 g (0.01 mol) of piperazine solution in 20 mL ethanol was added and this system stirred again for about 1 h at 100–110°C. The progress of reaction was monitored by TLC (thin layer chromatography). The reaction mixture was cooled and precipitated into 50/50 (v/v) water/acetone. The solid brown product was filtered and then reprecipitated from DMF in ethanol. The brown solid of SDFP was filtered and washed repeatedly with distilled water and acetone and dried in a vacuum oven to remove the trapped solvents, giving polymeric ligand in 70% yield.

2.2.3. Synthesis of the polychelates. Polychelates of SDFP were prepared by using equimolar ratio (1 : 1) of SDFP and metal salts. A typical procedure for the preparation of the Cu(II)-polychelate is carried out with 3.79 g (0.01 mol) of SDFP dissolved in a minimum quantity (~20 mL) of hot DMF and 1.99 g (0.01 mol) of Cu(II) salt dissolved in hot DMF (~10 mL) separately. Both the solutions were filtered and mixed while hot with constant stirring. Then the reaction mixture was refluxed at 100°C under stirring for 3–4 h. A dark green colored product was obtained, which was precipitated in distilled water. Finally, the product was filtered and washed with distilled water, alcohol and acetone and dried in a vacuum desiccator on calcium chloride (yield 75%).

A similar procedure was adopted for the synthesis of the other metal polychelates, such as SDFP-Mn(II), SDFP-Co(II), SDFP-Ni(II) and SDFP-Zn(II). The colored products were filtered, washed and dried (yield 70–76%).

2.2.4. Preparation of microbial cultures. The microorganisms used in this study were provided by the culture collection of the Microbiological Laboratory of J.N.U. In this work *Staphylococcus aureus*, *Escherichia coli*, *Salmonella typhi* and *Candida albicans*, *Aspergillus niger* were used to investigate the bacteriological and antifungal activities of the polymeric ligand and its polychelates. Bacterial strains were nourished in nutrient broth (Difco) and yeast in malt extract (Difco) and incubated for 24 and 48 h, respectively.

According to the agar well-diffusion method, bacteria were inoculated on a Mueller Hinton Agar (Difco) and Yeast on Saburoud Dextrose Agar (Difco). The SDFP and its metal polychelates (50 $\mu g\,mL^{-1}$) and (100 $\mu g\,mL^{-1}$) 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°C for 24 h; yeast samples were incubated at 30°C for 72 h. DMSO was used for control. The resulting inhibition zones on the dish were measured in mm and compared with Tetracyclines as a standard drug for the antibacterial activity and Miconazol for antifungal activity. The data reported in table 2 (a and b) are the average data of three experiments.

2.2.5. Measurements. 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 FTNMR instrument in dimethylsulfoxide (DMSO) solution and tetramethyl silane (TMS) as an internal standard. The elemental analyses of carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer model-2400 elemental analyzer (CDRI Lucknow). The percentage of metals was determined by complexometric titration against EDTA after decomposing with concentrated nitric acid (HNO_3). The solubilities of polymeric ligand and its metal polychelates were checked at room temperature in different solvents. The thermal stability of polymeric Schiff base and its metal polychelates have been evaluated with thermograms by TA analyzer 2000 at a heating rate of 20°C per minute under nitrogen. The electronic spectra of the metal polychelates were recorded on a Perkin-Elmer Lambda EZ-201 and magnetic susceptibility measurements were done with a vibrating sample magnetometer. The anti-bacterial and anti-fungal activities of Schiff base and its metal polychelates were done from the Microbiological Laboratory of J.N.U. against several microorganisms.

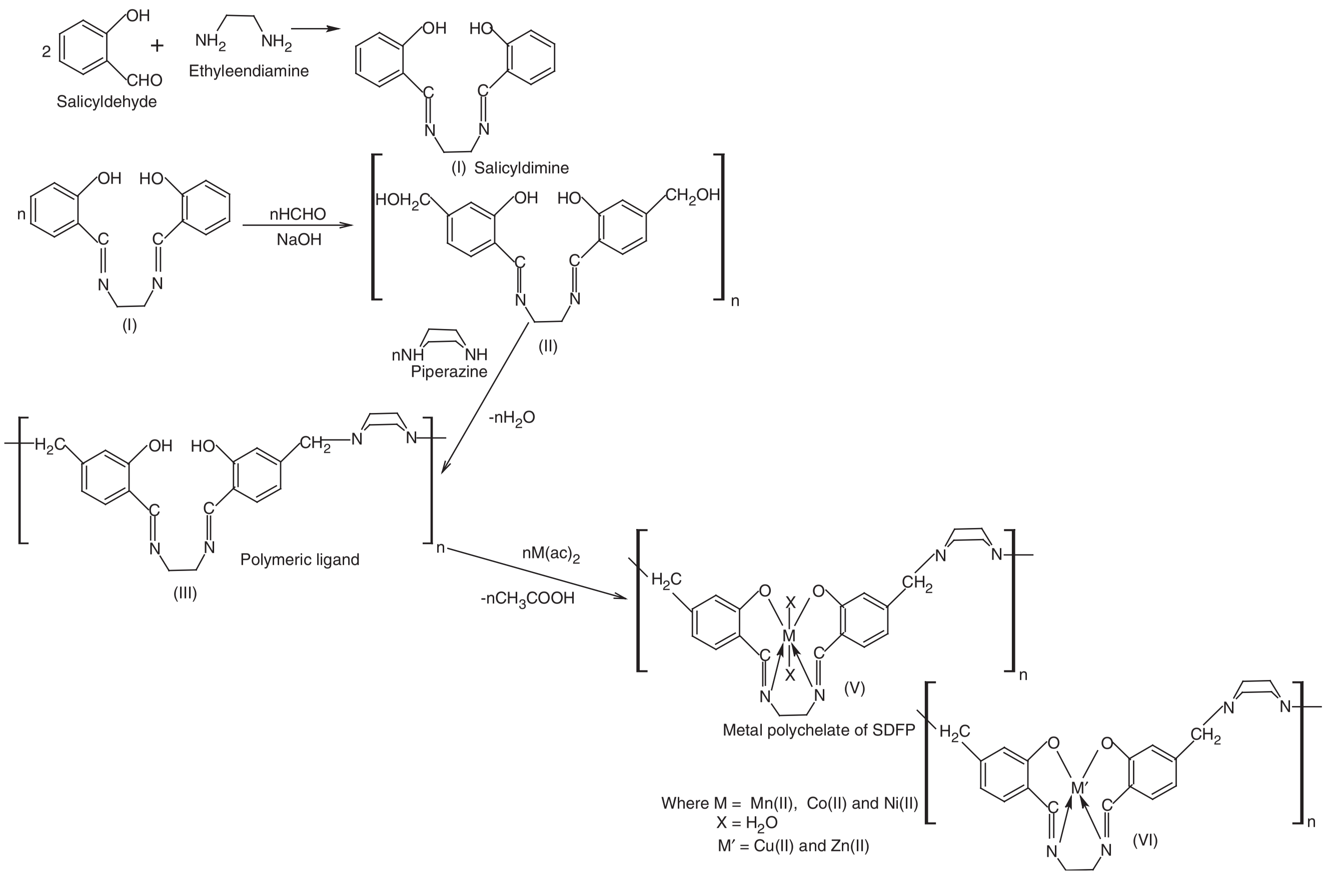
3. Results and discussion

The polymeric Schiff base (SDFP) was prepared by condensation in two steps. In the first step salicylaldehyde undergoes condensation with ethylenediamine in 2 : 1 molar ratio in refluxing ethanol, producing yellow crystals of salicylaldimine. In the second step salicylaldimine reacts with formaldehyde and piperazine in the molar ratio of 1 : 2 : 1 in alkaline medium, according to scheme 1, with DMF as solvent.

Metal polychelates of SDFP were prepared by reaction of SDFP with metal acetate in 1 : 1 molar ratio and obtained in good yield. The metal polychelates of SDFP were soluble in DMF and DMSO but insoluble in common organic solvents like methanol, THF, ethanol, $CHCl_3$, CCl_4, etc. The elemental and spectral analysis provide good evidence that the compounds are polymeric, and these data are also in agreement with the molecular structure given in scheme 1. The elemental analyses of the synthesized compounds are given in table 1.

3.1. *FTIR spectra*

A comparative study of polymeric Schiff base (SDFP) and its metal polychelates are given in table 3. In the IR spectra of ligand the absorption at $1677\,cm^{-1}$ attributed to azomethine (C=N) [20]; shifting this band to lower frequency (by $30–50\,cm^{-1}$) in all metal polychelates indicates participation of azomethine in chelation [21]. A broad band at $3450–3400\,cm^{-1}$ is due to phenolic–OH which disappears in the spectra of all metal polychelates, suggesting deprotonation of phenolic–OH by metal ion. The metal polychelates of SDFP display strong bands in the frequency range $1540–1560\,cm^{-1}$ that were ascribed to νC=C aromatic ring stretching. Two absorption bands at $2900\,cm^{-1}$ and $2800\,cm^{-1}$ are due to out of plane bending vibrations νCH symmetric and asymmetric stretching and a band at $1450\,cm^{-1}$ is due to νCH_2 bending mode. The νC–H out of plane bending vibration of the aromatic system is seen at $770–745\,cm^{-1}$ and the C–N band appears at $1020\,cm^{-1}$. The appearance of two new bands in the polychelates around $635–620\,cm^{-1}$ and $560–540\,cm^{-1}$ are due to



Scheme 1. Synthesis of polymeric Schiff base and its metal-polychelates.

Table 1. Elemental analysis of poly-SDFP and metal polychelates.

Compounds	Yield (%)	Temperature (°C)	Elemental analysis			
			%C	%H	%N	%M
$C_{22}H_{26}N_4O_2$	75	110	69.80 69.74	6.92 6.90	14.80 14.79	–
$C_{22}H_{28}N_4O_4$–Mn(II)	70	200	56.60 56.53	6.05 6.02	12.00 11.87	11.77 11.71
$C_{22}H_{28}N_4O_4$–Co(II)	74	180	56.12 56.07	5.99 5.86	11.95 11.71	12.51 12.43
$C_{22}H_{24}N_4O_2$–Ni(II)	70	210	60.72 60.54	5.56 5.36	12.88 12.65	13.49 13.23
$C_{22}H_{24}N_4O_2$–Cu(II)	75	260	60.10 59.84	5.50 5.43	12.73 12.57	14.44 14.32
$C_{22}H_{24}N_4O_2$–Zn(II)	70	235	59.80 59.69	5.48 5.25	12.68 12.51	14.80 14.68

Table 2(a). Antibacterial activity of poly-SDFP and metal polychelates.

Compounds	S. a.	E. c.	S. t.	A. n.	C. a.
SDFP	–	–	7.5	–	
SDFP-Mn(II)	7	–	8	11	8
SDEP-Ni(II)	8	–	9	–	–
SDFP-Cu(II)	10	12	7	13	13
SDFP-Zu(II)	–	–	–	9	–

Compound concentration = 50 μg mL^{-1}; (–) the compounds have any activity against the microorganism.

Table 2(b). Antibacterial activity of poly-SDFP and metal polychelates.

Compounds	S. a.	E. c.	S. t.	A. n.	C. a.
SDFP	–	–	8	7	9
SDFP-Mn(II)	9	–	10	13	11.5
SDFP-Ni(II)	10	8.5	10	9	9.5
SDFP-Cu(II)	12	15	11	15	14.5
SDFP-Zn(II)	8.5	10	10	9	9.5

Compound concentration = 100 μg mL^{-1}; the compounds have any activity against the microorganism.

coordination of metal ions with phenolic-oxygen (M–O) and azomethine-nitrogen (M–N), respectively [22]. Polychelates of Mn(II), Co(II) and Ni(II) show one common absorption band at 3400 cm^{-1} assigned to water within the coordination sphere as well as lattice water [23]. This band is not found in the spectra of Cu(II) and Zn(II) polychelates, which is also supported by electronic spectra and thermogravimetric analysis.

3.2. *^{1}H-NMR spectra*

The ^{1}H-NMR spectra of polymeric ligand (SDFP) and its Zn(II)-polychelate are shown in figures 1 and 2. The spectrum of Schiff base shows a signal at 8.25 ppm for

Table 3. Important IR spectral bands and their assignments of poly-SDFP resin and metal polychelates.

Assignments	Poly –SDFP	SDFP –Mn(II)	SDFP –Co(II)	SDFP –Ni(II)	SDFP –Cu(II)	SDFP –Zn(II)
Azomethine group (C=N)	1677	1636	1654	1676	1654	1677
Ar–OH or coordinated water	3450–3400	3400	3400	3400	3400	3400
C=C	1560–1540	1560–1540	1560–1540	1560–1540	1560–1540	1560–1540
C–H Asym – sym	2900–2800	2900–2800	2900–2800	2900–2800	2900–2800	2900–2800
CH_2	1480–1450	1480–1450	1480–1450	1480–1450	1480–1450	1480–1450
M–O	–	650–620	650–620	650–620	650–620	650–620
M–N	–	560–540	560–540	560–540	560–540	560–540

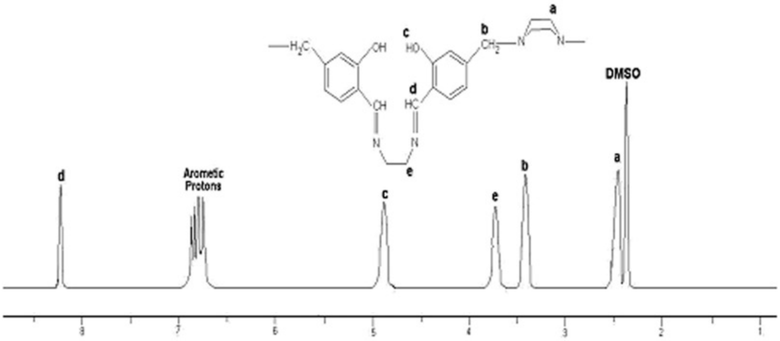


Figure 1. ^{1}H NMR spectra of polymeric ligand (SDFP).

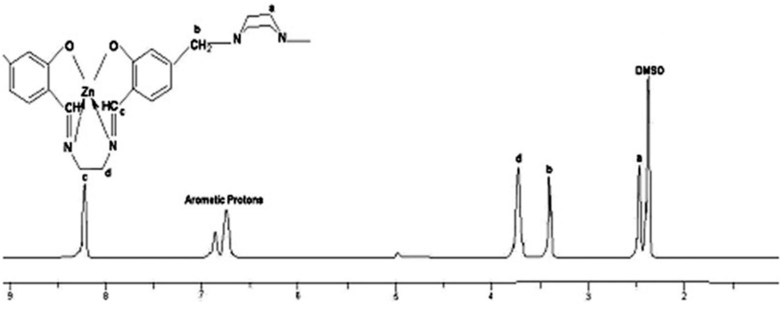


Figure 2. ^{1}H NMR spectra of Zn(II)-polychelate.

CH=N azomethine. The aromatic protons show multiple resonance signals between 6.67–6.85 ppm. The methylene protons of ethylenediamine appear at 3.64 ppm while the benzyl protons show a sharp resonance at 3.37 ppm. A resonance at 4.89 ppm appears due to the phenolic–OH group. A strong resonance observed at 2.49 ppm supports the presence of $–CH_2–CH_2–$ groups of the piperazine. The ^{1}H-NMR spectra reveal that the piperazine moieties are attached to the salicylaldimine with the methylene groups of formaldehyde. In the ^{1}H-NMR spectrum of Zn(II)-polychelate the phenolic–OH signal

Table 4. Magnetic susceptibility and electronic spectra of polymeric ligand (SDFP) and metal polychelates.

Compound (B.M.)	Magnetic moment transition (cm^{-1})	Electronic transition (cm^{-1})	Assignment	10 D_q (cm^{-1})	B (cm^{-1})	β	β%
SDFP-Mn(II)	5.11	23810	$^4E_{1g}(G) \leftarrow {}^6A_{1g}$				
		21739	$^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$	8811	801	0.83	17
		19231	$^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$				
SDFP-Co(II)	3.49	20000	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$				
		17857	$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$	11115	741	0.76	24
		10204	$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$				
SDFP-Ni(II)	2.96	24390	$^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$				
		16667	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$	8400	875	0.84	16
		13905	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$				
SDFP-Cu(II)	1.75	25300	$^2A_{1g} \leftarrow {}^2B_{1g}$	–	–	–	–
		16600	Charge transfer				

disappears confirming the bonding of phenolic–O–M. The aromatic protons become broad due to intermolecular interaction towards the metal ions and variation in the π-electron density around the protons.

3.3. *Electronic spectra and magnetic properties*

Electronic spectra and magnetic properties of metal polychelates of SDFP are given in table 4. The electronic spectra were recorded in DMSO. The Mn(II)-polychelate exhibited three bands at 19231 cm^{-1}, 21739 cm^{-1} and 23810 cm^{-1} due to the $^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$, $^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$ and $^4E_{1g}(G) \leftarrow {}^6A_{1g}$ transitions, respectively, suggesting octahedral environment [24]. The magnetic moment of Mn(II) was 5.11 B.M. and the value of ligand field parameters 10 D_q, B and β are 8811 cm^{-1}, 801 cm^{-1} and 0.83 cm^{-1}, respectively. The magnetic moment of Co(II) was 3.49 B.M. and this complex has three bands at 10204 cm^{-1}, 17857 cm^{-1} and 20000 cm^{-1} due to $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$, $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transitions, respectively, with values of 10 Dq, B and β 11115 cm^{-1}, 741 cm^{-1} and 0.76 cm^{-1}, suggesting an octahedral Co(II) [25]. Ni(II)-polychelate showed three bands at 13905 cm^{-1}, 16667 cm^{-1} and 24390 cm^{-1} due to $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ transitions. The magnetic moment of Ni(II)-polychelate was 2.96 B.M. and the ligand field parameters are 8400 cm^{-1}, 875 cm^{-1} and 0.84 cm^{-1}, also suggesting octahedral geometry. The Cu(II)-polychelate has two bands at 16600 cm^{-1} and 25300 cm^{-1} due to $^2A_{1g} \leftarrow {}^2B_{1g}$ and charge transfer band; the magnetic moment of Cu(II)-polychelate was 1.75 B.M. indicating square planar geometry for Cu(II).

3.4. *Thermogravimetric analysis*

The TGA of polymeric Schiff base (SDFP) and its metal polychelates were determined in nitrogen to 800°C to examine the thermal stability. The SDFP and Cu(II)-polychelate were both stable to 200°C, although 5–6% weight loss appeared at 100°C due to loss of absorbed water and solvents; in Mn(II), Co(II) and Ni(II)

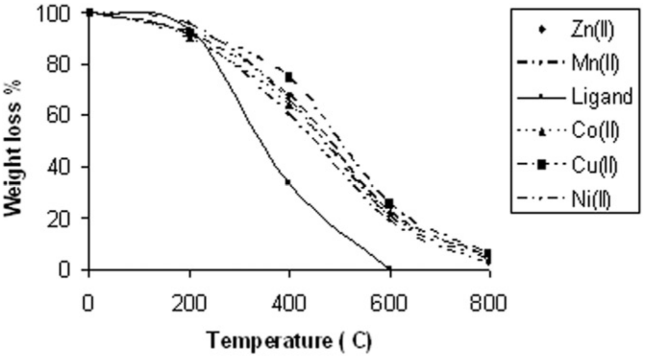


Figure 3. Thermograms of polymeric Schiff base and its metal-polychelates.

polychelates 10–12% weight loss was found to 160°C due to loss of two molecules of coordinated water. All the polychelates can be considered to decompose in two stages (figure 3). In the first stage of decomposition the polychelate showed 20.86–30% weight loss at 100–400°C due to the loss of uncoordinated parts and approximately 50–55% weight loss appeared in the temperature range 400–600°C due to the loss of coordinated parts during the second stage of decomposition. The decomposition of SDFP is almost complete at 600°C, whereas the decomposition of the polychelates was found to be complete at 700°C. The higher decomposition temperature in polychelates may result from the coordination and indicate that polychelates are more stable than the polymeric ligand (SDFP). The Cu(II) polychelate is the most stable metal polychelate due to the higher stability constant of Cu(II).

3.5. *Antibacterial activity*

The bacteriological and fungicidal effect of salicylaldimine containing formaldehyde and piperazine moiety and its metal polychelates were determined against three bacteria and two yeasts, as described in the experimental section. The agar well-diffusion method was employed for the bacteria and yeast with respect to Tetracyclin and Miconazol as standard drugs. The results showed that some compounds are very effective on some microorganisms [summarized in table 2 (a and b)]. The Cu(II)-polychelate exhibited high activity against *E. coli* (15 mm), *A. niger* (15 mm) and *Candida albicans* (Yeast) (14.5) and the others show mild activity against these microorganisms. The presence of N and O donor groups in the ligand and its metal polychelates inhibited enzyme production because enzymes that require free hydroxyl group for their activity appear to be especially susceptible to deactivation by the metal ion of polychelates. Chelation reduces the polarity of the central ion from partial sharing of its positive charge with the donor groups; π-electron delocalization in this chelating ring also increases the lipophilic nature of the central atom, favoring permeation through the lipid layer of the membrane. All the metal polychelates are more toxic than the ligand.

4. Conclusion

A newly developed polymeric ligand and its metal-polychelates were prepared in good yield and characterized by instrumental techniques. The polymeric ligand was soluble in DMF and DMSO, partially soluble in xylene, THF and $CHCl_3$ and insoluble in water, benzene, toluene and methanol, whereas all the metal-polychelates were soluble in DMF and DMSO and insoluble in water and common organic solvents. Attachment of metal ion in the polymeric backbone enhances thermal as well as antimicrobial activity. The Cu(II)-polychelate exhibited strong inhibitory effects on all bacteria, but other metal polychelates exhibited different antibacterial activities depending on the bacterium. All the metal polychelates were found to exhibit antibacterial activities and may be used as antifungal and antifouling coatings in various processes.

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