

New Antimicrobial Agents: The Synthesis of Schiff Base Polymers Containing Transition Metals and Their Characterization and Applications

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Received 27 August 2010; accepted 27 December 2010

DOI 10.1002/app.34100

Published online 29 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A new polymeric Schiff base containing formaldehyde and 2-thiobarbituric acid moieties was synthesized by the condensation of a monomeric Schiff base derived from 2-hydroxyacetophenone and hydrazine. Polymer-metal complexes were also synthesized by the reaction of the polymeric Schiff base with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) acetate. The polymeric Schiff base and its polymer-metal complexes were characterized with magnetic moment measurements, elemental analyses, and spectral techniques (infrared, $^1\text{H-NMR}$, and ultraviolet-visible). The thermal behaviors of these coordination polymers were studied by thermogravimetric analysis in a nitrogen atmosphere up to 800°C. The thermal data revealed that all of the polymer-metal complexes showed higher thermal stabilities

than the polymeric Schiff base and also ascribed that the Cu(II) polymer-metal complex showed better heat resistant properties than the other polymer-metal complexes. The antimicrobial activity was screened with the agar well diffusion method against various selected microorganisms, and all of the polymer-metal complexes showed good antimicrobial activity. Among all of the complexes, the antimicrobial activity of the Cu(II) polymer-metal complex showed the highest zone of inhibition because of its higher stability constant and may be used in biomedical applications. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2756–2764, 2011

Key words: infrared spectroscopy; monomers; synthesis; UV-vis spectroscopy

INTRODUCTION

Polymeric Schiff bases are an important class of ligands, and their relevant transition-metal complexes are still great interest in coordination chemistry,^{1–4} although this subject has been extensively studied.^{5–8} A number of reviews have appeared on the coordination chemistry of polymeric Schiff base complexes,^{9–11} which exhibit an interesting variety of stereochemical behaviors in this area. Polymeric Schiff base metal complexes have been widely studied because of their industrial and biological applications; most of them have been used as drugs. Polymeric Schiff bases, including conjugated bonding and active hydroxyl groups, have been of interest to many researchers for more than 60 years in the light of their potential applications in various diversified fields.¹² They are used in various fields of technol-

ogy because of several useful properties, such as paramagnetism, semiconductivity, and resistance to high energies.^{13,14} Because of these properties, they are used to prepare composites and graphite materials having high resistance at high temperatures, thermostabilizers, epoxide oligomers, block copolymers, photoresistors, antistatic and flame-resistant materials, and components of electrochemical cells.^{15–19} Additional useful properties can be profited by the introduction of other functional groups into these polymers. Polymeric Schiff bases demonstrate antimicrobial activity against bacteria, yeast, and fungi.^{20,21} They can be used for the purification of industrial wastewaters from heavy metals; this is significant for environmental protection. It seemed advantageous to attempt to design and prepare a polymer-bound chelating ligand, which would be able to form complexes with a variety of transition metals and, therefore, have a large range of applications. Coordination compounds of a salicylaldehyde Schiff base have been proven to be an excellent model system to study the enzymatic reactions of pyridoxal phosphate. Both of these systems are effectively catalyze transamination and racemization reactions.²² The development of antimicrobials for clinical use has been most successful in the targeting of essential components of five general areas of bacterial metabolism: cell wall synthesis, protein

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Contract grant sponsor: University Grants Commission (to Raza Rasool).

Contract grant sponsor: Third World Academy of Sciences; contract grant number: 00-047 RG/CHE/AS (for a PerkinElmer EZ-201 ultraviolet-visible spectrophotometer).

synthesis, RNA synthesis, DNA synthesis, and intermediary metabolism.²³ In recent years, the efforts of researchers have been devoted to the synthesis of coordination polymeric systems to prevent microbial infections. The coordination chemistry of these polymers with metal ions has increased their biological and pharmaceutical importance. The antimicrobial activity of coordination polymers depends on the central metal ions and the nature of the ligands and their spatial relationship. The chelated metal ions increase the lipophilic nature of the compounds, which in turn favors its permeation to the lipid layer of the cell membrane. Recently, we synthesized few antimicrobial coordination polymers by the complexation of polymeric Schiff bases with metal ions, which are used as antimicrobial coating materials.^{24,25} The metal ions also inhibited the bacterial cells for biosynthesis or affected protein synthesis because the metal could coordinate to active site residues to block the substrate or bind to the ribosomal subunits of the pathogens.²⁶ These facts inspired us to synthesize new coordination polymers with inadequate properties over organic polymers. This article deals with the synthesis, characterization, and antimicrobial activity of a polymeric Schiff base and its polymer-metal complexes [APHFB-M(II)] are polymer metal complexes, derived from Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) transition-metal ions.

EXPERIMENTAL

Reagents and strains

2-Hydroxyacetophenone, hydrazine, ethanol, formaldehyde (40% aqueous solution, S. D. Fine), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetone, sodium hydroxide (Merck), 2-thiobarbituric acid, transition-metal acetates (Qualingens), manganese(II) acetate tetrahydrate [$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$], cobalt(II) acetate tetrahydrate [$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$], nickel(II) acetate tetrahydrate [$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$], copper(II) acetate monohydrate [$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$], and zinc(II) acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] were used without further purification. All of the solvents were used as received. Microorganisms [*Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Staphylococcus aureus*, and *Salmonella typhi* (bacteria) and *Candida albicans*, *Microsporium canis*, and *Aspergillus niger* (yeasts)] were provided by the culture collection of the Microbiology Laboratory (Department of Microbiology, Aligarh Muslim University, Aligarh, India).

Test methods

Elemental analyses of all the polymeric compounds was carried out on a PerkinElmer model 2400 Waltham, Massachusetts, USA, elemental analyzer (In-

dian Institute of Technology Roorkee). The metal content of the polymer-metal complexes was determined by complexometric titration against ethylenediamine tetraacetic acid after the complexes were decomposed with concentrated nitric acid.²⁷ The Fourier transform infrared (FTIR) spectra were recorded over the 4000–400 cm^{-1} range on a PerkinElmer spectrometer model 621 with potassium bromide pellets. The ultraviolet-visible spectra were carried out on a PerkinElmer Lambda EZ-201 spectrometer with DMSO as a solvent. $^1\text{H-NMR}$ were recorded on a JEOL GX 300-MHz FX-1000 Fourier transform NMR spectrometer with DMSO- d_6 as a solvent and tetramethylsilane as an internal standard. The thermal behavior of the synthesized polymeric Schiff base and its polymer-metal complexes was determined on a TA Analyzer 2000 in a nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out at rates of 20 and 10°C/min. The solubilities of all of the synthesized polymeric compounds were tested in various solvents at room temperature. Apart from these, the antimicrobial activities of all of the polymeric compounds were also determined against various selected microorganisms with an agar well diffusion method from the Microbiological Laboratory (Department of Microbiology, Aligarh Muslim University).

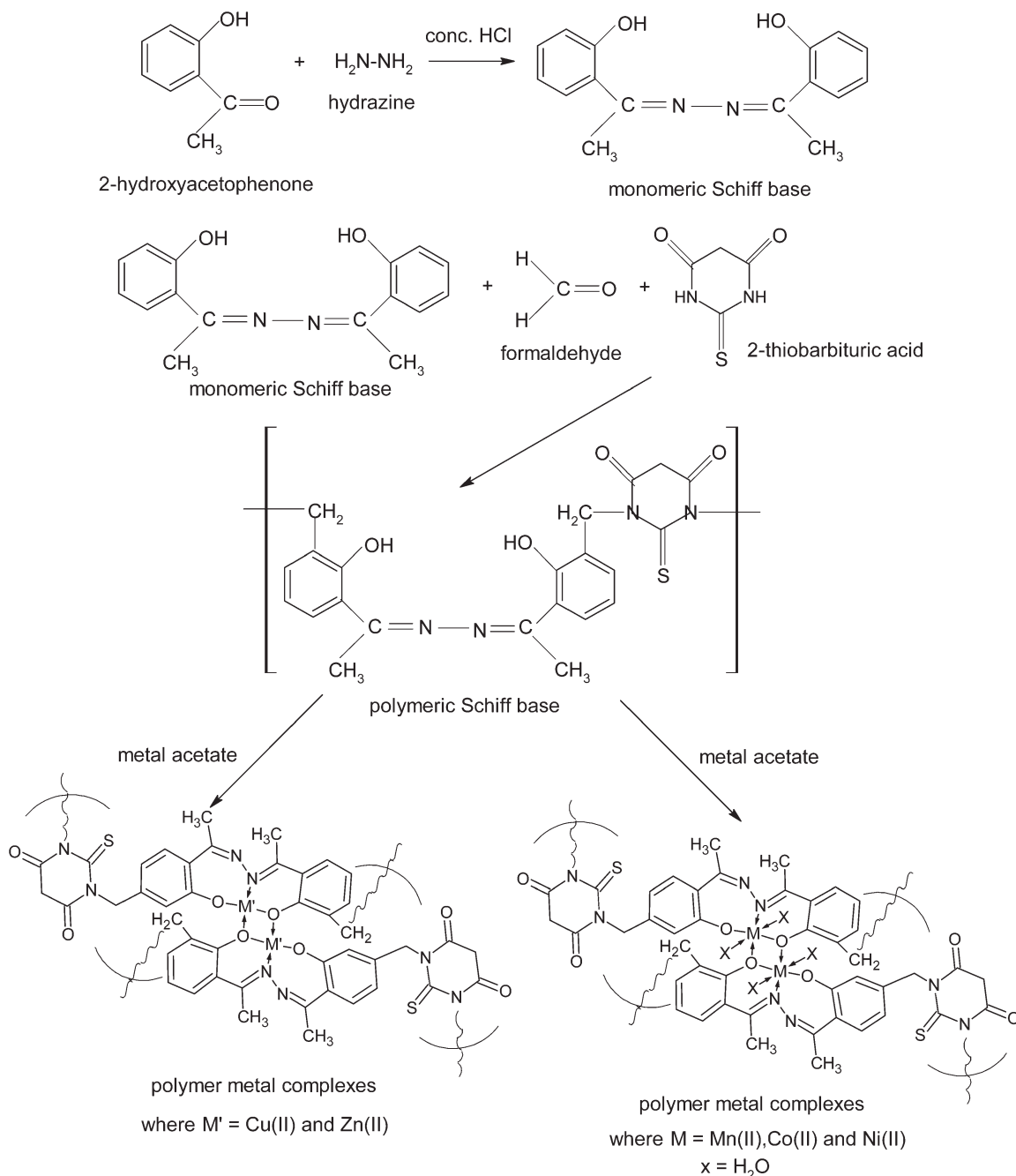
Synthesis

Synthesis of the monomeric Schiff base

The monomeric Schiff base was synthesized by the condensation of 2-hydroxyacetophenone with hydrazine in a 2 : 1 molar ratio (Scheme 1). In a 100-mL, round-bottom flask, a solution of 2-hydroxyacetophenone (0.02 mol) in ethanol (25 mL) was added dropwise to a solution of hydrazine (0.01 mol) in ethanol (25 mL). The reaction mixture was acidified with concentrated hydrochloric acid (HCl) and refluxed with constant stirring at room temperature for 2 h. When the reaction was completed, a yellow colored precipitate was obtained, which was filtered off, washed several times with distilled water and ethanol, and dried in a vacuum desiccator on calcium chloride (yield = 69%).

Synthesis of the polymeric Schiff base

In a 250-mL, three-necked, round-bottom flask equipped with a condenser, thermometer and a magnetic stirrer, a mixture of the monomeric Schiff base and formaldehyde (in 35 mL of DMF) was placed in a 1 : 2 ratio, and 2–3 drops of 40% aqueous sodium hydroxide was added to this solution. The temperature was raised up to 60°C, and the solution was stirred magnetically for 1 h. To this solution, 0.01 mol of 2-thiobarbituric acid dissolved in 15 mL of DMF



Scheme 1 Synthetic route for the preparation of the polymeric Schiff base and its polymer-metal complexes.

was added. The reaction mixture was again stirred continuously at 70°C for 3 h. The resulting brown viscous product was washed with distilled water, ethanol, and acetone. Finally, the product was dried in a vacuum desiccator on calcium chloride. The polymeric Schiff base was obtained in 70% yield.

Synthesis of the polymer-metal complexes

Polymer-metal complexes of Mn(II) , Co(II) , Ni(II) , Cu(II) , and Zn(II) were prepared with an equimolar ratio of polymeric Schiff base to metal salt of 1 : 1. A

typical procedure for the preparation of a polymer-metal complex of copper(II) was as follows. A solution of copper(II) acetate (0.01 mol) in 15 mL of DMF was added to a solution of the polymeric Schiff base (0.01 mol) in 20 mL of DMF. The reaction mixture was stirred and heated at 80°C . It turned brown and was precipitated in distilled water, washed with alcohol and acetone, and dried in a vacuum desiccator on calcium chloride. The yield was 75%.

The aforementioned procedure was adopted for the synthesis of the other polymer-metal complexes, and the yields are given in Table I.

TABLE I
Elemental Analyses of APHFB and Its Polymer–Metal Complexes

Compound	Yield (%)	Elemental analysis [calculated (observed)]			
		C (%)	H (%)	N (%)	M (%)
APHFB	70	60.54 (59.53)	4.62 (4.59)	12.83 (12.79)	—
APHFB–Mn(II)	68	50.29 (50.20)	4.22 (4.21)	10.66 (10.55)	10.45 (10.42)
APHFB–Co(II)	80	49.91 (49.85)	4.19 (4.10)	10.58 (10.53)	11.13 (11.09)
APHFB–Ni(II)	75	49.93 (49.80)	4.19 (4.09)	10.58 (10.55)	11.09 (11.29)
APHFB–Cu(II)	75	53.06 (52.97)	3.64 (3.57)	11.25 (11.10)	12.76 (12.62)
APHFB–Zn(II)	72	52.81 (52.28)	3.63 (3.56)	11.20 (11.21)	13.17 (12.59)

Preparation of the microbial cultures

The synthesized polymeric Schiff base and its corresponding polymer–metal complexes were screened *in vitro* for their antibacterial activity against *E. coli*, *B. subtilis*, *S. aureus*, *P. aeruginosa*, and *S. typhi* and for their antifungal activity against *C. albicans*, *M. canis*, and *A. niger* with the agar well diffusion method.²⁸ The wells were dug in the media with the help of a sterile metallic borer with centers of at least 24 mm. The recommended concentration (100 $\mu\text{L}/\text{mL}$) of the test sample (1 mg/mL in DMSO) was introduced into the corresponding wells. Other wells supplemented with DMSO and reference antibacterial drugs served as negative and positive controls, respectively. The plates were incubated immediately at 37°C for 20 h. The activity was determined by measurement of the diameter (millimeters) of zones showing complete inhibition. Kanamycin was used as a standard drug for antibacterial activity, and miconazole was used for antifungal activity.

RESULTS AND DISCUSSION

FTIR spectra

The significant infrared (IR) spectra of the polymeric Schiff base and its polymer–metal complexes with their assignments are given in Table II. The IR spectrum of the polymeric Schiff base showed a band at 3400–3100 cm^{-1} , which was assigned to the Ar–OH stretching. This band became broader on complexation. The spectra of polymer–metal complexes exhibited a broad band in the region 3350–3200 cm^{-1} ; this

suggested the presence of a coordinated or absorbed molecule.²⁹ The vibrational band observed at 827–834 cm^{-1} was assigned to C=S. The bands observed at 2900–2800 cm^{-1} corresponded to the CH₂ asymmetric and symmetric stretching vibrations. The IR spectra of the ligands showed a band at 1605 cm^{-1} due to C=N (azomethine group) stretching, which shifted slightly in all of the polymer–metal complexes; this suggested the participation of azomethine nitrogen in the formation of a coordinate bond with metal ions.³⁰ The bands observed at 1191–1198 and 1203–1298 cm^{-1} were assigned to the C–N of 2-thiobarbituric acid and phenolic C–O stretching vibrations, respectively, which shifted to a lower frequency in all of the polymer–metal complexes; this was consistent with coordination via the protonated phenolic oxygen.³¹ The participation of oxygen and nitrogen in the coordination in all of the polymer–metal complexes was further supported by the appearance of M–O and M–N modes in the regions 552–530 and 440–420 cm^{-1} , respectively.^{32,33}

Electronic spectra and magnetic moment measurements

The electronic spectra and magnetic properties of all of the polymer–metal complexes of polymeric schiff base (APHFB) were recorded at room temperature with DMSO-*d*₆ as a solvent, and the transitions with their assignments are given in Table III. The magnetic moment of the APHFB–Mn(II) complex was found to be 5.63 μ_{B} , and this suggested the presence of five unpaired electrons. The electronic spectrum of the APHFB–Mn(II) complex exhibited three bands

TABLE II
FTIR Spectral Bands and Their Assignments for APHFB and Its Polymer–Metal Complexes

Compound	Assignment						C=S
	Ar–OH/H ₂ O	CH (asymmetric–symmetric)	$\nu\text{C}=\text{N}$	$\nu\text{C}-\text{O}$	$\nu\text{M}-\text{O}$	$\nu\text{M}-\text{N}$	
APHFB	3400–3100	2900–2800	1605	1203	—	—	834
APHFB–Mn(II)	3400–3100	2900–2800	1600	1250	530	439	830
APHFB–Co(II)	3400–3100	2900–2800	1591	1243	540	430	832
APHFB–Ni(II)	3400–3100	2900–2800	1588	1298	552	440	827
APHFB–Cu(II)	—	2900–2800	1590	1247	530	420	830
APHFB–Zn(II)	—	2900–2800	1600	1296	544	435	827

TABLE III
Electronic Spectral Data, Magnetic Moments, and Ligand Field Parameters for the Polymer-Metal Complexes

Complex	Magnetic moment (μ_B)	Electronic spectral data		10Dq (cm^{-1})	B (cm^{-1})	β	β^0
		Electronic transition (cm^{-1})	Assignment				
APHFB-Mn(II)	5.63	22,890	${}^4A_{1g}(G) \leftarrow {}^6A_{1g}(F)$	5,520	920	0.96	4
		18,530	${}^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$				
		16,875	${}^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$				
APHFB-Co(II)	4.71	28,530	${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	17,120	951	0.85	15
		22,845	${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$				
		15,970	${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$				
APHFB-Ni(II)	3.10	23,690	${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$	8,690	790	0.73	27
		14,350	${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$				
		8,625	${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$				
APHFB-Cu(II)	1.70	24,570	Charge transfer				
		16,584	${}^2A_{1g} \leftarrow {}^2B_{1g}$				

at 16,875, 18,530, and 22,890 cm^{-1} , which may have reasonably corresponded to the ${}^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$, ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$, and ${}^4A_{1g}(G) \leftarrow {}^6A_{1g}(F)$ transitions, respectively. These data were used to calculate the crystal field splitting parameter (Dq), Racah parameter (B), and nephelauxetic effect (β) values. The 10 Dq value was found to be 5520 cm^{-1} , and B was 920 cm^{-1} . The β value was reduced to about 96% of the free-ion value for Mn^{2+} (960), and the covalency parameter (β^0) value of 4% indicated the covalent nature of the compound and suggested an octahedral environment around the Mn(II) ion.³⁴ The APHFB-Co(II) complex had a magnetic moment of

4.71 μ_B , which corresponded to four unpaired electrons and showed three bands at 15,970, 22,845, and 28,530 cm^{-1} , which were assigned to the ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$, ${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$, and ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transitions, respectively, and indicated an octahedral environment around the Co(II) ion.³⁵ The crystal field parameters of the compound were calculated accordingly:³⁶ 10Dq = 17,120 cm^{-1} , B = 951 cm^{-1} , $\beta = 0.85$, and $\beta^0 = 15\%$. The reduction of B from the free-ion values of 1120–951 cm^{-1} and the value of β indicated the covalent nature of the compound. The octahedral APHFB-Ni(II) was expected to be paramagnetic because of two unpaired d electrons, and

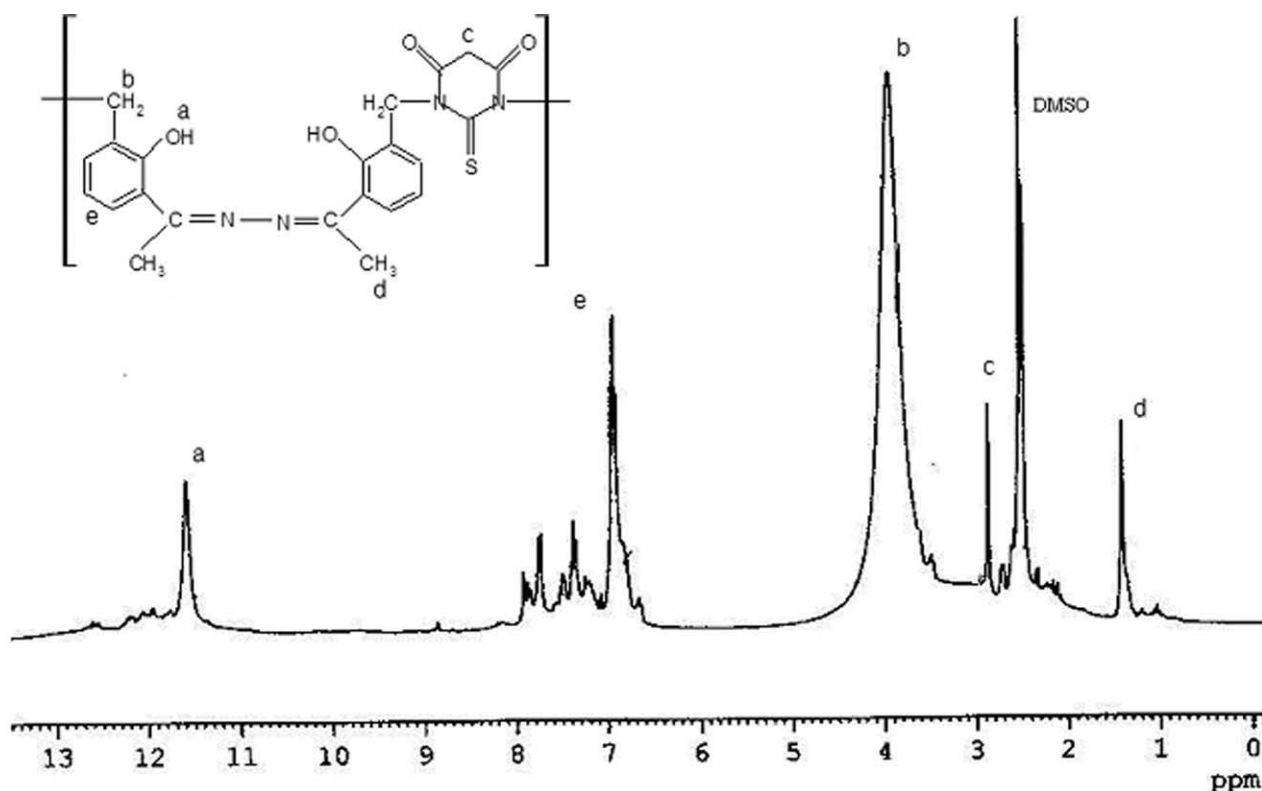


Figure 1 ${}^1\text{H}$ -NMR spectrum of the polymeric Schiff base (APHFB).

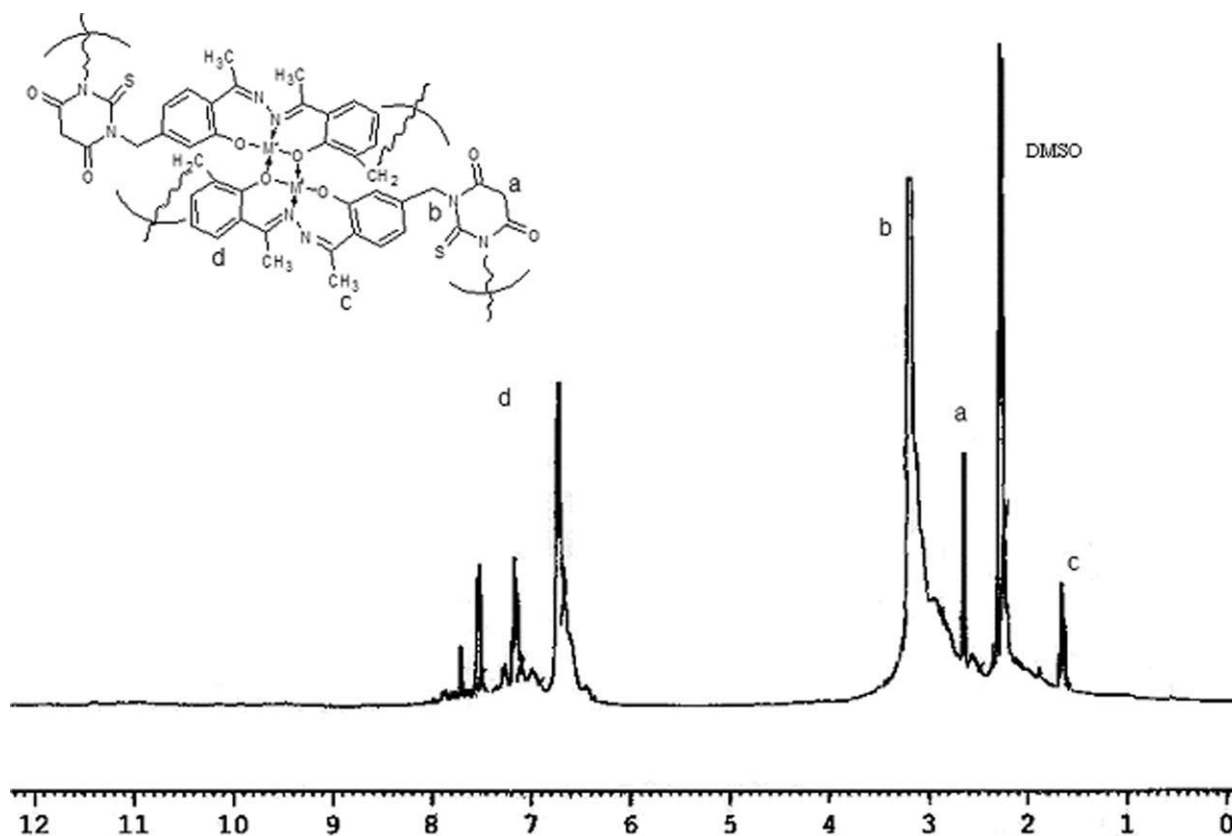


Figure 2 $^1\text{H-NMR}$ spectrum of APHFB-Zn(II).

the experimental magnetic moment was found to be $3.10 \mu_B$. The electronic spectrum showed three bands at 8625 , $14,350$, and $23,690 \text{ cm}^{-1}$, which were assigned to the $^3\text{T}_{2g}(\text{F}) \leftarrow ^3\text{A}_{2g}(\text{F})$, $^3\text{T}_{1g}(\text{F}) \leftarrow ^3\text{A}_{2g}(\text{F})$, and $^3\text{T}_{1g}(\text{P}) \leftarrow ^3\text{A}_{2g}(\text{F})$ transitions, respectively. The crystal field parameters were $10\text{Dq} = 8690 \text{ cm}^{-1}$, $B = 790 \text{ cm}^{-1}$, $\beta = 0.73$, and $\beta^0 = 27\%$; these data were in favor of an octahedral geometry for APHFB-Ni(II).³⁷ This data very strongly indicated an octahedral geometry around the central metal ion in the polymer-metal complex of Ni(II). It accounted for the occupation of two coordinating sites by water out of six in making the octahedral environment.

Polymer-metal complex APHFB-Cu(II) exhibited two bands, at $16,584$ and $24,570 \text{ cm}^{-1}$ due to $^2\text{A}_{1g} \leftarrow ^2\text{B}_{1g}$ and charge transfer, respectively, which indicates square-planar geometry. The magnetic moment value of APHFB-Cu(II) is found to be $1.70 \mu_B$, which is in accordance with square planar geometry.³⁸ The diamagnetic nature and the absence of $d-d$ transition in Zn(II) represent the tetrahedral geometry.

The above discussion very strongly indicates an octahedral geometry around the Mn(II), Co(II) and Ni(II) ions. It accounts for the occupation of two coordination sites by water out of six in the making of the octahedral environment.

$^1\text{H-NMR}$ spectra

The $^1\text{H-NMR}$ spectra of the polymeric Schiff base and its metal complex of Zn(II) are shown in Figures 1 and 2, respectively. The $^1\text{H-NMR}$ spectra of the polymeric Schiff base in $\text{DMSO-}d_6$ exhibited a

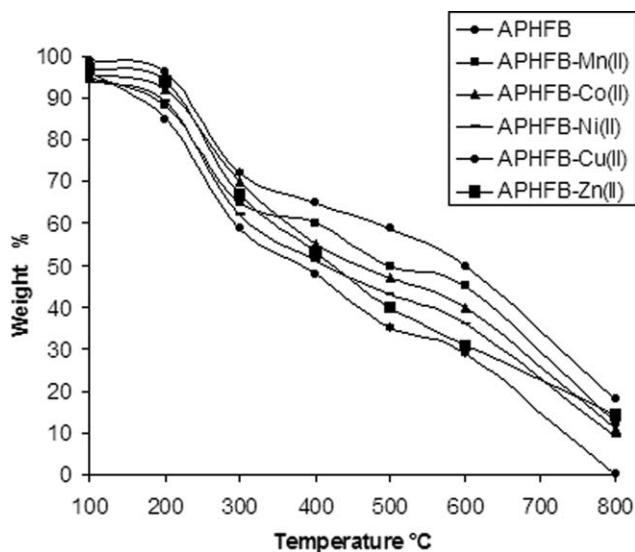


Figure 3 TGA of the polymeric Schiff base and its polymer-metal complexes.

TABLE IV
Thermal Properties of APHFB and Its Polymer–Metal Complexes

Compound	Weight loss (%)						Characteristic weight at 800°C (%)
	100°C	200°C	300°C	400°C	500°C	600°C	
APHFB	4	15	41	52	65	71	0
APHFB–Mn(II)	5	12	35	40	50	55	12.5
APHFB–Co(II)	4.5	8	30	45	53	60	11
APHFB–Ni(II)	6	11	38	49	57	64	9
APHFB–Cu(II)	1	4	28	35	41	50	18
APHFB–Zn(II)	3	6	33	47	60	69	14

resonance signal at 11.9 ppm, which was assigned to the phenolic –OH protons.³⁹ The aromatic proton showed multiple resonance signals between 6.67 and 7.93 ppm for the polymeric Schiff base and polymer–metal complex of Zn(II).⁴⁰ The methyl proton attached to the 2-hydroxyl acetophenone was observed at 1.39 ppm. The methylene proton of the Ph–CH₂–N– group showed a sharp resonance signal at 3.93 ppm, whereas the resonance signal found at 3.23 ppm indicated the presence of the O=C–CH₂–C=O group of 2-thiobarbituric acid. The results of the ¹H-NMR spectra reveal that the 2-thiobarbituric acid moiety was attached to the polymeric Schiff base with the methylene group of formaldehyde. In the ¹H-NMR spectra of the polymer–metal complex of Zn(II), the signal for the proton of phenolic OH disappeared; this suggested the participation of a phenolic OH proton in the metal centered in the formation of Ar–O–M, and a significant downfield shifting in all of the other peaks was observed. The peaks of the methyl proton were observed at 1.72 ppm; this indicated the involvement of azomethine nitrogen in the formation of a coordination bond with metal ions.

TGA

The thermal decompositions of the polymeric Schiff base and its polymer–metal complexes were studied by the thermogravimetric method. The TGA traces are shown in Figure 3, and the thermal data are pre-

sented in Table IV. These data revealed that the thermal stability of the polymer–metal complexes was higher than that of the parent ligand and that the complexes did not decomposed easily, even at high temperatures. The thermogravimetric curves confirmed the presence of water molecules in the polymer–metal complexes of Mn(II), Co(II), and Ni(II); the fact that water was eliminated up to 160°C may have been due to its coordination to the metal ions. In this study, the removal of water from the polymer–metal complexes of Mn(II), Co(II), and Ni(II) was completed up to 190°C; this water was probably considered crystalline or coordinated water. The thermogram in Figure 3 indicates that the decomposition of the polymer–metal complexes was very slow in the initial state, but above 300°C, the weight loss became fast. The thermal data indicated that the thermal and binding affinities of the polymer–metal complexes were higher than those of the polymeric Schiff base, and all of the polymer–metal complexes showed good thermal stability up to 300°C. The char yields at 800°C for the polymer–metal complexes are given in Table IV.

Biological activity studies

The polymeric Schiff base and its polymeric metal complexes individually exhibited varying degrees of inhibitory effects on the growth of bacterial and fungal strains. The results are presented in Tables V and VI and Figure 4(a,b); they show that the newly

TABLE V
Antibacterial Activities of APHFB and Its Polymer–Metal Complexes

Compound	Zone diameter showing complete growth inhibition (mm) ^a				
	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>B. subtilis</i>	<i>S. aureus</i>	<i>S. typhi</i>
APHFB	11	10	12	12	10
APHFB–Mn(II)	12	12	11	14	11
APHFB–Co(II)	11	10	12	13	11
APHFB–Ni(II)	12	13	12	13	14
APHFB–Cu(II)	15	14	14	16	16
APHFB–Zn(II)	13	12	11	12	11
Kanamycin ^b	20	18	18	20	18

^a Significant activity, 14–16 mm; moderate activity, 7–13 mm.

^b Standard drug.

TABLE VI
Antifungal Activities of APHFB and Its Polymer–Metal Complexes

Compound	Zone diameter showing complete growth inhibition (mm) ^a		
	<i>C. albicans</i>	<i>M. canis</i>	<i>A. niger</i>
APHFB	14	21	16
APHFB–Mn(II)	13	19	18
APHFB–Co(II)	15	18	21
APHFB–Ni(II)	16	20	20
APHFB–Cu(II)	21	20	22
APHFB–Zn(II)	20	19	21
Miconazole ^b	25	20	25

^a Significant activity, 14–22 mm; moderate activity, 7–13 mm.

^b Standard drug.

synthesized polymeric Schiff base and its Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes possessed good biological activity. All of the synthesized compounds were screened for their antibacterial activity against *E. coli*, *B. subtilis*, *S. aureus*, *P. aeruginosa*, and *S. typhi* and for their antifungal activity against *C. albicans*, *M. canis*, and *A. niger*. All of the compounds generally showed good antibacterial activity, but more significant antifungal activity was observed against most of the strains. A marked enhancement of activity was exhibited in all of the polymer–metal complexes against all of the bacterial/fungal strains. It was evident from the data that the antimicrobial activity of the entire polymeric compound increased on coordination. The enhancement in activity could

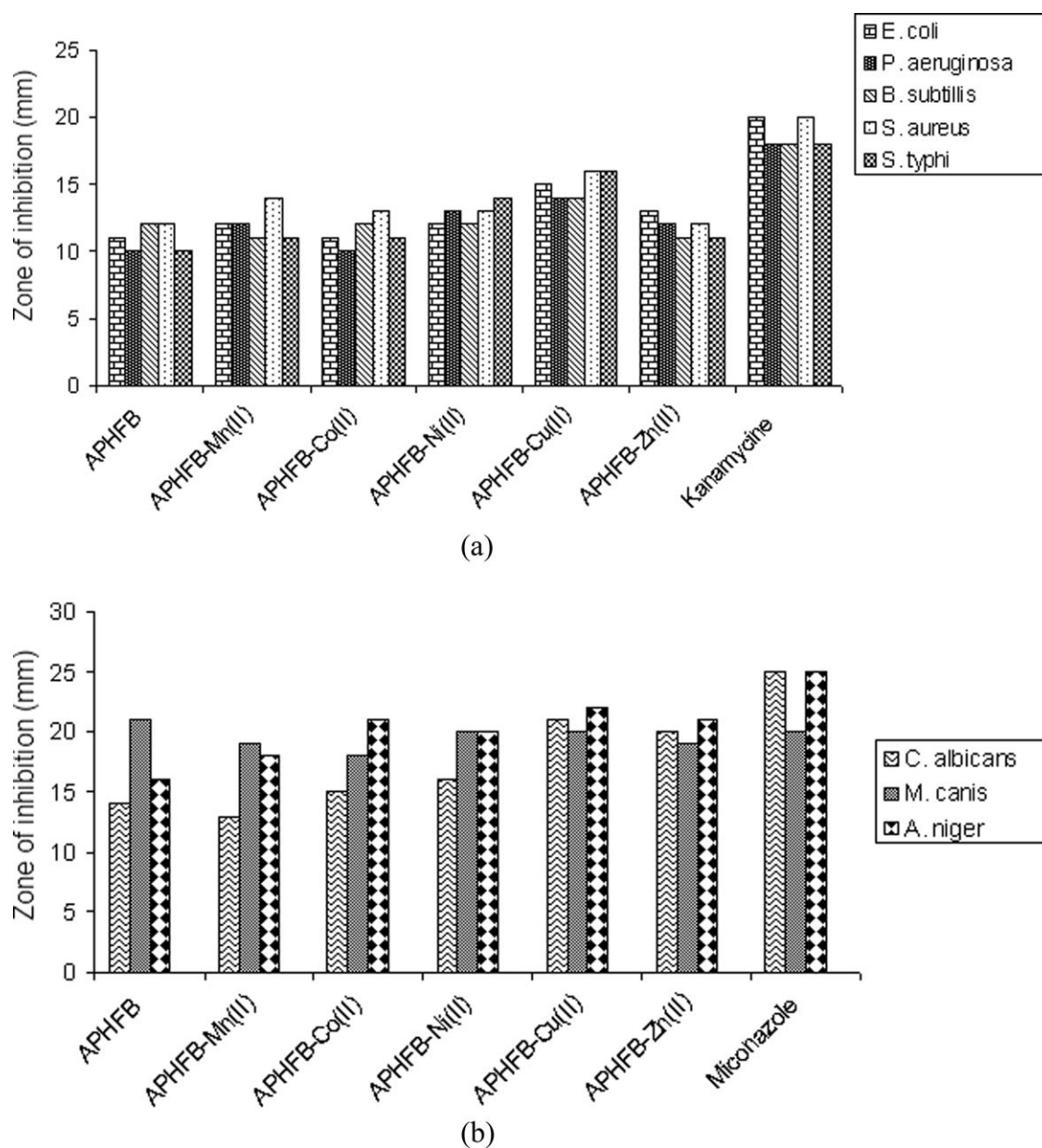


Figure 4 (a) Antibacterial activities and (b) antifungal activities of APHFB and its polymer–metal complexes.

be rationalized on the basis of their structures, which possessed an additional C=N bond. Moreover, chelation/coordination reduced the polarity of the metal ion by polarity sharing of its positive charge with the donor groups and the possibility of π -electron donor delocalization within the whole chelate ring. This process thus increased the lipophilic nature of the central metal atom, which in turn favored its greater penetration through the bacterial wall of the microorganism; this killed them more effectively. It has also been observed^{41,42} that the solubility, conductivity, and dipole moment are also influenced by the presence of metal ions; these could be significant factors responsible for increases in the hydrophobic character, liposolubility, and biological activity. The results of antifungal and antibacterial screening indicate that the polymer complexes of Cu(II) showed more activity than the other polymer-metal complexes. The result may have been due to the higher stability constant of the Cu(II) ion, which had a stronger interaction with nitrogen and oxygen donor atoms by which the lipophilic nature increased. The polymer complexes of Cu(II) showed more activity than the other polymer-metal complexes because of the presence of π electrons, which also increased the lipophilic nature of the Cu(II) ion.

CONCLUSIONS

A newly developed polymeric Schiff base and its polymer-metal complexes were prepared in good yield and characterized by various instrumental techniques. The polymeric Schiff base was soluble in DMF and DMSO, partially soluble in xylene and CHCl₃, and insoluble in water, benzene, toluene, and methanol, whereas the entire polymer-metal complexes were soluble in DMF and DMSO and were insoluble in water and common organic solvents. It was observed that the attachment of metal ions in the polymeric backbone enhanced the thermal and antimicrobial activities. The polymer-metal complexes of Cu(II) exhibited strong inhibitory effects on all of the bacteria, but other polymer-metal complexes exhibited different antibacterial activities, depending on the bacterium. All of the polymer-metal complexes were found to exhibit good antimicrobial activities and may be used as antifungal and antifouling coatings in various processes.

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