

Biocidal polymers: synthesis, characterization and applications of transition metals polychelates of formaldehyde-barbituric acid resin

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Abstract Novel polymeric ligand by polycondensation of Schiff base with barbituric acid and formaldehyde in acidic medium was synthesized followed by synthesis of polychelates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions. Structural and spectral properties were studied by elemental, spectral (FTIR, ¹HNMR and UV–vis) and thermogravimetric analysis (TGA). Antimicrobial screening against *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, (bacteria) and *Candida albicans*, *Microsporum canis*, *Cryptococcus neoformans* (fungi) was done by agar well- diffusion method. Metal polychelates showed more effective antimicrobial nature as compared to the polymeric Schiff base. The elemental analysis data show the formation of 1:1 [M:L] metal polychelates. Thermal behavior of these metal polychelates was studied by TGA in a nitrogen atmosphere upto 800 °C. The comparative TGA data revealed that metal polychelates were more stable than their corresponding ligand. Polymeric Schiff base (AGB) acted as a tetradentate ligand and coordinated through azomethine nitrogen and oxygen of carboxylic acid groups. On basis of analytical data, six coordinated geometry was assigned for Mn(II), Co(II) and Ni(II) complexes and four coordinated for Cu(II) and Zn(II) complexes, which were further supported by FTIR spectra and TGA data. Owing to enhanced antimicrobial and thermal behavior, these polymers have wide range of applications such as thermally resistant, antimicrobial and antifouling coating materials.

Keywords UV–visible spectroscopy · Metal polychelates · Transition metal acetates · Barbituric acid · Agar well diffusion method

Introduction

Development of metal polychelates by linking transition metal ions with polydentate ligands such as polymeric Schiff base, has been constantly growing over few past years, as these possess significantly improved biocidal behavior along with thermal resistivity after chelation with several donor systems. Polymer metal complexes are advantageous over organic polymers, as a metal ion insertion into a functional polymeric Schiff base alters its activity resulting in enhancement of thermal resistivity and biological activity. These metal-based polymers may be semiconducting, paramagnetic or have nonlinear optics properties [1, 2]. These are also useful in the preparation of composites, thermostabilizers and block copolymers [3–5].

Due to synergistic effects of Schiff base, its metal complex imine polymers have been studied currently [6, 7]. These possess wide variety of applications as viewed in the recent publications [8–10]. Most of the literatures have indicated that it is advantageous to prepare and design a polymer-bound chelated Schiff base.

In this study, we have developed Schiff base polymer metal complexes with barbituric acid which is known for its pharmacological activity. Its derivatives could be used as drugs which are valuable in medicine as soporifics, hypnotics, sedatives and anesthetics [11]. Barbituric acid is a nontoxic and thermally stable material [12]. The presence of potential donors such as two amine nitrogen and three carbonyl oxygen atoms makes barbiturates interesting as polyfunctional ligands in coordination and

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polymer chemistry [13]. The work emphasizes synthesis of novel biocidal polymeric coordination compounds with enhanced biocidal and thermal activity as compared to its ligand. All compounds were characterized by using various spectral and physicochemical techniques. Magnetic moment measurement, elemental analysis, thermal behavior and geometry of the central metal ion have been discussed. All of the synthesized polymers were screened for their antibacterial activity against several bacteria and fungi using agar well diffusion method. Research focus was to synthesize coordination polymers with biocidal and thermal resistant behavior that making them applicable for biomedical application.

Experimental

Materials

Glutaraldehyde 25 wt%, anthranilic acid and hydrochloric acid 35 wt% (Merck, India), barbituric acid (Qualingens, India), formaldehyde 37–41 wt% (SD Fine-Chem. Ltd, India), transition metal(II) acetates: $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (Merck, India) were used without further purification. Solvents like dimethylsulphoxide (DMSO), dimethylformamide (DMF), ethanol, methanol and acetone (Qualingens, India) were distilled before use. Microorganisms such as *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis* as bacteria and *Candida albicans*, *Microsporum canis* and *Cryptococcus neoformans* as fungi were provided by the culture collection of Microbiology Laboratory, Department of Microbiology, A.M.U. (Aligarh, India).

Methods

Elemental analyses of all polymeric compounds were carried out at IIT, Roorkee on a Perkin Elmer Model-2400 elemental analyzer (Waltham, MA, USA). Metal content was determined by the complexometric titration against EDTA after decomposing with conc. HNO_3 [18].

FTIR spectra were recorded over ($4000\text{--}400\text{ cm}^{-1}$) using a Perkin Elmer spectrometer model 621 (USA) by KBr pellets. UV–visible (Perkin Elmer Lambda Ez-201, USA) spectra were carried out with DMSO as a solvent. Magnetic susceptibility was measured on a vibrating sample magnetometer (model 155, NJ, USA). ^1H NMR spectra were recorded on a Jeol GXS 300 MHz FX-1000 FT-NMR spectrometer (JEOL, Japan) using $\text{DMSO-}d_6$ as a solvent and tetramethyl silane as an internal standard.

Thermal behavior of the synthesized polymeric Schiff base and its metal polychelates was determined on a TA

Analyzer 2000 (TA Instruments, USA) in nitrogen atmosphere and at a rate of $20\text{ }^\circ\text{C min}^{-1}$. Solubility of all the synthesized polymeric compounds was tested in various solvents at room temperature.

Apart from these, antimicrobial activity of all the polymeric compounds was also determined against various selected microorganism by using agar well diffusion method at Microbiological Laboratory of A.M.U. (Aligarh, India).

Synthesis of polymeric Schiff base (AGB)

Procedure to synthesize Schiff base from anthranilic acid and glutaraldehyde was adopted according to El-Reash et al. [14] with slight modification. Glutaraldehyde (1.0 g, 0.02 mol) was added drop wise into ethanolic solution of anthranilic acid (2.74 g, 0.02 mol) dissolved in 30 mL of ethanol at $65\text{ }^\circ\text{C}$ with continuous stirring (Scheme 1). Reaction mixture was stirred magnetically under reflux for 12 h, acidified with concentrated HCl. Dark oily product was formed which was allowed to cool at room temperature. Then, it was separated by using diethyl ether. The dark brown product was collected, washed with diethyl ether and dried in vacuum. The reaction yield was 65 %.

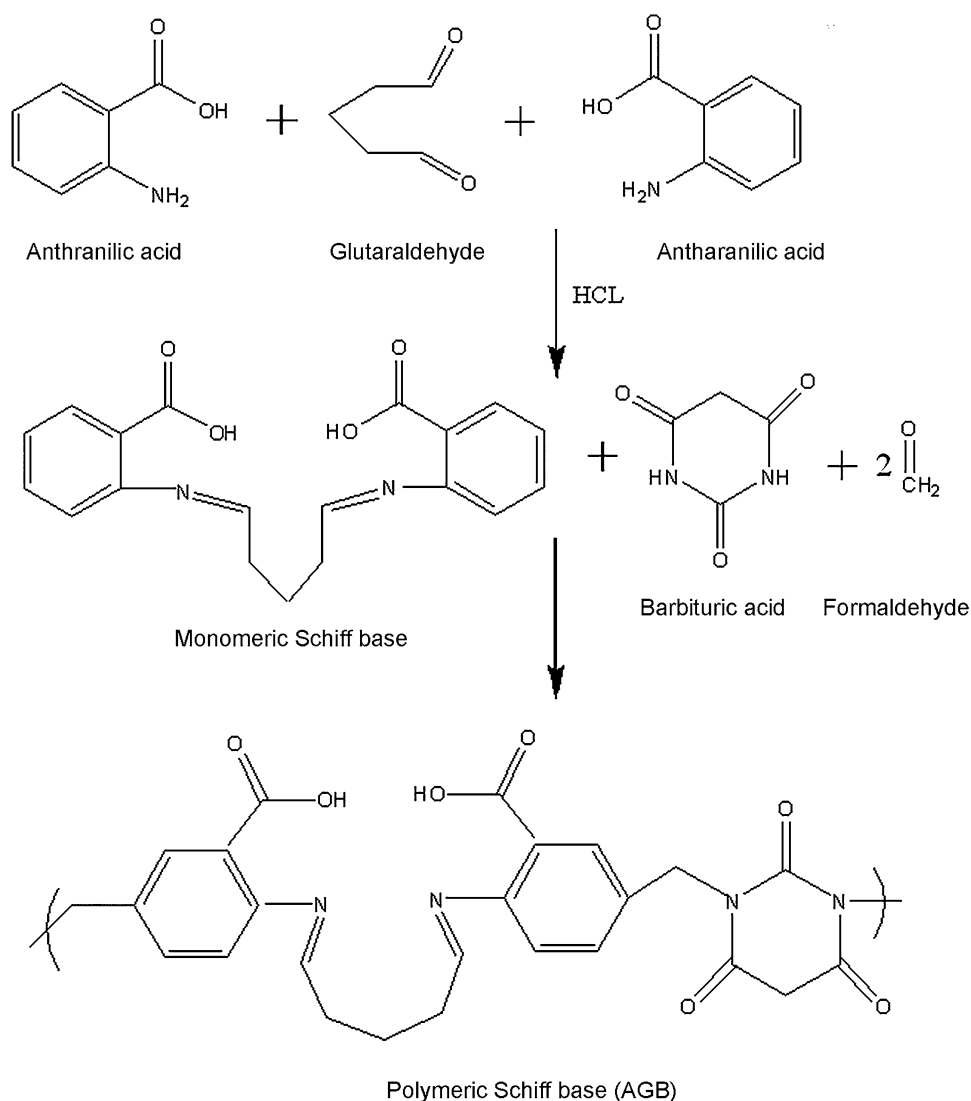
Elemental analyses

The elemental analyses for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_4$ (338.35 g/mol) were obtained as follows:

Obt.: C, 68.12 %; H, 5.49 %; N, 9.10 %. Cal.: C, 67.44 %; H, 5.36 %; N, 8.28 %.

IR (KBr pellet, $\nu\text{ (cm}^{-1}\text{)}$): 3345 (OH), 3133 (aromatic CH), 1715 (C=O), 1657 (CH=N). 2950–2844 ($-\text{CH}_2$ asym-sym).

In a 250 mL three necked round bottom flask equipped with a thermometer, condenser and magnetic stirrer, the prepared Schiff base (3.38 g, 0.01 mol) was dissolved in 30 mL DMF and 1.5 mL formaldehyde in 1:2 molar ratio, heated at $70 \pm 5\text{ }^\circ\text{C}$ for 3 h in the presence of 2–3 drops of hydrochloric acid with continuous stirring. Progress of reaction was monitored by thin layer chromatography. Then, barbituric acid (1.28 g, 0.01 mol) dissolved in 20 mL of DMF was added to the solution. The mixture was stirred again at $80\text{--}90\text{ }^\circ\text{C}$ for 24 h. The solution was made viscous by vaporizing excess solvent and was precipitated in excess amount of cold water. The resulting precipitate of polymeric Schiff base resin was filtered and washed with double distilled water and diethyl ether. The dark brown product of polymeric Schiff base AGB was dried in vacuum desiccator, while reaction yield was 58 %.

Scheme 1 Synthetic route of polymeric Schiff base (AGB)

Synthesis of metal polychelates

Metal polychelates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared by using equimolar ratio (1:1) of polymeric ligand (AGB) and metal(II) ions. Typical procedure for the preparation of metal polychelates of manganese (II) was as follows:

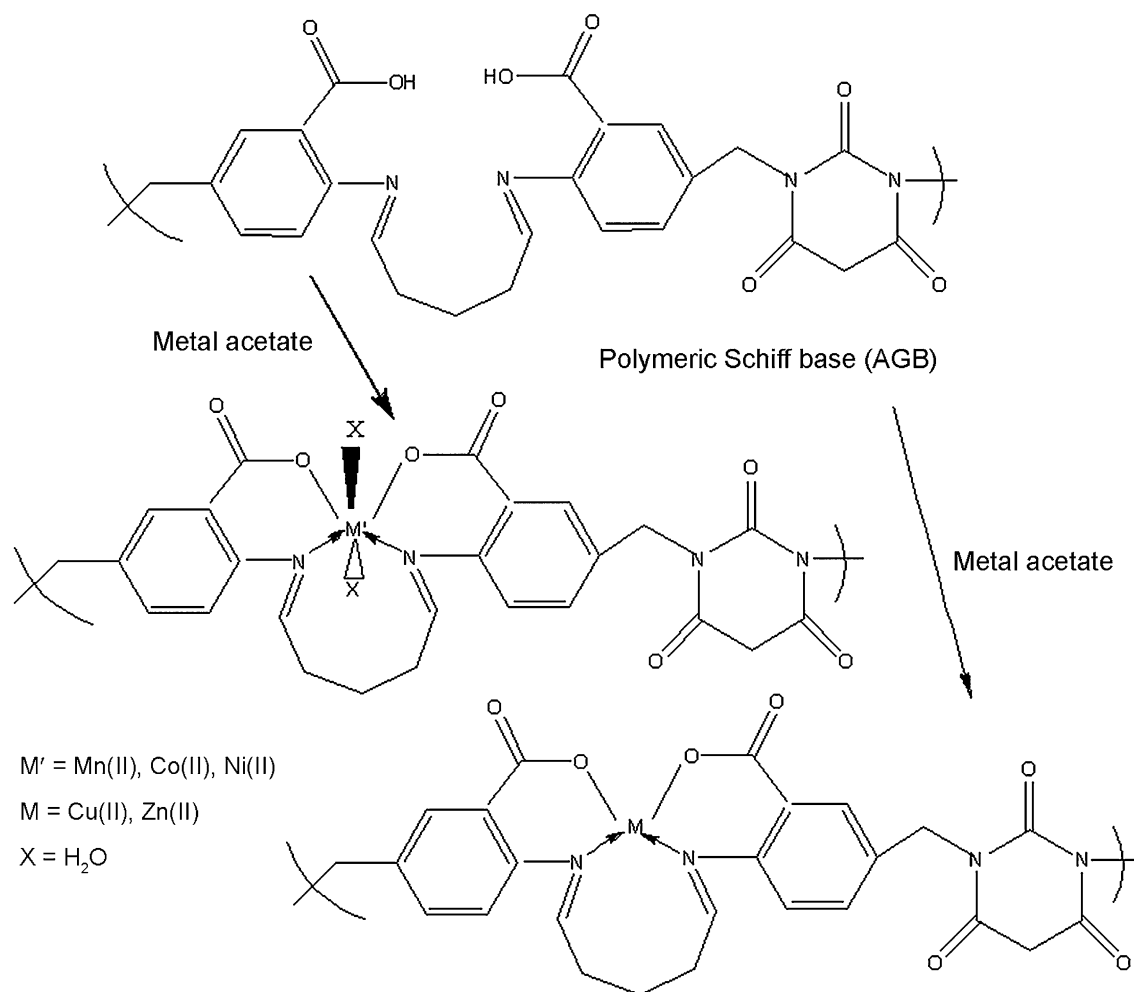
Hot solution of manganese (II) acetate tetrahydrate (2.45 g, 0.01 mol dissolved in 25 mL DMF) was mixed with the solution of polymeric Schiff base (0.01 mol dissolved in 25 mL DMF) in 1:1 molar ratio. The mixture was heated at 70 °C on a magnetic stirrer for 15 h. Brown viscous product was formed after slow evaporation of solvent. Ice cooled water was added to precipitate out the final product, which was filtered, washed with acetone and diethyl ether and dried in vacuum desiccator at room temperature, as yield of reaction was 67 %.

Similar procedure was adopted for the synthesis of other metal polychelates (Scheme 2) and yields are given in Table 1.

Antimicrobial assessment

Antimicrobial tests were carried out at the Department of Microbiology, Aligarh Muslim University, Aligarh, India. The antimicrobial activity of polymeric ligand and its metal polychelates was tested against different microorganisms in DMF as a solvent. The sample concentration was 50 $\mu\text{g mL}^{-1}$ for antibacterial and antifungal studies, respectively. Bacterial strains were nourished in a nutrient broth and yeasts in a malt-extract broth with incubation for 24 and 48 h, respectively, at room temperature (23–27 °C).

According to the agar well diffusion method, bacteria were incubated on Muller–Hinton agar and yeast on Sabouraud dextrose agar. The wells were dug in media with the



Scheme 2 Synthetic route of metal polychelates [AGB-M(II)]

Table 1 Elemental analysis data for polymeric Schiff base and its metal polychelates

Abbreviation	Empirical formula	Yield (%)	Calculated (%) (Observed %)			
			C	H	N	M
AGB	[C ₂₅ H ₂₂ N ₄ O ₇] _n	58	61.22 (61.30)	4.52 (4.50)	11.42 (11.53)	–
AGB-Mn(II)	[C ₂₅ H ₂₄ N ₄ O ₉ Mn] _n	67	51.82 (52.10)	4.17 (4.23)	9.67 (9.60)	9.48 (9.52)
AGB-Co(II)	[C ₂₅ H ₂₄ N ₄ O ₉ Co] _n	69	51.47 (51.62)	4.15 (4.21)	9.60 (9.57)	10.10 (10.11)
AGB-Ni(II)	[C ₂₅ H ₂₄ N ₄ O ₉ Ni] _n	68	51.49 (51.62)	4.15 (4.17)	9.61 (9.65)	10.06 (10.11)
AGB-Cu(II)	[C ₂₅ H ₂₀ N ₄ O ₇ Cu] _n	63	54.40 (54.46)	3.65 (3.66)	10.15 (10.19)	11.51 (11.62)
AGB-Zn(II)	[C ₂₅ H ₂₀ N ₄ O ₇ Zn] _n	70	54.21 (54.42)	3.64 (3.78)	10.12 (10.20)	11.81 (11.90)

n number of repeating units of polymeric chain

help of a sterile steel borer and then 0.1 mL of each sample was introduced in the corresponding well. Other wells were supplemented with solvent (DMF) for positive control and standard drug, viz. tetracycline (antibacterial) and fluconazole (antifungal), for negative control. The resulting zones of inhibition on the plates were measured in millimeters.

Results and discussion

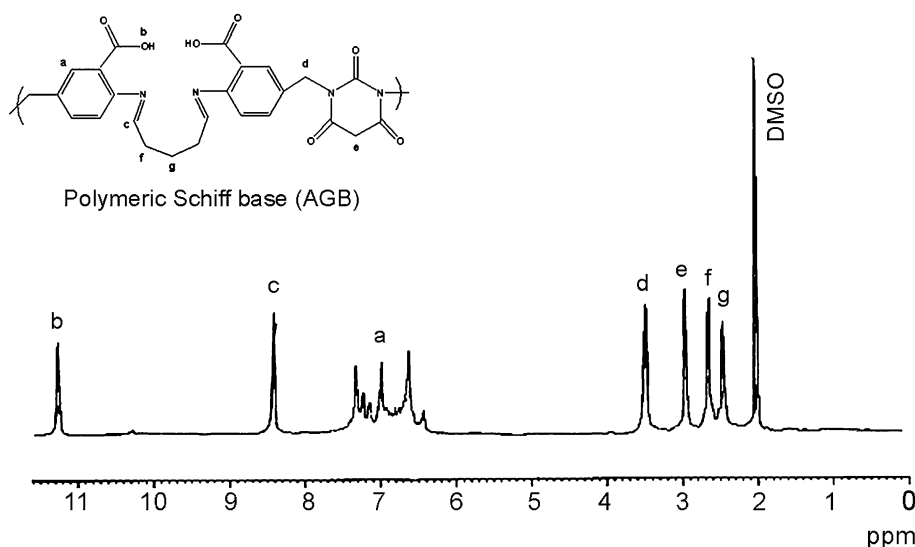
FTIR spectra

Fourier transform infrared spectroscopy was used for the structural analysis of polymeric ligand and its metal

Table 2 FTIR spectral bands and assignments of polymeric Schiff base and its metal polychelates

Compounds	Assignments						
	$\nu(\text{H}_2\text{O})$	(HOH) (ρ & ω)	$\nu(\text{COO}^-)$ (asym–sym)	$-\text{CH}_2$ (sym–asym)	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
AGB	–	–	1614–1411 (s)	2843–2954 (m)	1615 (m)	–	–
AGB–Mn(II)	3400 (m)	840 (s)	1588–1395 (s)	2843–2954 (m)	1590 (s)	528 (s)	453 (s)
AGB–Co(II)	3320 (m)	861 (s)	1567–1388 (s)	2843–2954 (m)	1597 (s)	540 (s)	438 (m)
AGB–Ni(II)	3365 (m)	897 (s)	1561–1376 (s)	2843–2954 (m)	1588 (s)	510 (s)	444 (s)
AGB–Cu(II)	–	–	1591–1363 (s)	2843–2954 (m)	1586 (s)	534 (m)	425 (s)
AGB–Zn(II)	–	–	1575–1381 (s)	2843–2954 (m)	1582 (s)	516 (s)	430 (m)

s strong, *b* broad, *m* medium, *w* weak, *sym* symmetric, *asym* asymmetric, ρ rocking, ω wagging

Fig. 1 $^1\text{H-NMR}$ spectrum of AGB sample

polychelates, results being illustrated in Table 2. The characteristic azomethine $\nu(\text{C}=\text{N})$ band appeared at 1615 cm^{-1} in metal free Schiff base sample. In metal polychelates, this band was shifted to lower frequencies by $18\text{--}33\text{ cm}^{-1}$. The shifting of peak to lower frequencies on complex formation indicated the coordination of nitrogen atoms of azomethine moieties [15, 16]. Bands responsible for symmetric stretching vibrations of the carboxylate ions were appeared in the range of $1411\text{--}1363\text{ cm}^{-1}$ while for asymmetric stretching vibrations were appeared at $1614\text{--}1561\text{ cm}^{-1}$; $\Delta\nu(\text{COO}^-) \sim 197\text{ cm}^{-1}$ indicated the unidenticity of carboxylate groups [17].

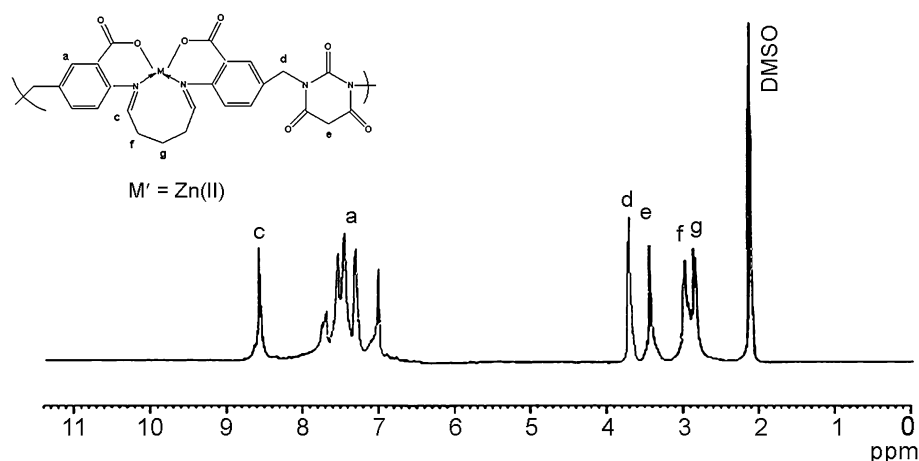
The spectra of Mn(II), Co(II), Ni(II) polychelates of AGB exhibited broad bands in the region of $3320\text{--}3365\text{ cm}^{-1}$ suggesting the presence of water molecules which is further confirmed by the appearance of a band in the region of $897\text{--}840\text{ cm}^{-1}$ assigned to rocking and wagging vibration modes of water molecules [18, 19]. The presence of coordinated water was also confirmed by TG analyses [20]. FTIR of AGB–M(II) show bands at $510\text{--}540$ and $425\text{--}453\text{ cm}^{-1}$ for $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$, respectively,

suggesting the coordination of metal ions with the oxygen and nitrogen donor atoms of the ligand [21, 22].

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

The $^1\text{H-NMR}$ spectra of AGB and AGB–Zn(II) in $\text{DMSO-}d_6$ are shown in Figs. 1 and 2, respectively, using tetramethylsilane (TMS) as an internal standard. Aromatic protons show multiple resonance signals at $6.40\text{--}7.80\text{ ppm}$ for AGB ligand and AGB–Zn(II) complex. The aromatic protons peak was broad due to intermolecular interactions toward the metal ions and variation in pi-electron densities around the protons. The peak observed at 11.3 ppm was assigned to proton of $-\text{COOH}$ groups of AGB [23] while signal for the protons of $-\text{COOH}$ groups was disappeared in the $^1\text{H-NMR}$ spectra of AGB–Zn(II) complex, suggesting the participation of $-\text{COOH}$ proton to the metal center in the formation of $\text{COO}-\text{M}$ coordination.

Azomethine linkage appeared at 8.40 ppm [24] in AGB, which showed downfield shifting in metal polychelates interpreting participation of nitrogen atom of azomethine in

Fig. 2 $^1\text{H-NMR}$ spectrum of AGB–Zn(II) complex**Table 3** Magnetic susceptibility, electronic spectra and ligand field parameters

Compounds	Magnetic moment (BM)	Electronic transitions (cm^{-1})	Assignment	Geometry	B	$10Dq$ (cm^{-1})	β	β°
AGB–Mn(II)	5.85	22,340	$^4A_{1g}(G) \leftarrow ^6A_{1g}(F)$	Octahedral	731	3658	0.76	0.24
		17,620	$^4T_{2g}(G) \leftarrow ^6A_{1g}(F)$					
		13,780	$^4T_{1g}(G) \leftarrow ^6A_{1g}(F)$					
AGB–Co(II)	4.25	21,415	$^4T_{1g}(P) \leftarrow ^4T_{1g}(F)$	Octahedral	948	9949	0.85	0.15
		17,350	$^4A_{2g}(F) \leftarrow ^4T_{1g}(F)$					
		8500	$^4T_{2g}(F) \leftarrow ^4T_{1g}(F)$					
AGB–Ni(II)	3.20	23,600	$^3T_{1g}(P) \leftarrow ^3A_{2g}(F)$	Octahedral	761	9135	0.70	0.30
		13,980	$^3T_{1g}(F) \leftarrow ^3A_{2g}(F)$					
		8240	$^3T_{2g}(F) \leftarrow ^3A_{2g}(F)$					
AGB–Cu(II)	1.78	15,571	$^2A_{1g} \leftarrow ^2B_{1g}(F)$	Square planar	–	–	–	–
		25,891	Charge-transfer					

M–N bond formation. Resonance signal at 2.90 ppm indicated the presence of methylene protons of barbituric acid. The peak at 3.40 ppm was due to the proton of benzylic methylene group in AGB.

Results of $^1\text{H-NMR}$ spectra revealed that barbituric acid moiety was attached to anthranilic acid with methylene groups of formaldehyde. Appearance and shifting of significant peaks confirmed the formation of ligand and metal polychelates.

Electronic spectra and magnetic moment measurements

Various crystal field parameters, ligand field splitting parameter (Dq), Racah inter-electronic repulsion parameter (B), ligand field splitting energy ($10Dq$), covalency and ionic character (β and β°) were calculated and results showed that the synthesized coordination polymers were stable and had good covalent character.

Electronic spectra of the synthesized metal polychelates were recorded in DMSO solution. Various crystal

field parameters, $10Dq$, B , β and β° were calculated and their values are given in Table 3. Magnetic moment of AGB–Mn(II) was 5.85 BM, which suggested the presence of five unpaired electrons. Electronic spectrum of AGB–Mn(II) exhibited three absorption bands at 22,340, 17,620, 13,780 cm^{-1} which were assigned to $^4A_{1g}(G) \leftarrow ^6A_{1g}(F)$, $^4T_{2g}(G) \leftarrow ^6A_{1g}(F)$, $^4T_{1g}(G) \leftarrow ^6A_{1g}(F)$ transitions, respectively. The spectral data were used to calculate ligand field parameters $10Dq$, B , β and β° and were 3658 cm^{-1} , 731, 0.76 and 0.24, respectively, which are listed in Table 3 indicating the covalent nature and suggested the octahedral environment around the Mn(II) ion [25].

Co(II) polychelate had a magnetic moment of 4.25 BM showing three absorption bands at 21415 cm^{-1} , 17350 cm^{-1} and 8500 cm^{-1} due to $^4T_{1g}(P) \leftarrow ^4T_{1g}(F)$, $^4A_{2g}(F) \leftarrow ^4T_{1g}(F)$, and $^4T_{2g}(F) \leftarrow ^4T_{1g}(F)$ transitions, respectively. The ligand field parameters $10Dq$, B , β and β° calculated with the help of spectral observations were 9949 cm^{-1} , 948, 0.85 and 0.15, respectively. While the magnetic moment 4.25 BM confirmed the octahedral geometry in Co(II) metal polychelate [26].

Table 4 Thermal properties of polymeric Schiff base (AGB) and its metal polychelates

Compounds	Weight left at the indicated temperature (%)							Characteristic weight left at 800 °C (%)
	100 (°C)	200 (°C)	300 (°C)	400 (°C)	500 (°C)	600 (°C)	700 (°C)	
AGB	95	81	64	50	41	29	14	4
AGB–Mn(II)	94	88	75	62	53	45	30	11
AGB–Co(II)	93	84	76	63	51	40	29	9
AGB–Ni(II)	95	87	70	59	48	39	25	7
AGB–Cu(II)	95	92	78	69	59	50	35	12
AGB–Zn(II)	96	91	82	71	63	52	38	14

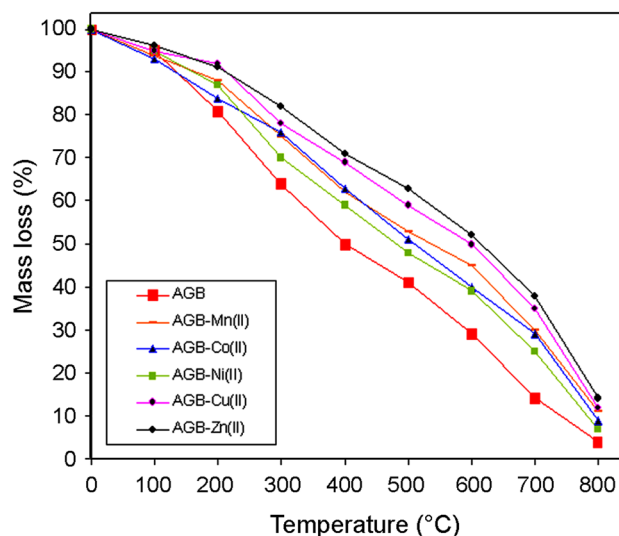
AGB–Ni(II) exhibited magnetic moment of 3.20 BM and show three bands at 23,600, 13,980, 8240 cm^{-1} assigned to spin-allowed transitions ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$, ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$, ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$, respectively. The ligand field parameters $10Dq$, B , β and β° were 9135 cm^{-1} , 761, 0.70 and 0.30, respectively, which supported its octahedral structure.

AGB–Cu(II) exhibited magnetic moment of 1.78 BM. The electronic spectrum of AGB–Cu(II) showed bands at 15,571 and 25,891 cm^{-1} which were assigned to ${}^2A_{1g} \leftarrow {}^2B_{1g}(F)$ and a charge-transfer band, respectively, indicating square planar geometry [27]. Thus, electronic spectral study further supported the proposed structures around the central metal ion.

Thermal behavior

Comparative study of the thermal degradation behavior of ligand (AGB) and its metal polychelates was carried out by a thermogravimetric analyzer. Thermal degradation was carried out at a linear heating rate of 20 °C/min in nitrogen atmosphere to the maximum temperature of 800 °C and the results are listed in Table 4. Thermograms of ligand and its metal polychelates are shown in Fig. 3. Thermal stability of the polychelates depends on the mode of complexation of the metal with the polymeric Schiff base and on the structure of polymeric Schiff base itself [28, 29].

The initial 6 % weight loss of AGB between temperatures of 100–120 °C is corresponded to the loss of moisture and other solvents. In the complexes of Mn(II), Co(II) and Ni(II), above 150 °C, further 2–6 % weight loss was observed which is due to the removal of coordinated water [30]. While no appreciable weight loss was observed for Cu(II) and Zn(II) polychelates, these polymers showed gradual degradation pattern that favors four coordinated geometry. This fact was also supported by elemental analysis, FTIR, magnetic moment and UV–visible analysis data. For AGB, above 200 °C, steep slope was observed in the TGA curve which was depicted rapid weight loss and about 50 % weight loss

**Fig. 3** Thermograms of AGB and its metal polychelates samples

was due to decomposition in the temperature range of 350–400 °C. On further increasing temperature, AGB was decomposed completely into a volatile substance.

Metal polychelates showed two-step continuous degradation, where the first degradation step was faster than the second one. This may be due to the decomposition of non-coordinated parts of complexes, while the actually coordinated parts of the all metal polychelates decomposed later [31] and finally resulted in the formation of char above 800 °C. It is also known that metal ions present in the polychelates are expected to impart greater effect on the thermal properties of the chelating polymer [32].

Results of thermal analysis revealed that the metal polychelate of Zn(II) followed by that of Cu(II) was comparatively more thermally stable than the other metal polychelates. Order of stability on the basis of thermal residual weight appeared to be AGB–Zn(II) > AGB–Cu(II) > AGB–Mn(II) > AGB–Co(II) > AGB–Ni(II) > AGB. Thus, the present study data clearly indicated that the improved thermal

Table 5 Antimicrobial activity of polymeric Schiff base (AGB) and its metal polychelates

Compounds	Zones of inhibition (mm)					
	<i>E. coli</i>	<i>S. aureus</i>	<i>B. subtilis</i>	<i>C. albicans</i>	<i>M. canis</i>	<i>C. neoformans</i>
AGB	10 ± 1	12 ± 1	13 ± 1	10 ± 1	11 ± 1	12 ± 1
AGB–Mn(II)	20 ± 1	20 ± 1	18 ± 2	16 ± 1	12 ± 2	16 ± 2
AGB–Co(II)	15 ± 2	14 ± 3	17 ± 1	16 ± 2	15 ± 2	20 ± 2
AGB–Ni(II)	18 ± 1	19 ± 1	20 ± 1	14 ± 3	15 ± 1	17 ± 1
AGB–Cu(II)	23 ± 1	21 ± 1	22 ± 2	20 ± 2	17 ± 2	22 ± 1
AGB–Zn(II)	17 ± 2	16 ± 1	19 ± 2	18 ± 1	14 ± 1	18 ± 1
Tetracycline ^a	15 ± 1	16 ± 2	18 ± 2	–	–	–
Fluconazole ^b	–	–	–	17 ± 2	15 ± 1	19 ± 1

^a Standard drug, antibacterial activity

^b Standard drug, antifungal activity

stability was due to the presence of transition metal in the polychelates.

Antimicrobial activity

Biocidal effect of the synthesized metal polychelates was determined against various bacteria and fungi. Agar well diffusion method was used to assess the antimicrobial action of bacteria and fungi with respect to tetracycline and fluconazole as standard drugs, respectively.

Results are summarized in Table 5 and shown in Fig. 4. AGB–Cu(II) polychelate exhibited highest antibacterial and antifungal activity against *E. coli*, *S. aureus*, *B. Subtilis*, *C. albicans*, *M. canis*, and *C. neoformans* (23, 21, 22, 20, 17, and 22 mm, respectively). AGB–Ni(II) and AGB–Mn(II) polychelates displayed promising antibacterial activity (18, 19, and 20 mm) and (20, 20, and 18 mm) against, *E. coli*, *S. aureus* and *B. subtilis*, respectively. While promising antifungal activity was observed for AGB–Co(II) (16, 15, and 20 mm) against *C. albicans*, *M. canis* and *C. neoformans* and for AGB–Zn(II) (18 and 18 mm) against *C. albicans* and *C. neoformans*, respectively. On comparing, antibacterial activity of the metal polychelates was better as reported by Nishat et al. [33] for similar kind of polychelates.

Antibacterial activity by AGB–Co(II) (15, 14, and 17 mm) was the lowest against *E. coli*, *S. aureus* and *B. subtilis*, respectively, while the lowest antifungal activities were observed for AGB–Ni(II) (14 mm) against *C. albicans* and AGB–Mn(II) (15 and 16 mm) against *M. canis* and *C. neoformans*, respectively. Most aldehydes, glutaraldehyde, glyoxal, succinaldehyde and *o*-phthalaldehyde have sporicidal activity but glyoxal and succinaldehyde are less active. The distance between two aldehyde groups in glutaraldehyde and possibly in *o*-phthalaldehyde may be optimal for interaction of these –CHO groups in nucleic acids and especially in proteins and enzymes [34].

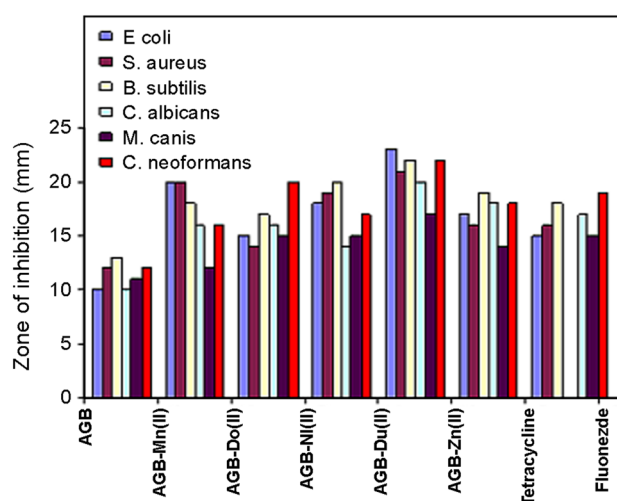


Fig. 4 Inhibition growth of AGB and AGB–M(II) samples

Metal-chelated polymers containing N and O donor systems might have inhibited enzyme production because enzymes that require a free hydroxyl groups for their activity appear to be especially susceptible to deactivation by the ions of complexes [35].

Polarity of metal ions was reduced by chelation, mainly because of partial sharing of its positive charge with donor groups and possibly π electron delocalization within whole chelate ring formed during coordination. This chelation process increases the lipophilic nature of the metal atom, which in turn favors its permeation through the lipid layer of the membrane.

Conclusion

Microanalytical, magnetic, spectroscopic and thermal analysis data favored successful synthesis of novel Schiff base polymer

metal complexes were discussed in this study. All the polymeric compounds were obtained in good yield and were soluble in DMF and DMSO, but insoluble in the common organic solvents. Thermal and antimicrobial activities were enhanced on incorporation of metal ions in the polymeric backbone. The results revealed that metal polychelate of Zn(II) followed by Cu(II) was comparatively more thermally stable than other metal polychelates. Cu(II) metal polychelate exhibited the best antibacterial as well as antifungal activity whereas better inhibitory effects were observed in the case of Mn(II) and Zn(II) metal polychelates for antibacterial and antifungal activity, respectively. The synthesized metal polychelates could be used as solvent resistant coating materials due to their insoluble nature. Moreover, since these polymers possess good biocidal activity and thermal stability, these can be used for biomedical applications requiring thermal sterilization.

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