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Biologically active and thermally stable polymeric Schiff base and its metal polychelates: Their synthesis and spectral aspects



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HIGHLIGHTS

- Results obtained, revealed that the synthesized polymers exhibited higher thermal stability than their corresponding ligands.
- Spectral studies confirmed the proposed structure of the metal polychelates.
- Antimicrobial studies show that biological activities of the polymers were enhanced after coordination with the metal.
- Antimicrobial activity and thermal stability of AGP-Cu(II) was the best amongst all synthesized metal polychelates.

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ABSTRACT

New metal polychelates 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 evaluated by elemental analysis, FT-IR and ¹H-NMR. Geometry of the chelated polymers was confirmed by magnetic susceptibility measurements, UV– Visible spectroscopy and Electron Spin Resonance. The molecular weight of the polymer was determined by gel permeation chromatography (GPC). Thermogravimetric analysis indicated that metal polychelates were more thermally stable than their corresponding ligand. All compounds were screened for their antimicrobial activities against *Escherichia coli, Staphylococcus aureus, Bacillus subtilis*, (bacteria) and *Candida albicans, Microsporum canis, Cryptococcus neoformans* (fungi) by agar well diffusion method. Interestingly, the polymeric Schiff base was found to be antimicrobial in nature but less effective as compared to the metal polychelates. On the basis of thermal and antimicrobial behavior, these polymers hold potential applications as thermally resistant antimicrobial and antifouling coating materials as well as antimicrobial packaging materials.

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Introduction

Continuous efforts have been made to make polymers more stable, increase their mechanical and chemical strengths and

http://dx.doi.org/10.1016/j.saa.2015.03.116 1386-1425/© 2015 Elsevier B.V. All rights reserved. to make them durable in the environment. Coordination polymers are usually known for their optical, mechanical and thermal stability [1]. Interest in construction of coordination polymers by linking transition metal ions with polydentate ligands has been constantly growing over the past years [2–4]. In addition to the above discussion, coordination polymers, derived from Schiff base have attractive physicochemical,

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chemical and biological properties, which make them highly processable [5]. Polymeric Schiff base are an important class of coordination polymers with multidentate donor sites, known to form polychelates with transition metal ions. Basic properties of polymeric Schiff base are due to the azomethine linkage in polymeric backbone [6]. They may serve as models in biologically important species, finding applications in biological, clinical, analytical and thermal activities.

Complexation of a metal ion to functional polymeric Schiff base changes its activity due to polymeric effect which has led to a variety of applications. Luminescent properties of polydentate Schiffbase coordination polymers have also been reported [7]. Various works on coordination complexes has revealed that the heterogeneous systems possess more economical potentials and advantages over homogeneous systems [8]. Several metallo-polymers containing metals in the backbone of polymer chain have already been prepared [9,10]. The preparation of polychelates from a polymeric ligand involving anthranilic acid and thiosemicarbazide, thiourea with formaldehyde resin has been reported [11,12]. Salicylidene anthranilic acid possesses antiulcer activity and complexation behavior with copper, increases its antiulcer activity [13]. Antimicrobial activity of coordination polymers depends on the central metal ion as well as nature of the ligand attached along their spatial relationship. So synthesis and structural studies of new compounds of this type have much interest as a first step in search for new Schiff base polymers as potential antimicrobial agents.

Keeping the foregoing facts in mind and in continuation to our research work in this domain, new Schiff base polymers containing transition metal ions in the main chain has been synthesized and their properties have been discussed. Its synthesis represents an attempt to give an organic polymer inorganic functionality.

Experimental

Materials and microbial strains

Anthranilic acid (Merck), 40% Glyoxal (S.D. fine), 35% hydrochloric acid (Merck), Formaldehyde 37–41% (S.D. Fine Chem), Piperazine (Qualingens), transition metal(II) acetates: Manganese(II) acetate tetrahydrate [Mn(CH₃COO)₂·4H₂O], Cobalt(II) acetate tetrahydrate [Co(CH₃COO)₂·4H₂O], Nickel(II) acetate tetrahydrate [Ni(CH₃COO)₂·4H₂O], Copper(II) acetate monohydrate [Cu(CH₃COO)₂·4H₂O], Copper(II) acetate tetrahydrate [Ni(CH₃COO)₂·4H₂O], Copper(II) acetate (Zn(CH₃COO)₂·2H₂O] (Merck), were used without further purification. Solvents like dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethanol, methanol and acetone (Qualingens) were distilled before use. Microorganisms, *Escherichia coli, Staphylococcus aureus, Bacillus subtilis*, (bacteria) and *Candida albicans, Microsporum canis, Cryptococcus neoformans* (fungi) were provided by the culture collection of microbiology laboratory, department of microbiology (A.M.U. Aligarh).

Synthesis

Synthesis of polymeric Schiff base (AGP)

Schiff base of anthranilic acid and glyoxal was synthesized by slightly modified method as described by Kurtoglu et al. [14]. Anthranilic acid (2.74 g, 0.02 mol) was dissolved in 30 mL ethanol then glyoxal (0.58 g, 0.01 mol) was added drop wise at 50 °C with continuous stirring. The reaction mixture was acidified with concentrated HCl and was stirred magnetically under reflux for a day at 60 °C. The formed dark yellow product was dissolved in

25 mL EtOH and left for crystallization at room temperature. Dark brown product was collected, washed with EtOH and dried in vacuum. Yield was 68%.

Elemental analysis for C₁₆H₁₂N₂O₄ (296.28 g/mol); *Cal.*: C, 64.86%; H, 4.08%; N, 9.46%. *Obt.*: C, 64.27%; H, 4.14%; N, 9.69%.

FTIR (KBr pellet, cm⁻¹): 3352 (OH), 2931 (=CH–CH=), 3132 (aromatic CH), 1657 (CH=N), 1717 (C=O).

To this synthesized Schiff base (0.01 mol), formaldehyde (0.02 mol) was added in presence of 40 mL DMF and 2–3 drops of conc. HCl. The three necked round bottom flask was equipped with thermometer, condenser and magnetic stirrer. Schematic representation is shown in Scheme 1.

Progress of reaction was monitored by thin layer chromatography. The resulting mixture was heated at 70 ± 5 °C for 1 h with continuous stirring. To this solution 0.86 g (0.01 mol) of piperazine dissolved in 15 mL of DMF was added. After that the reaction mixture was again stirred at 80–90 °C for 24 h. The obtained solution was poured into a beaker and made viscous by vaporizing the excess solvent. Then it was precipitated with an excess amount of cold water. The resulting light brown colored viscous product was washed with distilled water, acetone and diethyl ether. Finally, the product was dried in vacuum desiccators on calcium chloride. The polymeric Schiff base (AGP) was obtained in 62% yield.

Synthesis of metal polychelates

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

This metal polychelate was prepared by mixing a hot solution of manganese(II) acetate tetrahydrate (2.45 g, 0.01 mol dissolved in 25 mL DMF) with a solution of polymeric Schiff base (0.01 mol dissolved in 25 mL DMF). The reaction mixture was heated at 80 °C for 12 h, with continuous stirring as it becomes sticky and viscous. Brownish yellow product was precipitated by adding ice cooled water. The precipitate was filtered, washed several times with distilled water and acetone, and then dried under vacuum over anhydrous calcium chloride, yield 63%. Same procedure was adopted for the synthesis of other metal polychelates.

Characterization

Elemental analysis for the estimation of percentage of C, H and N present in metal polychelates was carried out by using elemental analyzer system GmbH Vario ELIII. Metal content of metal polychelates was determined by complexometric titration against ethylenediamine tetraacetic acid after decomposition of the complexes with concentrated nitric acid. FT-IR spectra were recorded on a Perkin Elmer IR spectrophotometer (Model 621) using KBr pellets in the range 4000–400 cm⁻¹. Proton NMR spectra was obtained from JEOL GXS 300-MHz FX-1000 Fourier transform NMR spectrometer, taking DMSO-d₆ as solvent and tetramethylsilane as an internal standard. Ultra violet-visible (UV-Vis) spectra were taken on a Perkin Elmer Lambda (EZ-201) spectrophotometer. Magnetic susceptibility was measured on a vibrating sample magnetometer (model 155). Electron Spin Resonance (ESR) of the copper complex was recorded on Varian E112 Xband Spectrometer. The number average (M_n) , weight average (M_w) , molecular weights were determined by gel permeation chromatography (Shimadzu, Japan) using tetrahydrofuran (THF) as mobile phase and polystyrene as a stationary phase.



Scheme 1. Synthetic route to polymeric Schiff base [AGP].

Thermal behavior of synthesized polymers was recorded with TA Analyzer 2000 at a heating rate of 20 °C/min in nitrogen atmosphere.

Antimicrobial assessment

Antimicrobial activity of polymeric ligand and its metal polychelates was tested against different microorganisms in DMSO as a solvent. The sample concentration was 50 μ g mL⁻¹. Bacterial strains were nourished in a nutrient broth and yeasts in a malt-extract broth and incubated for 24 and 48 h, respectively at room temperature (23–27 °C). According to the agar-diffusion method, bacteria were incubated on Muller-Hinton agar and yeast on Sabouraud dextrose agar. Wells were dug in media with the 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 DMSO for positive control and standard drugs, viz. Tetracycline (for bacterial strains) and Fluconazole (for antifungal strains) as negative control. The resulting zones of inhibition on the plates were measured in millimeters.

Results and discussion

Chemistry of the polymeric Schiff base and its metal polychelates

Nitrogen atom of anthranilic acid act as a nucleophile having a lone pair of electron, which attacks on carbon atom with positive charge of glyoxal, to form imine linkage (C=N). Mechanism involved during the formation of imine is given below:



The above synthesized Schiff base was subjected to react with formaldehyde in the presence of hydrochloric acid and mechanism for the preparation of polymeric Schiff base (AGP) is given as:

Polymeric Schiff base (AGP) and its metal polychelates were prepared by the procedure mentioned in experimental section and as shown in Schemes 1 and 2. The ligand and coordination polymers were colored compounds, soluble in DMSO and DMF but insoluble in common organic solvents.



Scheme 2. Synthetic route to metal polychelates [AGP-M(II)].



Analytical data of polymeric Schiff base (AGP) with its metal polychelates are given in Table 1, and are in good agreement with 1:1 metal to polymeric ligand molar ratio. It also revealed that coordination polymer of Mn(II) was coordinated with two molecules of water which is also corroborated by the FT-IR and TGA analyses discussed in the proceeding sections.

FT-IR analysis

IR spectra provide valuable information regarding the nature of functional groups attached to the metal atom. The polymeric Schiff base and its metal polychelates were characterized and their assignments are given in Table 2 and Fig. 1. Spectral band for v(C=N) appeared at 1622 cm⁻¹ in metal free Schiff base (AGP) while in metal polychelates, AGP-M(II), this bands shifted towards lower frequency by 15–22 cm⁻¹. Shifting of this band to lower energy on complex formation indicated the coordination of nitrogen atom of azomethine moiety [15,16]. Bands responsible for symmetric stretching vibration of carboxylate ion appeared at 1419–1375 cm⁻¹ while for asymmetric stretching it appeared at 1608–1555 cm⁻¹, Δv (COO⁻) ~230 cm⁻¹ for AGP polymers, indicating unidenticity of carboxylate group [17]. Spectra of AGP-Mn(II) exhibited a broad band at 3345 cm⁻¹ suggesting the presence of water molecule [11,12] which was further confirmed by the appearance of band at 855 cm⁻¹ assigned to rocking and wagging modes of water [18]. The presence of coordinated water was also confirmed by TG analyses. Spectra of other metal polychelates, AGP-M(II), showed bands in the range of $496-535 \text{ cm}^{-1}$ and 416–460 cm⁻¹ assigned to v(M–O) and v(M–N) vibrations respectively [19-20].

Table 1

Table 2

Elemental analysis data for polyment semin base and its metal polychelate.	Elemental	analysis d	lata for	polymeric	Schiff base	and its metal	polychelates
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Abbreviation	Empirical formula	(Yield %)	Calculated (obs	Calculated (observed) ^a (%)				
			С	Н	Ν	М		
AGP	$[C_{22}H_{22}N_4O_4]_n$	62	65.01 (64.35)	5.46 (5.55)	13.78 (13.89)	-		
AGP-Mn(II)	$[C_{22}H_{24}N_4O_6Mn]_n$	63	53.34 (54.10)	4.88 (4.96)	11.31 (11.44)	11.09 (11.02)		
AGP-Co(II)	$[C_{22}H_{20}N_4O_4Co]_n$	65	57.03 (56.88)	4.35 (4.40)	12.09 (12.15)	12.72 (12.76)		
AGP-Ni(II)	$[C_{22}H_{20}N_4O_4Ni]_n$	70	57.06 (56.98)	4.35 (4.37)	12.10 (12.13)	12.67 (12.64)		
AGP-Cu(II)	$[C_{22}H_{20}N_4O_4Cu]_n$	68	56.46 (56.71)	4.31 (4.35)	11.97 (12.10)	13.58 (13.46)		
AGP-Zn(II)	$[C_{22}H_{20}N_4O_4Zn]_n$	67	56.24 (56.31)	4.29 (4.33)	11.92 (12.02)	13.92 (14.04)		

a: Calculated value (observed).

n: number of repeating units of polymeric chain.

FT-IR spectral bands and assignments of polymeric Schiff base and its metal polychelates.

Compounds	Assignments	Assignments											
	v(H ₂ O)	(HOH) (ρ&ω)	v(COO ⁻) (<i>asym</i> -sym)	-CH ₂ (sym-asym)	v(C==N)	v(M—O)	v(M—N)						
AGP	-	-	1608-1419	2852-2926(m)	1622	-	-						
AGP-Mn(II)	3345	855(s)	1570-1406	2852-2926(m)	1607(s)	528(s)	460(s)						
AGP-Co(II)	-	-	1586-1401	2852-2926(m)	1605(s)	535(m)	453(s)						
AGP-Ni(II)	-	-	1555-1391	2852-2926(m)	1605(s)	517(s)	416(s)						
AGP-Cu(II)	-	-	1588-1375	2852-2926(m)	1603(s)	496(s)	437(m)						
AGP-Zn(II)	-	-	1595-1387	2852-2926(m)	1600(s)	520(m)	445(s)						

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

¹H NMR spectra

¹H NMR spectra of the synthesized polymers was recorded in DMSO-d₆ solvent, using tetramethylsilane (TMS) as an internal standard. Spectra of polymeric Schiff base AGP and AGP-Zn(II), are shown in Figs. 2 and 3 respectively. Aromatic protons show multiple resonance signals between 6.80 to 7.95 ppm for AGP and AGP-Zn(II). The peak of aromatic protons became broad due to intermolecular interaction towards metal ion and variation in the pi-electron density around protons. Peak observed at 11.10 ppm and 11.30 ppm was assigned to proton of -COOH group of AGP [21] while in the spectra of AGP-Zn(II), this signal disappeared, suggesting the participation of acidic proton to metal centre forming COO-M linkage. Azomethine linkage appeared at 8.30 ppm [22] in polymeric Schiff base, which showed downfield shifting in metal polychelate interpreting the participation of nitrogen of azomethine in the M-N bond formation. In AGP, resonance signal at 2.51 ppm indicated the presence of -CH₂-CH₂groups of piperazine moiety. Appearance of signal at 3.3 ppm was due to proton of benzylic methylene group in AGP. Results of ¹H-NMR spectra reveal that piperazine moiety was attached to anthranilic acid with methylene group of formaldehyde. Significant shifting of all peaks of AGP-Zn(II) were observed, which confirmed the formation of polymer metal complex.

Electronic spectra, magnetic property and Electron Spin Resonance

UV–Visible spectral analysis provides an accurate method for the determination of geometry of metal polychelates. The actual position of band maxima observed in electronic spectra is a function of geometry and strength of coordinating ligand. Various crystal field parameters, viz. ligand field splitting parameter (Dq), Racah interelectronic repulsion parameter (*B*), ligand field splitting energy (10 Dq), covalency and ionic character (β and β°) were calculated and the results revealed that the formed coordination polymers are stable and have good covalent character.

Electronic spectra of synthesized metal polychelates were recorded in DMSO. Various crystal field parameters, 10 Dq, *B*, β and β° were calculated and tabulated in Table 3. Magnetic moment of AGP-Mn(II) was 5.67 B.M., which suggested the presence of five unpaired electrons. The electronic spectrum exhibited bands at 21,252 cm⁻¹, 18,500 cm⁻¹, 14,450 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, suggesting an octahedral geometry [23]. Polymer complex of Co(II) had a magnetic moment of 4.54 B.M. [24] and the transitions appeared at 9213 cm⁻¹ and 16,598 cm⁻¹ corresponding to ⁴T₁ \leftarrow ⁴A₂ and ⁴T₁ \leftarrow ⁴A₂ respectively while v_3 was not visible due to broadness, which indicated tetrahedral geometry [25].

AGP-Ni(II) exhibited magnetic moment of 2.63 B.M. and three absorption bands were observed at 3994 cm⁻¹, 9497 cm⁻¹ and 16,465 cm⁻¹ corresponding to ${}^{3}T_{1}(P) {}^{3}T_{1}$, ${}^{3}A_{2} \leftarrow {}^{3}T_{1}$ and ${}^{3}T_{2} \leftarrow {}^{3}T_{1}$ transitions, respectively; suggesting tetrahedral geometry of the polychelate [26]. Magnetic moment for AGP-Cu(II) was 1.69 B.M. and the electronic spectrum showed spectral bands at 15,890 cm⁻¹ and 25,432 cm⁻¹ which were assigned to ${}^{2}A_{1g} \leftarrow {}^{2}B_{1g}(F)$ and a charge-transfer band respectively, indicating square planar geometry [27]. Thus, electronic spectral study further supports the structure proposed for metal polychelates.

Electron Spin Resonance (ESR) method is employed to understand the symmetry of surroundings of the paramagnetic ion and nature of its bonding to the neighboring ligands. ESR of Cu(II)



Fig. 1. FT-IR spectra of AGP and its metal polychelates.



chelated polymer was recorded in DMF at room temperature, which showed anisotropy with resolved hyperfine structure, with

the following values: gII = 2.326, $g \perp$ = 2.062, in which gII > $g \perp$. These values indicate that the ground state of Cu(II) is $dx^2 - y^2$,



Fig. 3. ¹H-NMR spectrum of AGP- Zn(II).

Table 3	
Magnetic susceptibility, electronic spectra and ligar	nd field parameter

Compounds	Magnetic moment (B.M.)	Electronic transitions (cm ⁻¹)	Assignment	Geometry	В	10 Dq (cm ⁻¹)	β	β°
AGP-Mn(II)	5.67	21,252 18,500 14,450	$\label{eq:4} \begin{array}{l} {}^{4}A_{1g}(G) \gets {}^{6}A_{1g}(F) \\ {}^{4}T_{2g}(G) \gets {}^{6}A_{1g}(F) \\ {}^{4}T_{1g}(G) \gets {}^{6}A_{1g}(F) \end{array}$	Octahedral	768	3838	0.79	0.21
AGP-Co(II)	4.54	9213 16,598	$\begin{array}{l} {}^4\!T_1(F) \leftarrow {}^4\!A_2 \\ {}^4\!T_1(P) \leftarrow {}^4\!A_2 \end{array}$	Tetrahedral	664	5975	0.59	0.41
AGP-Ni(II)	2.63	3994 9497 16,465	$ \begin{array}{c} {}^3T_1(P) \leftarrow {}^3T_1 \\ {}^3A_2 \leftarrow {}^3T_1 \\ {}^3T_2 \leftarrow {}^3T_1 \end{array} $	Tetrahedral	823	5763	0.76	0.24
AGP-Cu(II)	1.69	15,890 25,432	${}^{2}A_{1g} \leftarrow {}^{2}B_{1g}(F)$ Charge transfer	Square Planar	_	_	-	-

which supports square planar structure [28]. The *g*-values can be used to calculate *G*-value, which indicate weak field or strong field ligand. The equation used is:

$\textit{G} = (\textit{gII} - 2.002) / \textit{g} \perp -2.002$

If *G* is less than 4.0, the ligand forming Cu^{2+} complex is regarded as a strong field [29]. Since, *G*-value for AGP-Cu(II) is 5.4, therefore the ligand forms a weak field complex.

Molecular weight measurements

The average molecular weight of the AGP polymer was determined by gel permeation chromatography. The number average (M_n) and weight average (M_w) molecular weight were found 2998 and 3860 respectively. The polydispersity index (M_w/M_n) was found to be 1.28. The polydispersity index indicates the narrow distribution of molecular weights.



Fig. 4. Thermogram of AGP and its metal polychelates.

Thermal analysis

Thermal stability of the metal polychelates strongly depends on the structure of polymeric Schiff base and on the mode of complexation [30–31]. Fig. 4 shows TGA thermograms of all of the synthesized polymers. Degradation study was carried out at a linear heating rate of 20 °C/min. in nitrogen atmosphere to the maximum temperature of 800 °C. Thermal stability data (Table 4) of synthesized polymeric Schiff base and its metal polychelates is important to confirm the presence of metal ions, either as inclusion complexes or as absorbed species. Metal ions present in the ligand are expected to impart greater effect on thermal properties of the chelating polymer [32–33]. Thus thermal degradation behavior of

Table 4

Thermal properties of polymeric Schiff base (A	(AGP) and its metal polychelate
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Compounds	Weig temp	ht left eratur	(%) at e (°C)	Characteristic weight left (%) at				
	100	200	300	400	500	600	700	800 °C
AGP	93	79	60	48	35	23	12	2
AGP-Mn(II)	94	86	72	60	55	43	32	9
AGP-Co(II)	93	89	75	68	57	48	33	11
AGP-Ni(II)	94	91	73	65	55	43	31	7
AGP-Cu(II)	96	92	80	71	62	48	35	14
AGP-Zn(II)	95	91	77	68	56	42	30	12

Table 5

Antimicrobial activity of polymeric Schiff base (AGP) and its metal polychelates

ligand was compared to the polymers containing metal. For AGP, the initial weight loss was 8%, corresponds to the loss of moisture and other solvents. This loss was up to 11% due to loss of coordinated water in AGP-Mn(II) but no appreciable loss was observed for Ni(II), Co(II), Cu(II) and Zn(II) metal polychelates, thus favoring four coordinated geometry for these metal polychelates and as depicted from other data analysis. For AGP-M(II), up to 400 °C, 40–29% rapid weight loss was observed which shows the decomposition of organic part while slow and steady decomposition above 400 °C was due to the decomposition of inorganic part, finally resulting in the formation of char at 800 °C.

The results reveal that metal polychelate of Cu(II) was comparatively more thermally stable than other metal polychelates. Order of stability on the basis of thermal residual weight at 800 °C appeared to be AGP-Cu(II) > AGP-Zn(II) > AGP-Co(II) > AGP-Mn(II) > AGP-Ni(II). Data presented in the study clearly indicated that improved thermal stability was due to the presence of transition metal in the polymeric chain.

Antimicrobial evaluation

Agar well diffusion method was used for the assessment of antimicrobial action against some bacteria (*E. coli, S. aureus, B. subtilis*) and fungi (*C. albicans, M. canis, C. neoformans*). Tetracycline and Fluconazole were used as standard drugs for bacteria and fungi respectively. Results of the activity showed that polychelates are

Compound	Zones diameter showing complete growth inhibition (mm)										
	E. coli	S. aureus	B. subtilis	C. albicans	M. canis	C. neoformans					
AGP	08 ± 2	10 ± 1	11±1	08 ± 2	9 ± 1	11 ± 1					
AGP-Mn(II)	14 ± 2	14 ± 1	15 ± 1	14 ± 1	15 ± 2	16 ± 2					
AGP-Co(II)	20 ± 1	18 ± 1	18 ± 2	16 ± 1	13 ± 1	18 ± 1					
AGP-Ni(II)	14 ± 1	15 ± 2	13 ± 1	16 ± 1	12 ± 1	15 ± 3					
AGP-Cu(II)	22 ± 1	20 ± 1	20 ± 2	18 ± 3	16 ± 2	19 ± 1					
AGP-Zn(II)	16 ± 1	16 ± 2	18 ± 2	17 ± 1	18 ± 1	17 ± 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).



Fig. 5. Inhibition growth of AGP and AGP-M(II).

more biocidal in nature as compared to the ligand on some of the microorganisms as summarized in Table 5 and shown in Fig. 5. AGP-Cu(II) show high activity against E. coli, S. aureus, B. Subtilis, C. albicans and C. neoformans (22, 20, 20, 18 and 19 mm) respectively, while for *M. canis* AGP-Zn(II) shows high antifungal activity (18 mm).

AGP-Co(II) and AGP-Zn(II) polychelates display promising antibacterial activity (20, 18, 18 mm) and (16, 16, 18 mm) against E. coli, S. aureus, B. Subtilis while promising antifungal activity was also shown by AGP-Zn(II) 17 mm for C. albicans, AGP-Cu(II) 16 mm for M. canis, AGP-Co(II) 18 mm for C. neoformans. Lowest antibacterial activity was shown by AGP-Ni(II) (14, 13 mm) for E. coli, B. Subtilis and AGP-Mn(II) 14 mm against S. aureus, and lowest antifungal activity was shown by AGP-Ni(II) (12, 15 mm) for *M. canis*, C. neoformans and 14 mm for AGP-Co(II) against M. canis.

Results reveal that antimicrobial activity of these metal-chelated polymers is due to the presence of nitrogen and oxygen donor groups. Enhanced biological activity can be rationalized to the structures possessing additional C=N bond and chelation. It has been suggested that the compound with N and O donor system inhibit enzyme production because enzymes that require a free hydroxyl group for their activity appear to be especially susceptible to deactivation by the ions of the complexes [34].

Polarity of the metal ion is reduced by chelation, mainly because of partial sharing of its positive charge with the donor groups [35] and π electron delocalization within whole chelate ring thus formed during coordination. This chelation process thus increases lipophilic nature of metal atom [36], which in turn favors its permeation through the lipid layer of membrane.

Conclusions

Polymeric ligand (AGP) and its metal polychelates with M(II) acetates were synthesized in good yield. The identities of complexes were established by microanalytical, magnetic, spectroscopic and thermal analysis. All polymeric compounds were soluble in DMF and DMSO but insoluble in common organic solvents. Because of their insoluble nature, the synthesized metal polychelates can be used as solvent resistant coating materials. It was observed that the attachment of metal ions in the polymeric backbone enhanced thermal and anti-microbial activities. AGP-Cu(II) showed best antibacterial as well as antifungal activity whereas better inhibitory effects were observed in case of AGP-Co(II) and AGP-Zn(II) for antibacterial and antifungal activity respectively. Functional moieties such as azomethine group exhibit potential biological activities that may be responsible for the enhanced hydrophobic and lipophilic character of the molecule to cross-link the cell membrane of the microorganism and increase the biocidal activity of the polychelate. Being biologically active and thermally stable these polymers can be used for biomedical

applications requiring thermal sterilization due to stable nature at high temperatures.

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