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Coordination polymers of glutaraldehyde with glycine metal complexes: synthesis, spectral characterization, and their biological evaluation

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Glycine metal complexes were prepared by the reaction of glycine with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) in 1 : 2 molar ratio. Thereafter their condensation polymerization was done with glutaraldehyde to obtain polymer metal complexes. All the synthesized polymer metal complexes were characterized by elemental analysis, FT-IR, ¹H-NMR, and UV-Vis spectrometry, magnetic susceptibility, and thermogravimetric studies. The analytical data of all the polymers agreed with 1 : 1 molar ratio of metal complex to glutaraldehyde and magnetic moment data suggest that PGG–Mn(II), PGG–Co(II), PGG–Ni(II), and PGG–Cu(II) have an octahedral geometry around the metal atom, whereas the tetrahedral geometry was proposed for PGG–Zn(II) polymer. The PGG–Mn(II) and PGG–Cu(II) showed octahedral geometry. Thermal behavior of the polymer metal complexes was obtained at a heating rate of 10°C min⁻¹ under nitrogen atmosphere from 0°C to 800°C. The antimicrobial activities of synthesized polymers were investigated against *Streptococcus aureus*, *Escherichia coli*, *Bacillus sphaericus*, *Salmonella* sp. (Bacteria), *Fusarium oryzae*, *Candida albicans*, and *Aspergillus niger* (Yeast).

Keywords: Glycine metal complexes; Coordination polymers; Glutaraldehyde; Thermal properties; Antimicrobial activity

1. Introduction

Coordination polymers have potential applications as solid state materials as semi-conductors [1], heat resistant materials for aerospace [2], environmental protection [3], recovery of trace metal ions [4], and hydrolysis of cation exchange resins [5]. Incorporation of metals into the backbone of organic groups yields new coordination polymers whose properties are quite different from those of organic polymers. The polymer metal complexes also have catalytic activities differing from ordinary metal complexes. The complexation behavior of polymer supported ligand is different from the corresponding low molecular weight analog as a result of the polymeric support. Recently, we synthesized antimicrobial coordination polymers by complexation of polymeric ligand with metal ions and by the polymerization of monomeric metal

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complexes [6–8]. Thus, complexation parameters of polymeric materials are governed by the nature of the polymeric backbone and extent of functional groups of polymers.

Coordination polymers with nitrogen and oxygen containing ligands, such as amino acids, have been characterized earlier [9–11] and employed for applications such as those involving biodegradability, chelating agents for metal ions, and functional materials with desirable chemical and physical properties. Polymer-supported metal complexes are catalysts, models for various metalloenzymes, or biomedical controlled release agents [12, 13]. Polymers having antimicrobial properties are suitable in a variety of applications such as films used as food packaging materials, sanitary applications [14, 15], and many others.

As part of our research program to synthesize coordination polymers formed by condensation of glycine metal complexes with glutaraldehyde, this article deals with new metal polychelates. The spectral, magnetic and thermal properties and geometry around the central metal are also discussed. In addition, all metal polychelates were screened for their antimicrobial activities against selected microorganisms like *Streptococcus aureus*, *Escherichia coli*, *Bacillus sphaericus*, and *Salmonella* sp. (Bacteria) and also *Fusarium oryzae*, *Candida albicans*, and *Aspergillus niger* (Yeast).

2. Experimental

2.1. Materials

Glycine received from Loba Chemie of analytical reagent (AR) grade was used as received; glacial acetic acid and glutaraldehyde (25%) were supplied by Merck chemical company and used as received. Manganese(II) acetate tetrahydrate $[\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$, copper(II) acetate monohydrate $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}]$, nickel(II) acetate tetrahydrate $[\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$, cobalt(II) acetate tetrahydrate $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$, and zinc(II) acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ (Qualigens) were used without purification. *Streptococcus aureus*, *E. coli*, *B. sphaericus*, *Salmonella* sp., *F. oryzae*, *C. albicans*, and *A. niger* were collected by the culture collection center, Microbiology Laboratory, Department of Microbiology, Aligarh Muslim University (AMU), Aligarh.

2.2. Analytical procedure

The elemental analyses of polymers were carried out on Elemental analyzer system VarioEL CHNS (IIT Rookee). Metal content was determined by complexometric titration against EDTA after decomposing with a mixture of perchloric acid, sulfuric acid and concentrated nitric acid (HNO_3) [1 : 1.5 : 2.5]. FT-IR spectra were recorded from 4000 to 500 cm^{-1} on a Perkin Elmer infrared spectrophotometer model 621 using KBr pellets. UV-Vis spectra were recorded on a Perkin Elmer Lambda EZ-201 spectrophotometer using dimethyl sulfoxide (DMSO) as solvent and magnetic susceptibility measurements of these compounds were carried out on a Gouy balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a JEOL-GSX 300-MHz FX-1000 FT-NMR spectrometer in DMSO with tetramethylsilane (TMS) as an internal standard. Studies on thermal behaviors of the polymers were carried out on a TGA analyzer Perkin Elmer (Pyris Diamond) in nitrogen at a heating

rate of $10^{\circ}\text{C min}^{-1}$ (IIT Rookee). The solubilities of the polymers were tested in various solvents at room temperature. Antimicrobial tests of synthesized polychelates were carried out at the Department of Microbiology, AMU, Aligarh.

3. Synthesis

3.1. Synthesis of metal complexes

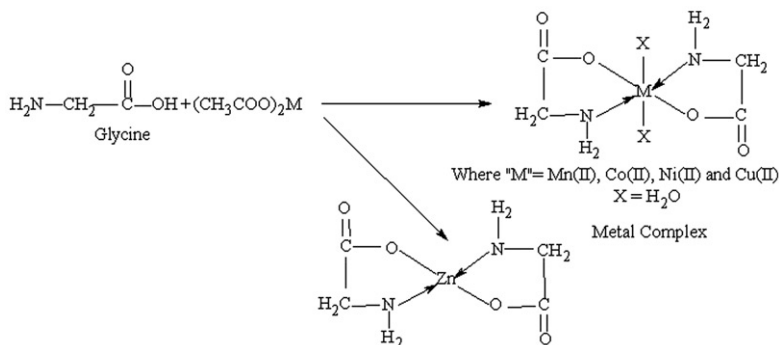
Metal complexes were prepared by the reaction of glycine with metal acetates using ethanol as solvent. Synthetic routes are given in scheme 1.

3.1.1. Synthesis of glycine metal complexes [(Gl)₂-M(II)]. Cobalt(II) [(Gl)₂-Co(II)] was synthesized by the reaction of cobalt(II) acetate tetrahydrate and glycine by analogous procedure of other metals. Pink precipitate was collected in 70% yield. Anal. [C₄H₈O₄N₂-Co(II)·2H₂O], Calcd: C, 19.76; H, 4.97; N, 11.52; and Co, 24.24. Found: C, 19.70; H, 5.01; N, 11.49; and Co, 24.23. FT-IR (KBr pellets) ν_{max} cm⁻¹ 3429–3438, 3200–3266, 2850–2940, 1588, 1408, 1500, 530, and 415. The same method was applied to carry out the reaction between glycine and other metal salts to obtain the metal complexes.

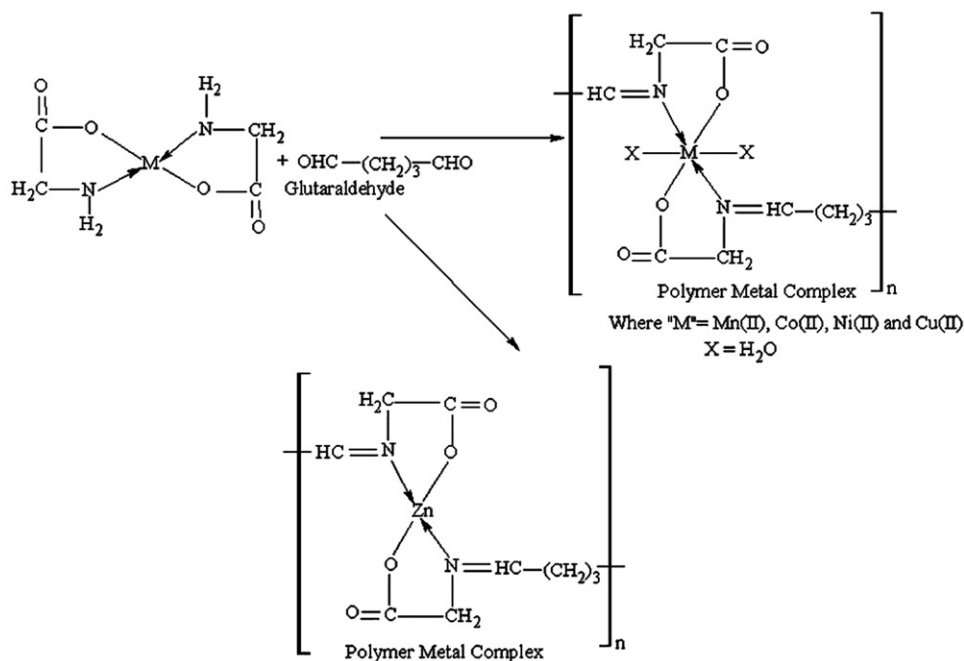
3.2. Synthesis of polymer metal complexes

The synthesis of polymer metal complexes is given in scheme 2.

3.2.1. [PGG-Mn(II)]. A solution of Mn(II) glycine complex (2.39 g, 0.01 mol, dissolved in 25 mL water) was placed in a round-bottom flask equipped with a thermometer. First, a few drops of glacial acetic acid and then 3.78 mL (0.01 mol) glutaraldehyde were added to this solution and stirred on a magnetic stirrer at 60°C for 4 h. Then, this reaction mixture was taken in a beaker and heated until it became adhesive and viscous. Reddish brown precipitate was obtained from this solution with excess methanol. The final



Scheme 1. Synthetic route to metal complex.



Scheme 2. Synthetic route to polymer metal complex.

product was separated by filtration and washed successively with acetone and dried in a vacuum desiccator for 12 h, yield 65%.

3.2.2. [PGG–Ni(II)]. Nickel(II) complex of glycine (2.42 g, 0.01 mol) was dissolved in 30 mL water in a round-bottom flask placed over a magnetic stirrer and equipped with condenser and thermometer. Glutaraldehyde (3.78 mL, 0.1 mol) was added to the above solution of complex with glacial acetic acid. This mixture was refluxed with continuous stirring for 3 h at 50°C and poured into a beaker and heated to reduce the solution until it becomes viscous and sticky. Metal complex was precipitated from solution using ethanol, filtered, washed with acetone, and then dried in a vacuum desiccator using fused calcium chloride, yield 67%.

3.2.3. [PGG–Zn(II)]. Zinc(II) glycine complex (2.13 g, 0.01 mol) was dissolved in 20 mL distilled water and glutaraldehyde (3.78 mL, 0.01 mol) in the presence of five drops of glacial acetic acid was added in a reaction flask equipped with a condenser, magnetic stirrer, and thermometer. Resulting mixture was refluxed with constant stirring at 50°C for 4 h. The mixture was poured into a beaker to evaporate. After concentration, methanol was added to this solution to precipitate the desired product. Precipitate was collected by filtration, washed several times, and then dried, yield 65%.

3.2.4. [PGG–Co(II)]. Metal complex of cobalt(II) was prepared according to the above method from cobalt(II) glycine complex and glutaraldehyde, yield 63%.

3.2.5. [PGG–Cu(II)]. Copper(II) complex of glycine was treated with glutaraldehyde to obtain its metal complex in 69% yield.

3.3. Biological activity

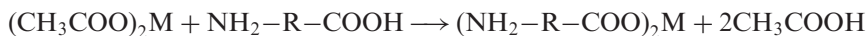
3.3.1. Anti-bacterial assessment. The complexes were screened *in vitro* for antibacterial activity against four bacterial strains (*S. aureus*, *E. coli*, *B. sphaericus*, and *Salmonella* sp.) using the agar well diffusion method. Also, 2- to 8-hour-old bacterial inoculums containing approximately 10^4 – 10^6 colony-forming units (CFU) per mL were used in these assays. Wells were dug in the media with a sterile metallic borer with centers at least 24 mm apart. The recommended concentration (100 μ L) of the test sample (1 mg in DMSO) was introduced into the respective wells. Other wells had DMSO and reference antibacterial drug, *imipinium*, which served as negative and positive controls, respectively. The plates were incubated immediately at 37°C for 20 h. Activity was determined by measuring the diameter of zones showing complete inhibition (mm) and compared with the standard drug *imipinium*. In order to clarify any role of DMSO, separate studies were carried out with the solutions of DMSO alone and they showed no activity against any bacterial strains.

3.3.2. Antifungal activity. Antifungal activities were studied against *F. oryzae*, *C. albicans*, and *A. niger*. Sabouraud dextrose agar was seeded with 10^5 CFU mL⁻¹ fungal spore suspensions and transferred to Petri plates. Discs soaked in 20 mL (10 μ g mL⁻¹ in DMSO) of all compounds were placed at different positions on the agar surface. The plates were incubated at 32°C for 7 days. The results were recorded as zones of inhibition in mm and compared with *miconazole*.

4. Results and discussion

4.1. Chemistry, composition, and characterization of the polymer metal complexes

Metal complexes of glycine were prepared by the reaction of metal(II) acetates in 2 : 1 molar ratio. The mechanism of the formation of complexes could be represented as



These amino acid complexes undergo polymerization with glutaraldehyde in the presence of glacial acetic acid in 1 : 1 molar ratio.

Elemental analysis of the synthesized polymer metal complexes shows agreement with theoretical values (table 1). The proposed structures of these polymers were established with the help of FT-IR and NMR methods and microanalytical data and they agreed with the 1 : 1 molar ratio of [(Gl)₂–M] to glutaraldehyde. The polymeric complexes were soluble in water and DMSO and insoluble in common organic solvents such as acetone, chloroform, tetrahydrofuran, toluene, benzene, etc. The suggested structure of polymer metal complexes is shown in scheme 2. Thermogravimetric analyses establish their thermal stabilities and ascertain the presence of water of crystallization.

Table 1. Elemental analysis of the metal polychelates.^a

Compound abbreviation	Empirical formula	Elemental analysis, calculated (observed)				Molar conductance ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)
		Carbon	Hydrogen	Nitrogen	Metal	
[PGG-Mn(II)] _n	[C ₉ H ₁₂ O ₄ N ₂ -Mn(II)·2H ₂ O]	35.7(35.15)	5.33(5.35)	9.27(9.25)	18.18(18.13)	28.3
[PGG-Co(II)] _n	[C ₉ H ₁₂ O ₄ N ₂ -Co(II)·2H ₂ O]	35.0(35.09)	5.23(5.20)	9.09(8.07)	19.12(19.19)	29.7
[PGG-Ni(II)] _n	[C ₉ H ₁₂ O ₄ N ₂ -Ni(II)·2H ₂ O]	35.21(35.27)	5.25(5.21)	9.12(9.18)	19.12(19.11)	29.5
[PGG-Cu(II)] _n	[C ₉ H ₁₂ O ₄ N ₂ -Cu(II)·2H ₂ O]	34.67(34.86)	5.17(5.11)	8.98(8.93)	20.38(20.41)	31.2
[PGG-Zn(II)] _n	[C ₉ H ₁₂ O ₄ N ₂ -Zn(II)]	38.97(38.83)	4.35(4.33)	10.09(10.00)	23.55(23.58)	30.8

n, Number of repeating units of polymeric chain.

^aMetal to ligand stoichiometry.

Table 2. The FT-IR spectral bands and their assignments.

Compounds	$\nu(\text{NH}_2)$	$\delta(\text{NH}_2)$	(HOH) (ρ and ω)	$\nu(\text{COO})$ (asym, sym)	$-\text{CH}_2$ (asym, sym)	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
PGG-Mn(II)	–	–	850(s)	1550, 1308	2940, 2850(m)	1608(s)	525(s)	420(s)
PGG-Co(II)	–	–	855(s)	1545, 1310	2940, 2850(m)	1610(s)	530(m)	415(s)
PGG-Ni(II)	–	–	860(s)	1543, 1314	2940, 2850(m)	1605(s)	530(s)	420(s)
PGG-Cu(II)	–	–	855(s)	1552, 1306	2940, 2850(m)	1604(s)	535(s)	420(m)
PGG-Zn(II)	–	–	–	1547, 1316	2940, 2850(m)	1612(s)	530(m)	415(s)

s, strong; m, medium; sym, symmetric; asym, asymmetric; ρ , rocking; ω , wagging.

5. Characterization

5.1. FT-IR spectra

FT-IR spectra of polymer metal complexes were recorded and the assigned absorption bands are consistent with the suggested structure. The frequencies of some significant bands of the synthesized polymer metal complexes are reported in table 2. All the polymer metal complexes exhibit a broad band at 3400–3000 cm^{-1} , supporting the presence of coordinated water [16, 17]. In addition, the rocking and wagging modes of water are observed at 850–860 cm^{-1} [18–20]. The amino acid was bidentate, bound to metal through carboxylic OH and amino NH_2 . Bands at 1586–1594 and 1408–1412 cm^{-1} , due to $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ of amino acids, appear in the complexes at 1543–1552 and 1306–1316 cm^{-1} , respectively. The shift suggests involvement of carboxylic groups of amino acids in complex formation [21]. After polymerization, IR spectra of the polymer metal complexes show no bands at 3200–3266 cm^{-1} for $\nu(\text{NH}_2)$ group and the stretching frequency of azomethine nitrogen in PGG-M(II) is at 1604–1612 cm^{-1} [22]. In the polymer metal complexes, bands at 1170–1181 cm^{-1} are assigned to $\nu(\text{C}-\text{N})$. Bands at 2940 and 2850 cm^{-1} are assigned to the asymmetric and symmetric frequencies of CH_2 [23]. Sharp bands at 525–535 cm^{-1} for all the metal complexes are due to $\nu(\text{M}-\text{N})$ [24], supporting involvement of nitrogen in coordination. Medium intensity $\nu(\text{M}-\text{O})$ bands in PGG-M(II) [25] have been observed at 415–420 cm^{-1} , confirming metal to oxygen coordination.

5.2. $^1\text{H-NMR}$ spectra

The $^1\text{H-NMR}$ spectra of PGG-Zn(II) in DMSO- d_6 and the spectral data with the possible assignment are depicted in the “Supplementary material”. $^1\text{H-NMR}$ data of PGG-Zn(II) show a signal at 4.69 ppm due to proton of α carbon near $-\text{COO}$ [26]. The resonances at 8.10 ppm was attributed to the azomethine proton ($-\text{HC}=\text{N}-$) [27]. Peaks at 1.75 and 1.65 ppm are assigned to other methylene protons.

5.3. $^{13}\text{C-NMR}$ spectra

Chemical shifts of carbons are based on the assigned labels of carbon represented in the “Supplementary material”. In $^{13}\text{C-NMR}$ spectra of PGG-Zn(II), peaks at 155.33 ppm are assigned to $-\text{HC}=\text{N}-$ carbons and peaks of $>\text{C}=\text{O}$ carbon are at 167.51 ppm [28].

Signal at 44.30 ppm was due to methylene carbons of $-\text{CH}_2-\text{N}$ and at 181.87 ppm due to $-\text{COO}$ [29]. The resonance signal at 38.63 ppm is assigned to other methylene carbons.

5.4. Magnetic moments and electronic spectra

The interpretation of structure and geometry of polymer metal complexes was confirmed by electronic spectra of polymer metal complexes. The electronic spectral band maxima with their tentative assignments and magnetic moment data are presented in table 3. The Mn(II) having a d^5 configuration generally forms high-spin complexes because of the additional stability of the half-filled d shell, magnetic moment value 5.64 B.M. is in the expected range of octahedral geometry [30]. The observed maxima of PGG–Mn(II) are at 16,910, 18,125, and 20,450 cm^{-1} , assigned to ${}^4\text{T}_{1g}(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$, ${}^4\text{T}_{2g}(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$, and ${}^4\text{A}_{1g}(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$, respectively. The magnetic moment of PGG–Co(II) in this case is 4.70 B.M., consistent with high-spin octahedral geometry [31]. The higher μ_{eff} of the Co(II) complex is attributed to the orbital contribution. The electronic spectrum of Co(II) complex shows three absorption bands similar to what have been observed for high-spin octahedral geometry. Lower energy absorptions at 9150 and 18,090 cm^{-1} have been assigned to ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$, respectively, and the band at 19,050 cm^{-1} to ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$. The absorption spectra of PGG–Ni(II) exhibit three bands at 10,200, 14,120, and 24,900 cm^{-1} attributed to ${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$, ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$, and ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\text{F})$, respectively, consistent with their octahedral configuration. The magnetic moment values 2.96 B.M. indicate two unpaired electrons for Ni(II) ions, confirming an octahedral geometry [32]. Magnetic moment of PGG–Cu(II) is 1.89 B.M., consistent with octahedral geometry [33]. Electronic spectra of PGG–Cu(II) complexes show broad bands at 15,365 cm^{-1} assigned to ${}^2\text{B}_{2g} \leftarrow {}^2\text{B}_{1g}$. Charge transfer bands for both cases were observed at 28,570 cm^{-1} . Because of the d^{10} system, Zn(II) is diamagnetic.

5.5. Thermogravimetric analysis

To evaluate thermal stability of the polymer metal complexes, thermogravimetric analysis has been employed (table 4). The TGA curves were obtained at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen in the temperature range of $0\text{--}800^\circ\text{C}$. The thermal results provide information regarding the number and nature of water present and also to propose intermediates and final products formed during decomposition. After the loss of lattice/coordinated water, the polymer metal complexes gradually degrade. For two-step degradation, the first step is faster than the second step, perhaps due to the non-coordinated part of the complex decomposes first, while the coordinated part decomposes later [34]. This step, in most cases, corresponds to the formation of stable metal oxide. Mostly higher oxides are formed. The TGA curves are shown in the "Supplementary material".

The presence of water can be seen in the TGA trace curves of PGG–Mn(II), PGG–Co(II), and PGG–Cu(II) showing the wt% loss in $50\text{--}150^\circ\text{C}$ and $50\text{--}200^\circ\text{C}$ range, respectively, corresponding to the loss of water of crystallization ($50\text{--}150^\circ\text{C}$) and coordinated water ($50\text{--}200^\circ\text{C}$) [35, 36]. PGG–Zn(II) does not show the presence of water. PGG–Mn(II), PGG–Co(II), and PGG–Cu(II) show wt% loss of 11.24–15.50%

Table 3. Magnetic susceptibility and electronic spectral parameters of metal polychelates.

Abbreviation	Magnetic moment ^a	Electronic spectral data	Electronic transition (cm ⁻¹)	Geometry	B	β	β (%)	Extinction coefficient (dm ³ mol ⁻¹ cm ⁻¹)	Color
PGG-Mn(II)	5.64	20,450	$4A_{1g}(G) \leftarrow 6A_{1g}(F)$	Octahedral	704	0.73	0.27	12	Pinkish brown
		18,125	$4T_{2g}(G) \leftarrow 6A_{1g}(F)$					11	
PGG-Co(II)	4.70	16,910	$4T_{1g}(G) \leftarrow 6A_{1g}(F)$	Octahedral	653	0.67	0.33	15	Dark pinkish brown
		19,050	$4T_{1g}(P) \leftarrow 4T_{1g}(F)$					11	
		18,090	$4A_{2g}(F) \leftarrow 4T_{1g}(F)$					12	
		9,150	$4T_{2g}(F) \leftarrow 4T_{1g}(F)$					14	
PGG-Ni(II)	2.96	24,900	$3T_{1g}(P) \leftarrow 3A_{2g}(F)$	Octahedral	784	0.72	0.28	11	Bluish brown
		14,120	$3T_{1g}(F) \leftarrow 3A_{2g}(F)$					11	
PGG-Cu(II)	1.89	10,200	$3T_{2g}(F) \leftarrow 3A_{2g}(F)$	Octahedral	-	-	-	13	Bluish brown
		28,570	Charge-transfer					13	
		15,365	$2B_{2g} \leftarrow 2B_{1g}$					14	

^aBohr magneton.

Table 4. Thermal behaviors of metal polychelate.

Materials	Percentage of weight loss at temperature (°C)							
	100	200	300	400	500	600	700	800
PGG–Mn(II)	4.48	12.63	24.77	45.28	62.28	65.06	67.39	70.5
PGG–Co(II)	4.11	12.22	24.1	31.07	51.31	62.13	69.46	74.31
PGG–Ni(II)	0.11	11.24	17.24	28.91	35.13	40.09	46.99	59.95
PGG–Cu(II)	5.80	15.50	26.28	35.45	37.81	39.97	42.6	45.48
PGG–Zn(II)	1.98	4.33	30.02	48.36	60.11	74.79	75.63	78.29

up to 200°C. At 400°C, a rapid decomposition of polymer metal complexes was observed because of degradation and volatilization of low molecular weight units of polymer metal complexes. PGG–Cu(II) shows wt% loss of 45.48% at 800°C, showing greater thermal stability compared to other polymer metal complexes. TG analysis data reveal that all the polymer metal complexes exhibit better heat-resistant features because of coordination with metal.

6. Antimicrobial effect

Polymer metal complexes were assayed *in vitro* for their ability to inhibit growth of *S. aureus*, *E. coli*, *B. sphaericus*, and *Salmonella* sp. The fungal strains of *F. oryzae*, *C. albicans*, and *A. niger* were also screened. The susceptibilities of certain strains of bacteria and fungi to the polymerized amino acid complexes were evaluated by the size of the bacteriostatic diameter. Each test microorganism was screened three times to obtain the most accurate results.

The results with error limits are given in table 5, which show that all polymer metal complexes exhibited inhibitory activity against bacterial and fungal strains. PGG–Mn(II) inhibits the growth of the fungi *C. albicans*, *F. oryzae*, and *A. niger* as well as bacteria *E. coli* and *B. sphaericus*, but it was inactive against *S. aureus*, and *Salmonella* sp. PGG–Co(II) exhibits higher activity against *Salmonella* sp., but it was inactive against *B. sphaericus*. PGG–Ni(II) shows higher activity against *A. niger*, minimum against *E. coli* and was inactive against *Salmonella* sp. PGG–Cu(II) exhibits high activity against *F. oryzae* and *A. niger*, whereas PGG–Zn(II) is highly active against *B. sphaericus* and *F. oryzae*. Marked enhancement in biocidal action on coordination with the metal ions against one or more testing bacterial strains is observed. This enhancement in activity is rationalized on the basis of the structures of metal complexes possessing an additional azomethine (C=N) linkage, important in elucidating the mechanism of transamination and resamination reactions in biological systems [37, 38]. The antimicrobial activities of the compounds also increase after metal chelation. Complexes having antimicrobial activity may act either by killing the microbe or by inhibiting multiplication of the microbe by blocking their active sites [39]. Other factors, namely stability constant, molar conductivity, solubility, and magnetic moment, are also responsible for increasing the antimicrobial activity of the complexes. The results are relevant to previously studied complex/polymer, which also show that copper complexes are more biocidal in nature than other transition metal complexes while the non-metal

Table 5. Antimicrobial activity.

Abbreviation	Zone of inhibition ^a (mm) 50 µg per disc						
	<i>S. aureus</i>	<i>E. coli</i>	<i>B. sphaericus</i>	<i>Salmonella</i> sp.	<i>F. oryzae</i>	<i>C. albicans</i>	<i>A. niger</i>
PGG	5 ± 1	6 ± 1	3 ± 1	5 ± 2	6 ± 1	4 ± 1	4 ± 2
PGG–Mn(II)	–	10 ± 2	12 ± 1	–	12 ± 1	11 ± 3	15 ± 1
PGG–Co(II)	8 ± 2	10 ± 1	–	13 ± 1	8 ± 2	10 ± 2	9 ± 1
PGG–Ni(II)	12 ± 2	8 ± 1	11 ± 1	–	9 ± 1	11 ± 1	16 ± 2
PGG–Cu(II)	13 ± 1	11 ± 1	15 ± 1	14 ± 1	16 ± 1	13 ± 1	17 ± 1
PGG–Zn(II)	11 ± 1	–	14 ± 1	10 ± 2	13 ± 3	8 ± 1	12 ± 2
<i>Miconazole</i> ^a	–	–	–	–	20 ± 1	15 ± 3	17 ± 2
<i>Imipinium</i> ^a	15 ± 1	19 ± 1	16 ± 2	15 ± 2	–	–	–
<i>DMSO</i> ^b	–	–	–	–	–	–	–
Mn(CH ₃ COO) ₂	15 ± 1	18 ± 1	15 ± 2	17 ± 1	22 ± 1	25 ± 1	24 ± 1
Co(CH ₃ COO) ₂	20 ± 2	22 ± 3	21 ± 1	21 ± 2	25 ± 2	24 ± 1	24 ± 1
Ni(CH ₃ COO) ₂	22 ± 1	22 ± 1	21 ± 1	20 ± 2	24 ± 2	21 ± 1	22 ± 1
Cu(CH ₃ COO) ₂	26 ± 1	28 ± 1	27 ± 1	26 ± 3	28 ± 1	27 ± 1	28 ± 1
Zn(CH ₃ COO) ₂	17 ± 2	18 ± 2	15 ± 1	15 ± 1	17 ± 1	16 ± 1	14 ± 2

^aStandard drug (positive control).

^bSolvent (negative control) antimicrobial activity.

PGG, non-metal containing polymer.

containing polymers were not active or very mildly active against any bacteria or fungi [40].

7. Conclusions

In this study metal polychelates have been synthesized by the reaction of glycine metal complexes with glutaraldehyde in 1:1 molar ratio and characterized on the basis of analytical, magnetic, spectral, and thermal data. Thermal analyses reveal that PGG–Cu(II) is more thermally stable than the other metal polychelates. The geometries of PGG–Mn(II), PGG–Co(II), PGG–Ni(II), and PGG–Cu(II) are octahedral, whereas PGG–Zn(II) exhibited tetrahedral geometry. Polychelate of Cu(II) showed more effective antibacterial and antifungal activities than metal polychelates due to the higher stability constant of Cu(II) ion.

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