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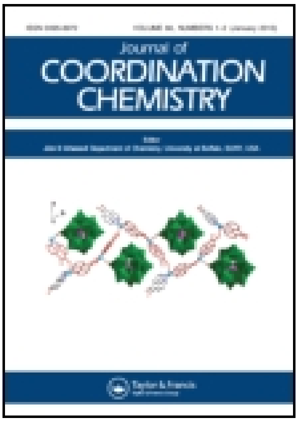

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis and characterization of metal-incorporated aniline formaldehyde resin modified by amino acid for antimicrobial applications

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Published online: 22 Nov 2011.

To cite this article: Nahid Nishat , Raza Rasool , Shamim Ahmad Khan & Shadma Parveen (2011) Synthesis and characterization of metal-incorporated aniline formaldehyde resin modified by amino acid for antimicrobial applications, Journal of Coordination Chemistry, 64:23, 4054-4065, DOI: 10.1080/00958972.2011.636426

To link to this article: http://dx.doi.org/10.1080/00958972.2011.636426

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Journal of Coordination Chemistry
Vol. 64, No. 23, 10 December 2011, 4054–4065

Synthesis and characterization of metal-incorporated aniline formaldehyde resin modified by amino acid for antimicrobial applications

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(*Received 14 July 2011; in final form 19 October 2011*)

Advances in metal incorporated resins are now an active field of research. To develop resin having better antimicrobial and thermal activity, a series of metal-chelated resins have been synthesized by the condensation of (4-aminobenzene-1,3-diyl)dimethanol with 2,6-diaminohexanoic acid in alkaline medium and then this polymeric ligand further reacts with transition metal ions forming various coordination polymers. (4-Aminobenzene-1,3-diyl)dimethanol was initially prepared by the reaction of aniline and formaldehyde in 1 : 2 molar ratio in alkaline medium. The analytical data reveal that the polymer metal complexes of Mn(II), Co(II), and Ni(II) are coordinated with two water molecules, which are further supported by FTIR spectra and TGA data. Comparative analyses of the polymer metal complexes in thermal curves show better thermal stability than the polymeric ligand. Since these resins are relatively stable at high temperatures, they can be used for medical and biomaterial applications requiring thermal sterilization, solvent-resist coating materials because of their insoluble nature, and antifouling coating materials owing to antimicrobial activity in fields such as life-saving medical devices and the bottoms of ships.

Keywords: Amino acid; Coordination polymers; Thermogravimetric analysis; Antimicrobial activity

1. Introduction

Coordination compounds are of importance in industries and also have important functional values in nature [1, 2]. Polymeric biomaterials are polymeric materials which are used in medicine or biotechnology. Polymers in biomedical applications is one rapidly growing area in polymer science, where the traditional sciences are connected to modern engineering to solve human health problems. Metal complexes have been explored for their catalytic and biological activities [3] and polymer metal complexes are developed as interdisciplinary involving chemistry, electrochemistry, metallurgy, environmental protection, and material science [4, 5]. Potential applications of such

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2011.636426

polymers are as surface coatings on metals and glasses, adhesives, electrical insulators, semiconductors, and electrochromic materials [6–9].

Thus, characterization and study of properties of chelate polymers are of great importance. In general, chelate polymers are insoluble in common organic solvents [10] and as a result, their application is somewhat limited due to processing difficulties. Their insolubility is explained by the formation of coordination networks. Therefore, efforts have been made to develop structurally modified chelate polymers having increased thermal stability and solubility by retentaining their good properties [11].

Coordination compounds in which amino groups are provided by amino acids have received attention due to their possible uses. Coordination compounds derived from several closely related multidentate amino acid-containing reduced Schiff-base ligands have been discussed in terms of their mode of binding and coordination to supramolecular structures [12]. Amino acid-based coordination polymers exhibiting unique properties in catalysis and biological aspects have been reported recently [13].

Coordination polymers containing amino acids exhibiting luminescence, homochirality, and dynamic porous properties have been reported [14–16]. Metal ions have been used to synthesize new drugs [17]. In view of this, it was interesting to synthesize new polymer metal complexes derived from amino acids and to study their biological activity. A number of papers on thermally stable and biologically active coordination polymers have been published in our laboratory [18–20], and as a continuation of our ongoing research work we report herein the synthesis of a new thermally stable, antimicrobial resin, prepared by the condensation of aniline-formaldehyde with lysine. Coordination polymers were synthesized using transition metal ions and were characterized by elemental analysis, spectral studies (FT-IR, UV-Visible, ^{1}H-NMR), magnetic susceptibility measurements, and thermal techniques. The synthesized polymeric ligand as well as all the coordination polymers were also tested for antimicrobial activity against a few bacteria and fungi such as *Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis*, *Aspergillus flavus*, *Candida albicans*, and *Aspergillus niger* by using agar well diffusion method.

2. Experimental

2.1. *Materials and strains*

Aniline (Qualinges Fine Chemicals, Mumbai), lysine, sodium hydroxide pellets, manganese(II) acetate tetrahydrate [$Mn(CH_3COO)_2 \cdot 4H_2O$], cobalt(II) acetate tetrahydrate [$Co(CH_3COO)_2 \cdot 4H_2O$], nickel(II) acetate tetrahydrate [$Ni(CH_3COO)_2 \cdot 4H_2O$], copper(II) acetate monohydrate [$Cu(CH_3COO)_2 \cdot H_2O$], and zinc(II) acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] (Merck, Mumbai) were commercially available and used as received. Ethanol (Changshu Yangyuan Chemical, China), methanol, diethyl ether, dimethylsulfoxide (DMSO), dimethylformamide (DMF), and formaldehyde 37–41% (S.D. Fine Chem. Ltd, Mumbai) were purified by standard procedures prior to use. Agar was purchased from Difco Laboratories. Microbial strains used for activity tests included three bacteria – *E. coli*, *S. aureus*, and *B. subtilis* and three fungi *A. flavus*, *C. albicans*, and *A. niger* kept at −80°C in a freezer [Culture collection of Microbiology Laboratory, Department of Microbiology (A.M.U. Aligarh)].

2.2. *Synthesis*

2.2.1. Synthesis of polymeric ligand (AFL). Aniline (0.02 mol) was dissolved in DMF (10 mL) and heated until it was completely dissolved. Formaldehyde (37% aqueous solution) (1.5 mL, 0.02 mol) was added and the pH was adjusted to 9 with sodium hydroxide. The reaction mixture was stirred on a magnetic stirrer and heated at 60°C for 4 h. The resulting mixture obtained was colorless. Lysine (0.01 mol) dissolved in DMF (10 mL) was added dropwise to the reaction mixture and stirred at 70°C for 3 h. A colorless liquid was formed and was digested at 35°C for 6 h. The ligand precipitated as a colorless solid when poured into water. It was then filtered and washed several times with water followed by diethyl ether and dried in a vacuum desiccator. The polymeric ligand (AFL) was soluble in DMSO and DMF, and insoluble in water, ethanol, methanol, chloroform, carbon tetrachloride, and benzene. Yield was 65%.

2.2.2. Synthesis of polymer metal complexes of AFL. A series of polymer metal complexes [Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)] were prepared by using equimolar ratio (1 : 1) of polymeric ligand (AFL) and metal(II) acetates. A typical procedure for the preparation of polymer metal complex of manganese(II) was as follows: a solution of ligand (0.01 mol) in DMF (25 mL) and solution of manganese(II) acetate tetrahydrate (0.01 mol) in a minimum quantity of DMF (15 mL) were mixed and heated at 60°C with constant stirring. The resulting viscous dark brown-colored product was precipitated by pouring it into excess distilled water, and then filtered. Finally, the precipitated AFL–Mn(II) was washed several times with water and acetone and dried at room temperature. Yield was 69%.

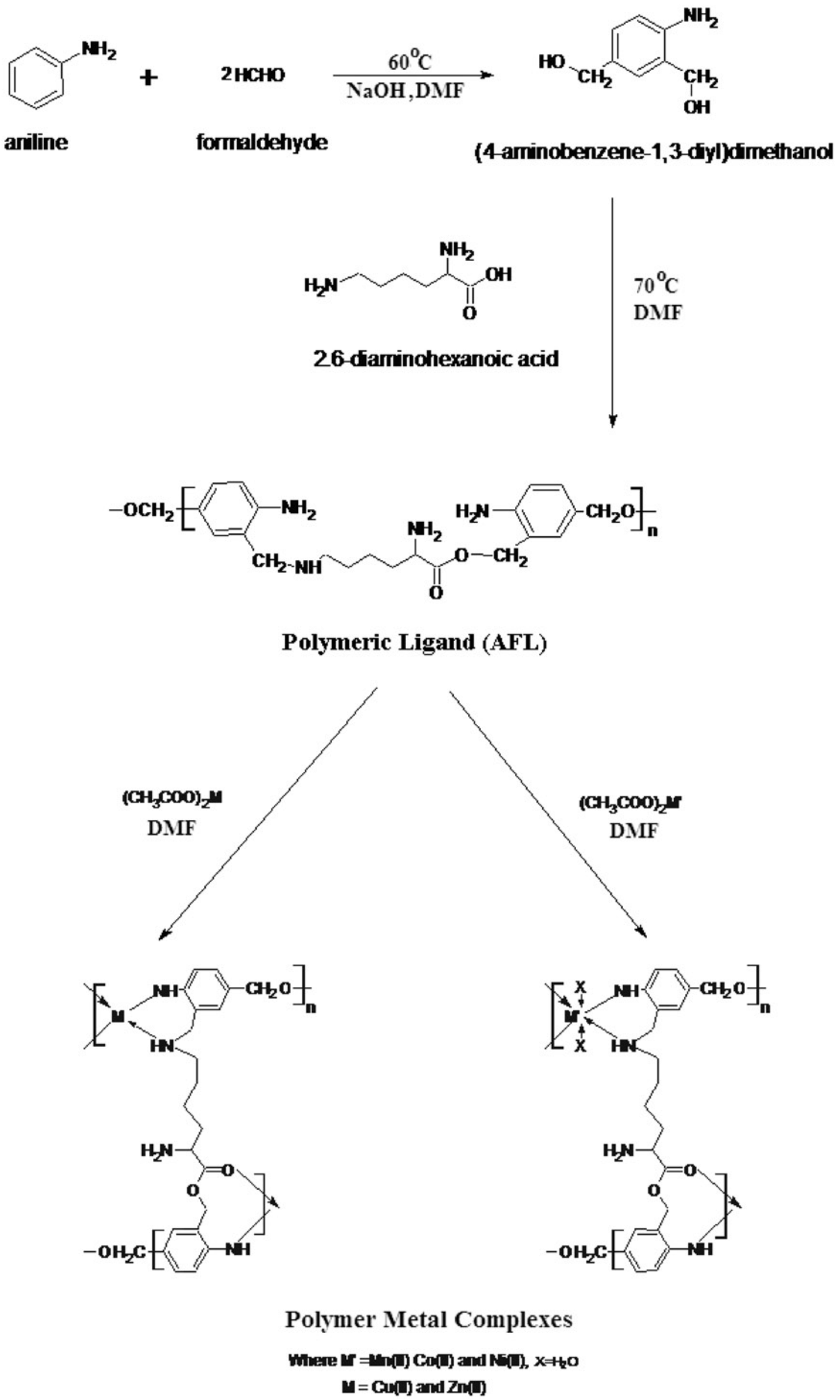
The above procedure was adopted for the synthesis of other polymer metal complexes (scheme 1) and the yields are given in table 1, ranging between 70% and 75%.

2.3. *Preparation of microbial culture*

All antimicrobial experiments were carried out at the Department of Microbiology, Aligarh Muslim University, Aligarh. The antimicrobial activities of the polymeric ligand and its polymer–metal complexes were tested against different microorganisms in DMF. The sample concentration was $50\,\mu g\,mL^{-1}$ for antibacterial and antifungal studies. Bacterial strains were nourished in a nutrient broth and yeasts in a malt-extract broth and incubated for 24 and 48 h, respectively. According to the agar-diffusion method, bacteria were incubated on Muller–Hinton agar and yeast on Sabouraud dextrose agar. The wells were dug in the 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 drug, namely kanamycin (antibacterial) and miconazole (antifungal), for negative control. The resulting zones of inhibition on the plates were measured in millimeters.

2.4. *Characterization*

Elemental analyses (C, H, and N) of the compounds were carried out using an elemental analyzer system GmbH Vario ELIII. The percentage of metals in the polymer metal



Scheme 1. Synthetic route for the preparation of AFL and its polymer metal complexes.

Table 1. Analytical and physical data of AFL and its polymer metal complexes.

Abbreviation	(Yield %)	Calcd (Found) (%) C	H	N	M
AFL	65	65.78 (65.47)	7.10 (7.23)	14.61 (14.42)	– –
AFL–Mn(II)	69	53.39 (52.98)	6.19 (5.95)	11.86 (11.80)	11.63 (11.45)
AFL–Co(II)	75	52.94 (53.14)	6.14 (6.20)	11.76 (11.88)	12.37 (12.55)
AFL–Ni(II)	73	52.97 (52.76)	6.14 (6.10)	11.77 (11.98)	12.33 (12.52)
AFL–Cu(II)	70	56.68 (56.27)	5.66 (5.71)	12.59 (12.48)	14.28 (14.43)
AFL–Zn(II)	72	56.44 (56.92)	5.64 (5.80)	12.54 (12.45)	14.64 (14.76)

complex was determined by complexometric titration with ethylenediaminetetraacetic acid (EDTA) after decomposition with fuming HNO_3. FT-IR spectra were recorded on a Perkin Elmer IR spectrophotometer (Model 621) using KBr discs from 4000 to 400 cm^{-1}. ^{1}H-NMR spectra were recorded on a JEOL-GSX 300 MHz FX 1000 FT NMR spectrometer. UV-Vis spectra were recorded on a Perkin Elmer Lambda (EZ-201) spectrophotometer in solution. Magnetic susceptibility of the powder samples were measured on a vibrating sample magnetometer (Model 155). The comparative thermal behaviors of polymeric ligand (AFL) and all polymer metal complexes were recorded with a TG analyzer (Perkin Elmer Pyris Diamond) at a heating rate of 20°C min^{-1} in nitrogen.

3. Results and discussion

3.1. *Composition and chemistry*

The structure of AFL is shown in scheme 1. AFL is a colorless solid, while the polymers were colored solids, soluble in DMSO and DMF but insoluble in common organic solvents. The molecular weight of the polymers could not be determined by GPC due to their insolubility. Analytical data of AFL with its polymer metal complexes are given in table 1, which are in good agreement with 1 : 1 metal to polymeric ligand molar ratio. The analytical data reveal that coordination polymers of Mn(II), Co(II), and Ni(II) were coordinated with two water molecules, corroborated by FT-IR and TGA analyses discussed in the following sections.

3.2. *FT-IR analysis*

FT-IR bands of AFL and polymer metal complexes are summarized in table 2. Presence of methylene was confirmed by the appearance of a strong band at 2950–2836 cm^{-1} that can be correlated to $\nu(CH_2)$ *asym* and *sym* stretching mode [21]. The band at 1447–1470 cm^{-1} for C–N stretch confirmed the reaction between aniline-formaldehyde and

Table 2. IR spectra of AFL and its polymer metal complexes.

	Assignments						
Compounds	ν(N–H)$_{asym.\ \&\ sym}$	ν(COO$^-$)$_{asym}$	ν(COO$^-$)$_{sym}$	ν(C–N)	ν(C–H)$_{asym.\ \&\ sym}$	ν(M–N)	ν(M–O)
AFL	3428–3250	1605	1417	1460	2950–2848	–	–
AFL–Mn(II)	3428–3250	1587	1400	1447	2950–2845	516	445
AFL–Co(II)	3428–3250	1568	1351	1441	2950–2840	527	430
AFL–Ni(II)	3428–3250	1590	1390	1465	2950–2850	538	425
AFL–Cu(II)	3428–3250	1547	1365	1470	2950–2845	550	445
AFL–Zn(II)	3428–3250	1585	1405	1454	2950–2836	545	436

amino acid. In the spectrum of AFL absorption bands at 3428–3250 cm^{-1} are assigned to *asymmetric* and *symmetric* ν(N–H) stretching [22], while in the spectra of polymers, ν(N–H) shifts to lower frequencies and ν(N–H) bending is observed at 1683–1650 cm^{-1} confirming chelation with metal ions and supporting formation of bond with metal.

Bands at 1605–1547 cm^{-1} were assigned to the asymmetric stretch of coordinated carboxylate. The symmetric stretch of coordinated carboxylate is at 1417–1351 cm^{-1}; $\Delta\nu(\mathrm{COO^-}) \sim 200\,\mathrm{cm^{-1}}$ indicates monodentate carboxylate [23]. Strong bands at 995–990 and 760–758 cm^{-1} in the complexes were assigned to rocking and wagging modes of coordinated water; the free ligand, Cu(II) and Zn(II) polymer metal complexes did not exhibit these bands. This confirms the presence of coordinated water in some complexes. New bands at 550–516 cm^{-1} can be attributed to ν(M–N) while bands at 445–425 cm^{-1} are correlated to ν(M–O) [24]. The FT-IR data confirm that nitrogen and carboxyl oxygen are involved in coordination with the metal ion in complexes.

3.3. *^{1}H-NMR spectra*

^{1}H-NMR spectra of AFL and its polymer complex with Zn(II) are shown in figures 1 and 2. The aromatic protons show multiple resonances between 7.9 and 6.2 ppm for AFL and its polymer metal complex [25], while methylene protons of lysine appear at 2.55 and 1.8 ppm and signal found at 1.4 ppm indicate the presence of –CH_2–CH_2– groups of lysine. The methylene groups of Ar–CH_2–N, Ar–CH_2–O, and Ar–NH_2 (primary amine group) show signals at 3.6, 3.9, and 4.6 ppm, respectively [26]. The spectrum of Zn(II) polymer shows a small peak at 4.8 ppm for Ar–NH (secondary amine group) with decreased intensity, confirming the formation of a M–N bond by the removal of one proton. Other peaks of the spectrum for the polymer metal complex do not show any shift compared with the spectrum of polymeric ligand.

3.4. *Electronic spectra and magnetic moment measurements*

The electronic spectra of polymer metal complexes were recorded in DMSO; electronic spectral bands and their magnetic properties are depicted in table 3. Obtained data were used to calculate the crystal field parameter (D_q), crystal field splitting energy ($10D_q$), Racah interelectronic repulsion parameter (B), nephelauxetic ratio (β), and covalency parameter (β°). The magnetic moment of the AFL–Mn(II) was 5.69 B.M. [27], which

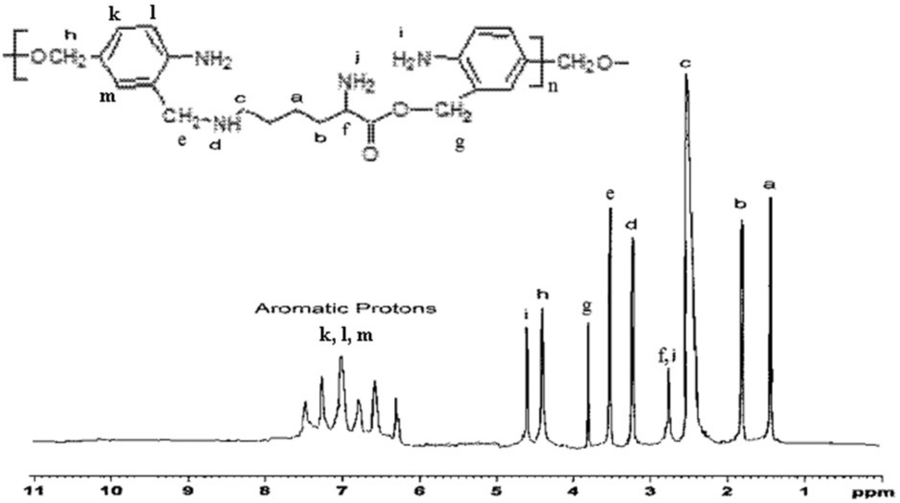


Figure 1. ^{1}H-NMR spectra of AFL.

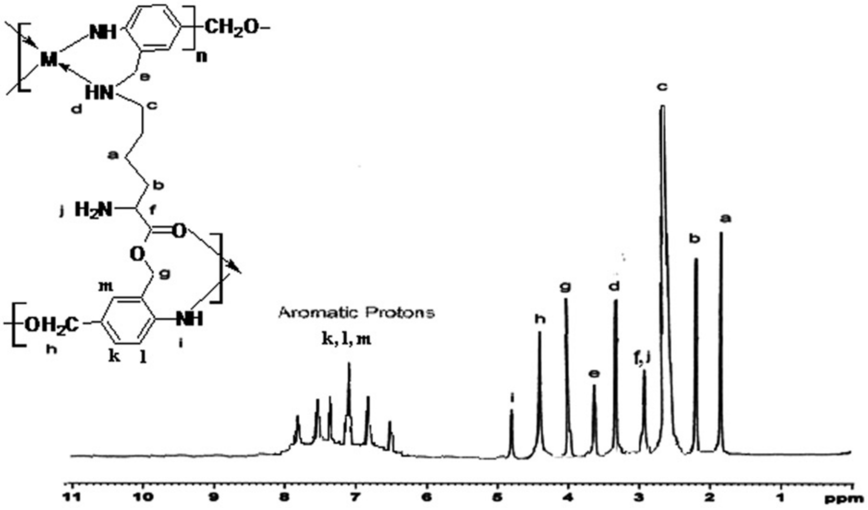


Figure 2. ^{1}H-NMR spectra of AFL–Zn(II).

suggested the presence of five unpaired electrons. The electronic spectrum of AFL–Mn(II) exhibited three bands at 18,600, 22,995, and 24,910 $\mathrm{cm^{-1}}$, which may reasonably correspond to $^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$, $^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$, and $^4A_{1g}(G) \leftarrow {}^6A_{1g}(F)$ transitions, respectively. The value of crystal field splitting energy ($10D_q$) of AFL–Mn(II) was 8550 $\mathrm{cm^{-1}}$ and the Racah parameter (B) was 776 $\mathrm{cm^{-1}}$. The nephelauxetic effect (β) value was reduced to about 80% of the free ion value for $\mathrm{Mn^{2+}}$ (960) and the covalency parameter (β°) value of 20% indicated the covalent nature of the compound. The AFL–Co(II) has a magnetic moment of 4.73 B.M. corresponding to four unpaired electrons

Table 3. Magnetic susceptibility and electronic spectra of AFL and its polymer metal complexes.

Compounds	Magnetic moment (B.M.)	Electronic transition (cm^{-1})	Assignments	$10D_q$ (cm^{-1})	B (cm^{-1})	β
AFL–Mn(II)	5.69	24,910	$^4A_{1g}(G) \leftarrow {}^6A_{1g}(F)$	8550	776	0.80
		22,995	$^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)$			
		18,600	$^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)$			
AFL–Co(II)	4.73	20,400	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	11000	785	0.81
		13,905	$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$			
		9820	$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$			
AFL–Ni(II)	2.95	24,048	$^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$	8620	867	0.81
		16,129	$^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$			
		13,869	$^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$			
AFL–Cu(II)	1.76	15,260	$^2A_{1g} \leftarrow {}^2B_{1g}(F)$	–	–	–
		24,450	Charge transfer			

and showed three bands at 9820, 13,905 and 20,400 cm^{-1} which were assigned to $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$, $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$, and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transitions, respectively, indicating octahedral environment around Co(II) [28, 29]. The values of different parameters for AFL–Co(II) were $10Dq = 11{,}000\,cm^{-1}$, $B = 785\,cm^{-1}$, $\beta = 0.81$ and $\beta^\circ = 19\%$. There was reduction in the Racah parameter (B) from the free ion values of 971 to 785 cm^{-1}. The nephelauxetic effect (β) value was reduced to about 81% of the free ion value and the covalency parameter (β°) value of 19% indicated the covalent nature of the compound. The octahedral AFL–Ni(II) was paramagnetic with two unpaired d-electrons, and the experimental magnetic moment was found to be 2.95 B.M. [30]. The electronic spectra showed three bands at 13,869, 16,129 and 24,048 cm^{-1}, assigned to $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$, and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ transitions, respectively. The values of different parameters for AFL–Ni(II) were $10D_q = 8620\,cm^{-1}$, $B = 867\,cm^{-1}$, $\beta = 0.81$, and β° value 19% which favors octahedral geometry for AFL–Ni(II) [31]. The reduction in the free ion value of 1080 to 867 cm^{-1} and the β value of 0.81 indicate the covalent nature of the compound.

The above discussion very strongly indicates an octahedral geometry around the central metal ion in all the above-discussed polymer metal complexes with two coordination sites by H_2O. Electronic spectra of AFL–Cu(II) exhibited two bands at 15,260 and 24,450 cm^{-1} due to $^2A_{1g} \leftarrow {}^2B_{1g}(F)$ and charge transfer, respectively, which indicate the square-planar geometry [32]. The magnetic moment value of AFL–Cu(II) was found to be 1.76 B.M. [33], in accord with square planar geometry.

3.5. *Thermogravimetric analysis*

TGA data of AFL and its polymer metal complexes were obtained at a heating rate of 20°C min^{-1} under N_2 from 20°C to 800. The TGA traces are shown in figure 3. Aliphatic chain present between two aromatic rings of polymeric unit decomposes rapidly followed by slow thermal degradation of aromatic rings. Slight decrease in weight loss (2–7%) depicted from the thermogram in the temperature range 60–130°C for the polymeric ligand (AFL) may be attributed to water.

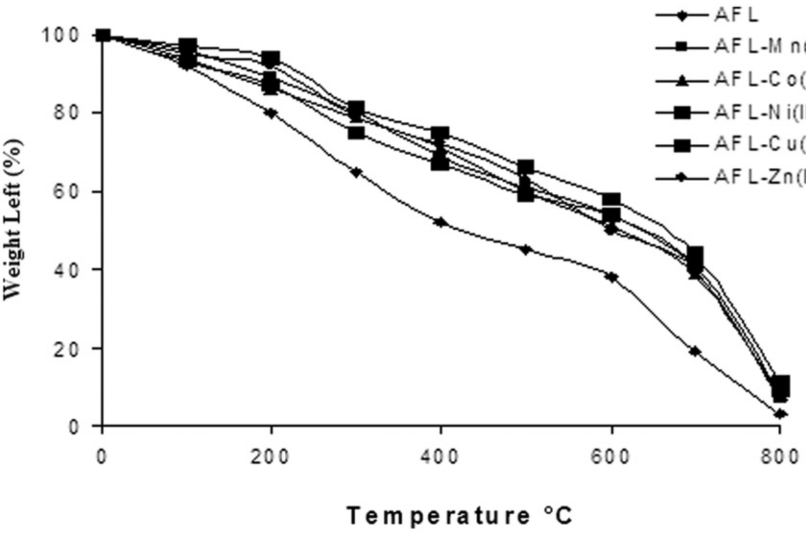


Figure 3. Thermograms of AFL and its polymer metal complexes.

The thermogravimetric curves confirmed the presence of water [34] in the polymer metal complexes of Mn(II), Co(II), and Ni(II) as the removal of water was completed at 180°C. IR studies also support the presence of water molecules in these polymers. For Cu(II) and Zn(II) polymers, weight loss corresponds to the loss of solvent or absorbed water molecules up to 130°C. The degradation of the polymer metal complexes is noticeable beyond 300°C and maximum at temperature between 400°C and 600°C. All these polymer metal complexes lost about 56–61% of weight when heated to 700°C.

Thermal results conclude that all the polymer metal complexes show higher thermal stability than the polymeric ligand (AFL) and do not decompose easily even at high temperature due to metal insertion into the polymeric chain as a result of chelation. The enhancement in thermal stability of the polymer metal complexes may be due to joining of two different polymeric chains. Polymer metal complex [AFL–Cu(II)] shows best heat-resistant characteristics among the polymeric compounds.

3.6. *Biological evaluation*

Biological activities of AFL and its polymer metal complexes were tested against three bacteria and three fungi (table 4 and figure 4). The highest zone of inhibition values, i.e., 23 and 21 mm, were measured for *E. coli* and *S. aureus*, respectively, for AFL–Cu(II) polymer. The AFL–Ni(II) polymer metal complex had the highest inhibition zone of 19 mm against *B. subtilis* while AFL–Mn(II) showed the lowest antibacterial activity compared to the other coordination polymers. The intermediate inhibition zone values were shown by AFL–Zn(II) and AFL–Co(II) complexes. The results reveal better antibacterial activity of polymer metal complexes than parent ligand.

Inhibition effect of the polymer metal complexes was found to be comparable to the standard drug (kanamycin). The antifungal activities of the polymers were tested

Table 4. Antimicrobial activity of AFL and its polymer metal complexes.

	Zone of inhibition (mm) 50 μg mL^{-1}					
Abbreviation	*E. coli*	*S. aureus*	*B. subtilis*	*A. flavus*	*C. albicans*	*A. niger*
AFL	11 ± 1	10 ± 2	11 ± 1	12 ± 1	9 ± 2	8 ± 1
AFL–Mn(II)	14 ± 2	13 ± 1	15 ± 1	13 ± 1	10 ± 1	12 ± 2
AFL–Co(II)	21 ± 1	17 ± 1	19 ± 1	13 ± 2	14 ± 1	12 ± 2
AFL–Ni(II)	16 ± 2	18 ± 1	19 ± 1	18 ± 1	15 ± 2	16 ± 1
AFL–Cu(II)	23 ± 1	21 ± 1	18 ± 2	19 ± 1	21 ± 1	18 ± 1
AFL–Zn(II)	17 ± 2	19 ± 1	17 ± 1	18 ± 1	20 ± 1	16 ± 3
Kanamycin[a]	20 ± 1	20 ± 1	18 ± 2	–	–	–
Miconazole[b]	–	–	–	23 ± 1	25 ± 2	25 ± 1

[a] Standard drug (positive control) antibacterial activity.
[b] Standard drug (negative control) antifungal activity.

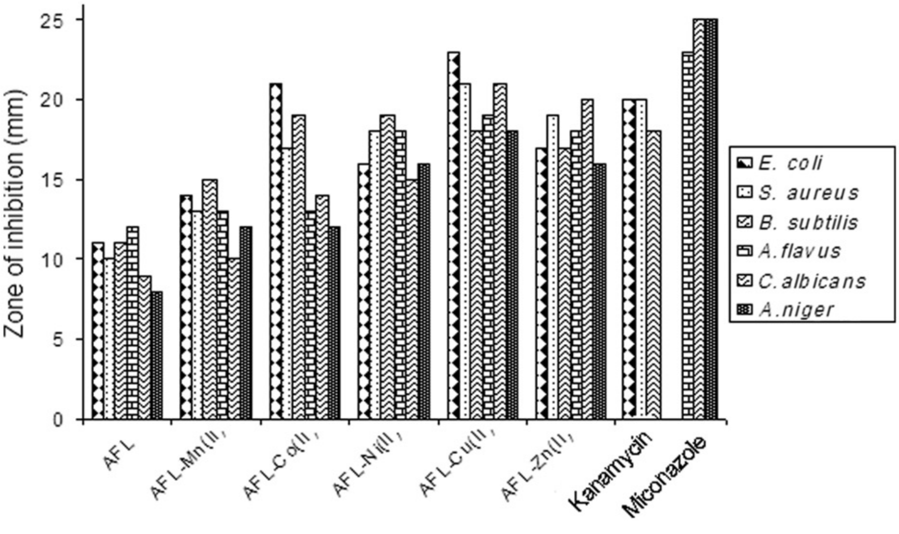


Figure 4. Antimicrobial activity of AFL and its polymer metal complexes.

against three fungi – *A. flavus*, *C. albicans*, and *A. niger* by the agar well diffusion method. The highest inhibition zones, i.e., 19, 21 and 18 mm, were measured for AFL–Cu(II) polymer metal complex against *A. flavus*, *C. albicans*, and *A. niger*, respectively. When AFL was screened against *A. flavus*, *C. albicans*, and *A. niger*, the zones of inhibition were found to be 12, 9, and 8 mm, respectively. The polymers of Mn(II) and Co(II) showed 13 mm inhibition zone against *A. flavus*, while Zn(II) and Ni(II) revealed similar inhibition effects of 16 mm against *A. niger*.

The results of these investigations indicated that the synthesized polymers showed good antimicrobial activity. The polymer metal complexes show moderate to high biocidal action compared to the ligand against most of the strains. These polymers show better antibacterial activity compared to polymers reported by Hasnain *et al.* [18] and Nishat *et al.* [19, 20], while the antifungal activities were better in latter cases.

Polymers containing amino acid cause membrane linkage, perhaps by interfering with the phosphate on phospholipids of the membranes [35]. Antimicrobial activity of the ligand increased after chelation because chelation reduces the polarity of the central metal by partial sharing of its positive charge with the donor groups [36]. Other factors, namely molar conductivity, solubility and magnetic moment, and stability constant, are also important for increasing antimicrobial activity of the complexes [37].

4. Conclusions

Newly synthesized polymer metal complexes were prepared in good yield and characterized by analytical, magnetic, spectral, and thermal data. The geometries of AFL–Mn(II), AFL–Co(II), and AFL–Ni(II) were octahedral while AFL–Cu(II) is square-planar and AFL–Zn(II) tetrahedral. Attachment of metal ions in the polymeric backbone enhances thermal stability and antimicrobial activity. All the polymeric compounds were soluble in DMF and DMSO, but insoluble in common organic solvents. The synthesized polymer metal complexes can be used as solvent-resistant coating materials and for biomedical applications requiring thermal sterilization due to stable nature at high temperatures. AFL–Cu(II) exhibit greater antimicrobial activity than other metal-coordinated polymers. Due to its effective antimicrobial activity, it can be used as antifungal and antifouling coating materials for various projects such as medical instruments and the bottoms of ships.

Acknowledgments

R. Rasool is thankful to UGC-CSIR (New Delhi, India) for financial assistance. The authors express their sincere thanks to "The Third World Academy of Sciences, Italy" for UV-Visible spectrophotometer EZ-201 (Perkin Elmer) through research grant scheme No. 00-047 RG/CHE/AS.

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