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Design and development of several polymeric metal–organic frameworks, spectral characterization, and their antimicrobial activity

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ABSTRACT

Coordination polymers were obtained by the reaction of metal acetates, $M(\text{CH}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$ {where $M = \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ } with AFP ligand (AFP = 5,5'-(piperazine-1,4-diylbis(methylene))bis(2-aminobenzoic acid)). The AFP ligand was prepared by the one-pot, two-step reaction of formaldehyde, 2-aminobenzoic acid, and piperazine. Structural and spectroscopic properties have been studied by elemental, spectral (FT-IR, ^1H NMR, ^{13}C NMR, and UV–vis), and thermogravimetric analysis. UV–vis spectra and magnetic moment values indicate that $\text{Mn}(\text{II}), \text{Co}(\text{II}),$ and $\text{Ni}(\text{II})$ polymer–metal complexes are octahedral, while $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ polymer–metal complexes are distorted octahedral and tetrahedral, respectively. The analytical data confirmed that the coordination polymers of $\text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}),$ and $\text{Cu}(\text{II})$ are coordinated with two water molecules, which are further supported by infrared spectra and thermogravimetric analysis data. The prepared polymer–metal complexes showed good antibacterial activities against all tested microorganisms; however, the AFP ligand was also found to be effective, but relatively less than their polymer–metal complexes. Along with antibacterial activity, all the polymer–metal complexes exhibit significant antifungal activity against most of the tested fungal strains. The results of antimicrobial activity reveals that the AFP– $\text{Cu}(\text{II})$ showed the highest antibacterial and antifungal activity than other polymer–metal complexes.

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1. Introduction

The synthesis and characterization of metal complexes with bioactive organic ligands to produce novel potential chemotherapeutic agents is an area of intense chemical research. Of particular note is the pressing need for new antibacterials to replace those losing their effectiveness because of the development of microorganisms' resistance [1]. Thus, the discovery of new antimicrobial agents or

increasing the effectiveness of previously known drugs is important [2a–c]. Several polymers with notable antibacterial activity have been synthesized by immobilization of low-molecular-weight antibacterial agents onto the polymers [3]. The controlled aggregation of small coordination complex–based building blocks to form large macromolecules is of great interest in both metal ligand and polyoxometalate chemistry [4]. Particularly, the ability to use both ligand design and adjustment of reaction conditions to understand and control the aggregation processes is crucial. The combination of these approaches yield the best chance of synthesizing sophisticated, potentially

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functional, and biologically active complexes and clusters [5a–d].

In recent years, profound research efforts on the synthesis and characterization of metal-organic coordination polymers has led to significant advances in their electronic, optical, magnetic, and physicochemical properties [6–8]. This includes the search for potential applications of these new materials [9]. There are reports that the transition metal complexes in polymer matrices show interesting chemical and catalytic reactivity toward various small gas molecules. This reactivity has been shown to take place under relatively mild conditions that are different from those of the corresponding free transition metal complexes or those in inorganic oxide-supported systems [10–12]. The characterization of transition metal ion-containing polymers has been the subject of numerous investigations. It has been demonstrated that the thermo-physical properties of ligands can be modified by coordination to transition metal ions [13–15]. In the present study, a novel AFP ligand whose 3-D molecular structure is given in Fig. 1 is reported. The structure is drawn using ChemBioDraw Ultra 13. The article describes the synthesis and characterization of the AFP ligand and its polymer–metal complexes containing Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) metal ions. Moreover, the AFP ligand and their polymer–metal complexes were also screened toward two kinds of organisms i.e. fungus and bacterium for their antimicrobial evaluation [16].

2. Experiment

2.1. Materials and strains

Piperazine (S D Fine-Chem Ltd.), 2-aminobenzoic acid, formaldehyde (37% aqueous solution), sodium hydroxide (Merck), and $M(\text{CH}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$, where $M = \text{Mn(II)}$, Co(II) , Ni(II) , Cu(II) , and Zn(II) and $x = 1, 2, 4$ (Qualigens fine chemicals) were used without further purification. Solvents such as acetone, methanol, diethyl ether, dimethyl formamide (DMF), dimethylsulfoxide (DMSO) (S D Fine-Chem Ltd.), and ethanol (Jiangsu Hauxi International) were purified by standard procedures before use. All the microorganisms were provided by the Culture Collection Center of

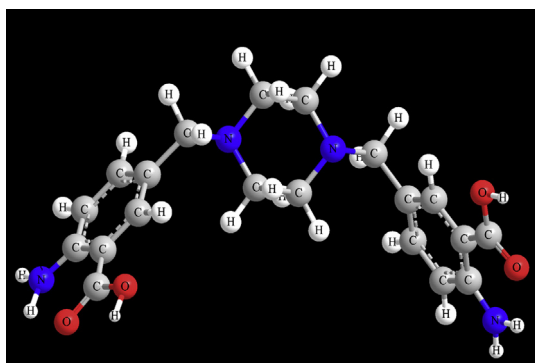


Fig. 1. Energy minimized cylindrical bonded 3-D molecular structure of the AFP ligand.

Microbiology laboratory, Department of Microbiology (AMU, Aligarh).

2.2. Synthesis of AFP ligand

2-aminobenzoic acid (0.01 mol) and formaldehyde (0.01 mol) in 1:1 M ratio were transferred to a 250 ml three-necked round bottom flask equipped with thermometer, condenser, and magnetic stirrer containing DMF (~50 mL) as a solvent, and the pH was adjusted in alkaline range with 40% aqueous NaOH. The reaction mixture was stirred magnetically at temperature up to 80°C for 3 h. A piperazine solution (0.01 mol) in 25 mL DMF was added to this system and stirred again for about 1 h up to 90–115°C. The progress of reaction was monitored by thin layer chromatography (TLC). The reaction mixture was cooled and precipitated using a 50/50 (v/v) water/acetone mixture. The obtained solid which is light brown in color (AFP–ligand) was filtered, and re-precipitated from DMF and ethanol. It was then filtered and washed repeatedly with distilled water and acetone and dried in a vacuum oven to remove the solvent (DMF and ethanol), yield 82% (2.05 gm).

2.3. Synthesis of polymer–metal complexes of AFP

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 AFP ligand and metal acetates. A typical synthesis of polymer AFP–Mn(II) is as follows.

The AFP ligand (3.84 gm, 0.01 mol) was dissolved in DMF (20 mL). Mn(II) acetate tetrahydrate (2.45 gm, 0.01 mol) was also dissolved in a minimum quantity of hot DMF (25 mL). Both the solutions were mixed and heated at reflux at 75°C with constant stirring. The resulting viscous dark brown colored product was precipitated by pouring it into excess of distilled water. The AFP–Mn(II) complex gets precipitated, and it was filtered and washed several times with water and acetone and dried at room temperature, yield 76%. Similar procedures were adopted for the synthesis of other polymer–metal complexes.

2.4. Measurements

The elemental analysis of carbon, hydrogen, and nitrogen were carried out on a Perkin–Elmer model-2400 elemental analyzer. The metals were determined by complexometric titration against EDTA after decomposing with concentrated nitric acid. The solubility of ligand and their polymer–metal complexes were investigated in different solvents at room temperature. The IR spectra were recorded on a PerkinElmer infrared spectrometer model 621 using KBr pellets. ^1H NMR spectra were recorded on a JEOL-FX-100 FT-NMR instrument in dimethylsulfoxide (DMSO- d_6) solution with tetramethylsilane as an internal standard. The thermal stability of ligand and their polymer–metal complexes were evaluated with a TA analyzer 2000 at a heating rate of 20°C/min under nitrogen. The electronic spectra of the polymer–metal complexes were recorded on a PerkinElmer Lambda-201, and magnetic susceptibility measurements were carried out with vibrating sample magnetometer. The antimicrobial activity of the ligand and

their polymer–metal complexes was tested against different bacterial and fungal strains.

3. Results and discussion

3.1. Composition and chemistry

The AFP ligand is composed of 2-aminobenzoic acid, formaldehyde, and piperazine. The preparation of the AFP ligand was carried out in two steps. In the first step, 2-aminobenzoic acid reacts with formaldehyde in (1:1) molar ratio and forms 2-amino-5-(hydroxymethyl)benzoic acid. In the second step, 2-amino-5-(hydroxymethyl)benzoic acid and piperazine undergo condensation reaction and forms the AFP ligand (Scheme 1). The polymer–metal complexes were obtained by the reaction of the AFP ligand with metal acetate in DMF in (1:1) molar ratio (Scheme 2). The AFP ligand and their polymer–metal complexes were soluble in DMF and DMSO and insoluble in most of the common organic solvents such as benzene, methanol, ethanol, and water.

All the polymer–metal complexes were colored and obtained in good yield. Various observations such as the nature of the AFP ligand, high thermal stability, metal to ligand ratio (1:1), and insolubility of the polymer–metal complexes in common organic solvents suggest their polymeric nature [17]. Elemental analysis, physical properties, and IR data provide good evidence that the compounds are polymeric [18]. The insolubility of the polymer–metal complexes in common organic solvents does not permit the determination of their molecular weight. The elemental analysis [Table 1] showed that AFP ligand to metal ratio in all the polymer–metal complexes was 1:1, in good agreement with the calculated values. The structures of AFP ligand and its polymer–metal complexes were also confirmed by IR, ^1H NMR, ^{13}C NMR, UV–visible, and magnetic susceptibility measurements. The magnetic moments were measured by placing the sample inside the uniform magnetic field at 25°C and 1 atm pressure. The vibrating sample magnetometer measures the magnetization of a small sample of magnetic material placed in an external magnetizing field by converting the dipole field of the sample into an AC electrical

signal which in turn is equated into magnetic moment values.

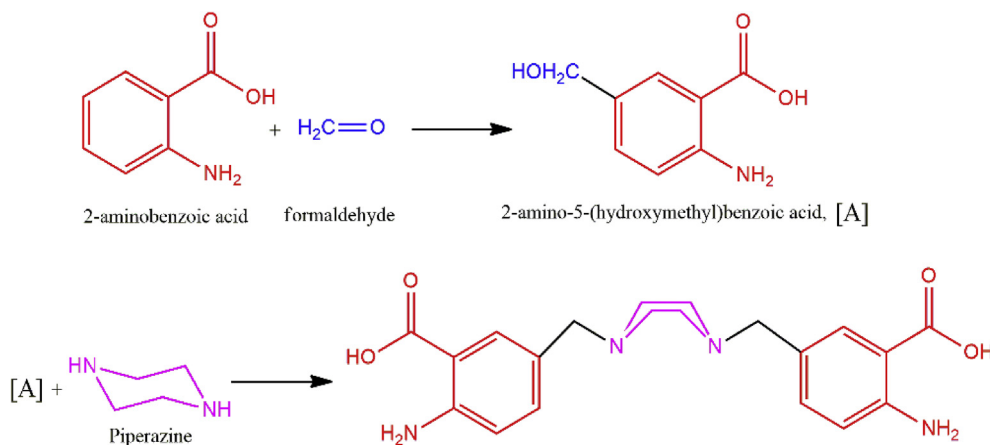
3.2. FT-IR spectra

The infrared spectra of the AFP ligand and their polymer–metal complexes are presented in Table 2. They resemble each other in their general shape, but the comparison of the IR spectrum of the ligand and their coordination polymers have revealed certain characteristics differences.

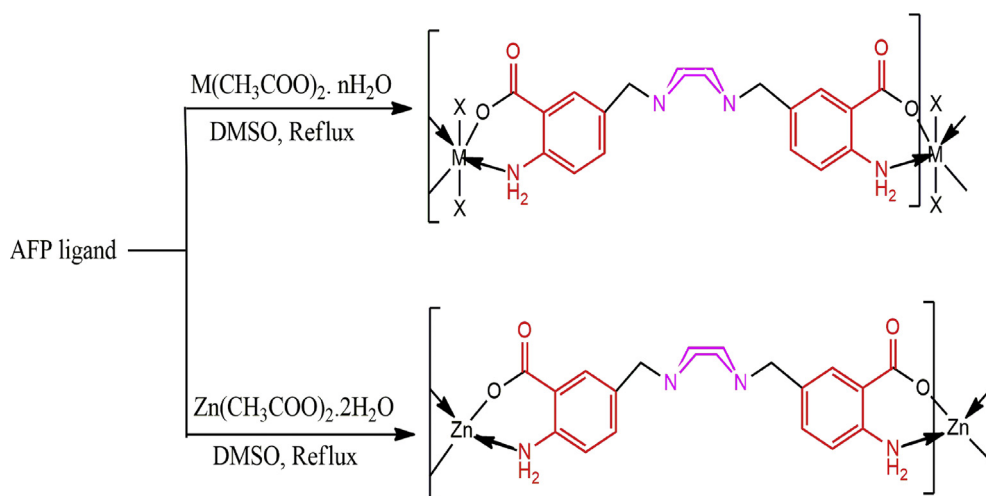
One of the significant differences in the IR spectrum of the AFP ligand and their coordination polymers is the presence of more broadened bands in the range of 3430–3452 cm^{-1} in the latter due to the formation of coordination bond between the O–H group of the ligand and the metal ions [19–21]. This is explained by the observation that water molecules might have strongly absorbed on to the polymer sample during their formation. In the spectrum of the AFP ligand, an absorption band appearing at 3360 cm^{-1} , which is assigned to the $\nu(\text{N–H})$ stretching, [22] is shifted toward higher frequency in the spectra of the coordination polymers, due to the formation of metal–nitrogen bonds. Another noticeable difference is the appearance of band due to the C=O stretching vibration at 1640 cm^{-1} of the AFP ligand which is shifted to lower frequency. The band at 1280 cm^{-1} of the AFP ligand assigned to in-plane OH deformation [23] is shifted toward lower frequency in the spectra of the coordination polymers due to the formation of metal–oxygen bond [24,25]. Bands appearing at 526–540 cm^{-1} and 480–498 cm^{-1} are attributed to M–O and M–N vibrations and support the involvement of nitrogen and oxygen atoms in complexation with metal ions [26] in polymer–metal complexes. Thus, all these characteristics features of the IR studies suggest the proposed structure of the coordination polymer as shown in Schemes 1 and 2.

3.3. ^1H NMR spectra

The ^1H NMR spectra of AFP ligand and their polymer complex of Zn(II) are shown in Figs. 2 and 3, respectively. The aromatic protons show multiple resonance signals



Scheme 1. Synthetic route of the AFP ligand.



M = Mn(II), Co(II), Ni(II) or Cu(II)
 X = H₂O, n = 1 for Cu(II) and 4 for rest

Scheme 2. Synthetic route of the polymer–metal complexes of the AFP ligand. DMSO, dimethylsulfoxide.

Table 1

Analytical data of AFP ligand and its polymeric metal complexes.

Compounds	Empirical formula	Formula weight of repeating units	Yield (%)	Calculated (found) (%)			
				C	H	N	M
AFP	C ₂₀ H ₂₄ N ₄ O ₄	384.43	82	62.49 (62.56)	6.29 (6.25)	14.57 (14.66)	–
[Mn(II)–AFP(H ₂ O) ₂] _n	[MnC ₂₀ H ₂₆ N ₄ O ₆] _n	473.38	76	50.74 (50.71)	5.54 (5.62)	11.84 (11.89)	11.61 (11.66)
[Co(II)–AFP(H ₂ O) ₂] _n	[CoC ₂₀ H ₂₆ N ₄ O ₆] _n	477.37	79	50.32 (50.34)	5.49 (5.45)	11.74 (11.83)	12.35 (12.34)
[Ni(II)–AFP(H ₂ O) ₂] _n	[NiC ₂₀ H ₂₆ N ₄ O ₆] _n	477.13	72	50.34 (50.38)	5.49 (5.55)	11.74 (11.80)	12.30 (12.28)
[Cu(II)–AFP(H ₂ O) ₂] _n	[CuC ₂₀ H ₂₆ N ₄ O ₆] _n	481.99	82	49.84 (49.82)	5.44 (5.38)	11.62 (11.67)	13.18 (13.23)
[Zn(II)–AFP] _n	[ZnC ₂₀ H ₂₂ N ₄ O ₄] _n	447.82	79	53.64 (53.70)	4.95 (5.01)	12.51 (12.55)	14.29 (14.26)

Table 2

IR spectral bands of AFP ligand and their polymer–metal complexes.

Compounds	Assignments							
	ν(–OH)/H ₂ O	CH (asym–sym)	ν(C=O)	ν(C=C)	ν(COO [–])	ν(C–N)	ν(M–O)	ν(M–N)
AFP	3452s	2900–2855	1640s	1462m	1280s	1392s
AFP–Mn(II)	3442b	2900–2855	1625s	1452m	1260s	1377w	540m	498m
AFP–Co(II)	3435b	2900–2855	1630s	1447m	1261s	1375w	538m	495m
AFP–Ni(II)	3430b	2900–2855	1620s	1440m	1267s	1379w	526m	490m
AFP–Cu(II)	3432b	2900–2855	1625s	1445m	1265s	1379w	527m	485m
AFP–Zn(II)	3440b	2900–2855	1635s	1455m	1268s	1380w	535m	480m

between 6.30–6.65 and 6.40–7.73 ppm for AFP ligand and AFP–Zn(II), respectively [27]. The singlet corresponding to one proton at 11.00 ppm is assigned to the –COOH group, and a resonance signal appeared at 5.5 ppm is due to the proton of the N–H group [28], whereas the resonance signal found at 2.4 ppm indicate the presence of the –CH₂–CH₂– groups of the piperazine moiety, and a resonance signal appearing at 3.35 is due to proton of the benzylic methylene group. The signals for the protons of the –COOH group are absent in the spectrum of AFP–Zn(II), suggesting the participation of the –COOH group to the metal center in the formation of COO–M. Similarly,

the protons of the N–H group were shifted toward down field at 5.4 ppm due to the coordination of nitrogen with metal ion. This significant shifting in all the peaks was observed, which confirms the formation of polymer–metal complexes. The peak of aromatic protons became broad due to the intermolecular interaction toward the metal ion and variation in the π-electron density around the protons.

3.4. ¹³C NMR spectra

The ¹³C NMR spectrum of AFP ligand is depicted in Fig. 4. Four prominent peaks are observed in the

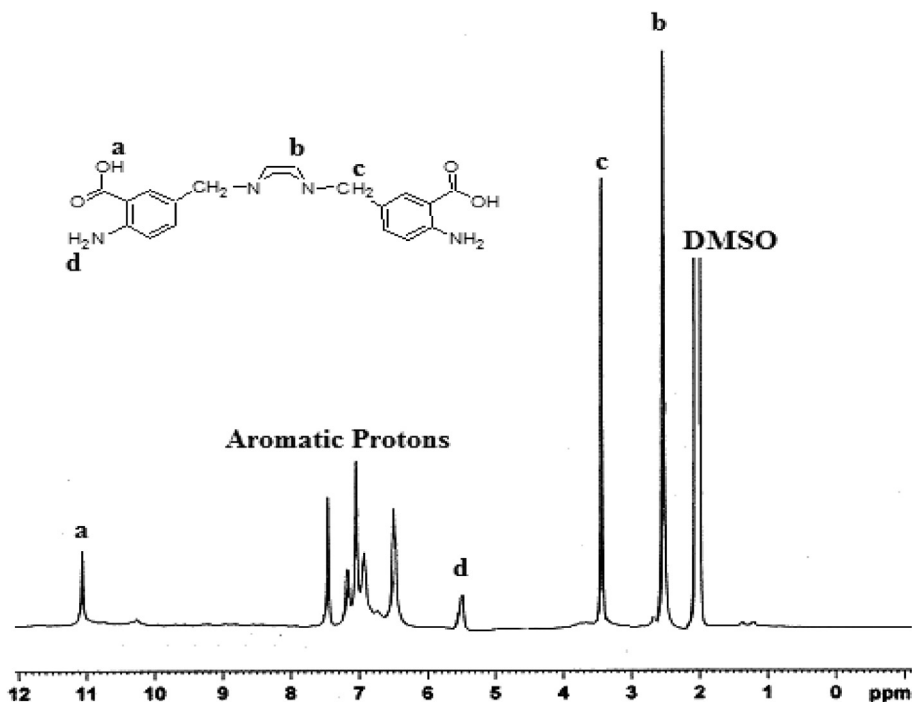


Fig. 2. ^1H NMR spectra of the AFP ligand in d^6 DMSO. DMSO, dimethylsulfoxide.

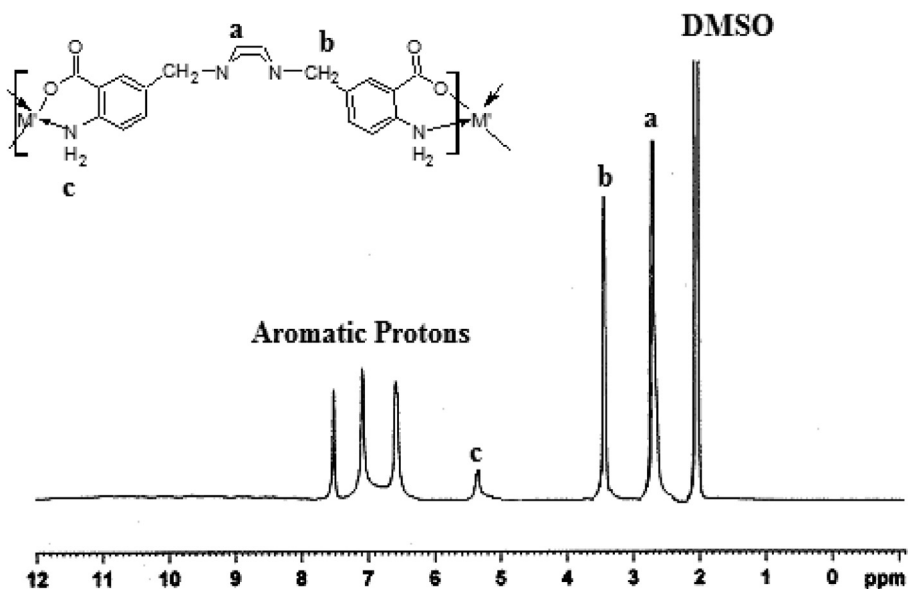


Fig. 3. ^1H NMR spectra of the AFP-Zn(II) in d^6 DMSO. DMSO, dimethylsulfoxide.

spectrum. The multiplets observed in the range of 112–140 ppm may be ascribed to the benzylic carbons while the piperazinic carbons were found to resonate in between 44 and 46 ppm. The carboxylic carbons of 2-aminobnzoic acid moiety were observed as a single sharp peak at 160 ppm while the formaldehydic carbons were observed as singlet at 62 ppm corroborating the proposed structure of the AFP ligand.

3.5. Electronic spectra and magnetic moments

Magnetic moments (μ_{eff}) of the polymer–metal complexes are given in Table 3. The data reveal that all the coordination polymers other than that of Zn(II) are paramagnetic while that of Zn(II) is diamagnetic.

The electronic spectrum of AFP–Mn(II) shows three bands at $14,222\text{ cm}^{-1}$, $19,431\text{ cm}^{-1}$, and $25,022\text{ cm}^{-1}$ which

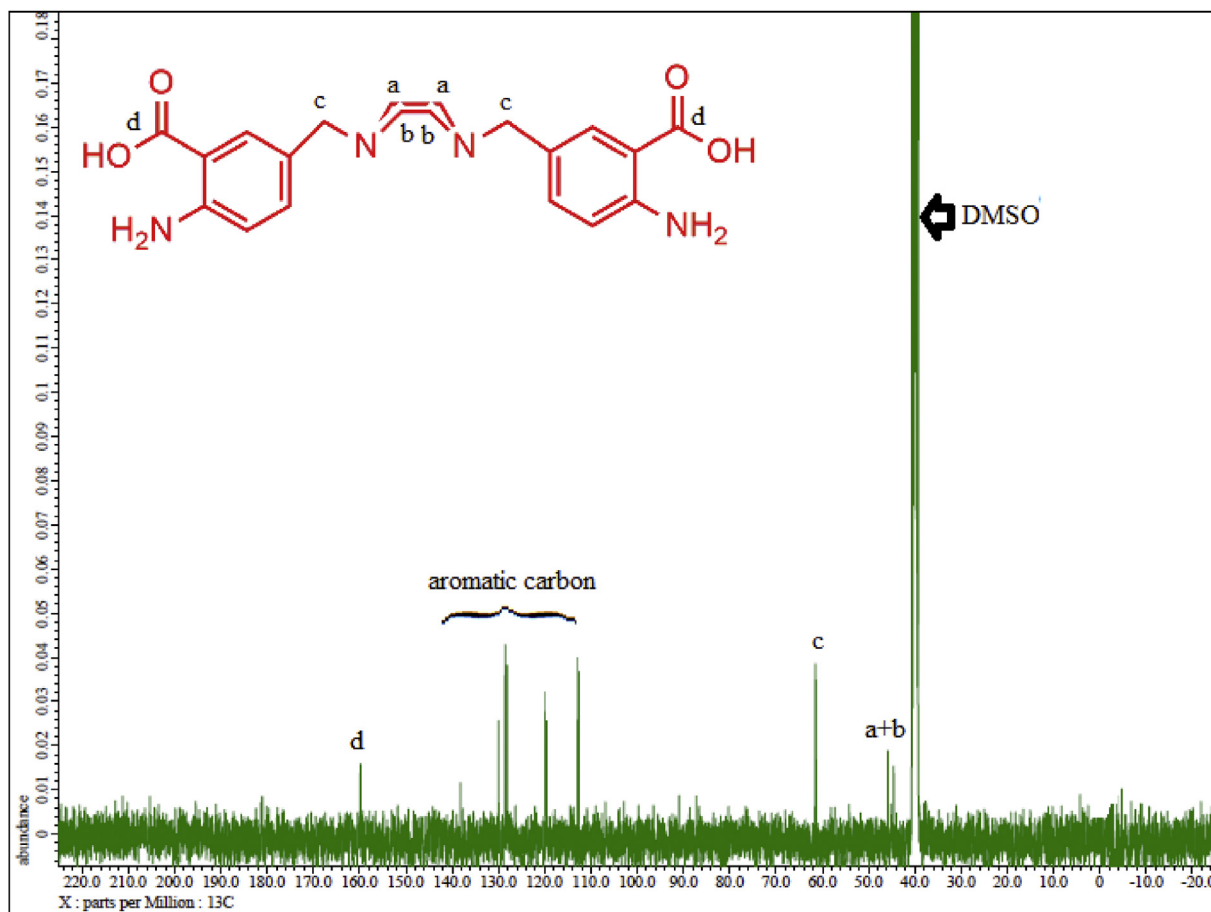


Fig. 4. ^{13}C NMR spectra of the AFP ligand in d^6 DMSO. DMSO, dimethylsulfoxide.

Table 3

Electronic spectra and magnetic moment of polymer–metal complexes.

Abbreviation	Magnetic moment (B.M.) ^a	Electronic spectral data		10 Dq	B	β	$\beta\%$	Geometry
		Electronic Trans. (cm^{-1})	Assignment					
AFP–Mn(II)	5.40	25022	$^4\text{T}_{1g}(\text{G}) \leftarrow ^6\text{A}_{1g}(\text{F})$	5292	882	0.91	9	Octahedral
		19431	$^4\text{T}_{2g}(\text{G}) \leftarrow ^6\text{A}_{1g}(\text{F})$					
		14222	$^4\text{T}_{1g}(\text{G}) \leftarrow ^6\text{A}_{1g}(\text{F})$					
AFP–Co(II)	4.84	24302	$^4\text{T}_{1g}(\text{P}) \leftarrow ^4\text{T}_{1g}(\text{F})$	7677	853	0.76	24	Octahedral
		18995	$^4\text{A}_{2g}(\text{F}) \leftarrow ^4\text{T}_{1g}(\text{F})$					
		14095	$^4\text{T}_{2g}(\text{F}) \leftarrow ^4\text{T}_{1g}(\text{F})$					
AFP–Ni(II)	3.39	24991	$^3\text{T}_{1g}(\text{P}) \leftarrow ^3\text{A}_{2g}(\text{F})$	12128	758	0.70	30	Octahedral
		18011	$^3\text{T}_{1g}(\text{F}) \leftarrow ^3\text{A}_{2g}(\text{F})$					
		11087	$^3\text{T}_{2g}(\text{F}) \leftarrow ^3\text{A}_{2g}(\text{F})$					
AFP–Cu(II)	2.15	25701	Charge transfer	–	–	–	–	Distorted Octahedral
		14999	$^2\text{T}_{2g} \leftarrow ^2\text{E}_g$					

^a Bohr magneton.

have been assigned to the transitions $^4\text{T}_{1g}(\text{G}) \leftarrow ^6\text{A}_{1g}$, $^4\text{T}_{2g}(\text{G}) \leftarrow ^6\text{A}_{1g}$, and $^4\text{T}_{1g}(\text{F}) \leftarrow ^6\text{A}_{1g}(\text{F})$, respectively, suggesting an octahedral structure of AFP–Mn(II) polymer–metal complex. The electronic spectrum of AFP–Co(II) polymer–metal complex shows three bands at 14,095, 18,995, and 24,302 cm^{-1} , which have been assigned to the transitions $^4\text{T}_{2g} \leftarrow ^4\text{T}_{1g}(\text{F})$, $^4\text{A}_{2g} \leftarrow ^4\text{T}_{1g}(\text{F})$, and $^4\text{T}_{1g}(\text{P}) \leftarrow ^4\text{T}_{1g}(\text{F})$, respectively, and are consistent with the values observed for an octahedral structure. The Ni(II) polymer–metal complex

[29] gave three bands at 11,087, 18,011, and 24,991 cm^{-1} , corresponding to the transitions $^3\text{T}_{2g}(\text{F}) \leftarrow ^3\text{A}_{2g}(\text{F})$, $^3\text{T}_{1g}(\text{F}) \leftarrow ^3\text{A}_{2g}(\text{F})$, and $^3\text{T}_{1g}(\text{P}) \leftarrow ^3\text{A}_{2g}(\text{F})$, respectively, corresponding to octahedral geometry. The electronic spectrum of the AFP–Cu(II) polymer–metal complex [30] exhibits a band at 14,999 cm^{-1} assigned to the $^2\text{T}_{2g} \leftarrow ^2\text{E}_g$ transition, implying a distorted octahedral geometry. Besides, a strong charge transfer band is observed at 25,701 cm^{-1} . The value of the ligand field splitting energy (10 Dq), Racah

interelectronic repulsion parameter (B), nephelauxetic ratio (β), and $\beta\%$ are presented in Table 3. The Zn(II) coordination polymer is diamagnetic in nature as expected for d^{10} system.

3.6. Thermogravimetric analysis

The thermal behavior of the coordination polymers was investigated by thermogravimetric analysis (TGA). The TGA data of all the samples are presented in Table 4, and the thermograms are shown in Fig. 5. The initial degradation temperature of the coordination polymers, as well as the AFP ligand begins from 25 to 50°C. A very slight decrease in weight loss (2–5%) depicted from the thermogram in the temperature range 25–150°C for the AFP ligand and may be attributed to unbound water molecules. However, the gradual weight loss that initially occurred below 150°C in all of the coordination polymers of AFP may be due to removal of hydrate water, whereas the loss obtained in the range of 150–200°C might be due to metal-coordinated water molecules [31]. The rate of decomposition for the entire coordination polymer is initially low up to 150°C and gradually increases to a maximum in the range of 250–600°C at which almost 65–85% loss in weight occurred. A remarkable difference is observed in the thermal degradation of the AFP ligand and its coordination polymer. The AFP ligand follows a two-step [32] mode as compared to a single-step thermal degradation of the coordination polymers. In AFP ligand, the first slow step of thermal degradation in the range of 250–340°C may be due to the decomposition of a more labile aliphatic bridge present between the two 2-aminobenzoic acid units, and the second step of thermal degradation may be in the anthranilic acid, initiated at 500°C, with a rapid weight loss at around 550°C which gets completed at 700°C.

These results revealed that all the polymer–metal complexes show higher thermal stability than the AFP ligand due to the incorporation of metal ions into the polymeric chain as a result of chelation. Another factor that may be responsible for the enrichment of the thermal stability of the polymer–metal complexes is the increase in the molecular weight due to the joining of two different polymer chains. The thermogram confirms that the polymer–metal complexes are thermally more stable than the AFP ligand.

3.7. Antimicrobial studies

The antibacterial and antifungal activities of the AFP ligand and their polymer–metal complexes were identified

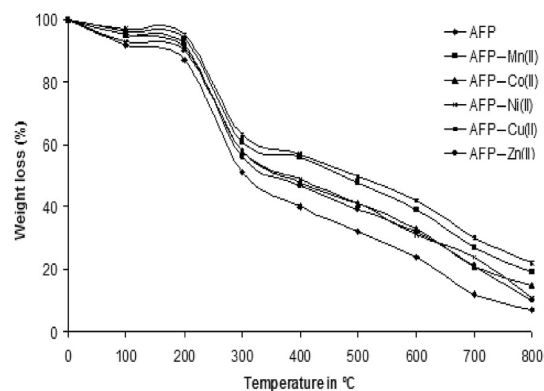


Fig. 5. Thermograms of the AFP ligand and its polymer–metal complexes.

based on the zone of inhibition for bacterial growth around the wells at one atmospheric pressure and ambient temperature. The results of activity were expressed as inactive, mild, moderate, and high. The results are summarized in Tables 5 and 6. The results reveal that all the compounds exhibited antibacterial and antifungal activities to a certain extent. All the compounds were screened for their antibacterial activity against *Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus*, *Pseudomonas fluorescens*, and *Salmonella typhi* and for their antifungal activity against *Candida albicans*, *Aspergillus niger*, and *Microsporum canis*. All the compounds generally showed good antibacterial activity, but more significant antifungal activity was observed against most of the strains. A marked enhancement of activity was exhibited in all the polymer–metal complexes against all the bacterial/fungal strains. It was evident from the data that the antimicrobial activity of all the polymeric compounds was increased relative to the AFP ligand. The chelation/coordination reduces the polarity of the metal ion by partial sharing of its positive charge with the donor groups and possibly π -electron delocalization takes place within the whole chelate ring [33]. This process thus increases the lipophilic nature of the central metal atom [34], which, in turn, favors its greater penetration through the bacterial wall of the microorganisms, thus killing them more effectively [35]. It has also been observed that the solubility, conductivity, and dipole moment are also influenced by the presence of metal ions; these could be the significant factors responsible for increasing the hydrophobic character and liposolubility of the molecule, hence enhancing the biological activity.

Table 4

Thermal properties of AFP ligand and its polymer–metal complexes.

Compounds	Weight left (%) at the indicated temperature (°C)							Characteristic weight left (%) at 800°C
	100	200	300	400	500	600	700	
AFP	92	87	51	40	32	24	12	7
AFP–Mn(II)	96	94	61	56	48	39	27	19
AFP–Co(II)	95	91	58	48	41	33	21	15
AFP–Ni(II)	93	90	58	49	41	31	24	11
AFP–Cu(II)	97	95	63	57	50	42	30	22
AFP–Zn(II)	95	92	56	47	39	32	21	10

Table 5
Antibacterial activity of AFP ligand and its polymer–metal complexes.

Compounds	Zones diameter showing complete growth inhibition (mm) ^a				
	<i>E. coli</i>	<i>P. fluorescence</i>	<i>B. subtilis</i>	<i>S. aureus</i>	<i>S. typhi</i>
AFP	17	16	20	14	15
AFP–Mn(II)	16	21	17	22	17
AFP–Co(II)	20	16	19	18	18
AFP–Ni(II)	17	18	18	19	17
AFP–Cu(II)	23	25	23	22	22
AFP–Zn(II)	21	20	18	19	19

^a 14–25 mm: significant activity; 7–13 mm: moderate activity.

Table 6
Antifungal activity of AFP ligand and its polymer–metal complexes.

Compounds	Zones diameter showing complete growth inhibition (mm) ^a		
	<i>C. albicans</i>	<i>M. canis</i>	<i>A. niger</i>
AFP	14	17	16
AFP–Mn(II)	14	13	15
AFP–Co(II)	17	14	16
AFP–Ni(II)	19	20	20
AFP–Cu(II)	22	23	22
AFP–Zn(II)	18	20	19

^a 14–22 mm: significant activity; 7–13 mm: moderate activity.

The results of antimicrobial activity reveal that the AFP–Cu(II) showed the highest antibacterial and antifungal activity than other polymer–metal complexes. This result may have been due to the higher stability constant of Cu(II) than the other polychelates [36,37]. According to the stability constant, the Cu(II) ion has stronger interactions with N and O donor atoms, by which its lipophilic nature was enhanced.

4. Conclusion

In the present work, some new coordination polymers of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) have been synthesized in good yield and characterized by analytical, magnetic, spectral, and thermal data. The IR spectral data confirmed the formation of coordination polymers. The monomeric ligand and all the coordination polymeric compounds were soluble in DMSO and DMF but insoluble in common organic solvents. The geometries of AFP–Mn(II), AFP–Co(II), and AFP–Ni(II) were octahedral, while AFP–Cu(II) is of distorted octahedral and AFP–Zn(II) has tetrahedral geometry. Attachment of transition metal ions in the polymeric structure increases thermal stability and antimicrobial activity. Owing to the enhanced antimicrobial activity, these coordination polymers have the potential to be used as antifungal and antifouling materials in various processes.

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