Antimicrobial Viscometric Studies of Thermally Stable Metal based Schiff Base Polymer derived from 4, 4-Methylene Bis Furfuraldehyde

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ABSTRACT

This paper presents antimicrobial viscometric studies of thermally stable metal based schiff base polymer derived from 4, 4-methylene bis furfuraldehyde. A new Antimicrobial Schiff base polymer is synthesized by condensing 4, 4-methylene bis (furfuraldehyde) with 1, 2-diaminopropane in 1:1 molar ratio. The experimental study determined this polymer found to react with Cu (II) acetate monohydrate and Ni (II) acetate, yielding poly chelates. The polymer and the polymetal chelates were characterized through elemental microanalysis and various spectroscopic techniques like FTIR, UV-Visible, Viscometry and Thermo-Analytical studies. The newly synthesized polymer and polymetal chelates were screened by using agar well diffusion method against various microorganisms. For antibacterial activity, Shigella Flexneri, Micrococcus Flavus, Staphylococcus Aureus, Bacillus Cirrofigellosus, Escherichia Coli and for antifungal activity A. Niger, Aspergillus Flavus, and Candida Albicans were produced.

Keywords: Agar Well Diffusion; Antibacterial; Antifungal; Antimicrobial; Poly Azomethine; Thermo-Analysis; Viscometry

1 INTRODUCTION

POLY Azomethine(s), or Schiff base polymers are synthesized by polycondensation of number of diamines with various dicarbonyl compounds, and are of significant interest due to their enormous applications and importance in numerous fields. They display remarkable properties which are related to their conjugated backbone and existence of imine sites [1]. These compounds exhibit nonlinear visual possessions, power or mechanical strength [2]. At high temperatures a number of Schiff base polymers form mesophases [3]. These polymeric compounds and their complexes possesses motivating factors; for example exposition of catalyst, thermally stable, photoluminescence properties and their remarkable coordinating behavior [4], [5], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15], and [16]. The antimicrobial agents as well as Schiff bases are found to exhibit additional carbinostatic and bacteriostatic character on coordination [17], [18], [19]. Numerous poly metal complexes have been synthesized, and exhibit remarkable possessions as antistatic agents, para magnetism, and metal ion uptake through oxidative polycondensation [20], [21], [22]. Polymeric Schiff base exhibit promising accomplishments against yeast, bacteria, and fungi [23], [24].

In the present study an attempt has been made to investigate the thermal stability and antimicrobial activity of newly synthesized Schiff base polymer and its poly chelates. All the synthesized compounds were characterized by using spectral as well as thermal and viscosity measurements. All the prepared compounds were screened against different bacteria and fungus by using agar well-diffusion method, and were motivating to find that the activity improved on coordination.

2 EXPERIMENTAL SETUP

2.1 Materials and Strains

1, 2-Propylenediamine, (E. Merck, Germany), dimethyl form amide (DMF), ethanol, diethyl ether and glacial acetic acid (E-Merck, Germany), Copper (II) acetate monohydrate [Cu(CH₃COO)₂ · H₂O] and Nickel (II) acetate tetrahydrate [Ni(CH₃COO)₂ · 4H₂O] (E-Merck, Germany) were used. The micro-organisms Staphylococcus Aureus, Micrococcus Flavus, Bacillus Cirrofigellosus, Shigella Flexneri, Escherichia Coli, Candida Albicans, A. Niger and Aspergillus Flavus, were also used.

2.2. Synthesis of 4, 4-Methylene Bis (Furfuraldehyde) (MBF)

The Monomer 4, 4-Methylene Bis (Furfuraldehyde) (MBF) was synthesized as reported in [25].

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2.3 Preparation of Poly 4, 4-Methylene bis (furfuraldehyde) 1, 2-Propylenediamine (PMBFPn)

MBF 0.1g was added to 20ml of Dimethyl Form Amide (DMF) and mixture was refluxed till its complete dissolution. The hot solution was filtered and added 0.041ml 1, 2-Propylenediamine, dissolved in DMF (1ml). The reaction mixture was refluxed with constant stirring for 24 hours. The mixture was concentrated to half the volume and 15ml of ethanol was added. Dark brown precipitate was filtered and washed with diethyl ether. The product was dried at 65–70°C for 7–8 hours. The melting point recorded was 350°C. The chemical scheme is shown in Fig-1.

2.4 Synthesis of Copper (II) and Nickel (II) Complexes (PMBFPnCu), (PMBFPnNi)

The metal complexes were synthesized by refluxing together in (1:1) ratio of ligand and metal salts. Poly 4, 4-methylene bis (furfuraldehyde) 1, 2- diamino propane was dissolved in (0.5g) dimethyl form amide (20–30ml). Into the resulting mixture, solution of Copper (II) acetate (0.4g) and Nickel (II) acetate (0.5g) already dissolved in tetrahydrofuran (20ml) and (1ml) acetic acid was added, and was refluxed for 15–20 min. The resulting mixture was allowable to cool at room temperature and was stirred continuously for the period of six days. The resulting precipitates were collected by filtration, washed with distilled water, ethanol diethyl ether and tetrahydrofuran and was kept for drying for 24 hours at 0.01mm pressure. The synthesized polymetal chelates exhibited dark brown color for nickel complex and light brown for copper complex. The polymer metal complexes decomposed at 355°C and were insoluble in number of organic solvents.

3 RESULTS AND DISCUSSION

The elemental microanalysis of the Schiff base polymer and their polymer metal complexes was carried out at HEJ Research Institute of Chemistry, University of Karachi, Pakistan. The FT-IR studies were recorded on Nicolet Avatar 330 FT-IR (Thermo Nicolet Electron Corporation, USA) with Attenuated Total Reflectance (ATR) accessory (Smart Partner) within the range 4000–6000 cm⁻¹. The ultraviolet and visible spectrophotometric studies were conducted at Institute of Advanced Research Studies In Chemical Sciences, University of Sindh Jamshoro and at HEJ Research Institute of Chemistry, University of Karachi, Karachi. The UV-Visible studies were conceded in DMF, by using Lambda 35 double beam spectrophotometer. Dual quartz cells of 1cm path length were used during the study, within 185–700 nm. The solubility of ligand and polymer metal complexes were tested in different organic solvents at room temperature. The ligand and polymer metal complex were found soluble in few and insoluble in various organic solvents, at room temperature. The thermal analysis of ligand and polymer metal complexes were examined by using Pyris Diamond TG/DTA thermal analyzer, from room temperature to 600°C with a nitrogen flow rate of 5 mL/min. Sample 2mg was placed in a platinum crucible and recorded against alumina as reference at heating rate of 20°C/min.

The viscosity measurements of the ligand and polymer metal complexes were carried out in dimethylformamide within, 0.024 – 0.064 g/dl concentration range.
The temperature range from 283—323ºK with an interval of 10ºK was established by using a suspended level viscometer (Technico ASTM 445). The flow time of the solvent (DMF) was noted and 15 ml solution was taken each time and average flow time was attained from minimum three readings. The reduced viscosity $\eta_{\text{reduced}}$ was calculated, by dividing specific viscosity $\eta_{\text{specific}}$, with concentration in (g/dl). Whereas intrinsic viscosity $\eta$ was calculated, by plotting $\eta_{\text{reduced}}$ against concentration and inducing to zero concentration, and for controlling the temperature throughout the experiment, Gallen kamp viscometer water bath was used. The thermodynamic parameters $\Delta G_v$, $\Delta H_v$ and $\Delta S_v$ of ligands and polymeric metal complexes were determined. The activation energy $\Delta G$ was calculated from the Eq.(1).

$$\Delta G = 2.303 \times R \times T \times \log \left( \frac{\eta_{\text{abs}}}{10^{-3}} \right) \quad \ldots (1)$$

Where $R$ is gas constant, $T$ is absolute temperature, and $\eta_{\text{abs}}$ is the viscosity at absolute temperature. A linear relationship was obtained by plotting log $\eta_{\text{abs}}$ verses $1/T$. The values of activation heat of flow $\Delta H_v$ were calculated from the slope $\text{Slope XR}$. The entropy of activation of viscous flow $\Delta S_v$ was calculated from the relation of Eq.(2) and Eq.(3).

$$\Delta G_v = \Delta H_v - T(\Delta S_v) \quad \ldots (2)$$

$$\Delta S_v = \frac{\Delta H_v - \Delta G_v}{T} \quad \ldots (3)$$

The antimicrobial activity of compounds under investigation was assessed by using agar well diffusion method. The ligand and polychelates possessed apparent antibacterial and antifungal activities against the microorganisms Staphylococcus Aureus, Micrococcus Flavus, Bacillus Cirroflegellosus, Shigella Flexneri, Escherichia Coli, Candida Albicans, A.Niger and Aspergillus Flavus.

The newly synthesized Schiff base polymer PMBFPn and its polymer metal complexes were prepared as shown in Fig-1 (Scheme-1). The monomer MBF was synthesizes [25], by following a reported method of 5, 5’-methylene bis (salicylaldehyde) and 5, 5’-methylene bis (2-hydroxyacetophenone) [26], [27], [28]. The polymer PMBFPn was prepared by polycondensing the dialdehyde MBF and 1, 2-diaminopropane. The product was achieved in good yield.

### 3.1 Elemental Microanalysis

The results of elemental micro-analysis for the prepared compounds are thoroughly associated to the probable values and favored the formation. Table-1 shows analytical and physical data of monomer, ligand and polymer metal complex.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M. Pt °C</th>
<th>Calculated (Found) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMBFPn</td>
<td>&gt; 300</td>
<td>62.90 (62.95) 4.99 (4.90) 9.88 (9.92)</td>
</tr>
<tr>
<td>PMBFPnCu</td>
<td>&gt; 394</td>
<td>54.99 (55.23) 4.61 (4.60) 9.16 (8.99)</td>
</tr>
<tr>
<td>PMBFPnNi</td>
<td>&gt; 400</td>
<td>55.87 (56.00) 4.68 (4.48) 9.30 (9.01)</td>
</tr>
</tbody>
</table>

**TABLE-1: Analytical and physical data of monomer, ligand and polymer metal complex**

Fig-2: FTIR Spectra of PMBFPn, PMBFPnCu (11) and PMBFPnNi (11)

### 3.2 Vibrational Spectra

The Schiff base polymer PMBFPn, show number of bands of varying intensities above 3000 cm$^{-1}$ due to aromatic $\mathrm{C-H}$ stretching, and bands around 2820—3000 cm$^{-1}$, are also seen due to aliphatic $\mathrm{C-H}$ group frequencies. The Nickel and Copper polychelates also show weak to medium intensity bands within 3100—2900 cm$^{-1}$ due to aromatic and aliphatic $\mathrm{C-H}$ stretching vibrations. The broad signals of Nickel complex, PMBFPnNi, was observed at 3325 cm$^{-1}$, followed by a sharp peak at 3490 cm$^{-1}$, due to coordination of polysaccharide water molecule whereas the similar band disappears for all the Copper complex that is for PMBFPnCu. PMBFPnCu polychelate showed medium intensity bands within 3000—2800 cm$^{-1}$, due to symmetrical and asymmetrical $\mathrm{C-H}$ stretching vibrations of $\mathrm{CH}_2$ group. The polymer PMBFPn also displayed bands around 1460—1440 cm$^{-1}$ due to $\mathrm{C=C}$ deformations. The bands appearing in the region 1100—850 cm$^{-1}$ are due to $\mathrm{C-H}$ vibrations and ring breathing. The polymer PMBFPn did not showed any absorption bands around 1700 cm$^{-1}$ due to $\mathrm{C=O}$ stretching vibrations, and showed strong absorption band at 1630 cm$^{-1}$ attributed to hydrogen bonded $\mathrm{C=N}$ stretching vibration. A shift of in-band position in the polymer as compared to monomers may be attributed to formation of azomethine groups. The nickel polychelate PMBFPnNi, showed strong absorption bands of hydrogen bonded $\mathrm{C=N}$ azomethine stretch at 1620 cm$^{-1}$, a shift of 10 cm$^{-1}$ towards lower frequency as compared to its Schiff base polymers and may be due to coordination of furyl $'\mathrm{O}'$ with metal ion. The copper polychelate PMBFPnCu has showed a sharp intense peak at 1610cm$^{-1}$ of hydrogen bonded $\mathrm{C=N}$ azomethine stretch and were also shifted 20 cm$^{-1}$ towards lower frequency as compared to their respective polymer PMBFPn is attributed to coordination with metal ion. Similar findings were observed and reported by [26], [27] and Schif base polymers PMSATen, di-PMSAS, and meso-PMSAS and their copper and nickel polychelates. A number of bands of varying intensities were seen for Nickel and Copper polychelates within 1515—1320 cm$^{-1}$ and at 1490 cm$^{-1}$ due to $\mathrm{C=O}$ ring breathing vibrations, $\mathrm{C-O}$ vibrations and $\mathrm{O-H}$ hydrogen bonded vibrations. The weak intensity absorption bands in all Nickel and Copper polychelates within 800—420 cm$^{-1}$ is due to metal ligand vibrations as shown in Fig-2.
3.3 Electronic Spectra

The UV/Visible spectra of ligand PMBFPn and polymetal chelates were recorded in DMF. The molecular weight of newly synthesized polymer PMBFPn and polymer metal complexes PMBFPnCu and PMBFPnNi was unknown, therefore 1% of its absorptivity was calculated. The results of spectrophotometric studies in DMF as solvent is depicted in Table-2.

The polymer PMBFPn indicated three to four bands. The polymer indicated first and second bands at 236nm with absorptivity (1% ε = 145.566 Lg\(^{-1}\)cm\(^{-1}\)) and at 289nm with absorptivity (1% ε = 96.9109 Lg\(^{-1}\)cm\(^{-1}\)) and third and fourth bands at 370nm and 410nm, with absorptivities one percent (1% ε = 112.65 Lg\(^{-1}\)cm\(^{-1}\)), and (1% ε = 47.2440 Lg\(^{-1}\)cm\(^{-1}\)) respectively. A bathochromic shift of 2-20 nm in the first, second and third absorption bands was observed in the polymer PMBFPn, as compared to the monomer. The bands could be assigned to π-π* transitions involving heteroaromatic rings, and due to π-π* transitions of heteroaromatic ring involving Oxygen π orbitals and due to π-π* transitions, heteroaromatic rings, and azomethine π electrons. The observation of a fourth new band in the polymer as compared to the monomer is due to conjugated azomethine (C = N) chromophore, merged in the polymer as a result of polycondensation.

The polymer metal complex PMBFPnCu and PMBFPnNi indicated bands within 242 - 425 nm and 248 - 445 nm with 1% absorptivity (ε 1% = 214.06 - 110.09 Lg\(^{-1}\)cm\(^{-1}\)) and (ε 1% = 180.58 - 60 Lg\(^{-1}\)cm\(^{-1}\)), due to π-π* transitions in heteroaromatic rings. The increase and shift of 6 - 15 nm in PMBFPnCu and 9 - 35 nm in PMBFPnNi as compared to Schiff base polymer PMBFPn was observed towards longer wavelengths (lower frequencies) that is a bathochromic shift, may be due to coordination with metal ion, and confirms the formation of complexes. The fourth band in copper polychelate at 425 nm and nickel polychelate at 445 nm is due to charge transfer band from metal towards the ligand. The UV Visible spectrum of PMBFPn, PMBFPnCu (11) and PMBFPnNi (11) is shown in Fig-3 with graph.

3.4 Solubility of Complexes

The Schiff base polymer and their polymetal complexes exhibited poor solubility in most of the organic solvents. The polymer PMBFPn showed partial solubility in DMF and DMSO but the polychelates were adequately soluble in DMF and DMSO to study their spectroscopic characteristics. The results are summarized in Table-3.

3.5 Thermal Analysis

The results of Thermo Gravimetric (TG) analysis recorded indicated that for polymer PMBFPn, loss in weight started at 265°C and loss of 68% occurred up to 480 degrees. 100% weight loss was observed at 500°C. Whereas the DTA showed a well-defined endothermic peak at 412°C, may be associated to the melting point of polymer. The TGA/DTA of poly metal chelate PMBFPnCu indicated weight loss in three stages, initial weight loss of 2% was observed at 351°C, may be due to the decomposition. Fig-4(a) reflects TGA/DTA curves of PMBFPnCu (11) with graph.

An additional weight loss of 26% at secondary decomposition step at 405°C was observed and was may be due to decomposition of aliphatic part of metal complex followed by tertiary and total weight loss of 100% at 500°C.

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>PMBFPn</th>
<th>PMBFPnCu</th>
<th>PMBFPnNi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorptivity, ε 1% (Lg(^{-1})cm(^{-1}))</td>
<td>(145)</td>
<td>(96)</td>
<td>(112)</td>
</tr>
</tbody>
</table>

Table-2: Results of Spectrophotometric Studies in DMF as Solvent

<table>
<thead>
<tr>
<th>H(_2)O</th>
<th>CH(_3)OH</th>
<th>C(_2)H(_5)OH</th>
<th>CHCl(_3)</th>
<th>Acetone</th>
<th>n-hexa</th>
<th>Ether</th>
<th>DMF</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMBFPn</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
</tr>
<tr>
<td>PMBFPnCu</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>PMBFPnNi</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>±</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Table-3: Solubility A, B Monomer, Ligand and Polymetal Complexes in Various Solvents

A: 0.05g compounds in 10ml solvent at 35°C.
B: (+) Soluble, (±) Partially soluble, (−) Insoluble.

Image captions:

Fig-3: UV Visible spectrum of PMBFPn, PMBFPnCu and PMBFPnNi

Fig-4(a): TGA/DTA curves of PMBFPnCu (11) with graph.
Between 355°C and 460°C, the material suffered rapid weight loss, the loss rate was 0.4% °C at 450°C, which is the temperature of maximum rate of weight loss \( T_{\text{max}} \). Well-defined endothermic peak was shown at 440°C which was may be due to the melting of poly metal chelate.

The TGA/DTA of poly metal chelate PMBFPnNi indicated, initial weight loss of 1.5% was at 355°C and was may be due to decomposition of non-coordinated part \( \text{CH}_4\text{CHCH}_2 \). Fig-4(b) reflects TGA/DTA curves of PMBFPnNi (11) with graph. An additional weight loss of 22% was observed at 430°C, followed by tertiary and total weight loss of 42% at 500°C was observed. Between 360°C and 450°C the material suffered rapid weight loss, the loss rate was 0.3% °C at 440°C, which is the temperature of maximum rate of weight loss \( T_{\text{max}} \). The DTA of poly metal chelate showed an endothermic peak at 465°C and may be associated to the melting of poly metal chelate.

3.6 Viscometric Analysis

The reduced viscosity \( \eta_{\text{red}} \) of ligand and Polymer metal complex was in the range 0.4689–0.3854 dl/g for PMBFPn and 0.4713–0.3878 dl/g for PMBFPnCu and 0.4696–0.3867 dl/g for PMBFPnNi Polymer metal complex. The nickel and copper complexes exhibit higher values of reduced viscosity as compared to the parent monomer.

The association between \( \eta_{\text{red}} \) and the concentration was linear, with which fulfilled the Huggins equation. The \( \eta_{\text{red}} \) increased with concentration within 0.024–0.064 g/dl and decreased with increase in the temperature within 282–323°C.

### TABLE 4: INTRINSIC VISCOSITY VALUES OF LIGAND AND POLYMETAL CHELATES (dl/g)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Temperature °C</th>
<th>283</th>
<th>293</th>
<th>303</th>
<th>313</th>
<th>323</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMBFPn</td>
<td></td>
<td>0.4570</td>
<td>0.4460</td>
<td>0.4160</td>
<td>0.3990</td>
<td>0.3970</td>
</tr>
<tr>
<td>PMBFPnCu</td>
<td></td>
<td>0.4508</td>
<td>0.4594</td>
<td>0.4210</td>
<td>0.4021</td>
<td>0.3815</td>
</tr>
<tr>
<td>PMBFPnNi</td>
<td></td>
<td>0.4483</td>
<td>0.4584</td>
<td>0.4198</td>
<td>0.4002</td>
<td>0.3813</td>
</tr>
</tbody>
</table>

Intrinsic viscosity \( \eta \) is associated with the polymer’s molecular size and as the molecular size increases, the molecule becomes huge and increases the value of \( \eta \).

The Schiff base polymer PMBFPn and Polymer metal complexes PMBFPnCu and PMBFPnNi presented the values of intrinsic viscosity \( \eta \) within the range 0.44–0.39 dl/g for PMBFPn, 0.4508–0.3815 dl/g for PMBFPnCu and 0.4483–0.3813 dl/g for PMBFPnNi respectively. Table 4 summarizes the intrinsic viscosity values of Ligand and Polymetal chelates (dl/g).

The copper complex exhibited the highest value of intrinsic viscosity 0.4508–0.3815 dl/g as compared to the nickel complex the values of intrinsic viscosity was 0.4483–0.3813 dl/g, agreeing that, intrinsic viscosity depends upon the molecular weight of the compounds. The absolute viscosity \( \eta_{\text{abs}} \) for the ligand PMBFPn, ranged between 0.4666–0.2591 mN.s/m². The polymer metal complexes exhibit values for \( \eta_{\text{abs}} \) within the range 0.5751–0.3676 mN.s/m² for PMBFPnCu and 0.5842–0.3767 mN.s/m² for PMBFPnNi respectively. The increase of absolute viscosity with concentration is due to rise in solution’s density, along with the possibility of development of acquaintances or associates.

The values of \( \Delta G_v \) for ligand PMBFPn were in the range 14.462–14.927 K.J.mol⁻¹. The polymer metal complex PMBFPnCu has \( \Delta G_v \) values in the range 14.954–15.866 K.J.mol⁻¹ and for PMBFPnNi 14.991–15.932 K.J.mol⁻¹. The energy of activation increased with an increase in concentration in dilute solution. This is due to the fact that polymer molecules have fragile or weaker connotations or associations and can simply astounded during the flow process, while at higher concentrations the associations are more or strong and little influenced during the flow process, therefore the values of \( \Delta G_v \) are high. The increase of \( \Delta G_v \) with rise in temperature indicates that shape conversion or transition of the polymer molecules takes place during flow process. The values of \( \Delta H_v \) for PMBFPn were in the range 11.407–11.409 K.J.mol⁻¹ and for polymer metal complexes 8.6581–8.308 for PMBFPnCu and 8.4836–8.5052 K.J.mol⁻¹ for PMBFPnNi complex.
Fig-5(a) and Fig-5(b) express the graph plot of $ln\eta$ and $\frac{1}{T}$ of PMBFpCu(11) and PMBFpNi(11) respectively. The entropy of activation of viscous flow $\Delta S_v$ is a mathematical measurement of the degree of uncertainty of a random variable. Entropy in this sense is essentially a measure of randomness.

In simple terms, the measure of the level of disorder in a closed but changing system, a system in which energy can only be transferred in one direction from an ordered state to a disordered state. Higher the entropy, higher the disorder and lower the availability of the system’s energy to do useful work. If the entropy of the system is positive, the system becomes more ordered during flow so the process of uncoiling and orientation of macromolecules takes place during the flow. The values of $\Delta S_v$ for the monomer MBF were from 0.00069-0.00175 J/K, while those of the polymers PMBFpN were $(-0.02224) - (-0.022163)$ J.mol$^{-1}$ and for polymer metal complexes PMBFpCu, PMBFpNi were in the range: $(-0.02246) - (-0.0221634)$ and $(-0.022994) - (-0.0229111)$ J.mol$^{-1}$.

The ligand PMBFpN and their polymer metal complexes PMBFpCu and PMBFpNi were evaluated for their in vitro antibacterial activity and antifungal activity, against various microorganisms like for antibacterial activity Shigella Flexneri, Micrococcus Flavus, Staphylococcus Aureus, Bacillus Cirrofilgellusos, Escherichia Coli and for antifungal activity A.Niger, Aspergillus Flavus, and Candida Albicans, were investigated using agar well diffusion method. Tetracycline, an antibacterial and miconazole, an antifungal were used as standard drugs. To apply the strains, Platinum wire loop was used. The cultures of all the samples were inoculated before pouring into the petri dishes. By using a sterilized cork borer (24mm) diameter, wells were dug in the culture plates. The concentrations recommended for making solutions for PMBFpN and PMBFpCu and PMBFpNi poly metal complexes was i.e. 1 mg.ml$^{-1}$ in DMF and were poured into the wells with the help of a micro pipette. For positive and negative controls the other wells were filled with DMF and reference antifungal and antibacterial drugs. The plates were incubated simultaneously at 37$^\circ$C for 24 hours. At the end of suggested time, inhibition zones formed on the medium were evaluated as millimeters (mm), offering thorough inhibition. The ligand PMBFpN and their polymer metal complexes showed noticeable activity against fungal and bacterial cultures. The results are summarized in Table-5.

### TABLE-5: ANTIMICROBIAL ACTIVITY OF LIGAND AND POLYMER METAL COMPLEX (ANTIBACTERIAL & ANTIFUNGAL)

<table>
<thead>
<tr>
<th>Compound</th>
<th>ZONE OF INHIBITION (mm) 50µg/ml$^{-1}$</th>
<th>ANTIMICROBIAL</th>
<th>ANTIMICROBIAL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M.FLAVUS</td>
<td>S.AUREUS</td>
<td>B.CIRROFILGELLUSOS</td>
</tr>
<tr>
<td>PMBFpN</td>
<td>+</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td>PMBFpCu</td>
<td>+ +</td>
<td>+ +</td>
<td>+</td>
</tr>
<tr>
<td>PMBFpNi</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Tetraacycline a</td>
<td>–</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Miconazole b</td>
<td>–</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

a Standard Drug: +ve control, Antibacterial Activity
b Standard Drug: –ve control, Antifungal Activity

- **INACTIVE** 5 mm
- **WEAKLY ACTIVE** 8-10 mm
- **MODERATELY ACTIVE** 11-15 mm
- **HIGHLY ACTIVE** 16-20 mm
- **MOST ACTIVE** 21-24 mm
The results uncovered the facts that the newly synthesized compounds exhibited remarkable biological activity. The ligand PMBFPh exhibited (10, 15, 5, 15, 10 mm) zones of inhibition against the reported bacteria and their copper polychelate PMBFPhCu, exhibit highest antibacterial activity against Shigella Flexneri, Micrococcus Flavus, Staphylococcus Aureus, Bacillus Cirrofillgellosus, Escherichia Coli, it exhibited (20, 24, 15, 20, 20 mm) zones of inhibition against the reported bacteria, and this could be due to Copper (11) ion higher stability constant than Ni (II). The Copper (11) ion has stronger collaboration with O and N donor atoms, and the presence of pi electrons also enhance the lipophilic nature. The polymer metal complex PMBFPhNi exhibited (10, 15, 15, 15 mm) zones of inhibition. All the compounds exhibit zones of inhibition against C. Albicans, A.Flavus and A.Niger for their antifungal activity. The ligand PMBFPh exhibited (15, 10, 15 mm), zones of inhibition, whereas the polymetal complex PMBFPhCu has the higher antifungal activity as compared to PMBFPhNi polychelate. PMBFPhCu exhibit (24, 20, 20 mm) and PMBFPhNi exhibit (15, 15, 20 mm) zones of inhibition against the reported fungus. All the newly synthesized compounds exhibit prominent antimicrobial activity against the reported microorganisms and zones of inhibition are evaluated in tables and was interesting to note that activity was enhanced on coordination.

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