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Synthesis, Characterization, Antimicrobial and Antioxidant Studies of Co(II), Ni(II), Cu(II) and Zn(II) Metal Complexes with the Ligands 2-{[4-(5-bromo thiophen-2-yl)-6- phenylpyrimidin-2-yl]carboimidoyl}phenol Derivatives

Sunanda Ravindranath¹, Nirdosh Patil², Shweta Patil³, Ambika Bhusange⁴

^{1, 2, 3}Department of Chemistry, Appa Institute of Engineering and Technology, Vidya Nagar, Kalabuaragi-585103, Karnataka, India

⁴Department of Chemistry, Godutai Engineering College for women, Vidya Nagar, Kalabuaragi-585103, Karnataka, India

Abstract: A few complexes 2-{[4-(5-bromo thiophen-2-yl)-6-phenyl pyrimidin-2-yl] carboimidoyl} phenol [HL^5] and 2-{[4-(5-bromo thiophen-2-yl)-6- phenyl pyrimidin-2-yl]carbon imidoyl}-5-methoxyphenol [HL^6] with first row transition metal ions have been reported in this paper. The stichiometry of type (1:1) $[M(L)]2H_2O$ is analysed by these complexes. Complexes with ligands (HL^5 and HL^6) of metal ions Co(II), Ni(II), Cu(II) and Zn(II) reveal co- ordination number six, by means of magnetic susceptibility, electronic, IR, ¹H NMR, X-ray diffraction and ESR spectrum data. Copper(II) complexes with (HL^5) and (HL^6) were studied spectrophotometrically at different temperatures having an absorption maxima of 535 nm. The findings demonstrate that copper(II) and (HL^5) and (HL^6) are combined at pH 5.0 at a molar ratio of 1:1. The stability constants of the complexes were calculated to be 13.06×10^4 , 14.51×10^4 and 10.40×10^4 and 13.18×10^4 , 15.06×10^4 , 11.23×10^4 for (HL^5) and (HL^6) respectively by Jobs continuous variation method and 0.24×10^4 , 0.57×10^4 , and 0.77×10^4 and 0.28×10^4 , 0.55×10^4 , 0.79×10^4 for (HL^5) and (HL^6) respectively by mole ratio method at 30, 35 and 40°C, respectively. Both ligands and their metal complexes were screened for their antibacterial and antifungal activity by cup plate method and antioxidant activity by using standard DPPH radical scavenging ability method.

Keywords: Antifungal, complexes, antioxidant, antibacterial, magnetic,

I. INTRODUCTION

In many physiologically active natural compounds nitrogen heterocycles, in general, and pyrimidine in particular, show substantial therapeutic promise. Pyrimidine is one of the most famous nucleic acid chemistry structures. Many chemotherapeutic drugs in the pyrimidine nucleus are now in clinical use, including antifungal (flucytocine), antifungal (pyrimethamine), antifungal (idoxuridine, trifluridine and zidovudine), antiviral (sulfadiazine, sulphamarazine and sulfamethazine), antimalarial (pyrimidamine) antifungal agents (flucytocine). The large spectrum of biological and pharmacological activities of pyrimidines, including anticarcinogenicity[1-3], antibacterial[4], anti-inflammatory[5], antiviral[6], anti HIV [7], anti-hypertensive[8-9], anticonvulsant and analgesic[10], is of particular concern. In recent years, an increase in drug-resistant bacterial strain isolates has created a therapeutic hurdle to physicians when choosing antimicrobials. Consequently, it is critically necessary to produce novel antibacterial medicines with strong antibacterial action and reduced adverse effects. 2-acetyl-5-bromothiophene produced equivalent chalcones when condensed with different aromatic aldehydes in the alcoholic KOH solution. The chalcones were then reacted in the presence of a base with ethanol guanidine hydrochloride that yielded pyrimidine derivatives. The freshly synthesized heterocycles were characterized by the NMR, IR, and mass spectroscopic data. The antibacterial characteristics of all freshly synthesized compounds were examined[11]. We have reported in the current research that certain novel amino pyrimidines, such as 2-{[4-(5-bromothiophen-2-yl)-6-phenylpyrimidin-2-yl]carboimidoyl} phenol [HL^1] and 2-{[4-(5-bromothiophen-2-yl)-6-phenylpyrimidin-2-yl] carboimidoyl}-5-methoxy phenol [HL^2] and their metal complexes.

II. MATERIALS AND METHODS

All the chemicals and solvents used were of AR grade and were obtained from Sisco-Chem Industries. The metal salts were purchased from commercial sources. Metal contents were estimated using standard methods[12]. The electronic spectra were recorded on an Elico SL 159 spectrophotometer in the 200-1000nm ranges in DMF solution (10-3). Elemental analyses were obtained from HERAEUS C, H, N-O rapid analyzer. ESR measurements were carried out on a VARAN E-109 GHz. The experiment was carried by taking DPPH as the reference with the field set at 3200 Gauss. Magnetic susceptibilities were determined by the Faraday method using a model 300 Lewis Coil Force Magnetometer of one Tesla field strength at room temperature. The instrument was calibrated with Hg [Co (SCN)₄][13]. All melting points were uncorrected and measured using an Electro-thermal IA 9100 apparatus (Shimadzu, Japan). IR spectra were recorded as potassium bromide pellets on a Perkin-Elmer 1650 spectrophotometer (Shimadzu). A Horiba F.8 pH meter, calibrated with standard buffer solutions, was used for pH measurements. Copper(II) sulphate pentahydrate was purchased from Merck, Germany. All other chemicals used were of analytical grade purchased from Merck, Germany. Double-distilled water was used throughout this study[14]. Both ligands and their metal complexes were screened for their antibacterial and antifungal activity by cup plate method and antioxidant activity by using standard DPPH radical scavenging ability method.

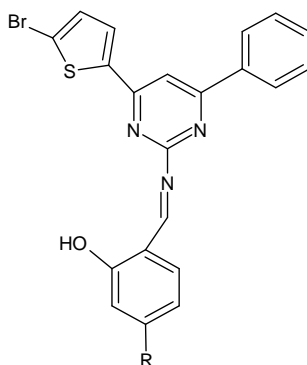


Fig. 1. Structure of ligands, $HL^1 = R = H$ and $HL^2 = R = OCH_3$

A. Preparation of Ligands

- 1) *Preparation of 1-(5-bromothiophen-2-yl)-3-phenylprop-2-en-1-one*: The substituted chalcones were prepared by reacting equimolar quantity of aromatic aldehydes (0.001mol) and 2-acetyl-5-bromothiophene iniethanol. 40% KOH was added to the reaction mixture at room temperature, drop by drop with regular stirring. After the completion of reaction, the precipitate thus obtained was separated by filtration, washed with cold ethanol, dried and purified by recrystallization from ethanol.
- 2) *Preparation of 4-(5-bromothiophene-2yl)-6-phenylpyrimidine-2- Amine*: Refluxing a combination of alternative chalcones (0.001mol), guanidine hydrochloride (0.001mol) and alkali (KOH), into 20ml ethanol, replaced pyrimidine. The reaction mixture was dumped into ice cold water when the reaction was finished. The resulting precipitation was filtered, washed with ethanol, dried and purified using ethanol recrystallation.
- 3) *Preparation of 2-[[4-(5-bromo thiophene-2-yl)-6-phenyl pyrimidin-2- yl] carbonimidoyl] phenol [HL^1] and 2-[[4-(5-bromothiophene-2-yl)-6- phenylpyrimidin-2- yl] carbon imido yl]-5-methoxyphenol [HL^2]*: Equimolar 4-(5-bromothiophene-2yl)-6-phenylpyrimidine-2-amine (0.001 mol) solutions and replaced salicylaldehyde (0.001mol) with 4 hour reaction mixture in 40 ml of ethanol reflux, with a 40% addition of KOH to the reaction mixture. Afterwards, for the reaction mixture, the precipitate was collected, washed with ethanol, dried and purified by ethanol recrystallization.

B. Microwave Irradiated Synthesis of Co(II), Ni(II) and Cu(II) metal complexes

Equimolar solution of Schiff base ligands of 2-[[4-(5-bromo thiophene-2-yl)-6-phenyl pyrimidin-2-yl] carbon imido yl] phenol [HL^1] / 2-[[4-(5-bromo thiophene-2-yl)-6-phenylpyrimidin-2-yl]carbonoimidoyl]-5-methoxyphenol [HL^2] (0.001 mol) and metal chloride (0.001mol) in ethanol, the reaction mixture was refluxed in microwave irradiation for 3 to 4 minutes, then the colour of the mixture was turned, it was treated with sodium acetate (0.5 g) the resultant reaction mixture was further refluxed in microwave irradiation for 2 more minutes, and then it was decomposed by pouring to distilled water (80 to 100 ml) with stirring. The separated solid (complex) was allowed to settle and collected by filtration, washed several times with distilled water and then with hot ethanol. The solid complex obtained was dried in desiccators over anhydrous calcium chloride.

III. RESULTS AND DISCUSSION

The analytical data shown in Table-1: indicate that all the metal ions from 1:1 (M:L) complexes with both the ligands. All the complexes are coloured and are soluble in DMF, DMSO and acetonitrile and are sparingly soluble in other organic solvents. Molar conductance measurements of these complexes in DMF correspond to electrolytes. The cobalt(II) complexes magnetic moment is 5.22-5.38 B.M. The magnetic moment of the cobalt(II) octahedral complex is shown to be between 4.46 and 5.33 B.M.[15]. Thus, the reported magnetic moment for the investigated Co(II) complexes demonstrates that they are octahedral geometry. Nickel (II) is a d^8 ion with two electrons unpaired which may form six coordinated octahedral complexes[16]. The magnetic moments reported in the octahedral Ni(II) complexes vary from 2.82 to 3.4, depending on the magnitude of the orbital contribution B.M.[17-18]. In this study 3.17-3.34 B.M. were discovered to be magnetic moments at room temperature for the Ni(II) complexes. This investigation implies the octahedral structure of Ni(II) complexes. The copper(II) complexes magnetic moment is 1.85 to 1.90 B.M., which is the same as the spin only value. It is reported that the distorted octahedral geometry of copper (II) complexes devoid of spin interaction exhibit magnetic moment in the range of 1.80-1.93 B.M[19]. Hence it may be concluded that copper (II) complexes have major spin interaction. The electronic spectral band maxima with their assignments for the complexes were discussed, In the present Co(II) complexes, the transitions may be ascribed to three bands: 14725.28 cm^{-1} , 18192.32 cm^{-1} , and 32233.05 cm^{-1} . These transitions indicate the octahedral structure of the present Co(II) complexes. The investigated Ni(II) complexes were having transition of three bands: 10210.05 cm^{-1} , 12825.55 cm^{-1} , and 22730.32 cm^{-1} , respectively, to ν_1 , ν_2 and ν_3 , indicating the octahedral geometry of the Ni(II) ion.

Table 1: Elemental analysis and Conductance data for ligands and metal complexes.

Sl. No.	Ligands / Complexes	Analysis % Found (Calculated)						Molar Conductance $\square^{-1}\text{cm}^2\text{mol}^{-1}$
		C	H	N	S	Br	M	
	HL ¹ C ₂₁ H ₁₄ BrN ₃ OS	57.82 (57.78)	3.24 (3.20)	9.67 (9.62)	7.28 (7.33)	18.25 (18.31)	---	-
01	Co(L ¹)2H ₂ O Co(C ₂₁ H ₁₃ BrN ₃ OS)2H ₂ O	47.45 (47.43)	3.15 (3.20)	7.95 (7.90)	6.05 (6.02)	15.11 (15.04)	11.13 (11.09)	73.00
02	Ni(L ¹)2H ₂ O Ni(C ₂₁ H ₁₃ BrN ₃ OS)2H ₂ O	47.48 (47.45)	3.25 (3.21)	7.97 (7.91)	5.98 (6.03)	15.13 (15.05)	11.10 (11.05)	84.29
03	Cu(L ¹)2H ₂ O Cu(C ₂₁ H ₁₃ BrN ₃ OS)2H ₂ O	47.10 (47.03)	3.13 (3.17)	7.90 (7.84)	6.03 (5.97)	14.96 (14.91)	11.80 (11.85)	84.96
04	Zn(L ¹)2H ₂ O Zn(C ₂₁ H ₁₃ BrN ₃ OS)2H ₂ O	46.92 (46.87)	3.21 (3.16)	7.86 (7.81)	6.00 (5.95)	14.90 (14.85)	12.10 (12.15)	85.40
	HL ² C ₂₂ H ₁₆ BrN ₃ O ₂ S	56.55 (56.61)	3.38 (3.43)	9.05 (9.00)	6.92 (6.86)	17.18 (17.13)	---	92.63
05	Co(L ²)2H ₂ O Co(C ₂₂ H ₁₅ BrN ₃ O ₂ S)2H ₂ O	47.10 (47.03)	3.42 (3.38)	7.43 (7.48)	5.65 (5.70)	14.26 (14.23)	10.57 (10.50)	93.00
06	Ni(L ²)2H ₂ O Ni(C ₂₂ H ₁₅ BrN ₃ O ₂ S)2H ₂ O	47.09 (47.05)	3.45 (3.39)	7.52 (7.49)	5.76 (5.70)	14.31 (14.24)	10.40 (10.46)	85.02
07	Cu(L ²)2H ₂ O Cu(C ₂₂ H ₁₅ BrN ₃ O ₂ S)2H ₂ O	46.58 (46.65)	3.42 (3.35)	7.36 (7.42)	5.63 (5.65)	14.07 (14.12)	11.17 (11.22)	93.40
08	Zn(L ²)2H ₂ O Zn(C ₂₂ H ₁₅ BrN ₃ O ₂ S)2H ₂ O	46.55 (46.50)	3.37 (3.34)	7.46 (7.39)	5.69 (5.63)	14.12 (14.06)	11.25 (11.18)	92.32

The values shown in the parenthesis are calculated ones.

Three bands are seen at 14735.81 cm^{-1} , 18155.21 cm^{-1} , and 32260.06 cm^{-1} in this study, which can be assigned to the transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ respectively. According to these findings, the Cu(II) complexes have six-coordinated octahedral structure. In the IR spectra of ligands 2-[[4-(5-bromo thiophen-2-yl)-6-phenyl pyrimidin-2-yl] carbonimidoyl] phenol [HL^1] and 2-[[4-(5-bromo thiophen-2-yl)-6-phenyl pyrimidin-2-yl] carbonimidoyl]-5-methoxyphenol [HL^2] and their complexes, The azomethine group found in the Schiff bases is attributed to the significant absorption in the 1620 cm^{-1} region. The azomethine group[20] in metal complexes is moved to a lower frequency in the range $1600 - 1580\text{ cm}^{-1}$. The appearance of a new band around this region $1618 - 1610\text{ cm}^{-1}$ due to $\nu_{C=N}$ [21] adds to this. The C=N changes to a higher frequency area in the present complexes, showing that azomethine nitrogen is involved in coordination. The spectrum of the base ligands HL^1 and HL^2 displayed a medium intensity band (O-H), which is absent from the complexes spectrum, of 3364 cm^{-1} and shows that the base ligands HL^1 and HL^2 were deprotonated before coordination by the oxygen atom. In ligands, HL^1 and HL^2 a medium intensity band is observed in the range of $1090-950\text{ cm}^{-1}$ are assigned to the $\nu_{(C-S)}$ vibrations[22], In complexes these bands are shifted to lower frequency due coordination through S atom to central metal. Metals have respectively heavy mass and M-S and M-O bonds have low bond order and hence the group vibration due to these occurs in the far infrared region. Based on the literature data in the present study the complexes of ν_{M-S} vibration occur in the region $540-490\text{ cm}^{-1}$ and ν_{M-O} occur in the region $450-400\text{ cm}^{-1}$ have been assigned[23]. 1H NMR spectra of ligands HL^1 and HL^2 shows two singlets $2.20\text{ }\delta(\text{ppm})$ at $3.83\text{ }\delta(\text{ppm})$ methoxy (OCH_3) protons. But the ligands also shows a multiplet at $6.90-7.56\text{ }\delta(\text{ppm})$ due to aromatic protons. In the complexes the multiplet observed between $6.66 - 7.25\text{ }\delta(\text{ppm})$ due to aromatic protons and the signals at $3.62 - 3.77\text{ }\delta(\text{ppm})$ are due to methoxy protons, were shifted to down field due to the complexation through oxygen and S of thiophene group and nitrogen of C=N group. A signal at $11.40 - 11.51\text{ }\delta(\text{ppm})$ due to resonance acting of phenolic OH protons, in complexes these signals were absent due to complexation through oxygen of phenolic OH group were shifted to down field due to the complexation through nitrogen of C=N and S of thiophene group to the metal ion respectively. ESR studies of the complex have been made. The magnetic parameters have been evaluated from the spectra and $g_{\parallel} > g_{\perp}$ observed in the g^{\prime} values suggests the presence of an unpaired electron in the $d_{x^2-y^2}$ orbital[24]. Based on these observations copper(II) complex may have octahedral geometry. The covalent character of the metal-ligand relation has a g value less than 2.3 and larger than 2.3 for ionic character has been reported by Kivelson and Neiman[25]. $Cu(L^2)2H_2O$, complex has a g value of 2.47 in this study, indicating that the metal-ligand interactions are more ionic in nature. The powder x-ray diffraction for $Cu(C_{21}H_{13}BrN_3OS)2H_2O$ have been studied. It is seen that the complexes consists of some reflections between $8 - 69^{\circ}$ (2θ). In Bragg's relation, interplanar spacing(d), is computed using the locations of the intense peak ($n\lambda = 2d \sin \theta$), where λ is the wavelength of the x-ray utilised ($Cu\text{ k}\lambda = 1.54056\text{ \AA}$). The calculated spacing together with relative intensities with respect to most intense peaks are recorded in table. All main peaks have index[26] and their $\text{Sin}^2 \theta$ values are compared with the calculated values. The comparison of these values reveals that there is good agreement with the calculated and observed values. The complex shown broad peaks indicates that amorphous nature of the complexes. On the basis of elemental analysis, magnetic susceptibility, conductivity, electronic, IR, 1H NMR, ESR spectral data and powder X-ray powder diffraction observations indicated the tentative structures of these complexes for the coordination number six having octahedral geometry have been proposed.

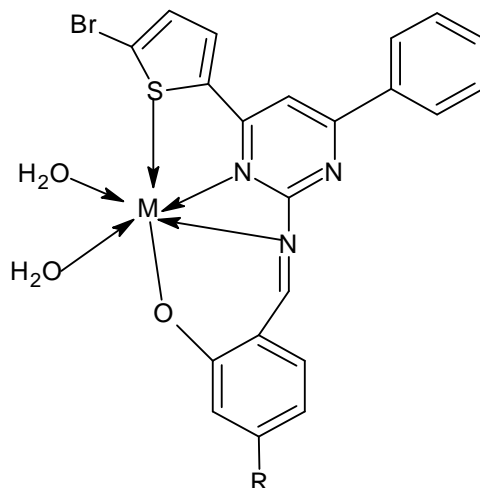


Fig.2. Proposed structure of complexes, where M= Co(II), Ni(II), Cu(II) and Zn(II)

A. Determination of stability constant of Cu(II) complexes by spectrophotometric method:

- 1) *Determination of λ_{max}* : A solution of (10^{-2} M) Cu (II) is mixed a solution of (10^{-2} M) ligands 2-{{[4-(5-bromo thiophen-2-yl)-6-phenyl pyrimidin- 2-yl] carbonimidoyl} phenol [HL¹] and 2-{{[4-(5-bromo thiophen-2-yl) -6- phenyl pyrimidin-2-yl]carbonimidoyl}-5-methoxyphenol [HL²] solution a distinct greenish colored complexes are formed. The absorbance at 5nm wavelength interval of the complex solutions were measured in the visible range at [350-750nm], it is found that both the complexes having maximum absorbance (λ_{max}) at 535nm.
- 2) *Effect of pH*: The following method was used to investigate the effect of pH on the colour intensity of the reaction mixture. In a 25 ml standard flask, 1 ml of copper(II) solution (1×10^{-3} M) and 10 of buffer solution of known pH (Range 1 to 10) and 1 ml of HL¹ and HL² (1×10^{-2} M) solutions were taken and diluted up to the mark with distilled water. The absorbance of the reaction mixture was measured at 535nm at different p^H and plot the graph absorbance versus p^H, It is found that maximum absorbance at p^H = 5. In view of the above reasons the author has selected a pH of 5 for further studies[27].
- 3) *Job's method*: Prepare a series of solutions, copper(II) penthydrate sulphide standard solution 0 to 40×10^{-4} M was pippered into seven volumetric flasks and the mole ratio was maintained by adding an aliquot of 40×10^{-4} to 0 M HL¹ and HL², respectively. All measurements were made at 3 different temperatures at 535 nm, i.e. 30, 35 and 40 °C. The curve revealed a maximum of $\chi_{metal} = 0.5$ in a mole fraction indicating the development of a complex with aratio of 1:1 metal to ligand[28]. The following is the Job's approach equation used in this study:

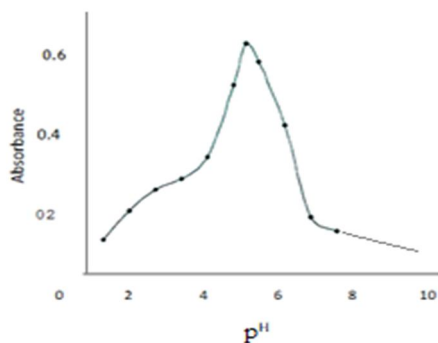


Fig 3: Effect of pH on absorbance

$$K_f = \frac{[ML]}{[m][L]}$$

$$K_f = \frac{A_2 / A_1}{[1 - A_2 / A_1] \times [C_L - C_M \times A_2 / A_1]}$$

Where, A₁ = absorbance at break point, A₂ = actual absorbance, C_M = concentration of metal, and C_L = concentration of ligand.

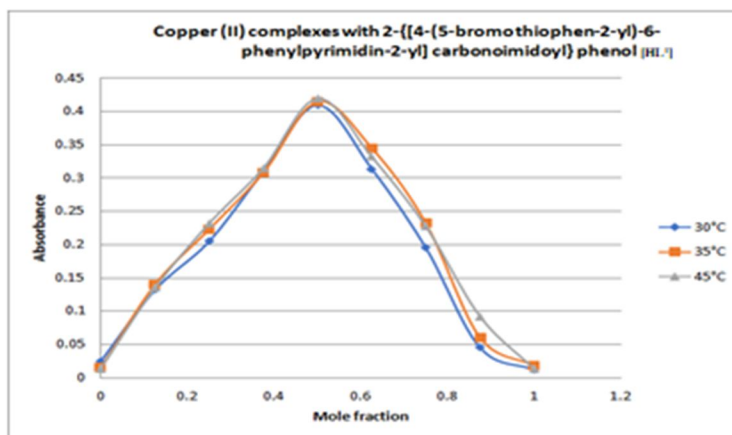


Fig. 4: Representative Job's curves of equimolar solutions of Cu(II) complexes with (HL¹) at 30°C, 35°C and 40°C

4) **Mole Ratio Method:** By using the mole ratio method[29], at constant Cu (II) concentration (20×10^{-4}) and varying HL^1 and HL^2 concentrations (0 to 40×10^{-4}) at 535nm and at these three temperatures, a sharp bands were observed at 1:1mole ratio of HL^1 and HL^2 with Cu(II). A graph is plotted between HL^5 and HL^6 ligands volume and the absorbance (Fig.5.). Mole ratio method also confirms that the ratio between the metal ion and the reagent is 1:1(M:L). The corresponding equation for mole ratio method is as follows:

$$K_f = \frac{\frac{A}{\epsilon b}}{\left[C_M - \frac{A}{\epsilon b} \right] \times \left[C_L - \frac{A}{\epsilon b} \right]}$$

Where ϵb = molar absorptivity constant, and A = absorbance at peak point. The stability constant has been determined using Job's and mole ratio approaches, based on the data provided[30-31], and the mean value of K_f obtained using two separate approaches is in fair agreement (Table-2).

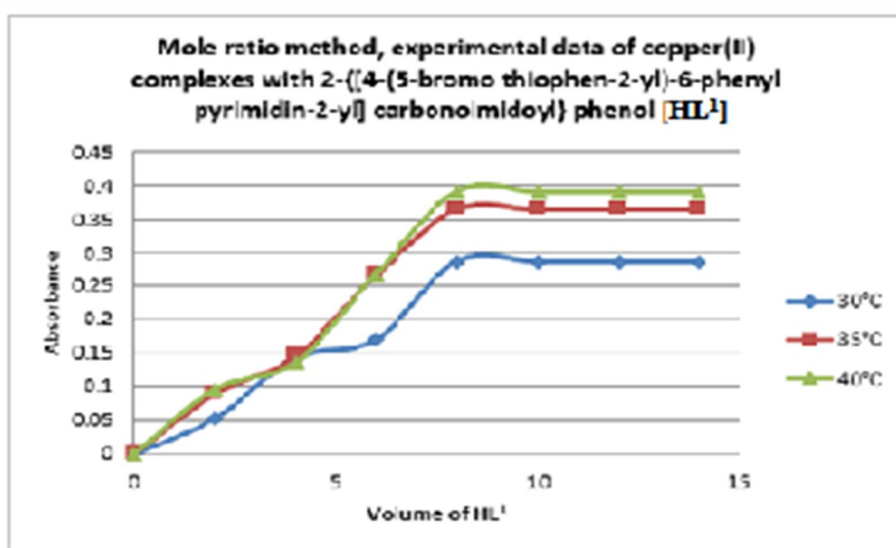


Fig. 5.: Representative Mole ratio curves for Copper(II) complexes with HL^1 at $30^\circ C$, $35^\circ C$ and $40^\circ C$

Table 2: Metal-ligand formation constants calculated from Job's continuous variation method and mole ratio method at $30^\circ C$, $35^\circ C$ and $40^\circ C$ and P^H of 5 ± 0.05

S.No	Methods	Metal: Ligand	Formation Constants at temperatures		
			$25^\circ C$	$35^\circ C$	$45^\circ C$
1	Job's method	1:1	13.06×10^4	14.51×10^4	10.40×10^4
a.	Copper(II) complexes with (HL^1)				
b.	Copper(II) complexes with (HL^2)	1:1	13.18×10^4	15.06×10^4	11.23×10^4
2	Mole ratio method	1:1	0.24×10^4	0.57×10^4	0.77×10^4
A	Copper(II) complexes with (HL^1)				
B	Copper(II) complexes with (H_2L^2)				

B. Antimicrobial Activities

Both the investigated ligands, of 2-{{4-(5-bromo thiophene-2-yl)-6-phenyl pyrimidin-2-yl} carbon imidoyl} phenol [HL¹] and 2-{{4-(5-bromo thiophene-2-yl)-6-phenylpyrimidin-2-yl}carbonimidoyl}-5-methoxyphenol [HL²] and their metal complexes were screened for their antibacterial and antifungal activity by cup plate method, at different concentrations in DMSO solvent by minimum inhibitory concentration (MIC) method. Antibacterial activity in opposition to *Escherichia coli* and *Staphylococcus aureus* and Antifungal activity in opposition to *Aspergillus niger* and *Cladosporium* were carried out. A normal drugs gentamycine and fluconazole were also tested for their antibacterial and antifungal activity at the same concentration under the circumstances analogous to that of the test compound. The results (given in Table-3) suggest that the among all the complexes Cu(II) complexes have exhibited good bacterial and fungal activities which is due to the faster diffusion of the Cu(II) complexes[32-33], whereas, ligands (HL¹) and (HL²) have shown moderate activity.

Table 3: The antimicrobial activity of ligands and their Co (II), Ni(II), and Cu(II) complexes evaluated by (mm).

Ligands / Complexes	Zone of inhibition in mm			
	Antibacterial activity		Antifungal activity	
	<i>Escherichia Coli</i>	<i>Staphylococcus Aureus</i>	<i>Aspergillus Niger</i>	<i>Cladosporium</i>
HL ¹	13	12	14	13
Co(II) with HL ¹	18	17	15	17
Ni(II) with HL ¹	16	18	16	18
Cu(II) with HL ¹	24	22	23	24
HL ²	15	17	17	18
Co(II) with HL ²	15	14	13	14
Ni(II) with HL ²	16	17	19	16
Cu(II) with HL ²	15	18	17	17
Gentamycine	22	23	24	22
Fluconazole	18	16	16	17

C. Antioxidant Activity

The utilization the stable free radical diphenylpicrylhydrazyl is one such approach that is currently popular (DPPH)[34]. This approach is based on the creation of the non-radical form DPPH-H when DPPH is reduced in methanol solution in the presence of a hydrogen donating antioxidant[35]. Therefore, the present study has been carried out to assess the antioxidant activity of the newly synthesized Co(II), Ni(II), Cu(II) and Zn(II) metal complexes of the Schiff's base ligands 2-{{4-(5-bromothiophen-2-yl)-6-phenylpyrimidin-2-yl}carbon imidoyl} phenol [HL⁵] and 2-{{4-(5-bromothiophen-2-yl)-6-phenylpyrimidin-2-yl} carbon imidoyl}-5 methoxyphenol [HL⁶].The ligands and their complexes were diluted in methanol to a final concentration of various stock solutions (mg/ml), 2.5 ml of test solution of various concentrations was added to 1 ml of DPPH solution (0.1 mmol) and allowed to react at room temperature. The absorbance was measured at 517 nm after 30 minutes, using butylated hydroxyl anisole (BHA) as standards. On the y-axis, percentage scavenging effects were plotted, and on the x-axis, concentration (g/ml)[36]. The results of DPPH scavenging activity both the ligands and their metal complexes were presented in figure-6.The analysis revealed that metal complexes of Co(II), Ni(II), Cu(II), and Zn(II) scavenge DPPH more efficiently than ligands, implying that they have better free radical scavenging and antioxidant characteristics.

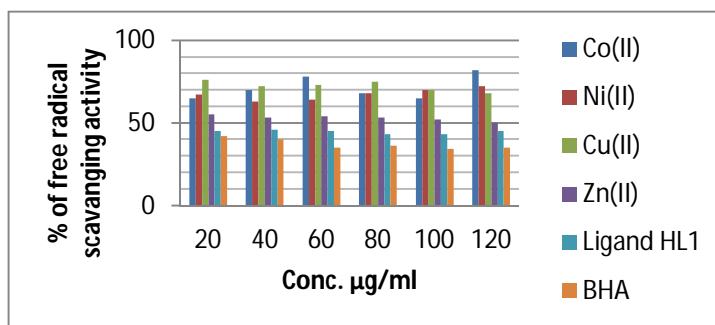


Fig. 6. Antioxidant results of ligands 2-{{4-(5-bromo thiophene-2-yl)-6-phenyl pyrimidin-2-yl} carbon imidoyl} phenol [HL¹] and their metal (II) complexes

IV. CONCLUSION

A few complexes of 2-[[4-(5-bromo thiophen-2-yl)-6-phenyl pyrimidin-2-yl] carbonimidoyl] phenol [HL¹] and 2-[[4-(5-bromo thiophen-2-yl) -6- phenyl pyrimidin-2-yl]carbon imidoyl]-5-methoxyphenol [HL²] with first row transition metal ions have been reported in this chapter. These complexes analyze for the stoichiometry of the type (1:1) [M(L)]2H₂O. The conductivity data shows the electrolytic nature of these complexes. The magnetic susceptibility measurements obtained at room temperature for Co(II), Ni(II) Cu(II) complexes agrees with the spin only values. The electronic, IR, ¹H NMR, ESR spectral data and X-ray diffraction data suggest that Co(II), Ni(II), Cu(II) and Zn(II) complexes with ligands (HL¹ and HL²), exhibit coordination number six. The formation of copper(II) complex with ligands has been studied spectrophotometrically at an absorption maximum of 535 nm at different temperatures. The data shows that copper(II) and (HL¹) and (HL²) combine in the molar ratio of 1: 1 at p^H 5.0. The stability constants of the complexes were calculated to be 13.06×10⁴, 14.51×10⁴ and 10.40×10⁴ and 13.18×10⁴, 15.06×10⁴, 11.23×10⁴ for (H₂L¹) and (H₂L²) respectively by Jobs continuous variation method and 0.24×10⁴, 0.57×10⁴, and 0.77×10⁴ and 0.28×10⁴, 0.55×10⁴, 0.79×10⁴ for (HL¹) and (HL²) respectively by mole ratio method at 30, 35 and 40°C, respectively. The results of antimicrobial activity data suggest that the among all the complexes Cu(II) complexes have exhibited good bacterial and fungal activities which is due to the faster diffusion of the Cu(II) complexes, whereas, ligands (HL¹) and (HL²) have shown moderate activity. Antioxidant analysis results of DPPH scavenging activity both the ligands and their metal complexes were studied. The analysis revealed that metal complexes of Co(II), Ni(II), Cu(II), and Zn(II) scavenge DPPH more efficiently than ligands, implying that they have better free radical scavenging and antioxidant characteristics.

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