



Synthesis, characterization, antimicrobial and antioxidant activity of 2-hydroxy-4-methoxybenzaldehyde-4-phenylthiosemicarbazone and its Pd(II), Ni(II) and Cu(II) complexes having heterocyclic bases

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ABSTRACT

The Schiff base ligand 2-hydroxy-4-methoxybenzaldehyde-4-phenylthiosemicarbazone (HMBPTSC) and its Pd(II) complex was presented. The Cu(II) and Ni(II) mixed ligand complexes with HMBPTSC, heterocyclic bases (2,2-bipyridyl, 1,10-phenanthroline) and bisdiphenylphosphinomethane respectively were reported. The ligand and metal complexes were characterized by LCMS, NMR and FT-IR & UV-Vis studies which clearly indicated the formation of metal complexes. EPR spectral studies were carried out for Cu(II) complexes, and single crystal XRD studies were presented for the Ni(II) complex. The results revealed that Cu(II) complexes were of elongated tetragonal and Ni(II) and Pd(II) were of square planar geometry. The ligand HMBPTSC and all the prepared complexes were tested for their biological activities. The evaluated antimicrobial, antifungal, and antioxidant activity of the ligand and metal complexes were compared with the standard drugs.

Keywords- Antimicrobial, Antioxidant activity, 2-hydroxy-4-methoxybenzaldehyde, heterocyclic bases.

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INTRODUCTION

The chemistry of thiosemicarbazones has received huge attention given their variable binding modes as ligands in coordination chemistry leading to diverse molecular structures, promising biological implications and ion-sensing ability [1–3]. Thiosemicarbazones are now well established as an important class of sulfur donor ligands particularly for transition metal ions [4–6]. The metal complexing ability of the thiosemicarbazones with transition metals made the complexes remarkable in showing biological activities. These compounds present a great variety of biological activities ranging from antiviral [7] to anticancer [8], antitumor [9,10], antibacterial [11–13], anti-inflammatory and antiamebic [14–16] activities. The inhibitory action of these compounds is attributed to their chelating properties [17]. The activity of these compounds is strongly dependent upon the nature of the hetero atomic ring and the position of attachment of thiosemicarbazone group to the ring as well as the form of thiosemicarbazone moiety [18]. These compounds are studied extensively due to their flexibility, their selectivity and sensitivity towards the central metal atom, their structural similarities with natural biological substances and the presence of imine group(–N CH–) which imparts the biological activity [19]. Collins *et al.* have reported the correlation between structure and anti-mycobacterial activity in a series of 2-acetylpyridinethiosemicarbazones [20]. In many cases, due coordination to different transition metal ions that can be found in biological systems, it is possible to obtain complexes that are more efficient drugs than the corresponding free ligands [21–24]. In recent thermodynamic studies of some metal complexes, potentiometric methods were used. Also the coordination chemistry and biological activity and analytical application, thiosemicarbazides and thiosemicarbazones, as well as their metal complexes have been the subject of many studies [25]. We now report the synthesis and spectral characterization of Pd(II), Ni(II), Cu(II)bipy and Cu(II)phen complexes containing 2-hydroxy-4-methoxybenzaldehyde-4-phenyl thiosemicarbazone as the primary ligand. The ligand used in the study is depicted in Scheme 1.

EXPERIMENTAL

Materials: All the chemicals used were of analytical grade and used without further purification for the preparation of the free ligand (HMBPTSC) as well as metal complexes. 2-hydroxy-4-methoxybenzaldehyde, 1,10-phenanthroline (phen), bis(diphenyl) phosphine methane (PPh₂-CH₂-PPh₂) and palladium (II)

chloride were purchased from Sigma–Aldrich. 4-phenyl-3-thiosemicarbazide was purchased from Alfa Aesar chemicals. Copper (II) acetate, nickel (II) chloride and 2,2-bipyridyl (bipy) were purchased from Sd-fine chemicals.

Synthesis of ligand: Hot ethanolic solution of 0.01 mol/2.12 g of 2-Hydroxy-4-methoxybenzaldehyde is mixed with hot ethanolic solution of 0.01mol/1.67g of 4-phenyl-3-thiosemicarbazide. The mixture obtained is refluxed for an hour and then stirred for 5 h at 60–70 °C. The reaction was monitored by thin layer chromatography (TLC) and set aside to attain room temperature. The obtained yellow colored precipitate was filtered and washed with ethanol and dried under vacuum with anhydrous P₄O₁₀. The synthesis scheme is shown in **Scheme 1**. Yellow colored solid: M.P: 202 °C; ¹H NMR: (400 MHz) δ (ppm) DMSO-d₆: δ 10.36 (1H, s, NH); 9.69 (1H, s, NH), δ 8.35(1H, s, -OH), δ 8.10 (1H, s, H-C=N), 7.56 (2H, d, J= 8.0 Hz, Ar-H) 7.42 (2H, d, J= 8.0 Hz, Ar-H), 7.30(1H, t, J= 8.0 Hz, Ar-H), 7.17 (1H, d, J= 8.0 Hz, Ar-H), 6.55-6.51 (2H, m, Ar-H): ¹³C NMR (400 MHz) δ (ppm) CDCl₃-d₃: δ 175.07, 163.45, 159.44, 148.15, 137.44, 133.20, 128.96, 126.76, 125.20, 110.34, 107.77, 101.43, 55.56.

Synthesis of metal complexes

Synthesis of Pd (II) complex: HMBPTSC (0.0602g, 0.0002 mol) and metal chloride, PdCl₂ (0.0177g, 0.0001 mol) were dissolved in hot methanol (30mL) and the mixture was refluxed for 6 h. After cooling the reaction mixture to room temperature (≈ 30 °C), the obtained brown color solution was further evaporated to yield brown color precipitate of corresponding Pd(II) complex.

Synthesis of Ni (II) complex: To a solution of HMBPTSC (0.0602g, 0.0002 mol) in acetonitrile solid NiCl₂.6H₂O salt (0.0474g, 0.0002 mol) was added followed by the addition of Et₃N base (3mL) and the mixture was stirred for 1h. To this mixture solid PPh₂-CH₂-PPh₂ (0.768g, 0.002 mol) was added and further stirred for 4h. The clear red colored solution was allowed to evaporate at room temperature which yielded red crystals along with formation of Et₃NH⁺Cl⁻ salt.

Synthesis of [Cu (II) (bipy/phen)] complex: To a solution of HMBPTSC (0.002 mol, 0.602 g) in hot ethanol was added an ethanolic solution of Cu(OAc)₂.2H₂O (0.002 mol, 0.398 g) with constant stirring. After 5h the heterocyclic base (0.002 mol, bipy/ phen) was added in solid form. The stirring was continued for another hour. The green colored compound that formed was filtered, washed with cold ethanol and ether and then dried.

Physical measurements: NMR spectrum was recorded with BRUKER Biospin AG-400 MHz (School of Chemistry, University of Hyderabad) using DMSO-d₆ as a solvent. Mass spectrum of the ligand was recorded in a Quattro LC-Micro mass. Elemental analyses (CHN) were performed by using FLASH 1112 series. FT-IR spectra (KBr pellet) were recorded in the region 4000-400 cm⁻¹ on a FT-IR spectrum Thermo Scientific Nicolet-380 spectrophotometer. The electronic spectra were recorded with the help of a UV Shimadzu 3600 spectrometer. BRUKER-ER073 instrument equipped with an EMX micro X source was used to record EPR spectra of polycrystalline samples at 298K.

Biological studies

Collection of microorganisms: *Bacillus subtilis* (B. subtilis), *Escherichia coli* (E. coli), *Pseudomonas fluorescens* (P. fluorescent), *Staphylococcus aureus* (S. aureus) and fungal cultures of (*Aspergillus niger*, Penicillin, A. Davis and A. Mucor) were obtained from Institute of Microbial Technology (IMTECH), Chandigarh and Department of Biochemistry, Sri Venkateswara University, Tirupati, India were used for antimicrobial test organisms. The bacteria were maintained on nutrient broth (NB) at 37 °C, and fungus was maintained on Potato dextrose agar (PDA) at 28 °C.

Antimicrobial activity: The antimicrobial activity of different compound was describing using agar diffusion method according to Goni *et al.* (2009) with modifications each sterile Petri plate (90 mm) was prepared with 20 ml nutrient agar and PDA medium after solidifying, 100 µl of bacterial suspension was spread on the plates. After 5 minutes, a sterile filter paper disc (6 mm) containing 5 µl of compound was placed on the surface of plate. Afterwards the microbial plates were incubated at 37 °C for 24 hours for bacterial growth and 28 °C for 48 hours for fungal growth. The antimicrobial activity of different compound was expressed by measuring the diameter of inhibition zone (DIZ). Streptomycin and fluconazole drugs were served as reference drugs. The zone of inhibition was measured (Diameter in mm)

Anti-Oxidant activity: The hydrogen atom or electron donation ability of the compounds was measured from the purple colored methanol bleaching solution of 1, 1-diphenyl-1-picrylhydrazyl (DPPH). The spectrophotometric assay uses the stable radical DPPH as a reagent. 1 ml of various concentrations of the test compounds (25, 50, 75, and 100 µg/mL) in methanol was added to 4 ml of 0.004% (w/v) methanol solution

of DPPH. After a 30 min incubation period at room temperature, the absorbance was read against blank at 517 nm. The percent of inhibition (I %) of free radical production from DPPH was calculated by the following equation:

$$\% \text{ of scavenging} = \frac{(\text{A control} - \text{A sample})}{(\text{A control})} \times 100$$

Where A control is the absorbance of the control reaction (containing all reagents except the test compound) and A sample is the absorbance of the test compound. Vitamin-c was used as a reference. Tests were carried in triplicate.

RESULTS AND DISCUSSION

Crystal structures studies: The crystal structure of Ni complex was presented in **Fig. 1**. The crystallographic data of compound was given in **Table 1**. The complex crystallizes in the monoclinic P2(1)/c space group and single crystal X-ray diffraction analysis reveals that the asymmetric unit consists of one complex molecule and unit cell comprises four molecules. In the complex the Ni(II) metal ion was centered in distorted ONSP square planar coordination sphere comprised of one PPh₂-CH₂-PPh₂ ligand and one ONS donor HMBPTSC ligand. The bond distances Ni – O (1.839 Å), Ni – S (2.036 Å), Ni – N (1.889 Å) and the Ni – P (2.208 Å) are very consistent with the values reported for similar kind of compounds [26]. The ONS donor Schiff-base forms a six membered and one five membered chelate rings and these chelate rings are fused. The chelate bite angles are also comparable with the similar structures reported in the literature [26].

NMR and Mass spectra of HMBPTSC: ¹H NMR and ¹³C NMR spectra of HMBPTSC are recorded in DMSO-d₆ solution. ¹H NMR and ¹³C NMR spectra of HMBPTSC are given in **Fig. 2** and **Fig. 3** respectively. The data analysis represented as follows. The proton of N-H functionality attached to azomethine resonates at 10.36 ppm. The signal at 9.68 ppm is corresponds to the proton of N-H group lies in between phenyl and C=S groups. The phenolic OH proton shows a singlet at 8.35 ppm. The proton attached to azomethine moiety resonates at 8.10 ppm. The signals appear in the range 6.51 – 7.56 ppm are attributed to eight aromatic protons. ¹³C NMR signal are very consistent to the number of carbons present in the compound. The signal appeared at 175.07 ppm is corresponding to C=S carbon center. The azomethine carbon displays a signal at 163.45 ppm. The aromatic carbons show signals in the range 101.43 – 159.44 ppm. The carbon atom belongs methoxy group resonate at 55.56 ppm as expected. The ESI mass spectrum of HMBPTSC is represented in **Fig. 4**, showed a molecular ion peak

at $m/z = 302.09$ corresponding to species ($C_{15}H_{15}N_3O_2S$) which confirms the proposed molecular formula.

FT-IR spectral studies: The FT-IR spectra of HMBPTSC and its complexes were presented in the Fig. 5. The significant FT-IR spectral bands (cm^{-1}) along with assignments of HMBPTSC and its Pd (II), Ni(II) and Cu(II)-bipy, Cu(II)-phen complexes are presented in Table 2. Presence of thioamide moiety (-HN-C(S) NH) of free HMBPTSC in thione form was confirmed by the absence of bands in the range $2500-2600\text{ cm}^{-1}$ [27]. The strong IR band present in the spectra of HMBPTSC at 1628 cm^{-1} is corresponding to the azomethine group $\nu(HC=N)$. Where as in the spectra of Pd(II), Ni(II), Cu-bipy and Cu-phen metal complexes the band appears at 1610 cm^{-1} , 1606 cm^{-1} , 1604 cm^{-1} and 1602 cm^{-1} respectively. The shift of this band to a lower frequencies clearly suggesting the participation of azomethine nitrogen in the coordination to the metal ions [28-29]. The band corresponding to C=S functional group of free HMBPTSC appears at 1035 cm^{-1} , but in the complexes 750 cm^{-1} , 815 cm^{-1} , 804 cm^{-1} , 842 cm^{-1} Pd (II), Ni(II) and Cu(II)-bipy, Cu(II)-phen complexes the band was appeared and indicating that the coordination of thione sulfur with metal ion [30-31]. In the spectra of complexes new bands observed at 414 cm^{-1} , 430 cm^{-1} , 432 cm^{-1} , 423 cm^{-1} are assigned to $\nu(Pd-M)$, $\nu(Ni-M)$, (Cu(II) bipy-M), $\nu(Cu(II)\text{ phen-M})$ respectively.

Electronic absorption spectra: Electronic spectra of HMBPTSC and its corresponding complexes of Cu(II) and Pd(II) were recorded in their methanolic solutions whereas Ni(II) complex was recorded in acetonitrile solution. The absorption patterns of the ligand is comparable with similar types of thiocarbazones reported [32] and display a group of bands at 257, 295, 304 nm corresponding to $\pi - \pi^*$ transition and band observed at 350 nm is attributed to $n - \pi^*$ transition. All the complexes display similar bands corresponding to Intra-ligand transitions below 350nm and an expected blue shift was observed when compared to ligand. The Cu(II)bipy and Cu(II)phen complexes display a broad band with considerable intensity in the range 388 – 404nm corresponding to Ligand to Metal Charge Transfer transitions (Fig. 6.) [26]. The Ni(II) complex with $PPh_2-CH_2-PPh_2$ as ancillary ligand and Pd(II) complex is shown Fig. 7 and Fig. 8 are also show a similar kind of absorption bands compared to Cu(II) complexes in the region of 375 – 408nm, which are also attributed to Ligand to Metal Charge Transfer transitions.

Electron paramagnetic resonance (EPR) spectrum: EPR spectra of Cu(II) complexes of 2-

Hydroxy4-methoxybenzaldehyde-4-phenylthiosemicarbazone were recorded in polycrystalline form, on X band at frequency of 9.68GHz under the magnetic-field strength of 3200G. Room temperature X-band EPR spectra of (Cu(II) bipy complex-1 and Cu(II) phen complex-2 are presented in Fig. 9 and Fig. 10 respectively. The spectrum of Cu(II) bipy complex-1 is a superposition of a very broad component due to strong dipole-dipole interactions. From the EPR spectrum of Cu(II) bipy complex-1, it is observed that the characteristic of mononuclear copper complexes with axial symmetry, and lacks the hyperfine splitting like concentrated solid Cu(II) complexes. The analysis of spectra gives $g_{\perp}=2.094$ and, $g_{\parallel}=2.130$ and $g_{\perp}=2.094$ values for the Cu(II) bipy complex-1 and Cu(II) phen complex-2 respectively [33]. The observed g_{\perp} values for the complexes are less than 2.3 indicate that covalent character of the metal ligand bond. The calculated g values provide valuable information on the electronic ground state of the ion. For g values, $g_{\parallel} > g_{\perp} > g_e$, the ground state of the ion is $d_{x^2-y^2}$ which suggests an elongated tetragonal symmetry. The exchange coupling interaction between two copper ions is obtained from the expression given by Hathaway.

$$G = (g_{\parallel} - 2.0023) / (g_{\perp} - 2.0023).$$

According to Hathaway, if $G > 4$, the exchange interaction is negligible, but $G < 4$ indicates considerable exchange interaction in the solid complexes. The complexes reported in this paper, given the “G” value is 1.392 i.e. $G < 4$ indicating the exchange interaction in the prepared Cu(II) phen complex-2.

Biological studies

Anti-microbial activity: Antibacterial activity of the ligand and its complex were tested against different gram positive and negative bacteria. The activities of the ligand and its complexes were compared with standard antibiotic Streptomycin. The minimum inhibitory concentration (MIC) is the lowest concentration of visible growth after overnight incubation. MICs are important in diagnostic laboratories to confirm the resistance of microorganisms to antimicrobial agents and also to monitor the activity of the new microbial agents. We used modified agar well diffusion method to measure the MIC values and tabulated in Table 3. The Ligand, Ni(II) and Pd(II) complexes showed a good effect against gram negative bacteria than gram positive. However, other compounds inactive against either of the organisms. Among the two complexes, Ni complex showed more activity against bacterial isolates. The reason for greater activity of complexes could be explained by Chelation theory [34]. According to the chelation theory, the polarity of the metal ion is found to be

reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups especially with sulfur and nitrogen donors. Finally, the growth of antibacterial activity for all compounds following in the order of Ni(II) > Pd(II) > ligand.

Antifungal activity: Antifungal activity of the ligand and its Cu(II) bipy, Cu(II) phen, Pd(II), Ni(II) complex were tested against three fungal strains. The activities of the ligand and its complexes were compared with standard antibiotic Fluconazole as given in **Table 4**. All the complexes showed the moderate activity against *A. niger* and *Rhizopus*. However, none of the complexes was effective against *A. flavus*. The mode of action may involve the formation of a hydrogen bond through the azomethine nitrogen atom with the active centers of the cell constituents in the fungi resulting in interference with the normal cell process [35-36].

Anti-Oxidant activity: DPPH method is a rapid, simple and inexpensive method to measure the antioxidant capacity of natural or synthesized compounds *in vitro*. The principle for the reduction in DPPH free radicals was that the antioxidant reacts with stable free radical DPPH and converts it to 1,1-diphenyl-2-picrylhydrazine. The ability to scavenge the stable free radical DPPH is measured by a decrease in the absorbance at 517 nm. The synthesized ligand and its complexes were

screened for a reduction in DPPH free radicals [37]. The free ligand exhibited comparative activity in DPPH scavenging as seen in the case of standard antioxidant Vit-c. All are the complexes showed good antioxidant properties as shown in the table. Moreover, Pd(II) complex showed the best antioxidant activity at any given concentration than Vit-c as shown in the **Fig .11** respectively.

Conclusion

In this study, we present the synthesis and characterization of HMBPTSC with coordinating through the sulfur and nitrogen atom forming metal complexes with Pd(II), Ni(II) and [Cu(II)bipy/phen]. The EPR and electronic spectral studies of the Cu(II) complex indicated tetragonal symmetry for the metal ion. The result of antibacterial activity all compounds clearly show that the biological behavior of Ni (II), Pd (II) and ligand exhibited considerable antibacterial activity. Pd(II) complex showed the moderate antioxidant activity.

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Scheme 1: Synthesis of ligand (HMBPTSC).

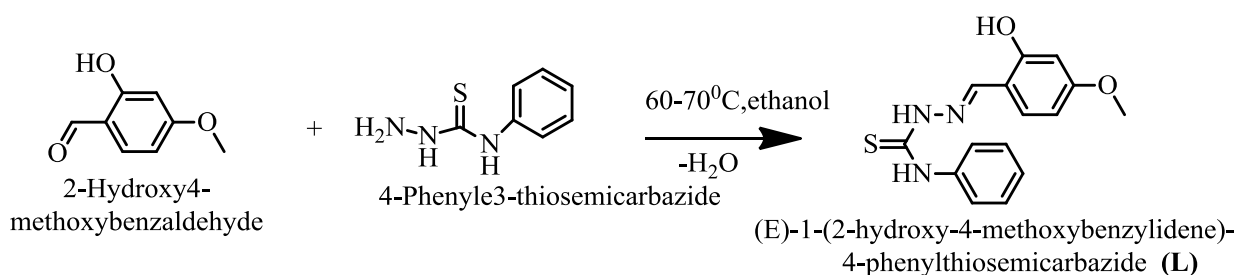


Table 1. Crystal data and structure refinement for Ni(II)HMBPTSC.

Empirical formula	C ₄₀ H ₃₅ N ₃ NiO ₂ P ₂ S
Formula weight	742.42
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/C
Unit cell dimensions	$a = 9.2094(18)$ Å $\alpha = 90^\circ$.
	$b = 16.213(3)$ Å $\beta = 96.08(3)^\circ$.
	$c = 24.057(5)$ Å $\gamma = 90^\circ$.
Volume	3571.8(12) Å ³
Z	4
Density (calculated)	1.381 Mg/m ³
Absorption coefficient	0.731 mm ⁻¹
F(000)	1544
Crystal size	0.3 x 0.4 x 0.5 mm ³
Theta range for data collection	2.51 to 27.74°.
Index ranges	-11 ≤ h ≤ 11, -21 ≤ k ≤ 21, -31 ≤ l ≤ 31
Reflections collected	78494
Independent reflections	8238 [R _(int) = 0.4036]
Completeness to theta = 27.74°	98.20%
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8238 / 0 / 447
Goodness-of-fit on F ²	1.015
Final R indices [I > 2σ(I)]	R ₁ = 0.0963, wR ₂ = 0.1368
R indices (all data)	R ₁ = 0.2338, wR ₂ = 0.1719
Largest diff. peak and hole	0.415 and -0.630 e.Å ⁻³

Table 2: IR values with assignments for the complexes.

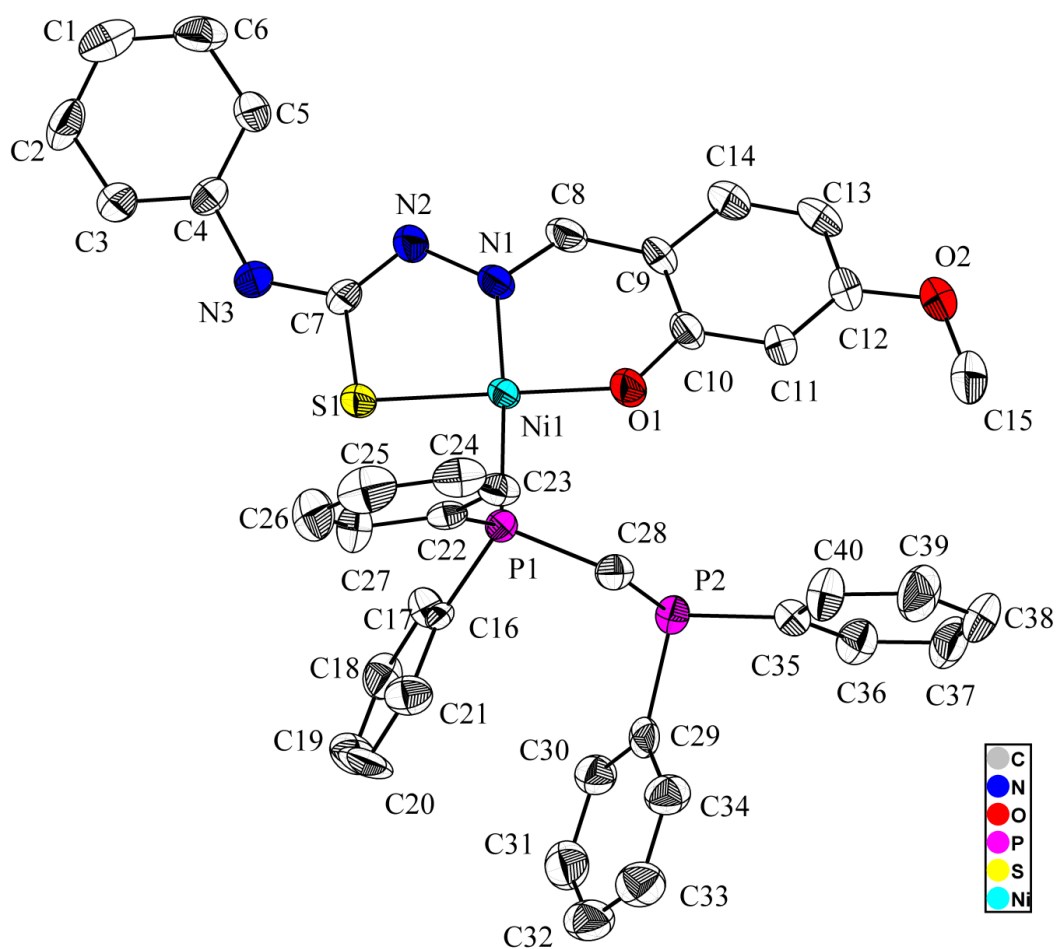
Ligand	Pd (II)	Ni(II) (P-C _{ph})	Cu(II) bipy	Cu(II) phen	Assignments
3147	3440	3404	3457	3402	ν _{sy} N-H
1628	1610	1606	1604	1602	ν(C=N)
1035	750	839	804	842	ν (C=S)
-	414	482	432	423	M-N

Table 3: Anti-bacterial activity of ligand and their Cu(II)bipy, Cu(II)phen, Pd(II) and Ni(II) complexes.

Compound	<i>B.subtilis</i>	<i>E.coli</i>	<i>P.fluorescens</i>	<i>K.pneumonea</i>	<i>S.aureus</i>
L	1.5	1.3	0	1.3	0
Cu(II) bipy	0	0	0	0	0
Cu(II) phen	0	0	0	0	0
Pd(II)	0.6	0	0	1.3	0.9
Ni(II)	1.9	1.0	0	1.5	0
Streptomycin	2.3	1.2	0.7	3.1	2.4

Table 4: Antifungal activity of of ligand and their Cu(II) bipy, Cu(II) phen, Pd(II) and Ni(II) complexes.

Compound	<i>A.niger</i>	<i>A.flavus</i>	<i>Rhizopus</i>
L	1.0	0	1.5
Cu(II) bipy	1.2	0	0
Cu(II) phen	0.9	0	0.6
Pd(II)	1.0	0	0.8
Ni(II)	1.4	0	1.7
Fluconazole	2.3	1.3	2.3

Figure 1. Molecular structure of complex Ni(PPh₂-CH₂-PPh₂)

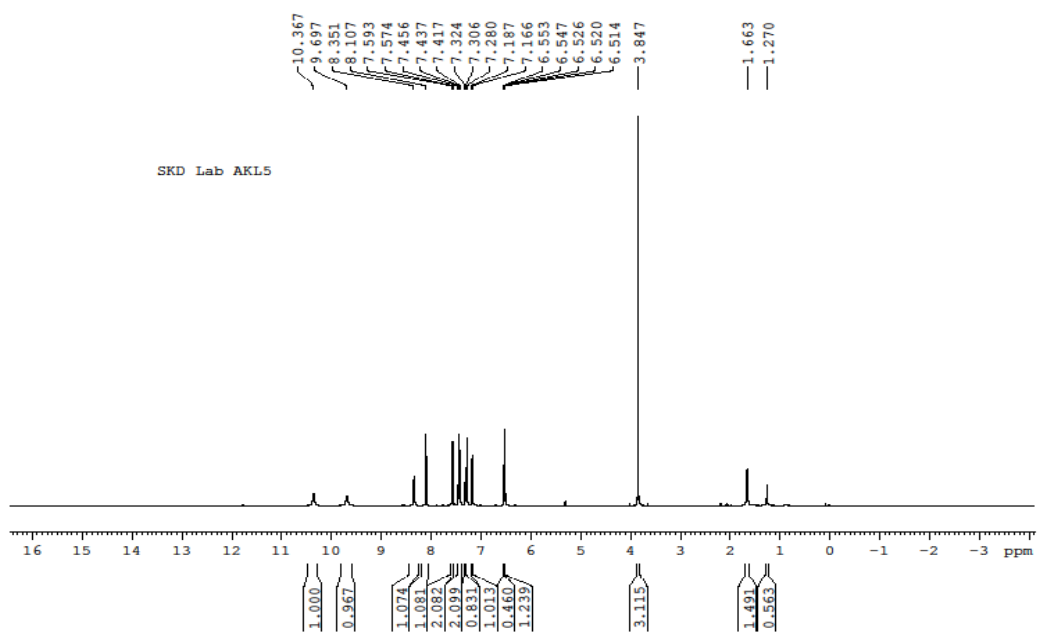


Figure 2 . ^1H NMR spectrum of the ligand

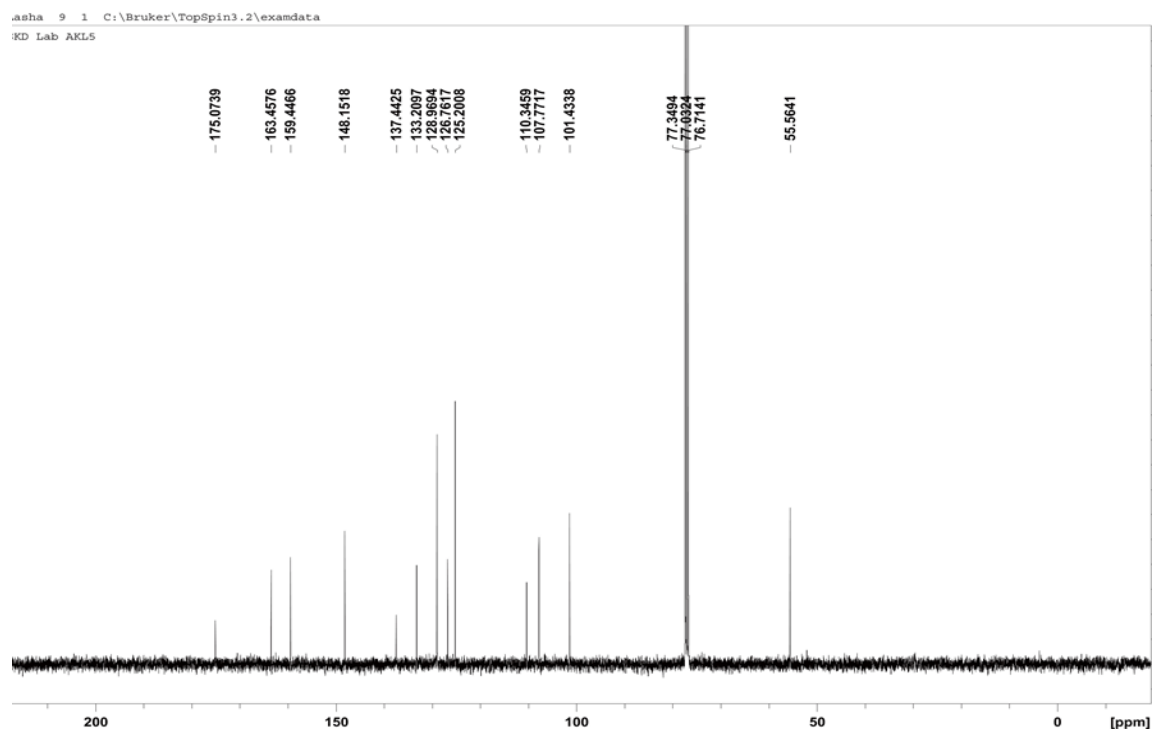


Figure 3 . ^{13}C NMR spectrum of the ligand

**LCMS-2010A DATA REPORT
SHIMADZU**

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 Inj. Volume : 5.000
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 Method Name : C:\LCMSsolution\User\Method\esi.qlm

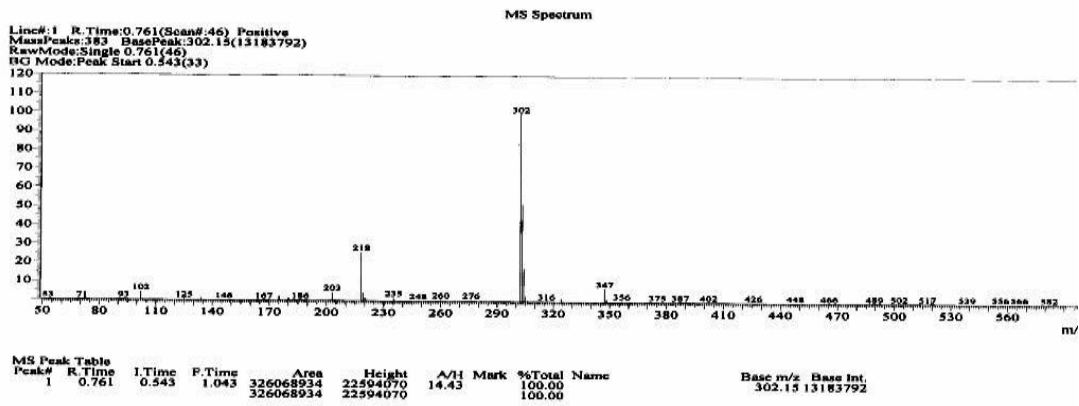


Figure 4. Mass spectrum of the ligand

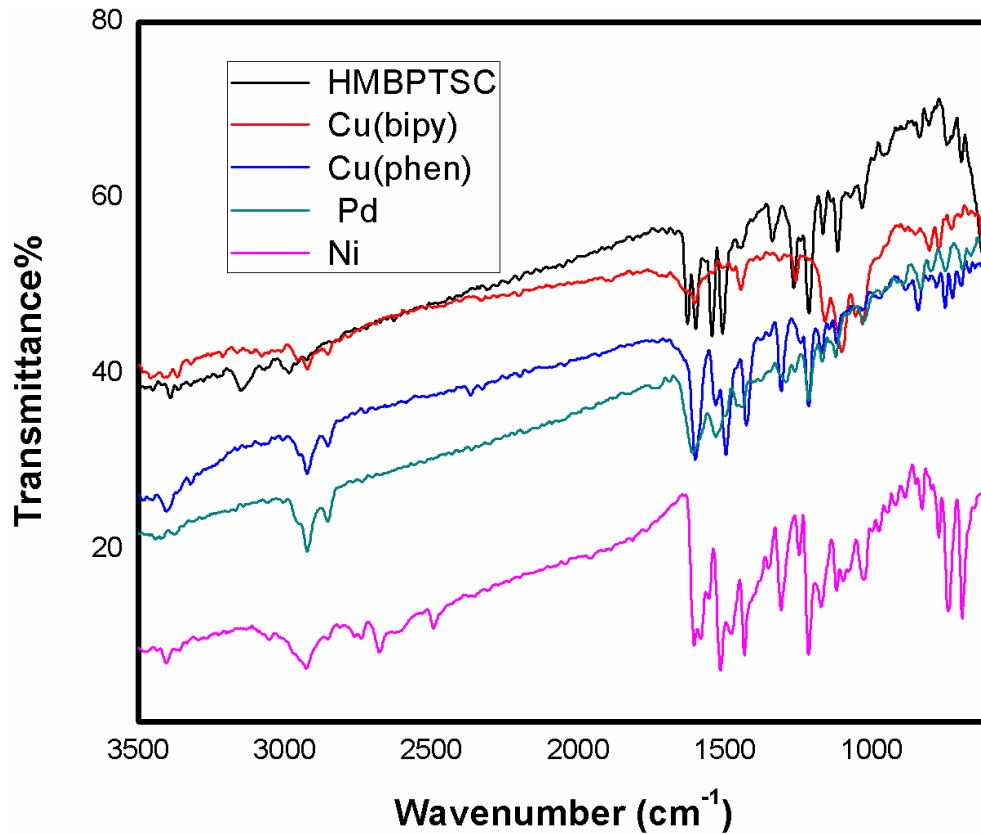


Figure 5. FT-IR spectra of Ligand, Pd(II), Ni(II), Cu(II)Bipy, Cu(II)Phen Complexes of respectively.

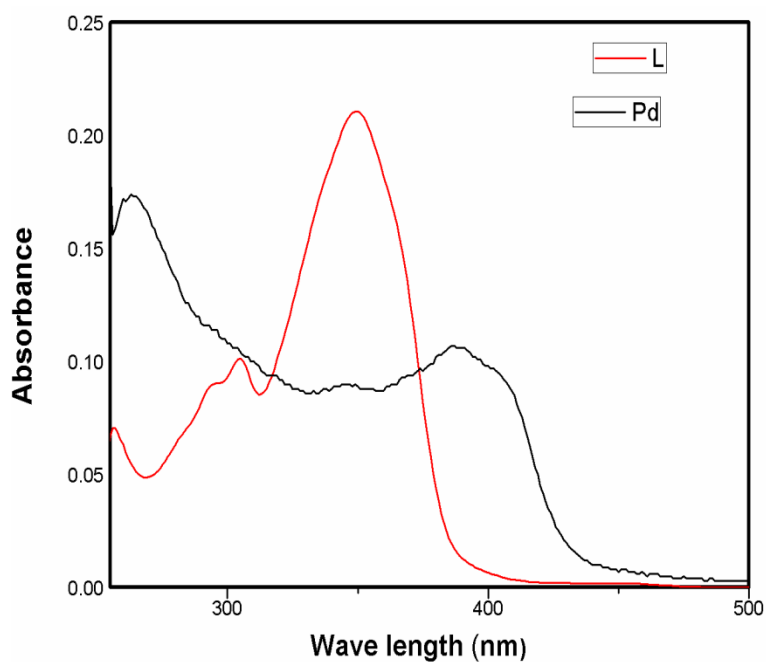


Figure 6. Electronic spectrum of the Ligand and Pd(II) complex

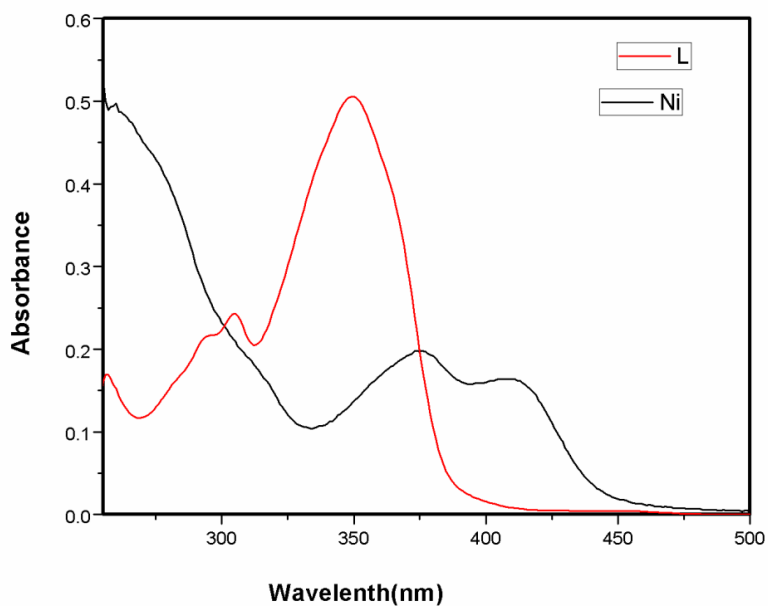


Figure 7. Electronic spectrum of the Ligand and Ni(II) complex

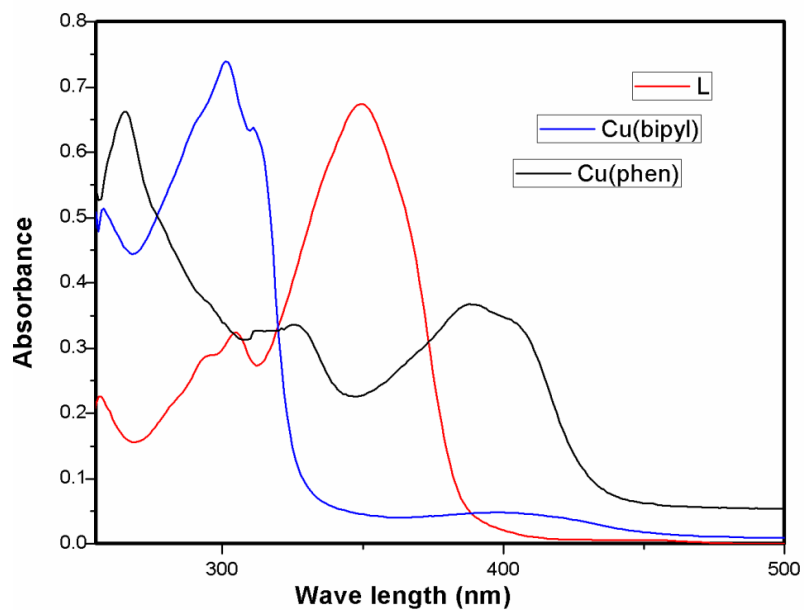


Figure 8. Electronic spectrum of the Ligand and Cu(II)bipy, Cu(II)phen complexes

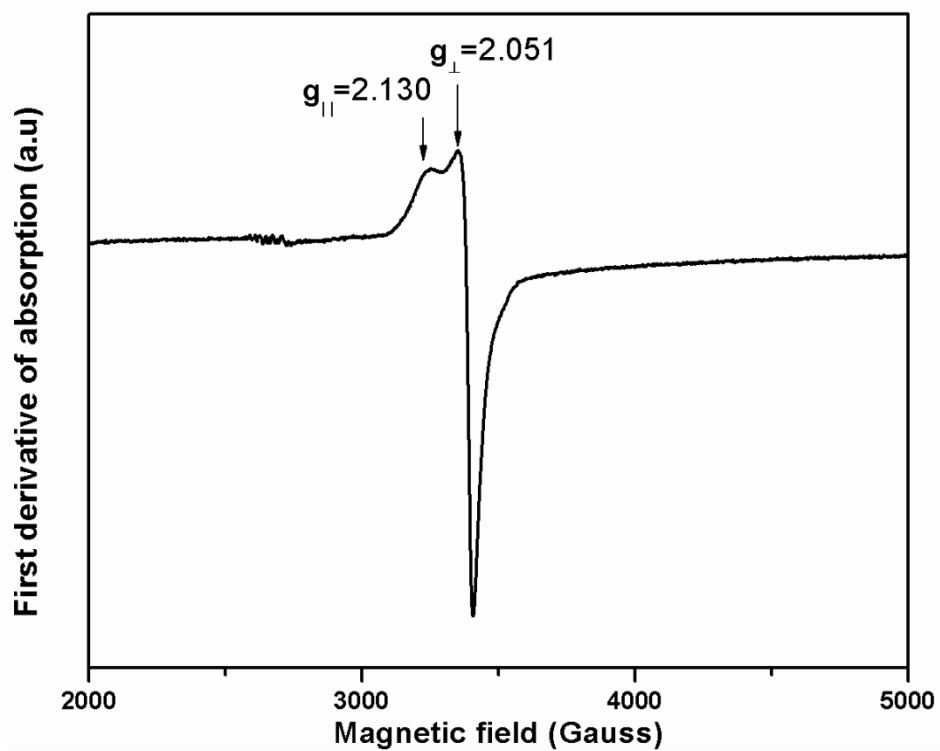


Figure 9. EPR Spectrum of Cu (II) bipy complex-1

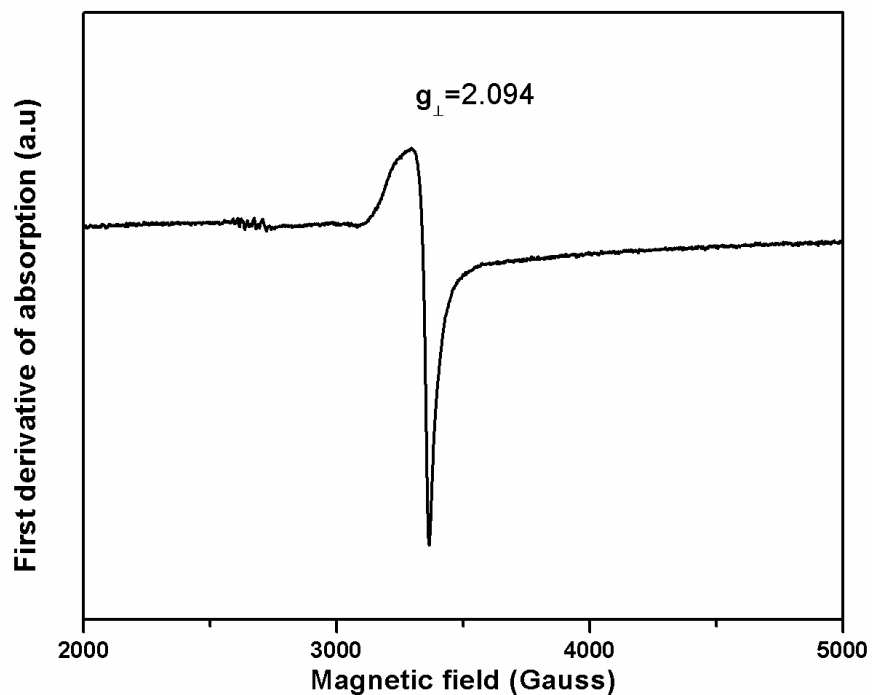


Figure 10. EPR Spectrum Cu(II) phen complex-2

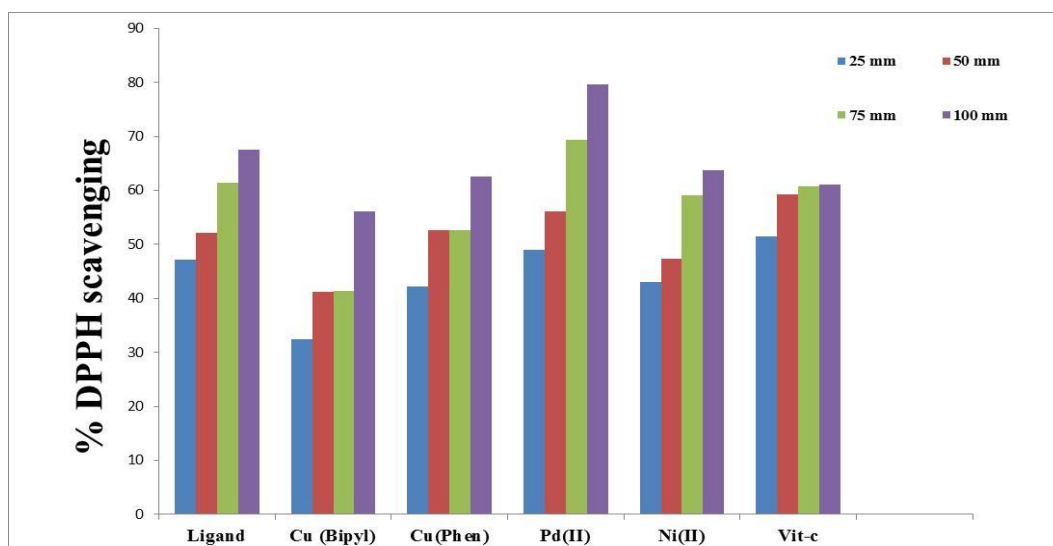


Fig 11. DPPH Scavenging activity of Ligand and their Cu(II)bipy, Cu(II)phen, Pd(II) and Ni(II) complexes.

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