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Synthesis, Characterization Antimicrobial and Antioxidant Activities of 2,4-dihydroxybenzaldehyde-4-phenyl-3-thiosemicarbazone (DHBPTSC) and its Pd(II), Ni(II)dppm Mixed Ligand and Cu(II) Complex having Heterocyclic Bases

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ABSTRACT

A series of four new Pd(II), [Ni(II)dppm], [Cu(II)bipy] and [Cu(II)phen] complexes of 2,4-dihydroxybenzaldehyde-4-phenyl-3-thiosemicarbazone (DHBPTSC). The DHBPTSC (ligand) and complexes were established by using means of IR, ^{1}H NMR, Mass, electronic, EPR spectra and elemental analysis discussed. The FT-IR spectral data intimate the coordination of sulphur and azomethine nitrogen with the central metal ion. The EPR spectra of absorbance were observed for Cu(II)bipy and Cu(II)phen complexes the g values $g_{\|} = 2.126$ and $g_{\|} = 2.108$, respectively. The g values are found in both the complexes had suggested elongated tetragonal geometry for the molecules. These compounds were further tested with antibacterial, antifungal and antioxidant activities.

INTRODUCTION

In the opinion of during continue infrequent depraved continuing interest in the coordination behavior of thiosemicarbazones. Past decades mainly thiosemicarbazones have exposed class of compounds have multi-donor ligands still growing attracts in the research group. This class of compounds has absorbed in the pharmacological and biological activity of thiosemicarbazone and several transition metal complexes have received considerable attention in the chemistry. Thiosemicarbazones have shown biology importance because of their variable biological applications as some of them have present antitumor, antiviral, antifungal, antibacterial and antimalarial *suitability* (Scovill *et al*., 1982; Hu *et al*., 2006; Belwal *et al*., 1999; Casas *et al*., 2000; Offiong *et al*., 1994; Singh *et al*., 2001; Garcia *et al*., 2003; Mishra *et al*., 2006; Prasad and Agarwal, 2007; Singh et al., 2000). They reported on a wide range of activities such as identify tumors, bacteria and fungi activities (Kizilcikh *et al*., 2004). Particular properties of these compounds due to their chelating ability and bonding modes to the central metal atom. The imine group (-N=CH-) becomes a suitable donor for coordination to grant. The versatile ligands to show chelating behavior and various biological properties (Chandra *et al*., 2001). In the course of these synthetic studies were also observed under certain conditions carbonyl thiosemicarbazones undergo in cyclization

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reaction many cases, thiosemicarbazones act as bidentate and tridentate ligands that coordinate to through Sulphur, Azomethine nitrogen and heteroatom and their coordinative behavior followed depends on the transition metal ions occupy (Campbell *et al*., 1975; Padhye *et al*., 1985; West *et al*., 1993; Singh *et al*., 2006; Sahin *et al*., 2009; Bermejo *et al*., 2001). A strong interacts with the heterocyclic Aldehydes or ketones depending upon coordination with ligand and complexes has stable in bioactivities (John *et al*., 2004; Belicchi-Ferrari *et al*., 2005; Gulea *et al*., 2004; Birca *et al*., 2004). In the present paper, we report synthesis, characterization of newly synthesized metal compounds Pd(II), Ni(II)dppm and [Cu(II)bipyl/phen] complexes of 2,4-dihydroxybenzaldehyde-4-phenyl-3-thiosemicarbazone. By using spectroscopic techniques ^{1}NMR, Mass, FT-IR, UV-Vis and EPR spectra. Furthermore, the antioxidant, antibacterial and antifungal activities were evaluated.

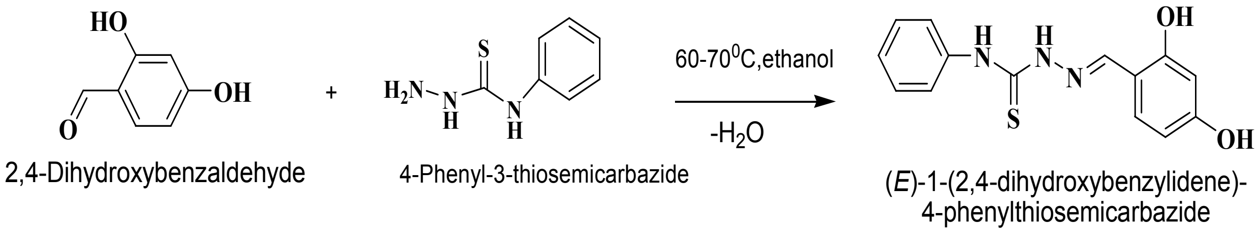
EXPERIMENTAL

Starting materials and methods

The chemicals were reagent grade without refinement of the preparation of DHBPTSC and l complexes. Palladium (II) chloride, bisdiphenylphospinomethan(dppm), 2,2 bipyridyle(bipy), 1,10-phenanthroline (phen), 2,4-dihydroxybenzaldehyde were obtained from Sigma-Aldrich. 4-phenyl-3-thiosemicarbazide was purchased from Alfa-Aesar chemicals. Whereas copper (II) acetate, nickel (II) chloride, were buying from Sd-fine chemicals.

Synthesis of ligand (DHBPTSC)

Two of the reactants 2,4-dihydroxybenzaldehyde (1.381 g, 0.01 mol) and 4-phenyl-3-thiosemicarbazide (1.673 g, 0.01 mol) were separately dissolved in 20 mL of ethanol and subsequently, they were mixed. To this mixture 2 drops of glacial acetic was added, this mixture was refluxed for 6 h at 60–70°C. The obtained yellow color precipitate is collected thoroughly filtered off washed with ethanol. Finely dried over $P_4O_{10.}$ Purity was checked by thin layer chromatography (TLC) techniques. The synthesis rote is Scheme 1.



Scheme 1: General synthesis of DHBPTSC.

Synthesis of complexes

Synthesis of $NiCl_2(PPh_2\text{-}CH_2\text{-}PPh_2)$

To 10 mL of DHBPTSC (0.574 g, 0.002 mol) was dissolved in acetonitrile solution and 10 mL of acetonitrile solution containing solid $NiCl_2$ salt (0.474 g, 0.002 mol) and 3 mL of the Et_3N base were added and stirred for one hour. To the reaction mixture under stirring, solid $PPh_2\text{-}CH_2\text{-}PPh_2$ (0.768 g, 0.002 mol) was added and further continued stirring for 4-5 h. Finally, the obtained red color compound was allowed to evaporate at room temperature to yielded which afforded red crystals along with the formation of $Et_3NH^+Cl^-$ salt.

Synthesis of $PdCl_2$-DHBPTSC complex

The hot methanolic solution 10 mL of DHBPTSC (0.574 g, 0.002 mol), 5 mL of a methanolic solution of $PdCl_2$ (0.0177 g, 0.0001 mol) were slowly dissolved and then mixed. This mixture was refluxed for 6-7 h at 60–70°C to get a brown colored solution. The progress of the reaction was monitored by TLC. The solution was further evaporated slowly on cooled to stand at room temperature. To get a brown colored precipitate, the obtained precipitate was separated by filtration and washed with hot ethanol and ultimately dried.

Synthesis of [Cu(II)bipy/phen]

The new Copper(II) mixed ligand complexes were synthesized general procedure. To 10 mL of DHBPTSC (0.574 g, 0.002 mol) in hot ethanol solution was added an ethanolic solution of $Cu(OAc)_2.H_2O$ (0.398 g, 0.002 mol) which constant stirring for 4-5 h, To this mixture, the solid heterocyclic base (0.002 mol, bipy/phen) was added and then content continued stirring for another one hour. The obtained green colored precipitate was formed and filtered. Finally, washed in ethanol ultimately dried.

Physical measurement

^{1}HMR spectrum of the DHBPTSC (L) was recorded on Bruker Bio spin AG-400 MHz (School of Chemistry, University of Hyderabad) using DMSO-d^6 with TMS an internal reference compound. Mass spectra of the ligand was carried out in the University of Hyderabad on a Quattro LC-Micro mass. Elemental analysis (CHN) was executed by using FLASH 1112 series. FT-IR spectra (KBr pellet) were obtained in the solid state the range of 4000–400 cm^{-1} utilizing a thermo scientific nicolet -380 spectrophotometers. The electronic spectra were recorded with the help of a UV Shimadzu-3600 spectrometer. EPR spectra of the polycrystalline sample at 298 k Bruker-ER073 apparatus equipped with an EMX micro X source for X band measurement were these compounds were used to carry out.

Biological studies

Collection of microorganisms

The microorganisms such as *Bacillus subtilis* (*B. subtilis*), *Escherichia Coli* (*E. coli*) Pseudomonas (*P. fluorescencs*), *Staphylococcus aureus* (*S. aureus*) and fungal development of *Aspergillus niger*, Penicillin, A. Ravis and A. Mucor) were obtained from Institute of Microbial Technology (IMTECH), Chandigarh and Department of Biochemistry, Sri Venkateswara University, Tirupati, India. In the present study were used for testing antimicrobial 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 synthesized DHBPTSC (ligand) and its Pd(II), Ni(II) dppm and [Cu(bipy/phen)] complexes are subjected to *in-vitro* antimicrobial and antifungal activity. The antimicrobial activity of different compounds described using agar diffusion method according to Goñi *et al*. (2009) with modifications. Each sterile Petri plate (90 mn) was prepared with 20 mL of nutrient agar and PDA medium. After solidifying, 100 µL of bacterial apprehension was spread on the plates. After 5 minutes, a sterile filter paper disc (6 mn) containing 5 µl of the compound was placed on the surface of each plate. Afterward, the microbial plates were incubated at 37°C for 24 h bacterial development and at 28°C for 48 h for fungal produce. The antimicrobial activity of various compounds represented by measuring the diameter of inhibition zone (DIZ) in mm streptomycin and fluconazole drug was served reference drug.

Anti-oxidant activity

The free radical scavenging activity of ligand and the Pd(II), Ni(II)dppm, Cu(II)-bipy and Cu(II)-phen complexes compounds was measured with bleaching of a colored methanolic solution of 1,1-diphenyl-1-picrylhydrazyl (DPPH). 1 ml of various concentrations of the ligand and metal complex compounds (25, 50, 75, and 100 µg/mL) dissolved in 4 ml of 0.004% (w/v) methanol solution of DPPH. After a 30 min incubation at room temperature, the absorbance was read against blank at 517 nm. The presence of inhibition (%) of formation of free radical from DPPH was determined by the following equation:

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

where A control is the absorbance of the regulate reaction (containing all reagents expects the test compound) and A sample is the absorbance of the test compounds Vitamin-C was used and citation. The test was carried in triplicate.

RESULTS AND DISCUSSION

^{1}NMR and mass spectra

^{1}H NMR spectra of DHBPTSC is recorded in DMSO-d_6 solution using TMS internal reference compound. ^{1}H NMR spectra is presented in Figure 1. The data analysis represented as follows. The peak at 11.57 ppm attributes the N-H functionality attached to azomethine. The singlet signal at 9.91 ppm is the corresponding to the proton of N-H group appear in between phenyl and C=S groups. The phenolic ortho –OH proton shows a singlet at 8.36 ppm. Whereas, the signal at 7.85 ppm represents the phenolic para –OH proton. The proton attached to azomethine moiety resonates at 8.10 ppm. The signals appear in the range of 7.56–6.28 ppm are attributed to eight aromatic protons. Yellow color solid: M.P:215°C: ^{1}HNMR: (400 MHz) δ (ppm) DMSO-d_6: δ 11.57 (1H, s, NH); 9.91 (1H, s, NH), δ 8.36 (lH, s, –OH), δ 7.85 (1H, d, –OH), 7.56 (3H, d, $J = 8.0$ Hz, Ar-H) 7.35 (3H, d, $J = 8.0$ Hz, Ar-H), 7.17 (1H, t, $J = 8.0$ Hz, Ar-H), 7.17 (1H, d, $J = 8.0$ Hz, Ar-H), 6.32-6.28 (2H, m, Ar-H): The mass spectrum of ligand presented in Figure 2 owed a molecular ion m/z (M+1) peaks at 287.34 amu corresponding to species ($C_{14}H_{13}N_3O_2S$) it prove in good conformance with the suggested structure of the formula. Elemental and chemical analysis data are demonstrated in Table 1.

Table 1: Analytical data for the ligand and its Pd(II), Ni(II)dppm and [Cu(II)bipy/phen] complexes.

S. No	Compounds	Color	M.Wt	M.P (ºC)	% Yield	Elemental analyses data(%) Expt. (calculated)		
						C	H	N
1	Ligand	Yellow	287.07	215	75	58.45 (58.41)	4.62 (4.59)	14.48 (14.47)
2	Pd(II)	Orange	680.05	>300	62	49.32 (49.35)	3.81 (3.80)	12.45 (12.42)
3	Ni(II)dppm	Redish brown	729.13	>300	65	64.26 (64.16)	4.75 (4.81)	5.68 (5.71)
4	Cu(II)bipy	Green	530.07	>300	61	56.62 (56.58)	4.31 (4.34)	13.65 (13.67)
5	Cu(II)-phen	Light Green	506.07	>300	61	58.81 (58.80)	4.23 (4.25)	13.07 (13.11)

FT-IR spectra

The IR spectral investigation is one of the evidence to find out the structural confirmation of the synthesized compounds by the identifying the bands corresponding to the important functional groups. The conformance specification vibrational band with structural results provide evidence the ligand coordination through complexation. The significant vibrational bands corresponding to the DHBPTSC and its Pd(II), Ni(II) dppm, Cu(II)-bipy and Cu(II)-phen are assigned and compared carefully. The important vibrational bands are carefully assigned and presented in Table 2. The spectra of DHBPTSC is confirmed on the absence of the band in the range from 2853−2924 cm^{-1} which indicates the presence of thione form (Sampath *et al*., 2013) and appearance of strong IR band of ligand at 1603 cm^{-1} confirms the conversion of the carbonyl group to imine group. Further the coordination of the ligand with metal complexes of Pd(II), Ni(II) dppm Cu(II)-bipy, Cu(II)-phen complexes, the appearance of shift of this band at 1627 cm^{-1}, 1601 cm^{-1}, 1600 cm^{-1} and 1654 cm^{-1} in the complexes corresponding to the coordination of azomethine υ(HC=N) respectively, shown in Figure 3. It indicating the involvement of the azomethine nitrogen in equalizing to the metal ion. Coordination of azomethine nitrogen, in turn, affects the band order between the carbon and nitrogen shift of vibrations to lower frequencies (Yudhvir *et al*., 1983; West *et al*., 1988). The participation of thione (C=S) functional group of ligand has shown IR band at 833 cm^{-1}, after coordination with the central metal ion is observed from the appearance of vibrational band at 847 cm^{-1}, 854 cm^{-1}, 849 cm^{-1}, and 848 cm^{-1} in the spectra of Pd(II), Ni(II)-dppm, Cu(II)-bipy, Cu(II)-phen complexes, respectively, (Lobana *et al*., 2014; Lobanaa *et al*., 2013). The metal-nitrogen bond formation is again confirmed with the presence of weak yet new bonds at 466 cm^{-1}, 485 cm^{-1}, 466 cm^{-1} are designated to (Pd(II)-N), (Ni(II) dppm-N), (Cu(II)-bipy-N), and Cu(II)-phen-N) complexes are, respectively.

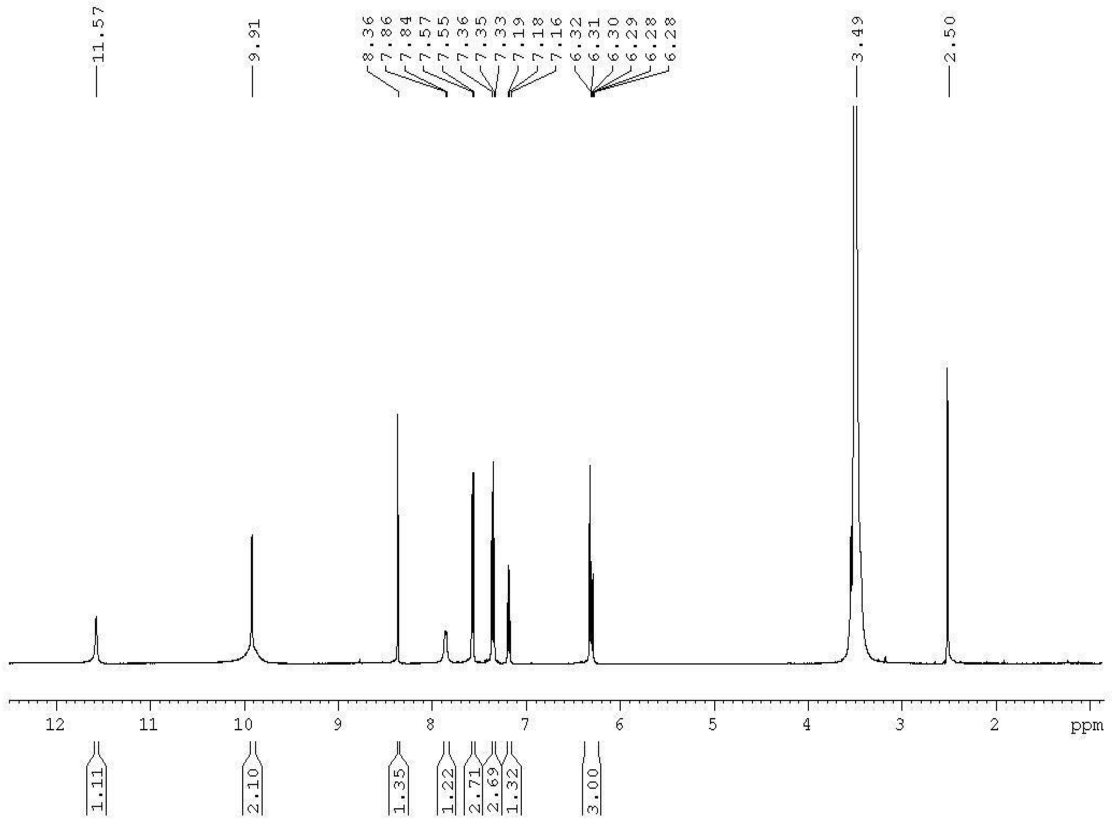


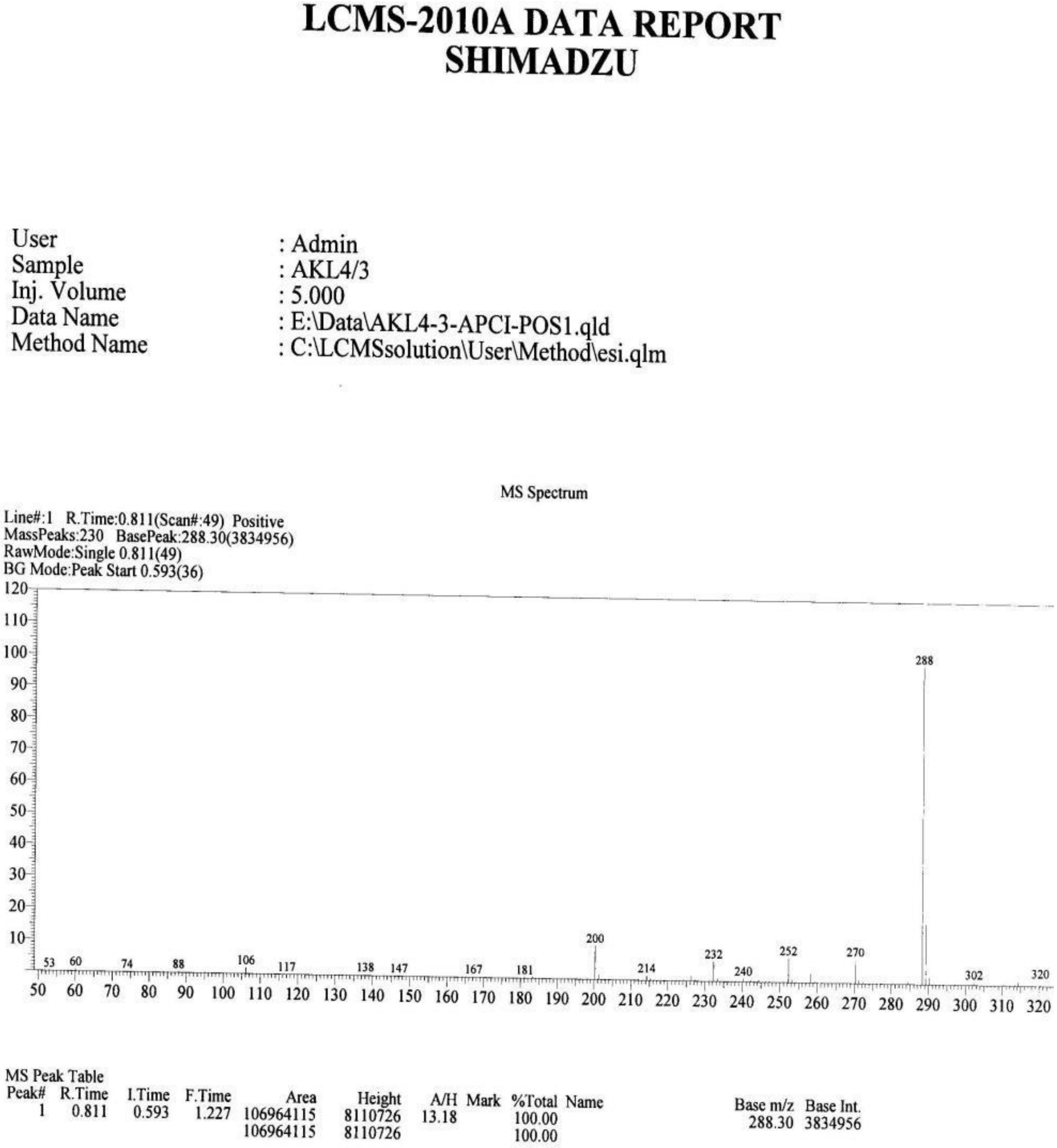
Fig. 1: ^{1}H NMR spectrum of the DHBPTSC.

Table 2: IR values with assignments for the DHBPTSC, Pd(II), Ni(II)dppm and [Cu(II)bipy] and [Cu(II)phen] complexes.

Ligand	Pd (II)	Ni(II)-dppm	Cu(II)-bipy	Cu(II)-phen	Assignments
3318	3347	3051	3320	3403	υsyN-H
1603	1627	1601	1600	1654	υ (C=N)
852	847	854	849	848	υ (C=S)
487	466	485	481	425	M-N

Electronic absorption spectra

The UV-Vis spectra of the ligand with corresponding complexes of Cu(II)-bipy, Cu(II)-phen, and Pd(II) were recorded in methanolic solution. Whereas Ni(II)dppm complexes were collected in acetonitrile solution. The absorption pattern of the ligand is comparable with exact types of thiosemicarbazones ligands reported (Jagadeesh *et al*., 2015). The display a group of bands at 256, 293, and 306 nm corresponds to the **π-π^*** transitions. All the complexes display similar bands corresponding to the intra-ligand transitions below 350 nm and an expected blue shift was observed compared to the ligand. The electronic transition found in thiosemicarbazones due to imine function was shifted on complexation. The Cu(II) mixed ligand complex with 2,2 bipyridyl and 1,10-phenanthroline ancillary ligands exhibit a broad band with tolerable intensity near 402 nm corresponding to the ligand to metal charge transfer transitions (Lobana *et al*., 2014). The Ni(II) complexes with $(PPh_2\text{-}CH_2\text{-}PPh_2)$ as ancillary ligand and Pd(II) complex are also showing a similar kind of absorption bands parallel to Cu(II)bipy and Cu(II)phen complex in the region of 400–450 nm, which are also attributed to transitions. The spectrum of two complexes Cu(II)-bipy and Cu(II)-phen show a red shift approximately 30 nm was observed for ligand centered bands, but in case of Ni(II)-dppm and Pd(II) complexes has the maximum red shift was only about 15 nm. This observation transparently indicates the stabilization of exited state in complexes. The Ni(II)dppm complex as ancillary ligand confirms square planar nature of the complex and Pd(II) complex suggest a square planar geometry involving transition in the spectra shown in Figures 4 and 5, respectively.



LCMS-2010A DATA REPORT
SHIMADZU

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Sample : AKL4/3
Inj. Volume : 5.000
Data Name : E:\Data\AKL4-3-APCI-POS1.qld
Method Name : C:\LCMSsolution\User\Method\esi.qlm

MS Spectrum

Line#:1 R.Time:0.811(Scan#:49) Positive
MassPeaks:230 BasePeak:288.30(3834956)
RawMode:Single 0.811(49)
BG Mode:Peak Start 0.593(36)

MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name	Base m/z	Base Int.
1	0.811	0.593	1.227	106964115	8110726	13.18		100.00		288.30	3834956
				106964115	8110726			100.00			

Fig. 2: Mass spectrum of the DHBPTSC.

Electron paramagnetic resonance spectra (EPR)

EPR spectra of the Cu(II) complex of 2,4-dihydroxybenzaldehyde-4-phenyl-3-thiosemicarbazone were recorded in polycrystalline samples at 298 K on X band at a frequency of 9.68 GHz under the magnetic field stamina of 320 G. room temperature X-band. The spectrum of Cu(II)-bipy complex-1 and Cu(II)-phen complexes-2 are presented in Figures 6 and 7, respectively. The spectra of the complexes have shown some variations with a change in the ligand all the complexes exhibit a superposition of very broad constituent due to strong dipole-dipole interactions. From the spectrum of Cu(II) bipy complexes, it performs that the characteristic of mononuclear copper complexes with axial symmetry, and lakes the hyperfine splitting like concentrated solid Cu(II) complexes. The g values provided inconstant information is reported by the modulation $G = (g_{\|} - 2)/(g_{\perp} - 2)$, that use full in measuring the exchange interaction between copper(II) centers has been considered in the polycrystalline solid, The analyses of spectra gives $g_{\|} = 2.126$ and $g_{\|} = 2.108$ values for the Cu(II)bipy and Cu(II)phen complexes, respectively (Martins *et al*., 2016). In the causes, if G > 4, an expression that conversion interaction is insignificant, G < 4 it indicates the important significant between copper(II) ions. Our present paper study, the obtained 'G' value, suggest that is appreciable exchange interaction between copper(II) ions.

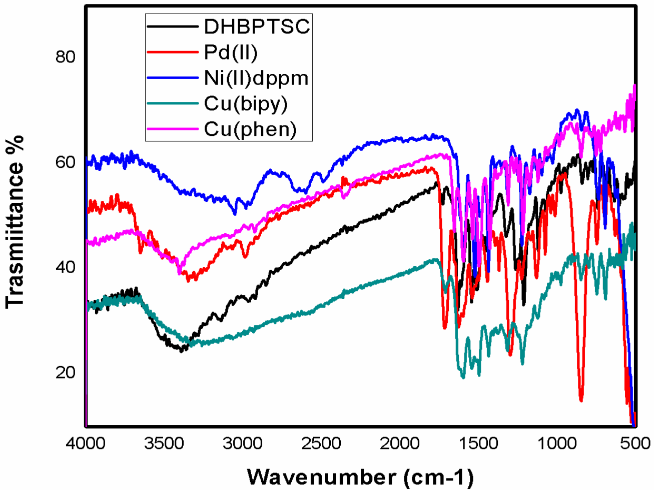

Fig. 3: FT-IR spectra of DHBPTSC, Pd(II), Ni(II)-dppm, Cu(II)-bipy, Cu(II)-phen Complexes respectively.

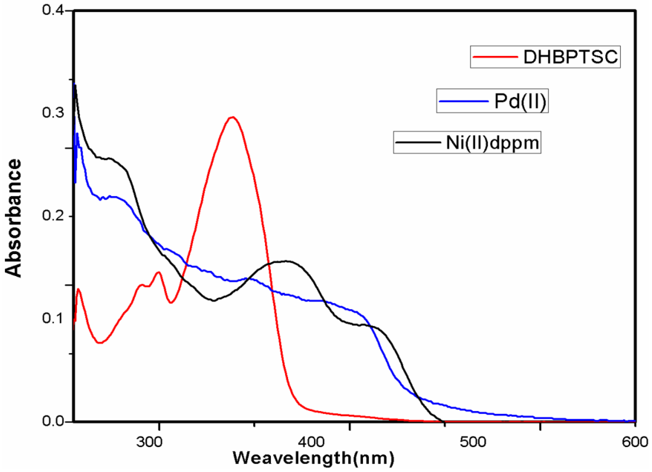

Fig. 4: Electronic absorption spectrum of the DHBPTSC, Pd(II) and Ni(II)-dppm complexes.

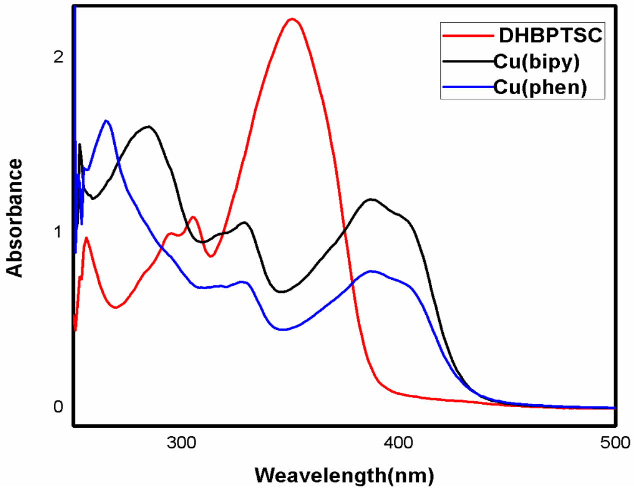

Fig. 5: Electronic absorption spectrum of the DHBPTSC, Cu(II)-bipy, and Cu(II)-phen complexes.

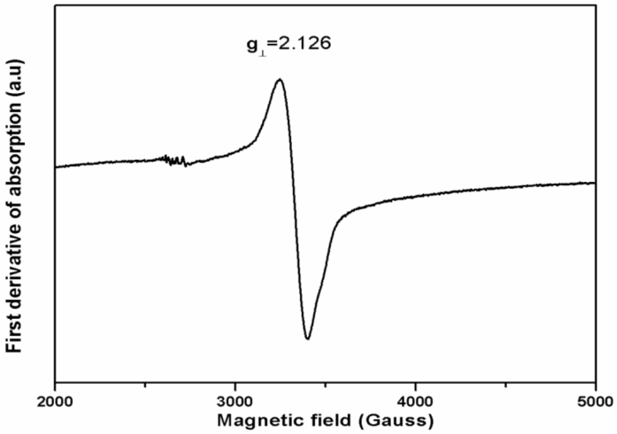

Fig. 6: X-band EPR spectrum of Cu(II)-bipy complex.

BIOLOGICAL STUDIES

Anti-microbial activity

Antimicrobial activity of the synthesized ligand and metal complexes were tested against for different gram positive and negative bacteria. The activity of the ligand and their Pd(II), Ni(II)dppm, Cu(II)bipy, and Cu(II)phen complexes were compared with criterion antibiotic streptomycin. The quantity of minimum inhibitory concentration (MIC) is the least concentration of transparent development after overnight incubation. Modified agar well diffusion method was used to find out the MIC values tabulated in Table 3. The Ni(II)dppm complexes shown excellence effect against both gram-negative and are positive bacteria. However, other compounds have moderate activity against all organisms. Cu(II)-bipy shown an excellent effect against gram-negative k. pneumonia. The chelation theory explains the reason behind the better activity of these thiosemicarbazone complexes (Agh-Atabay *et al*., 2005), the polarity of the metal ion is determined to be minimized to an advanced level, due to the responsibility of the ligand and unfinished of positive charge of the metal ion with donor groups especially with sulfur-nitrogen donors. Finally, included in the development of antibacterial activity for all compounds are in the order of Ni(II)dppm > Cu(bipy) > Cu(phen) > Pd(II) > ligand.

Antifungal activity

The preliminary antifungal activity of the DHBPTSC and its Cu(II)bipy, Cu(II)phen Pd(II), and Ni(II)dppm complexes were performed tested *in vitro* against three different fungal strains. The activities of the ligand and its complexes were parallel with standard antibiotic Fluconazole and shown in Table 4. On comparing the antifungal activity of the synthesized ligand and its metal complexes, it is observed that the metal complexes are capable of exhibiting higher antifungal activity than the free ligand. The antifungal activity of the increase in antifungal activity was better explained on the basis of chelation theory. All the complexes have been proved to be the better antifungal activity against the fungal strain *A. niger* and Rhizopus. Cu(II)-bipy has been proved to be the showed better antifungal activity against *A. niger*. However, none of the complexes display effective against *A. flavus*. The way of action may interfere the formation of a hydrogen bond through the azomethine nitrogen atom with the active centers of the cell constituents. The fungi conclusion in involvement through common cell procedure (Goñi *et al*., 2009; Chandra *et al*., 2009).

Table 3: Antibacterial activity of DHBPTSC and their Pd(II), Ni(II)-dppm, Cu(II)-bipy and Cu(II)-phen complexes.

Compound	*B. subtilis*	*E. coli*	*P. fluorescens*	*K. pneumonea*	*S. aureus*
L	0.3	0.4	0	1.7	0
Pd(II)	0.5	0	0.6	0.8	0
Ni(II)dppm	1.3	1.0	0.7	3.2	0.6
Cu(II)bipy	0.3	0.9	0	2.5	0
Cu(II)phen	0.6	0.6	0	0.9	0
Streptomycin	2.3	1.2	0.7	3.1	2.4

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

Compound	*A. niger*	*A. flavus*	*Rhizopus*
L			0
Pd(II)	1.2	0	0.4
Ni(II)-dppm	0.9	0	0.4
Cu(II)-bipy			0
Cu(II)-phen	2.0	0.7	0.6
Fluconazole	2.3	1.6	2.3

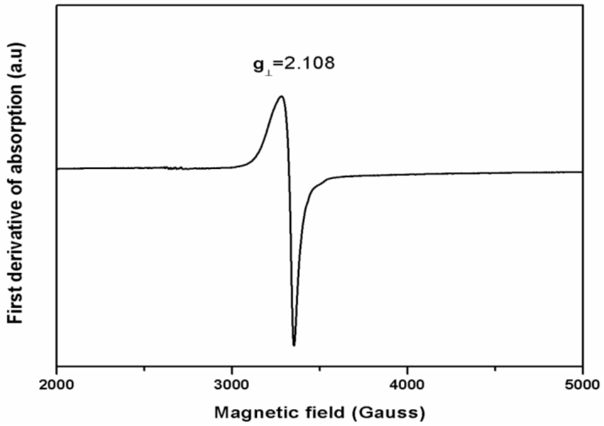

Fig. 7: X-band EPR spectrum of Cu(II)-phen complex.

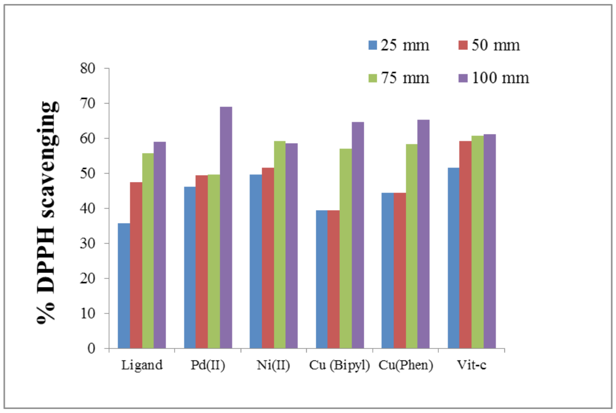

Fig. 8: DPPH Scavenging activity of ligand and their Pd(II), Ni(II)dppm, [Cu(II) bipy], and [Cu(II)phen] complexes.

Anti-oxidant activity

DPPH method is a prompt, simple and inexpensive method to measure the antioxidant ability of natural or synthesized compounds *in vitro*. The postulate for the reduction of DPPH free radicals is that the antioxidant reacts with stable free radical DPPH and reorganize it to 1,1 diphenyl-2-picrylhydrazine (Baraca *et al*., 2001). It shows the visible spectrum due to the presence of an unpaired electron occupation of a free radical scavenger the electron becomes paired off and absorbance decreases with respect to the number of electron capture higher. The free ligand exhibited comparative activity in DPPH scavenging as seen in the case of standard antioxidant Vitamin-C. All the complexes demonstrate good antioxidant properties in a concentration-dependent manner as shown in the Figure 8. Moreover, Pd(II) complex shown better activity than the standard Vitamin-C.

CONCLUSIONS

Synthesis of Pd(II), Ni(II)dppm and [Cu(II)bipy/phen] complexes with the ligand of 2,4-dihydroxybenzaldehyde-4-phenyl-3-thiosemicarbazone and were characterized by different spectral characterization methods. The IR and NMR spectroscopy provided a convenient approach to elucidate the structure of the synthesized compounds. The electronic spectral studies suggested that Pd(II) complex has found to be square planar, EPR spectrum of each complex has confirmed the existence of characteristic of the Cu(II) ion with axial symmetry. Further, the investigations are underway the antibacterial and antifungal activities of the synthesized ligand its metal complexes shown moderate activity and Pd(II) complex appeared excellence antioxidant activity.

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