Synthesis, UV Visible Spectroscopic Characterization and Antimicrobial Activity of Cu (II) and Ag (II) Metal complexes with 2-(4,5-dihydro-1H-pyrazol-5-yl) phenol.

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Abstract : In the present work the entitled ligand 2-(4,5-dihydro-1H-pyrazol-5-yl)phenol prepared by (E)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one and phenyl hydrazine while its metal complexes (M = Cu, Ag) are prepared by refluxing in ethanol solution. The ligand and its metal complexes are characterised by UV Visible spectra, which suggesting M:L ration 1:2 and 1:1 for Cu(II) and Ag(II) metal ion chelate respectively.

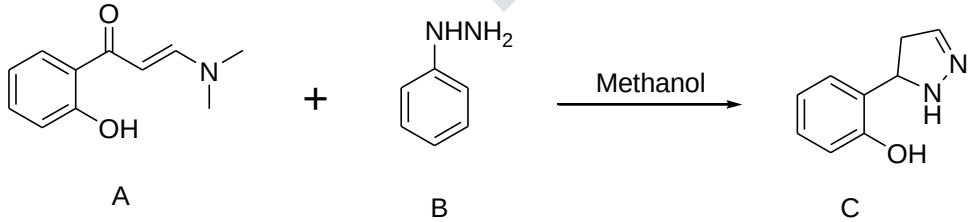
KEY WORDS :- Ligand, metal complexes and spectra.

I. INTRODUCTION

The Transition metals like Nickel, Copper, Zinc, Iron etc playing an important role in the various biological process occurs in the living organism like plants, animals, human etc. Haemoglobin carries oxygen to vital areas of body by binding it to the iron atom contained within it. Metal ions such as zinc provide the structural framework for the zinc fingers that regulates the functions of the genes in the nuclei of cells minerals containing calcium are the bases of bones, the framework of human body[12]. Metals such as zinc, copper iron and manganese are incorporated into catalytic proteins which facilitate a number of chemical reactions needed for life1.There has been enough interest organic ligand if at least one atom other than carbon forms a part of the ring system that it is designated as a heterocyclic compound[1]. Parasol, which are five members two nitrogen containing heterocycle. Nitrogen, oxygen and sulphur are the most common hetero atom but heterocyclic rings containing O, N, S, donor atoms because of the Varity of ways in which they are bonded to metal ion. Benzimidazole, pyrazole, isoquinoline, derivatives are the different types of heterocyclic used as anthelmintics. Albendazole is the most active benzamidazole antihelminitic drug[10]. Coordination compounds have been extensively used in industrial, biological, analytical, biochemical, clinical, antimicrobial[2], analgesic[3], antibacteral[4], antihypersensive[5] anticancer, antifungal and antitumor activity. The ligand plays an important role in complex formation, ligand act as electron donor to a single cation, they also acts as bridging groups to form stable metal chelates. The metal Chelates depends on the affinity of metal ion reacts with towards chelating and its coordination[5]. The rapidly developing field of bioinorganic chemistry is centered on the study of coordination compounds present in living systems.

II. EXPIRMENTAL

Synthesis of Ligand: In the synthesis of 2-(4,5-dihydro-1H-pyrazol-5-yl)phenol (C) , the equimolar mixture of (E)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one (A) and phenyl hydrazine (B) are dissolved in a 30 ml Ethanol. The reaction mixture was stirred under reflux condition for 10 to 12 hour. TLC monitoring of the reaction showed complete transformation. After completion of reaction, mixture was poured into crushed ice. The resulting product having black colur were filtered off, washed with cold water and dried in vacuum.



A B C

Synthesis of metal complex (CuL_2) The Metal complex (CuL2) i.e. bis(2-(4,5-dihydro-1H-pyrazol-5-yl) phenoxy)copper (D) is prepared by following method. A weighed quantity of ligand (0.02 mol) and metal chelate i.e. $CuCl_2$ (0.01mol) were separately dissolved in 100 ml of ethanol solution. Clear solution of cupper chloride and ligand solution were mixed in stoichiometric ration 1:1, the solution were reflux for two hours with constant steering . The pH of solution was adjusted 6.0 to 6.5 by alcoholic ammonia. After cooling the resultant precipitate was digested for one hour. The precipitate was filtered, washed with hot ethanol (40-60 ^{0}C) and dried in vacuum desiccators over anhydrous granular calcium chloride and stored in a air tight glass bottle.

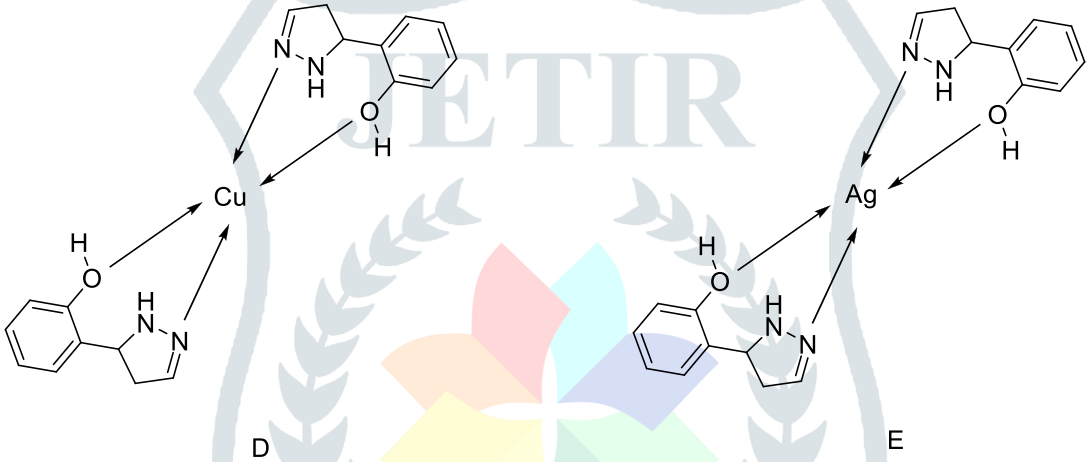
Synthesis of metal complex (Ag_2L_2) The Metal complex (Ag_2L_2) i.e. bis(2-(4,5-dihydro-1H-pyrazol-5-yl) phenoxy)silver (E) is prepared by following method. A weighed quantity of ligand (0.01 mol) and metal chelate i.e. $AgNO_3$ (0.01mol) were separately dissolved in 100 ml of ethanol solution. Clear solution of cupper chloride and ligand solution were mixed in stoichiometric ration 1:1, the solution were reflux for two hours with constant steering . The pH of solution was adjusted 6.0 to 6.5 by alcoholic

ammonia. After cooling the resultant precipitate was digested for one hour. The precipitate was filtered, washed with hot ethanol (40-60 ^{0}C) and dried in vacuum desiccators over anhydrous granular calcium chloride and stored in a air tight glass bottle.

III. RESULT AND DISCUSSION

Table 1: Analytical Data of 2-(4,5-dihydro-1H-pyrazol-5-yl)phenol and Cu(II), Ag(II) metal Complexs with 2-(4,5-dihydro-1H-pyrazol-5-yl)phenol.

Ligand / Complex	Colour	Yield (%)	Formula	Mol. Wt.	%Analysis Found(Calculated)			
					C	H	N	M
2-(4,5-dihydro-1H-pyrazol-5-yl)phenol	Black	65	$C_9H_{10}N_2O$	162.08	66.60 (66.65)	6.15 (6.21)	17.22 (17.27)	
bis(2-(4,5-dihydro-1H-pyrazol-5-yl) phenoxy)copper	Brown	52	$C_{18}H_{18}CuN_4O_2$	387.09	55.96 (56.02)	4.61 (4.70)	14.63 (14.52	16.35 (16.47)
bis(2-(4,5-dihydro-1H-pyrazol-5-yl) phenoxy)silver	Gray	54	$C_{18}H_{18}Ag_2N_4O_2$	539.97	50.1 (50.25)	4.46 (4.22)	13.10 (13.02)	24.98 (25.0)



Visible Spectral studies:- Electronic spectral data of the ligand and mononuclear complexes of the copper and silver complexes have been recorded in the DMSO solution, in the range 200nm to 700nm. The electronic spectrum of ligand shows strong band in the ultraviolet region 260nm-400nm this shows that the transition $\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$ the aromatic ring or diazomethane (C=N) group for free ligand6-7.

Table 2 : U.V. Visible Spectral data of transiton metal Chelate

Sr. No.	Ligand/metal Chelate	Absorbance	Transition
1 (L)	$C_9H_{10}N_2O$	260nm 295nm 400nm	$n \longrightarrow \pi^*$ $\pi \longrightarrow \pi^*$ $\pi \longrightarrow \pi^*$
2 (CuL_2)	$C_{18}H_{18}CuN_4O_2$	260nm 315nm 434nm	$\pi \longrightarrow \pi^*$ $\pi \longrightarrow \pi^*$ LMCT
3 (Ag_2L_2)	$C_{18}H_{18}Ag_2N_4O_2$	276nm 343nm 402nm	$\pi \longrightarrow \pi^*$ $\pi \longrightarrow \pi^*$ LMCT

Electronic spectra of metal complexes the bond of high and low wavelength side shows to its free ligand in different solution the absorption bands between 260nm-402nm in the free ligand changed in the metal complexes the absorption shift and the intensity change in the spectra of metal complex changed because of conjugation and delocalization of the whole electronic system and result in the energy change of $\pi \longrightarrow \pi^*$ transition of conjugation chromophore[8-9]. In case of copper complex the absorption bands in the visible region are 260nm to 434nm similarly for the silver complex, the absorption bands in the visible region are 276nm to 402nm the nature of Cu(II) and Ag(II) affects the position of absorption bands.

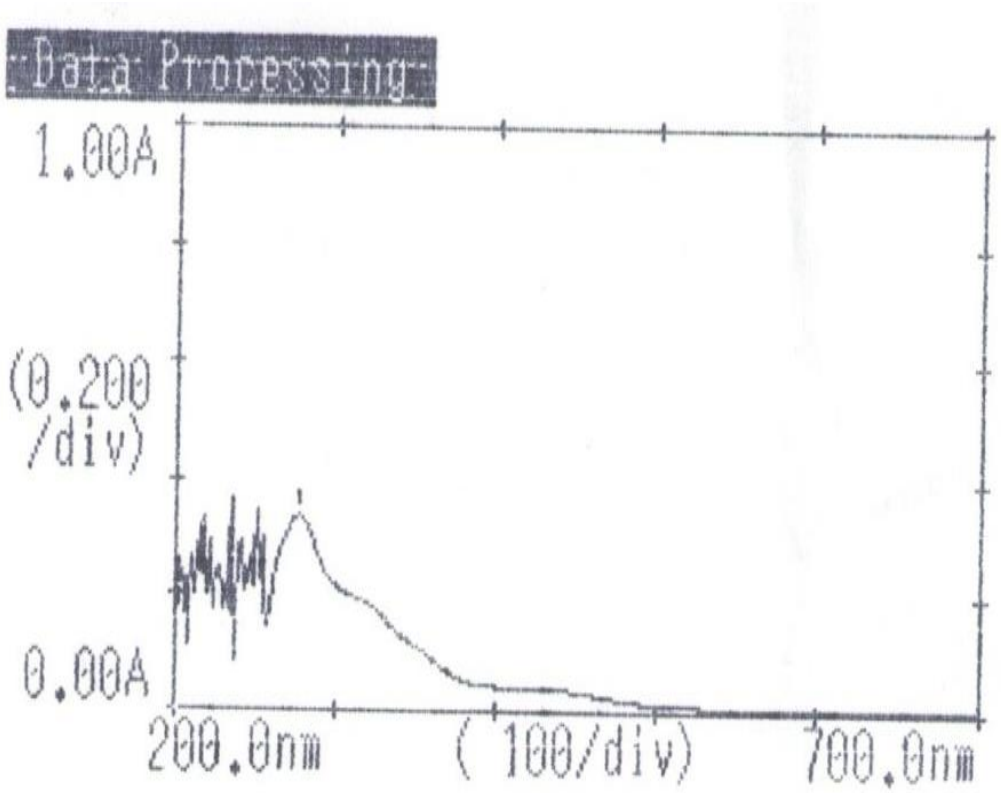


Figure 1: Electronic specra of Ligand

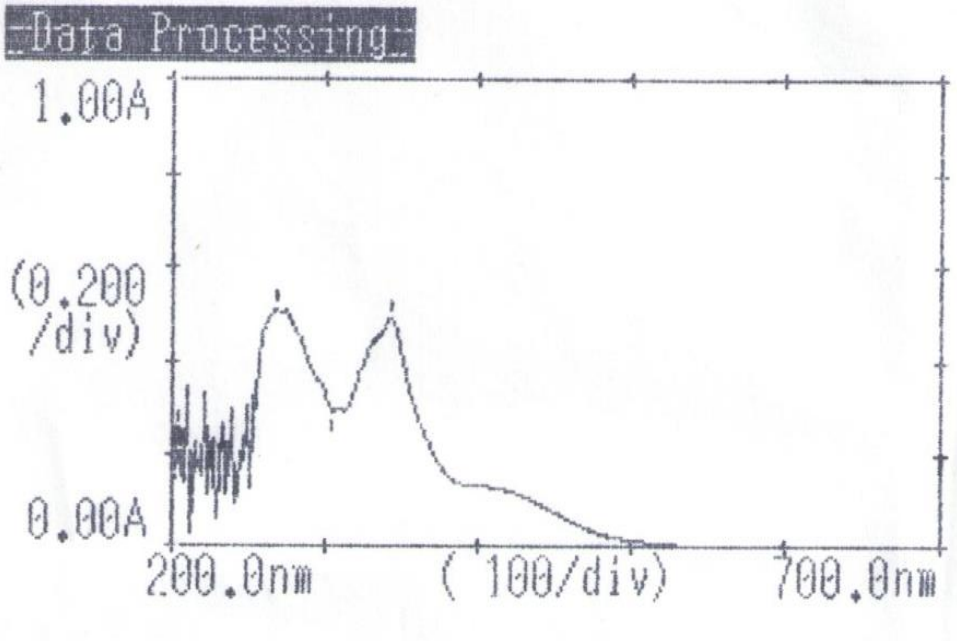


Figure 2: Electronic specra of $(CuL_2)_1$

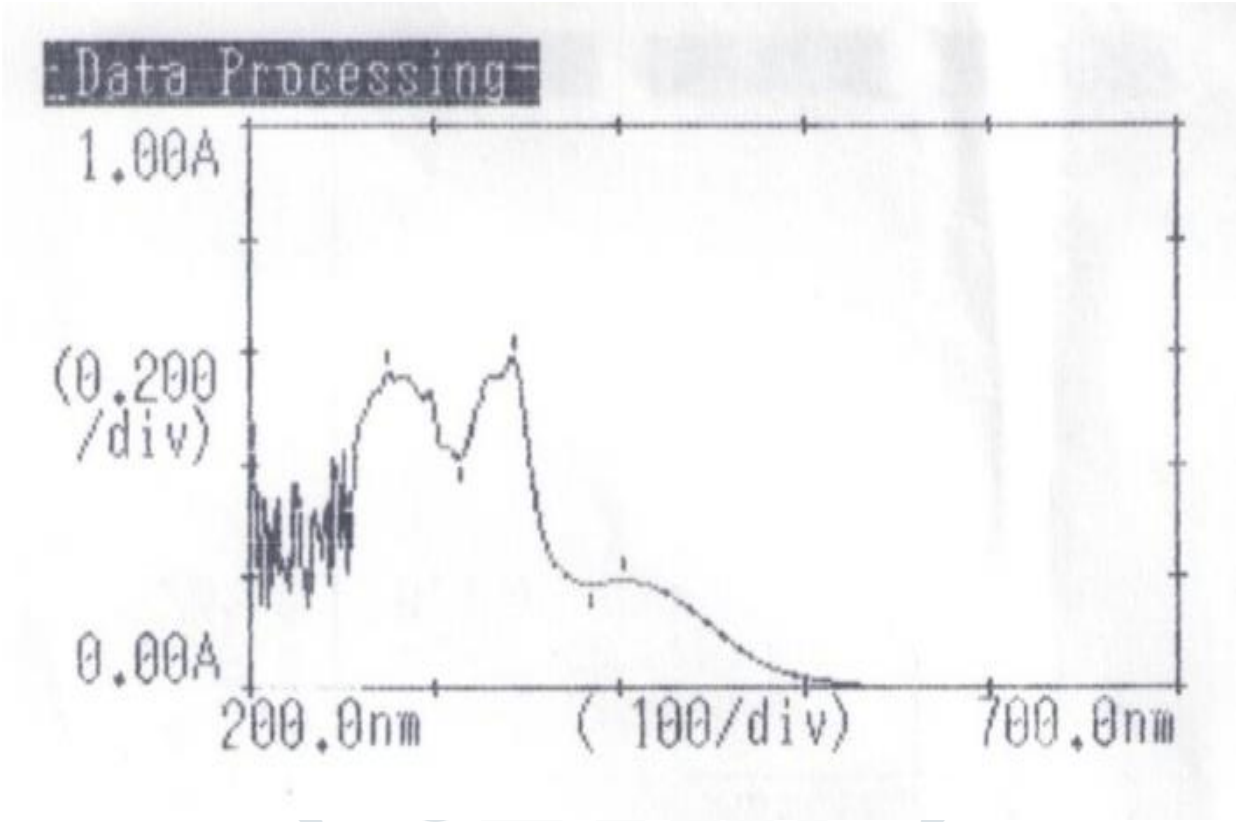


Figure 3: Electronic specra of (Ag_2L_2)

Antimicrobial Activity

Preparation of culture of media

The antimicrobial activity of test compounds was tested by disc diffusion method. The test compound (1 mg/mL) was dissolved in dimethyl sulphoxide and loaded on a sterile filter paper disc of 6 mm diameter. The petriplates containing nutrient agar medium (HiMedia) were spread with 100µL of actively growing both culture of the test bacteria using sterile cotton swab and allowed to dry for 10 min. For fungal species, 100 µL of active culture was spreaded on CzapekDox agar (HiMedia).Then the impregnated discs were placed on the surface of inoculated agar medium.

Discs loaded with dimethyl sulphoxide (Sd Fine Chemicals) were served as control. Streptomycin and fluconazole (HiMedia) discs were used as positive control for bacterial and fungal species respectively18. The nutrient agar plates were incubated at 37 °C for 24 h and CzapekDox agar plates at 30 °C for 7 days. The development of inhibition zone around the disc was recorded in terms of mm and compared with controls.

Observation

Microscopic organism, Bacteria and fungus are responsible for various diseases. They are also responsible for the some biochemical reactions. The previous studies indicate that the heterocyclic ligands with transition metal ions increases or retards the antibacterial and antifungal activity. Complex formation reduces the polarity of the metal ion due to the partial sharing of its positive charge with the donor groups and delocalization of π electrons. This process increases the lipophilic nature of the central metal atom, which is responsible for increasing the hydrophobic character and liposolubility of the molecule in crossing cell membrane of the microorganism, and hence enhances antibacterial activity[13].

(CuL_2) exhibited the maximum antibacterial activity against Bacillus subtilis The growth of Aspergillus flavus was effectively inhibited by (Ag_2L_2). The maximum antibacterial activity was displayed by (Ag_2L_2) against Bacillus subtilis (24 mm). The antimicrobial activity of Metal Complexes are summarized in the following table.

Table 3: Antimicrobial Activity of Metal Complexes.

Sr. No.	Compound Code	Zone of Inhibition in mm			
		Fungal species		Bacterial species	
		Aspergillus flavus	*Aspergillus niger*	*Escherichia coli*	*Bacillus subtilis*
01	(Ag_2L_2)	30	22	20	24
05	(CuL_2)	15	10	24	36

Figure 4: Antimicrobial Activity of CuL_2

Figure 4: Antimicrobial Activity of Ag_2L_2

IV. CONCLUSION

The Copper(II) and Silver(II) complexes were synthesized and characterized by UV-Visible Spectroscopy and biological studies were carried out. The complexes are soluble in DMF and DMSO. The observation shows that both the copper and silver complexes are positively antimicrobial in action. They seems to be bacterial and fungicidal. However their toxic effects are to be tested. They can also be used against plant pathogens as plant protection agents.

REFERENCES

1. KATRIZKY. A. R. Handbook of heterocyclic chemistry, pergaman press, Newyork **(1985)**
2. Demirayak. T. S. Karaburum. A. S. Beis. R. Eur. J. Med.Chem, 9.1089**(2004).**
3. Menonni,G,Mosti,L,Schenone,P,D,Amico,M,,Falciani,M,W,Farmaco.,49,115, **(1994).**
4. Premkumar, T, Govindarajan, S, World J, Microb, Biot. 21,479, **(2005)**.
5. Baily, D.M., Hasen,P.E,Halvac, A.G,Baizman,E.R,Pearl,J.J.Med.Chem. 28,256. **(1985)**.
6. Z. Chen, Y.Wu, D.Gu,F.Gan, dyes.Pigm, 3,624, **(2008)**.
7. H.Temel, S.Khan, J.Cordi. Chem.61 (9), 1443, **(2009)**.
8. A.Vogt.S.Wolvoiec, R.L.Pras, Polyhedron 17,8,1231, **(1998)**.
9. K.N.Kumar, R.Ramaesh, Polyhsron, 24,14.1985, **(1998)**.
10. Sayed, L.El. and Lakandar, M.F.J.Inorg.Nucl. Chem.33,435, **(1971)**.
11. Saxena, N., Juneja, H.D and Munshi, K.N.J. Indian Chem. Soc. 70,943, **(1993)**.
12. Brandht, W. W., Dwyer F. P. and Gyarfas E.C., Chem. Rev., 54, 959. 1954.
13. Goodman, L. S, Wintrobe, M. M, Damesheck, W, Goodman, M. J. and Lennan, M. I. Mc. Jour. Ame. Med. Associ. 132, 126, 1946.