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Studies on Copper (II), Nickel (II), and Cobalt (II) complexes of some new 2-hydroxychalcones and evaluation their antimicrobial activity

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Abstract

After having prepared a new series of Cu(II), Co(II) and Ni(II)complexes with 2-Hydroxy chalcone as ligand, the structures of these synthesized complexes is verified by using spectroscopic methods and elemental analysis. UV-Visible and IR spectra recorded of these prepared complexes, moreover the structures of complexes were confirmed by magnetic moments and molar conductance in DMSO. All these complexes are non electrolytes as the conductivity data confirms. In addition Analytical data confirmed were 1:2 stoichiometry. According to the suggestion of electronic spectral data the geometry of Cu(II) complexes is square planar and octahedral geometry for all Ni(II) and Co(II) complexes. From the antimicrobial screening done it shows enhanced activity of metal complexes as compared to their corresponding ligands.

Keywords: Acetophenone, Aldehyde, Metal complexes, Spectral analysis, Antimicrobial activity.

Introduction

The chalcones play an important role as intermediates in organic synthesis[1-3] which used in wide range of pharmacological activities as antioxidant, antimalarial[4], antitumor[5], antiinflammatory[6], anticancer[7], antimicrobial[8] and antileishmanial[9]. Transition metal having ability bound to 2-Hydroxy chalcone to form metal complexes which possess different activities and find wide applications in catalytical, analytical, medicinal and biological activity such as anticancer[10], cytotoxic[11,12], antifungal[13]and antibacterial[14] activities.

Materials and methods

Materials: The chemicals used were of A.R grade and were obtained from known chemical companies like Lancaster and Sigma–Aldrich. The purification required solvents was done by standard methods. The determination of melting points was done by open capillary tube method and are uncorrected. Thin layer chromatography on pre-coated sheets of silica gel-G was used to monitor the completion of reaction.

Instrumentation: Determination of the ratio of elements in coordination compounds / chelate, was done by SHIMADZU AA 7000. The other usual method of structural analysis is IR spectroscopy particularly to get the used information quickly regarding the structure of molecule. IR spectra in CsCl υmax in cm-1 were recorded on SHIMADZU 8600 S FTIR spectrometer. AVANCE-400 MHz spectrometer is used to record 1HNMR spectra of all synthesized compounds (in DMSO-d6), TMS used as internal standard. To record ESR spectra (Electron Spin Resonance) which used in order to get information about covalency and magnetic behaviour of complexes, Varian E-112X- band ESR spectrometer was used at 100KC modulation and 9 inch electromagnet.

General procedure for the synthesis of 2'-hydroxychalcone: Mixture of substituted acetophenone (0-01mol), substituted aldehyde (0.01mol) dissolved in ethanol (20 ml), and KOH (0.02mol in minimum H_2O) gradually drop by drop added. Reaction mixture was stirred at 50-60°C temperature for about and reaction mixture was kept in bulb oven for 14-16 hr. The reaction was monitored by using TLC method. After completion the reaction mixture were poured on crushed ice-water folloed by acidification made by dil HCl. The solid separated was filtered and washed with cold water. The crude product obtained was then recrystallized by using glacial acetic acid in order to get pure product. IR, ^{1}HNMR and Mass Spectral analysis was done to confirm the structure of the synthesized compound.

Synthesis of metal complexes: By refluxing solution of ligands and metal acetate in 2:1 molar ratio, i.e 0.02 moles of ligand [in slight excess] taken in RB flask containing 20 ml of DMF. 0.01moles of metal acetate was dissolved in 10 ml of DMF to synthesis the metal complex. This metal solution added in hot solution of ligand drop by drop with constant stirring. For a period of 3 hours the contents were refluxed and then poured on ice-cold water. The resultant metal complex then filtered and washed with a small amount of cold DMF to remove excess amount of ligand that have not reacted, the product was then washed with petroleum-ether and dried over calcium chloride in a vacuum desiccators.

Results and discussion

These metal complexs are colored compounds, stable at room temperature, they are non soluble in water and in most of the common organic solvents but highly soluble in DMF and DMSO. Analytical data showed that stoichiometry may be represented as 1:2 metal to ligand ratio of these complexes. Their conductivity experiments in DMF solution showed that these complexes have low conductivity, which supported non-electrolytic nature of the metal complexes[15] (Table-1).

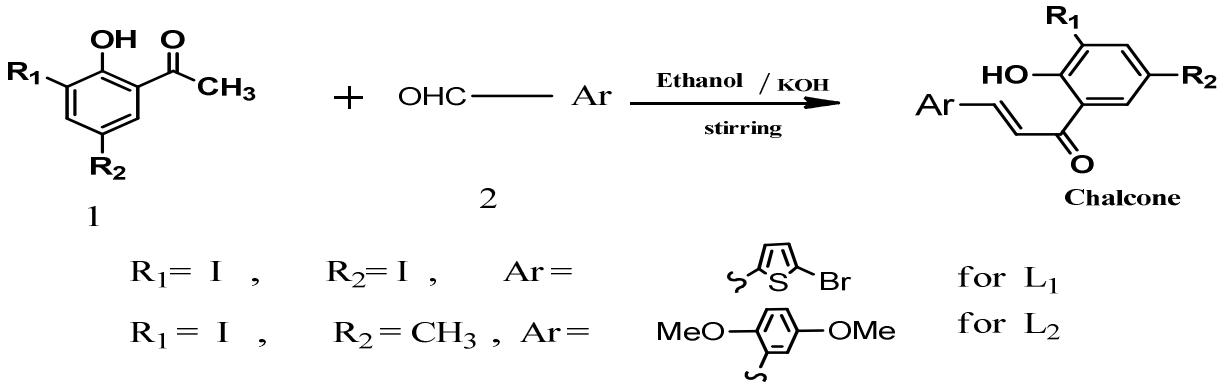
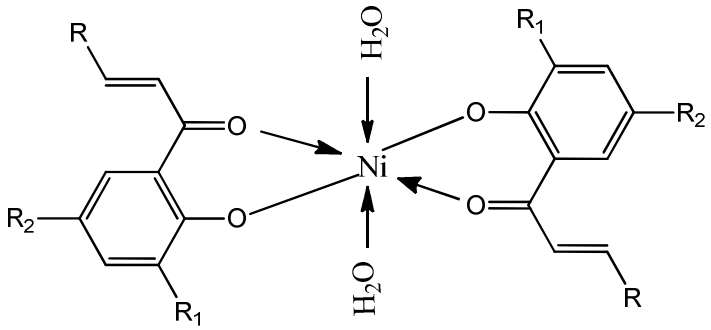


Figure-1: Synthesis of Chalcones ligands.

Table-1: Physical Parameters and analytical data of Co (II), Ni (II) and Cu (II) complexes.

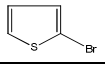
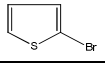
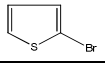
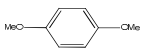
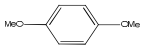
Molecular Formula	Colour	M. P./ D.P. ºC	Elemental Analysis		Molar Conductivity S cm2 mol-1 × 10-4	µeff. B. M.
			Halogen Found (Calcd)	Metal Found (Calcd)		
$C_{26}H_{12}O_4I_4Br_2S_2Cu$	Brown	227	56.11 (56.39)	5.37 (4.98)	11.16	1.74
$C_{26}H_{16}Br_2I_4NiO_6S_2$	Greenish Brown	289	54.50 (54.95)	4.32 (4.83)	19.61	2.91
$C_{26}H_{16}Br_2CoI_4O_6S_2$	Brown	189	55.21 (54.93)	4.92 (4.85)	12.37	4.64
$C_{36}H_{32}CuI_2O_8$	Dark Brown	291	44.13 (44.77)	6.13 (5.61)	10.14	1.81
$C_{36}H_{36}I_2NiO_{10}$	Dark Brown	253	43.91 (43.58)	5.34 (5.04)	14.24	2.87
$C_{36}H_{36}CoI_2O_{10}$	Brown	271	43.26 (43.57)	5.26 (5.06)	12.91	5.09



M = Ni (II) , Co(II)

Scheme-1:

Table-2: Metal Complexes Substitute.

Sr. No	Complexes	R_1	R_2	R
1.	[Cu $(L_1)_2$]	I	I	
2.	[Ni $(L_1)_2$].2H_2O	I	I	
3.	[Co $(L_1)_2$].2H_2O	I	I	
4.	[Cu $(L_2)_2$]	I	CH_3	
5.	[Ni $(L_2)_2$].2H_2O	I	CH_3	
6.	[Co $(L_2)_2$].2H_2O	I	CH_3	

IR spectra: Presence of phenolic –OH group in the ligand confirmed by a broad band in the range 3425-3440 cm^{-1}, this band is absent in Cu(II), Co(II) and Ni(II) complexes due to deprotonation forms covalent bond with central atom through oxygen atom. A new intense broad band appeared in IR spectra of Ni (II) and Co (II) complexes in the range of 2997-3287cm^{-1} due to the presence of coordinated water molecule[16]. For ν(C=O) In the IR spectra of all the ligands the value of this band showed at the range of 1625-1631 cm^{-1} [17]. This band in the IR spectra of the complexes is shifted to lower or higher wave number indicating coordination through oxygen of (C=O) group. Similarly the medium intensity band appeared in the range of 1215-1276 cm^{-1} assigned to υ (C-O) in the ligands also this value is shifted to lower or higher in IR spectra of metal complexes, new band appeared in IR spectra of metal complexes at range 453-466 cm^{-1} which did not present in the ligand due to υ(M-O) in the complexes[18].

Table-3: IR bands of ligands and its Cu(II), Ni(II) and Co(II) complexes.

Ligand and Metal Complexes	*v* (OH) cm^{-1}	*v*(H_2O) cm^{-1}	*v*(C=O) cm^{-1}	*v* (C=C) cm^{-1}	*v*(C-O) cm^{-1}	*v*(Cu-O) cm^{-1}
L_1	3425	--	1625	1546	1249	--
Cu $(L_1)_2$	--	--	1613	1540	1215	466
[Ni$(L_1)_2$]. 2H_2O	--	3190	1620	1566	1257	466
[Co$(L_1)_2$].2H_2O	--	3228	1627	1542	1276	455
L_2	3440	--	1631	1562	1245	--
Cu $(L_2)_2$	--	--	1612	1566	1226	466
[Ni$(L_2)_2$]. 2H_2O	--	2997	1635	1562	1242	453
[Co$(L_2)_2$].2H_2O		3287	1604	1545	1220	461

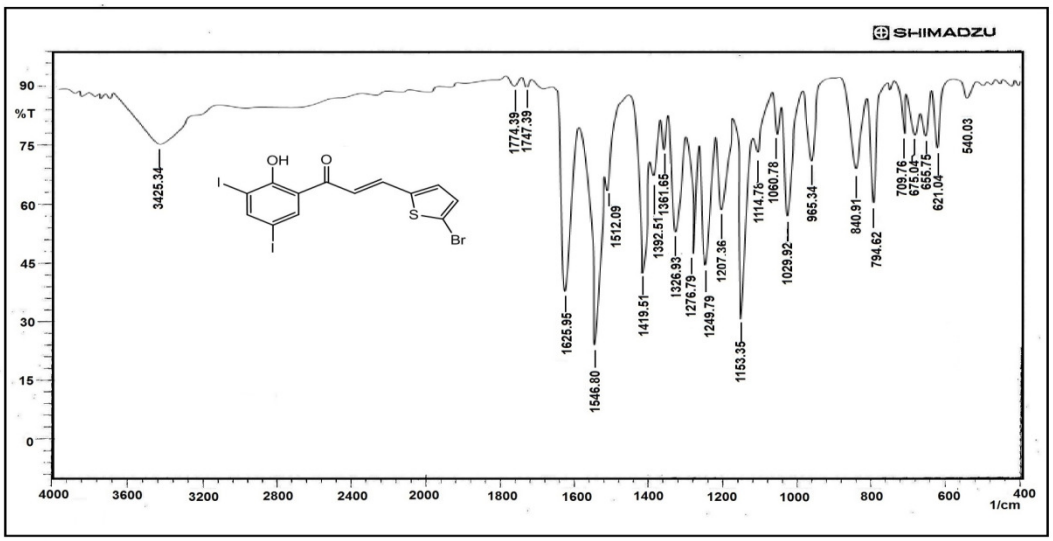


Figure-2: Infra Red Spectrum of **L_1** 3-(5-bromothiophen-2-yl)-1-(2-hydroxy-3,5-diiodophenyl)prop-2-en-1-one.

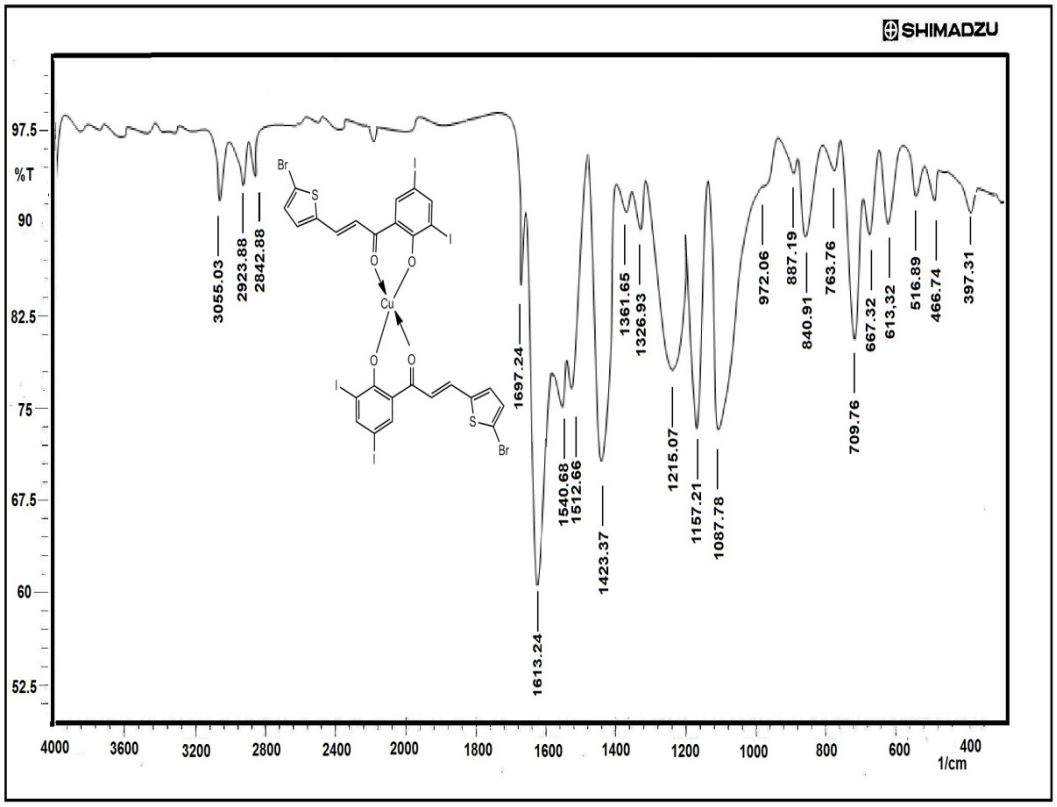


Figure-3: Infra Red Spectrum of $Cu(L_1)_2$.

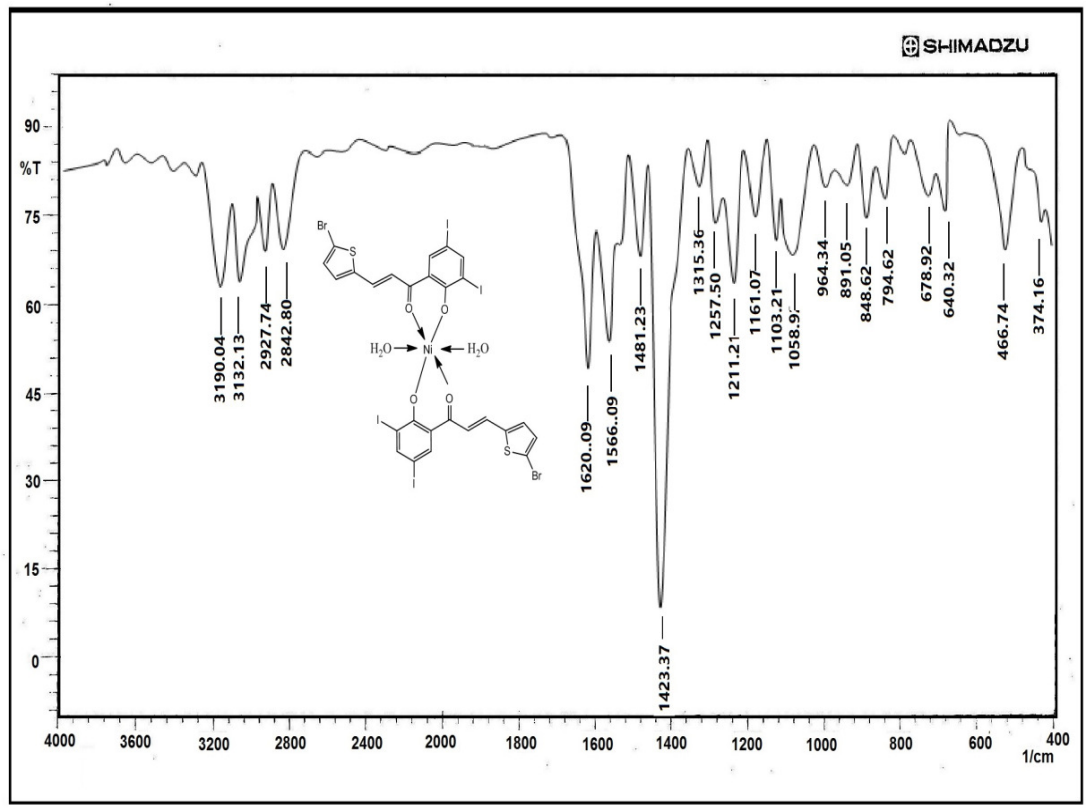


Figure-4: Infra Red Spectrum of $[Ni(L_1)_2].2H_2O$

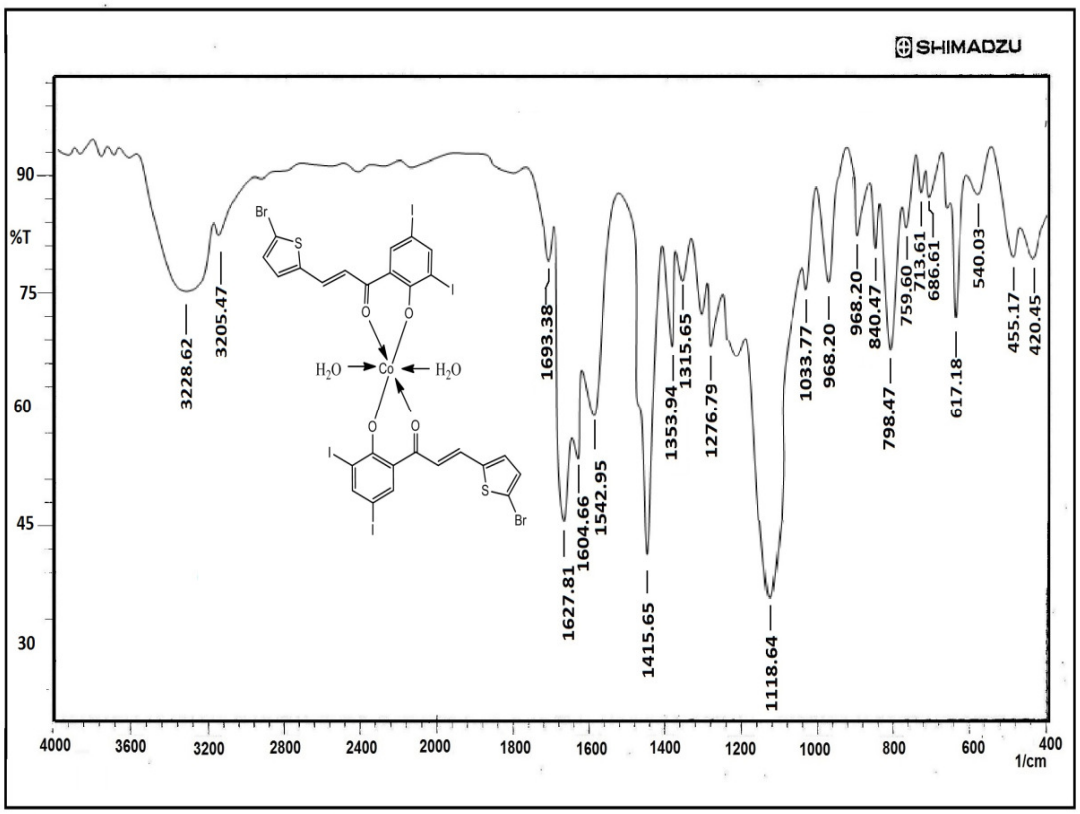


Figure-5: Infra Red Spectrum of $[Co(L_1)_2].2H_2O$.

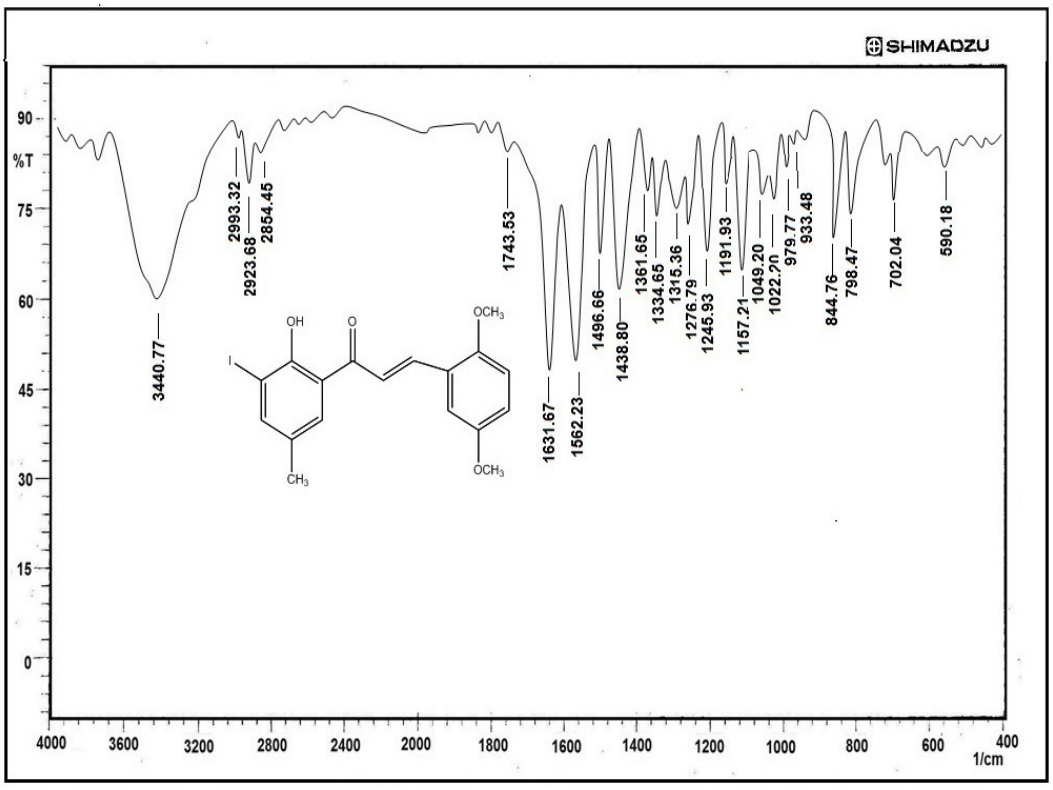


Figure-6: Infra Red Spectrum of **L_2** 3-(2,5-dimethoxyphenyl)-1-(2-hydroxy-3-iodo-5-methylphenyl)prop-2-en-1-one.

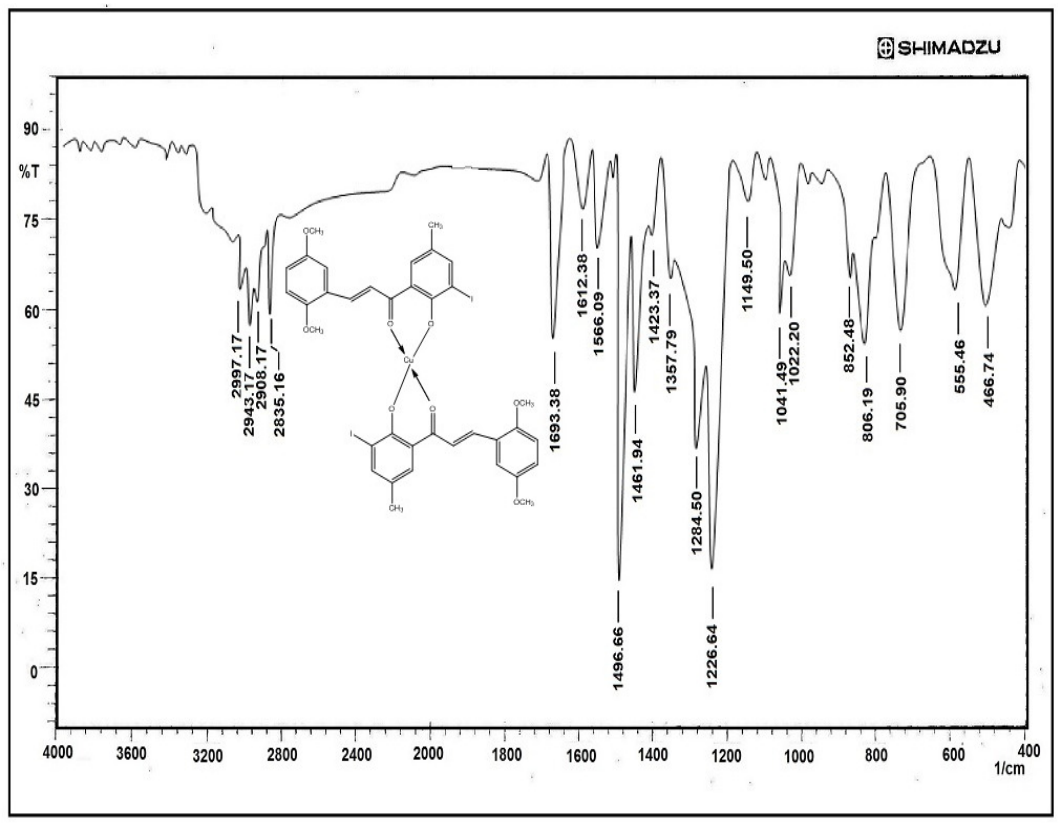


Figure-7: Infra Red Spectrum of $Cu(L_2)_2$

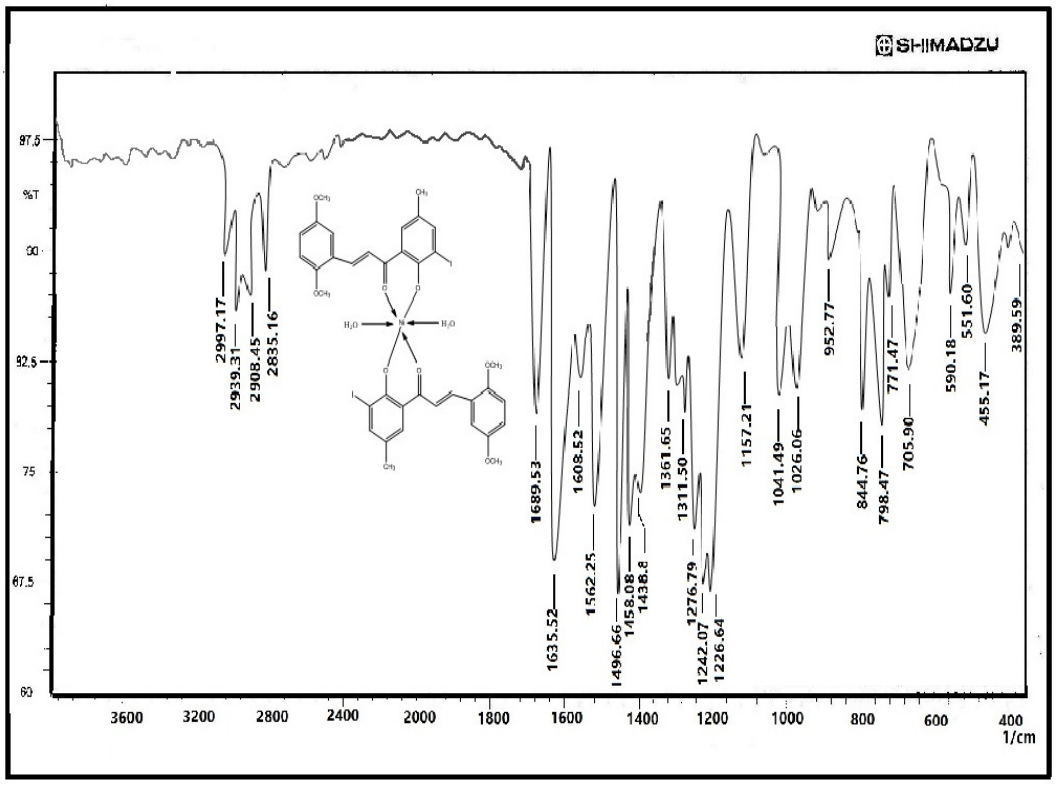


Figure-8: Infra Red Spectrum of $[Ni(L_2)_2].2H_2O$.

Thermal analysis: TGA analysis is very important which carried out to confirm presence of water molecule in these complexes as well as to know their decomposition pattern. This analysis correlate the information obtained from the IR spectral studies. In Ni(II) and Co(II) complexes, the TGA curve showed lose in weight in the temperature range ~200-250 indicates the presence of coordinated water in the complex[19], but in case of Cu (II) complexes the thermogram show that, the complex starts decomposing gradually till 146ºC, which indicated presence of one mole water of hydration.

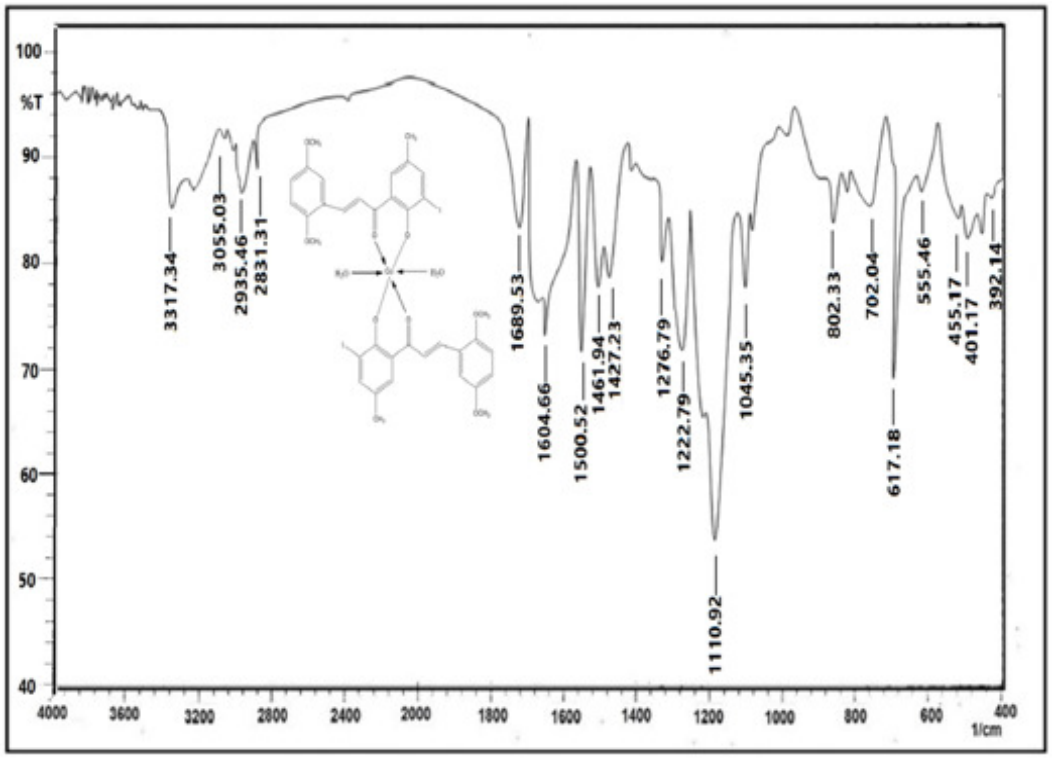


Figure-9: Infra Red Spectrum of $[Co(L_2)_2].2H_2O$.

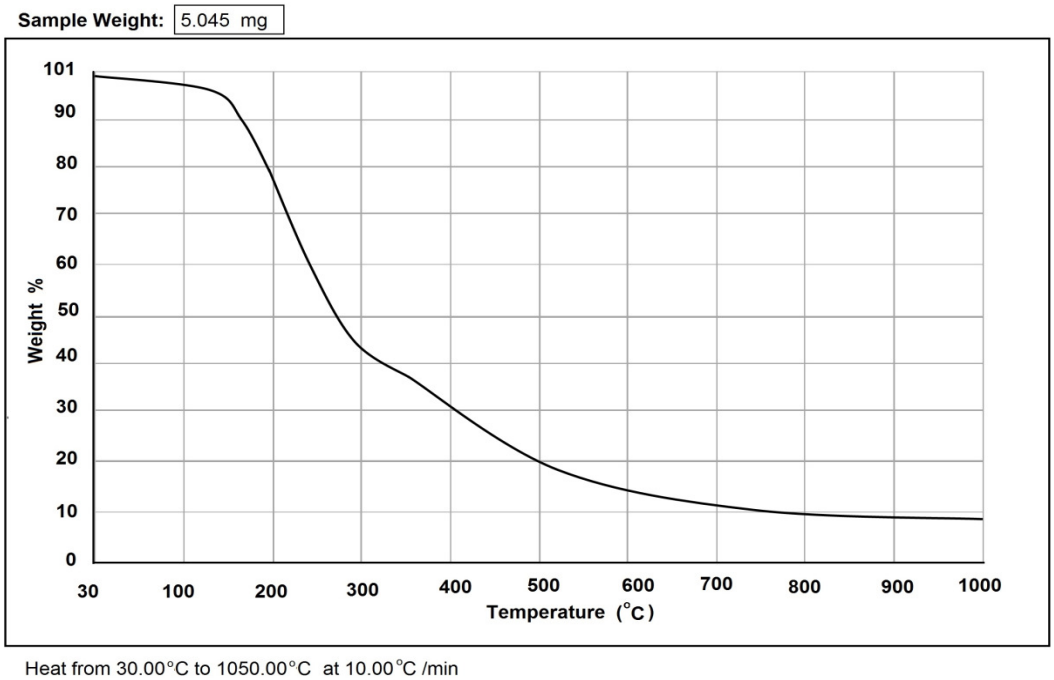


Figure-10: TGA Curve of $[Cu(L_1)_2].H_2O$.

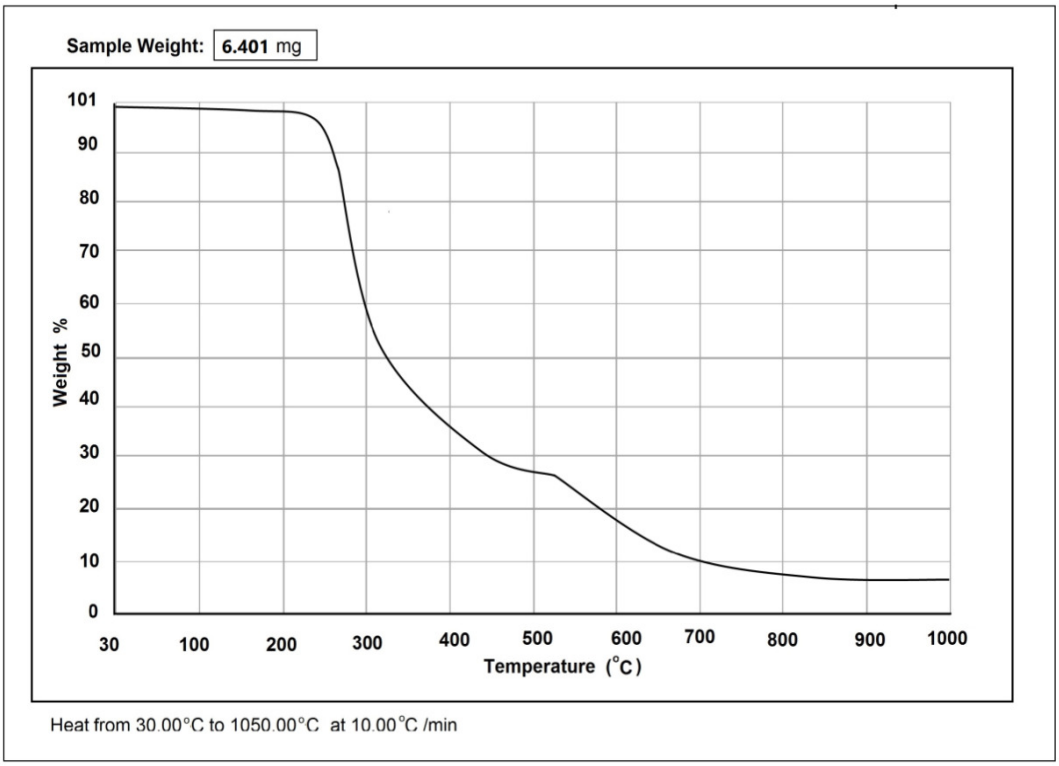


Figure-11: TGA Curve of $[Ni(L_2)_2].2H_2O$.

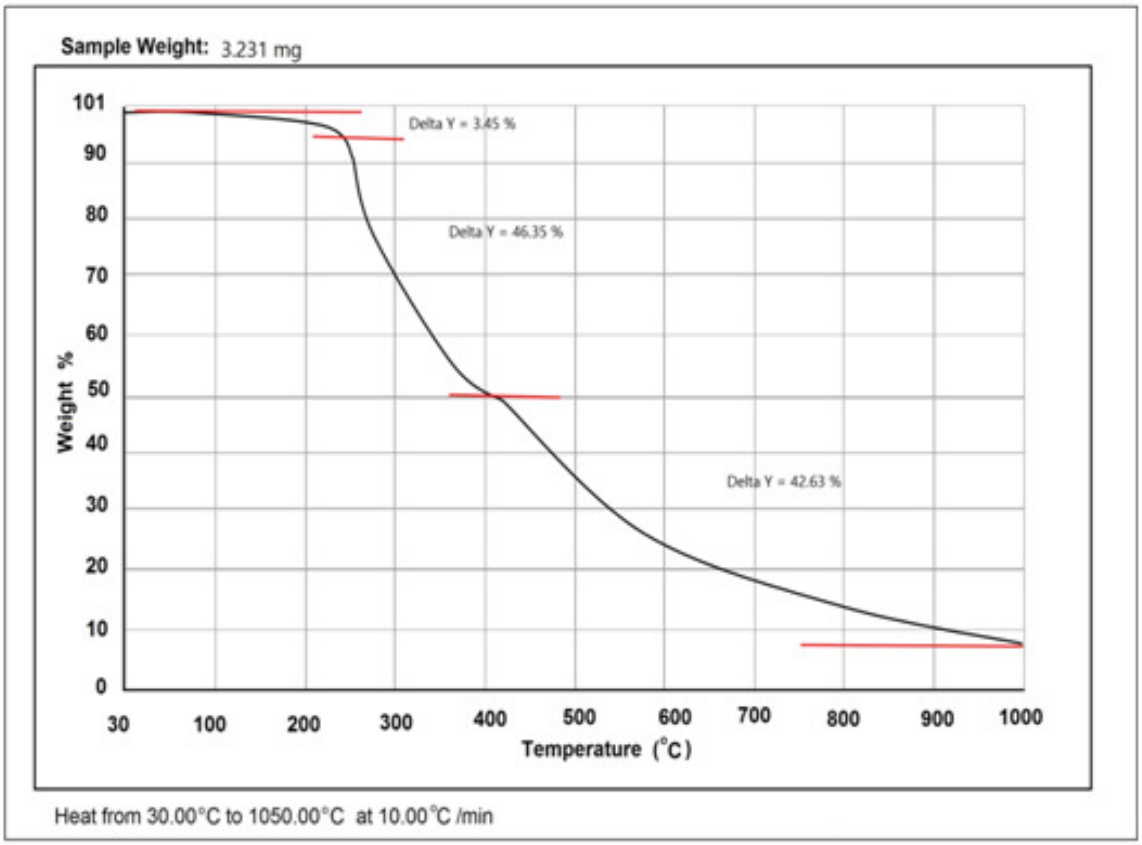


Figure-12: TGA Curve of $[Co(L_2)_2].2H_2O$.

Magnetic moment: For all metal complexes magnetic moment was conducted at room temperature, results showed square planar geometry of Cu (II) complexes was confirmed by the value around 1.74-1.81 B.M.[20] Octahedral geometry of Ni (II) [21], and Co (II) complexes at 25˚C [22] which confirmed through magnetic moment studies, Ni (II) and Co (II) complexes have values in the range of 2.91-2.81 and 4.64-5.09 B.M. respectively.

Electron spin resonance study: The ESR spectra of the complexes were recorded at room temperature as polycrystalline samples, two peaks are showed, one at high field with intense absorption and the other at low field has less intensity. By adopting Kneubehls method we have calculated the values of g‖ and g$^{\perp}$.[23] From ESR spectra, g values observed are g‖ > g⊥ indicates that the unpaired electron is in the dx^2-y^2 orbital See (Table4). This suggests a square planar structure of the Cu(II) ion.[24-26] Covalent character of the metal-ligand bond for the Cu (II) complexes due to g‖ obtained was less than 2.3.[27] The value of the axial symmetry parameter (G) for the complexes was greater than 4, this indicates to absence of interaction between copper centers in the solid state[28].

Antimicrobial activity: By using disc diffusion method[29] at a concentration of 500 µg/ml, antimicrobial screening was done. Penicillin and streptomycin are used as standard references. All ligands and their metal complexes were screened against the bacteria (*Staph aureus, Bacillus subtilis, Escherichia coli, Salmonella typhi*) and fungi (*Aspergillus oryzae, Aspergillus niger*). The results obtained are tabulated in Table-5. From the table we can see Cu(II) complexes ($Cu(L_1)_2$) shows the moderate activity against all selected bacteria except *Staph aureus* than it's ligand (L_1) which gives high activity only on *Staph aureus*. $Cu(L_2)_2$ showed same activity with *Staph aureus* compared with it's ligand (L_2) and modrate activite with with the other bacteria, while other complexes Ni(II) and Co(II) did not show significant activity against bacteria except moderately active against *Staph aureus and Salmonella typhi*. All compounds did not stop the growth of *Aspergillus oryzae* fungus and all compounds were not effective towards *Aspergillus niger* fungus (Figure-13).

Table-4: ESR spectral date of Cu(II) Complexes.

Sr. No.	Complex Code	g‖	g⊥	g_{av}	G axial Symmetry Parameter	μ_{eff}. B.M. from Gouy Balance
1.	$Cu(L_1)_2$	2.1723	2.0711	2.1048	4.2434	1.74
2.	$Cu(L_2)_2$	2.1641	2.0618	2.0959	4.2259	1.82

Table-5: Antimicrobial activity of synthesized compounds.

Compounds / code	Gram positive bacterias		Gram negative bacterias		Fungus	
	Staph aureus	*Bacillus subtilis*	*Escherichia coli*	*Salmonella typhi*	*Aspergillus oryzae*	*Asperillus niger,*
L_1 / (a1)	++	-	-	-	-	-
$Cu(L_1)_2$ / a2	+	+	+	+	-	-
$[Ni(L_1)_2].2H_2O$ / a3	-	-	-	-	-	-
$[Co(L_1)_2].2H_2O$/ a4	-	-	-	-	-	-
L_2 / b1	+	-	+	-	-	-
$Cu(L_2)_2$ / b2	+	+	-	+	-	-
$[Ni(L_2)_2].2H_2O$ / b3	+	-	-	-	-	-
$[Co(L_2)_2].2H_2O$ / b4	-	-	-	+	-	-
Penciline 1	+	+	+	+	x	x
Streptomycin 2	++	++	++	++	x	x
Greseofulvin	x	x	x	x	-	-

+ = Minimum Zone of Inhibition - Greseofulvin (fungus), ++ = Clear Zone of Inhibition - Standerd [1] Penciline +, - = No Effect, Standerd [2] Streptomycin ++, X = Not applicable

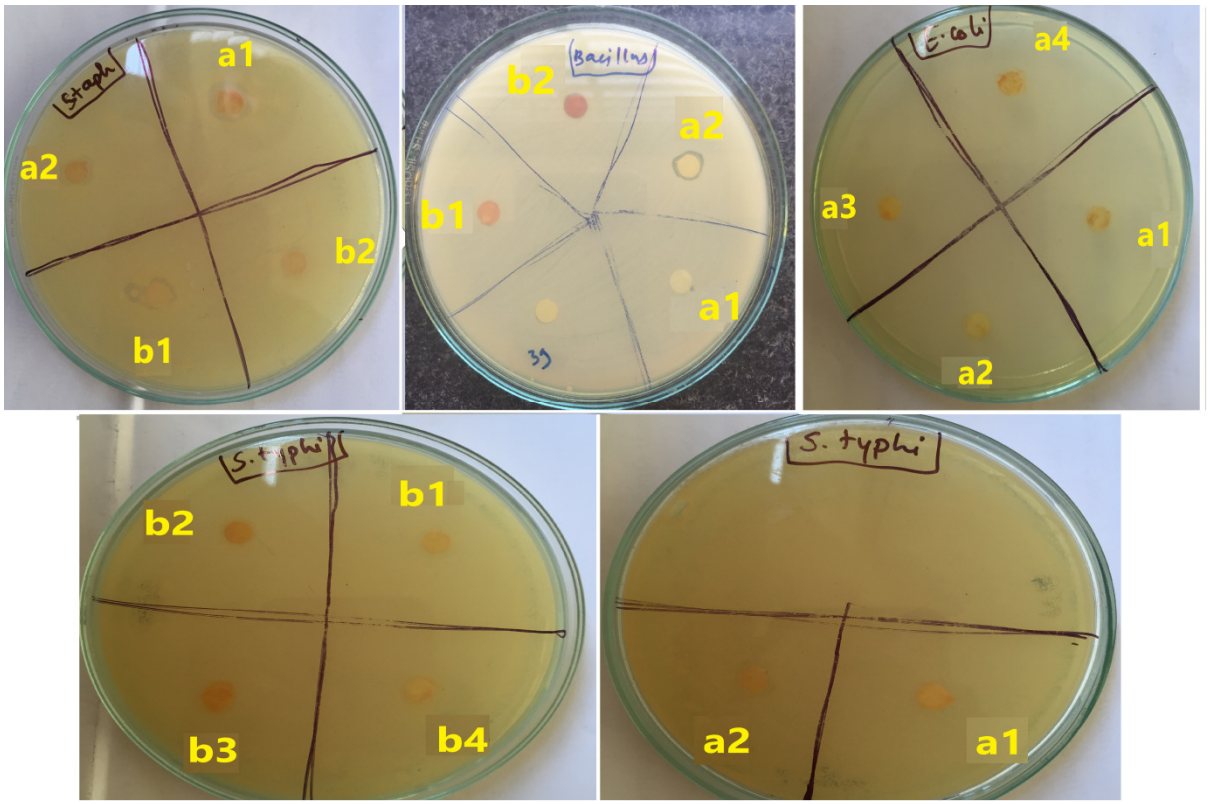


Figure-13: Antimicrobial activity for some samples of Cu(II), Ni(II) and Co(II) and their ligands.

Conclusion

According to discussion the results of this study a square planar geometry for the Cu(II) complex and an octahedral geometry for the Ni(II) and Co(II) complexes are proposed. In this study only Cu (II) complexes shows the moderate activity against different bacteria. Comparing with Ni(II) and Co(II) complexes, $[Ni(L_2)_2]$. $2H_2O$ shows moderate activity on *S.aureus* and $[Co(L_2)_2].2H_2O$ shows moderate active on *P. aeruginosa.*

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