

# Measurement of temperature dependence conductivity and antimicrobial screening of four co-ordinate Ni (II) complexes

J. R. Gujarathi, Associate Professor

Department of Chemical Science, Pratap College, Amalner, Dist-Jalgaon (M.S.) India,

H.J.Nawate, Assistant Professor,

Department of Physical Science and Information Technology ,

Pratap College Amalner, Dist-Jalgaon (M.S.) India.

**Abstract :-** Hydrazone ligands were synthesized by the reaction of acetohydrazone with 3,5-dichloro-2-hydroxy acetophenone, 5-chloro-2-hydroxy acetophenone and 4,5-dichloro-2-hydroxy acetophenone. Ni (II) complexes were synthesized by reaction of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  with hydrazone ligand in mole ratio 1:2. The ligands and complexes were characterized by Elemental analysis, ESI-MS, Infrared (FT-IR) spectroscopy, electronic spectra, Nuclear Magnetic Resonance ( $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR) magnetic measurement and conductivity at different temperature. The metal complexes and corresponding ligands were screened against bacterial parasites. It is observed that the complexes synthesized are more biologically active than corresponding hydrazone ligands. exhibited growth inhibitory activity against bacterial species.

**Keywords:** 1:2 ratio, bioactive metal complexes, diamagnetism,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ .

## INTRODUCTION

Many transition metal complexes have been used in catalysis and in biological fields as potential drugs [1,2]. Nickel is divalent metal and exists as Ni. Ni (II) complexes usually exhibit four coordinate square planer or tetrahedral geometries. Six coordinate octahedral complexes of Ni (II) are also known [3,4]. Ni (II) complexes are generally diamagnetic. But some paramagnetic complexes have also been studied [5]. Hydrazides and complexes synthesized from them possess biological properties such as antibacterial [6-8], antifungal [9], anti-tumor [10-13], anti-malarial [14], anti-cancer [15], anti-inflammatory [16]. Metal complexes of Schiff base ligands possess wide range of applications in the biological, analytical, clinical, and industrial areas [17]. The transition metal complexes of Schiff base ligands are important, not only due to their spectroscopic properties and applications [18] but also due to their antifungal, antibacterial and antitumor activities [19]. Schiff bases have a vital position in metal coordination chemistry even almost a century since their discovery. Large number of metal coordination complexes of Schiff bases have been used as antibacterial, antifungal, cytotoxic, anti-inflammatory and cytostatic agents [20-23].

In this article the synthesis, spectral characterization and biological studies of four coordinate complexes of Ni (II) with hydrazone ligands have been reported.

## II MATERIALS AND METHODS

Chemicals used are of A.R. grade. Magnetic susceptibility measurement was carried out by Faraday method at room temperature. IR spectra were recorded in solid state in the range  $4000\text{-}200\text{ cm}^{-1}$  range. Thermogravimetric analysis was carried out in the temperature range  $30\text{-}800^\circ\text{C}$ . Metal was estimated by standardized E.D.T.A using xylenol orange as an indicator and hexamine as buffer.

## III EXPERIMENTAL

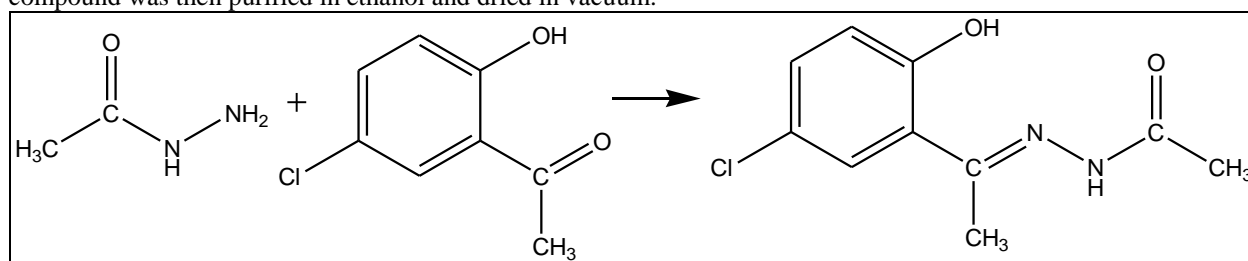
### Synthesis of acetohydrazone:

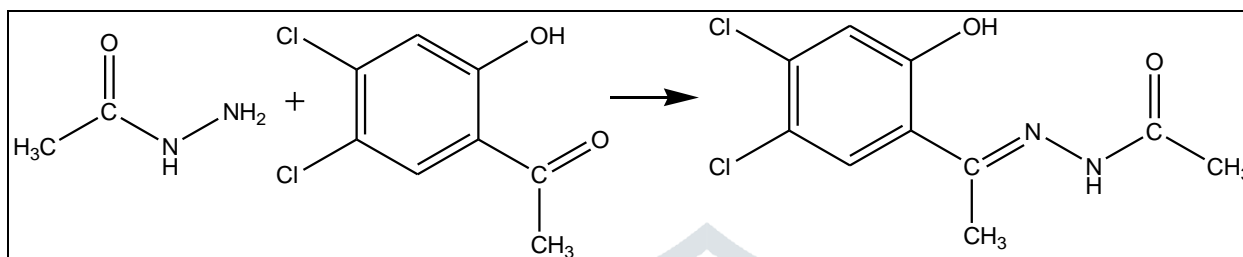
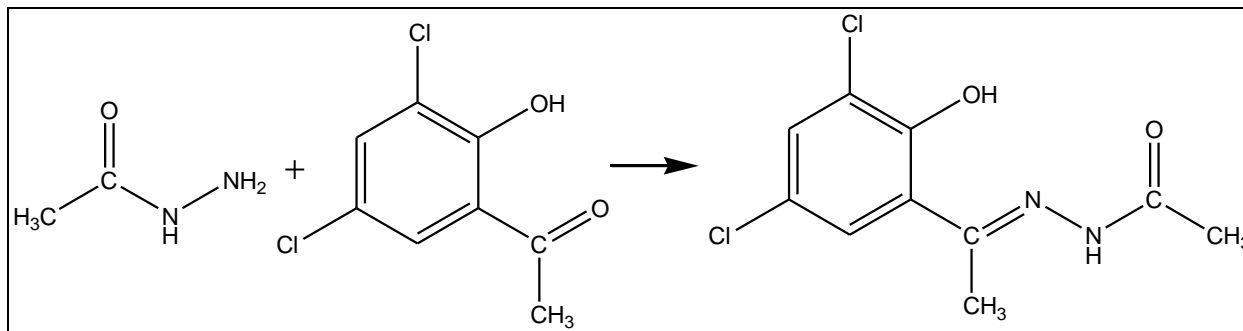
Ethanol solution of glacial acetic acid (0.01 mole) was added to ethanol solution of hydrazine hydrate (0.01 mole) in the mole ratio 1:1. The reaction mixture was refluxed for three hours. Pale yellow product on cooling was filtered and washed with hot water then cold ethanol and finally with ether. Purified in ethanol and dried in vacuum.



Scheme I

Ethanol solution of acetohydrazone (0.01 mole) was added to ethanol solution 5-chloro-2-hydroxy acetophenone/3,5-dichloro-2-hydroxy acetophenone/4,5-dichloro-2-hydroxy acetophenone (0.01 mole) in the mole ratio 1:1. The reaction mixture was refluxed for three hours. Yellow product was filtered and washed with hot water then cold ethanol and finally with ether. The compound was then purified in ethanol and dried in vacuum.





### Synthesis of complex

Ni.L<sub>2</sub> was synthesized by adding slowly ethanolic solution of NiCl<sub>2</sub>.6H<sub>2</sub>O (0.01 mole) to the hot ethanolic solution of 5-chloro 2-hydroxy acetophenone acetohydride/3,5-dichloro 2-hydroxy acetophenone acetohydride/4,5-dichloro 2-hydroxy acetophenone acetohydride (0.01 mole) in the ratio 1:2 and starting reaction mixture for half hour at 30°C temperature. The complex obtained was filtered and washed with hot water to remove excess metal salt, cold ethanol and diethyl ether and dried in vacuum.

### Physical measurements

Magnetic measurement was carried out at room temperature by Faraday method. IR spectra were recorded in the range 4000-200 cm<sup>-1</sup>. NMR spectra were recorded in the mixture of CDCl<sub>3</sub> and DMSO-d<sub>6</sub> (1:1 v/v) with a Bruker AC-300F 300MHz spectrometer. Conductivity measurement was carried out at room temperature. UV-Visible solution spectra were measured on Jasco UV-visible double beam spectrophotometer. Metal in the complex and adducts was estimated by E.D.T.A using murexide as an indicator.

**Table 1 Physical measurements**

Compounds	Colour	Empirical Formula	Magnetic Moment B.M.
L	Yellow	C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> OSCl <sub>2</sub>	-
Ni-L.H <sub>2</sub> O	Reddish Brown	C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> SCl <sub>2</sub> Ni	Diamagnetic
Ni-L.Py	Reddish Brown	C <sub>16</sub> H <sub>16</sub> N <sub>4</sub> OSCl <sub>2</sub> Ni	Diamagnetic
Ni-L.2-Cl Py	Reddish Brown	C <sub>16</sub> H <sub>15</sub> N <sub>4</sub> OSCl <sub>3</sub> Ni	Diamagnetic
Ni-L. 3-Cl Py	Reddish Brown	C <sub>16</sub> H <sub>15</sub> N <sub>4</sub> OSCl <sub>3</sub> Ni	Diamagnetic
Ni-L.4-Cl Py	Reddish Brown	C <sub>16</sub> H <sub>15</sub> N <sub>4</sub> OSCl <sub>3</sub> Ni	Diamagnetic

### Conductivity measurement

The conductivity was measured in DMF solution and equivalent conductance was calculated. The 0.001 M solution of complexes was prepared in different percentages of DMF-ethanol mixture and the parameter of solution under study was calculated at temperature 300 K, 305 K and 310 K.

Equivalent conductance at 300 K			
DMF-Ethanol mixture	Ni.L <sub>2</sub> .	Ni.L <sub>2</sub> '	Ni.L <sub>2</sub> ''
75%	32.0	35.3	37.5
80%	35.6	40.5	39.8
85%	42.4	41.6	41.7
90%	45.8	48.4	44.3
95%	50.1	50.3	47.9

100%	53.5	52.2	49.2
<b>Equivalent conductance at 305 K</b>			
DMF-Ethanol mixture	Ni.L <sub>2</sub> .	Ni.L <sub>2</sub> '	Ni.L <sub>2</sub> ''
75%	39.4	39.3	40.1
80%	41.5	40.2	42.4
85%	46.2	44.2	44.4
90%	51.2	49.3	46.2
95%	54.2	50.4	48.7
100%	58.2	55.3	51.4

<b>Equivalent conductance at 310 K</b>			
DMF-Ethanol mixture	Ni.L <sub>2</sub> .	Ni.L <sub>2</sub> '	Ni.L <sub>2</sub> ''
75%	41.5	39.2	40.1
80%	43.7	42.2	43.5
85%	47.4	44.5	49.4
90%	51.3	50.3	51.2
95%	56.2	52.4	53.7
100%	60.5	56.5	59.1

**<sup>1</sup>H-NMR (L)**

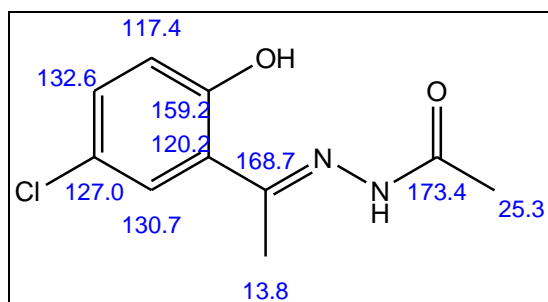
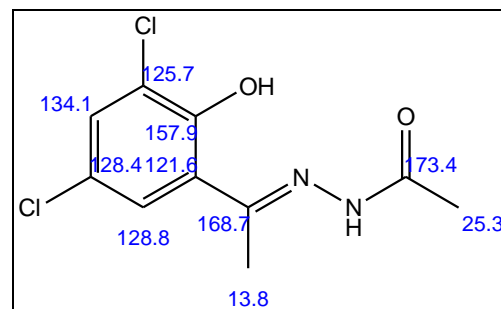
NMR signals at 10.00 and 2.05 ppm and 0.8 ppm are assigned to –OH and O=C-CH<sub>3</sub> and –N=C-CH<sub>3</sub> protons respectively. Signal at 7.2 ppm corresponds to NH. Aromatic protons show multiplets at 7.2, 7.4, 6.8, ppm.

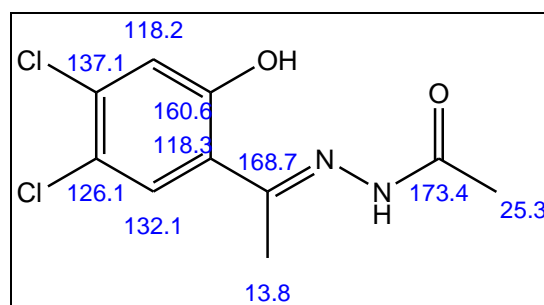
**<sup>1</sup>H-NMR (L')**

NMR signals at 10.01 and 2.03 ppm and 0.8 ppm are assigned to –OH and O=C-CH<sub>3</sub> and –N=C-CH<sub>3</sub> protons respectively. Signal at 7.2 ppm corresponds to NH. Aromatic protons show multiplets at 7.2, 7.4 ppm.

**<sup>1</sup>H-NMR (L'')**

NMR signals at 10.02 and 2.03 ppm and 0.8 ppm are assigned to –OH and O=C-CH<sub>3</sub> and –N=C-CH<sub>3</sub> protons respectively. Signal at 7.1 ppm corresponds to NH. Aromatic protons show multiplets at 7.5, 6.8 ppm.

**<sup>13</sup>C-NMR (L) δppm****<sup>13</sup>C-NMR (L') δppm**

**<sup>13</sup>C-NMR (L'') δppm****ESI-MS m/z, ion M<sup>+</sup>(Calcd) found**

C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>SCl<sub>2</sub> (306.19) 306.72, C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>SCl<sub>2</sub>Ni (380.88) 380.13, C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>SCl<sub>2</sub>Ni (427.96) 427.34, C<sub>16</sub>H<sub>15</sub>N<sub>4</sub>O<sub>2</sub>SCl<sub>3</sub>Ni (462.40) 462.812, C<sub>16</sub>H<sub>15</sub>N<sub>4</sub>O<sub>2</sub>SCl<sub>3</sub>Ni (462.40) 462.82, C<sub>16</sub>H<sub>15</sub>N<sub>4</sub>O<sub>2</sub>SCl<sub>3</sub>Ni (462.40) 462.74.

**Table.2 Analytical data**

Compounds	Elemental Analysis Found (Calculated) %				
	Metal%	%C	%H	%N	%O
L	-	52.21 (52.99)	4.80 (4.28)	12.30 (12.71)	14.80 (14.12)
L'	-	46.70 (46.00)	3.10 (3.86)	10.15 (10.73)	12.75 (12.27)
L''	-	46.88 (46.00)	3.05 (3.86)	10.15 (10.73)	12.75 (12.27)
Ni.L <sub>2</sub>	12.08 (12.67)	41.18 (41.56)	3.82 (3.27)	9.83 (9.09)	6.12 (6.93)
Ni.L' <sub>2</sub>	12.12 (12.67)	41.05 (41.56)	3.88 (3.27)	9.84 (9.09)	6.17 (6.93)
Ni.L'' <sub>2</sub>	12.10 (12.67)	41.16 (41.56)	3.89 (3.27)	9.87 (9.09)	6.20 (6.93)

**Electronic Spectral data (cm<sup>-1</sup>) in solid state****Table 3 .Electronic spectral data (cm<sup>-1</sup>)**

Compound	d-d	L→M	n→π*	π→π*
L	-	-	25,977	40,860
L'	-	-	25,890	40,220
L''	-	-	25,352	40,145
Ni.L <sub>2</sub>	17,540	23,787	32,140	43,150
Ni.L' <sub>2</sub>	17,650	23,689	32,456	42,225
Ni.L'' <sub>2</sub>	17,752	23,890	32,326	42,960

**Infrared Spectroscopic data (cm<sup>-1</sup>)****IR-spectral data**

- 1.L:** ν (- OH) 3250; ν (C = N) 1671, ν (N - N) 1052; ν (<sup>2</sup>N-H) 3257; ν (C - O) 1296.
- 2.L':** ν (- OH) 3255; ν (C = N) 1677, ν (N - N) 1075; ν (<sup>2</sup>N-H) 3258; ν (C - O) 1287.
- 3.L'':** ν (- OH) 3288; ν (C = N) 1687, ν (N - N) 1081; ν (<sup>2</sup>N-H) 3261; ν (C - O) 1289.
- 4.Ni.L<sub>2</sub>:** ν (- OH) 3215, ν (C = N) 1565, ν (N-N) 1167, ν (N-H) 3259, ν (M - N) 452, ν (M - O) 532, ν (C - O) 1215.
- 5.Ni.L'<sub>2</sub>:** ν (- OH) 3266, ν (C = N) 1567, ν (N-N) 1172, ν (N-H) 3264, ν (M - N) 462, ν (M - O) 542, ν (C - O) 1222.
- 6.Ni.L''<sub>2</sub>:** ν (- OH) 3296, ν (C = N) 1572, ν (N-N) 1182, ν (N-H) 3270, ν (M - N) 466, ν (M - O) 547, ν (C - O) 1226.

**TGA ANALYSIS DATA:**

TGA was carried out in the temperature range 25 °C to 800 °C

- 1.Ni.L<sub>2</sub>:** First step, 116 °C, Mass loss 4.52 % second step, 140.0 °C, Mass loss, 18.38 % Third Step 245.0 °C, Mass loss, 38.00 % Fourth Step, 372.0 °C, Mass loss .67.0 %, Residue 800 °C, % of NiO, 20.90(20.36).
- 2.Ni.L'<sub>2</sub>:** First step, 121 °C, Mass loss 10.24 % second step, 352.0 °C, Third Step 242.0 °C, Mass loss, 40.05 % Fourth Step, 375.0 °C, Mass loss .65.0 %, Mass loss, 57.0 % , Residue, 782 °C, % of NiO, 18.60 (18.04).
- 3.Ni.L''<sub>2</sub>:** First step, 120 °C, Mass loss 10.55 % second step 364 °C, Mass loss, 59.2 % , Third Step 257.0 °C, Mass loss, 45.04 % Fourth Step, 372.0 °C, Mass loss .68.5 %, Residue 782 °C, % of NiO, 16.06 (16.66).

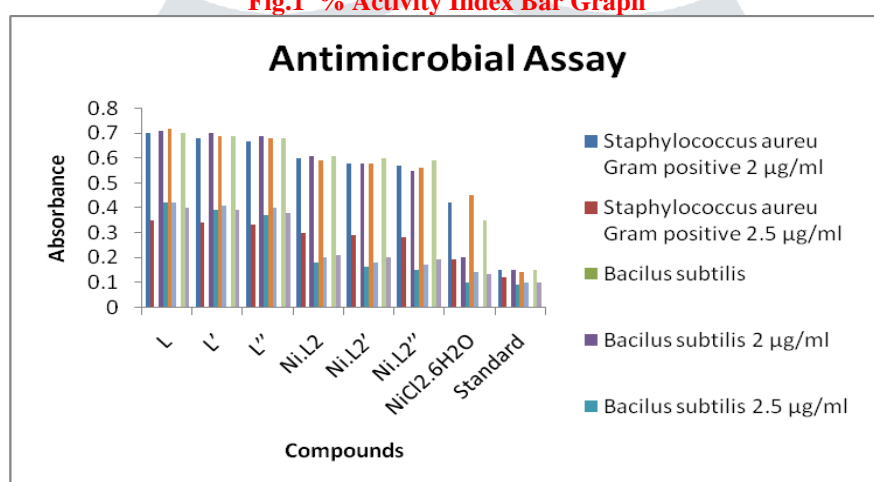
## IX BIOLOGICAL ACTIVITY (AGAR PLATE DIFFUSION METHOD)

Table.6 Minimum Inhibitory concentration L, Ni (II) complexes and standered

Compound	<i>Staphylococcus aureu</i>		<i>Bacillus subtilis</i>		<i>Escherichia Coli</i>		<i>Pseudomonas aeruginosa</i>	
	Gram positive				Gram negative			
	2 µg/ml	2.5 µg/ml	2 µg/ml	2.5 µg/ml	2 µg/ml	2.5 µg/ml	2 µg/ml	2.5 µg/ml
L	0.72	0.37	0.70	0.43	0.70	0.40	0.72	0.41
L'	0.69	0.35	0.71	0.40	0.70	0.42	0.70	0.40
L''	0.70	0.35	0.65	0.38	0.69	0.42	0.69	0.39
Ni.L <sub>2</sub>	0.62	0.32	0.62	0.19	0.60	0.22	0.62	0.22
Ni.L <sub>2</sub> '	0.59	0.30	0.59	0.17	0.59	0.19	0.62	0.22
Ni.L <sub>2</sub> ''	0.58	0.30	0.56	0.18	0.57	0.18	0.58	0.18
NiCl <sub>2</sub> .6H <sub>2</sub> O	0.43	0.20	0.21	0.11	0.46	0.15	0.36	0.14
Standard	0.14	0.13	0.17	0.10	0.15	0.11	0.16	0.11

(Std-Amphiciline)

Fig.1 % Activity Index Bar Graph



## RESULTS AND DISCUSSION

Elemental analysis data showed 1:2 ratio of metal ion and ligand in all complexes. The complexes are insoluble in polar and non polar solvents. The conductivity measurements were made in DMF. All complexes showed non electrolyte behaviour [24]. Mass spectral data confirmed the structure of ligands and complexes. The magnetic susceptibility measurement was carried out at room temperature showed complexes are diamagnetic in nature.

The equivalent conductance of electrolyte solution depends on concentration of solution and temperature. It is found that equivalent conductance of an electrolyte increases upon dilution. In dilute solution conductance is more. All complexes showed increasing value of conductance with increase in the dilution at 300 K, 305K, 310 K. The conductivity of an electrolyte depends upon the temperature. The conductivity of an electrolyte increases with increase in temperature. This may be due to at higher temperature the mobility of ions increases and hence conductivity.

No bands observed below 10,000 cm<sup>-1</sup> clearly distinguish the planer complexes from octahedral and tetrahedral complexes. The electronic spectra showed band in the range 40,000-41,000 cm<sup>-1</sup> and 25,000 – 26,000 cm<sup>-1</sup>, these can be assigned to  $\Pi - \Pi^*$  (aromatic ring) and  $n - \Pi^*$  transitions respectively. The broad bands in 32,000 – 33,000 range are assigned to  $n - \Pi^*$  transitions in all complexes [25]. The shifting of  $\Pi - \Pi^*$  bands to the longer wavelength region in all complexes. The spectral data showed d-d transitions in the range 17,000 – 18,000 cm<sup>-1</sup>. These are assigned to  $^1A_{1g} \rightarrow ^1E_g$  and  $^1A_{1g} \rightarrow ^1A_{2g}$  [26]. The d-d bands appearing as weak shoulders centred around 17000 cm<sup>-1</sup> region are of square planer Ni (II) complexes [27]. The bands at 23,000 – 24,000 cm<sup>-1</sup> range correspond to  $L \rightarrow M$ .

$\nu(C = N)$  shifted to lower wavenumbers due to coordination of azomethine nitrogen.  $\nu(N-N)$  shifted to higher wavenumbers confirms coordination of azomethine nitrogen [28]. The new band at 450 – 470 cm<sup>-1</sup> is assignable to  $\nu(Ni - N)$  confirmed the coordination of azomethine nitrogen. The bands at 530-545 cm<sup>-1</sup> is assignable to  $\nu(Ni-O)$ . The band due to N-H in all complexes is not affected. The band due to OH in the complexes is not affected.

Lattice water molecule was removed at a temperature about 115-120°C corresponding to mass loss 4.0-10.0 %. The TGA data indicated that the decomposition proceeded in several steps. In between temperature 30-120 °C, hydration of water molecules were lost. No change observed up to ~200 °C after that there is break in the curves due to evaporation of part of molecule of organic ligand. The remaining hydrazine molecule was removed from the coordination sphere at ~600°C. The metal oxides were formed above 600°C. The decomposition was completed at ~800 °C. It has been found that Ni (II) complexes are stable up to 200°C and decomposition took place above this temperature and completed in the temperature range 300-370°C. The second steps are in the range of 315-380 °C. The solid oxide residue was of Ni-O [29].

The antibacterial assay was carried out by the agar plate diffusion method. Activity was measured by measuring the absorbance at 520 nm. Ligands were found less active. The minimum inhibitory concentration was determined by liquid dilution method [30]. The solutions of ligand and complexes with 2 µg/ml, 2.5 µg/ml and 3 µg/ml concentrations were prepared in the solvent



DMF. The solutions of standard drug ampicillin and metal salt were also prepared in the same concentration. Inoculums of the overnight culture were prepared. 0.2 ml of the inoculums was added to the test tubes containing the solutions of the compounds of different concentrations. Sterile water to each of the test tubes was added and these were incubated for 24 hours and observed for turbidity. The absorbance of the turbid solutions was measured at 530 nm. The same procedure was carried out for standard [31]. More absorbance was observed at 2 µg/ml concentration, less absorbance at 2.5 µg/ml and no absorbance at 3 µg/ml. The metal salt solution showed better inhibition than ligand and complexes. The minimum inhibitory concentration is 2.5 µg/ml. Thus coordination of metal ion to ligand enhances microbial activity. The free metal ion was found more effective than ligand and complexes. In general, complexes are found more effective than the free ligands and the same was observed in this study, that the complexes are more active than the parent ligands. The effective activity is exhibited by Ni(II) complexes towards bacterial species. The ligands show less activity. The variation in the activity of different complexes against different organisms depends either on the impermeability of cells of the microbes or differences in the ribosomes of microbial cells [32]. The higher antibacterial activity of complexes can be explained by chelation theory of the ligand with metal ions [33] as metal chelates possess both polar and nonpolar properties. This makes them suitable for permeation into cells and tissues. The polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital upon chelation, and partial sharing of the positive charge of the metal ion with donor groups. Chelation increases the delocalization of  $\pi$ -electrons over the entire chelate ring and enhances the penetration of the complexes into lipid membranes [33], [34]. It also increases the hydrophilic and lipophilic nature of the central metal ion, probably leading to lipo-solubility and permeability through the lipid layer of cell membranes. Further, lipophilicity, which controls the rate of entry of molecules into the cell, is modified by coordination, so the metal complex can become more active than the free ligand [35].

### Conclusion:

All complexes of Ni (II) are square planer in nature. Magnetic moment studies and conductance studies prove the assigned geometries. Ligands and the synthesized complexes were tested for antibacterial assay. The antimicrobial activity of metal complexes is depended more on the metal center itself than on the geometry around the metal ion.

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