



ISSN: 0976-3376

Available Online at <http://www.journalajst.com>

ASIAN JOURNAL OF  
SCIENCE AND TECHNOLOGY

Asian Journal of Science and Technology  
Vol. 11, Issue, 09, pp.11187-11196, September, 2020

## RESEARCH ARTICLE

### COMPLEXES OF N-SUBSTITUTED PHENOTHIAZINES WITH NI(II): SYNTHESIS, CHARACTERISATION AND THEIR BIOLOGICAL STUDIES

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#### ARTICLE INFO

##### Article History:

Received 17<sup>th</sup> June, 2020

Received in revised form

09<sup>th</sup> July, 2020

Accepted 24<sup>th</sup> August, 2020

Published online 30<sup>th</sup> September, 2020

##### Key words:

N-substituted Phenothiazines,  
Metal Complexes,  
Antibacterial, Spectral Studies.

#### ABSTRACT

New series of Nickel(II) complexes were synthesized and formulated as  $[M L L^1(CH_3COO)(H_2O)_2]$ , and  $[M L L^1(CH_3COO)H_2O]$  where  $L=N$ -substituted phenothiazines and  $L^1=1,10$ -phenanthroline. The newly synthesized complexes have been characterized by elemental analysis, molar conductance, UV-Visible, IR, mass spectra and magnetic properties. The spectral studies have shown that the complexes are paramagnetic and tentative structure has been proposed for the prepared complexes. The complexes were screened for antibacterial, antifungal and antioxidant activities, some of the complexes exhibit good biological activity.

**Citation:** Kohila, M., Jeyalalitha, T. and Amutha, A., 2020. "Complexes of n-substituted phenothiazines with ni(ii): synthesis, characterisation and their biological studies", *Asian Journal of Science and Technology*, 11, (09), 11187-11196.

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## INTRODUCTION

N-substituted phenothiazines fulfill the basic prerequisite for an active ligand possessing three active coordinate sites in the forms of a heterocyclic nitrogen and sulphur atoms in the side chain. Due to these multifaceted characteristic, they find widespread utilization in biology, medicine and chemical analysis. Recently, N-substituted phenothiazines have attracted a large interest in the photo ionization studies performed for solar energy conversion processes. It is used for pre-anesthetic medication, as a muscle relaxant and in the treatment of tetanus (Perumal, 2001). N-substituted phenothiazines are versatile compounds possessing anticholinergic, antihistaminic, antiameobic and antiemetic activities. These compounds are found to be exhibiting fungicidal and antibacterial activities. They are extensively used in the field of psychiatry and chemotherapy (Satoskar, 1976). It has now been discovered that some derivatives of N-substituted phenothiazines show surprisingly high stabilizer activity and more solubility in a broad range of mineral and synthetic oils. Thus the subject matter of the instant invention is a lubricant composition comprising synthetic oils, mineral oils, mixtures thereof and an antioxidative compound.

Such antioxidant combinations may show a synergistic action that is the stabilizing effect of such a mixture being greater than the sum of the performances of the individual antioxidant. Such synergistic performance can be obtained when combining the instant compounds along with certain aromatic amines or hindered phenols or with both types of antioxidants. Nickel shows a range of oxidation states from (+1) to (+IV). It is predominantly divalent and ionic in simple compounds, and exists as Ni (II) in most of its complexes. Nickel forms four, five and six coordinate complexes. Five coordinate nickel complexes are rather unusual. The nickel complexes compounds with multidentate ligands has attracted particular attention, because this metal in complex, is able to exhibit several oxidation states in the complexes<sup>3,4</sup>. These complexes can also act as potential catalysts<sup>5,6</sup>. Such complexes with different oxidation states have a strong role in bioinorganic chemistry and provide the basis of models for active sites of biological systems (Prakash, 2011). Nickel complex of N-benzoyl-N'-(2-aminophenyl)thiocarbamide was shown to exhibit antifungal activity (Satpathy, 1981). Depending on the ligands the balance can lie between square planar and tetrahedral forms indeed in the case of dibromobis (benzylidiphenylphosphine) nickel(II),  $Ni[P(CH_2C_6H_5)_2]_2Br_2$ , both tetrahedral and square planar forms coexist in the same crystal lattice. The biological experiments showed that the nickel complexes have many number of applications as antiepileptic (Bombicz, 2001) anticonvulsant (Morgant, 2006) agents or vitamins and showed significant antibacterial

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(Kurtaran, 2005) anticancer/antiproliferative (Afrasiabi, 2007; Zhong) antifungal and antimicrobial (Luo, 2007) activities. The survey reveals the transition metal ion interactions with substituted phenothiazines drug have been extensively studied. The nitrogen and sulphur present in the N-substituted phenothiazines act as excellent electron donors and possess good biological activity. Due to the multifaceted activity the author has prepared nickel (II) complexes and the structure of newly synthesized complexes were accomplished by spectral characterization *via.*, IR, UV-visible mass, elemental analysis and thermo gravimetric analysis. The biological properties were evaluated *via* antimicrobial, antioxidant activities.

## MATERIALS AND METHODS

The ligands [L] were prepared as described in the literature for phenothiazine and 2-chloro phenothiazine (Chandrashekara, 2016). Metal salt, Nickel acetate and 1,10-phenanthroline was obtained from padmashree scientific. All organic solvents such as methanol, ethanol, diethyl ether, dimethyl formamide, dimethyl sulfoxide and DMSO- $d_6$  were of ACS reagent grade and were used without further purification. Double distilled water was used in all preparations. The CT-DNA was purchased from Bangalore, the Trisbuffer, sodium chloride and hydrochloric acid (AR) was purchased from Merck.

Elemental analyses of complexes were estimated *in* an elementorvairo-EL instrument. Molar conductivity measurement in DMF was made on an ELICO-CM-180 conductivity bridge with a conductivity cell having cell constant  $0.51\text{cm}^{-1}$ . UV-Visible spectra were recorded using a Shimadzu UV1601 spectrophotometer. IR spectra were recorded in KBr using a perkin Elmer 157 FT-IR spectrometer from  $4000$  to  $400\text{cm}^{-1}$ . Mass magnetic susceptibilities of the complexes were measured in Johnson Matthey magnetic susceptibility balance which uses  $\text{HgCo}(\text{SCN})_4$  as a calibrant, at room temperature. Melting points were determined on a Melt-Temp apparatus in laboratory devices. The mass spectra of ligands were recorded on TOF MS ES+ 9.25e4 spectrometer. The thermal analysis of the complexes were recorded using an instrument TGA Q50 V20.13 Build 39, samples were placed in platinum pan and heated with  $10^\circ\text{C}/\text{min}$  from room temperature to  $900^\circ\text{C}$  under the flow of  $20\text{mL}/\text{min}$  in dried argon. Nitrogen content was analyzed by micro-combustion Dumas. The metal content was determined by atomic absorption spectrometry (perkin elmer Analyst 400 spectrophotometer). Metal and chloride estimations were done by standard procedures after decomposition in nitric acid [16]. The electronic spectra were recorded at  $25^\circ\text{C}$  on a Jasco V560 in diffuse reflectance technique.

## EXPERIMENTAL

### General procedure for the preparation of metal Complexes

#### Synthesis of 1:1:1 ratio complexes

A known concentration of nickel acetate (1 m mol) in a minimum volume of methanol, is added drop wise with stirring to a concentrated methanolic solution of ligand (1 m mol) followed by addition of 1:10-phenanthroline (1 m mol) in limited amount of methanol. The mixture was refluxed for 6 hr at  $50^\circ\text{C}$ - $60^\circ\text{C}$  on water bath.

On cooling, colored solid product was obtained, the obtained metal complexes were collected by filtration and purified by washing with cold distilled ethanol and then with ether and dried over fused calcium chloride in vacuum. Each of the new complexes does not possess a sharp melting points ranging. Some complexes have high melting point which indicate their greater thermal stability.

| Complex Formula   | Complex Numbers |
|---|-----------------|
| $[\text{Ni}(\text{L}_1)(\text{L}')(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ | 1               |
| $[\text{Ni}(\text{L}_2)(\text{L}')(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ | 2               |
| $[\text{Ni}(\text{L}_3)(\text{L}')(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ | 3               |
| $[\text{Ni}(\text{L}_4)(\text{L}')(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ | 4               |
| $[\text{Ni}(\text{L}_5)(\text{L}')(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ | 5               |
| $[\text{Ni}(\text{L}_6)(\text{L}')(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ | 6               |

## BIOLOGICAL ACTIVITY

All the newly synthesized compounds are screened for biological activity such as antibacterial antimicrobial and antioxidant activity,

**Antibacterial activity:** The antibacterial activity were carried out against both gram positive and gram negative species like *B.subtilis*, *Ralstonia Solanacearum*, *Pseudomonas aeruginosa* and *Esherichia coli*, it is performed by disc diffusion technique method using nutrient agar medium (Katritzky, 1968). The test organisms were sub-cultured in the agar medium and were incubated for 24 hat  $37^\circ\text{C}$ . Standard antibacterial drug, Ciprofloxacin was used for comparison. The discs of 4 mm diameter were soaked in the test solutions and then placed on medium previously seeded with organisms in Petri plates and incubated for 24 h at  $37^\circ\text{C}$ . The inhibition zone circling each disc was measured and the results have been noted in the form of inhibition zones. In order to clarify any effect of solvent (DMF) on the microbial screening, individual studies were performed with solution alone of DMF and they showed no activity against any microbial strains. The stock solution (1 mg/ml) of the test compounds was prepared in DMF. The test was carried out in triplicate and the average is represented.

**Antifungal Activity:** *In vitro* antifungal activity was tested against *Aspergillus flavus*, *Fusarium* and *phoma*. The test organisms were sub-cultured in potato dextrose agar medium and incubated at room temperature by well diffusion method<sup>18</sup>. The fungal strains were into each compound and standard drug of 10 mg was dissolved in 10 mL of DMSO to get a concentration of 1 mg/ mL. Fungal subculture was inoculated on the solidified media. With the help of 6 mm cork borer the cups were punched and scoped out of the set agar. The cups of inoculated plates were then filled with 0.1 mL of the test solution, standard solution and DMSO (negative control). The plates were allowed to stay for three days at room temperature and zone inhibition (mm) was then measured.

**Antioxidant Activity Investigation:** The evaluation of the *in vitro* antioxidant activity was carried out using DPPH radical scavenging assay followed by the procedure (Blois, 1958).

## RESULT AND DISCUSSION

The molecular formula and structure of the complexes were assigned on the basis of elemental analysis, mass, molar conductance, UV-visible, IR, magnetic studies and TGA.

Table 1. Physical characteristics and analytical data of the complexes

| Complexes | Color | Melting point (°C) | Molar conductance (mho cm <sup>2</sup> mol <sup>-1</sup> ) (ionic ratio) | Yield (%) |
|-----------|-------|--------------------|--|-----------|
| 1         | Green | >250°C             | 12.4   | 69        |
| 2         | Green | >250°C             | 12.8   | 72        |
| 3         | Green | >250°C             | 11.7   | 85        |
| 4         | Green | >250°C             | 13.1   | 71        |
| 5         | Green | >250°C             | 10.8   | 89        |
| 6         | Green | >250°C             | 10.5   | 85        |

Table 2. Elemental analysis of metal complexes

| Complexes | Molecular formula   | C Exp(Theor)% | H Exp(Theor)% | N Exp(Theor)% | M Exp(Theor)% |              |
|-----------|---|---------------|---------------|---------------|---------------|--------------|
| 1         | C <sub>26</sub> H <sub>27</sub> ClN <sub>3</sub> O <sub>4</sub> SNi | 610           | 54.97(54.96)  | 4.45(4.44)    | 6.87(6.88)    | 9.59(9.58)   |
| 2         | C <sub>27</sub> H <sub>26</sub> ClN <sub>3</sub> O <sub>4</sub> SNi | 623           | 55.63(55.52)  | 4.50(4.48)    | 7.21(7.18)    | 10.11(10.08) |
| 3         | C <sub>28</sub> H <sub>28</sub> ClN <sub>3</sub> O <sub>4</sub> SNi | 637           | 56.33(56.30)  | 4.73(4.71)    | 7.04(7.03)    | 9.87(9.86)   |
| 4         | C <sub>30</sub> H <sub>30</sub> N <sub>4</sub> O <sub>4</sub> SNi   | 642           | 59.90(59.85)  | 5.03(5.00)    | 9.31(9.30)    | 9.80(9.79)   |
| 5         | C <sub>31</sub> H <sub>32</sub> N <sub>4</sub> O <sub>4</sub> SNi   | 656           | 60.48(60.46)  | 5.24(5.23)    | 9.10(9.09)    | 9.57(9.56)   |
| 6         | C <sub>32</sub> H <sub>34</sub> N <sub>4</sub> O <sub>4</sub> SNi   | 674           | 61.04(61.02)  | 5.44(5.42)    | 8.90(8.88)    | 9.36(9.35)   |

Table 3. UV-visible spectral data of ligand and its metal complexes

| Ligands and Complexes | $\lambda_{max}$ (nm) | Molar absorptivity ( $\epsilon$ )(10 <sup>4</sup> ,M <sup>-1</sup> cm <sup>-1</sup> ) | transition  |
|-----------------------|----------------------|---|-------------|
| L <sub>1</sub>        | 262                  | 0.280   |             |
| 1                     | 272                  | 0.680   | $\pi-\pi^*$ |
| L <sub>2</sub>        | 265                  | 0.137   |             |
| 2                     | 271                  | 0.440   | $\pi-\pi^*$ |
| L <sub>3</sub>        | 265                  | 0.173   |             |
| 3                     | 269                  | 0.950   | $\pi-\pi^*$ |
| L <sub>4</sub>        | 269                  | 0.081   |             |
| 4                     | 273                  | 0.500   | $\pi-\pi^*$ |
| L <sub>5</sub>        | 265                  | 0.210   |             |
| 5                     | 270                  | 1.420   | $\pi-\pi^*$ |
| L <sub>6</sub>        | 265                  | 0.208   |             |
| 6                     | 272                  | 0.522   | $\pi-\pi^*$ |

Table -4: IR absorption of ligand and its metal complexes

| Ligands and Complexes | Absorption (C=O)(cm <sup>-1</sup> ) | Absorption N)(cm <sup>-1</sup> ) | (Ar-C)(cm <sup>-1</sup> ) | Absorption (C-S-N)(cm <sup>-1</sup> ) | Absorption (M-(H <sub>2</sub> O)(cm <sup>-1</sup> ) | Absorption (CH <sub>3</sub> COO)(cm <sup>-1</sup> ) |
|-----------------------|-------------------------------------|----------------------------------|---------------------------|---------------------------------------|---|---|
| L <sub>1</sub>        | 1674                                | 1323                             | 690                       | -                                     | -   | -   |
| 1                     | 1673                                | 1310                             | 688                       | 435                                   | 3335  | 1445  |
| L <sub>2</sub>        | 1675                                | 1325                             | 690                       | -                                     | -   | -   |
| 2                     | 1672                                | 1309                             | 689                       | 438                                   | 3445  | 1470  |
| L <sub>3</sub>        | 1670                                | 1365                             | 697                       | -                                     | -   | -   |
| 3                     | 1669                                | 1339                             | 697                       | 440                                   | 3440  | 1475  |
| L <sub>4</sub>        | 1671                                | 1352                             | 692                       | -                                     | -   | -   |
| 4                     | 1669                                | 1332                             | 691                       | 445                                   | 3410  | 1500  |
| L <sub>5</sub>        | 1683                                | 1369                             | 683                       | -                                     | -   | -   |
| 5                     | 1681                                | 1340                             | 682                       | 440                                   | 3455  | 1500  |
| L <sub>6</sub>        | 1686                                | 1374                             | 687                       | -                                     | -   | -   |
| 6                     | 1686                                | 1350                             | 687                       | 435                                   | 3545  | 1450  |

The complexes are soluble in acetone, methanol, ethanol, acetonitrile, DMF and DMSO.

**Physical properties of the complexes:** The analytical data and physical properties of ligands and metal complexes are given in table 1. Complexes are colored, and stable at room temperature as indicated by the melting point. The prepared complexes were found to have formula [M L L<sup>1</sup>(CH<sub>3</sub>COO)(H<sub>2</sub>O)<sub>2</sub>], and [M L L<sup>1</sup>(CH<sub>3</sub>COOH)(H<sub>2</sub>O)] Where M = Ni (II), L=N-Substituted phenothiazines, L<sup>1</sup> is 1:10-phenanthroline

**Molar Conductivity Measurements:** The molar conductance for the prepared complexes were measured at room temperature in DMF solution at 10<sup>-3</sup>mol/dm<sup>3</sup> were measured to establish the charge on the metal complexes The conductance values in the range of 10-14 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, indicates that all the complexes exhibit non-electrolytic nature, is due to no counter ions in the proposed structures of the metal complexes (Made Gowda, 1992).

**Elemental analysis:** The greenish complex exhibited three bands at 10250, 15245 and 26134 cm<sup>-1</sup> attributed to the <sup>3</sup>A<sub>2g</sub>-<sup>3</sup>T<sub>2g</sub> (v<sub>1</sub>), <sup>3</sup>A<sub>2g</sub>-<sup>3</sup>T<sub>1g</sub> (F) (v<sub>2</sub>) and <sup>3</sup>A<sub>2g</sub>-<sup>3</sup>T<sub>1g</sub> (P) (v<sub>3</sub>) transitions

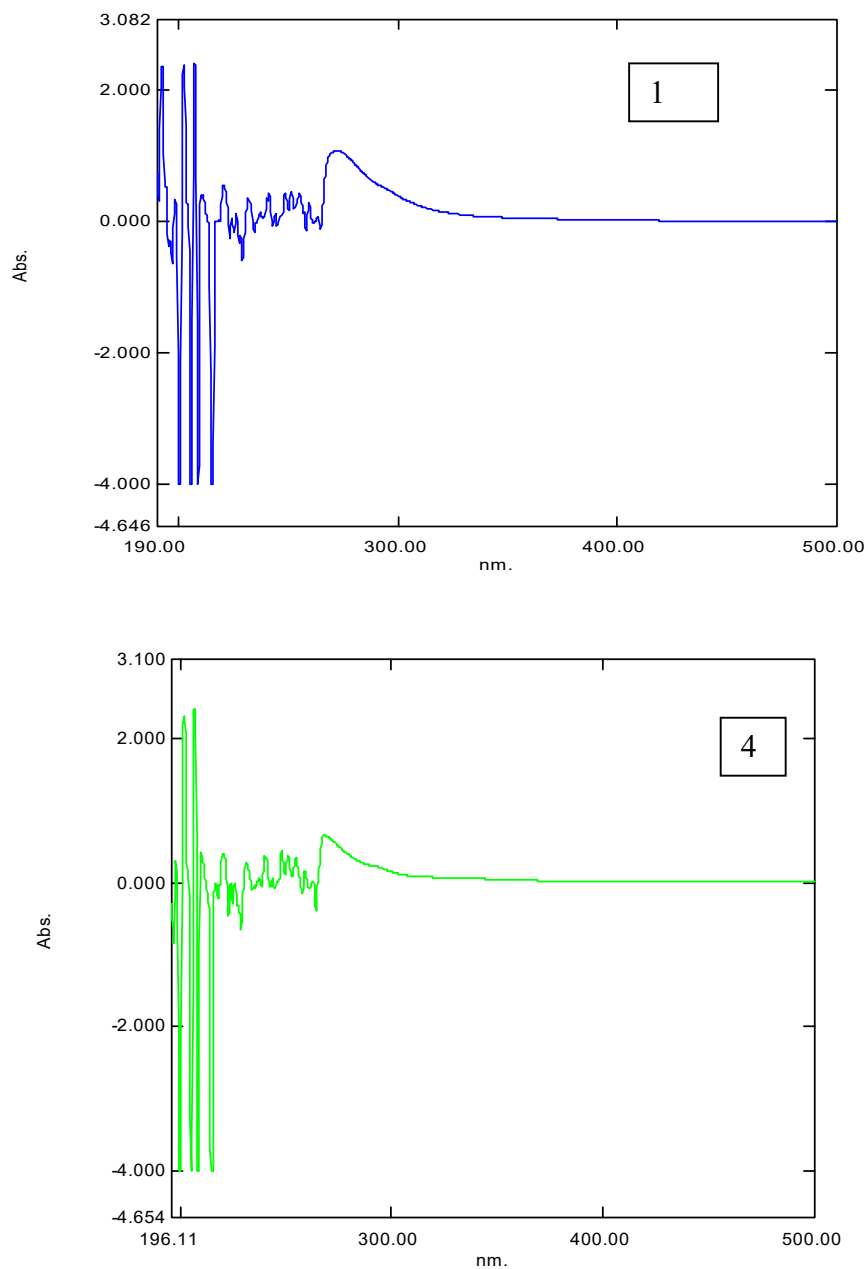


Figure 1: UV spectra of complexes 1 and 4

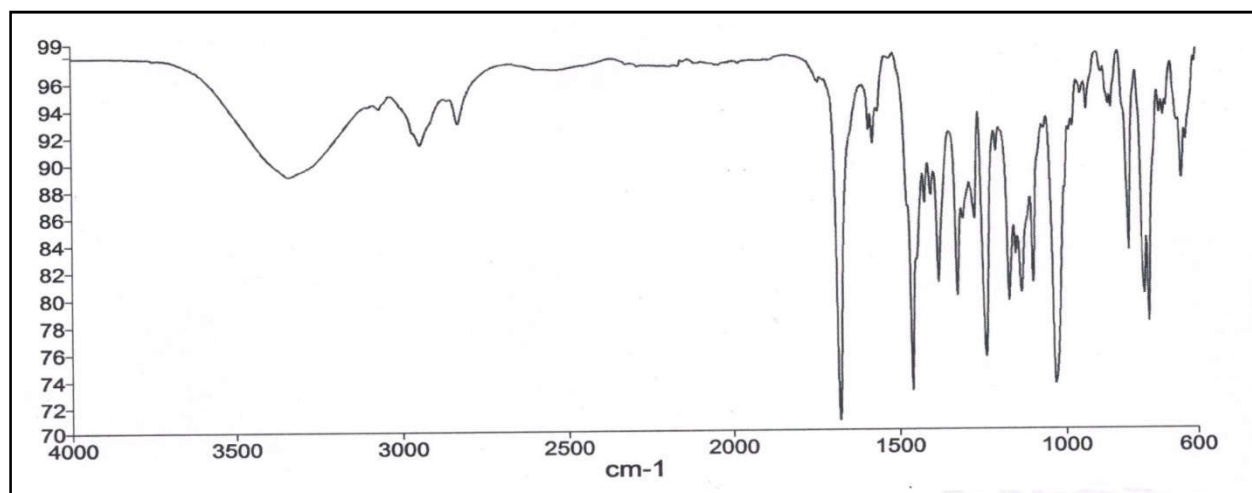


Figure 2: IR spectra of complex 1

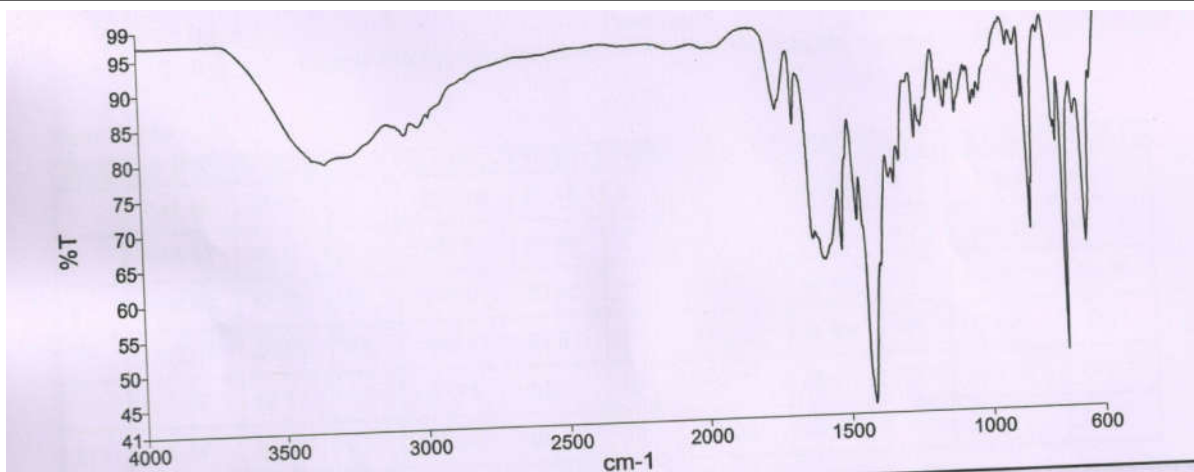


Figure 2: IR spectra of complex. 3

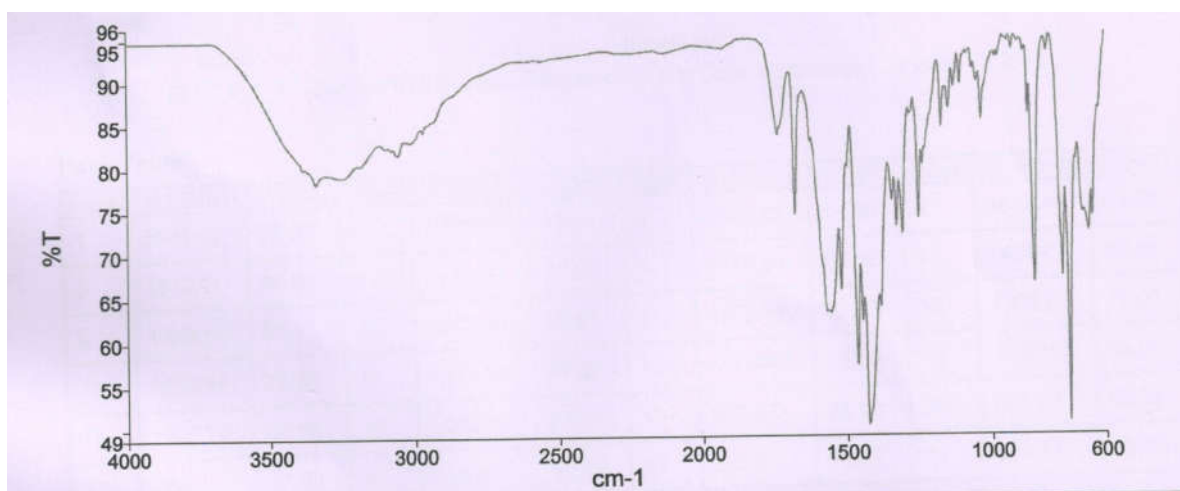


Figure 2: IR spectra of complex 5

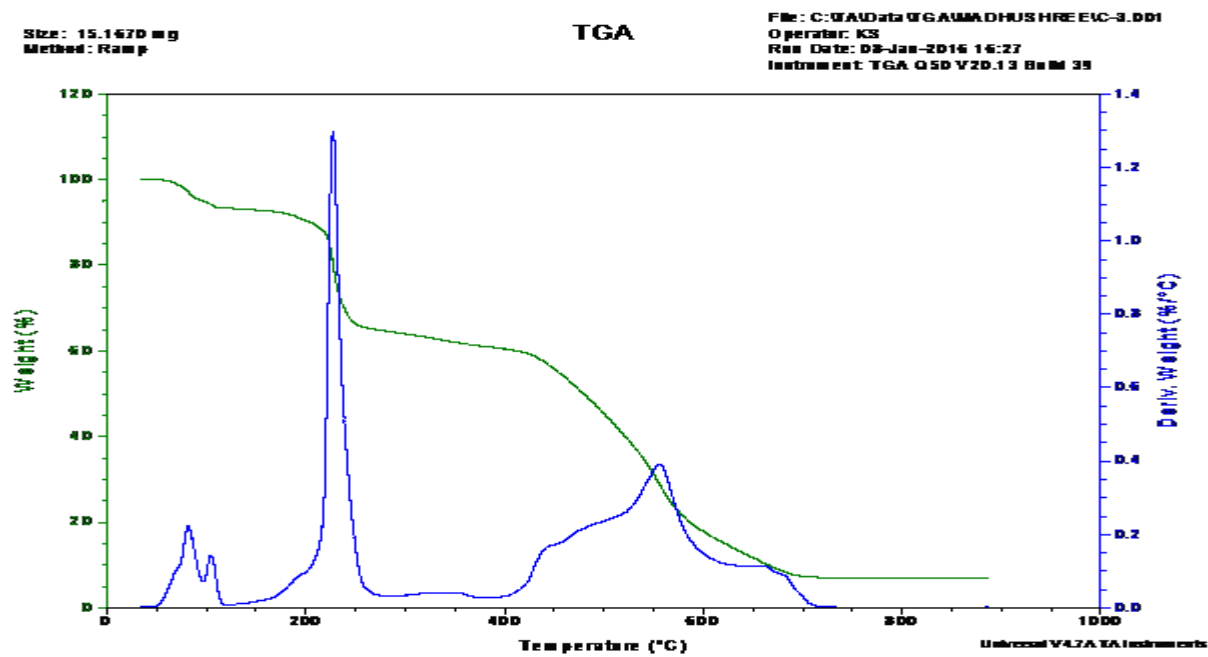


Figure 3: TGA spectra of complex.1

respectively, which indicate an octahedral geometry around Ni(II) ion. The value of  $v_2/v_1$  is found to be 1.47 and the  $\mu_{\text{eff}}$  value is 3.178 which are within the range of 3.15-3.22 BM, suggesting the octahedral environment. The values of the nephelauxetic parameter  $\beta$ , indicate low covalent character of the metal-ligand  $\sigma$  bonds (Makode, 2003; Mohamed, 2001):

**UV-Visible spectra:** The UV-Visible spectral data of the ligands and its metal complexes are presented in table 3. The broad bands observed in the region of 260-275 nm in the spectra of all complexes, can be attributed to the intraligand transitions. The molar absorptivities of the metal complexes falling in the range of  $0.24 \times 10^4 \text{ L mol}^{-1}$  to  $1.69 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ , are comparably higher than that of the ligand in the free state which is  $0.60 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The shift in the bands in UV- Visible spectra are attributed to the intramolecular transitions of  $\pi \rightarrow \pi^*$  type. This may be taken as an indirect evidence for the involvement of N atoms of ligand in the coordination process. The electronic spectra confirm the complex formation between the ligand and metal ions<sup>23</sup>

**Infrared spectra:** The type of bonding in metal complexes was studied by comparing the IR spectra of ligands with the spectra of metal complexes. Relevant IR absorption frequencies of the ligand and its metal complexes are presented in table 4. The functional groups of the ligands and their metal complexes have been detected by infrared spectra. The  $\nu(\text{Ar-N})$  frequency in the complex is observed around  $1300\text{-}1340 \text{ cm}^{-1}$  which is lower than that observed in free ligand and this evidence supports to the coordination of phenothiazines nitrogen. Involvement of phenothiazines nitrogen in the complexation is also supported by the presence of a new band at  $458\text{-}436 \text{ cm}^{-1}$ , assignable to  $\nu(\text{M-N})$  for these Ni(II) complexes (Palaniandavar, 1980). The IR spectra of free ligands shows characteristic bands due to lactam  $\nu(\text{C=O})$  in the region  $1675\text{-}1657 \text{ cm}^{-1}$  and  $\nu(\text{C-S-C})$  in the region  $680\text{-}699 \text{ cm}^{-1}$ . These band were not shifted in the IR spectra of the Ni(II) complexes, indicating the non participation of carbonyl oxygen and sulphur in coordination.

It was pointed out that the heterocyclic nitrogen atom to the alkyl group (aromatic or aliphatic) gives a characteristic band in the region  $2860\text{-}2850 \text{ cm}^{-1}$ , this band disappeared in the complexes 4, 5 and 6, which indicates the hetero cyclic nitrogen being the site of coordination. This shows that ligand act as a bidentate ligand with heterocyclic nitrogen (Keshavan, 1999). The absorption bands of the coordinated acetate groups in nickel complexes observed at  $1520$  and  $1425 \text{ cm}^{-1}$  are indicating a mono-dentate acetate anion character. In addition, complexes show a broad band in the  $3250\text{-}3560 \text{ cm}^{-1}$  region, suggesting the hydrogen bonded OH interactions of the water molecules and sharp peak in the range of  $1618\text{-}1624 \text{ cm}^{-1}$ , these peaks can be assigned to OH bending and stretching vibration which indicates the presences of coordinate water molecule in the complexes. The presence of water molecule in complexes is also supported by TGA studies (Gupta, 2006).

**Magnetic properties:** The magnetic susceptibility measurements of the complexes were obtained at room temperature using Gouy balance. Pure  $\text{Hg}[\text{Co}(\text{SCN})_4]$  was synthesized and used as calibration standard. The magnetic susceptibility of the complexes is given in table-5. The greenish Ni(II) complexes except exhibited the  $\mu_{\text{eff}}$  value is

around 3.02 and 3.12 B.M, suggesting the octahedral environment around Ni(II) ion (Bellamy, 1964).

### Magnetic moments

#### Thermo gravimetric Analysis

The thermal analysis of the compounds gave idea about the compound stability and suggested a decomposition pathway. TGA analysis was carried out in the temperature range  $900^\circ\text{C}$ . A heating rate of  $10^\circ\text{C}/\text{min}$  and flow rate  $20^\circ/\text{min}$ . The thermal decomposition of complexes takes place in four steps, until  $900^\circ\text{C}$ . In the first step, between  $70\text{-}180^\circ\text{C}$ , the compound is losing water molecule from the coordination sphere. The decomposition of ligand and anion starts above  $230^\circ\text{C}$ . The final step of thermal decomposition takes place between  $460\text{-}900^\circ\text{C}$ . The weight losses becomes constant at  $670^\circ\text{C}$  in both complexes. The weight loss observed in each case was good agreement with weight loss calculated on the basis of the stoichiometry proposed for the complexes in static air and corresponding to the total degradation of organic molecule, part of the carbon atoms remaining as a product in the crucible as metallic oxide.

#### Mass Spectra

Mass spectrometry has been widely applied to the characterization of coordination compounds<sup>28-30</sup>. The mass spectra of all the Ni(II) complexes have been recorded. All the spectra exhibit parent peaks due to molecular ions. The proposed molecular formula of these complexes was confirmed by comparing their molecular formula weights with  $m/z$  values. Mass spectral studies provide evidence for the proposed constitution of the complexes. The two complexes 1, 2 and 4 are selected as representative show the molecular ion peaks  $[\text{M}^+] = 610.9690.$ ,  $[\text{M}^+ + 2] = 612.9815$ ,  $[\text{M}^+] = 622.2171$ ,  $[\text{M}^+ + 2] = 623.2220$  and  $[\text{M}^+] = 642.9634$ ,  $[\text{M}^+ + 2] = 644.9577$  that correspond to the formula weight respectively, for monomeric complexes. Besides, the spectra show some prominent peaks corresponding to various ion fragments. The peak intensity gives an idea of the stability of the fragments.

## BIOLOGICAL ACTIVITY

The newly synthesized Ligands and complexes were screened for their antimicrobial activities against the selected species of bacteria and fungi such as *Ralstonia Solanacrum*, *Pseudomonas aeruginosa*, *E.coli*, *Aspergillus flavus*, *Fusarium* and *phoma*. The activities were compared with standard antibacterial and antifungal drugs such as Chloromphicol and Nystalin, respectively. The result were compared with standard drugs and depicted in table 6 and 7. The results of antimicrobial of Ni(II) complexes are shown in Table 5.

**Table –5: Magnetic measurements**

| Complexes | $\mu_{\text{eff}}$ (BM) | Proposed Geometry |
|-----------|-------------------------|-------------------|
| 1         | 3.06                    | Octahedral        |
| 2         | 3.02                    | Octahedral        |
| 3         | 3.08                    | Octahedral        |
| 4         | 3.05                    | Octahedral        |
| 5         | 3.10                    | Octahedral        |
| 6         | 3.11                    | Octahedral        |

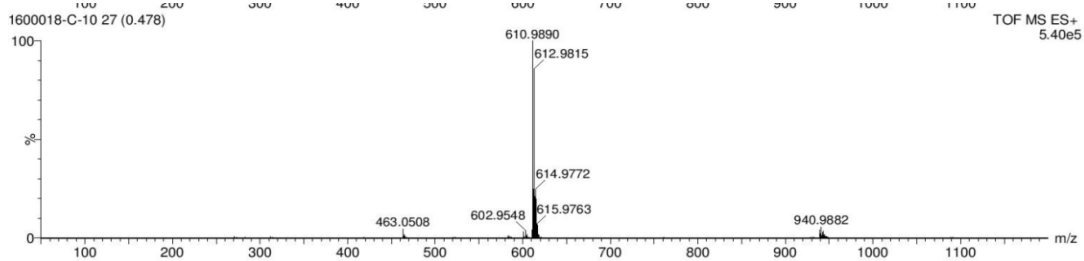


Figure 4: Mass spectra of complex. 1

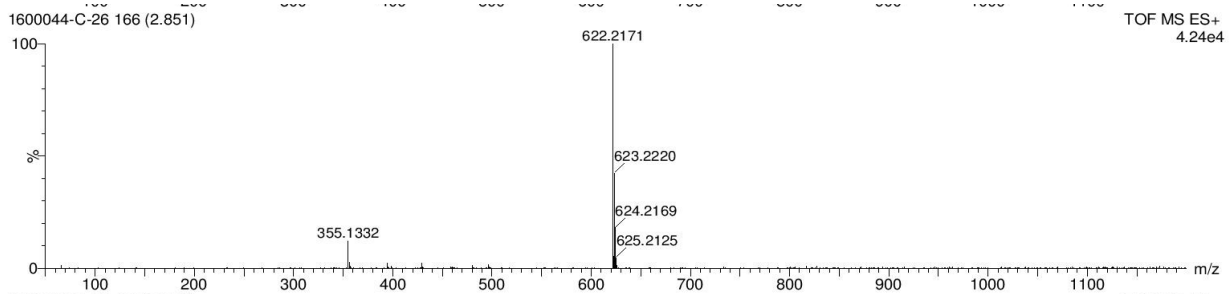


Figure 4: Mass spectra of complex. 2

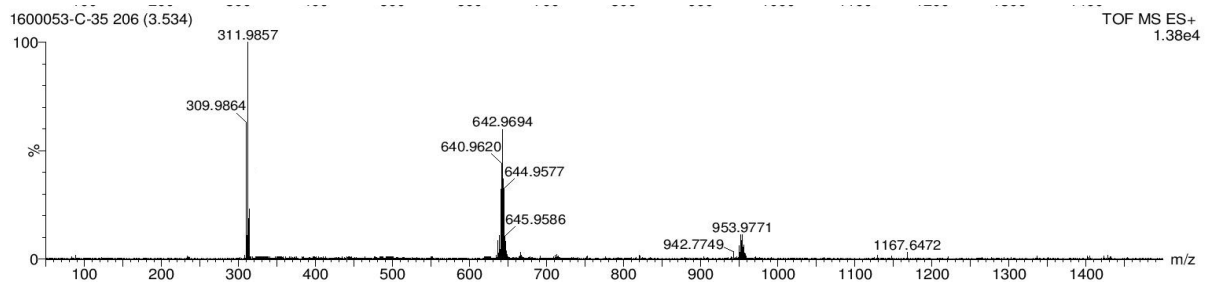


Figure 4: Mass spectra of complex. 4

Table-6: Antibacterial activity of ligands and their metal complexes

Zone of inhibition in mm

| compounds      | B.Subtilis | Ralstonia Solanacearum | Pseudomonas aeruginosa | Escherichia coli |
|----------------|------------|------------------------|------------------------|------------------|
| L <sub>1</sub> | 7.5        | 6.5                    | 5                      | 7                |
| 1              | 12         | 12                     | 14                     | 14               |
| L <sub>2</sub> | 8          | 6                      | 8                      | 7.2              |
| 2              | 12         | 12.5                   | 14                     | 14               |
| L <sub>3</sub> | 9          | 8                      | 6                      | 9.5              |
| 3              | 14         | 16                     | 15                     | 14.5             |
| L <sub>4</sub> | 7          | 3.5                    | 13                     | 8                |
| 4              | 8          | 11                     | 12                     | 13.5             |
| L <sub>5</sub> | 7.2        | 9                      | 2                      | 6.8              |
| 5              | 9          | 15.8                   | 14                     | 14               |
| L <sub>6</sub> | 7.4        | 4                      | 4                      | 7                |
| 6              | 12         | 9.1                    | 12.5                   | 11               |
| Standard       | 12         | 15                     | 15                     | 15               |

Table-7: Antifungal activity of ligands and their metal complex Zone of inhibition in mm

| compounds      | Aspergillus flavour | Fusarium | Phoma |
|----------------|---------------------|----------|-------|
| L <sub>1</sub> | 8                   | 8        | 10    |
| 1              | 10.1                | 12.1     | 16.9  |
| L <sub>2</sub> | 7.5                 | 8        | 12    |
| 2              | 12.5                | 13.4     | 20.1  |
| L <sub>3</sub> | 12                  | 6        | 8.1   |
| 3              | 16                  | 14       | 19    |
| L <sub>4</sub> | 14                  | 12       | 8     |
| 4              | 18                  | 18       | 15    |
| L <sub>5</sub> | 16                  | 7        | 12    |
| 5              | 18.2                | 16.5     | 18    |
| L <sub>6</sub> | 14                  | 7        | 8     |
| 6              | 19                  | 15       | 20    |
| Standard       | 15                  | 20       | 20    |

Table 8: Free radical scavenging activity of the ligands and their metal complexes.

Antioxidant activities of the compounds

| IC <sub>50</sub> valves (µg/ml) compounds | DPPH radical scavenging assay |
|---|-------------------------------|
| 1   | 87.1ng/ml                     |
| 2   | 86.21ng/ml                    |
| 3   | 75.5ng/ml                     |
| 4   | 67.79ng/ml                    |
| 5   | 80ng/ml                       |
| 6   | 35.71ng/ml                    |
| BHT                                       | 57.69ng/ml                    |

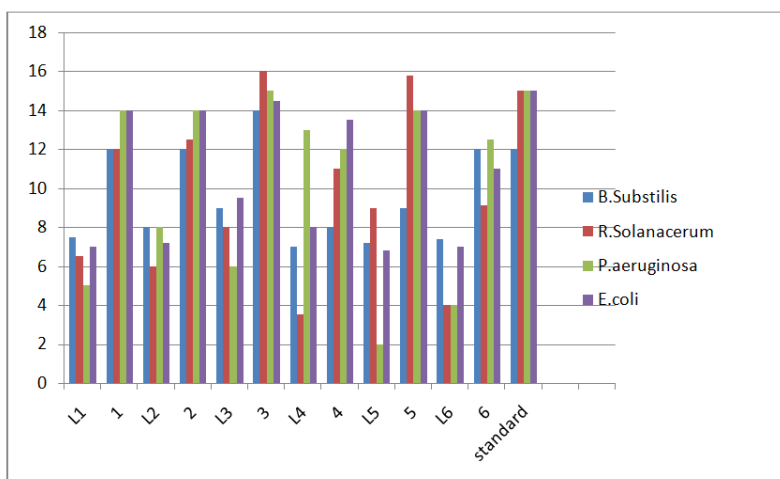


Figure 5. Graphical representation of antibacterial growth inhibition

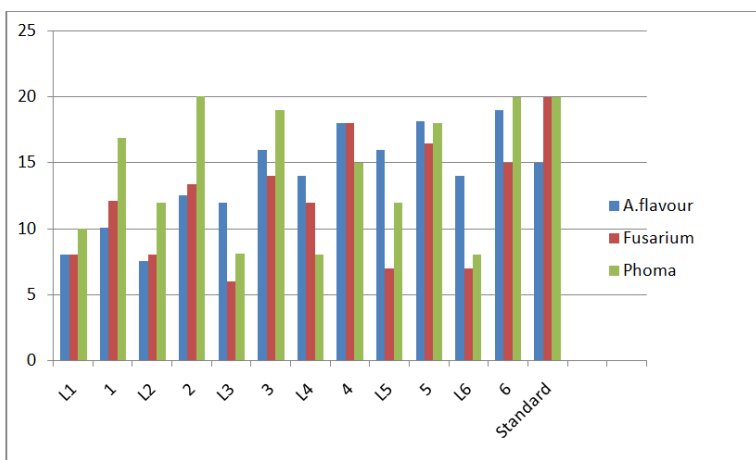


Figure 6: Graphical representation of antifungal growth inhibition.

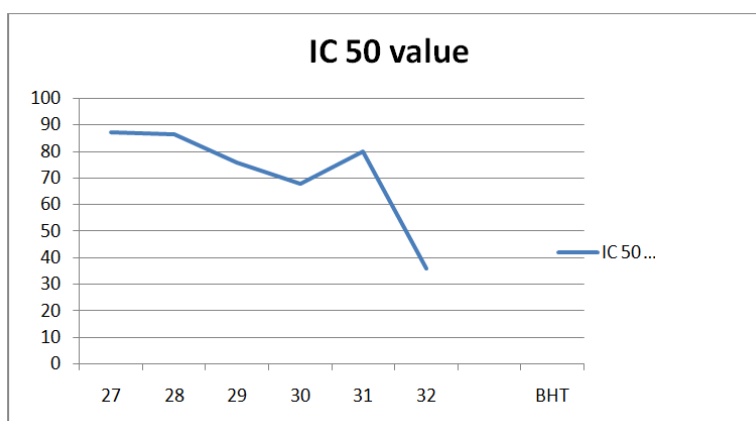
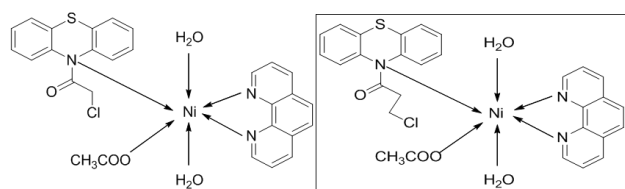
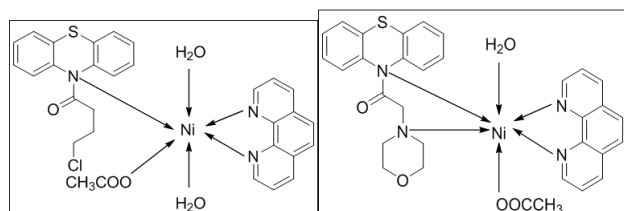


Figure-7: Antioxidant activity of metal complexes

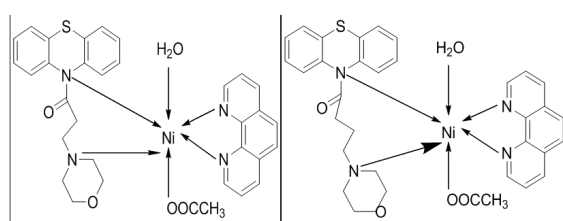




Structure of complex 1 and 2



Structure of complex 3 and 4



Structure of complex 5 and 6

Figure 8. Tentative structure of complexes based on spectroscopic analysis

Almost all the synthesized Ni(II) complexes were found to exhibit moderate to good activity against a wide variety of Gram bacteria's. Among the tested complexes, 1, 2, 3, 4 and 5 showed good activity. The complex 6 are showing moderate activity. This may be due to the presence of morpholine group in complexes 5 and 6 is responsible for the enhancement of activity. In all other complexes, the presence of phenanthroline moiety is responsible for good activity. All Compounds were showing good antifungal activity than antibacterial. All of the ligands showed lowest antimicrobial activity, but all the metal complexes under study were definitely showing better antimicrobial activity compared to the ligands and standard antibiotics Chloromphericol and Nystalin. It was suggested that in the chelated complex, the positive charge of the metal is partially shared with donor atoms and there is  $\pi$ -electron delocalization over the whole chelate ring. This increases the lipophilic character of the metal chelate and favours its permeation through lipid layers of the fungus of the fungus membranes.

### Antioxidant Activity Investigation

**Antioxidant Assay:** The antioxidant potential of mixed ligand complexes against DPPH radical, to different concentrations of the complexes varying from 0 to 100  $\mu$ M and the results are shown in table 4. The 50 % inhibitory concentration (IC<sub>50</sub>) value of complexes varies from 6.00  $\mu$ M to 9.00 $\mu$ M against DPPH radical. The DPPH radical scavenging activity shown by the ligands and complexes because of its H-donating

capacity. In the present investigation compounds complexes showed high DPPH radical scavenging activity with IC<sub>50</sub> value, activity of compound 5 is almost similar to that of the reference compound BHT. The synthesized complexes undergo Antioxidant activity by using DPPH assay. We tested all metal complexes with DPPH assay. We tested all metal complexes with DPPH assay method and the complex shows effective free radical scavenging property and the remaining complexes shows moderate free radical scavenging activity. The reason would be the presence of electron releasing groups or electron donating nitrogen groups in ligand moiety endowed notable improvement in radical scavenging activity. After the complexation with metal ions reveals that the antioxidant activity increase due to the presence of positively charged metal ions as well as different groups present in the moiety. Compound 6 has showed more DPPH radical scavenging activity with IC<sub>50</sub> value of 35.71 mg/ml and also Compound 4 Showed moderate DPPH radical scavenging activity with the IC<sub>50</sub> value of 67.79ng/ml when compared to the BHT with an IC<sub>50</sub> value of 57.69 $\mu$ g/ml. The remaining compounds showed less DPPH radical scavenging activity with the IC<sub>50</sub> value (Table 8). These metal complexes have the following order of DPPH radical scavenging activities: 6 > 4 > 3 > 5 > 2 > 1. BHT standard anti oxidant is taken as a reference & IC 50 value for BHT was found to be 57.69ng/ml. when compared to the reference compound, Ligand - I series, Ligand - II along with the complexes were showing significant scavenging activity as their IC 50 values ranges between 14.93ng to 100ng/mL. Metal complexes were better in scavenging the proton radical as compared to the ligand series-I and ligand series II, of all the metal complexes, 1 and 4 were the best scavengers with an IC<sub>50</sub> value ranging from 14.93ng to 18.18ng/mL

### Proposed structure of metal complexes

The *N*-substituted phenothiazine complex crystal were poor in quality such that to permit X-ray crystallographic analysis of the structure .Therefore tentative complex structure for the compounds proposed based on various physic-chemical methods.

### Conclusion

The synthesized complexes have been characterized by utilizing the various physic-chemical methods. The molar conductance of all the complexes in DMF shows that they are non-electrolytes. The magnetic and electronic spectral studies support an octahedral geometry for all the metal complexes. Thermal studies suggested that metal complexes show two or three steps thermal degradation. Mass spectrum of the complexes shows two or three steps thermal degradation. Mass spectrum of the complex confirms the proposed structure. The proposed geometry of the complexes is given in figure 5. The importance of the prepared metal complexes was studied by subjecting them to biological activities. The metal complex compounds were screened against three bacteria and three fungi using *In vitro* disc diffusion method. The results revealed that most of the synthesized complex compounds were found to be highly active against some of the bacterial and fungal species than compared to ligands. The antioxidant reactivity was carried out using DPPH radical scavenging, it results that metal complexes were better in scavenging the proton radical as compared to the ligand series.

### Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this article.

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