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# A Study on Electrochemical, Catalytic and Biological Properties of New Nickel Coordinated Schiff Base Materials

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***Abstract:*** *Four new Schiff bases have been derived from the condensation of acenapthoquinone and naphthylamines in 1:2 molar ratios. These Schiff base ligands were used to synthesise novel mononuclear Ni(II) complexes with square planar geometry. The ligands and the complexes have been investigated by elemental analyses, spectroscopic methods (FT-IR and UV-Vis.,), molar conductance and magnetic susceptibility studies. The electrochemical properties of Ni(II) complexes have been studied by cyclic voltammetry technique. The catalytic efficacy of the complexes has been analysed in the oxidation of toluene to benzyl alcohol, using $H_2O_2$. Biological activities of these ligands and complexes were checked against selected bacterial strains (E. coli and S. Aureus).*

*Keywords: Schiff base, FT-IR spectroscopy, cyclic voltammetry, toluene, chelation*

## 1. INTRODUCTION

Through the decades, Schiff bases derived by the condensation of primary amines and carbonyl compounds (aldehyde/ketone) have played a significant role as chelating agents in transition metal coordination chemistry. This is due to their stability under a variety of oxidative and reductive conditions and to the fact that imine ligands are borderline between hard and soft Lewis bases [1-3]. Transition metal complexes with multidentate Schiff base ligands have been extensively investigated as catalysts for a number of organic redox reactions and electrochemical reduction processes. Furthermore, the metallation of Schiff base ligands leads to the many important applications such as antifungal, antibacterial, DNA binding and cleavage studies [4, 5]. In this context, Ni(II) Schiff base complexes have been vastly reported, because Schiff base ligands can bind with one, two or more metals involving various coordination modes and allow the synthesis of homo and/or heteronuclear nickel metal complexes with interesting stereochemistry. Moreover, the nickel complexes with multidentate Schiff base ligands have been found to be significant, and such complexes have an important role in bioinorganic chemistry and redox enzyme systems [6-9].

Cyclic voltammetry (CV) has been widely used to investigate the mechanisms of catalysis by Schiff base metal complexes, structure-activity relationship and the electrochemical properties of these compounds [10-12]. Numerous electrochemical studies have been made for large number of Ni(II) complexes derived from Schiff bases. These investigations have revealed that redox behaviour of Ni(II) complexes have been markedly influenced by structural and electronic factors. Hence, the study of electrochemical properties of Ni(II) metal centre in the coordination complexes has been shown greater attention.

All the above facts encouraged us to synthesise the Ni(II) complexes of various Schiff bases obtained from acenapthoquinone and substituted naphthylamines (Scheme 1). The characterization of the synthesized compounds has been also reported. In addition, the redox properties of the complexes have been studied by CV technique. This work has also included the evaluation of antibacterial activities of complexes against E.coli and S. aureus and their catalytic ability in toluene oxidation with hydrogen peroxide as oxidant.

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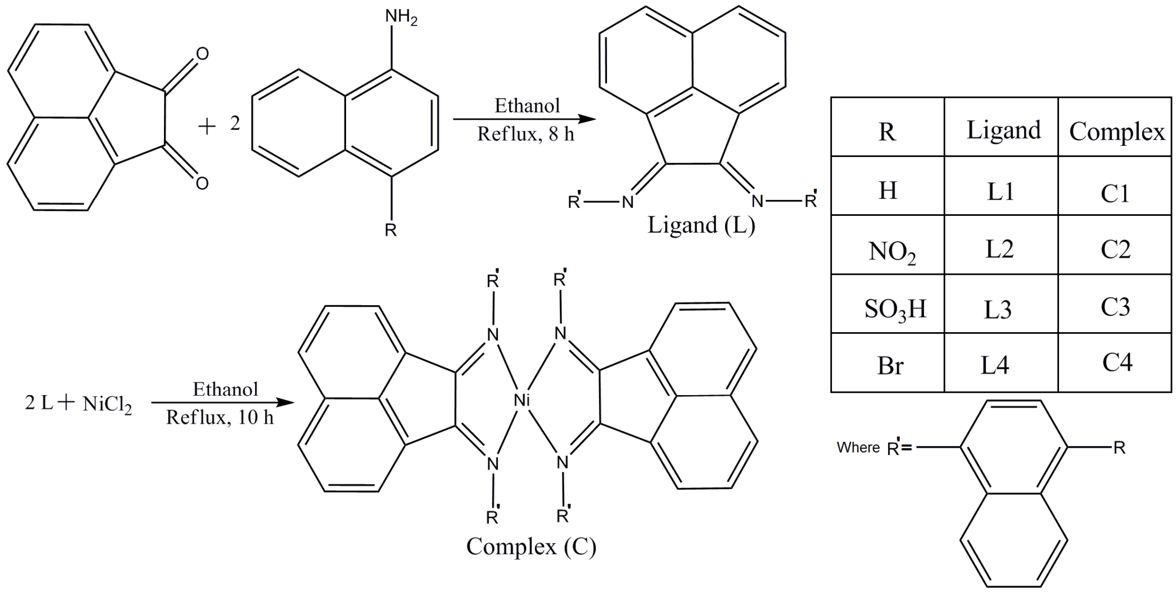

| R | Ligand | Complex |
|---|---|---|
| H | L1 | C1 |
| $NO_2$ | L2 | C2 |
| $SO_3H$ | L3 | C3 |
| Br | L4 | C4 |

Scheme 1. Synthesis of ligands and Ni(II) complexes

## 2. MATERIALS AND METHODS

The chemicals used were of AnalaR grade purchased from Merck chemicals. All the manipulations and reactions were carried out under aerobic conditions.

Elemental (C, H and N) analysis of ligands and the complexes was computed by a Carlo Erba 1108 model elemental analyzer. The percentage of nickel present in the complexes was experimentally calculated as given in the procedure [13]. FT-IR spectra of the compounds were recorded on Jasco FT-IR/4100 spectrophotometer at 4 $cm^{-1}$ resolution between the wave number range 4000 and 400 $cm^{-1}$. UV-Vis. spectral studies for the compounds in DMSO solutions were carried out using a Shimadzu UV-1601 spectrophotometer in the wavelength range of 200-800 nm. A Bruker 300 Avance DRX 300 FT-NMR spectrometer was used to record $^1H$ NMR of the ligands in 1% $HCl/D_2O$ solution. The magnetic measurements of the metal complexes were measured on a modified Hertz SG8-5HJ model Gouy type magnetic balance. Molar conductivity of the complexes was evaluated at room temperature with a Deep vision model-601 digital conductivity meter.

### 2.1. Synthesis of ligand (L1)

50 ml ethanolic mixture of acenapthoquinone (5 mmol) and naphthylamines (10 mmol) was refluxed in a 100 ml round bottom flask equipped with a magnetic stirrer. After 8 h, the solution turned into brown colour and solvent was evaporated from this solution. The obtained product (L1) after evaporation was washed with hot water and dried in the vacuum oven for 5 h. The procedure was repeated for the synthesis of L2, L3 and L4 with different substituted naphthylamines.

### 2.2. Synthesis of complex (C1)

L1 and $NiCl_2$ were taken in 2:1 ratio for the synthesis of complex, C1. This mixture was dissolved in 50 ml ethanol and refluxed in a 100 ml RB flask equipped with a magnetic stirrer. After 10 h of the reaction, the solvent was allowed to evaporate from the solution and the final product was washed with hot water and dried in vacuum oven for 12 h. The above procedure was also followed for synthesis of complexes C2, C3 and C4 from L2, L3 and L4, respectively.

### 2.3. Electrochemical studies

CV experiments were performed in a single compartmental cell at 25 °C with freshly distilled DMSO on CHI 620C electrochemical analyzer. A three electrode configuration was used, comprised of a glassy carbon as working electrode, Pt wire as auxiliary electrode and Ag/AgCl electrode as reference electrode. All the electrochemical measurements were carried out in a 10 mL electrolytic cell using 5mM Tris-HCl/50 mM NaCl buffer (pH=7.2) as the supporting electrode. Solutions were purged with Nitrogen to maintain inert atmosphere for measurements.

### 2.4. Antibacterial studies

Qualitative evaluation of antibacterial activity was carried out using the disc diffusion method. The complexes were dissolved in DMSO for the analysis of their antibacterial studies against *E. coli* and *S. aureus*.

Suspensions in sterile peptone water from the 24 h cultures of microorganisms were adjusted to 0.5 McFarland. Muller-Hinton Petri discs of 90 mm were inoculated using these suspensions. Paper discs (6 mm in diameter) containing 10 μL of the substance to be tested were placed in a circular pattern in each inoculated plate. Discs were impregnated with DMSO and used as negative controls. Toxicity tests show that the used concentration of DMSO did not interfere with the growth of microorganisms. The antibacterial activity of the complexes was evaluated from their zone of inhibition (in mm) which did form around the discs impregnated with complex solution.

### 2.5. Oxidation of toluene

Oxidation of toluene was achieved with 0.05 g of complex as catalyst with $H_2O_2$ as oxidant in 10 ml acetonitrile at room temperature under aerobic conditions. This reaction was done in a 25 ml flask equipped with a magnetic stirrer. After 12 h stirring, the aliquots were collected from the reaction mixture and concentrated for the product analysis. The Hewlett–Packard gas chromatogram (HP 6890) having FID detector was used for analysing the products of the toluene oxidations. Blank experiment was also done without the catalyst in order to investigate the importance of catalyst in toluene oxidation.

## 3. RESULTS AND DISCUSSION

The synthesized compounds are found to be air stable. They are soluble in organic solvents like ethanol, DMSO and DMF. The elemental analysis data are given in Table 1, and are well comparable with the theoretically calculated values and this proves the formation of ligands and complexes with the expected stoichiometry.

### 3.1. FT-IR spectroscopy

The FT-IR spectra of free ligands and their complexes are used to confirm the structure of the ligands and complexes. Ligands and Ni(II) complexes show similar absorption bands, except some shifts due to metallation in the spectra of the complexes. In all the ligands, the band observed at ~1640 $cm^{-1}$ is assigned to C=N streching and this confirms the formation of Schiff base from acenapthoquinone and napthylamine [14]. The coordination modes of the ligands to the Ni(II) ions are obtained by comparing the IR spectra of the free ligands with their metal complexes.

In Figure 1, the FT-IR spectroscopy of L1 shows C=C streching at 1443 $cm^{-1}$. This confirms the presence of aromatic groups in L1. All the ligands show this characteristic band for C=C streching at ~1450 $cm^{-1}$. In all the complexes, the C=N streching frequency is slightly shifted to the lower region which assures the coordination of the imino nitrogen atom to Ni(II) [15, 16].

### 3.2. UV-Vis. spectroscopy and magnetic studies

UV-Vis. spectral studies and magntic susceptibility data are used to investigate the geometry of the complexes.

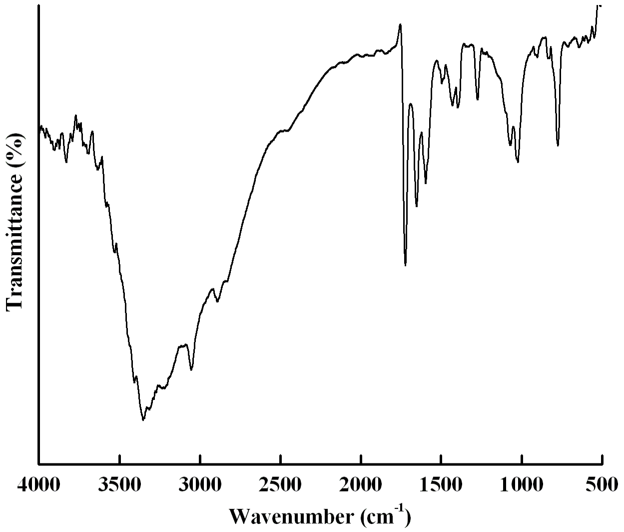

Figure 1. FT-IR spectra of L1

Electronic spectra of ligands and their mononuclear Ni(II) complexes were recorded in the 200-800 nm wavelength range in DMF solutions. In the UV-Vis. spectra of the ligands, the bands observed at ~240 nm could be assigned to their π-π* and n-π* transitions of aromatic π-electrons or C=N chromophore [17]. These absorption bands of the complexes are shifted towards longer wave length. This could be due to the metallation, which causes increased conjugation and delocalization of the whole electronic system, resulting in the energy change of π-π* and n-π* transitions of the conjugated chromophore [18].

The UV-Vis. spectra of the complexes exhibit another band at ~600-620 nm due to the d-d transition of Ni(II) centre. This band is significant in characterising the geometry of the complexes. This band is assigned to $^1A_{1g}\rightarrow{}^1A_{2g}$ and $^1A_{1g}\rightarrow{}^1B_{1g}$ transitions [19], which predicts square planar geometry around the Ni(II). All the Ni(II) complexes in the present study are diamagnetic in nature which supports the square planar geometry of the S=0 ($d^8$), Ni(II) system.

Table 1. Elemental analysis data (C, H, N and Ni) and molar conductance data of the complexes

| Compound | Calculated (%) (Found (%)) | | | | Molar conductance ($\lambda_M$) ($\Omega^{-1}cm^2\ mol^{-1}$) |
|---|---|---|---|---|---|
| | C | H | N | Ni | |
| L1 | 88.86 (88.71) | 4.66 (4.58) | 6.47 (6.43) | - | - |
| L2 | 73.55 (73.24) | 3.47 (3.40) | 10.72 (10.64) | - | - |
| L3 | 65.10 (65.07) | 3.07 (2.96) | 4.74 (4.65) | - | - |
| L4 | 64.85 (64.70) | 3.40 (3.31) | 4.72 (4.58) | - | - |
| Complex 1 | 77.28 (77.16) | 4.05 (3.99) | 5.63 (5.57) | 5.90 (5.72) | 113 |
| Complex 2 | 65.44 (65.08) | 3.08 (3.0) | 9.54 (9.44) | 4.99 (4.76) | 108 |
| Complex 3 | 58.65 (58.02) | 2.77 (2.63) | 4.27 (4.20) | 4.48 (4.38) | 99 |
| Complex 4 | 58.46 (58.35) | 3.07 (2.97) | 4.26 (4.21) | 4.46 (4.37) | 110 |

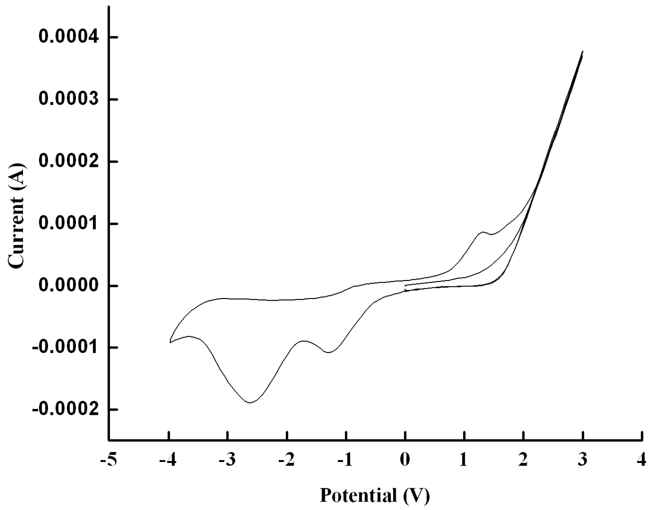

Figure 2. CV pattern of C1 in DMSO solution

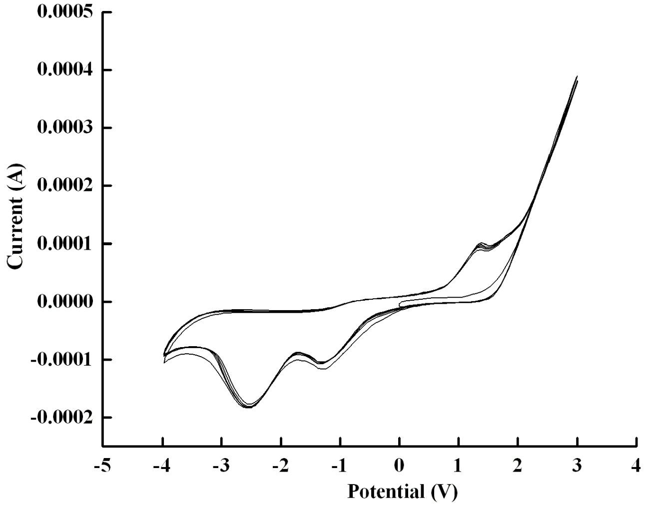

Figure 3. CV patterns of C1 in DMSO solution for various scan rates

### 3.3. Molar conductance studies

Molar conductance studies are used to study the electrolytic nature of the complexes. This study was carried out room temperature in $10^{-3}$ M DMSO solution of complexes on Deep vision model-601 digital conductivity meter. The blank conductivity measurement was made for DMSO and it was below 10 $\Omega^{-1}cm^2\ mol^{-1}$. Then molar conductivties for DMSO solutions of complexes were found to be in the range of 99-113 $\Omega^{-1}cm^2\ mol^{-1}$ (Table 1). It suggests electrolytic nature of the complexes [20] and also proves that the presence of chloride ions in outside of coordiantion sphere. This was further confirmed by Volhard's test.

### 3.4. Electrochemical studies

The electrochemical properties of the mononuclear Ni(II) complexes were studied by using cyclic voltammetry in DMSO solution containing 5mM Tris-HCl/50 mM NaCl buffer (pH=7.2) and the supporting electrode in the potential range +4 to -5 V. The cyclic voltammogram of complex, C1 is shown in Figure 2. Generally, the electrochemical properties of the complexes depend on a number of factors such as chelate ring/size [21,22] axial ligation [23,24], degree and distribution of unsaturation [25] and substitution pattern [26] in the chelate ring.

In Figure 2, the complex C1 shows two different electrochemical behaviours. The first one is due to the electrochemical oxidation of Ni(II) metal centre of the complex to the unstable Ni(III). These Ni(III) species are unstable and they are rapidly reduced into Ni(II) species. There is no corresponding cathodic peak for the reduction of Ni(III) to Ni(II) because of the speed of the reaction. The parameters obtained for this one electron electrochemical process are: $E_{pa}$=-2.7 V and $i_{pa}$= -85 μA.

The second electrochemical process for C1 is reversible due to the equality of anodic and cathodic currents observed for this reversible process ($i_{pc}$=$i_{pa}$). This may be attributed to the one electron transfer which invoves in the redox reaction of Ni(II)/Ni(I) in metal centre of complex. In this reversible process, Ni(II) is initially reduced into Ni(I) with the cathodic peak ($E_{pc}$=1.2 V and $i_{pc}$= 90 μA) and this Ni(I) is oxidized into Ni(II) with the anodic peak ($E_{pa}$=-1.2 V and $i_{pa}$= -90 μA). The scan rate is altered during the electrochemical analysis of C1 for the investigation of dependence of redox behavior on the scan rate. The changes in scan rate do not cause much variation in the electrochemical properties of the complexes, as shown in Figure 3.

The electrochemical investigation of the other complexes, C2,C3 and C4 shows similar electrochemical properties as C1. They also exhibit one electron transfer processes. First one is the electrochemical oxidation of Ni(II) to Ni(III) and the second one is the elecrochemical redox reaction of Ni(II)/Ni(I). But, the position of peaks are slightly different compare to C1 and this might be due to the presence of different subsitutent groups in different complexes. The CV parameters for all the complexes are given in Table 2. It was observed that the ligand moiety had a significant effect on $E_{1/2}$ for all the complexes; because electron-withdrawing group anion makes the complex more positive and favours the reduction of metal ion.

### 3.5. Antibacterial studies

The antimicrobial activities of Ni(II) complexes were expored against two disease causing bacterial srains such as *E.coli* and *S.aureus*. The comparative antibacterial activity of all the complexes with the commerical drug, chloramphenical is given in Figure 4. All the complexes show good biocidal activity against *E.coli* than *S.aureus*. This difference could be due to the Gram-status. The membrane of Gram-negative bacteria is surrounded by an outer membrane containing lipopolysaccharides. The antibacterial activity of mononuclear Ni(II) Schiff base complexes C1, C2, C3 and

Table 2. Electrochemical parameters obtained for the complexes from their CV studies.

| Number | Complex | $E^1_{pa}$ | $E^2_{pc}$ | $E^2_{pa}$ | $E^2_{1/2}$ (V) |
|---|---|---|---|---|---|
| 1 | C1 | -2.70 | 1.23 | -1.23 | 1.23 |
| 2 | C2 | -2.82 | 1.15 | -1.23 | 1.19 |
| 3 | C3 | -2.75 | 1.21 | -1.24 | 1.22 |
| 4 | C4 | -2.94 | 1.08 | -1.25 | 1.11 |

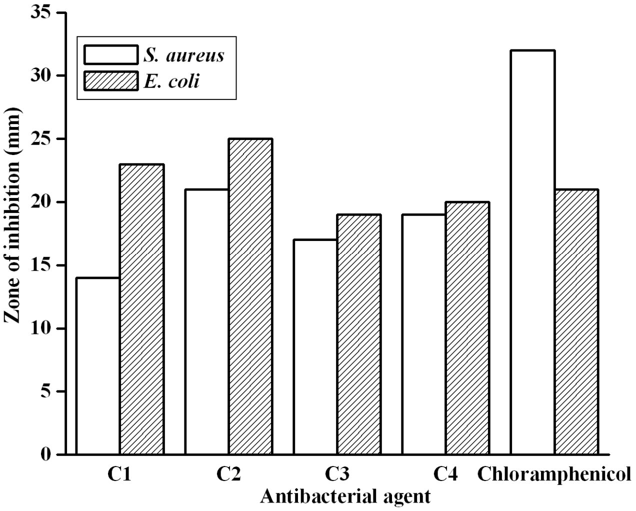

Figure 4. Antibacterial activity of Ni(II) complexes against *E. coli* and *S. aureus*

C4 can be explained on the basis of chelation theory [27]. On chelation, the polarity of Ni(II) ion is reduced to greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of the metal ion with donor groups. These Ni(II) complexes also disturb the respiration process of bacterial cell and thus block the synthesis of proteins that restricts further growth of bacteria.

### 3.6. Catalytic studies

Catalytic properties of the complexes were examined with industrially important toluene oxidation using environmental friendly oxidant, $H_2O_2$ under room temperature conditions. The separate blank experiments show that no conversion of toluene is observed without Ni(II) complex and oxidant, $H_2O_2$. The catalytic efficacy of complexes is shown in Figure 5. Toluene is successfully converted into benzyl alcohol and there is no further oxidation of benzyl ancohol to benzaldehyde. Complex C1 yields maximum conversion of toluene since all other complexes contain electron withdrawing substituents. The key point in the conversion of toluene to benzyl alcohol is the reduction of Ni(II)–L to Ni(I)–L and it was further confirmed by CV measurements.

## 4. CONCLUSIONS

Four different mononuclear Ni(II) complexes have been synthesized from Schiff bases of acenapthoquinone and napthylamines (1:2). The stoichiometry of complexes have been confirmed by elemental analyses, FT-IR spectral data and molar conductance studies. Tetra coordinated (N, N, N, N) square planar geometry has been suggested to complexes by UV-Vis. spectroscopy and magnetic data. Electrochemical studies of complexes reveal that Ni(II) has irreversibly oxidized into Ni(III) and reversible redox behavior obtained for one electron transfer Ni(II)/Ni(I) system. All Ni(II) complexes have been comparatively active against E. coli and S. aureus as compare to chloramphenicol, the standard. The reported complexes have shown good catalytic activity in toluene oxidation for the production of benzyl alcohol.

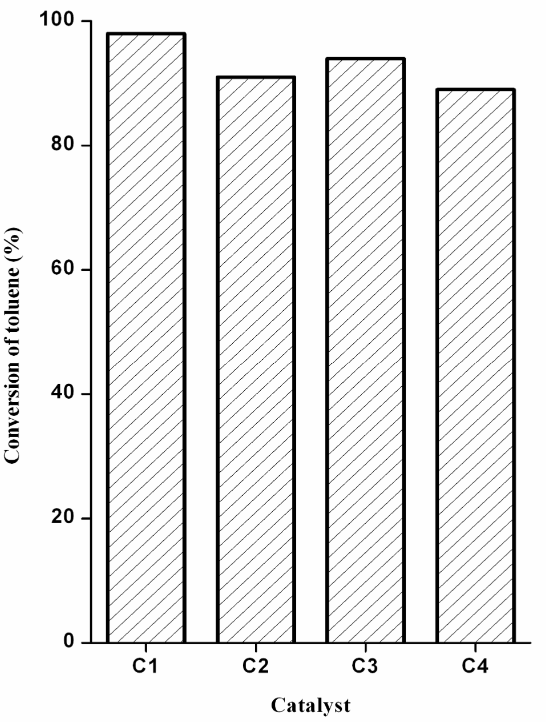

Figure 5. Catalytic activity of Ni(II) complexes in toluene oxidation

## 5. ACKNOWLEDGEMENT

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