



Synthesis, Spectral Investigation of Ni(II) Schiff Base Complexes: Antimicrobial Activities and Catalytic Oxidation of Alcohols

R. MADASELVI^{1,2}, N. PADMA PRIYA³, M. JEYARAJ^{2,3}, C. ARUN PAUL⁴, K. KALAIVANI⁴, H. SHAHUL MEERAN^{2,5} and S. ARUNACHALAM^{2,3,*}

¹Department of Chemistry, Arulmigu Kalasalingam College of Education, Virudhunagar-626 126, India

²Research and Development Centre, Bharathiar University, Coimbatore-641046, India

³Department of Chemistry, Sri Krishna College of Engineering and Technology, Coimbatore-641 008, India

⁴Department of Physics, Sri Krishna College of Engineering and Technology, Coimbatore-641 008, India

⁵Department of Chemistry, United Institute of Technology, Coimbatore-641 032, India

*Corresponding author: E-mail: drarunachalam.s@gmail.com

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Air stable Ni(II) Schiff base complexes viz. $[\text{Ni}(\text{L}^1)(\text{PPh}_3)]$ and $[\text{Ni}(\text{L}^2)(\text{PPh}_3)]$ [where L^1 and L^2 are dianions of Schiff base ligands, respectively] have been synthesized and characterized by analytical and spectral (electronic, FT-IR, ^1H , ^{13}C and ^{31}P NMR) methods. The assignment of all the aromatic carbon-hydrogen resonances is made on the basis of ^1H - ^{13}C HSQC spectrum of the complexes. The Schiff base ligands behave as a bibasic tridentate ligands and bonded through ONO and ONS mode. A square planar structure has been proposed on the basis of spectral data. Novel Ni(II) Schiff base complexes exhibited good antimicrobial activity towards the strains *Staphylococcus epidermidis* and *Escherichia coli*. Thermal and air stability of the complexes offer the advantage of oxidation of alcohols.

Keywords: Nickel(II), Schiff base complexes, Square planar nickel, Tridentate ligands, Oxidation of alcohols.

INTRODUCTION

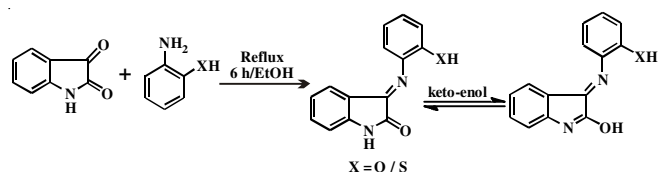
The chemistry of transition metal complexes with coordinated phosphorous ligands has been known for a long time. During the previous years we have been working on the coordination chemistry and biological properties of different metal complexes of isatin and other Schiff base ligands in order to establish a possible relationship between chemical structure and biological activity. Schiff bases have been reported to show a variety of biological actions by virtue of the azomethine linkage, which is responsible for various antibacterial, antifungal, herbicidal, clinical and analytical activities [1-7]. Following this research line, here we report the synthesis and characterization of Schiff bases of isatin with *o*-aminophenol and *o*-aminothiophenol (**Scheme-I**) as well as some of their nickel(II) complexes.

EXPERIMENTAL

All the reagents used were of AnalaR grade and purchased from Sigma Aldrich chemicals and was used without further purification. Melting points were recorded on a Veego VMP-DS melting point apparatus and are uncorrected. The analysis of carbon, hydrogen, nitrogen and sulphur were performed in Vario EL III CHNS analyzer at Cochin University, Kerala,

India. Infrared spectra were recorded as KBr pellets in the 4000-400 cm^{-1} region using a Perkin Elmer FT-IR 8000 spectrophotometer. Electronic spectra of all the complexes were taken in dichloromethane solution in quartz cells. The concentration of the complexes ranges around 0.02-0.3 N. The spectra were recorded on a Systronics double beam UV-visible spectrophotometer 2202 in the range 200-800 nm at room temperature. ^1H and ^{13}C NMR spectra for the ligand were recorded using Bruker 500 MHz instrument in CDCl_3 at room temperature in Indian Institute of Science, Bangalore. Minimum quantities of ligands were dissolved in deuterated CDCl_3 . ^1H NMR chemical shifts were referenced to tetramethylsilane (TMS) as an internal solvent standard resonance and ^{13}C NMR chemical shifts were referenced to the internal solvent resonance. Signals are quoted in parts per million as δ downfield from internal reference.

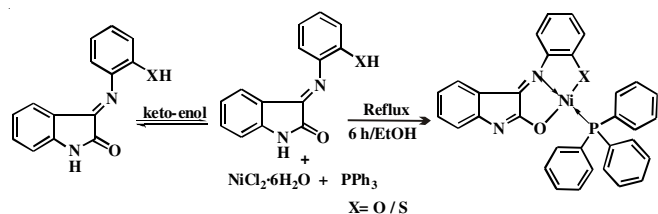
Preparation of new tridentate Schiff base ligands: To an ethanolic solution of isatin (0.147 g: 0.1 mmol) with *o*-aminophenol (0.109 g: 0.1 mmol)/*o*-aminothiophenol (0.125 g: 0.1 mmol) was added in 1:1 ratio with stirring in the magnetic stirrer for about 0.5 h and then refluxed in a round bottomed flask fitted with double surface condenser on the water bath for about 6 h (**Scheme-I**). The resultant product was washed with ethanol and the purity of the ligands were checked by TLC



Scheme-I: Synthesis and keto-enol form of Schiff base ligands

and was column chromatographed on silica gel (petroleum ether:ethyl acetate) (Yield \approx 79 %). The C, H, N, S analysis were recorded.

Preparation of new Ni(II) Schiff base complexes: To a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol) in ethanol (20 cm^3) the appropriate Schiff base (0.1 mmol) was added with PPh_3 (0.1 mmol) in 1:1 molar ratio and heated under reflux in a round bottomed flask fitted with a double surface condenser for 6 h under anhydrous condition (Scheme-II). The solution was then concentrated on the water bath to 3 cm^3 and cooled. The complex was precipitated by the addition of small quantity of petroleum ether (60-80 $^\circ\text{C}$) and recrystallized from CH_2Cl_2 /petroleum ether and dried *in vacuo* (Yield about 76 %).

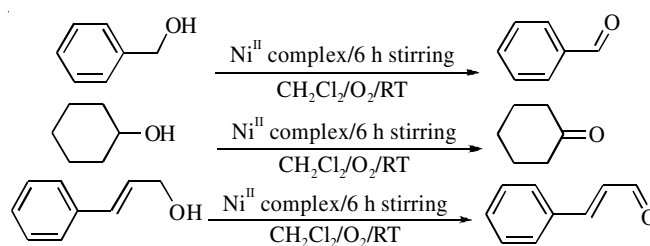


Scheme-II: Synthesis of new Ni(II) Schiff base complexes

Antimicrobial activities: The *in vitro* cytotoxicity of the complexes were screened in order to evaluate activity against *Staphylococcus epidermidis* and *Escherichia coli* at 0.25 %, 0.50 % and 1 % concentration by disc diffusion method. Streptomycin was used as a standard. The bacteria (*Staphylococcus epidermidis*, *Escherichia coli*) were grown in nutrient broth and incubated at 37 $^\circ\text{C}$ for 48 h followed by frequent subculture to fresh medium and were used as test bacteria. Then the petriplates were inoculated with a loop full of bacterial culture and spread throughout the petriplates uniformly with a sterile glass spreader. To each disc, the test samples and reference antibiotic (streptomycin) were added with a sterile micropipette. The plates were then incubated at 35 ± 2 $^\circ\text{C}$ for 24 h for bacteria. Plates with disc containing respective solvents served as control. Inhibition was recorded by measuring the diameter of the inhibitory zone after the period of incubation [6].

Catalytic oxidation reactions by Ni(II) Schiff base complexes: Catalytic oxidation of alcohols to corresponding carbonyl compounds by Ni(II) Schiff base complexes was carried out in the presence of oxygen atmosphere at ambient

temperature (Scheme-III). A typical reaction using the complexes $[\text{Ni}(\text{L})(\text{PPh}_3)]$ as a catalyst and alcohols as substrates at a 1:100 molar ratio is described as follows. A solution of Ni(II) Schiff base complexes (0.01 mmol) in 20 cm^3 CH_2Cl_2 was added to the solution of alcohol (1 mmol) under 1 atm oxygen atmosphere at ambient temperature. The solution mixture was stirred at room temperature for 6 h and the solvent was then evaporated from the mother liquor under reduced pressure. The residue was then extracted with petroleum ether (60-80 $^\circ\text{C}$) (20 cm^3) and the carbonyl compounds were treated with 2,4-dinitrophenylhydrazine, methanol and few drops of sulphuric acid. The yellow colour product obtained is quantified as 2,4-dinitrophenylhydrazone derivatives [5-7].



Scheme-III: Catalytic oxidation of alcohols

RESULTS AND DISCUSSION

The Ni(II) Schiff base complexes of the type $[\text{Ni}(\text{PPh}_3)(\text{L})]$ were synthesized by reacting equimolar solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Schiff base ligands (H_2L^1 and H_2L^2) and triphenyl phosphine in ethanolic medium, refluxed for 6 h. The complexes are non-hygroscopic and are soluble in common organic solvents. In all the reactions, it was found that Schiff bases behave as bidentate tridentate ligands. The analytical data obtained for the new Ni(II) Schiff base complexes are agreed well with proposed molecular formulae (Table-1).

Infrared spectra: The IR spectra of the ligands were compared with those of the nickel complexes in order to confirm the binding mode of the Schiff base ligands to the nickel(II) atom in the complexes (Table-2). The free Schiff base ligands showed a strong band in the region 1617-1615 cm^{-1} , which is characteristic of the azomethine $\nu(\text{C}=\text{N})$ group. Coordination of the Schiff bases to the metal through the nitrogen atom is expected to reduce the electron density in the azomethine link and lower the $\nu(\text{C}=\text{N})$ absorption frequency. The band due to $\nu(\text{C}=\text{N})$ is shifted to lower frequencies and appears around 1592-1580 cm^{-1} , indicating coordination of the azomethine nitrogen to the nickel metal [1-6]. A strong band observed at 1343 cm^{-1} in the free Schiff base H_2L^1 has been assigned to phenolic C-O stretching. On complexation, this band is shifted to a higher frequency at 1438 cm^{-1} , indicating

TABLE-1
ANALYTICAL DATA OF Ni(II) SCHIFF BASE COMPLEXES

Ligands and Complexes	Colour	m.p. ($^\circ\text{C}$)	m.f.	m.w.	Elemental analysis (%): Calcd. (Found)			
					C	H	N	S
H_2L^1	Brown	128	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2$	238.24	70.57 (70.21)	4.22 (4.15)	11.75 (11.56)	–
H_2L^2	Orange	135	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{OS}$	254.31	66.11 (66.01)	3.95 (3.76)	11.01 (10.93)	12.6 (12.34)
$[\text{Ni}(\text{L}^1)(\text{PPh}_3)]$	Green	230	$\text{C}_{32}\text{H}_{23}\text{N}_2\text{O}_2\text{PNi}$	557.20	68.98 (68.86)	4.16 (4.09)	5.03 (4.91)	–
$[\text{Ni}(\text{L}^2)(\text{PPh}_3)]$	Brown	283	$\text{C}_{32}\text{H}_{23}\text{N}_2\text{OPSNi}$	573.27	7.04 (66.97)	4.04 (3.91)	4.89 (4.79)	5.59 (5.49)

coordination through the phenolic oxygen. This has been further supported by the disappearance of the broad band $\nu(\text{OH})$ around 3000 cm^{-1} in the complex $[\text{Ni}(\text{PPh}_3)(\text{L}^1)]$, indicating deprotonation of the phenolic proton prior to coordination [4-7]. In the IR spectra of the Schiff base H_2L^2 , a very weak absorption band appeared at 2834 cm^{-1} corresponding to $\nu(\text{S-H})$ disappeared in the spectra of the complexes due to the fact that coordination has taken place through the sulphur atom after deprotonation. Moreover, the absorption due to $\nu(\text{C-S})$ of the ligand at 1224 cm^{-1} is shifted to a higher frequency 1256 cm^{-1} in the complexes $[\text{Ni}(\text{PPh}_3)(\text{L}^2)]$, indicating that the other coordination is through thiophenolic sulphur atom. The characteristic bands due to triphenylphosphine were observed in the expected region. The characteristic band for $\nu(\text{C=O})$ and $\nu(\text{NH})$ disappears on complexation. This may be due to the enolization and subsequent coordination through the deprotonated oxygen atom [8].

Ultraviolet-visible spectra: The electronic spectra of both ligands and their Ni^{2+} complexes in dichloromethane showed four to seven bands in the 230-494 nm regions. The electronic spectra of Ni(II) Schiff base complexes and the positions are similar to the one that have been observed for other nickel(II) square planar complexes showed one to four bands at the region 230-440 nm due to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ transition in a square planar geometry. The results are in accordance with the electronic spectra of other similar square planar Ni(II) complexes [9,10]. The UV-visible spectral data are given in Table-2.

${}^1\text{H}$, ${}^{13}\text{C}$ and ${}^{31}\text{P}$ NMR spectra of the Ni(II) complexes: The ${}^1\text{H}$ NMR spectra of all the complexes were recorded to confirm the binding of Schiff bases to the nickel ion (Table-3). Multiplets are observed around 5.4-7.6 ppm in all the complexes have been assigned to aromatic protons of triphenylphosphine and Schiff base ligands. The disappearance of signals due to phenolic, enolic and thiolato hydrogen atoms in the ${}^1\text{H}$ NMR spectra of all the Ni(II) complexes indicates the deprotonation of these groups and the Schiff bases are coordinated to metal ions as dianionic ligands, which indicates the coordination of nickel(II) through the Ph-O, Ph-S and enolic-O atoms.

The ${}^{13}\text{C}$ NMR data for the complexes have been recorded and summarized in Table-3. The assignment of all the aromatic carbon resonances is made on the basis of ${}^1\text{H}$ - ${}^{13}\text{C}$ HSQC spectrum of the complex $[\text{Ni}(\text{PPh}_3)(\text{L}^1)]$ and $[\text{Ni}(\text{PPh}_3)(\text{L}^2)]$ are given in Figs. 1 and 2, respectively. The chemical shifts for the aromatic carbon atoms of triphenylphosphine and phenyl groups in the complexes appear at 109-137 ppm. In all the complexes, Ph-C-O and Ph-C-S appears at 137 and 134 ppm, respectively and also for Ph-C=N-Ph and Ph-N=C-O in the complexes appears in the range 136-153 ppm and 145-159 ppm, respectively.

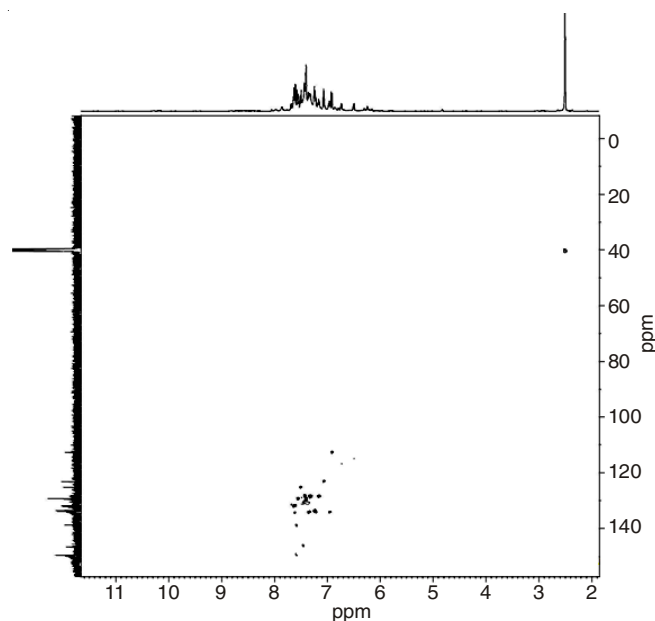


Fig. 1. ${}^1\text{H}$ - ${}^{13}\text{C}$ HSQC Spectrum of the complex $[\text{Ni}(\text{L}^1)(\text{PPh}_3)]$

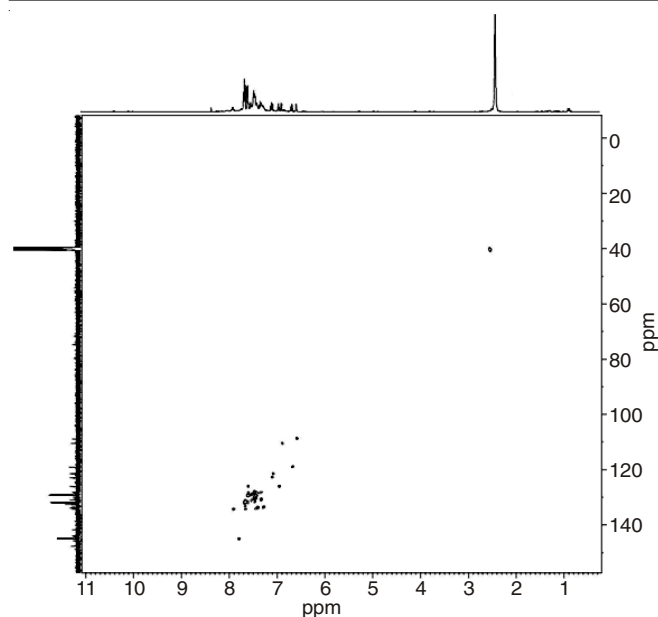
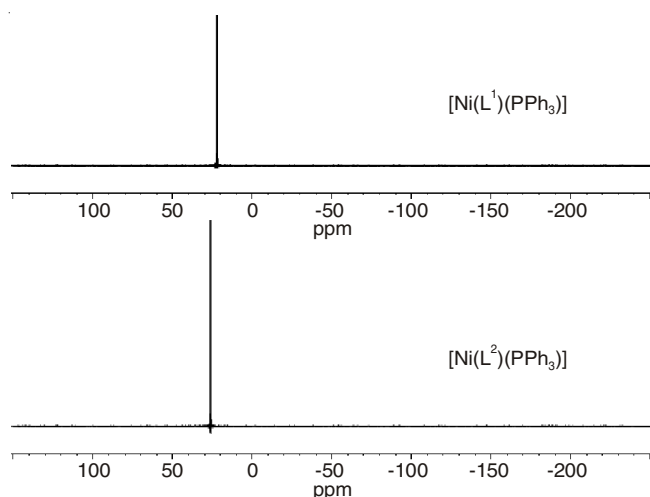
${}^{31}\text{P}$ NMR spectra were recorded for two complexes in order to confirm the presence of triphenylphosphine group of the complexes. The complexes $[\text{Ni}(\text{PPh}_3)(\text{L}^1)]$ and $[\text{Ni}(\text{PPh}_3)(\text{L}^2)]$ exhibits only one signal at 23.91 and 26.00 ppm confirming the presence of triphenylphosphine, respectively (Fig. 3).

TABLE-2
FT-IR SPECTRAL AND UV-VISIBLE DATA OF NEW Ni(II) SCHIFF BASE COMPLEXES

Ligands & Complexes	IR spectra (cm^{-1})			UV-visible λ_{max} (nm)
	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{C-S})$	
H_2L^1	1615	1343	–	255, 296, 369, 401
H_2L^2	1617	–	1224	256, 297, 369, 404, 435, 472, 494
$[\text{Ni}(\text{L}^1)(\text{PPh}_3)]$	1592	1438	–	290, 330, 322, 412
$[\text{Ni}(\text{L}^2)(\text{PPh}_3)]$	1580	–	1260	266, 322, 428

TABLE-3
 ${}^1\text{H}$, ${}^{13}\text{C}$ AND ${}^{31}\text{P}$ NMR SPECTRAL DATA OF Ni(II) SCHIFF BASE COMPLEXES

Ligands and complexes	${}^1\text{H}$ NMR (ppm)	${}^{13}\text{C}$ NMR (ppm)
H_2L^1	6.2-7.6 (m, aromatic), 10.8 (s, Ph-OH), 12.8 (s, enolic-OH)	110, 114, 116, 122, 136, 143, 153 (aromatic C), 155 (Ph-C-OH), 158 (Ph-C=N-Ph), 163 (Ph-N=C-OH)
H_2L^2	6.4-7.8 (m, aromatic), 3.4 (s, Ph-SH), 10.4 (s, enolic-OH)	108, 116, 121, 125, 130, 135, 141 (aromatic C), 154 (Ph-C-SH), 158 (Ph-C=N-Ph), 176 (Ph-N=C-OH)
$[\text{Ni}(\text{L}^1)(\text{PPh}_3)]$	6.3-7.6 (m, aromatic)	111, 115, 118, 123, 128, 129, 137 (aromatic C), 137 (Ph-C-O), 153 (Ph-C=N-Ph), 159 (Ph-N=C-O)
$[\text{Ni}(\text{L}^2)(\text{PPh}_3)]$	5.4-7.5 (m, aromatic)	109, 120, 124, 126, 129, 130, 131, 132 (aromatic C), 134 (Ph-C-SH), 136 (Ph-C=N-Ph), 145 (Ph-N=C-O)

Fig. 2. ^1H - ^{13}C HSQC Spectrum of the complex $[\text{Ni}(\text{L}^2)(\text{PPh}_3)]$ Fig. 3. ^{31}P NMR Spectra of the complexes

Microbial studies: The *in vitro* cytotoxicity of ligands and the complexes were screened in order to evaluate activity against *Staphylococcus epidermidis* and *Escherichia coli* at 0.25 %, 0.50 % and 1 % concentration and the results are shown in Table-4. From the results, it is inferred that the Ni(II) Schiff base complexes show higher efficiency when compared with the standard (co-trimoxazole), parent ligands, nickel(II) precursors and standard reference against same microbes under identical experimental conditions. This would suggest that the chelation could facilitate the ability of a complex to cross a

cell membrane and can be explained by Tweedy's chelation theory [11]. Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with donor groups and possible π -electron delocalization over the whole chelate ring. Such a chelation could enhance the lipophilic character of the central metal atom, which subsequently favours its permeation through the lipid layer of the cell membrane. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and blocking the metal binding sites on enzymes of microorganism. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restrict the further growth of the organism [11-13]. The variation in the effectiveness of different compounds against different organisms depends either on the impermeability of the cells of the microbes or on differences in the ribosome of microbial cells. A number of new nickel(II) Schiff base complexes exhibits a greater activity when compared with the Ru(III) Schiff base complexes[6], which contains the same ligands.

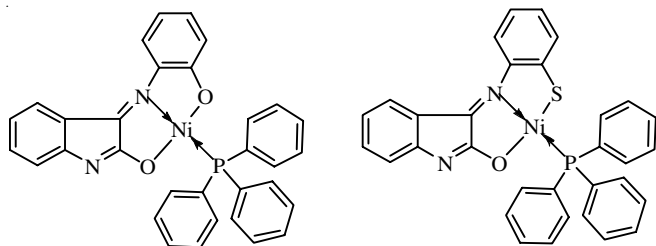
Oxidation of alcohols: Catalytic oxidation of cyclohexanol, benzyl alcohol and cinnamyl alcohol by the synthesized nickel(II) Schiff base complexes were carried out in CH_2Cl_2 under an oxygen atmosphere at ambient temperature which is a green technique and the results are summarized in Table-4. Activation of molecular oxygen by transition metals for the catalytic oxidation of organic substrates has been of continued interest in organic synthesis [14]. Cyclohexanone, benzaldehyde and cinnamaldehyde were formed from cyclohexanol, benzyl alcohol and cinnamyl alcohol, respectively, after stirring for about 6 h and the carbonyl compounds were quantified as 2,4-dinitrophenylhydrazone derivatives. Only a very little amount of carbonyl compound is formed when the reaction is carried out without the catalyst in presence of oxygen atmosphere at ambient temperature. This is an insignificant amount compared with the yields of carbonyl compounds that have been obtained from the reaction catalyzed by nickel complexes. The relatively higher product yield obtained for oxidation of cinnamyl alcohol and benzyl alcohol compared with cyclohexanol is due to the fact that α -CH unit of benzyl alcohol is more acidic than cyclohexanol [14].

Conclusion

Nickel(II) complexes with dibasic tridentate Schiff bases have been prepared and characterized by (FT-IR, UV-visible and NMR). The Ni(II) ion is assigned a square planar geometry and coordination of the ligands through ONO/ONS atoms (**Scheme-IV**). The $[\text{Ni}(\text{L}^1)(\text{PPh}_3)]$ complex can serve as good catalyst for the oxidation of alcohols to corresponding carbonyl compounds reactions. All complexes were screened for their

TABLE-4
OXIDATION OF ALCOHOLS AND BIOCIDAL ACTIVITY OF NEW Ni(II) SCHIFF BASE COMPLEXES

Complexes	Benzyl alcohol		Cyclohexanol		Cinnamyl alcohol		Inhibition zone (mm)					
	Yield (%)	Turnover number	Yield (%)	Turnover number	Yield (%)	Turnover number	<i>Staphylococcus epidermidis</i>			<i>Escherichia coli</i>		
							0.25 %	0.5 %	1 %	0.25 %	0.5 %	1 %
$[\text{Ni}(\text{L}^1)(\text{PPh}_3)]$	71	73	59	61	47	49	24	24	26	27	27	29
$[\text{Ni}(\text{L}^2)(\text{PPh}_3)]$	69	71	59	61	43	45	26	27	27	29	29	30
Standard							Co-trimoxazole (21)			Co-trimoxazole (22)		



Scheme-IV: Tentatively proposed structure of Ni(II) complex

antimicrobial studies. The Ni(II) Schiff base complexes show higher efficiency when compared with the standard (cotrimoxazole), parent ligands, nickel(II) precursors and standard reference. The $[\text{Ni}(\text{L}^2)(\text{PPh}_3)]$ complex is more active due to the presence of thiophenolic moiety in the ligand. Thermal and air stability of the complexes offer the advantage of oxidation of alcohols and antimicrobial activities.

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