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Synthesis, spectroscopy and biological studies of nickel (II) complexes with tetradentate Schiff bases having N_2O_2 donor group

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Complexes of nickel(II) of N,N'-disalicylidene-3,4-diaminotoluene(H2L1), N,N'-bis(3,5-di-tert-butylsalicylidene)-1,3-diaminopropane(H2L2),tetrathiafulvalene-N,N'-phenylene bis (salicylideneimine)(H2L3), o-hydroxybenzaldehyde, o-hydroxyacetophenone ethylene diamine (H2L4) and 1-phenylbutane-1,3-dionemono-S-methylisothio- semicarbazone with 5-phenylazo- o-hydroxybenzaldehyde (H2L5) have been synthesized and characterized by elemental analysis, electronic, (Infra-Red) IR, 1H NMR, magnetic susceptibility measurement, molar conductance and thermal studies. The complexes are found to be non- ionic in nature. The analytical studies show tetrahedral, square planar and octahedral geometries of the complexes. The complexes have been found to posses 1:1 (M:L) stoichiometry. The bioefficacy of the ligands and their complexes have been examined against the growth of bacteria *in vitro* to evaluate their anti-microbial potential.

Key words: Tetradentate schiff base, Nickel (II) ions, N_2O_2 group, spectra.

INTRODUCTION

Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility and diverse range of applications (Taylor and Relinski, 2004; Yamada, 1999). Tetradentate Schiff base complexes of nickel afford two main differences relative to macrocyclic ligands, easier access to mixed donor environments and an open equatorial ring, the hole size of which can in principle accommodate more easily the expected changes in metal size upon oxidation/reduction (Cristin and de Castro, 1988). The coordination chemistry of nickel metal complexes with salen-type ligands had achieved a special status (Klein et al., 2000; Isse et al., 1992), because of their very interesting O_2-binding reactivity, redox chemistry, unusual magnetic and structural properties, as well as their usage as catalysts for the oxidation and epoxidation reactions (Veli et al.,

2005; Zhang et al., 1990). Salen complexes have also been recently used as catalytically active materials to develop surface-modified electrodes for sensoring applications and as sources of planar supramolecular building blocks (Aubert et al., 1999; Mao et al., 2000; Jager et al., 1997; Chiehak et al., 2002). In the area of bioinorganic chemistry, interest in Schiff bases complexes had centered on synthetic applications (Khaddar et al., 2005), whereas, unsymmetrical Schiff base ligands have clearly offered many advantages over their symmetrical counterparts in the elucidation of the composition and geometry of the metal ion binding sites in the metal-proteins and enzymes and selectivity of natural systems with synthetic materials (Daneshvar et al., 2003; Bu et al., 1997). Salen-type Schiff base complexes exhibiting potentially large nonlinear optical (NLO) responses have attracted attention in last decades (Bella, 2000, 2002; Chiang et al., 1996). In such compounds having generally a planar or a pseudo planar structure, the metal atom is strategically placed at the center of the charge-transfer system, allowing the d electrons of the metal to take part in the conjugation scheme of the organic ligands. As a

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result enhanced optical nonlinearities are observed after complexation.

EXPERIMENTAL

Materials and methodology

All the chemicals were used of analytical grade and used as procured. Solvents used were of analytical grade and were purified by standard procedures. The stoichiometric analyses (C, H and N) of the complexes were performed using Elementar vario EL III (Germany) model. Metal contents were estimated on an AA-640-13 Shimadzu flame atomic absorption spectrophotometer in solutions prepared by decomposing the complex in hot concentrated HNO_3. The molar conductances at 10^{-3} molar dilution were measured by Elico-Conductometer Bridge.

The IR spectra were recorded on Perkin-Elmer FTIR spectro-photometer in KBr and polyethylene pellets. The UV-visible spectra were recorded in water on Beckman DU-64 spectrophotometer with quartz cells of 1 cm path length. 1H NMR spectra were recorded in DMSO solvent (solvent peak 3.8 ppm) on a Bruker Advance 400 instrument.

Synthesis of ligands

Synthesis of H2L1

It was prepared by dissolving 3.05 gm (25 mmol) of 3, 4-diaminotoluene in 100 ml of ethanol and stirred for 3 h. After that 50 mmol (6.10 ml) of salicylaldehyde was mixed in 150 ml of ethanol. The 3, 4-diaminotoluene solution was added to the salicylaldehyde solution using an overhead stir for complete mixing. The crude product obtained was recrystallised from dichloromethane.MP 120°C.

Synthesis of H2L2

It was prepared by refluxing 20 mmol of 3, 5-di-tertbutylsalicylaldehyde and 10 mmol of the 1, 3-diaminopropane in 60 ml of ethanol for 1 h. The product was recrystallised from ethanol and dried (melting point, 144°C).

Synthesis of H2L3

A solution of 5,6-diamino-2-(4,5-bis (propylthio)-1,3-dithio-2-ylidene)-benzo 1,3-dithiole (5 mmol) and salicylaldehyde (10 mmol) in ethanol was stirred for 6 h. The resulting precipitate was filtered, washed with ethanol and dried in vacuum. The analytical pure ligand was obtained as an orange powder (melting point (MP) 185°C).

Synthesis of H2L4

Hot ethanolic solution of ethylene diamine (0.61 g, 10 mmol) was added drop-wisely with continuous stirring to a hot ethanolic solution of o-hydroxy acetophenone (10 mmol) followed by o-hydroxybenzaldehyde (10 mmol). The mixture had been refluxed on water bath for about 1 h then allowed to cool at room temperature. The solid product was filtered off and recrystallised from ethanol (MP 170°C).

Synthesis of complexes (general method)

One millimole of $NiAc_2.4H_2O$ was dissolved in ethanol and stirred for 2 h and 1 mmol of requisite ligand was suspended in hot ethanol and stirred for 3 h. Ethanolic solutions of the Schiff base were added to ethanolic Nickel (II) acetate tetra hydrate solutions and the resulting mixtures refluxed; after cooling, solids were filtered off, washed with ethanol and diethyl ether and dried under vacuum over P4O10.

Synthesis of ligand (H2L5) and complex (NiL5)

A warm solution of $NiAc_2.4H_2O$ (1.0 mmol) in methanol (10 cm^3) was added to a solution containing phenylbutane-1, 3-dionemono-S-methylisothiosemicarbazone (1.0 mmol), 5-phenylazo-salicylaldehyde (0.2 cm^3, 1.5 mmol) and triethylamine (1 cm^3). Precipitation of complex occurred immediately. The precipitate was washed with methanol and dried (Abe et al., 2004).

RESULT AND DISCUSSION

The synthesized compounds are crystalline colored, non-hygroscopic, insoluble in water, partially soluble in ethanol but soluble in chloroform, acetone, Dimethylformamide DMF and Dimethyl sulfoxide (DMSO). They were obtained with excellent yield because of the intramolecular hydrogen bond between the fairly acidic phenolic hydrogen and the azomethine nitrogen atom in salicylaldehyde or its derivatives, which catalyzes the condensation reactions. The coordination of the Ni metal of the quadridentate (ONNO) ligands is realized by means of nitrogen atoms N1 and N4 of the ligands and two oxygen of the ligands. Composition and identity of the assembled system were deduced from elemental analysis and IR, UV-vis, NMR, TGA and molar conductance. The analytical data of the complexes indicated 1:1 metal to ligand stoichiometry. The complexes were decomposed in the range of 200 to 270°C. Possible compositions of the complexes were calculated and compared with the experimental values as presented in Table 1.

Molar conductance

The complexes were dissolved in DMF and the molar conductivities of 10^{-3} M of their solutions at room temperature were measured. Table 2 shows the molar conductance values of the complexes. It is concluded from the results that complexes are found to have molar conductance values in the range of 2 to 14 ohm^{-1} mol^{-1} cm^2 indicating the non-electrolytic nature of these complexes (Figure 1) (Prakash et al., 2010; Rabie et al., 2008).

I.R. spectra

The IR spectra of the complexes were interpreted by

Table 1. Composition, colours, melting point and elemental analyses.

Complexes composition	Melting point	Colour	Yield	Elemental analyses (found|calcd.)			
				C	H	N	Ni
NiL^1 $C_{21}H_{14}N_2O_2Ni$	240	Red	86	64.45 (64.40)	3.70 (3.76)	7.54 (7.51)	15.72 (15.74)
NiL^2 $C_{33}H_{48}N_2O_2Ni$	205	Green	83	71.43 (70.33)	9.35 (8.58)	5.55 (4.97)	1 8.98 (18.19)
NiL^3 $C_{30}H_{26}N_2O_2S_6Ni$	215	Orange	87	51.85 (51.65)	3.75 (3.76)	4.08 (4.02)	9.12 (8.42)
NiL^4 $C_{17}H_{20}N_2O_2Ni$	200	Yellow	84	54.66 (54.44)	5.32 (5.37)	7.75 (7.47)	16.00 (15.66)
NiL^5 $C_{25}H_{21}N_5O_2SNi$	270	Brown	83	58.70 (58.39)	4.25 (4.12)	13.48 (13.63)	11.87 (11.42)

Table 2. I. R., Electronic spectra, Magnetic moment, Molar conductance and Geometry of the complexes.

Complexes	I.R. ν (C=N) (cm^{-1})	Electronic (nm)	$\mu_{eff.}$ B. M..	Geometry	Molar Conductance (Ω^{-1} mol^{-1} cm^2)
NiL^1	1600	478,448,378	Diamagnetic	Square planar	14
NiL^2	1605	270,340,600	Diamagnetic	Square planar	6
NiL^3	1588	280,310,350	Diamagnetic	Square planar	2
NiL^4	1578	340,360,410	2.50	Octahedral	8
NiL^5	1585	290,380,490	2.40	Tetrahedral	10

comparing the spectra with that of the free ligands. The absence of the broad band at 2500 to 3200 cm^{-1} due to ν(OH) of the intra molecularly bonded N-H-O in the spectra of the complexes indicated the de-protonation of the salicylaldimine moiety of H_2Lx in the Complexation (Abe et al., 2004; Rigamonti et al., 2006). The shift of the characteristic imines (CH=N) band from 1590 to 1620 to 1578 to 1605 cm^{-1} indicated coordination of the azomethine nitrogen's to the nickel atom (Gradinaru et al., 2007). Further coordination of azomethine is confirmed with the presence of new bands at 430 to 480 cm^{-1} region assignable to ν (Ni-N) for these complexes. A new band in the 400 to 450 cm^{-1} region in the spectra of the complexes is assignable to ν (Ni-O) (Garg and Kumar., 2003). A very broad band at about 3300 to 3446 cm^{-1} is present in the spectra of NiL^4 complex. The presence of this broad band is associated with coordinated water molecules. The presence of coordinated water in the complex had been inferred on the basis of a medium intensity at 728 to 777 cm^{-1} (OH- rocking) Figure 2 (El-Wahab and.El-Sarrag, 2004).

Magnetic susceptibility measurement and ^{1}H NMR spectroscopy

The complexes NiL^1, NiL^2, NiL^3 are diamagnetic at RT indicates their square planar geometry around Ni(II) ion while the complexes NiL^4 and NiL^5 having magnetic tetrahedral geometry, respectively. The TGA study of the NiL^4 complex shows the presence of two coordinated water molecules which is in the support of its octahedral geometry.

All tetradentate Schiff bases showed a narrow intense singlet in the region of δ 13.00 to 13.99 ppm assigned to hydrogen bonded salicylic proton. The presence of a doublet signal in the region of δ 7.42 to 8.40 ppm indicated the presence of two azomethine groups, as two signals are recorded for the azomethine protons. The ^{1}H NMR spectra of all the complexes showed a down-field shift in the frequency of azomethine protons confirming coordination of the metal ion. In all the complexes, no signal was recorded for phenolic hydrogen in the 12.5 to 14.00 ppm region, as in the case of the Schiff base, indicating deprotonation of the orthohydroxyl group (Tas et al., 2006) and confirmed coordination through phenolic oxygen. Protons of the bridging methylene groups attached to a nitrogen atom, N-CH$_2$-, resonances in the region of δ 3.57 to 3.91 ppm as a triplet pattern and doublet pattern in H_2L^2 and H_2L^4, respectively (Figure 3).

Electronic absorption spectra

The UV-vis spectra of the complexes 15 in chloroform are reported in Table 2. They show essentially three sets of common bands, falling in the range 270 to 600 nm. Thevery intense bands at low wavelengths have been assigned to charge transfer transition, for complexes with aromatic bridges these bands occur at longer wave-lengths, as expected from the higher aromaticity of the ligands which eases delocalization of electron density.
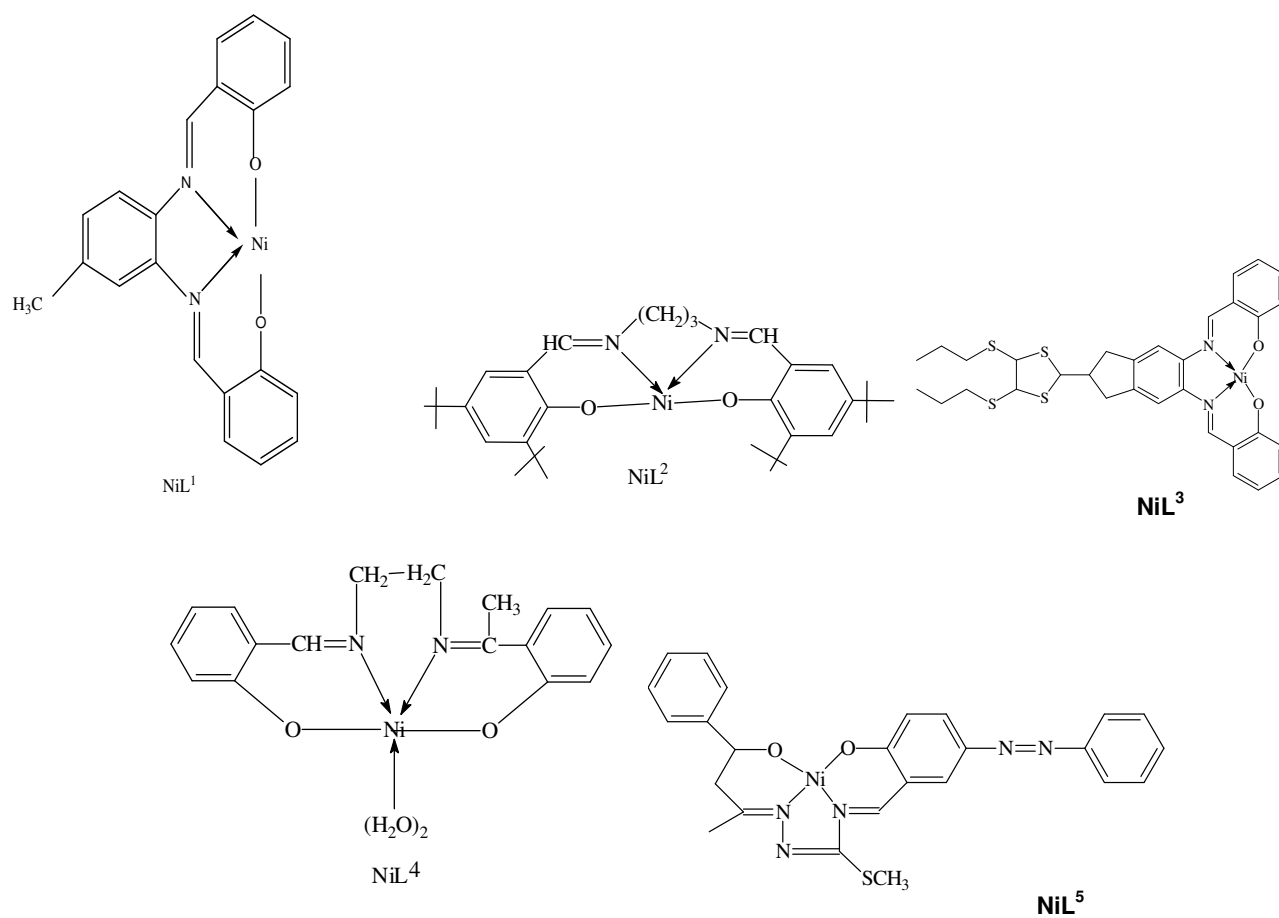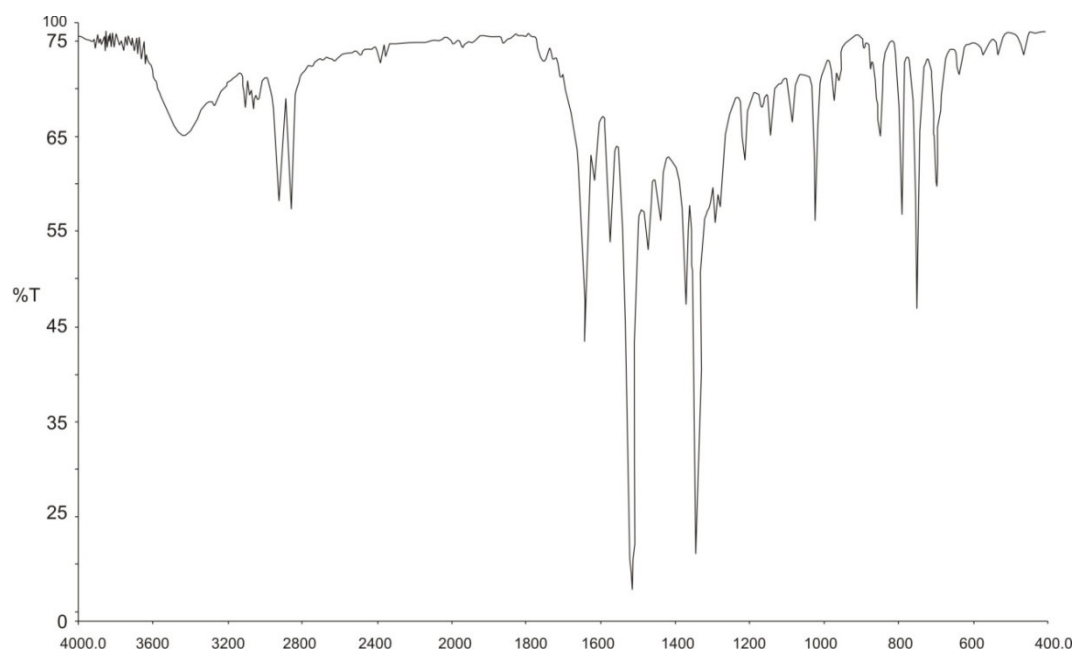
Figure 1. Structures of the complexes.

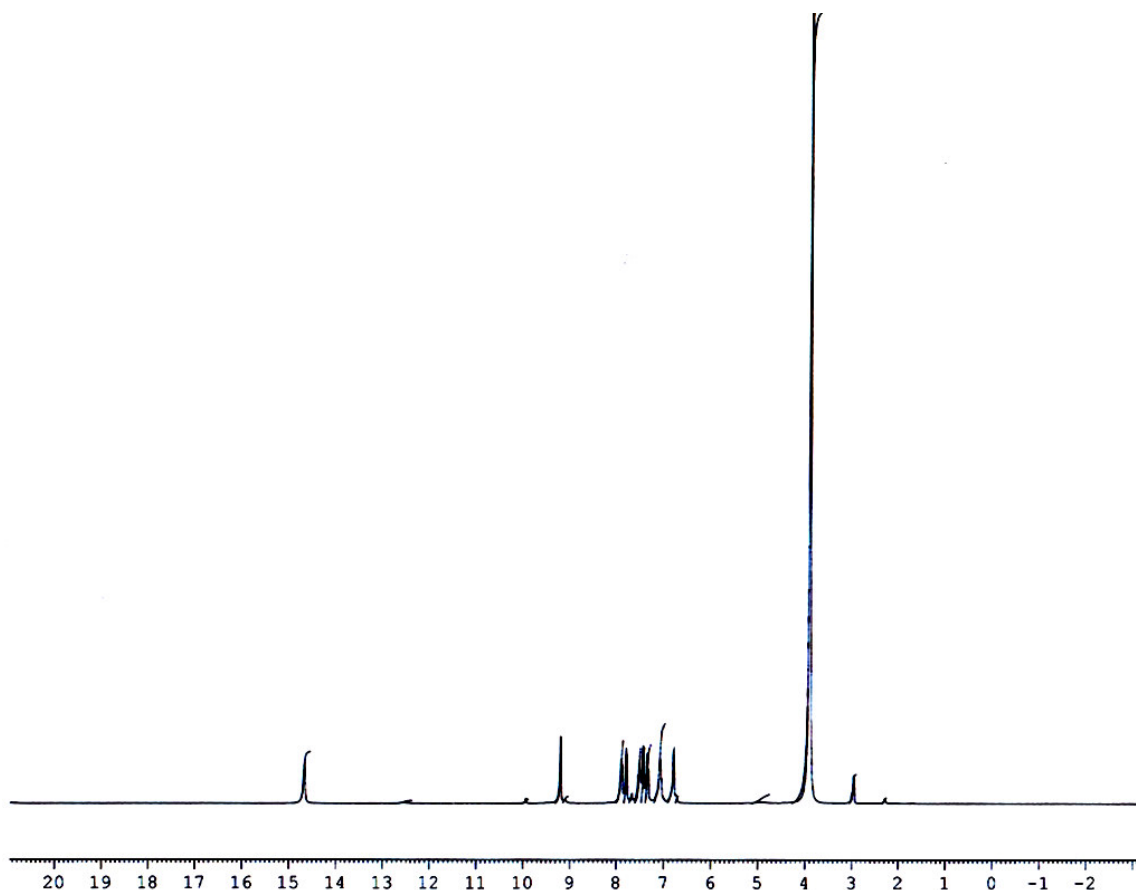**Figure 2.** I.R. spectrum of complex NiL^4.

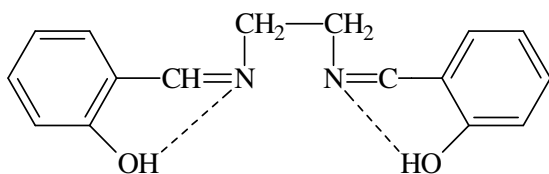**Figure 3.** ^{1}H NMR (300 MHz) spectra NiL^1 in DMSO-d6.

Figure 4. Intramolecular H-bonding H2L4.

On the other hand, the observed new shoulder around 450 nm in the spectra of the complexes solutions can be likely ascribed to an intermolecular transition from the ligands molecules to the vacant orbitals localized on the coordinated metal ions, that is, L→MCT (Figure 4).

The weaker band in the region 520 to 600 nm in the spectra of complexes with aliphatic imines is assigned to unresolved transitions from the four low-lying d-orbitals to the empty dxy orbital (Hoyt and Everett, 1969). This band could not be observed for complexes with aromatic imines bridges since it is masked by the high-intensity charge transfer transitions (Figure 5).
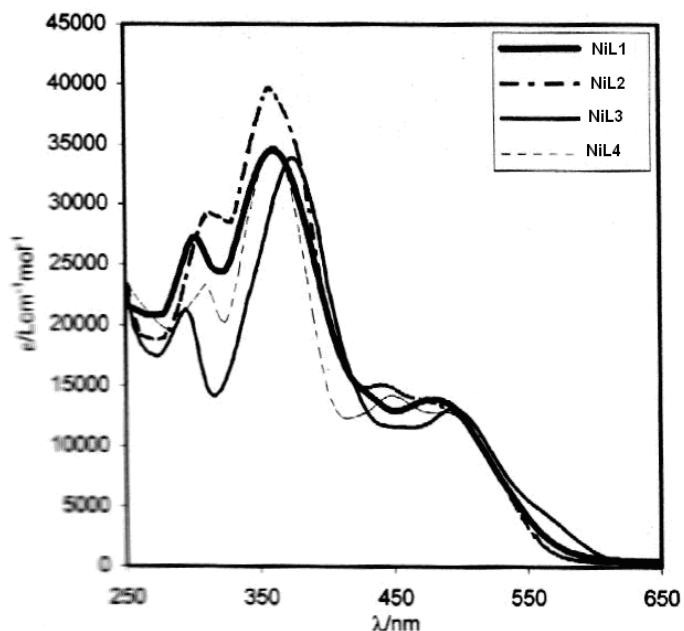
Electronic absorption spectra of NiL^1 to NiL^3 are characterized by a broad band in the range of 270 to 600 nm. This behavior can be assigned to $^1A_{1g}{\rightarrow}^1A_{2g}$, $^1A_{1g}{\rightarrow}^1B_{1g}$ and $^1A_{1g}{\rightarrow}^1E_{1g}$ transitions confirmed square planar geometry of these complexes (Garg and Kumar., 2003). The electronic spectra of NiL^4 are characterized by a broad band covering the long wavelength region 390 to 435 nm. This behavior can be assigned to an octahedral $^3A_{2g}{\rightarrow}^3T_{1g}(P)$ transitions. In NiL^5, the band at 290 to 490 nm is assigned to $^3T_1{\rightarrow}^3T_1(P)$ transitions which are also in support of a tetrahedral geometry (Lever, 1984).

Thermal analysis

TG and DTA studies were carried out on the ligands and their complexes in the temperature range of 30 to 650°C. The thermal analyses show that there are two endothermic peaks in the DTA curve of the ligands. The first is the melting point of the ligands, because no loss of weight was observed in the TG curve and second corresponds to decomposition of the ligands. TG studies of NiL^1, NiL^2, NiL^3 and NiL^5 complexes showed no weight loss upto 170°C, indicating the absence of coordinated

Table 3. Antibacterial activity of the synthesized compounds.

S/N	Compound	Diameter of zone of inhibition in mm for *E. coli*		Diameter of zone of inhibition in mm for *S. aureus*	
		50 ppm	100 ppm	50 ppm	100 ppm
1	H_2L^1	7	6	2	4
2	NiL^1	10	11	8	7
3	H_2L^2	2	3	2	2
4	NiL^2	4	6	4	4
5	H_2L^3	5	6	2	4
6	NiL^3	7	10	8	12
7	H_2L^4	6	5	5	6
8	NiL^4	6	7	10	11
9	H_2L^5	4	5	5	4
10	NiL^5	7	6	4	10
11	Chloramphenicol (Reference)	11	22	10	20

Figure 5. Experimental UV-vis spectra of complexes.

water molecules in the complexes. The complex NiL^4 showed weight loss at about 170°C, corresponding to two water molecules, this suggests the presence of two coordinated water molecules in this complex.

Biological studies

The free ligands and their Ni(II) complexes were screened against *Escherchia coli* and *Staphylococcus aureus* bacteria to assess their potential antimicrobial activity. The results are quite promising. The bacterial

screening results (Table 3) reveal that the free ligand (H_2L^1) and complex I showed maximum activity against *E. coli* bacteria, but the complex III and IV show maximum activity against *S. aureus* whereas ligand (H_2L^3) and complex III showed the better activity against *E. coli* bacteria and the complex III shows better agent for *S. aureus* bacteria. The antimicrobial data reveal that the complexes are more bioactive than the free ligands. The enhanced activity of the metal complexes may be ascribed to the increased lipophilic nature of the complexes arising due to chelation. It is probably due to faster diffusion of the chelates as a whole through the cell membrane or due to the chelation theory.

Conclusion

Metal complexes are found to be monomer and involved coordination of metal ion through azomethine nitrogen atom, phenolic oxygen atom and water molecules of the ligand molecules and forms different types of geometry. Kinetic decomposition studies reveals the first order kinetics and proceeds in two/ three step decomposition. The ligands and their metal complexes exhibit noble anti microbial activity against the reported bacterial species.

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