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Binuclear Ni(II) complexes with (11E)-4-((E)-4-(2-amino-5-nitrobenzylideneamino)phenoxy)-N-(2-amino-5-nitrobenzylidene)benzenamine Schiff base : Investigation of spectral, electrochemical and antimicrobial studies

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ABSTRACT

A new Schiff base ligand (11E)-4-((E)-4-(2-amino-5-nitrobenzylideneamino)phenoxy)-N-(2-amino-5-nitrobenzylidene)benzenamine and its nickel complexes $[Ni_2L_2(OAc)_4].H_2O$ (1), $[Ni_2L_2(ClO_4)_4].H_2O$ (2) and $[Ni_2L_2Cl_2]Cl_2.H_2O$ (3), have been synthesized and characterized by elemental analyses, molar conductance, spectroscopic and electrochemical methods. The spectral data and conductivity measurements show that Schiff base is coordinated to metal ions, from azomethine nitrogen, primary amine and as monobasic anion. Electronic and magnetic studies revealed complex 1 and 2 are octahedral and complex 3 is square pyramidal geometry. The electrochemistry of the complexes was tested studied by cyclic voltammetry. The ligand and complexes were tested for their efficiency towards antimicrobial activity and MIC data revealed that complexes are higher activity compared with ligand and not strong activity in comparison to the standard drugs.

Keywords: Schiff base, nickel(II), binuclear complexes, Antimicrobial activity

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INTRODUCTION

Schiff bases and transition metal ions complexes, with attractive desired features, have experienced long standing applications in biology, pharmacology, photochromism, catalysis, purification of toxic metal ions [1-4]. The symmetric nature of a number of homodinuclear transition metal derived metallo-biosites and of the ability of the individual metal ions to have quite distinct roles in the functioning of the metalloenzyme concerned has led to a search for symmetrical dinucleating ligands which will give binuclear complexes capable of acting as models for the metallobiosites [5,6] Currently nickel complexes a great deal of attention due to the environmental toxicity and carcinogenic nature of certain nickel compounds and the chemotherapeutic properties of other groups VIII metal complexes [7].

Nickel compounds are also present in the active sites of urease [8]. The Schiff base properties of nickel complex are high in demand in bioinorganic chemistry as well as in the redox enzyme reactions [9]. The cleavage of plasmid DNA in the presence of iodosulbenzene or magnesium mono peroxyphthalic acid (MPPA) by square planner nickel salen [bis(salicylidene)ethylenediamine] was observed by Morrow and Kolasa [10]. Novel nickel complexes have potential applications in medicine and research, such as inhibitors of cancer proliferation and useful DNA or RNA probes [11, 12].

The present study deals with the preparation of novel Schiff base ligand and its nickel binuclear complexes have been studied by elemental analysis, molar conductance, IR, electronic, and electrochemical studies. The biological activity of the parent Schiff base and its complexes was also studied.

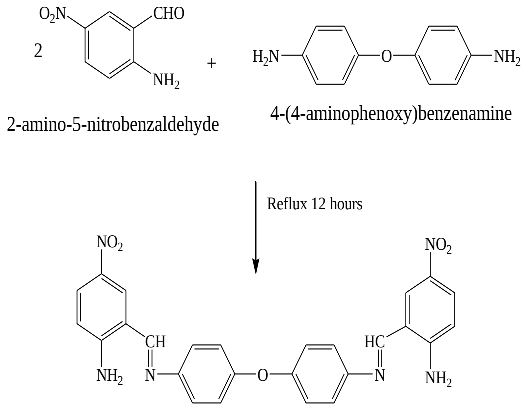
MATERIALS AND METHODS

All chemicals used were of the analytical reagent grade and of highest purity available. 2-nitrobenzaldehyde, 4,4'-diaminodiphenylether, n-Bu_4NClO_4, Nickel acetate, nickelperchlorate and nickel chlordie was purchased from Loba chemie, Aldrich. The precursor 2-amino-5-nitrobenzaldehyde was prepared with modifications in the literature [13]. Melting points of all newly prepared compounds were determined in open capillaries and are uncorrected. The C, H and N were analyzed on Carlo Erba 1106 elemental analyzer. The metal content of the complexes were determined according to the literature methods [14]. The molar conductance of the Schiff base complexes was determined on a Systronic direct reading conductivity meter with a cell having cell constant of 1.1. The The IR spectra of all complexes were recorded on FT-IR spectrophotometer (Jasco FT-IR-410) in the range 4000-400 cm^{-1}, potassium bromide disc method was employed for sample preparation. The UV-Visible in 200-800 nm range was recorded on UV/Vis Jasco 550 double beam, spectrophotometer in DMSO solvent. The magnetic measurements were made by Gouy's method at room temperature by using $Hg[Co(SCN)_6]$ as calibrant. Cyclic voltammograms were obtained using a CHI 1120A electrochemical analyzer in DMSO containing 0.1M n-Bu_4NClO_4 as the supporting electrolyte. A three-electrode system was employed with a carbon electrode working electrode, a Pt-wire as the auxiliary electrode, and an Ag/AgCl electrode as the reference electrode.

EXPERIMENTAL

Synthesis of ligand

The Schiff base ligand (11E)-4-((E)-4-(2-amino-5-nitrobenzylideneamino)phenoxy)-N-(2-amino-5-nitrobenzylidene)benzenamine (L) was prepared by the literature method [15]. 2-amino-5-nitrobenzaldehyde (0.25 g, 1.5 mmole) was dissolved in a mixture of acetonitrile (10 ml) and dichloromethane (10 ml), to with methanolic solution of 4,4'-diaminodiphenylether (0.75 mmole) was added. The solution was refluxed for 12 hours and then allowed to stand for 3 days. The solvent was removed under vacuum and, upon addition of diethylether, a coloured powder precipitated; this was recovered by filtration washed with diethylether (**Scheme 1**).

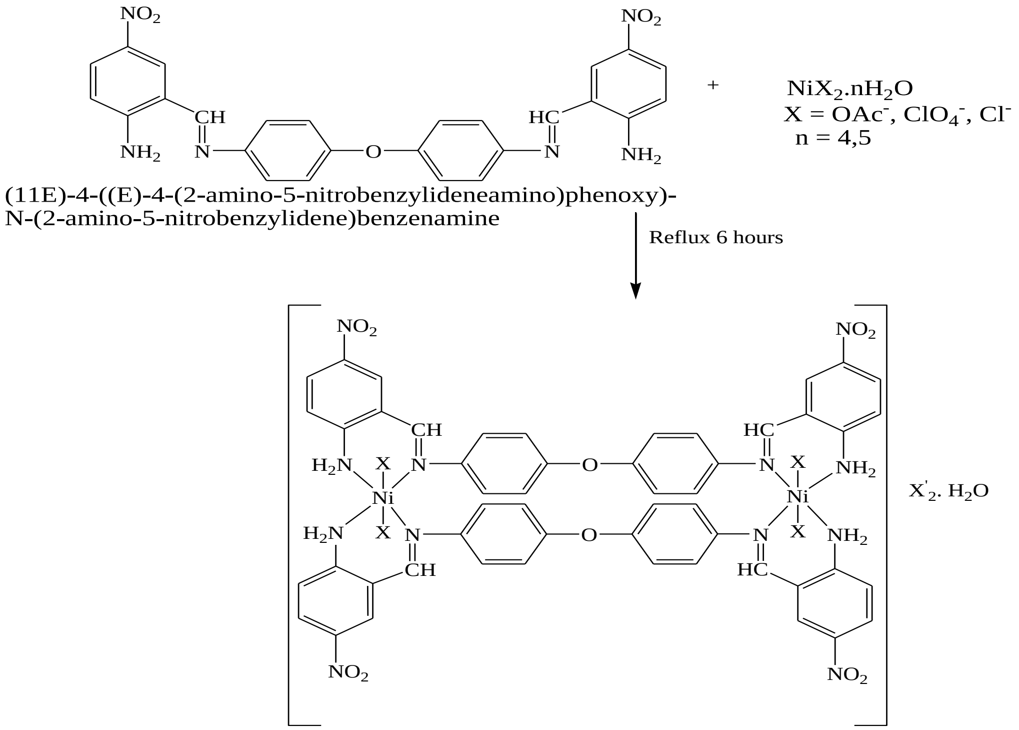


(11*E*)-4-((*E*)-4-(2-amino-5-nitrobenzylideneamino)phenoxy)-*N*-(2-amino-5-nitrobenzylidene)benzenamine

Scheme 1. Synthesis of ligand

Synthesis of nickel complexes

Ligand (L) (0.62 mmole) was dissolved in dry tetrahydrofuran (10 ml) to which $NiX_2.nH_2O$ (0.62 mmole) X = OAc^-, ClO_4^- and Cl^-, n = 4,5 in methanol (10 ml) was added and the reaction mixture was stirred for an hour. The solution was refluxed for 8-10 hours. The refluxed solution was allowed to stand overnight and reduced to half its volume under vaccum, after which a color solid precipitated; this was filtered off, washed with diethylether (10 ml) (**Scheme 2**).



Complex (1), $X = OAc^-$, $X' = 0$
Complex (2), $X = ClO_4^-$, $X' = 0$
Complex (3), $X = Cl^-$, $X' = Cl^-$

Scheme 2: Synthesis of nickel(II) complexes

Biological studies

Four pathogenic microbial were used to test the antimicrobial potential of the Schiff base metal complexes: *Staphylococcus aureus, Bacillus subtilis, Pseudomonas aeruginosa* and *Salmonella typhi*. The antimicrobial activity of the ligand and complexes were qualitatively determined by well diffusion methods. A lawn of microorganisms was prepared by pipetting and evently spreading inoculums on to agar set in petri dishes, using Muller Hinton nutrient agar for the bacteria. The bacteria were then cultured for 24 h at 36°C in an incubator. The compounds (25 µg/ml, 50 µg/ml and 100 µg/ml) to be tested were dissolved in DMSO. The inhibition zone, which appeared around the discs in each plate, was measured. Commercially available Ciprofloxacin, tetracycline, kanamycin and chloramphenicol were used for antibacterial control.

RESULTS AND DISCUSSION

The present study is based upon the employment of Schiff base ligand, which is obtained by reacting 2-amino-5-nitrobenzaldehyde with 4,4'-diaminodiphenylether (scheme1). Three new Ni(II) complexes were obtained by different Nickel(II) salts including CH_3COO^-, ClO_4^- and Cl^- anions. All the nickel(II) complexes are colored, non hygroscopic solids and stable in air. They are insoluble in common organic solvent, but soluble in DMF and DMSO. The general composition for all nickel complexes have $[M_2L_2X_2]$ and $[M_2L_2X_2]X'_2$, (M=Ni(II), X= CH_3COO^- (or)

ClO_4^- (or) Cl^-). All the complexes provide proper C, H and N results which were in good agreement with those calculated for the suggested formulae. The results of elemental analysis with molecular formula and melting points were listed in Table1.

In an effort to obtain a crystalline product suitable for X-ray diffraction studies, a range of solid metal complexes have not been isolated until now. Therefore, the structural studies of the ligand and their complexes were done by spectroscopic methods.

Table -1 Elemental analysis and physical data of ligand and binuclear nickel(II) complexes

Compounds	Molecular Formula	FM	Color	Yield	M.p., (°C)	Calcd. (found) %			
						C	H	N	M
Ligand (L)	$C_{26}H_{20}N_6O_5$	496.47	Yellow	80	140	62.90 (62.88)	4.06 (4.03)	16.93 (16.91)	-
$[Ni_2L_2(OAc)_4].H_2O$ (1)	$C_{60}H_{54}N_{12}O_{19}Ni_2$	1363.38	Pale green	70	> 250	52.80 (52.79)	3.81 (3.80)	12.32 (12.30)	8.60 (8.58)
$[Ni_2L_2(ClO_4)_4].H_2O$ (2)	$C_{52}H_{42}N_{12}O_{27}Cl_4Ni_2$	1525.38	Green	75	> 250	40.90 (40.88)	2.62 (2.61)	11.01 (11.00)	7.69 (7.67)
$[Ni_2L_2Cl_2]Cl_2.H_2O$ (3)	$C_{52}H_{42}N_{12}O_{11}Cl_4Ni_2$	1251.38	Green	72	> 250	49.15 (49.12)	3.15 (3.14)	13.26 (13.24)	9.24 (9.22)

Molar conductivity

The molar conductivity measurements have been demonstrated to be a very useful tool in the investigation of geometrical structure of inorganic compounds. The complexes were dissolved in DMSO and molar conductivities of 10^{-3} M of their solutions at room temperature were measured (Table 2). The complexes 1 and 2 showed a lower molar conductivity values in the range10.28 and 14.37 $ohm^{-1}cm^2\ mol^{-1}$. It was concluded that the complexes are non electrolytic in nature. The molar conductance value suggested that the anions were inside the coordination sphere and bonded to the metal ion therefore, these complexes may be formulated as $[M_2L_2X_2]$ [16]. The complex 3 shows the value of molar conductance 55.13 $ohm^{-1}cm^2\ mol^{-1}$, which indicates the electrolytic nature, the chloride ion present in inner and outer coordination sphere.

Table 2 Molar conductance and magnetic moment data of nickel(II) complexes

Compounds	Solvent	Molar conductance Λ_m ($ohm^{-1}cm^2\ mol^{-1}$)	Magnetic moment μ_{eff} B.M
$[Ni_2L_2(OAc)_4].H_2O$ (1)	DMSO	10.28	3.33
$[Ni_2L_2(ClO_4)_4].H_2O$ (2)	DMSO	14.37	3.34
$[Ni_2L_2Cl_2]Cl_2.H_2O$ (3)	DMSO	55.13	3.20

Infrared spectral studies

The characteristic vibrational frequencies and their tentative assignments for the HL ligand and its transition metal complexes are listed in Table 3 and figure 1. The assignments were aided by comparison with the vibrational frequencies of the free ligand and its related compounds

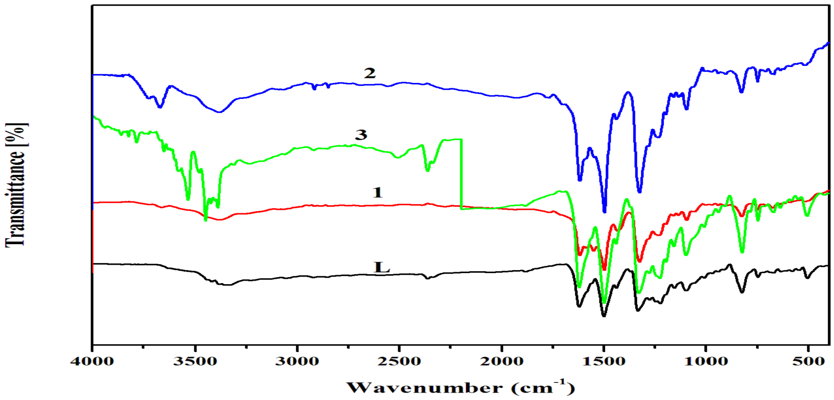


Figure 1.Infrared spectra of ligand and nickel(II) complexes

Table 3 Infrared spectra data (cm^{-1}) of ligand and nickel(II) complexes

Compounds	υ(NH$_2$)$_{as/s}$ & υ(H$_2$O) (cm^{-1})	υ(C=N) (cm^{-1})	υ(C=C) (cm^{-1})	υ(COO)$_{as/s}$ (cm^{-1})	υ(ClO$_4$) (cm^{-1})	υ(M-N) (cm^{-1})
Ligand (L)	3418, 3383	1620	1499	-	-	-
[Ni$_2$L$_2$(OAc)$_4$].H$_2$O (1)	3382	1617	1497	1583,1321	-	431
[Ni$_2$L$_2$(ClO$_4$)$_4$].H$_2$O (2)	3390	1617	1493	-	1095,625	437
[Ni$_2$L$_2$Cl$_2$]Cl$_2$.H$_2$O (3)	3418,3326,3234	1619	1495	-	-	427

The IR spectrum of the free ligand exhibits two bands at 3418 and 3383 cm^{-1} characteristic of the asymmetric and symmetric stretching vibrations of the NH$_2$ substituent on the phenyl ring [17]. In complexes the amine and lattice water peak observed one broad band at 3430-3234 cm^{-1}. The most intense band at 1620 cm^{-1} is assigned to the –C=N- stretching frequency of the ligand and is characterized for azomethine moiety of most Schiff base compounds. The shift of the stretching frequencies of the azomethine υ(C=N) group of the metal complexes to lower frequencies which lie in the range of 1617-1619 cm^{-1} compared with the free ligand may be due to the coordination of the azomethine groups to metal ions [18,19]. Weak band at 427-437cm^{-1} is assigned to υ(M–N) in the complexes. These shifts and new bands further confirm that the nitrogen of the imino-group bonds to the nickel ions [20]. The various absorption bands in the region 1460-1500 cm^{-1} may be assigned due to υ(C=C) aromatic stretching vibrations of the aromatic ring [21].

The IR spectrum of complex 1 revealed two intense bands at 1583 and 1321 cm^{-1} for υ$_{asym}$(OCO) and υ$_{sym}$ (OCO), respectively. Comparison of the Δυ value of the acetate complex with the Δυ value of sodium acetate can be used as a guideline in assigning the acetate coordination mode [22,23]. The Δυ= 262 cm^{-1} value of the acetate complex is larger than that reported for sodium acetate (Δυ= 164 cm^{-1}) which indicates two acetate groups coordinates to the metal atoms.

The binuclear nickel(II) complex 2 showed two peak at near 1095 cm^{-1} and a peak at around 625 cm^{-1}, which are assigned to perchlorate ions [24]. The peak shows splitting indicating the presence of coordinated perchlorate ions.

Electronic spectral studies

The electronic spectrum of the ligand L and binuclear Ni(II) complexes are recorded in DMSO solution (Table 4, Figure 2). The absorption band appearing at 239-264 nm (41,841-37,878 cm^{-1}) is attributable to $\pi \rightarrow \pi^*$ within the phenyl rings and the lower energy side at 306-316 nm (32,679-31645 cm^{-1}) is arise from $n \rightarrow \pi^*$ transitions associated with the azomethine chromophores [25]. The absorption bands of the complexes are shifted to longer wavelength region compared to those of the ligand [26]. A intense band at 380-383 nm (26,315-26,109 cm^{-1}) is attributable to the LMCT transitions of complexes, respectively. This shift may be attributed to the donation of the lone pairs of electron of the nitrogen atoms of the Schiff base to the metal ion (M←N).

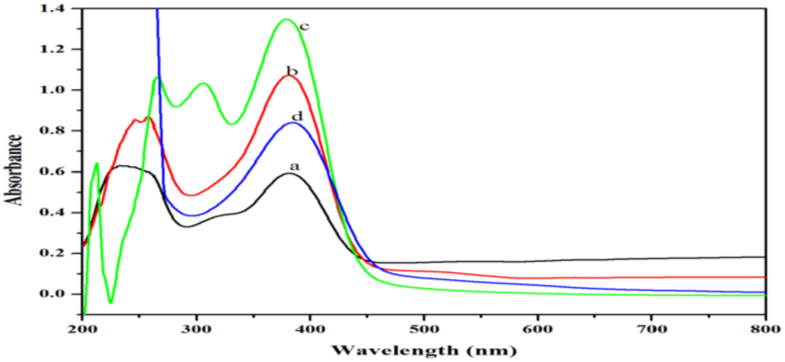


Figure 2. Electronic spectra of ligand and nickel(II) complexes

Table 4 Electronic spectral data of ligand and nickel complexes

Compound	$\pi \rightarrow \pi^*$ (cm^{-1})	$n \rightarrow \pi^*$ (cm^{-1})	LMCT (cm^{-1})	d-d transition (cm^{-1})	Geometry
Ligand (L)	41,841	31,645	26,315	-	-
$[Ni_2L_2(OAc)_4].H_2O$ (1)	39,215	-	26,178	19,455, 15,772, 12,987	Octahedral
$[Ni_2L_2(ClO_4)_4].H_2O$ (2)	37,878	-	25,839	15,105	Octahedral
$[Ni_2L_2Cl_2]Cl_2.H_2O$ (3)	38,167	-	26,109	16,863	Square pyramidal

Typically octahedral Ni(II) complex is expected to exhibit three bands which are assignable to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transitions. The Ni(II) complex 1 in this study exhibit three absorption bands at 514 nm (19,455 cm^{-1}), 634 nm (15772 cm^{-1}) and 770 nm (12,987 cm^{-1}) assignable to above transition, while the complex 2 exhibit only one broad band at 662 nm (15,105cm^{-1}) due to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition [27].

The diamagnetic Ni(II) complex 3 showed band at 593 nm (16,863 cm^{-1}), assigned to $^3B_1(F) \rightarrow {}^3E(F)$ transition. The λmax value is consistent with a penta coordinate environment around the Ni(II) ion [28].

Magnetic moment studies

The measurement of the magnetic moment of coordination compounds containing unpaired electron spins is useful in the establishment of the valence electron of the metal atom, and in many cases also helps to determine the geometrical structure of the complex. The magnetic susceptibilities of the solid-state complexes under discussion were measured by the Gouy balance method. The magnetic moments of the Ni(II) complexes obtained at room temperature are listed in Table 2. The Ni(II) complexes 1 and 2 shown magnetic moment value 3.32 and 3.34 B.M. respectively which indicates weak antiferromagnetic coupling interaction between the metal ions which further confirm the dinuclear nature of the complexes [29].

Table 2 Molar conductance and magnetic moment data of nickel(II) complexes

Compounds	Solvent	Molar conductance Λ_m ($ohm^{-1}cm^2\ mol^{-1}$)	Magnetic moment μ_{eff} B.M
$[Ni_2L_2(OAc)_4].H_2O$ (1)	DMSO	10.28	3.33
$[Ni_2L_2(ClO_4)_4].H_2O$ (2)	DMSO	14.37	3.34
$[Ni_2L_2Cl_2]Cl_2.H_2O$ (3)	DMSO	55.13	3.20

Cyclic Voltammetry studies

The cyclic voltammetric data of the nickel complexes are presented in Fig. 3 and Table 5. A 10^{-3} M solution of each complex in DMSO containing 0.1 M tetrabutylammonium perchlorate as asupporting electrolyte at a scan rate of 100 mV/s. All the complexes display two well-defined oxidation–reduction waves at positive and negative potentials. The voltammogram show two cathodic peaks (E_{pc}) at -1.537 to 0.724 V with anodic peaks at -0.911 to 1.305 V, and large peak to peak separation (ΔE) indicating quasi reversible nature for nickel complexes. The two half wave potential of nickel complexes 1, 2 and 3 shows at -1.22, 0.14, -1.01, 0.30 and 0.07, 0.29 V. It would seem the electrode reaction of nickel complexes of two one electron reductive responses is

$$Ni^{II}\text{-}Ni^{II} + e^- \rightarrow Ni^{II}\text{-}Ni^{I}$$
$$Ni^{II}\text{-}Ni^{I} + e^- \rightarrow Ni^{I}\text{-}Ni^{I}$$

The stability of mixed valance form can be qualified by the conproportionation equilibrium constant (K_{con}). It is observed that larger the K_{con} is, the greater the electronic coupling [30]. From the difference in Ni^{II}/Ni^{I} couples of binuclear complexes ($\Delta E_{1/2}$), the K_{con} for the formation of the Ni^{II}/Ni^{I} mixed valance.

$$Ni^{II}\text{-}Ni^{II} + Ni^{II}\text{-}Ni^{I} \leftrightarrow 2(Ni^{II}\text{-}Ni^{I})$$

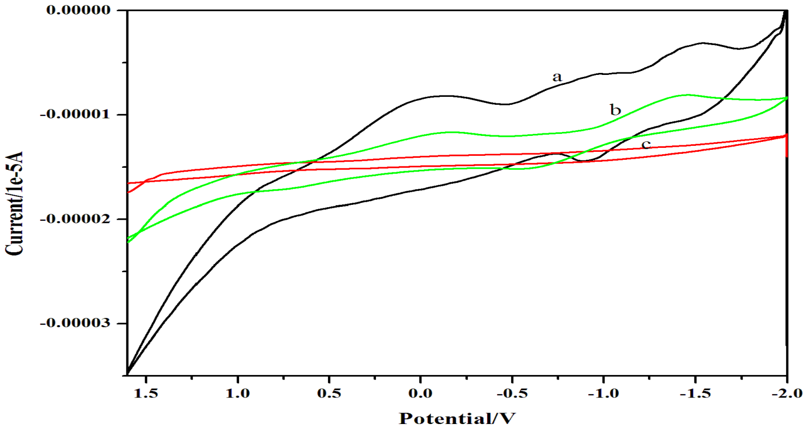


Figure 3. Cyclic voltammogram of nickel(II) complexes

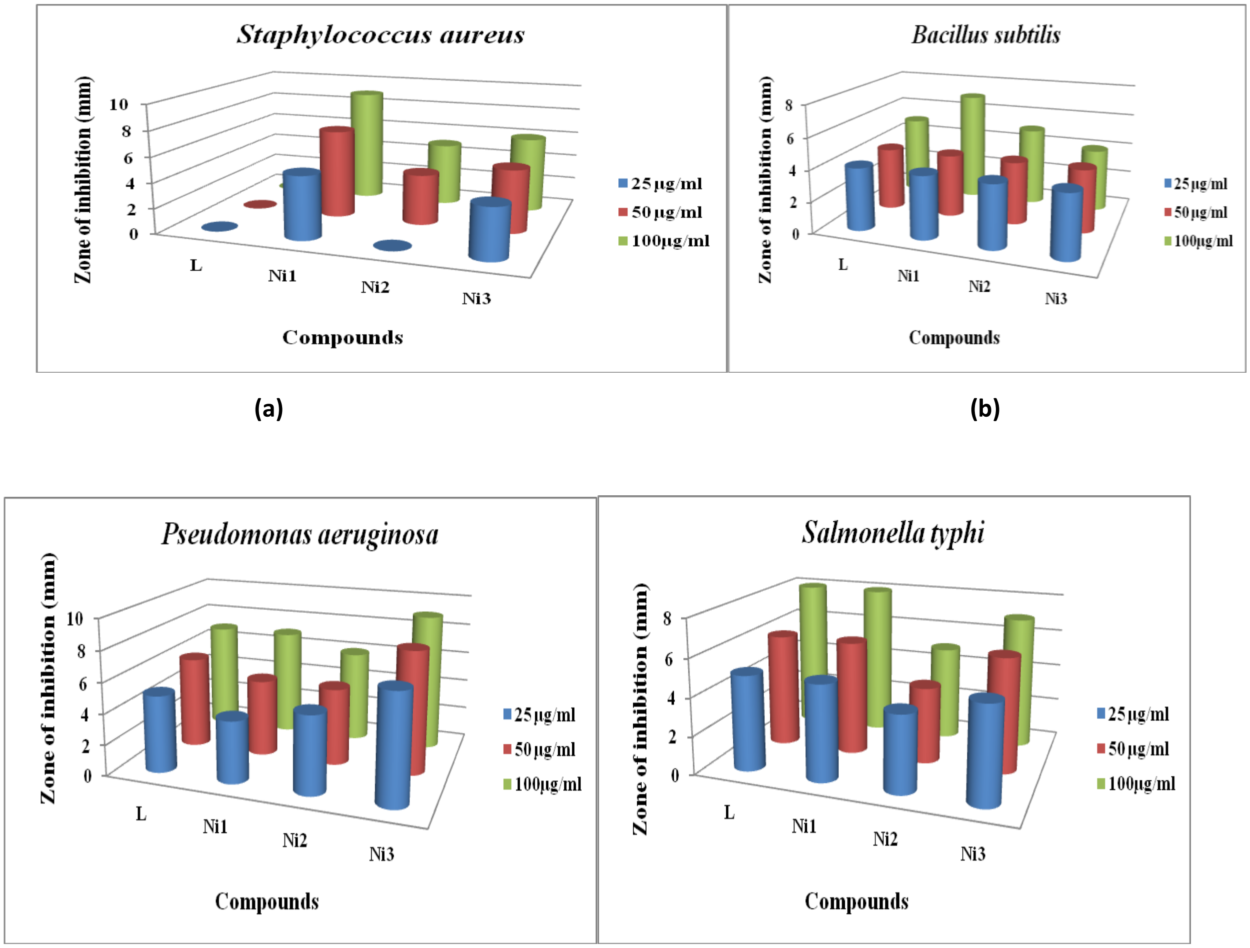
Table 5 Electrochemical data of the nickel complexes

Complexes	E^1_{pc} (V)	E^1_{pa} (V)	$E^1_{1/2}$ (V)	ΔE (mV)	E^2_{pc} (V)	E^2_{pa} (V)	$E^2_{1/2}$ (V)	ΔE (mV)	K_{con}
$[Ni_2L_2(OAc)_4].H_2O$ (1)	-1.53	-0.91	625	-1.22	-0.10	-0.39	0.14	502	1.79 x 10^{18}
$[Ni_2L_2(ClO_4)_4].H_2O$ (2)	-1.45	-0.57	-1.01	879	-0.17	0.78	0.30	963	9.08 x 10^{11}
$[Ni_2L_2Cl_2]Cl_2.H_2O$ (3)	-0.12	0.28	0.07	414	0.72	1.30	0.50	581	1.80 x 10^{7}

Antimicrobial activity

The antibacterial activities of the synthesized compounds were tested against *Staphylococcus aureus, Bacillus subtilis,* and *Salmonella typhi* bacteria by MIC method. The activity of the Schiff base ligand and their nickel complexes increases as the concentration increases because it is a well known fact that concentration plays a vital role in increasing the Zone of inhibition. The inspection of microbial results are presented in Table 6 and figure 5, which reveals that the newly synthesized Schiff base is biologically active and their metal complexes showed increased antibacterial activity than the free ligand. It can be explained by on the basis of Tweedy's theory [31].

The order of antibacterial activity of nickel complexes and ligand are $[Ni_2L_2(OAc)_4].H_2O$ (1) > $[Ni_2L_2Cl_2]Cl_2.H_2O$ (3) > L > $[Ni_2L_2(ClO_4)_4].H_2O$ (2). All the compounds have higher antimicrobial activity in gram negative bacteria compared with gram positive bacteria can be explained by considering the effect on lipo-polysaccharide (LPS), a major component of the surface of gram negative bacteria [32]. LPS is an important entity in determining the outer membrane barrier function and the virulence of Gram negative pathogens. The Schiff base can penetrate the bacterial cell membrane by coordination of metal ion through nitrogen donor atom to LPS which leads to the damage of outer cell membrane and consequently inhibits growth of the bacteria. Though there is sufficient increase in the bacterial activity of complexes as compared to the free ligands [33].



(a)

(b)

(c)

(d)

Figure 4. Antimicrobial activity against a) *Staphylococcus aureus*, b) *Bacillus subtilis*, c) *Pseudomonas aeruginosa* d)*Salmonella typhi*, with L – Ligand Ni1-[$Ni_2L_2(OAc)_4$].H_2O (1), Ni2-[$Ni_2L_2(ClO_4)_4$].H_2O (2), Ni3-[$Ni_2L_2Cl_2$]Cl_2.H_2O (3),

CONCLUSION

In this paper, we presented three nickel(II) complexes with Schiff base ligand. All the complexes are bimetallic and the proposed structure of ligand and complexes are well sustained by spectral, magnetic and conductivity studies. The metal centers in complexes 1 and 2 are octahedral and complex 3 is square pyramidal geometry. Metal complexes are higher antimicrobial activity than ligand.

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