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New Acyclic Schiff-Base Nickel(II) Complexes and their Electrochemical, Kinetic, and Antimicrobial Studies

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Five new nickel(II) complexes were synthesized. All the complexes were characterized by elemental and spectral analysis. Electronic spectra of the complexes show d–d transition in the range of 500–800 nm. Electrochemical studies of the complexes show an irreversible one-electron reduction process around –0.65 to –0.91 V and an irreversible one-electron oxidation process around 0.87 to 1.00 V. The reduction and oxidation potential of nickel(II) complexes shifts toward cathodic and anodic directions, respectively, upon increasing the chain length. The catalytic activity of the nickel(II) complexes on the hydrolysis of 4-nitrophenylphosphate was determined. All the nickel(II) complexes were screened for antibacterial activity.

Keywords antimicrobial activity, cyclic voltammetry, nickel(II) complexes, Schiff-base ligand, urease activity

INTRODUCTION

Schiff bases and their structural analogues, as ligating compounds containing acyclic and cyclic imine (C = N) bonds, are of great importance in modern coordination chemistry.[1–6] Interest in metal complexes of these ligands[7–10] is related to wide variability of their fine structures (rational design[5]) and obtaining of polyfunctional materials. Among them, we note luminescent complexes,[11,12] magnetoactive[13–15] and liquid crystal[16,17] structures, chemosensors[[18–20] and other useful metal-containing azomethine compounds.[21] Bioinorganic and biomimetics are widely represented.[22–24] Practically all coordination compounds of Schiff bases were synthesized using chemical and electrochemical techniques.[2] All factors forming mononuclear coordination compounds of Schiff bases are taken into account. Thereupon, a systematization of various types of Schiff-base complexes is offered.

The field of acyclic chemistry of metals is developing very rapidly because of its application[25,26] and importance in the area of coordination chemistry.[27,28] Studies on complexes of acyclic Schiff-base ligands with different size, and number and donor atoms for coordination with a variety of metal centers have been published.[29–31] Many transition metal ions in living systems work as enzymes or carriers in a macrocyclic ligand environment. Meaningful research in this direction might generate simple models for biologically occurring metalloenzymes,[32–34] and thus help in further understanding biological systems. The development of the field of bioinorganic chemistry has been another important factor in spurring the growth of interest in macrocyclic compounds.[35] The stability of acyclic metal complexes depends upon a number of factors, including the number and types of donor atoms present in the ligand and their relative positions within the macrocyclic skeleton, as well as the number and size of the chelate rings formed on complexation.

Nickel is recognized as an essential trace element for bacteria, plants and animals.[36–39] The active sites of enzymes such as urease, carbon monoxide dehydrogenase, [NiFe]-hydrogenase, and methyl-S-coenzyme-M methylreductase are known to contain nickel centers, which are intimately involved in the catalytic cycles.[40] Until the recent reports of the structures of urease[41] and [NiFe]-hydrogenase,[42] x-ray structural data on nickel enzymes was lacking. The quest for information about the structures and modes of action of nickel active sites continues to generate interest in the development of synthetic models for the various nickel biosites and in the coordination chemistry of nickel in general.[40,43–48] Apart from their potential to form the basis of models for the polynuclear active sites of Ni containing enzymes, complexes of macrocyclic ligands and their derivatives are ideal for studying magnetic exchange interactions[44,45] and the redox properties of nickel(II) centers in close proximity.[46] Parashar et al.[49] reported copper(II), cobalt(II), and nickel(II) complexes of the Schiff-base ligands obtained from 2-substituted anilines

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and salicylaldehyde, which exhibit good antifungal and antibacterial activity. Tagenine et al.[50] reported antibacterial activity of Zn(II), Cu(II), and Ni(II) Schiff-base complexes derived from 2,3-diamino pyridine and salicylaldehyde. Julieta Gradinaru et al.[51] reported Ni(II), Cu(II), Zn(II), and VO(II) Schiff-base complexes from 1-phenylbutane-1,3-dione mono-*S*-methylisothiosemicarbazone with *o*-hydroxybenzaldehyde that exihibit nonlinear optical (NLO) properties. Kianfar et al.[52] reported the electrochemical activity of VO(IV) Schiff-base complexes, salen type of aldehydes with diamine. Rahimi et al.[53] reported Cu(II) Schiff-base complexes derived from ethylene diamine, 2,3-diaminobenzene with 5-methylsalicylaldehyde that exhibit good electrochemical activity. We reported recently Cu(II) Schiff base complexes in 2011.[55] The present work deals with the influence of ligand modification on spectral, electrochemical, and kinetic studies, reporting the synthesis and characterization of acyclic mononuclear nickel(II) complexes.

EXPERIMENTAL

Chemicals and Reagents

5-Methylsalicylaldehyde[54] was prepared following the literature method. Analytical-grade methanol, acetonitrile, and dimethyl formamide were purchased from Qualigens. TBAP (tetra(*n*-butyl)ammonium perchlorate) used as supporting electrolyte in electrochemical measurements was purchased from Fluka and recrystallized from hot methanol. *N,N*-Bis-(3-aminopropyl) piperazine, *N,N*-bis-(3-aminopropyl) ethylene diamine, and tris-(2-aminoethyl)amine were purchased from Aldrich. Triethylenetetramine and diethylenetriamine were purchased from Qualigens.

Physical Measurements

Elemental analysis of the complexes was obtained using a Haereus CHN rapid analyzer. IR spectra were recorded on a PerkinElmer FT-IR 8300 series spectrophotometer on KBr disks from 4000 to 400 cm^{-1}. ^{1}H-Nuclear magnetic resonance (NMR) spectra were recorded using a JEOL GSX 400-MHz NMR spectrometer. Electrospray ionization (ESI) mass spectra were obtained on a JEOL DX-303 mass spectrometer. Electronic spectral studies were carried out on a PerkinElmer 320 spectrophotometer. Cyclic voltammograms were obtained on a CHI-600A electrochemical analyzer under oxygen-free conditions using a three-electrode cell in which a glassy carbon electrode was the working electrode, a saturated Ag/AgCl electrode was the reference electrode, and platinum wire was the auxiliary electrode. A ferrocene/ferrocenium couple was used as an internal standard and $E_{1/2}$ of the ferrocene/ferrocenium (Fc/Fc^+) couple under the experimental condition was 470 mV. Tetra(*n*-butyl)ammonium perchlorate (TBAP) at 1×10^{-1} *M* was used as the supporting electrolyte. Catalytic hydrolysis of 4-nitrophenylphosphate by the nickel complexes was monitored by following the ultraviolet–visible (UV-vis) absorbance change at 420 nm (assigned to the 4-nitrophenolate anion) as a function of time. A plot of $\log[A_\alpha/(A_\alpha - A_t)]$ versus time was made for each complex and the rate constants for the catalytic oxidations and the hydrolysis of 4-nitrophenylphsophate were calculated.

Synthesis of Ligands

Synthesis of L^1 [55]

An absolute methanol solution (10 mL) containing diethylenetriamine (0.1030 g, 1 mmol) was added dropwise to a stirred solution of 5-methylsalicylaldehyde (0.2720 g, 2 mmol). The solution was refluxed for 8 h (Scheme 1). The resulting yellow solution was cooled in ice. The yellow precipitate formed was filtered and washed with hexane and dried under vacuum. The crude product on recrystalization from THF gave yellow crystals.

Yield (54.8%). m.p.: 163°C. Anal.: Calcd. for $C_{20}H_{25}N_3O_2$ (%): C, 70.77; H, 7.42; N, 12.38. Found: C, 70.72; H, 7.31; N, 12.30. ESI MS: (*m/z*) 339.19 [MH^+]. Calcd. av. *m/z* 338.10. IR data (KBr) (ν, cm^{-1}): 3405 ν [b,(OH)], 1637 [s, ν(C = N)]. ^{1}H-NMR (ppm in $CDCl_3$, 400 MHz): 2.94 ($2CH_3$, s, 6H), 3.11(N-H, d, 1H, J = 8 Hz), 3.24 (N-CH_2, t, 8H, J = 12 Hz), 6.84 (Ar-H, t, 6H, J = 8Hz), 8.29 (-CH = N, d, 2H, J = 12 Hz), 9.78 (2Ar-OH, s, 2H). ^{13}C-NMR ($CDCl_3$, 400 MHz): 20.15 ($2CH_3$), 55.98 ($2CH_2$), 57.98 ($2CH_2$), Ar(CH) 116.42, 118.40, 127.28, 131.59, 132.76, 158.59, 166.28.

Ligands L^2, L^3, L^4, and L^5 were synthesized by following the already-described procedure using tris-(2-aminoethyl)amine (0.1490 g, 1 mmol), triethylenetetramine (0.1420 g, 1 mmol), *N,N*-bis-(3-aminopropyl)ethylenediamine (0.1740 g, 1 mmol), and *N,N*-bis-(3-aminopropyl)piperazine (0.2000 g, 1 mmol), respectively, instead of diethylenetriamine.

Synthesis of L^2

Yield (35.2%). m.p.: 138°C. Anal.: Calcd. for $C_{22}H_{30}N_4O_2$ (%): C, 69.08; H, 7.91; N, 14.65. Found: C, 69.01; H, 7.34; N, 14.61. ESI MS: (*m/z*) 382.24. Calcd. av. *m/z* 382.10. Selected IR data (KBr) (ν, cm^{-1}): 3485 [b, ν(OH)], 1635 [s, ν(C = N)]. ^{1}H-NMR (ppm in $CDCl_3$ 400 MHz): 2.35 ($2CH_3$, s, 6H), 3.49 (N-CH_2, t, 10H, J = 8 Hz), 5.82 (NH_2, s, 2H), 6.94 (Ar-H, t, 6H, J = = 8 Hz), 7.93 ($2CH_2$, s, 4H), 8.24 (-CH = N, d, 2H, J = 12 Hz), 9.89 (2Ar-OH, s, 2H). ^{13}C-NMR ($CDCl_3$, 400 MHz): 21.43 ($2CH_3$), 35.28 (CH_2-NH_2) 54.59 ($2CH_2$), 57.29 (CH_2-N), 59.10 ($2CH_2$), Ar(CH) 115.39, 119.49, 128.24, 134.59, 135.10, 159.43, 164.59.

Synthesis of L^3

Yield (41.5%). m.p.: 125°C. Anal.: Calcd. for $C_{22}H_{30}N_4O_2$ (%): C, 69.08; H, 7.81; N, 15.65. Found (%): C, 69.01; H, 7.64; N, 15.61. ESI MS: (*m/z*) 383.24 [MH^+]. Calcd. av. *m/z* 382.10. Selected IR data (KBr) (ν, cm^{-1}): 3445 ν(OH), 1630 [s, ν(C = N)]. ^{1}H-NMR (ppm in $CDCl_3$, 400 MHz): 2.32 ($2CH_3$, s, 6H), 2.97 (2N-H, d, 2H, J = 8 Hz), 3.77 (2N-$(CH_2)_2$, d, 12H, J = 12 Hz), 6.94 (Ar-H, t, 6H, J = 8 Hz), 8.32 (-CH = N, d, 2H, J = 8 Hz), 9.87 (2Ar-OH, s, 2H). ^{13}C-NMR ($CDCl_3$, 400 MHz): 20.88

TABLE 1
Physical properties and analytical data of [Ni(II)L^1] to [Ni(II)L^5]

Complexes	Molecular formula	Yield (%)	M.P. (°C)	Elemental analysis (%)				
				C found (calcd.)	H found (calcd.)	N found (calcd.)	Ni found (calcd.)	Mol. wt. found (calcd.)
[Ni(II)L^1]	$C_{20}H_{23}NiN_3O_2$	59	312	60.12 (60.65)	5.72 (5.88)	10.22 (10.61)	14.61 (14.85)	394.12[MH^+] (393.95)
[Ni(II)L^2]	$C_{22}H_{28}NiN_4O_2$	71	321	60.02 (60.17)	6.25 (6.42)	12.49 (12.72)	13.26 (13.31)	437.15[MH^-] (438.10)
[Ni(II)L^3]	$C_{22}H_{28}NiN_4O_2$	69	325	60.30 (59.51)	6.20 (6.36)	12.80 (12.62)	13.39 (14.31)	436.20[MH^-] (438.69)
[Ni(II)L^4]	$C_{24}H_{31}NiN_4O_2$	74	329	61.11 (61.77)	6.56 (6.72)	12.11 (12.02)	12.13 (12.45)	464.20[MH^-] (466.28)
[Ni(II)L^5]	$C_{26}H_{34}NiN_4O_2$	61	341	63.12 (63.31)	6.80 (6.97)	11.17 (11.31)	11.69 (11.94)	490.27[MH^-] (492.25)

($2CH_3$), 49.82 ($2CH_2$), 51.39 ($2CH_2$), 56.91 ($2CH_2$), Ar(CH) 115.88, 118.39, 129.39, 132.81, 134.73,158.90, 163.89.

Synthesis of L^4

Yield (29.5%). m.p.: 141°C. Anal.: Calcd. for $C_{24}H_{34}N_4O_2$ (%): C, 70.21; H, 8.34; N, 13.69. Found (%): C, 70.13; H, 8.29; N, 13.53. ESI MS: (*m/z*) 410.30. Calcd. av. *m/z* 410.10. Selected IR data (KBr) (ν, cm^{-1}): 3475 ν(OH), 1637 [s, ν(C = N)]. ^{1}H-NMR (ppm in $CDCl_3$, 400 MHz): 2.60($2CH_3$, s, 6H), 2.88 (2N-H, d,2H, J = 8 Hz), 3.71 (N-$(CH_2)_2$, d, 4H, J = 8 Hz), 7.09 (Ar-H, s, 6H), 7.81 (CH_2, s,12H), 8.16 (-CH = N, s, 2H), 9.81 (2Ar-OH, s, 2H). ^{13}C-NMR ($CDCl_3$, 400 MHz): 20.98 ($2CH_3$), 32.49 ($2CH_2$), 46.89 ($2CH_2$), 49.48 ($2CH_2$), Ar(CH) 116.81, 125.39, 131.49, 133.53, 135.33,158.89, 163.84.

Synthesis of L^5

Yield (29.5%). m.p.: 171°C. Anal.: Calcd. for $C_{26}H_{36}N_4O_2$ (%): C, 71.53; H, 8.32; N, 12.80. Found (%): C, 71.41; H, 8.24; N, 12.77. ESI MS: (*m/z*) 436.35 [MH^+]. Calcd. av. *m/z* 435.20. Selected IR data (KBr) (ν, cm^{-1}): 3435 ν(OH), 1631 [s, ν(C = N)]. ^{1}H-NMR (ppm in $CDCl_3$, 400 MHz): 2.28 ($2CH_3$, s, 6H), 3.54 (2N-$(CH_2)_2$, d, 8H, J = 12 Hz), 5.71 (CH_2, s, 12H), 7.24 (Ar-H, s, 6H), 8.25 (-CH = N, s, 2H), 9.79 (2Ar-OH, s, 2H). ^{13}C-NMR ($CDCl_3$, 400 MHz): 22.49 ($2CH_3$), 31.10 ($2CH_2$), 50.39 ($2CH_2$),53.39($4CH_2$), Ar(CH) 118.39, 124.39, 132.41, 134.49, 137.10, 157.79, 160.83.

Synthesis of Metal Complexes

An absolute methanol solution containing $Ni(ClO_4)_2 \cdot 6H_2O$ (0.036 g, 0.1mmol) was added dropwise to a stirring solution of L^1 (0.0339 g, 0.1 mmol) in 20 mL of absolute methanol. The solution was refluxed for 8 h. On cooling the solution, green color microcrystals were formed, which were filtered and washed with methanol followed by diethyl ether and dried in vacuum. The crude product was recrystallized from methanol and acetonitrile (1:3, v/v). [Ni(II)L^2], [Ni(II)L^3], [Ni(II)L^4], and [Ni(II)L^5] were synthesized by following the already-described procedure using L^2 (0.038 g, 0.1 mmol), L^3 (0.0382 g, 0.1 mmol), L^4 (0.0426 g, 0.1 mmol), and L^5 (0.0468 g, 0.1 mmol). Physical and analytical data of the complexes are given in Table 1. All the nickel(II) complexes are neutral.

Synthesis of [Ni(II)L^1]

^{1}H-NMR (ppm in $CDCl_3$,, 400 MHz): 2.94 ($2CH_3$, s, 6H), 3.53 (N-CH_2, t, 8H, J = 12 Hz), 6.94 (Ar-H, t, 6H, J = 8 Hz), 8.12 (-CH = N, d, 2H, J = 12 Hz).

Synthesis of [Ni(II)L^2]

^{1}H-NMR (ppm in $CDCl_3$, 400 MHz): 2.30 ($2CH_3$, s, 6H), 2.95 (N-CH_2, t, 12H, J = 8 Hz), 2.1 (NH,s,IH), 7.25 (Ar-H, t, 6H, J = 8 Hz), 8.20 (-CH = N, d, 2H, J = 12 Hz).

Synthesis of [Ni(II)L^3]

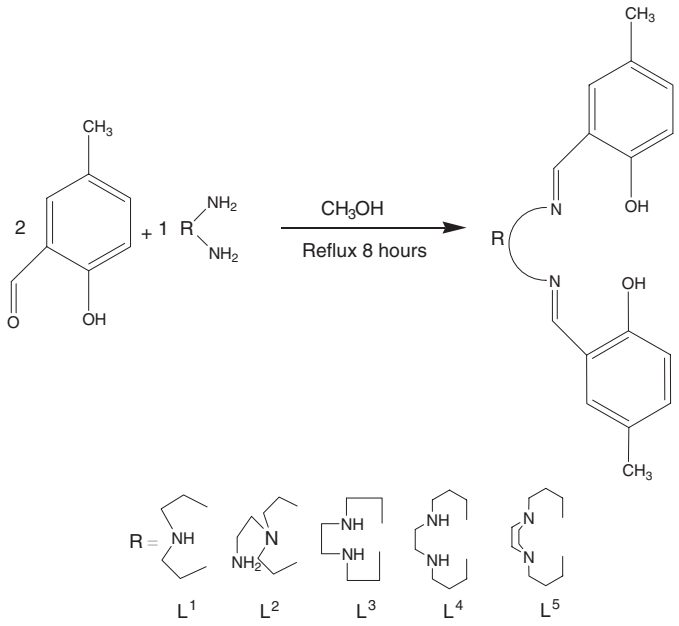
^{1}H-NMR (ppm in $CDCl_3$, 400 MHz): 2.35 ($2CH_3$, s, 6H), 2.79 (2N-$(CH_2)_2$, d, 12H, J = 12 Hz), 6.94 (Ar-H, t, 6H, J = 8 Hz), 8.12 (-CH = N, d, 2H, J = 8 Hz).

Synthesis of [Ni(II)L^4]

^{1}H-NMR (ppm in $CDCl_3$, 400 MHz): 2.55 ($2CH_3$, s, 6H), 2.81 (N-$(CH_2)_2$, d, 4H, J = 8 Hz), 3.05 ($6CH_2$, s, 12H), 7.20 (Ar-H, s, 6H), 8.16 (-CH = N, s, 2H).

Synthesis of [Ni(II)L^5]

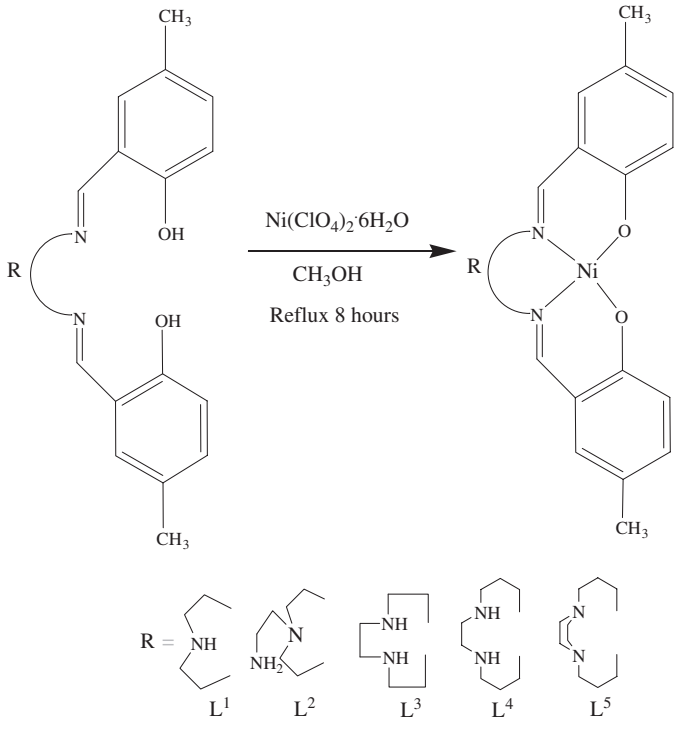
^{1}H-NMR (ppm in $CDCl_3$, 400 MHz): 2.22 ($2CH_3$, s, 6H), 2.53 (2N-$(CH_2)_2$, d, 8H, J = 12 Hz), 2.82 ($6CH_2$, s, 12H), 7.33 (Ar-H, s, 6H), 8.29 (-CH = N, s, 2H).



SCH. 1. Schematic diagram for the synthesis of ligands.

RESULTS AND DISCUSSION

A series of acyclic mononuclear nickel(II) complexes was synthesized by the Schiff-base condensation of the precursor compounds with diamines in presence of metal ion. The synthetic pathway of mononuclear complexes is shown in Scheme 2. All attempts to grow single crystals of the complexes (e.g., by the diffusion of diethyl ether vapor into DMF solutions or recrystallization of the complexes from acetonitrile) have failed and only green powder or micro crystals were obtained. Spectral, electrochemical, catalytic, and antimicrobial studies of the complexes were carried out.



SCH. 2. Schematic diagram for the synthesis of complexes.

Spectroscopic Studies

The Fourier-transform infrared (FT-IR) spectra of the ligands show a broad band around 3400 cm^{-1} due to the presence of the phenolic OH group. 5-Methy1salicylaldehyde shows a sharp band peak at 1655 cm^{-1} corresponding to ν(-CHO). Ligands and complexes show a sharp band at 1620–1640 cm^{-1} due to the C = N group. The presence of this new peak and the absence of ν(C = O) in the complexes indicate Schiff-base condensation.[56–61] The absence of a peak around 3400 cm^{-1} in all the complexes indicates the absence of ν(-OH) due to deprotonation followed by complexation. For the complexes, bands at 420–460 cm^{-1} could be assigned to the -(M–O) bond. Other weak bands at lower frequency could be assigned to the -(M–N) bond.[62] The spectra of all the complexes are dominated by bands at 3150–3070 cm^{-1} due to the aromatic C–H stretching vibration. A strong band at 1260 cm^{-1} in the free Schiff bases has been assigned to phenolic C–O stretching. Upon complexation, this band shifts to a higher frequency (1300 cm^{-1}), showing coordination through phenolic oxygen[63]; the IR data are given in Table 2. In the proton NMR spectra of all the nickel(II) complexes the peak due to phenolic OH group is absent. This indicates that the phenolic protons are deprotonated during complexation. The nickel(II) complexes are all neutral.

ESI Mass Spectral Analysis

The ESI mass spectra of the mononuclear complexes [Ni(II)L^3], [Ni(II)L^4], and [Ni(II)L^5] show the molecular ion peak (M^+) at m/z = 436.20, 464.20, and 490.27 respectively The spectra show some prominent peaks corresponding to the various fragments of the complexes. The appearance of many peaks is due to the presence of isotopic atoms. The ESI mass spectra of the mononuclear complexes [Ni(II)L^3], [Ni(II)L^4], and [Ni(II)L^5] are shown in Figure 1.

Electronic Spectra

Electronic spectra for all the complexes were obtained in DMF medium. The electronic spectra of all the complexes show a single weak d–d band in the region 410–750 nm due to $^1A_1g \rightarrow {}^1A_2g$ associated with square-planar geometry.[64] A red-shift in the λ_{max} value of the d–d band[65] with increase in the chain length between imine nitrogen has been observed. This red-shift may be due to the distortion from planar geometry as the chain length increases. The moderately intense band observed in the region of 260–330 nm is associated with ligand-to-metal charge transfer transition. An intense band observed in the region 210–240 nm is associated with intraligands transition. The absorption spectral data are given in Table 2.

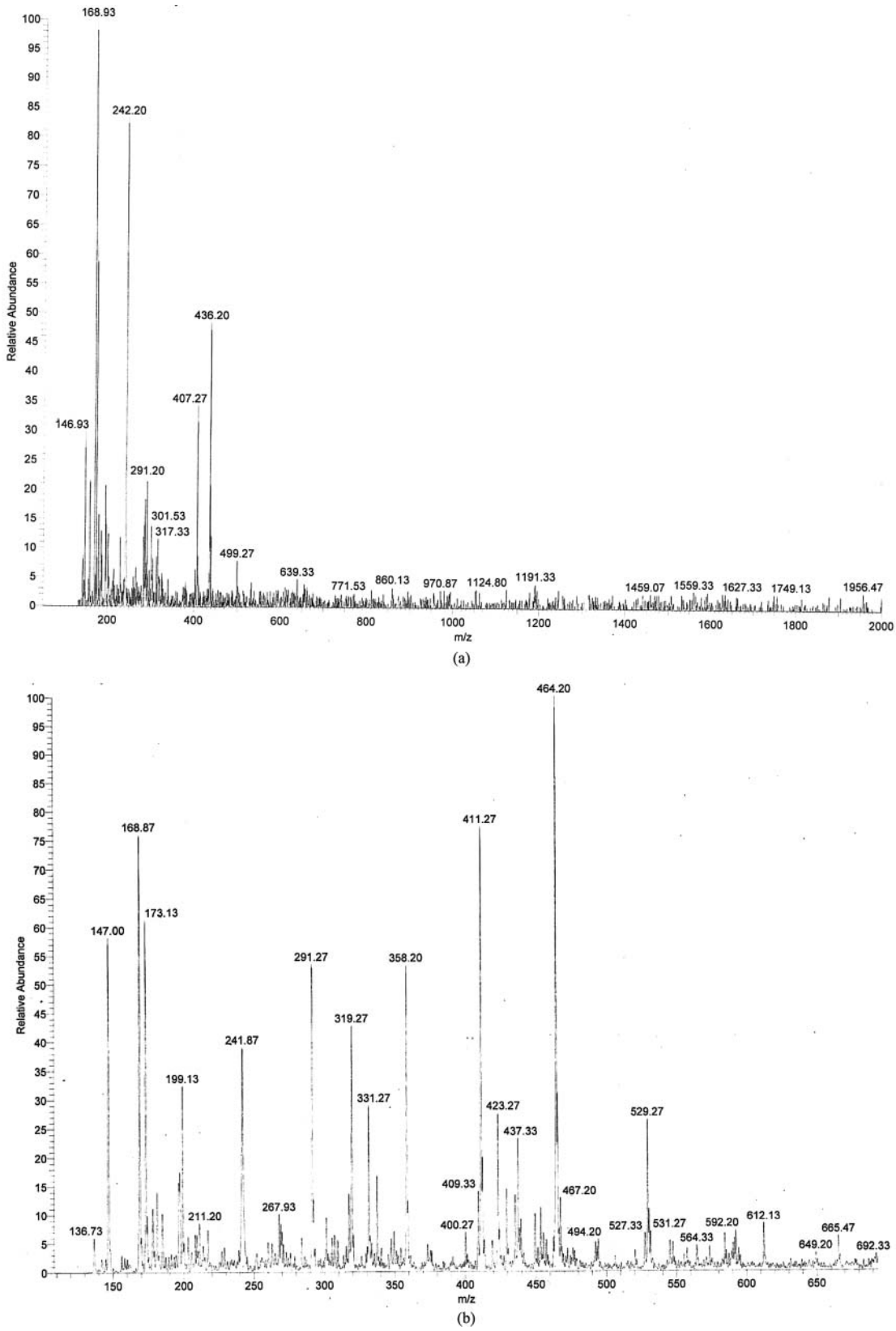
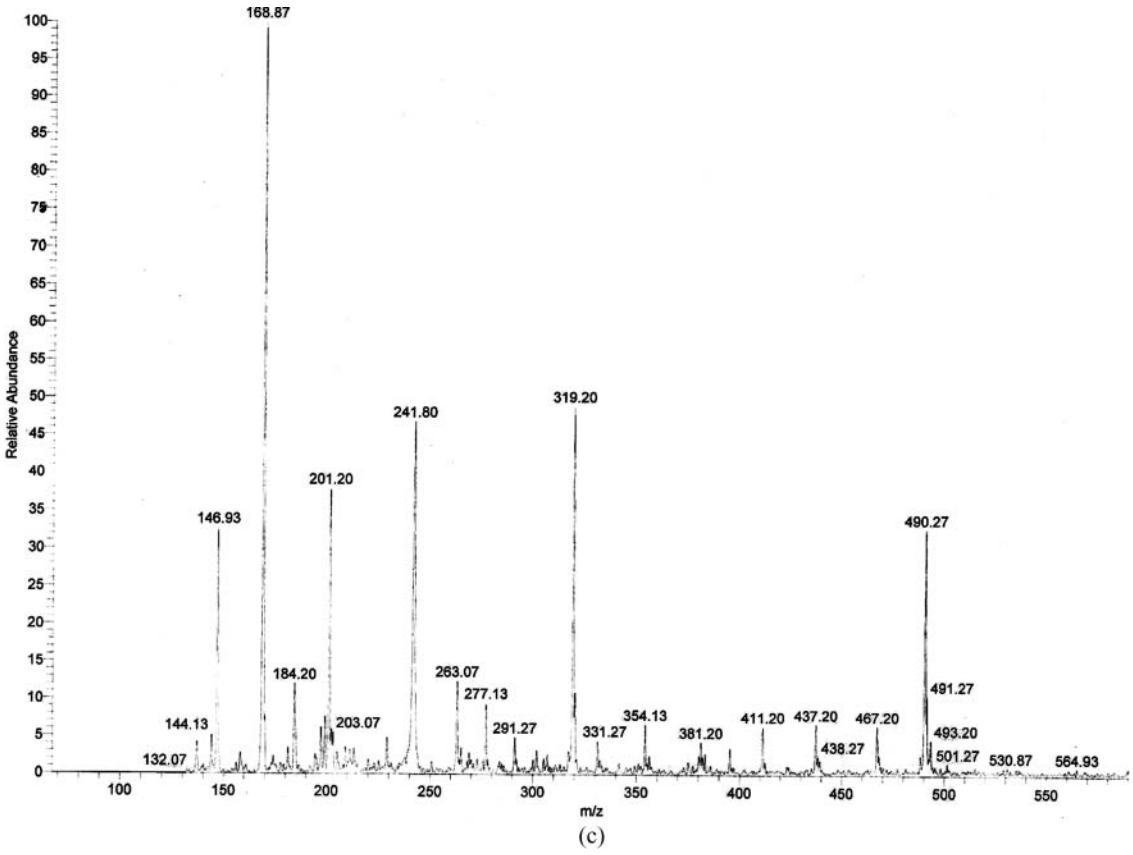


FIG. 1. (a) ESI mass spectrum of [Ni(II)L^3] complex *m/*z 436.20 [MH^-]; (b) ESI mass spectrum of [Ni(II)L^4] complex *m/z* 464.20 [MH^-]; (c) ESI mass spectrum of [Ni(II)L^5] complex *m/z* 490.27 [MH−] (continued on next page).



(c)

FIG. 1. (Continued.)

Electrochemistry of the Complexes

Reduction Process at Negative Potential

The electrochemical properties of the mononuclear complexes were studied by cyclic voltammetry in DMF solution containing TBAP as supporting electrolyte in the potential range to 0 to −1.200 V (Figure 2). The electrochemical data of nickel(II) complexes are given in Table 3. Generally the electrochemical properties of the complexes depend on a number of factors, such as chelate ring/size, axial ligation, degree and distribution of unsaturation, and substitution pattern in the chelate ring. Each voltammogram shows a one-electron irreversible reduction wave at a negative potential in the range –0.400 V to –1.100 V. The controlled potential electrolysis carried out at 100 mV more negative than the reduction wave conveys the consumption of one electron per molecule. It is very interesting to compare the electrochemical behavior of [Ni(II)L] complexes. The reduction potential shifts toward the anodic direction for the complexes [Ni(II)L^1] to [Ni(II)L^5] from –0.910 V to –0.650 V, as the number of methylene groups increases.[66,67] This shows that as the number of methylene groups between the imine nitrogen (chain length) increases, the entire acyclic ring becomes more flexible, which causes a distortion of the geometry of the

TABLE 2
Characteristic IR bands (cm^{-1}) of metal complexes and UV-Vis data of the prepared complexes

Complexes	ν(C = N) (cm^{-1})	ν(N-H) (cm^{-1})	ν(M-N) (cm^{-1})	ν(M-O) (cm^{-1})	λmax (nm) (ε ($M^{-1}cm^{-1}$) in DMF
[Ni(II)L^1]	1624 s	3375 s	616 s	436 s	541 (251), 320 (17,843)
[Ni(II)L^2]	1635 s	—	623 s	421 s	573 (191), 339 (17,230)
[Ni(II)L^3]	1629 s	3359 s	609 s	431 s	631 (178), 351 (17,020)
[Ni(II)L^4]	1632 s	3370 m	611 s	459 s	650 (148), 390 (16,710)
[Ni(II)L^5]	1621 s	—	605 s	440 s	725 (129), 410 (16,430)

S = strong, w = weak, m = medium.

TABLE 3
Electrochemical data for the complexes' reduction (at cathodic potential), oxidation (at anodic potential), and hydrolysis of 4-nitrophenylphosphate data for the complexes

Complexes	Reduction (at cathodic) (V)	Oxidation (at anodic) (V)	Rate constant (k) $\times 10^{-3}$ min^{-1} NPP
$[Ni(II)L^1]$	–0.910	0.870	2.688
$[Ni(II)L^2]$	–0.810	0.920	4.516
$[Ni(II)L^3]$	–0.750	0.950	5.822
$[Ni(II)L^4]$	–0.700	0.970	6.888
$[Ni(II)L^5]$	–0.650	1.000	8.533

Measured by CV at 50 mV s^{-1} scan rate. E vs. Ag/AgCl conditions: GC working electrode and Ag/AgCl reference electrodes; supporting electrolyte TBAP; concentration of complex 1×10^{-3} *M*, concentration of TBAP 1×10^{-1} *M*. Measured spectrophotometrically in DMF. Concentration of the complexes: 1×10^{-3} *M*. Concentration of 4-nitrophenylphosphate: 1×10^{-1} *M*.

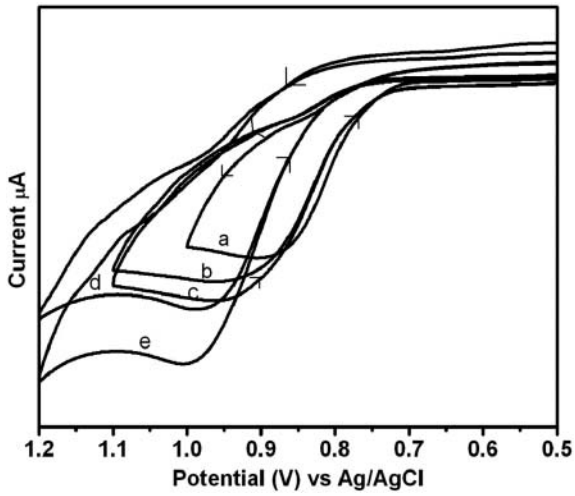


FIG. 3. Voltammogram of mononuclear nickel(II) complexes: (a) $[Ni(II)L^1]$,(b) $[Ni(II)L^2]$, (c) $[Ni(II)L^3]$, (d) $[Ni(II)L^4]$, and (e) $[Ni(II)L^5]$ (oxidation process).

nickel(II) complexes and makes the system more flexible, which stabilizes the low-valent Ni(I).

Oxidation Process at Positive Potential

The oxidation potential shifts toward the cathodic direction for the complexes $[Ni(II)L^1]$ to $[Ni(II)L^5]$ from 0.870 V to 1.000 V as the number of methylene groups is increased (Figure 3). This is because as the ring size increases the flexibility the planarity of the complexes decreases, and the electrochemical oxidation process occurs with difficulty. The electrochemical data are given in Table 3.

Kinetic Studies of Hydrolysis of 4-Nitrophenylphosphate

The catalytic activity of the nickel(II) complexes on the hydrolysis of 4-nitrophenylphosphate was determined spectrophotometrically by monitoring the increase in the characteristic absorbance of the 4-nitrophenolate anion at 420 nm over time in dimethylformamide at 25°C. For this purpose, 10^{-3} mol dm^{-3} solutions of complexes in dimethylformamide were treated with 100 equivalents of 4-nitrophenyl phosphate in the presence of

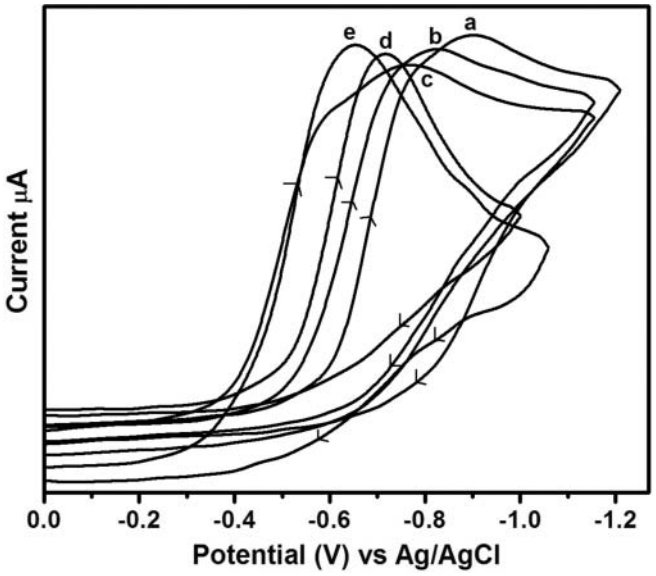


FIG. 2. Voltammogram of mononuclear nickel(II) complexes: (a) $[Ni(II)L^1]$, (b) $Ni(II)L^2]$, (c) $[Ni(II)L^3]$, (d) $[Ni(II)L^4]$, and (e) $[Ni(II)L^5]$ (reduction process).

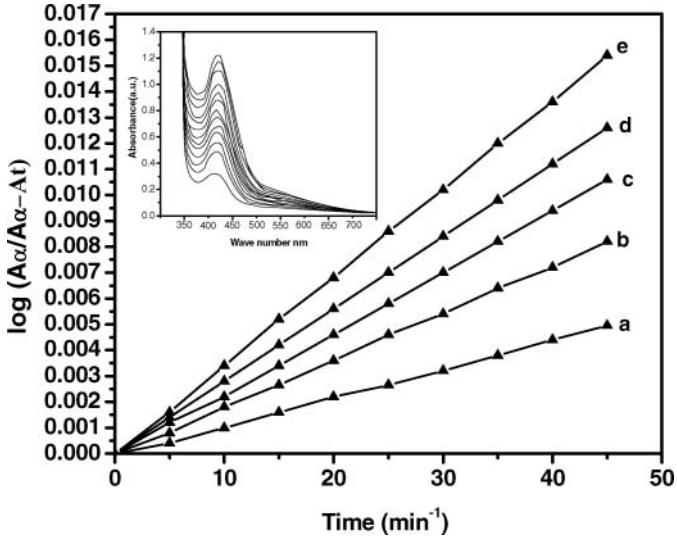


FIG. 4. Catalysis of 4-nitrophenylphosphate by the nickel(II) complexes: (a) $[Ni(II)L^1]$, (b) $[Ni(II)L^2]$, (c) $[Ni(II)L^3]$, (d) $[Ni(II)L^4]$, and (e) $[Ni(II)L^5]$. The inset is the time-dependent growth of *p*-nitrophenolate chromophore in the presence of $[Ni(II)L^5]$.

TABLE 4
Antibacterial activity data of nickel(II) complexes

	Zone of inhibition (mm)					
	Bacillus subtilis			*Staphylococcus aureus*		
Compound	10 mg	20 mg	30 mg	10 mg	20 mg	30 mg
$[Ni(II)L^1]$	24.0 ± 0.80	29.0 ± 1.0	30.0 ± 1.0	14.0 ± 0.80	24.0 ± 1.38	33.0 ± 1.0
$[Ni(II)L^2]$	29.0 ± 0.69	32.0 ± 1.0	33.0 ± 1.0	12.0 ± 0.69	22.0 ± 1.26	31.0 ± 1.0
$[Ni(II)L^3]$	20.0 ± 1.16	25.0 ± 1.0	26.0 ± 1.0	—	14.0 ± 1.80	17.0 ± 1.0
$[Ni(II)L^4]$	21.0 ± 1.20	22.0 ± 1.0	25.0 ± 1.0	—	14.0 ± 0.80	15.0 ± 1.0
$[Ni(II)L^5]$	—	—	13.0 ± 1.0	—	—	—
Std-1		43.0			38.0	

Std-1 = Azithromycin (15 mg/mL).

air. The course of the reaction was followed at 420 nm for nearly 45 min at regular time intervals. The slope was determined by the method of initial rates by monitoring the growth of the 420 nm band of the product 4-nitrophenolate anion. A linear relationship for all the complexes shows a first-order dependence on the complex concentration for the systems. Plots of $\log[A\alpha/(A\alpha - At)]$ versus time for hydrolysis of 4-nitrophenylphosphate activity of the complexes are obtained and shown in Figure 4. The inset in Figure 4 shows the time dependent growth of p-nitrophenolate chromophore in the presence of $[Ni(II)L^5]$. The observed initial rate constant values for all the nickel(II) complexes are given in Table 3. The catalytic activities of the nickel(II) complexes are founded to increase as the chain length increases due to the flexibility resulting from the distraction of the coordination sphere; i.e., increasing in the chain length enhances the rate constant of hydrolysis fairly well by producing distortion in the geometry around the metal ion that enhances the accessibility of the metal ion for the bonding of phosphate and OH group.[68–70] The rate constant value for the mononuclear nickel(II) complex $[Ni(II)L^5]$ is higher (8.533×10^{-3} min^{-1}) than that of the complex $[Ni(II)L^4]$ (6.888×10^{-3} min^{-1}), which in turn is higher than the nickel(II) complex $[Ni(II)L^1]$ (2.688×10^{-3} min^{-1}).

Antimicrobial Activity

Test Organisms

The axenic cultures *Bacillus subtilis* (MTCC 441), *Staphylococcus aureus* (MTCC 96), *Pseudomonas aeruginosa* (MTCC 424), *K. pnemonia* (MTCC), and *Candida albicans* (MTCC 227) were obtained from Microbial Type Culture Collection (MTCC), Chandigarh, India.

Muller Hinton agar (MHA)

Commercially available Muller Hinton agar (MHA) and sabouraud dextrose agar (SDA) purchased from Himedia Pvt. Ltd, Mumbai, India were used in this study. Agar was suspended in 1600 mL of distilled water in a 2-L flask, stirred, boiled to dissolve, and then autoclaved at 15 lb and at 121°C for 15 min. The pH range was maintained between 7.0 and 7.5. Incubation was maintained at 37°C for 24 h.

Nutrient agar (NA) plates were seeded separately with active growth of 10^5 test organisms such as *B. subtilis*, *S. aureus*, *K. pneumonia*, *P. aeruginosa,* or *C. albicans*, distributed by a sterile cotton swab on the surface of the MHA medium and left for 5 min in a laminar airflow cabinet to dry. Yeast was grown on SDA medium for antimicrobial activity. After drying, a well was created by a cork borer (9 mm) and 10, 20, and 30 mg/well was separately transferred to the well and left for 30 min at 5°C until the diffusion of compounds was completed. A well received a similar volume of 0.4% DMSO, which served as control.[71] The plates were incubated for 24 h at 37°C. The development of an inhibition zone around the well was measured and recorded.

Results

The antibacterial activity of the complexes $[Ni(II)L^1]$ to $[Ni(II)L^5]$ against human bacterial and yeast pathogens was determined by agar diffusion method with azithromycin as reference control and was represented in the Table 4. For the antibacterial activity against *S. aureus* the zone of inhibition observed for the compound $[Ni(II)L^1]$ was found to be maximum, followed by $[Ni(II)L^2]$, $[Ni(II)L^3]$, and $[Ni(II)L^4]$. Zone of inhibition was absent in $[Ni(II)L^5]$. For the antibacterial activity against *B. subtilis* the zone of inhibition observed for the compound $[Ni(II)L^2]$ is found to be maximum, followed by $[Ni(II)L^1]$, $[Ni(II)L^4]$, $[Ni(II)L^3]$, and $[Ni(II)L^5]$. $[Ni(II)L^2]$ and $[Ni(II)L^1]$ showed similar antibacterial activity with a zone of inhibition 33 ± 1.0 mm at 30 mg concentration in both *B. subtilis* and *S. aureus*. $[Ni(II)L^5]$ showed less antibacterial activity against *B. subtilis* and had no activity against *S. aureus*. The nickel complexes showed no antibacterial activity against *P. aeruginosa, K. pnemonia*, and *Candida albicans* even at 30 mg/mL concentration. The results show that all derivative compounds were able to inhibit gram-positive bacterial organisms but there was no zone of inhibition in gram-negative bacterial and yeast organisms. Therefore, the inhibition mode of these

compound derivatives was cell wall dependent, which might be the structural–activity relationship (SAR) correlation for inhibition in gram-positive organisms. Hence, the results of these compounds were promising for gram-positive antibacterial therapeutic agents.

CONCLUSIONS

In conclusion, five Schiff-base nickel(II) complexes have been synthesized and their coordination chemistry and antibacterial activity have been investigated. The electronic spectra of [Ni(II)L] complexes indicates square planar geometry, and there is a red-shift due to the increase in the chain length. Cyclic voltammograms exhibit a one-electron quasi-reversible process. The reduction potential shifts to more negative potential on increasing chain length and oxidation potential shifts to more positive potential on increasing chain length. All the [Ni(II)L] complexes show good catalytic activity on increasing the chain length. Increase in the chain length causes a greater distortion of the geometry of the complexes. This flexibility in the geometry may favor the observed higher rate of the reaction. The complexes showed remarkable activity against the two organisms tested. [Ni(II)L^1] and [Ni(II)L^2] have the highest activity against *Bacillus subtilis* and *Staphylococcus aureus,* and all derivative compounds were able to inhibit gram-positive bacterial organisms. All these studies of the complexes agree well with the established trend.

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