

Synthesis, Characterization and Antibacterial Evaluation of Some New Nickel(II) Complexes of a Tetraazamacrocycle

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Abstract

Condensation of 1,2-diaminopropane with acetone in the presence of quantitative amount of perchloric acid, yielded a 14-membered octamethyl tetraazamacrocyclic dihydroperchlorate salt, $\text{Me}_8[14]\text{diene} \cdot 2\text{HClO}_4$ ($\text{L} \cdot 2\text{HClO}_4$), which on extraction with chloroform at pH above 12 produced free ligand, L. The reaction between nickel(II) nitrate hexahydrate and the free ligand L resulted in a five coordinated square pyramidal light violet complex $[\text{NiL}(\text{NO}_3)](\text{NO}_3)$. Moreover some substituted nickel(II) salts, $\text{Ni}(\text{NCS})_2$, NiCl_2 , NiBr_2 , NiI_2 and $\text{Ni}(\text{NO}_2)_2$ prepared in solution (with a possibility of existence of negligible amount of NO_3^- ion) by the interaction of nickel(II) nitrate hexahydrate with KX ($\text{X}=\text{SCN}$, Cl , Br or I) and NaNO_2 respectively on reactions with the concerned ligand L furnished orange yellow $[\text{NiL}(\text{SCN})_2]$ and light pink $[\text{NiL}(\text{NCS})](\text{SCN})$, light purple $[\text{NiLCl}]\text{Cl}$, brownish $[\text{NiLBr}]_2$ and light purple $[\text{NiLBr}]\text{Br}$, light purple $[\text{NiLI}]\text{I}$ and light pink $[\text{NiL}(\text{NO}_2)](\text{NO}_3)$ respectively. Among them, $[\text{NiL}(\text{NCS})](\text{SCN})$, $[\text{NiLCl}]\text{Cl}$, $[\text{NiLBr}]\text{Br}$, $[\text{NiLI}]\text{I}$ and $[\text{NiL}(\text{NO}_2)](\text{NO}_3)$ were analysed as five coordinated square pyramidal and $[\text{NiL}(\text{SCN})_2]$ and $[\text{NiLBr}]_2$ as four coordinated square planar in geometry. All these complexes have been characterized on the basis of analytical, spectroscopic, conductometric and magnetochemical data. The antimicrobial activities of the ligand and its new nickel(II) complexes have been evaluated against some selected gram positive and gram negative bacteria.

Keywords: Tetraazamacrocyclic Ligand; Nickel(II) Complexes; Spectral Analysis; Antibacterial Evaluation

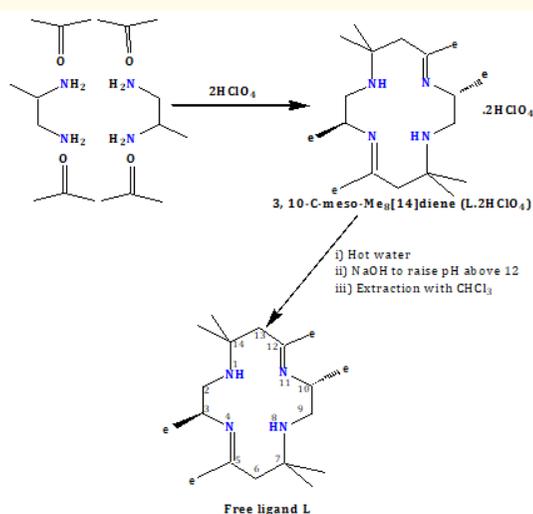
Introduction

The structural, thermodynamic and kinetic studies of polyazamacrocyclic ligands and their complexes have drawn a great attention due to their significant implication in analytical, biological and other applications [1-10] in the field of coordination chemistry. However, there is a similarity in structure and biomedical applications of these complexes with some natural macrocycles such as erythromycin A, vancomycin, amphotericin B etc. which are important in the area of medicinal chemistry [2]. The interest of exploring the macrocyclic structures and macrocyclization reaction is due to their biological activities including antiviral, anticarcinogenic [3], antifertility [4], antibacterial and antifungal [5] activities. The biological analysis of these compounds also give a strong evidence about their anticancer [6], antitumor [7] anti-inflammatory

[8] antioxidant [9] and anti-HIV activities [10]. Metal like nickel, copper, cobalt and manganese have high ability for coordination because of their smaller size and higher nuclear charge [11].

An exhaustive number of nickel(II) complexes with different macrocycles are available in literature [12-19]. In our previous study, metal complexes of 3,10-C-*meso*- $\text{Me}_8[14]\text{diene}$ (L) (Scheme 1) and its reduced isomeric anes (L_A , L_B and L_C) [20-23] and few N-pendent derivative ligands of the isomeric ligands, $\text{Me}_8[14]\text{anes}$ [i.e. L_B and L_C] and their metal complexes have been reported [24-25]. Moreover one study [23] on analogous zinc(II) complexes reveals that the square pyramidal zinc(II) complex can undergo subsequent axial addition and axial substitution reactions. As per previous reports [26,27], our group was successful in preparing

an octahedral diperchlorotocopper(II) complex, $[\text{CuL}(\text{ClO}_4)_2]$ of $\text{Me}_8[14]$ diene and its axial substitution products and the structure of mother complex, $[\text{CuL}(\text{ClO}_4)_2]$ was confirmed by X-ray crystallography [27]. So it was interesting to see whether four or five coordinated complexes of free $\text{Me}_8[14]$ diene ligand (L) could be prepared using nickel(II) salt or substituted nickel(II) salt. Thus an effort to prepare some new nickel(II) complexes of free ligand L [26] was successful. This study reveals that the concerned free ligand L undergoes complexation with nickel(II) nitrate hexahydrate to result a five-coordinated square pyramidal complex $[\text{NiL}(\text{NO}_3)](\text{NO}_3)$ with sp^3d hybridization. It is also noticed that attempts to produce some nickel(II) complexes of the ligand L with substituted nickel(II) salts (produced from nickel(II) nitrate hexahydrate) were successful. Thus interaction of the ligand L with metal salts like $\text{Ni}(\text{SCN})_2$, NiCl_2 , NiBr_2 , NiI_2 and $\text{Ni}(\text{NO}_2)_2$ [produced by the reactions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with KX ($\text{X}=\text{SCN}$, Cl , Br or I) and NaNO_2 respectively] resulted in square planar $[\text{NiL}(\text{SCN})_2]$ and square pyramidal $[\text{NiL}(\text{NCS})](\text{SCN})$, square pyramidal $[\text{NiLCl}]\text{Cl}$, square planar $[\text{NiLBr}_2]$ and square pyramidal $[\text{NiLBr}]\text{Br}$, square pyramidal $[\text{NiLI}]\text{I}$ and $[\text{NiL}(\text{NO}_2)](\text{NO}_3)$ respectively. The free ligand L and its nickel(II) complexes have been characterized on the basis of analytical, spectroscopic, conductometric and magnetochemical data. The antibacterial activities of the ligand and its new nickel(II) complexes have been investigated against both gram positive and gram negative bacteria. Thus herein we report, the synthesis, characterization and antibacterial evaluation of the concerned ligand and its new nickel(II) complexes.



Scheme 1: Preparation of free ligand 3,10-C-meso-Me₈[14]diene (L).

Materials and Methods

All chemicals were of analytical grade (Sigma Aldrich) or equivalent grades and were used without further purification. The solvents were of reagent grade and dried according to standard procedure. Equipment used were of standard ones. Microanalysis of C, H and N of the complexes has been carried out on a C, H, N analyzer at the Department of Chemistry, Friedrich Schiller University, Jena, Germany. IR spectra were recorded on a Shimadzu IR 20 spectrophotometer as KBr disks. UV-visible spectra were recorded on a Shimadzu UV-visible spectrophotometer in DMSO, Acetonitrile and H_2O . Conductance measurements were carried out on a conductivity bridge Hanna instrument HI-8820 in pure DMSO, Acetonitrile and H_2O . Magnetic measurements were performed on Gouy Balance which was calibrated using $\text{Hg}[\text{Co}(\text{NCS})_4]$. $^1\text{H-NMR}$ spectra were recorded in DMSO with a 400 MHz Bruker DPX-400 spectrometer using TMS as internal standard at the BCSIR Laboratory, Dhaka, Bangladesh.

Syntheses

Free ligand, L

Synthesis of free ligand $\text{Me}_8[14]$ diene. 2HClO_4 (L) (Scheme-1) was carried out as procedure adopted in our earlier studies [26].

Nickel(II) complexes of free ligand L

Preparation of nickel(II) complex $[\text{NiL}(\text{NO}_3)](\text{NO}_3)$ by the direct reaction of L with nickel(II) nitrate hexahydrate

0.291 g (1.0 mmol) nickel(II) nitrate hexahydrate was dissolved in 30 mL of methanol and the solution was heated until concentrated to 5 mL and cooled. The precipitate was filtered off. 30 mL methanolic solution of 0.308 g (1.0 mmol) L was added to the filtrate in a round bottom flask. The solution was refluxed for 4 hours. On evaporation of the solvent, solid material was obtained which was extracted with chloroform leaving behind an insoluble solid. On evaporation of the chloroform extract a small amount of greenish product was obtained which was very negligible in amount to be characterized. However the insoluble part in chloroform was treated with ethanol and the ethanolic solution was dried. The light violet product was resulted which was stored in a vacuum desiccator.

$[\text{NiL}(\text{NO}_3)](\text{NO}_3)$ ($\text{C}_{18}\text{H}_{36}\text{N}_6\text{O}_6\text{Ni}$): Color: Light violet. Decomposition point: 194°C . Anal. Calcd. (%): C, 44.01; H, 7.39; N, 17.10. Found (%): C, 44.07; H, 7.35; N, 17.07. IR (KBr disc, cm^{-1}): $\nu_{\text{N-H}}$ 3190w; $\nu_{\text{C-H}}$ 2964s; ν_{CH_3} 1383s; $\nu_{\text{C-C}}$ 1150s; $\nu_{\text{N-Ni}}$ 538w; ν_{NO_3} 831s(ν_2), 1383vs(ν_3), 668s(ν_4), 1325w, 1440w. Conductance (ohm⁻¹

$1\text{cm}^2\text{mol}^{-1}$): in DMSO 114; in Acetonitrile 250; in H_2O 217. UV-vis [λ_{max} in nm (ϵ_{max} in $\text{M}^{-1}\text{cm}^{-1}$): in DMSO 795(15), 570(32), 356(25), 285(4000); in Acetonitrile 790(17), 555(13), 342(30), 275(2801); in H_2O 796(28), 566(11), 465(92), 356(24), 280(3800). Magnetic moment μ_{eff} (BM): 3.006.

Preparation of nickel(II) complexes by the reactions of L with substituted nickel(II) salts

[NiL](SCN)₂ and [NiL(NCS)](SCN)

0.291 g (1.0 mmol) of nickel(II) nitrate hexahydrate and 0.194 g (2.0 mmol) of potassium thiocyanate were dissolved in 30 mL of methanol and the solution was heated until concentrated to 5 mL and cooled. The precipitate was filtered off. 30 mL methanolic solution of 0.308 g (1.0 mmol) L was added to the filtrate in a round bottom flask. The solution was refluxed for 2 h. On evaporation of the solvent, solid material was obtained which was extracted with chloroform leaving behind an insoluble solid. On evaporation of the chloroform extract, yellow product of [NiL](SCN)₂ was obtained which was no more soluble in chloroform. On the other hand the insoluble part in chloroform was treated with ethanol and the ethanolic solution was dried. The light pink product of [NiL(NCS)](SCN) was resulted which was stored in vacuum desiccator.

[NiL](SCN)₂ (C₂₀H₃₆N₆S₂Ni): Color: Yellow. Decomposition point: 190°C. Anal. Calcd. (%): C, 49.69; H, 7.51; N, 17.39. Found (%): C, 49.65; H, 7.57; N, 17.34. IR (KBr disc, cm^{-1}): $\nu_{\text{N-H}}$, 3064s; $\nu_{\text{C-H}}$, 2970s; ν_{CH_3} , 1383s; $\nu_{\text{C-C}}$, 1145s; $\nu_{\text{N-Ni}}$, 585s; ν_{NCS} , 2035vs. ¹H NMR (δ , ppm): Geminal dimethyl and Methyl proton on chiral carbon, 0.884 (ov, 12H, e), 1.282 (s, 6H, a); Methyl protons on sp^2 carbons, 1.602 (s, 6H, e); CH₂ and CH protons, 2.000, 2.250, 2.600, 4.000, 4.900; NH proton, 7.220. Conductance ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$): in DMSO 95; in Acetonitrile 214; in H_2O , 191. UV-vis [λ_{max} in nm (ϵ_{max} in $\text{M}^{-1}\text{cm}^{-1}$): in DMSO 435(109), 565(64), 615(81); in Acetonitrile 445(74); in H_2O , 436(81); 436(81), 340(76), 287(3966). Magnetic moment μ_{eff} (BM): Diamagnetic.

[NiL(NCS)](SCN) (C₂₀H₃₆N₆S₂Ni): Color: Light pink. Melting point: 188°C. Anal. Calcd. (%): C, 49.69; H, 7.51; N, 17.39. Found (%): C, 49.62; H, 7.59; N, 17.31. IR (KBr disc, cm^{-1}): $\nu_{\text{N-H}}$, 3152w; $\nu_{\text{C-H}}$, 2961s; ν_{CH_3} , 1383vs; $\nu_{\text{C-C}}$, 1150s; $\nu_{\text{N-Ni}}$, 538s; ν_{NCS} , 2051vs; ν_{CS} , 835s; δ_{NCS} , 482s. Conductance, ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$): in DMSO 104; in H_2O , 241. UV-vis [λ_{max} in nm (ϵ_{max} in $\text{M}^{-1}\text{cm}^{-1}$): in DMSO 798(15), 545(27), 340(25); in H_2O 796(11), 550(15), 468(95), 340(35). Magnetic moment μ_{eff} (B.M.): 3.006.

[NiL(NO₂)](NO₃)

The complex was prepared by following the above mentioned procedure adopted for preparation nickel(II) thiocyanate complexes by adding sodium nitrite instead of KSCN. But in this preparation, a small amount of chloroform soluble brownish product was obtained which was very negligible in amount to be characterized. However the other insoluble part in chloroform was treated with ethanol and the ethanolic solution was dried. The light pink product was resulted which was stored in a vacuum desiccator.

[NiL(NO₂)](NO₃) (C₁₈H₃₆N₆O₅Ni): Color: Light pink. Decomposition point: 188-190°C. Melting point: 204°C, Anal. Calcd. (%): C, 45.49; H, 7.64; N, 11.79. Found (%): C, 45.51; H, 7.62; N, 11.74. IR (KBr disc, cm^{-1}): $\nu_{\text{N-H}}$, 3166w; $\nu_{\text{C-H}}$, 2962m; ν_{CH_3} , 1383s; $\nu_{\text{C-C}}$, 1157s; $\nu_{\text{N-Ni}}$, 543w; $\nu_{\text{asym}(\text{NO}_2)}$, 1459 w; $\nu_{\text{sym}(\text{NO}_2)}$, 1320w, δ_{NO_2} , 650w, ν_{NO_3} , 1383s. Conductance ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$): in DMSO 96; in H_2O 231. UV-vis [λ_{max} in nm (ϵ_{max} in $\text{M}^{-1}\text{cm}^{-1}$): in DMSO 798(22), 543(35), 371(54); in H_2O 794(4), 553(6), 356(43). Magnetic moment μ_{eff} (B.M.): 3.035.

[NiLX_m]_n (X=Cl, Br or I, m=0 or 1 and n=2 or 1)

These complexes were also prepared by the procedure adopted for nickel(II) thiocyanate complexes by adding KX in the proper ratio. On evaporation of the solvent, solid material was obtained which was extracted with chloroform leaving behind an insoluble solid. On evaporation of the chloroform extract a small amount of brownish product was obtained which was very negligible in amount for chloride and iodide complex to be characterized but it was sufficient for bromide complex. However the extracted brownish [NiL]Br₂ product with CHCl₃ was no more soluble in CHCl₃. On the other hand the insoluble part in chloroform was treated with ethanol and the ethanolic solution on drying resulted in the light purple product in all cases which were stored in a vacuum desiccator.

[NiLCl]Cl (C₁₈H₃₆N₄Cl₂Ni): Color: Light purple. Decomposition point: 190°C. Anal. Calcd. (%): C, 49.35; H, 8.28; N, 12.79. Found (%): C, 49.29; H, 8.31; N, 12.71. IR (KBr disc, cm^{-1}): $\nu_{\text{N-H}}$, 3167w; $\nu_{\text{C-H}}$, 2962w; ν_{CH_3} , 1383s; $\nu_{\text{C-C}}$, 1158s; $\nu_{\text{N-Ni}}$, 536w. Conductance ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$): in DMSO, 73; in H_2O , 256. UV vis [λ_{max} in nm (ϵ_{max}): in DMSO 797(5), 536(7), 348(11); in H_2O 794(9), 551(12), 485(102), 340(25). Magnetic moment μ_{eff} (BM): 3.073.

[NiL]Br₂ (C₁₈H₃₆N₄Br₂Ni): Color: Brownish. Decomposition point: 195°C. Anal. Calcd. (%): C, 41.02; H, 6.89; N, 10.63. Found

(%): C, 41.08; H, 6.83; N, 10.69. IR (KBr disc, cm^{-1}): $\nu_{\text{N-H}}$, 3140w; $\nu_{\text{C-H}}$, 2950w; ν_{CH_3} , 1383s; $\nu_{\text{C-C}}$, 1155s; $\nu_{\text{N-Ni}}$, 530w. Conductance ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$): in DMSO 75; in H_2O 208. UV vis [λ_{max} in nm (ϵ_{max})]: in DMSO 448(44); in H_2O 443(47). Magnetic moment μ_{eff} (BM): Diamagnetic. ^1H NMR (δ , ppm): Geminal dimethyl and Methyl proton on chiral carbon, 1.26 (s, 6H, e), 1.36 (s, 6H, a), 1.05 (d, 6H, e); Methyl protons on sp^2 carbons, 2.09 (s, 6H, e); CH_2 , CH and NH protons, 1.90 (s, 4H), 2.75 (m), 3.20 (m).

[NiLBr]Br ($\text{C}_{18}\text{H}_{36}\text{N}_4\text{Br}_2\text{Ni}$): Color: Light purple. Melting point: 197-201°C. Anal. Calcd. (%): C, 41.02; H, 6.89; N, 10.63. Found (%): C, 41.06; H, 6.87; N, 10.58. IR (KBr disc, cm^{-1}): $\nu_{\text{N-H}}$, 3159w; $\nu_{\text{C-H}}$, 2961w; ν_{CH_3} , 1383vs; $\nu_{\text{C-C}}$, 1156s; $\nu_{\text{N-Ni}}$, 534w. Conductance ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$): in DMSO, 90; in H_2O , 250. UV vis [λ_{max} in nm (ϵ_{max})]: in DMSO, 585(54), 675(81), 797(27), 541(18), 348(67); in H_2O 798(17), 550(29), 468(92), 348(77). Magnetic moment μ_{eff} (BM): 3.09.

[NiLI]I ($\text{C}_{18}\text{H}_{36}\text{N}_4\text{I}_2\text{Ni}$): Color: Light purple. Decomposition point: 224°C. Anal. Calcd. (%): C, 34.81; H, 5.84; N, 9.02. Found (%): C, 34.75; H, 5.81; N, 9.08. IR (KBr disc, cm^{-1}): $\nu_{\text{N-H}}$, 3138w; $\nu_{\text{C-H}}$, 2961s; ν_{CH_3} , 1383s; $\nu_{\text{C-C}}$, 1149s; $\nu_{\text{N-Ni}}$, 534s. Conductance ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$): in DMSO, 92; in H_2O 214; UV-vis [λ_{max} in nm (ϵ_{max} in $\text{M}^{-1}\text{cm}^{-1}$)]: in DMSO 795(37), 543(13), 340(78); in H_2O 798(12), 548(15), 475(97), 346(28). Magnetic moment μ_{eff} (B.M.): 3.023.

Antibacterial activities

Antibacterial activities of the ligand and its nickel(II) complexes were performed by the disc diffusion method against selected gram-positive and gram-negative bacteria. Solutions of known concentration (0.1%) of the test samples were made by dissolving the samples in definite volume of solvents. Dried and sterilized filter paper discs (4 mm in diameter) are then impregnated with known amount of test substances using micropipette and these were then allowed to dry. Discs containing the test material were placed on nutrient agar medium uniformly seeded with the test microorganism. A control plate was also maintained in each case with DMSO. These plates were then kept at low temperature (4°C) for 2-4 h to allow maximum diffusion. During this time dried discs absorbed water from the surrounding media and then the test materials were dissolved and diffused out of the media. The plates were then incubated at (35±2)°C for the growth of test organisms and were observed at 48 hours intervals. The activity was expressed in terms of zone of inhibition in mm. The activities of non-coordinated metal salt $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, a commercial standard (Ampiciline) were also

tested against all bacteria accordingly for the comparison. Tests were repeated thrice for statistical analysis.

Results and Discussion

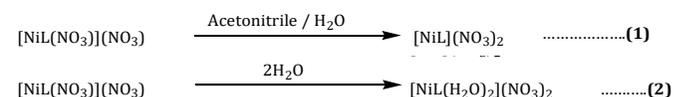
Ligands

The free ligand L was prepared (Scheme 1) and characterized by the procedure adopted in our previous study [26].

Characterization

[NiL(NO₃)](NO₃)

Interaction between the nickel(II) nitrate hexahydrate and free ligand L in methanol produced five coordinated square pyramidal light violet product, [NiL(NO₃)](NO₃). The infrared spectrum of this complex (Table-2) displays $\nu_{\text{N-H}}$, $\nu_{\text{C-C}}$, $\nu_{\text{C-H}}$, $\nu_{\text{N-N}}$ and ν_{CH_3} bands at 3190 cm^{-1} , 1150 cm^{-1} , 2964 cm^{-1} , 538 cm^{-1} and 1383 cm^{-1} respectively. The complex [NiL(NO₃)](NO₃) exhibits bands at three frequencies assigned to vibrational modes $\nu_2=831$ cm^{-1} , $\nu_3=1383$ cm^{-1} and $\nu_4=668$ cm^{-1} for ν_{NO_3} [26]. Moreover this complex displays bands at 1325 cm^{-1} and 1440 cm^{-1} showing separation of bands by 115 cm^{-1} indicating unidentate mode of coordination [28]. Further appearance of a band at 1383 cm^{-1} is due to ionic NO_3^- group overlapped with the band for ν_{CH_3} . The complex [NiL(NO₃)](NO₃) reveals molar conductivity value 114 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in DMSO (in this solvent it retains its color intact) corresponding to 1:1 electrolyte as expected for formula assigned. However the molar conductivity values of 250 and 217 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ of the complex in acetonitrile and H_2O corresponding to 1:2 electrolyte [29] can be accounted for expulsion of an anion i.e. (NO_3^-) from coordination sphere to form square planar complex [NiL(NO₃)₂] as expressed by the expression-1 or for the conversion of square pyramidal to octahedral aqua complex in H_2O as shown by the expression-2.



The magnetic moment value of 3.006 BM of the complex [NiL(NO₃)](NO₃) demonstrates that the complex is paramagnetic corresponding to two unpaired electrons as expected for square pyramidal complex with sp^3d hybridization [30]. Electronic spectrum of [NiL(NO₃)](NO₃) reveals bands at 342-356 nm, 555-570 nm, 790-796 nm in concerned solvents assignable to the $^3\text{B}_{1g} \rightarrow ^3\text{E}_g$ [$\text{T}_{1g}(\text{P})$], $^1\text{B}_{2g} \rightarrow ^1\text{B}_{1g}$, $^3\text{B}_{1g} \rightarrow ^3\text{B}_{2g}$ [$\text{T}_{2g}(\text{F})$] transitions respectively, which are characteristic bands expected for a high-spin d^8 nickel(II) ion

[31]. This study supports the square pyramidal geometry of the complex $[\text{NiL}(\text{NO}_3)](\text{NO}_3)$ having sp^3d hybridization. But the value 456 nm in H_2O supports the existence of square planar species too. However the bands at 275-285 nm for this complex can be accounted for charge transfer transitions. Since this is a paramagnetic complex and NMR spectra of paramagnetic complexes are less informative, so $^1\text{H-NMR}$ spectrum of this complex has not been measured. However the stereochemistry (axial-equatorial orientation) of this complex has been assigned as corresponding square pyramidal zinc(II) complex [32] and square planar nickel(II) complexes of this study. The similar assignment has been made for other paramagnetic square pyramidal complexes of this study. Thus based on these evidences, the structure-I can be assigned for $[\text{NiL}(\text{NO}_3)]$

Str.- I $[\text{NiL}(\text{NO}_3)](\text{NO}_3)$

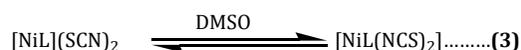
Figure a

(NO_3) complex.

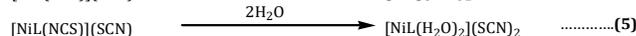
$[\text{NiL}(\text{SCN})_2]$ and $[\text{NiL}(\text{NCS})](\text{SCN})$

Reaction between $\text{Ni}(\text{NCS})_2$ (produced by the interaction of nickel(II) nitrate hexahydrate with potassium thiocyanate in methanol) and free ligand L afforded four coordinated square planar yellow complex, $[\text{NiL}(\text{SCN})_2]$ and five coordinated square pyramidal light pink complex $[\text{NiL}(\text{NCS})](\text{SCN})$ in methanol. The infrared spectra of $[\text{NiL}(\text{SCN})_2]$ and $[\text{NiL}(\text{NCS})](\text{SCN})$ display all characteristic bands due to $\nu_{\text{N-H}}$, $\nu_{\text{C-C}}$, $\nu_{\text{C-H}}$, $\nu_{\text{Ni-N}}$ and ν_{CH_3} stretching bands in the expected region. Further very strong band at 2035-2051 cm^{-1} implies that NCS^- is attached as ionic SCN^- or coordinated with nickel by Ni-N bond [33,34]. The present complex $[\text{NiL}(\text{NCS})](\text{SCN})$ displays a peak at 835 cm^{-1} which is due to ν_{CS} band responsible for N-bonded NCS^- group [33]. Further the appearance of band at 482 cm^{-1} for this complex can be accounted for δ_{NCS} for N-bonded isothiocyanato complex. However this band does not correspond to

ligand in this region and are therefore assigned for fully N-bonded thiocyanate group [28,30,33,36-37]. Therefore the complex can be identified as N-bonded isothiocyanato complex. The conductance values of $[\text{NiL}(\text{SCN})_2]$ are 214 and 191 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in acetonitrile and water (Table-3) respectively which demonstrate that this complex is 1:2 electrolyte i.e. two thiocyanate ions are out of coordination sphere as expected. It is to be noted that this complex retain its color in these solvents. Again the molar conductivity value of 95 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in DMSO solution of this complex corresponding to 1:1 electrolyte [29] can be assigned for equilibrium between square planar and octahedral geometry as shown in expression-3.



The complex $[\text{NiL}(\text{NCS})](\text{SCN})$ exhibits molar conductivity value 104 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in DMSO (in this solvent it retained its color intact) corresponding to 1:1 electrolyte as expected for formula assigned. However the molar conductivity value of 241 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ of the complex $[\text{NiL}(\text{NCS})](\text{SCN})$ in water corresponding to 1:2 electrolyte can be accounted for expulsion of an anion i.e. NCS^- from coordination sphere to form square planar complex $[\text{NiL}(\text{SCN})_2]$ as expressed by the expression-4 or for the conversion of square pyramidal to octahedral diaqua complex as shown by expression-5.

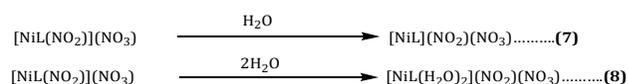


The magnetic moment value of $[\text{NiL}(\text{SCN})_2]$ indicates it's diamagnetic character whereas the magnetic moment value (3.006 B.M) for the complex $[\text{NiL}(\text{NCS})](\text{SCN})$ corresponds to two unpaired electrons as expected for paramagnetic square pyramidal complex. The electronic spectrum of square planar nickel(II) dithiocyanate complex $[\text{NiL}(\text{SCN})_2]$ displays d-d bands at 435 nm, 436 nm and 445 nm in DMSO, water and acetonitrile respectively can be assigned to the $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ transition for square planar nickel(II) complexes. But the values 565-615 nm in DMSO supports the equilibrium between octahedral and square planar species. However in case of $[\text{NiL}(\text{NCS})](\text{SCN})$, all characteristic bands in different solvents are observed expected for a high-spin d^8 nickel(II) ion [31]. This study supports the square pyramidal geometry of the complex $[\text{NiL}(\text{NCS})](\text{SCN})$ with sp^3d hybridization.

The $^1\text{H-NMR}$ spectrum of $[\text{NiL}(\text{SCN})_2]$ shows one overlapped

singlet with a doublet at 0.884 ppm and two singlets at 1.282 ppm and 1.602 ppm corresponding to 12H, 6H and 6H respectively. The overlapped signal can be accounted for a singlet corresponding to 6H for equatorial components of gem-dimethyl groups and a doublet arising out of six protons of methyl groups having equatorial orientation on chiral carbons. However the singlet at 1.282 ppm can be assigned to the gem dimethyl groups having axial orientation. The other singlet at 1.602 ppm corresponding to 6H can be accounted for protons of methyl groups on sp^2 carbons at C_5 and C_{12} positions. So an all equatorial arrangement of imine methyls and chiral methyls can be assigned for this complex. The other multiplets at 2.000 ppm, 2.250 ppm, 2.600 ppm, 4.000 ppm and 4.900 ppm can be attributed to the methine and methylene protons. However the signal at 7.220 ppm can be attributed to NH protons. Since $[NiL(NCS)](SCN)$ is a paramagnetic compound and 1H -NMR spectra of paramagnetic substances are less informative, so 1H -NMR spectrum of this complex has not been measured. Based on the discussed evidences, the following structures, II and III can be

This complex exhibits molar conductivity value $96 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in DMSO (in this solvent it retains its color intact) corresponding to 1:1 electrolyte [29] as expected for formula assigned. However the molar conductivity value of $231 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ of this complex in water corresponding to 1:2 electrolyte can be accounted for expulsion of an anion i.e. (NO_2^-) from coordination sphere to form square planar complex $[NiL(NO_2)(NO_3)]$ (expression-7) or to form an octahedral diaqua complex, $[NiL(H_2O)_2](NO_2)(NO_3)$ as expressed by the expression-8.



The magnetic moment value of 3.035BM of the complex is an indication that the complex $[NiL(NO_2)](NO_3)$ is paramagnetic corresponding to two unpaired electrons as expected for square pyramidal complex with sp^3d hybridization. The electronic spectrum of this complex in the visible region reveals all characteristic bands in different solvents as expected for a high-spin d^8 nickel(II) ion [31]. This assignment also supports the square pyramidal geom-

Figure b

assigned to $[NiL](SCN)_2$ and $[NiL(NCS)](SCN)$ respectively.

$[NiL(NO_2)](NO_3)$

Interaction between free ligand L and $Ni(NO_2)_2$ (produced by the reaction of nickel(II) nitrate hexahydrate with sodium nitrite) in methanol furnished a five coordinated square pyramidal light pink complex $[NiL(NO_2)](NO_3)$. Infrared spectrum of this complex shows ν_{N-H} , ν_{C-H} , ν_{C-C} and ν_{Ni-N} stretching bands at the expected regions. The band of ν_{CH_3} is overlapped with the band of NO_3^- group. Moreover the complex exhibits the $\nu_{asym(NO_2)}$ band at 1459 cm^{-1} , $\nu_{sym(NO_2)}$ hump at 1320 cm^{-1} and stretching δ_{NO_2} band at 650 cm^{-1} . Presence of ν_{Ni-N} band at 543 cm^{-1} and other bands in the proper region strongly support the complex to be N-bonded nitro complex.

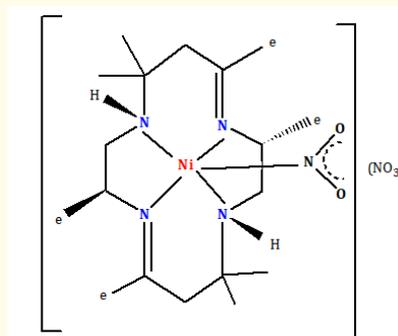

 Str.-IV $[NiL(NO_2)](NO_3)$

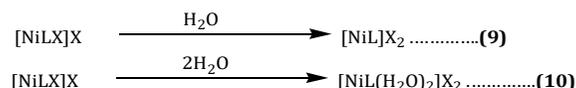
Figure c

etry of this complex having sp^3d hybridization. Thus the following structure-IV can be assigned to $[NiL(NO_2)](NO_3)$ complex.

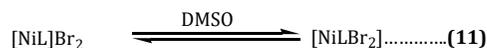
$[NiLX_m]X_n$ (Where X=Cl, Br or I, m= 0 or 1 and n = 2 or 1)

These halonickel(II) complexes were synthesized by the same procedure followed for nickel(II) thiocyanate complexes by adding KX in the proper ratio. The infrared spectra of these complexes exhibit all characteristic bands due to ν_{N-H} , ν_{C-C} , ν_{C-H} , ν_{Ni-N} and ν_{CH_3}

stretching bands in the proper positions. The band for Ni-X could not be detected as the IR spectrum has not been carried out below 400 cm^{-1} . All complexes showed expected molar conductivity values in DMSO (colour is retained as solid) corresponding to 1:1 electrolytes as expected for formula assigned. However the prospective values of these complexes in water corresponding to 1:2 electrolyte can be accounted for expulsion of an anion i.e. Cl⁻, Br⁻, I⁻ from coordination sphere to form square planar complex [NiL]X₂ (expression-9) or octahedral diaqua complex, [NiL(H₂O)₂]X₂ as expressed by the expression-10 [21].



But the conductance value of [NiL]Br₂ is $208\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in water indicates that this complex is 1:2 electrolyte i.e. two bromide ions are out of coordination sphere as expected. It is to be noted that this complex retains its colour in this solvent. Again the value of $75\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in DMSO solution corresponding to 1:1 electrolyte can be assigned for equilibrium between square planar and octahedral geometry as shown in expression-11.



The magnetic moment values 3.073 BM, 3.09 BM and 3.023 BM of the complexes [NiLCl]Cl, [NiLBr]Br and [NiLI]I respectively demonstrate that these complexes are paramagnetic corresponding to two unpaired electrons as expected for square pyramidal complex with sp³d hybridization. Whereas, the magnetochemical study of the complex [NiL]Br₂ corresponds to diamagnetic compound as expected for square planar orientation with dsp² hybridization. The electronic spectra of these paramagnetic complexes in the visible region reveal three absorption bands in the proper region in different solvents which are characteristic bands expected for a high-spin d⁸ nickel(II) ion [31]. This study supports the square pyramidal geometry of these complexes having sp³d hybridization. On the other hand the electronic spectrum of the complex, [NiL]Br₂ displays d-d bands at 448 nm and 443 nm in DMSO and water respectively which can be assigned to the ¹A_{1g} → ¹B_{1g} transition for square planar nickel(II) complexes. Moreover the values 585-797 nm in DMSO indicates the equilibrium between octahedral and square planar species.

The ¹H-NMR spectrum of this complex shows four sharp sin-

glets at 1.26 ppm, 1.36 ppm, 1.90 ppm and 2.09 ppm corresponding to 6H, 6H, 4H and 6H respectively. The singlets at 1.26 ppm and 1.36 ppm can be assigned to the dimethyl groups having equatorial and axial orientation respectively. The 3rd singlet at 1.90 ppm corresponding to 4H can be accounted for CH₂ protons at C6 and C13. The 4th downfield singlet at 2.09 ppm corresponding to 6H can be attributed to protons of methyl groups on sp² carbons at C3 and C10 position. The upfield doublet appearing at 1.05 ppm corresponding to 6H can be assigned to protons of methyl groups having equatorial orientation on chiral carbons. So an all equatorial arrangement of imine methyls and chiral methyls can be assigned for this complex, as like as other complexes of this study. The other multiplets 2.75 ppm, 3.20 ppm can be due to the methine, methy-

Figure d

lene and NH protons. Thus the following structures-V, VI, VII and VIII can be assigned for [NiLCl]Cl, [NiLBr]Br, [NiLI]I and [NiL]Br₂ respectively.

Antibacterial activities

Studies on antimicrobial activity of macrocyclic ligands and their different metal complexes against different bacteria are available in the literature [36-43]. But the antibacterial activity of the nickel(II) complexes of concerned free ligand L have not been studied so far. In this context antibacterial activity of concerned macrocyclic ligand and its nickel(II) complexes have been carried out against some important and selected gram positive and gram negative bacteria. As seen from the Table 1, the concerned free ligand did not show any activity but the concerned

nickel(II) complexes show different amount of activity against different bacteria. However, all the complexes except nickel(II) dithiocyanate (C-02) showed remarkable activity against *B. cereus* but monochloridonickel(II) chloride (C-05) was the most potent among them. On the other hand, monoiodidonickel(II) iodide (C-08) complex against *S. aureus* and *E. coli*, nickel(II) dithiocyanate (C-02), mononitronickel(II) nitrate (C-04), nickel(II) dibromide (C-06) and monobromidonickel(II) bromide (C-07) complex against *E. coli*, monobromidonickel(II) bromide (C-07) complex against *P. aeruginosa* showed good activity. However some complexes showed ineffectiveness against bacteria but a minute comparison on the result (Table 1) reveals that monoiodidonickel(II) iodide (C-08), monobromidonickel(II) bromide (C-07), nickel(II) dibromide (C-06) exhibited good activity against all bacteria. Similarly mononitronickel(II) nitrate (C-04) was active against all bacteria except *P. aeruginosa*, monochloridonickel(II) chloride (C-05), monoisothiocyanatonickel(II) thiocyanate (C-03) and mononitratonickel(II) nitrate (C-01) were also effective against all bacteria except *E. coli*. Antibacterial activity of solvent DMSO (as control) was also performed for the comparison which was inactive in all cases. Antibacterial activity of the metal complexes can

Table 1: Antibacterial data for the nickel(II) complexes.

Sample Code	Ligand and their complexes	Zone of inhibition in diameter (mm)			
		Gram-negative bacteria		Gram-positive bacteria	
		<i>E. coli</i>	<i>P. aeruginosa</i>	<i>S. aureus</i>	<i>B. cereus</i>
L ₁	L	0	0	0	0
C-01	[NiL(NO ₃)](NO ₃)	0	9	8	21
C-02	[NiL](SCN) ₂	10	0	8	0
C-03	[NiL(NCS)](SCN)	0	9	10	14
C-04	[NiL(NO ₂)](NO ₃)	10	0	9	20
C-05	[NiLClCl]	0	9	11	23
C-06	[NiL]Br ₂	11	8	9	16
C-07	[NiLBr]Br	11	10	10	16
C-08	[NiLI]I	11	8	12	16
	Ampicillin(Standard)	34	25	22	24
	Ni(NO ₃) ₂ ·6H ₂ O	9	8	10	7
	DMSO(Control)	0	0	0	0

be explained by using the chelation theory [42]. To restricts further growth of organism, chelation helps to block the metal binding

sites on enzymes of bacteria by enhancing the lipophilicity of central metal atom thereby block the synthesis of proteins [43].

Conclusion

This study reveals that interaction of macrocyclic ligand, L with nickel nitrate hexahydrate resulted in a five coordinated square pyramidal complex [NiL(NO₃)](NO₃). Moreover a number of new five coordinated (high spin) square pyramidal complexes [NiL(NCS)](SCN), [NiL(NO₂)](NO₃), [NiLCl]Cl, [NiLBr]Br and [NiLI]I as well as four coordinated square planar [NiL](SCN)₂ and [NiL]Br₂ were produced by the reaction of L with substituted nickel(II) salts. Antibacterial evaluation of the ligand and its nickel(II) complexes shows that, though the ligand was ineffective against the bacteria but most of the complexes showed good antibacterial activities.

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