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Nickel(II) Complexes of Octamethyl Tetraazamacrocycle and its *N*-Pendent Derivative: Syntheses, Characterization, Electrolytic Behaviour and Antimicrobial Activities

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Octamethyl tetraazamacrocycle, $Me_8[14]diene\cdot 2HClO_4$ and its three isomeric ligands (L_A, L_B and L_C) were synthesized and characterized using analytical and spectroscopic data, and the antibacterial activities were evaluated against selected bacteria and yeast. Interaction of L_C with excess acrylonitrile resulted in an *N*-pendent derivative (L_{CX}). Square planar nickel(II) diperchlorate complex of L_C, $[NiL_{C\alpha}](ClO_4)_2$, underwent axial addition reactions with KI and $NaNO_2$ to yield six coordinated octahedral species, $[NiL_{C\alpha}I_2]\cdot 2H_2O$ and $[NiL_{C\alpha}(NO_2)(ClO_4)]$. Five coordinated square pyramidal Ni(II) complexes, $[NiL_{CX}Cl](ClO_4)$, $[NiL_{CX}(NCS)](NO_3)$ and $[NiL_{CX}I](NO_3)$, were synthesized from Ni(II) salts and tetraazamacrocyclic ligand L_{CX}. Among the complexes, $[NiL_{CX}Cl](ClO_4)$ was synthesized through the direct interaction of $NiCl_2$ with L_{CX}, followed by the subsequent addition of $NaClO_4\cdot 6H_2O$. On the other hand, $[NiL_{CX}(NCS)](NO_3)$ and $[NiL_{CX}I](NO_3)$ as well as octahedral $[NiL_{CX}Br_2]$ and $[NiL_{CX}(NO_2)(NO_3)]$ were synthesized by the interaction of L_{CX} with different Ni(II) salts.

Keywords: Azamacrocyclic ligands, *N*-Pendent derivative, Ni(II) complexes, Spectroscopic studies, Antibacterial activities.

INTRODUCTION

Macrocyclic complexes of transition metals have widespread applications as antibacterial [1], antifungal [2], antitumor [3] and anticancer [4] agents. Moreover, because of resemblances with naturally occurring macrocycles, *e.g.*, porphyrin [5], vitamin B_{12}, hemoglobin [6] and so forth, multidentate ligands are used in both diagnostic and therapeutical sectors [7-10]. Hence, research on macrocyclic ligands and their metal complexes is receiving widespread interest [11-14]. The literature survey demonstrates the interests of researchers in developing metal complexes of *N*-pendent derivatives [15-19], along with their X-ray structures [20]. Four-coordinated Ni(II) with tetrahedral or square planar and hexa-coordinated octahedral structures are the most common [11,18,19,21]. Although penta-coordinated square pyramidal Ni(II) complexes are rarely available in the literature [21-23], our research group reported some new square pyramidal Ni(II) complexes of a macrocyclic ligand [21].

In previous study, a square planar Ni(II) complex of the *N*-pendent ligand (L_{CX}) has been reported [19]. However, in other studies, square planar Ni(II) [24] and Cu(II) [25] complexes were found to undergo addition reactions at the axial sites of metal ions. From this point of view, it appeared motivating to go forward with previously synthesized square planar Ni(II) complex of L_{CX} for further investigation to determine whether this complex undergoes an axial addition reaction [19]. Although Ni(II), Cu(II) and Cd(II) complexes of analogous L_{BX} undergo axial addition and substitution reactions with various ligands, *e.g.*, NCS^-, Br^-, I^- and NO_2^- to form six coordinated complexes [16,18], our attempts to achieve the same were not successful with Ni(II) complex of L_{CX}. However, some new complexes of L_{CX} by direct interaction of the ligand with Ni(II) salts, as well as some substituted Ni(II) salts, have been synthesized.

Synthesis of axial addition products of square planar Ni(II) complex of L_C was also carried out. In this context, 14-membered octamethyl tetraazamacrocycle salt, Me_8[14]diene·2HClO$_4$ (L·2HClO$_4$), reduced isomeric ligands (L_A, L_B and L_C) [26,27] and *bis*(cyanoethyl) *N*-pendant derivative L_{CX} of isomeric ligand L_C were synthesized [19]. Current work reports the synthesis, characterization and antibacterial activities of some new Ni(II) complexes of L_C and it's *N*-pendent derivative (L_{CX}).

EXPERIMENTAL

Analytical grade chemicals as procured from Sigma-Aldrich (St. Louis, MO) were used without further purification.

Characterization: CHNS-932 elemental analyzer from LECO Corporation (St. Joseph, USA) was used for elemental analyses (C, H and N). ^{1}H NMR experiment was carried out in DMSO with the help of an AVANCE 400 spectrometer from Bruker AG (Karlsruhe, Germany). A UV-visible spectrophotometer from Shimadzu (Kyoto, Japan) was used to produce the UV-visible spectra (solvents: DMSO, chloroform and acetonitrile). Conductivity Bridge HI-8820 from Hanna Instruments (Padova, Italy) was used to measure conductance in DMSO, chloroform and acetonitrile. A Gouy balance, calibrated using Hg[Co(NCS)$_4$], was used to measure magnetic moments. IR 20 spectrophotometer from Shimadzu (Kyoto, Japan) was used to generate the infrared spectra.

Syntheses

Isomeric ligand L_C and its *N*-pendent derivative L_{CX}: The synthesis of ligand, Me_8[14]diene·2HClO$_4$ (L·2HClO$_4$) was described earlier by Curtis *et al.* [26]. Three isomers, L_A, L_B and L_C of the reduced form of L·2HClO$_4$ were separated and isolated following the method described by Bembi *et al.* [27]. The *N*-pendent ligand L_{CX} was synthesized following the protocol mentioned in Dey *et al.* [19] (**Scheme-I**).

Ni(II) complexes of L_C

[NiL$_{C\alpha}$](ClO$_4$)$_2$: [NiL$_{C\alpha}$](ClO$_4$)$_2$ was synthesized following the protocol reported by Roy *et al.* [28].

Axial addition products of [NiL$_{C\alpha}$](ClO$_4$)$_2$

[NiL$_{C\alpha}$I$_2$]·2H$_2$O: [NiL$_{C\alpha}$](ClO$_4$)$_2$ (1.0 mmol, 0.496 g) and KI (2.0 mmol, 0.332 g) were dissolved or suspended separately in methanol (40 mL). Then, both the solutions or suspensions were mixed and evaporated to dryness. The obtained orange yellow product was extracted with chloroform. After filtration, the chloroform extract was dried and then orange-yellow powder of [NiL$_{C\alpha}$I$_2$]·2H$_2$O was collected. Colour: orange-yellow, *m.w.*: 661.07; Anal. calcd. (found) %: C, 32.72 (32.70); H, 6.72 (6.71); N, 8.49 (8.48); IR (cm^{-1}): ν_{N-H}, 3177 w; ν_{C-H}, 2974 s; ν_{CH_3}, 1380 s; ν_{C-C}, 1138 s; ν_{OH}, 3461 vs; δ_{H_2O}, 1650 w. Molar conductivity (ohm^{-1} cm^2 mol^{-1}): 64 (in DMSO), 0 (in CHCl$_3$), 188 (in acetonitrile). Magnetic moment (μ_{eff}, B.M.): 2.81, paramagnetic. UV vis [λ_{max} in nm (ε_{max})]: 334(14), 466(83), 705(4) and 775(5) (in DMSO); 243(2201), 332(149), 478(50), 660(3) and 768(2) (in CHCl$_3$); 245(2047), 329(128), 470(76), 680(4) and 780(4) (in acetonitrile).

[NiL$_{C\alpha}$(NO$_2$)(ClO$_4$)]: This complex was also synthesized in a similar manner as described except using NaNO$_2$ instead of KI. Colour: yellow, *m.w.*: 516.69. Anal. calcd. (found) %: C, 41.93 (41.84); H, 7.82 (7.80); N, 13.59 (13.55); IR (cm^{-1}): ν_{N-H}, 3194s; ν_{C-H}, 2974s; ν_{CH_3}, 1377s; ν_{C-C}, 1144 vs; ν_{ClO_4}, 1118 vs & 625 vs; $\nu s_{asym(NO_2)}$, 1459m, δ_{NO_2}, 807w. Molar conductivity (ohm^{-1} cm^2 mol^{-1}): 62 (in DMSO), 0 (in CHCl$_3$), 181 (in acetonitrile). Magnetic moment (μ_{eff}, B.M.): 2.45, paramagnetic. UV vis [λ_{max} in nm (ε_{max})]: 369(15), 465(71) and 591(6) (in DMSO); 242(1763), 362(25), 475(52), 668(7) and 776(5) (in CHCl$_3$); 366(17), 466(48), 587(6) and 741(2) (in acetonitrile).

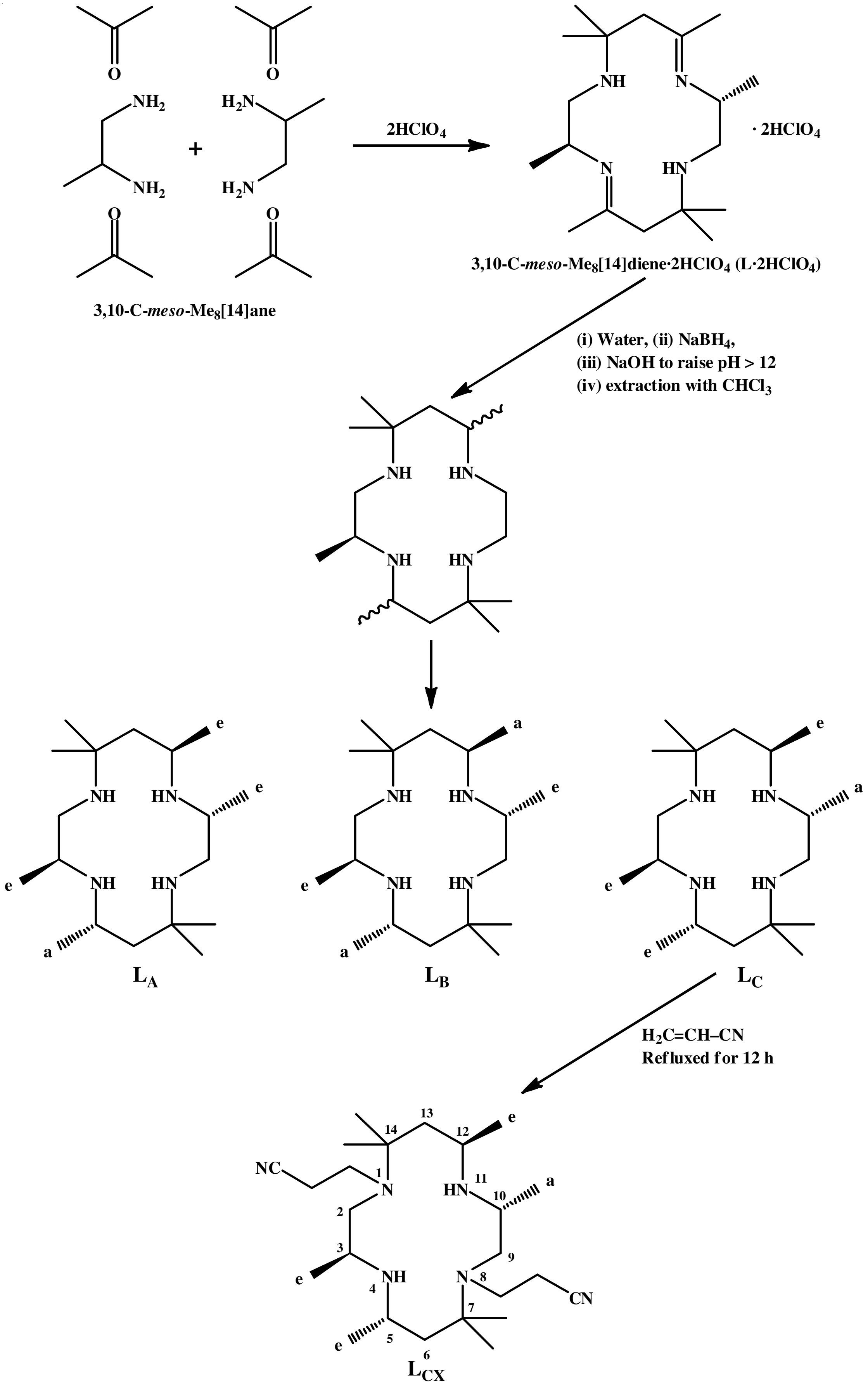
Ni(II) complexes of L_{CX}

[NiL$_{CX}$Cl](ClO$_4$): NiCl$_2$·6H$_2$O (0.238 g, 1.0 mmol) and L_{CX} (0.418 g, 1.0 mmol) were dissolved separately in methanol (30 mL). Both solutions were mixed in a round bottom flask, 1-2 mL of acrylonitrile was added and refluxed for 2 h. Then, the solution was transferred to a beaker and 0.3675 g (3.0 mmol) of NaClO$_4$·6H$_2$O was added. The obtained sticky product was dissolved in ethanol, concentrated again and then diethyl ether was added. The orange-coloured sticky material was separated by decanting the liquid portion, dried in a desiccator to obtain the orange-coloured powder complex, [NiL$_{CX}$Cl](ClO$_4$). Colour: orange, *m.w.*: 610.23. Anal. calcd. (found) %: C, 47.20 (47.08); H, 7.60 (7.57); N, 13.77 (13.73); calcd.: C, 47.20; H, 7.60; N, 13.77%; IR (cm^{-1}): ν_{N-H}, 3187s; ν_{C-H}, 2978s; ν_{CH_3}, 1385s; $\nu_{C\equiv N}$, 2250s; $\nu_{Ni\text{-}N}$, 547w, ν_{ClO_4}, 1098 vs, 625 v; ^{1}H NMR (δ, ppm in DMSO-d_6): (for CH$_3$), 1.134 (ovs, 6H, e), 1.357 (ovs, 6H, a), 1.134 (d, 9H, e) 1.357 (ovd, 3H, a), (for CH$_2$, CH and NH), 2.000 (m), 4.500 (m), 5.600 (m), 7.100 (b), 8.702 (b), 8.968 (b). Molar conductivity (ohm^{-1} cm^2 mol^{-1}), 103 (in DMSO), 290 (in acetonitrile). Magnetic moment (μ_{eff}, B.M.): diamagnetic. UV vis [λ_{max} in nm (ε_{max})]: 260(1923), 417(25), 483(40) and 725(7) (in DMSO); 403(46), 490(58), 650(30) and 757(27) (in acetonitrile).

Ni(II) complexes of L_{CX} from substituted Ni(II) salts

[NiL$_{CX}$(NCS)](NO$_3$): Ni(NO$_3$)$_2$·4H$_2$O (1.0 mmol, 0.291 g) and KSCN (0.194 g, 2.0 mmol) were dissolved in methanol (30 mL). The solution was heated for 15 min and cooled. The precipitate was filtered off. L_{CX} (0.418 g, 1.0 mmol) was dissolved in methanol (30 mL) and mixed with the filtrate in a round bottom flask. Acrylonitrile (1.0 mL) was added to the round bottom flask and the solution was refluxed for 2 h. A light violet precipitate of [NiL$_{CX}$(NCS)](NO$_3$) was formed on concentration, which was filtered and washed with methanol, followed by diethyl ether and stored. Colour: light violet, *m.w.*: 597.44. Anal. calcd. (found) %: C, 50.31 (50.26); H, 7.77 (7.76); N, 18.79 (18.76); IR (cm^{-1}): ν_{N-H}, 3220 m; ν_{C-H}, 2968 s; ν_{CH_3}, 1369 w; ν_{C-C}, 1133 s; $\nu_{C\equiv N}$, 2249 s; $\nu_{Ni\text{-}N}$, 543w; $\nu_{NO_3^-}$, 1383s; ν_{CN}, 2078 vs; ν_{CS}, 850 w. Molar conductivity (ohm^{-1} cm^2 mol^{-1}): 96 (in DMSO), 255 (in acetonitrile). Magnetic moment (μ_{eff}, B.M.): 3.006, paramagnetic. UV vis [λ_{max} in nm (ε_{max})]: 458 (121), 571(47), 645(37) and 730(32) (in DMSO); 351(309) and 462(207) (in acetonitrile).

[NiL$_{CX}$Br$_2$], [NiL$_{CX}$I](NO$_3$) and [NiL$_{CX}$(NO$_2$)(NO$_3$)]: [NiL$_{CX}$Br$_2$], [NiL$_{CX}$I](NO$_3$) and [NiL$_{CX}$(NO$_2$)(NO$_3$)] were synthesized similarly as the procedure adopted for the synthesis of [NiL$_{CX}$(NCS)](NO$_3$) by using KBr, KI and NaNO$_2$, respectively, instead of KSCN.



Scheme-I: Preparation of isomeric ligand L$_C$ and *N*-pendent derivative L$_{CX}$

[$NiL_{CX}Br_2$]: Colour: orange, *m.w.*: 634.15. Anal. calcd. (found) %: C, 45.42 (45.34); H, 7.31 (7.28); N, 13.25 (13.19); IR (cm^{-1}): $\nu_{N–H}$, 3021s; $\nu_{C–H}$, 2974s; ν_{CH_3}, 1396s; $\nu_{C–C}$, 1138s; $\nu_{C\equiv N}$, 2247s; ν_{Ni-N}, 550w; Molar conductivity ($ohm^{-1}\,cm^2\,mol^{-1}$), 40 (in DMSO), 0 (in $CHCl_3$), 103 (in acetonitrile). Magnetic moment (μ_{eff}, BM): 2.89, paramagnetic. UV vis [λ_{max} in nm (ε_{max})]: 479(39) (in DMSO); 486(35) and 658(7) (in $CHCl_3$); 369(50), 484(37), 655(9) and 742(4) (in acetonitrile).

[$NiL_{CX}I$](NO_3): Colour: orange, *m.w.*: 639.2. Anal. calcd. (found) %: C, 45.06 (45.03); H, 7.25 (7.24); N, 13.14 (13.13); IR (cm^{-1}): $\nu_{N–H}$, 3023s; $\nu_{C–H}$, 2972s; ν_{CH_3}, 1394w; $\nu_{C–C}$, 1158s; $\nu_{C\equiv N}$, 2247s; $\nu_{NO_3^-}$, 1383s; ν_{Ni-N}, 544w. ^{1}H NMR (δ, ppm in DMSO-d_6): (for CH_3), 1.108 (ovs, 6H, e), 1.347 (ovs, 6H, a), 1.030 (d, 6H, e), 1.108 (ovd, 3H,e), 1.347 (ovd, 3H, a), (for CH_2, CH and NH), 1.550 (m), 1.750 (m), 2.000 (m), 2.200 (m), 2.785 (m), 3.161 (m), 8.016 (b), 8.506 (b). Molar conductivity ($ohm^{-1}\,cm^2\,mol^{-1}$): 84 (in DMSO), 267 (in acetonitrile). Magnetic moment (μ_{eff}, B.M.): diamagnetic. UV vis [λ_{max} in nm (ε_{max})]: 484(34) and 778(2) (in DMSO); 360(160), 484(38) and 712(4) (in acetonitrile).

[$NiL_{CX}(NO_2)(NO_3)$]: Colour: grey, *m.w.*: 584.29. Anal. calcd. (found) %: C, 49.29 (49.24); H, 7.93 (7.92); N, 19.17 (19.14); IR (cm^{-1}): $\nu_{N–H}$, 3208s; $\nu_{C–H}$, 2971s; ν_{CH_3}, 1326s; $\nu_{C–C}$, 1138w; $\nu_{C\equiv N}$, 2246w; $\nu_{NO_3^-}$, 1340–1456m; $\nu_{asym(NO_2^-)}$, 1456w; $\nu_{sym(NO_2^-)}$, 1339m, δ_{NO_2}, 828s. Molar conductivity ($ohm^{-1}\,cm^2\,mol^{-1}$): 40 (in DMSO), 0 (in $CHCl_3$), 120 (in acetonitrile). Magnetic moment (μ_{eff}, B.M.): 2.44, paramagnetic. UV-vis [λ_{max} in nm (ε_{max})]: 366(118), 457(53) and 578(26) (in DMSO); 364(134), 465(34), 575(28) and 697(7) (in $CHCl_3$); 362(109), 457(41), 576(22) and 793(5) (in acetonitrile).

Antimicrobial activities: Disc diffusion method was used to investigate the activity of ligands and their Ni(II) complexes against some selected bacteria and yeast. Freshly prepared and sterilized suspension of nutrient agar (melted at 45 ºC) medium uniformly seeded with the test microorganism was used in 70 mm diameter petri plates. Paper discs (6 mm) were placed at the inoculated pour plates after soaking with the chemicals dissolved in DMSO (1 mg mL^{-1}) along with a control. A 4 h waiting period at 4 ºC allowed to diffuse the test chemicals from the disc to the surrounding medium. Then, the plates were incubated at 35 ± 2 ºC, followed by observations at 24 and 48 h. The activity was expressed in mm in terms of the zone of inhibition. All tests were performed in triplicates.

RESULTS AND DISCUSSION

Analytical, spectroscopic, magnetochemical and molar conductivity data were used to characterize metal complexes of ligands L_C and L_{CX}. Since ^{1}H NMR spectra of paramagnetic compounds are less informative, ^{1}H NMR spectral analysis of diamagnetic compounds were investigated. The substituted salts of $Ni(NO_3)_2$ may contain a negligible amount of NO_3^-, so the inclusion of NO_3^- in some complexes of L_{CX} synthesized from substituted salts of $Ni(NO_3)_2$ indicates that Ni(II) has a greater fascination for NO_3^- ion in case of the concerned ligand L_{CX}.

Isomeric ligand L_C and Its *N*-pendent derivative L_{CX}: Isomeric ligand L_C [27] and its *N*-pendent derivative L_{CX} [19] (**Scheme-I**) were synthesized and characterized. The molecular structure (Fig. 1) of *N*-pendent ligand L_{CX} has also been reported by Chakraborty *et al.* [29].

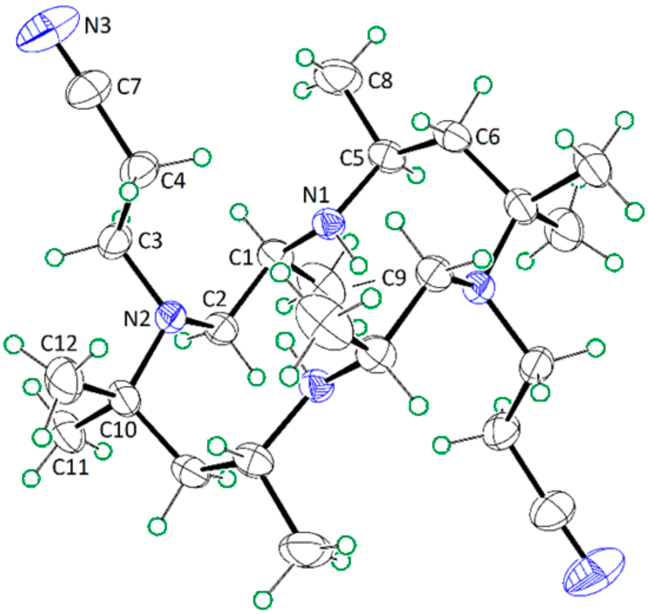


Fig. 1. Molecular structure of L_{CX}

Ni(II) complexes of L_C and L_{CX}

[$NiL_{C\alpha}$](ClO_4)$_2$: The square planar Ni(II) complex, [$NiL_{C\alpha}$](ClO_4)$_2$, were synthesized and characterized as described in Roy *et al.* [28].

[$NiL_{C\alpha}I_2$]·$2H_2O$ and [$NiL_{C\alpha}(NO_2)(ClO_4)$]: [$NiL_{C\alpha}$]($ClO_4$)$_2$ underwent axial addition with KI and $NaNO_2$ to result in the formation of [$NiL_{C\alpha}I_2$]·$2H_2O$ and [$NiL_{C\alpha}(NO_2)(ClO_4)$], respectively. The infrared spectra of these complexes display ν_{N-H}, ν_{C-H}, ν_{CH_3} and ν_{C-C} bands in 3194-3177, 2974, 1380-1377 and 1144-1133 cm^{-1}, respectively. Strong bands at 3461and 1650 cm^{-1} for [$NiL_{C\alpha}I_2$]·$2H_2O$ indicate the presence of lattice water [30]. The IR of [$NiL_{C\alpha}(NO_2)(ClO_4)$] further exhibits bands at 1118 and 625 cm^{-1} due to the presence of ClO_4^-. The band's splitting at 1118 cm^{-1} indicates the presence of unidentate coordinated perchlorate [31]. [$NiL_{C\alpha}(NO_2)(ClO_4)$] exhibits $\nu_{asym(NO_2)}$ and δ_{NO_2} bands at 1459 and 807 cm^{-1}, respectively. The $\nu_{sym(NO_2)}$ band would be overlapped with the band of $-CH_3$ group. So, this band couldn't be identified properly.

The conductance value of 0 $ohm^{-1}\,cm^2\,mol^{-1}$ for both complexes in $CHCl_3$ (colour remains intact) strongly supports the non-electrolytic nature of the complexes, *i.e.* the anions are in the coordination sphere as expected for the hexa-coordinated octahedral complexes. The molar conductance values of 64 and 62 $ohm^{-1}\,cm^2\,mol^{-1}$ for [$NiL_{C\alpha}I_2$]·$2H_2O$ and [$NiL_{C\alpha}(NO_2)(ClO_4)$], respectively, in DMSO corresponding to 1:1 electrolyte can be assigned for the equilibrium between octahedral and square planar geometry (eqns. 1 and 2) or conversion of octahedral to square pyramidal species (eqns. 3 and 4), respectively.

$$[NiL_{C\alpha}\,I_2]\cdot 2H_2O \xleftrightarrow{DMSO} [NiL_{C\alpha}]I_2\cdot 2H_2O \qquad (1)$$

$$[NiL_{C\alpha}(NO_2)(ClO_4)] \xleftrightarrow{DMSO} [NiL_{C\alpha}](NO_2)(ClO_4) \qquad (2)$$

$$[NiL_{C\alpha}I_2]\cdot 2H_2O \xrightarrow{DMSO} [NiL_{C\alpha}\ I]I\cdot 2H_2O \qquad (3)$$

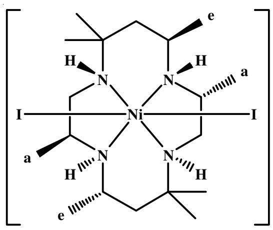
$$[NiL_{C\alpha}(NO_2)(ClO_4)] \xrightarrow{DMSO} [NiL_{C\alpha}(NO_2)](ClO_4) \qquad (4)$$

On the other hand, in acetonitrile, the molar conductance values of 188 and 181 ohm^{-1} cm^2 mol^{-1} for $[NiL_{C\alpha}I_2]\cdot 2H_2O$ and $[NiL_{C\alpha}(NO_2)(ClO_4)]$, respectively, indicated the 1:2 electrolytic nature. Therefore, it is evidence for converting octahedral to square planar geometry as expressed by eqns. 5 and 6:

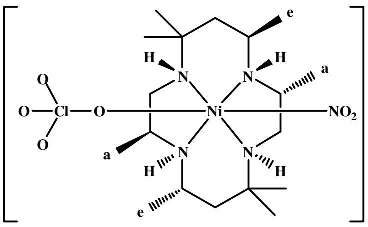
$$[NiL_{C\alpha}I_2]\cdot 2H_2O \xrightarrow{Acetonitrile} [NiL_{C\alpha}]I_2\cdot 2H_2O \qquad (5)$$

$$[NiL_{C\alpha}(NO_2)(ClO_4)] \xrightarrow{Acetonitrile} [NiL_{C\alpha}(NO_2)](ClO_4) \qquad (6)$$

The electronic spectrum of the complex $[NiL_{C\alpha}I_2]\cdot 2H_2O$ shows *d–d* bands at 334 nm in DMSO, 332 nm in chloroform and 329 nm in acetonitrile, which can be assigned as $^3A_{2g}(P) \rightarrow {}^3T_{1g}$ transition [32]. In $[NiL_{C\alpha}(NO_2)(ClO_4)]$, $^3A_{2g}(P)\rightarrow{}^3T_{1g}$ transition can be shown at 369 nm in DMSO, 362 nm in chloroform and 366 nm in acetonitrile, which are evidence of octahedral geometry. Again, bands at 660-680 nm are the evidence of octahedral geometry, which can be assigned to $^3A_{2g}(F)\rightarrow{}^3T_{1g}$ transition. But, the appearance of bands at 465-478 nm can be accounted for the equilibrium between square planar and octahedral species. It would be due to conversion to square planar species. Further, the bands at the region 768-780 nm are due to the presence of octahedral to square pyramidal equilibrium. The band at 245 nm with a high molar extinction coefficient in acetonitrile for $[NiL_{C\alpha}I_2]\cdot 2H_2O$ and in chloroform for $[NiL_{C\alpha}(NO_2)(ClO_4)]$ is the charge transfer band. Furthermore, the magnetic moment values of $[NiL_{C\alpha}I_2]\cdot 2H_2O$ and $[NiL_{C\alpha}(NO_2)(ClO_4)]$ were corresponded to paramagnetism due to two unpaired electrons. It is clear that both complexes exhibit sp^3d^2 hybridization. Based on the above discussion and the fact that axial addition takes place without a change of conformation and configuration of the ligand of the original compound [33,34], Str. 1 and 2 are assigned to $[NiL_{C\alpha}I_2]\cdot 2H_2O$ and $[NiL_{C\alpha}(NO_2)(ClO_4)]$, respectively.



Str. 1



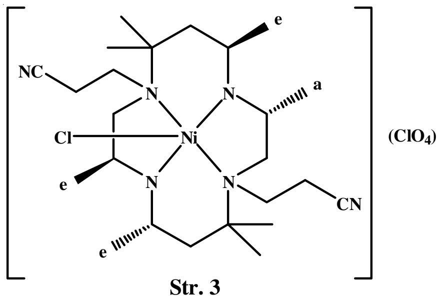
Str. 2

Ni(II) complexes of L_{CX}

$[NiL_{CX}Cl](ClO_4)$: $[NiL_{CX}Cl](ClO_4)$ was synthesized by the interaction of L_{CX} and $NiCl_2\cdot 6H_2O$ with the subsequent addition of $NaClO_4\cdot 6H_2O$. The IR spectrum of this complex displayed $\nu_{N\text{-}H}$, $\nu_{C\text{–}H}$, ν_{CH_3}, $\nu_{C\equiv N}$ and $\nu_{Ni\text{–}N}$ bands in the expected regions. A non-splitting band at around 1080 cm^{-1} of ClO_4^- strongly supports the non-coordination of this ion in the complex [35]. The ClO_4^- band was so broad that it overlapped with $\nu_{C\text{–}C}$ band. So, this complex's C–C band couldn't be detected. $[NiL_{CX}Cl](ClO_4)$ exhibits molar conductivity values of 103 ohm^{-1} cm^2 mol^{-1} in DMSO (retained the colour intact) and 290 ohm^{-1} cm^2 mol^{-1} in acetonitrile, respectively. The molar conductivity value in DMSO corresponds to 1:1 electrolytes, as anticipated for the formula assigned. However, the molar conductivity value of the complex in acetonitrile corresponding to 1:2 electrolyte [36] can be accounted for the expulsion of an anion, *i.e.* Cl^- from the coordination sphere to form square planar complex $[NiL_{CX}](Cl)(ClO_4)$ as expressed in eqn. 7:

$$[NiL_{CX}Cl(ClO_4)] \xrightarrow{Acetonitrile} [NiL_{CX}](Cl)(ClO_4) \qquad (7)$$

The magnetic moment value of this complex indicated diamagnetic character, which supports the low spin dsp^3 hybridized square pyramidal structure of this complex [35]. Diamagnetic $[NiL_{CX}Cl](ClO_4)$ displays *d–d* bands at 403 nm (ε = 46), 490 nm (ε =58), 650 nm (ε =30) and 757 nm (ε =27). The *d–d* bands at 650 and 757 nm in acetonitrile solution can be assigned to the $^3B_1\rightarrow{}^3A_2$ transition, which strongly supports the square pyramidal geometry [37]. But, bands at 403 and 490 nm in acetonitrile also revealed the presence of some square planar species. The ^1H NMR spectrum of $[NiL_{CX}Cl](ClO_4)$ is not well resolved may be due to the mixing of some paramagnetic species. However, the signals corresponding to peripheral methyl protons can be divided into two parts. One signal at 1.134 ppm corresponding to 15H can be assigned to equatorial components of *gem*-dimethyl protons (6H) and due to protons (9H) of three equatorially oriented methyls on three chiral carbons. The other overlapped signal of a singlet (6H) with a doublet (3H) corresponding to 9H at 1.357 ppm can be attributed to axial components of *gem*-dimethyl protons (6H) and axially oriented one methyl protons (3H) on the rest chiral carbon. Thus, a tri-equatorial-axial orientation of chiral methyls can be assigned to this complex. The spectrum further displays some multiplets at 2.000, 4.500, 5.600 ppm and so forth for methine and methylene protons. The signals at 7.100, 8.702 and 8.968 ppm may be due to NH protons. Therefore, based on the above discussion, Str. 3 is assigned to the corresponding square pyramidal complex $[NiL_{CX}Cl](ClO_4)$.



Str. 3

$[NiL_{CX}(NCS)](NO_3)$, $[NiL_{CX}I](NO_3)$, $[NiL_{CX}Br_2]$ and $[NiL_{CX}(NO_2)(NO_3)]$: Substituted Ni(II) salts, $Ni(NCS)_2$, NiI_2, $NiBr_2$ and $Ni(NO_2)_2$ were synthesized by the interaction of $Ni(NO_3)_2\cdot 4H_2O$ with KSCN, KI, KBr and $NaNO_2$, respectively. The substituted salts on interaction with L_{CX} yielded $[NiL_{CX}(NCS)](NO_3)$, $[NiL_{CX}I](NO_3)$, $[NiL_{CX}Br_2]$ and $[NiL_{CX}(NO_2)(NO_3)]$, respectively. IR spectra of these complexes display all the expected bands due to $\nu_{N\text{–}H}$, $\nu_{C\text{–}H}$, ν_{CH_3}, $\nu_{C\text{–}C}$ and $\nu_{C\equiv N}$ in the foreseeable positions. Bands at the region between 1456 to1326 cm^{-1} for three complexes out of four indicate the presence of NO_3^- ion. The inclusion of NO_3^- in all three complexes demonstrates that Ni(II) of this ligand has a greater fascination for NO_3^- ion as received from substituted salts of $Ni(NO_3)_2$, which may contain a negligible amount of NO_3^- ion. Coordination of unidentate NO_3^- group gives two bands at higher and lower frequencies than 1390 cm^{-1}, showing a separation of bands by about 115 cm^{-1}, whereas it is about 180 cm^{-1} for the bidentate complexes [38-40]. IR spectrum of $[NiL_{CX}(NO_2)(NO_3)]$ exhibits bands at 1456 and 1340 cm^{-1} differing by 116 cm^{-1}, which can be reported for a unidentate mode of coordination of NO_3^- group. On the other hand, the presence of a single band at 1383 cm^{-1} in both $[NiL_{CX}(NCS)](NO_3)$ and $[NiL_{CX}I](NO_3)$ is due to the ionic NO_3^- group. Moreover, $[NiL_{CX}(NO_2)(NO_3)]$ exhibits $\nu_{asym(NO_2)}$ band at 1456 cm^{-1}, $\nu_{sym(NO_2)}$ band at 1339 cm^{-1} and stretching δ_{NO_2} band at 668 cm^{-1}. $[NiL_{CX}(NCS)](NO_3)$ display peaks at 850 and 2078 cm^{-1} due to ν_{CS} and ν_{CN} bands, respectively. But, the band of δ_{NCS} is obscured by other bands, which can be assigned to the *N*-bonded thiocyanate group [38,41-44].

Molar conductance values of $[NiL_{CX}(NCS)](NO_3)$ and $[NiL_{CX}I](NO_3)$ in DMSO were found to be 96 and 84 $ohm^{-1} cm^2 mol^{-1}$, which correspond to 1:1 electrolytes as expected and in acetonitrile, these values were 255 and 267 $ohm^{-1} cm^2 mol^{-1}$ corresponding to 1:2 electrolytes [36]. It is due to the expulsion of one ion in acetonitrile from the coordination sphere to form square planar species from a square pyramidal structure, which can be expressed by eqn. 8. Consequently, conductance values ($ohm^{-1} cm^2 mol^{-1}$) of 0 in $CHCl_3$ and 40 in DMSO for $[NiL_{CX}Br_2]$ and $[NiL_{CX}(NO_2)(NO_3)]$, respectively, can be identified as non-electrolytic nature in both solvents for six coordinated octahedral complexes. The 103 and 120 $ohm^{-1} cm^2 mol^{-1}$ conductance values in acetonitrile can be assigned as 1:1 electrolytes, which indicate the equilibrium of octahedral to square planar geometry as expressed in eqns. 9 and 9a. An alternative explanation of the same could be the conversion of octahedral to square pyramidal geometry as per eqns. 10 and 10a:

$$[NiL_{CX}X](NO_3) \xrightarrow{\text{Acetonitrile}} [NiL_{CX}]X(NO_3)[X = NCS^- \text{ or } I^-] \quad (8)$$

$$[NiL_{CX}Br_2] \xleftrightarrow{\text{Acetonitrile}} [NiL_{CX}]Br_2 \quad (9)$$

$$[NiL_{CX}(NO_2)(NO_3)] \xleftrightarrow{\text{Acetonitrile}} [NiL_{CX}](NO_2)(NO_3) \quad (9a)$$

$$[NiL_{CX}\,Br_2] \xrightarrow{\text{Acetonitrile}} [NiL_{CX}\,Br]Br \quad (10)$$

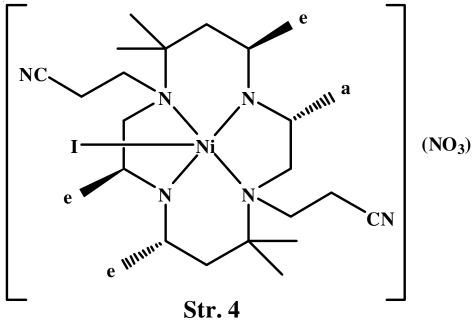
$$[NiL_{CX}(NO_2)(NO_3)] \xrightarrow{\text{Acetonitrile}} [NiL_{CX}(NO_2)](NO_3) \text{ or } [NiL_{CX}(NO_3)](NO_2) \quad (10a)$$

In case of $[NiL_{CX}I](NO_3)$ and $[NiL_{CX}(NCS)](NO_3)$, *d–d* bands at 634 and 645 nm in DMSO are due to the $^3B_1 \rightarrow ^3A_2$ transitions [31]. The bands at 730, 712 and 778 nm in acetonitrile and DMSO solutions indicate the conversion of square pyramidal to octahedral geometry [37]. The bands at 458, 462 and 484 nm in solutions are responsible for $^1A_{1g} \rightarrow ^1B_{1g}$ transition, which indicates the conversion of square pyramidal to square planar geometry. The magnetic moment data indicated that diamagnetic $[NiL_{CX}I](NO_3)$ and paramagnetic $[NiL_{CX}(NCS)](NO_3)$ exhibit the dsp^3 and sp^3d hybridization due to low-spin and high spin-orbital structures, respectively, which supports five coordinated square pyramidal structure of the complexes [45].

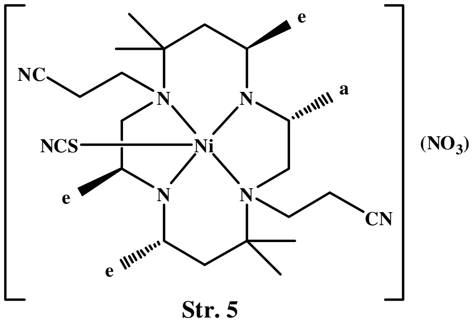
The electronic spectral data of $[NiL_{CX}Br_2]$ and $[NiL_{CX}(NO_2)(NO_3)]$ strongly supports $^3A_{2g} \rightarrow ^3T_{1g}$ *d–d* transition at 658, 655 and 697 nm, which is evidence of the octahedral geometry. The band at 742 nm in acetonitrile of $[NiL_{CX}Br_2]$ may be due to the conversion of octahedral geometry to square pyramidal. But, the bands at 457-486 nm in DMSO and acetonitrile, which are comparatively shorter wavelengths, can be assigned to the square planar species. Additionally, both $[NiL_{CX}(NO_2)(NO_3)]$ and $[NiL_{CX}Br_2]$ are paramagnetic as accounted for the high spin six coordinated sp^3d^2 hybridized octahedral structure [45].

The ^1H NMR spectrum of $[NiL_{CX}I](NO_3)$ displays a doublet at 1.030 ppm, an overlapped singlet with a doublet at 1.108 ppm and another overlapped singlet with a doublet at 1.347 ppm. The doublet at 1.030 ppm corresponding to 6H can be assigned to equatorially oriented two equivalent methyl protons on two chiral carbons. The overlapped signal at 1.108 ppm corresponding to 9H can be due to equatorial components of *gem*-dimethyl groups (6H) and a doublet arising out of one equatorially oriented methyl protons (3H) on a chiral carbon. However, the other overlapped signal at 1.347 ppm corresponding to 9H can be assigned to axial components of *gem*-dimethyl proton (6H) and a doublet due to one axially oriented methyl protons (3H) on a chiral carbon. Thus, a tri-equatorial-axial orientation of methyls on chiral carbons can be assigned for this complex as assigned to $[NiL_{CX}Cl](ClO_4)$. The spectrum exhibits multiplets at 1.850, 1.750, 2.000, 2.200, 2.785 and 3.161 ppm due to the methine and methylene protons and the signals at 8.016 and 8.506 ppm can be assigned for NH protons. From all the evidence, Str. 4 is suggested for $[NiL_{CX}I](NO_3)$. ^1H NMR of diamagnetic compounds is more informative than paramagnetic ones. So, $[NiL_{CX}(NCS)](NO_3)$, which has similar properties to $[NiL_{CX}I](NO_3)$, can be represented by Str. 5. The structures of paramagnetic octahedral complexes $[NiL_{CX}Br_2]$ and $[NiL_{CX}(NO_2)(NO_3)]$ can be assigned according to previously published Co(III) complexes of L_{CX} [19] using Str. 6 and 7.

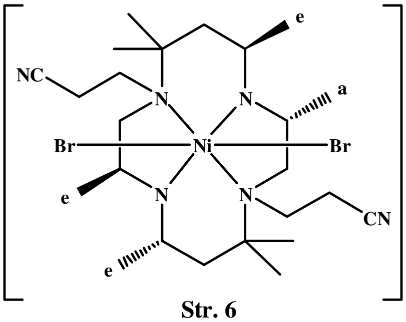
Antimicrobial activities: The antimicrobial potential of the ligand L_{CX} and its different metal complexes against some Gram-positive and Gram-negative bacteria, as well as against some pathogenic fungi, were reported earlier by Dey *et al.* [19]. In continuation of that work, antimicrobial activity evaluation of the new Ni(II) complexes with L_C and L_{CX} was conducted using Gram-positive bacteria (*B. subtilis* and *B. cereus*), Gram-negative bacteria (*S. abony* and *P. aeruginosa*) and yeast (*C. albicans*). The results are summarized in Table-1, confirming that several of these complexes have some antimicrobial activity, as observed in earlier studies [15,19,33,34,46,47]. However, the other complexes have not shown any activity against the tested Gram-positive bacteria, so the results are excluded from Table-1. Although the ligands and solvent DMSO did not show any activity, metal salts showed little activity. However, the activity demonstrated by the complexes is not due to metal ions as the complexes are very stable even in solution. Moreover, the complexes exhibited activity comparable to standard Ampicillin in some cases. As per the results listed in Table-1, the inhibiting capacity of the complexes against different bacteria as well as yeast did not follow any specific trend. However, further studies should be performed based on the observations



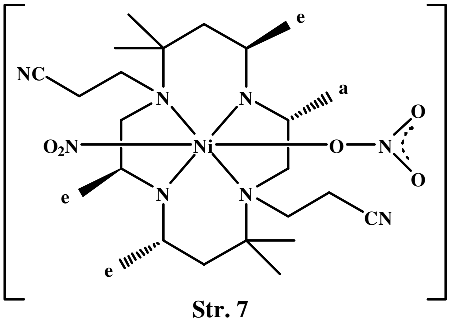
Str. 4



Str. 5



Str. 6



Str. 7

TABLE-1
ANTIMICROBIAL ACTIVITIES OF
THE LIGANDS AND Ni(II) COMPLEXES

Test organisms	Diameter of zone of inhibition (mm)		
	Yeast	Gram-negative bacteria	
	Candida albicans	*Salmonella abony*	*Pseudomonus aeruginosa*
Ligands and Ni(II) complexes	48 h	48 h	48 h
L_C	0	0	0
L_{CX}	0	0	0
$[NiL_{CX}Cl](ClO_4)$	0	9	10
$[NiL_{CX}(CNS)](NO_3)$	0	10	9
$[NiL_{CX}I](NO_3)$	0	0	11
$[NiL_{CX}(NO_2)(NO_3)]$	13	9	14
$[NiL_{CX}Br_2]$	11	0	15
$[NiL_{C\alpha}I_2]\cdot 2H_2O$	0	9	10
$[NiL_{C\alpha}(NO_2)(ClO_4)]$	14	0	9
$NiCl_2\cdot 6H_2O$	5	3	6
DMSO (control)	0	0	0
Ampicillin (std.)	20	18	21

of the current work. Although the mode of action of complexes against microorganisms is a matter of extensive research, chelation theory can be suggested in this case [48-50].

Conclusion

Macrocyclic ligand, L_{CX}, underwent facile complexation when treated with $NiCl_2$ with the subsequent addition of $NaClO_4$ to yield five coordinated square pyramidal complex, $[NiL_{CX}Cl](ClO_4)$ with *dsp*^{3} hybridization. Attempts to carry out axial addition or substitution reactions of this complex were unsuccessful. On the other hand, some Ni(II) complexes of the ligand L_{CX} with substituted Ni(II) salts synthesized from $Ni(NO_3)_2$ were successful. Thus, interaction of L_{CX} with $Ni(NCS)_2$, NiI_2, $NiBr_2$ and $Ni(NO_2)_2$ resulted in square pyramidal $[NiL_{CX}(NCS)](NO_3)$ and $[NiL_{CX}I](NO_3)$ with *sp*^{3}*d* and *dsp*^{3} hybridization and octahedral $[NiL_{CX}Br_2]$ and $[NiL_{CX}(NO_2)(NO_3)]$ with *sp*^{3}*d*^{2} hybridization. Square pyramidal Ni(II) complex of *N*-pendent ligand L_{CX} did not undergo any axial addition or substitution reaction. However, square planar Ni(II) diperchlorate complex $[NiL_{C\alpha}](ClO_4)_2$ of L_C underwent axial addition reactions with KI and $NaNO_2$ to generate six coordinated octahedral species $[NiL_{C\alpha}I_2]\cdot 2H_2O$ and $[NiL_{C\alpha}(NO_2)(ClO_4)]$ with *sp*^{3}*d*^{2} hybridization. The stereochemistry of the addition complexes was established based on axial addition taking place without a change of conformation and configuration of the ligand of the original compound. The antimicrobial activities of these newly synthesized Ni(II) complexes can provide a new dimension to the research on medicinal chemistry.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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