

Nickel(II) Complexes with N-pendent Macrocyclic Ligands: Synthesis, Characterization and Antimicrobial Activities

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Abstract

The tetraazamacrocyclic ligand salt $\text{Me}_8[14]\text{diene} \cdot 2\text{HClO}_4$ ($\text{L} \cdot 2\text{HClO}_4$) was synthesized by the condensation of 1, 2-diaminopropane with acetone in presence of quantitative amount of HClO_4 . Three isomeric ligands L_A , L_B & L_C of its reduced analogues were separated by the reduction of $\text{L} \cdot 2\text{HClO}_4$ with NaBH_4 followed by fractional crystallization from xylene. Isomeric ligands, L_B and L_C on reaction with CH_3I under reflux produced N, N' -dimethyl derivatives L_{BZ} and L_{CZ} . The reactions of L_{BZ} and L_{CZ} with nickel(II) acetate followed by addition of $\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ produced square planar complexes, $[\text{NiL}_{BZ}](\text{ClO}_4)_2$ and $[\text{NiL}_{CZ}](\text{ClO}_4)_2$ respectively. These square planar complexes underwent axial addition reactions with KNO_2 and KNO_3 to produce corresponding octahedral derivative complexes $[\text{NiL}_{BZ}(\text{NO}_2)(\text{ClO}_4)]$ & $[\text{NiL}_{CZ}(\text{NO}_2)_2]$ and $[\text{NiL}_{BZ}(\text{NO}_3)(\text{ClO}_4)]$ & $[\text{NiL}_{CZ}(\text{NO}_3)_2]$ respectively. In addition the square planar complex, $[\text{NiL}_{BZ}](\text{ClO}_4)_2$ underwent self axial addition reaction to form octahedral axial addition product $[\text{NiL}_{BZ}(\text{ClO}_4)_2]$ by addition of two ionic ClO_4^- on its two axial positions when extracted with chloroform. All these compounds have been characterized by different analytical and spectroscopic techniques. All the complexes are found to be nonelectrolytes and octahedral in CHCl_3 . Antimicrobial activities of these complexes have been investigated against a few phytopathogenic bacteria and fungi.

Keywords: Azamacrocyclic ligands; Nickel(II) complexes ; Spectroscopic studies; Antibacterial activities; Antifungal activities.

1. Introduction

In the field of modern science, polyazamacrocyclic ligands and their different metal complexes have achieved a fascinating position due to their applications in different sectors like industrial [1], analytical [2] field etc. Moreover the macrocyclic compounds are playing a very important role in pharmacological [3] and medicinal sectors because of their antibacterial [4], antifungal [5], anticancer [6] and therapeutic criteria [7]. In addition the N-pendent ligands are more significant due to their greater ligating activity. In this connection it is reasonable to carry out more studies on the macrocyclic ligands and their complexes. Different metal complexes with macrocyclic ligands and their N-pendent derivatives have been reported in the literature

[8-14]. Some nickel (II) complexes with the concerned N-pendent ligands, L_{BZ} and L_{CZ} have already been reported [15]. But it was our interest to bring some new nickel(II) complexes as axial addition reaction products in this field, which are expected to have antimicrobial activities. With this point of view the ligand salt, $\text{L} \cdot 2\text{HClO}_4$ and three isomeric ligands, L_A , L_B & L_C of its reduced form (Scheme-1) [16-18] as well as N-pendent derivatives L_{BZ} and L_{CZ} [14] of the isomeric ligands L_B & L_C respectively with N, N'-dimethyl groups have been prepared as per literature. Moreover nickel (II) diperchlorate complexes, $[\text{NiL}_{BZ}](\text{ClO}_4)_2$ and $[\text{NiL}_{CZ}](\text{ClO}_4)_2$ of L_{BZ} and L_{CZ} respectively were also prepared according to the procedure adopted in the

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literature [15] on which some axial addition reactions were carried out. Herein we report studies on some new axial addition reaction products of the mentioned nickel (II) diperchlorate complexes of the concerned N-pendent macrocyclic ligands L_{BZ} and L_{CZ} .

2. Experimental

2.1 Material and Equipment

All chemicals were of analytical grade (Sigma Aldrich) or of equivalent grades and were used without further purification. The solvents were of reagent grade and dried according to standard procedure. Equipments used were of standard ones.

2.2 Syntheses of ligands

2.2.1 Syntheses of isomeric ligands (L_A , L_B & L_C)

Synthesis of the parent ligand, 3,10-C-meso-Me₈[14]diene dihydroperchlorate (L_2HClO_4), reduction of this diene and resolution of isomeric Me₈[14]anes, (L_A , L_B & L_C) were carried out by the literature method [16-18].

2.2.2 Syntheses of N, N'-dimethyl pendent ligands L_{BZ} and L_{CZ}

Syntheses of the N-pendent derivatives, L_{BZ} and L_{CZ} of the isomeric ligands L_B and L_C respectively were carried out by the procedure adopted in the literature [15].

2.3 Synthesis of complexes

2.3.1. $[NiL_{BZ}](ClO_4)_2$ and $[ZnL_{CZ}](ClO_4)_2$

The complexes, $[NiL_{BZ}](ClO_4)_2$ and $[ZnL_{CZ}](ClO_4)_2$ were prepared as per our earlier report [15].

2.4. Syntheses of axial addition products

2.4.1 Syntheses of axial addition products of $[NiL_{BZ}](ClO_4)_2$

2.4.1.1 $[NiL_{BZ}(ClO_4)_2]$

0.299 g (0.5 mmol) of synthesized yellow square planar complex $[NiL_{BZ}](ClO_4)_2$ was heated on a steam bath with 10 mL of $CHCl_3$ for 15 minutes. The solution turned pink. Then the solution was heated on a steam bath till completely dried. Thereafter the pink product was extracted with chloroform. The

pink chloroform extract was heated to dryness on a water bath to yield the pink solid product, $[NiL_{BZ}(ClO_4)_2]$, which was recrystallized from chloroform- methanol mixture and stored in a vacuum desiccator over silicagel.

2.4.1.2 $[NiL_{BZ}(NO_2)(ClO_4)]$

0.299 g (0.5 mmol) of $[NiL_{BZ}](ClO_4)_2$ and 0.085 g (1.0 mmol) of $NaNO_2$ were suspended separately in 25 mL dry and hot methanol and mixed while hot. The solution turned yellow. The resulting mixture was then stirred on a magnetic stirrer for about 2 hours. The mixture was completely dried on a water bath. The dry product was extracted with chloroform and undissolved product rejected. The violet chloroform extract was heated to dryness on a steam bath to result a violet product $[NiL_{BZ}(NO_2)(ClO_4)]$ which was dried under vacuum over silica gel.

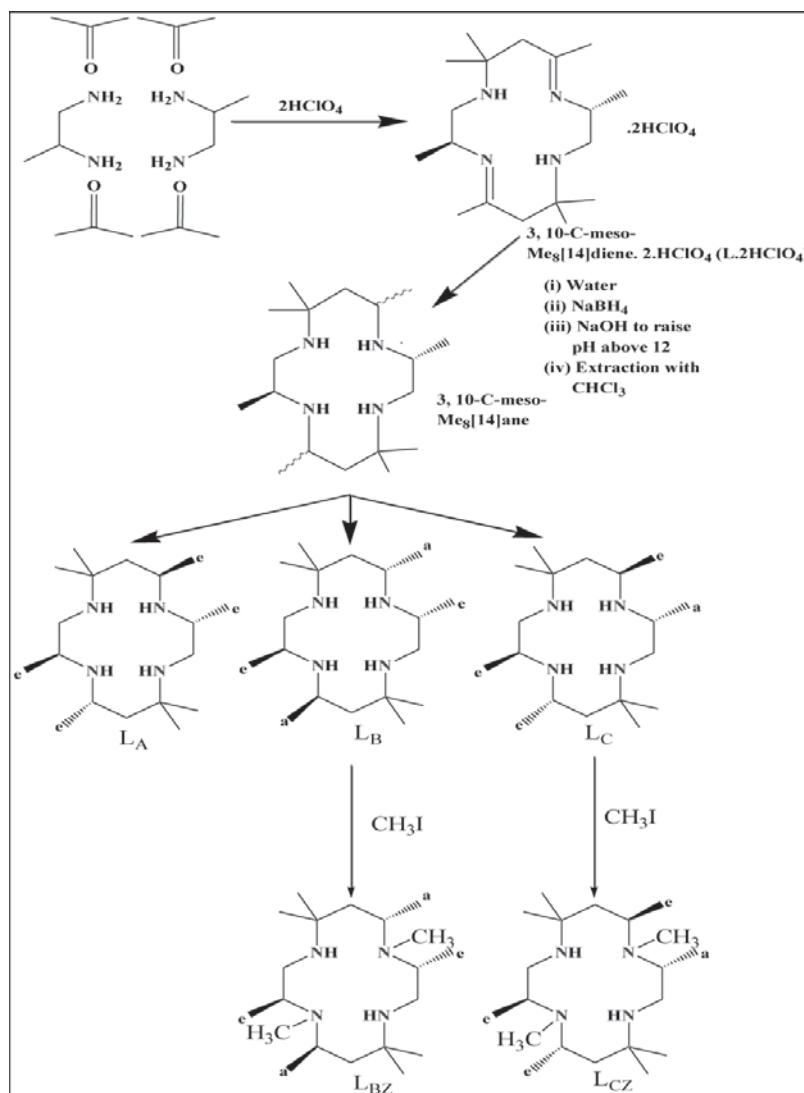
2.4.1.3 $[NiL_{BZ}(NO_3)(ClO_4)]$

0.299 g (0.5 mmol) $[NiL_{BZ}](ClO_4)_2$ and 0.101 g (1.0 mmol) KNO_3 were suspended separately in 30 mL of dry and hot methanol and mixed while hot. The solution turned yellow. The resulting mixture was then stirred on a magnetic stirrer for about 1.5 hours. The mixture was completely dried on a water bath. The dry product was extracted with chloroform and undissolved product rejected. The violet chloroform extract was heated to dryness to yield a violet product, $[NiL_{BZ}(NO_3)(ClO_4)]$ which was dried under vacuum over silicagel. However the violet product was found to convert into yellowish in open air i.e in presence of moisture.

2.4.2 Syntheses of axial addition products of $[NiL_{CZ}](ClO_4)_2$

2.4.2.1 $[NiL_{CZ}(NO_2)_2]$

0.299 g (0.5 mmol) $[NiL_{CZ}](ClO_4)_2$ and 0.085 g (1.0 mmol) $NaNO_2$ were suspended separately in 25 mL hot dry and hot methanol and mixed while hot. The solution turned yellow. The resulting mixture was then stirred on a magnetic stirrer for about 2-3 hours. The mixture was completely dried on a water bath. The dry product was extracted with



Scheme-1: Syntheses of diene ligand, isomeric ligands and N-pendent derivatives

chloroform and undissolved material rejected.

The bluish chloroform extract was heated to dryness to produce a bluish product, [NiL_{CZ}(NO₂)₂] which was dried under vacuum over silicagel.

2.4.2.2 Preparation of [NiL_{CZ}(NO₃)₂]

A suspension of 0.299 g (0.5 mmol) [NiL_{CZ}](ClO₄)₂ in 30 mL dry methanol and a suspension of 0.101 g (1.0 mmol) of KNO₃ in 30 mL of same solvent were mixed together. A yellow color appeared immediately. The resulting mixture was stirred on a magnetic

stirrer for about 2-3 hours. The reaction mixture was heated on a steam bath and completely dried. The orange product was treated with hot chloroform which gave a pink-violet color to the chloroform solution. The mixture was then filtered off. The filtrate was evaporated to dryness by heating on a steam bath to result a pink-violet solid product, [NiL_{CZ}(NO₃)₂] which was stored hot under vacuum over silica gel. However the violet product was found to convert into yellowish in open air i.e in presence of moisture.

2.5 Physical measurements

Microanalysis (C, H, N analysis) of the complexes have been carried out on a C, H, N analyzer at the Inorganic Research Laboratory of the Institut der Anorganische und Angewandte Chemie, Hamburg Universitaet, Germany and at Department of Chemistry, Kyungpook National University, Daegu, South Korea. The percentage of nickel(II) was estimated by using the complexometric titration method in the Department of Chemistry, University of Chittagong. IR spectra were recorded on a Shimadzu IR 20 spectrophotometer as KBr disks in Kyungpook National University, Daegu, South Korea. UV-visible spectra were recorded on a Shimadzu UV-visible spectrophotometer in CHCl_3 and H_2O . Conductance measurements were carried out on a conductivity bridge Hanna instrument HI-8820 in CHCl_3 and H_2O . Magnetic measurements were performed on Gouy Balance which was calibrated using $\text{Hg}[\text{Co}(\text{NCS})_4]$ at Department of Chemistry, University of Chittagong.

2.6 Antibacterial activities

Antibacterial activities of the ligands and their complexes against selected gram-positive and gram-negative bacteria were investigated by the disc diffusion method. Paper disc (6 mm in diameter) and Petri plates (70 mm in diameter) were used throughout the experiment. Pour plates were made with sterilized melted nutrient agar NA (45°C) and after solidification of pour plates, the test organisms (suspension in sterilized water) were spread uniformly over the pour plates with sterilized glass rod separately. The paper discs after soaking with test chemicals (1.0 mg/1mL in DMSO) were placed at the center of the inoculated pour plates. A control plate was also maintained in each case with DMSO. At first the plates were left for four hours at low temperature (4°C) and the test chemicals diffused from disc to the surrounding medium by this time. The plates were then incubated at $(35\pm 2)^\circ\text{C}$ for growth of test organisms and were observed at 24-hours. The activity was expressed in terms of zone of inhibition in mm. The results for all concerned complexes have been reported after subtracting values for solvent DMSO itself. Tests were repeated thrice for statistical analysis.

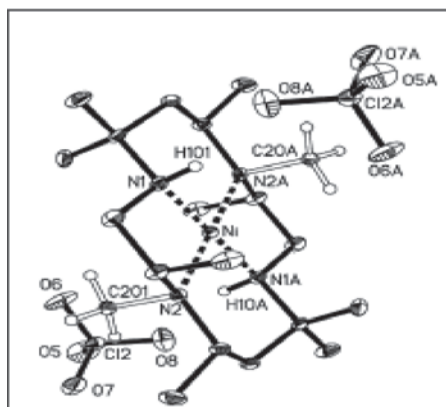
2.7 Antifungal activities

The in vitro antifungal activities of the complexes against selected phytopathogenic fungi were assessed by the poisoned food technique. Potato Dextros Agar (PDA) was used as a growth medium. Dimethylsulphoxide was used as the solvent to prepare solutions of the tested compounds. The solutions were then mixed with the sterilized PDA so as to maintain concentrations of the compounds of 0.01%. 20 ml of these solutions were each poured into a petri dish. After the medium had solidified, a 5 mm mycelial disc of each fungus was placed in the center of each assay plate, along with a control. Linear growth of the fungus was measured in mm after five days of incubation at $25 \pm 2^\circ\text{C}$.

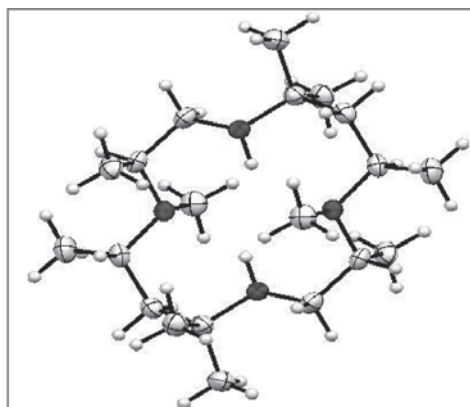
3. Results and Discussion

The ligand salt ($\text{L} \cdot 2\text{HClO}_4$) and isomeric ligands (L_A , L_B & L_C) of its reduced form were isolated as per literature [16-18] (Scheme-1). The N-pendent derivatives (L_{BZ} & L_{CZ}) of isomeric ligands (L_B & L_C) and nickel(II) diperchlorate complexes $[\text{NiL}_{BZ}](\text{ClO}_4)_2$ and $[\text{NiL}_{CZ}](\text{ClO}_4)_2$ of them have been prepared and characterized as procedure adopted in the literature [15]. The X-ray crystallographic structures (Fig-1) of the N-pendent ligand L_{BZ} and its nickel(II) diperchlorate complex $[\text{NiL}_{BZ}](\text{ClO}_4)_2$ have also been reported [15]. These square planar complexes, $[\text{NiL}_{BZ}](\text{ClO}_4)_2$ and $[\text{NiL}_{CZ}](\text{ClO}_4)_2$ underwent axial addition reactions to give a variety of trans-derivatives on reactions with NaNO_2 & KNO_3 in proper ratio. Moreover the complex, $[\text{NiL}_{BZ}](\text{ClO}_4)_2$ on extraction with CHCl_3 and subsequent dryness of CHCl_3 extract produced six coordinated axial addition product $[\text{NiL}_{BZ}(\text{ClO}_4)_2]$. The molar conductivity values of $0 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ of these complexes in chloroform supported the formation of six coordinate non-electrolytic octahedral complexes as reported earlier for analogous complexes [18]. All these nickel(II) complexes are found to be paramagnetic as expected. Since $^1\text{H-NMR}$ spectra of paramagnetic compounds are less informative so $^1\text{H-NMR}$ spectra of all the derivative complexes have not been measured. In this relation, the stereochemistry of all derivatives has been assigned on the basis that axial addition takes place without change of conformation and

configuration of the ligand of original complex [14, 19, 20]. The details of characterization of these six coordinate octahedral complexes have been described as follows.



$[\text{NiL}_{\text{BZ}}](\text{ClO}_4)_2$



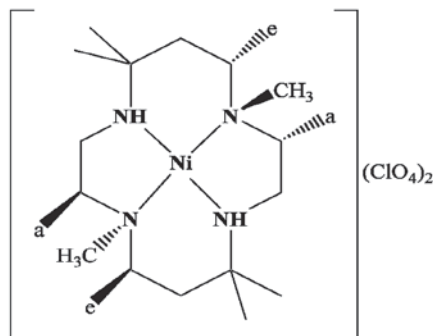
L_{BZ}

Fig. 1: X-ray structures L_{BZ} and $[\text{NiL}_{\text{BZ}}](\text{ClO}_4)_2$

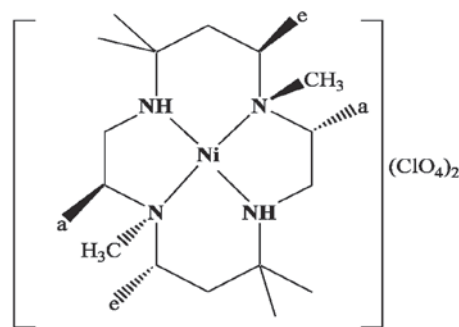
adopted in the literature [14]. The structure of L_{BZ} (Fig-1) has been confirmed by X-ray crystallography [14].

3.2 Nickel (II) diperchlorate complexes

The complexes, $[\text{NiL}_{\text{BZ}}](\text{ClO}_4)_2$ (Stru-I) and $[\text{ZnL}_{\text{CZ}}](\text{ClO}_4)_2$ (Stru-II) were characterized as per our earlier report [14] and the structure of



Stru- I
 $[\text{NiL}_{\text{BZ}}](\text{ClO}_4)_2$



Stru- II
 $[\text{ZnL}_{\text{CZ}}](\text{ClO}_4)_2$

spectrum (Table 2) of this complex shows the $\nu_{\text{N-H}}$, $\nu_{\text{C-C}}$, $\nu_{\text{C-H}}$, $\nu_{\text{C=O}}$, $\nu_{\text{N-H}}$ bands at the proper positions. The spectrum further exhibits bands at 1100 cm^{-1} , 1180 cm^{-1} , 910 cm^{-1} , and 620 cm^{-1} due to ClO_4^- ion. The splitting of a band at 1080 cm^{-1} into 1140 cm^{-1} and 910 cm^{-1} is an indication [20] of presence of coordinated perchlorate (ClO_4^-). The positions of these perchlorate bands strongly support the

3.1 Ligands

Characterization of the N-pendent derivatives, L_{BZ} and L_{CZ} of the isomeric ligands L_{B} and L_{C} respectively were carried out by the procedure

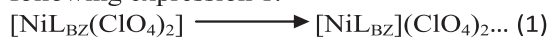
$[\text{NiL}_{\text{BZ}}](\text{ClO}_4)_2$ (Fig-1) has been confirmed by X-ray crystallography [14].

3.3 Diperchloratonickel (II) complex

Extraction of $[\text{NiL}_{\text{BZ}}](\text{ClO}_4)_2$ with hot chloroform gave pink product, $[\text{NiL}_{\text{BZ}}](\text{ClO}_4)_2$ where two ClO_4^- ions have been incorporated into the cavity of the macrocycle in trans positions. Infrared

unidentate mode of coordination [21]. The conductivity value of 0 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ in chloroform is an indication of nonelectrolytic nature of the complex (Table-3) i.e. two ClO_4^- groups are in the coordination sphere. The color of the complex in chloroform remained (pink-violet) intact as in the solid state, i.e. the geometry and conformation of this complex remained unchanged in chloroform. But the

conductance value of $168 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ of yellow aqueous solution of this complex, corresponds to 1:2 electrolytes. i.e. the octahedral diperchloratonickel(II) complex converts into square planar complex in water as observed for analogous complexes [15]. This conversion can be explained by the following expression 1.



The magnetic moment value of this complex is 2.89 B.M. (Table-4) which corresponds to two unpaired electrons as expected for octahedral nickel(II) complex. The d-d bands at 924 and

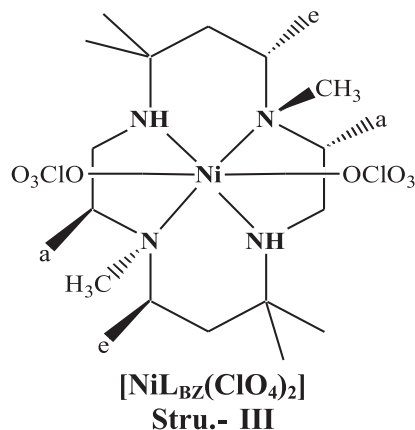


Table-1: Analytical data of nickel(II) complexes

Complexes	% of C		% of H		% of N		% of Ni	
	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found
[NiL _{BZ} (ClO ₄) ₂]	40.15	40.13	7.36	7.38	9.36	9.34	9.82	9.80
[NiL _{BZ} (NO ₂)(ClO ₄)]	44.10	44.06	8.08	8.02	12.86	12.80	10.78	10.75
[NiL _{CZ} (NO ₂) ₂]	48.90	48.98	8.96	8.94	17.11	17.08	11.96	11.99
[NiL _{BZ} (NO ₃)(ClO ₄)]	42.84	42.80	7.85	7.88	12.49	12.50	10.47	10.43
[NiL _{CZ} (NO ₃) ₂]	45.91	45.87	8.41	8.45	16.07	16.10	11.23	11.21

Table-2: Infrared spectral data of nickel (II) complexes

Complexes	Assignment (cm ⁻¹)					
	$\nu_{\text{N-H}}$	$\nu_{\text{C-H}}$	ν_{CH_3}	$\nu_{\text{C-C}}$	$\nu_{\text{Ni-N}}$	Others
[NiL _{BZ} (ClO ₄) ₂]	3200	2985	1370	1140	540	ν_{ClO_4} , 1140, 1080, 980, 620
[NiL _{BZ} (NO ₂)(ClO ₄)]	3180	2970	1380	1193	550, 440	ν_{ClO_4} , 1115, 1085, 980, 625 $\nu_{\text{NO}_2(\text{asym})}$, 1455; $\nu_{\text{NO}_2(\text{sym})}$, 1370, δ_{NO_2} , 820
[NiL _{CZ} (NO ₂) ₂]	3182	2968	1380	1195	570, 440	$\nu_{\text{NO}_2(\text{asym})}$, 1465; $\nu_{\text{NO}_2(\text{sym})}$, 1375, δ_{NO_2} , 825
[NiL _{BZ} (NO ₃)(ClO ₄)]	3100	2985	1375	1165	540	ν_{ClO_4} , 1120, 1065, 965, 622; ν_{NO_3} , 1440, 1325
[NiL _{CZ} (NO ₃) ₂]	3090	2980	1360	1180	540	ν_{NO_3} , 1445, 1330

745 nm (Table 4) in its electronic spectrum of CHCl₃ solution and lower molar extinction coefficient values strongly support the octahedral structure. Thus the following structure (Str.-III) has been proposed for the complex [NiL_{BZ}(ClO₄)₂].

3.4 Nitro nickel(II) complexes

In the reactions of square planar [NiL_{BZ}](ClO₄)₂ and [NiL_{CZ}](ClO₄)₂ with KNO₂ in the molar ratio of 1:2 yielded violet [NiL_{BZ}(NO₂)(ClO₄)₂] and bluish [NiL_{CZ}(NO₂)₂] respectively. The infrared spectra (Table-2) of both complexes display bands corresponding to $\nu_{\text{N-H}}$, $\nu_{\text{C-C}}$, $\nu_{\text{C-H}}$, $\nu_{\text{Ni-N}}$ and ν_{CH_3} in the proper regions and appearance of bands at 820-825 cm⁻¹ can be assigned for δ_{NO_2} stretching frequencies; presence of band at 440 cm⁻¹ due to $\nu_{\text{Ni-N}}$ and other bands strongly support the complexes to be of N-bonded nitro complex. Absence of any band around 1100 cm⁻¹ and 620 cm⁻¹ due to ν_{ClO_4} indicated that both the ClO₄ in [NiL_{CZ}(NO₂)₂] are completely replaced by NO₂ ions. Both the complexes exhibit the bands at 1445-1465 cm⁻¹ and 1370-1375 cm⁻¹ due to $\nu_{\text{NO}_2(\text{asym})}$ and $\nu_{\text{NO}_2(\text{sym})}$ respectively. The infrared spectrum of [NiL_{BZ}(NO₂)(ClO₄)₂] further displays bands at 1115 cm⁻¹, 1085 cm⁻¹, 980 cm⁻¹ and 625 cm⁻¹ due to ClO₄⁻ ion. The splitting of a band at

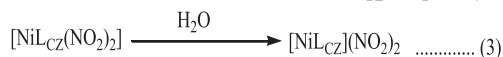
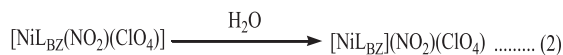
Table-3: Molar conductivity data of nickel(II) complexes

Complexes	Color in solid	In chloroform		In water	
		Color	Conductance (ohm ⁻¹ cm ² mole ⁻¹)	Color	Conductance (ohm ⁻¹ cm ² mole ⁻¹)
[NiL _{BZ} (ClO ₄) ₂]	Pink	Pink	0	Yellow	168
[NiL _{BZ} (NO ₂)(ClO ₄)]	Violet	Violet	0	Yellow	154
[NiL _{CZ} (NO ₂) ₂]	Bluish	Bluish	0	Yellow	185
[NiL _{BZ} (NO ₃)(ClO ₄)]	Pale- Yellow	Violet	0	Yellow	185
[NiL _{CZ} (NO ₃) ₂]	Pale- Yellow	Pink- Violet	0	Yellow	207

Table-4: Electronic spectral and magnetic moment data of nickel(II) complexes

Complexes	λ_{\max} nm (ϵ_{\max})		μ_{eff} (B.M)
	In water	In chloroform	
[NiL _{BZ} (ClO ₄) ₂]	761, 536, 345	924, 745, 256	2.89
[NiL _{BZ} (NO ₂)(ClO ₄)]	-	889(3), 478(39)	2.85
[NiL _{CZ} (NO ₂) ₂]	-	772(6), 492, 253	2.82
[NiL _{BZ} (NO ₃)(ClO ₄)]	442, 246	909, 763, 269	0.85
[NiL _{CZ} (NO ₃) ₂]	455	809, 476, 255	1.05

1085 cm⁻¹ into 1115 cm⁻¹ and 980 cm⁻¹ is an indication of presence of coordinated perchlorate (ClO₄⁻) ion. The position of these perchlorate bands strongly supports the unidentate mode of coordination [22]. Thus the IR-spectral analyses gave the evidence of coordination of perchlorate ion (ClO₄⁻) as well as of nitro (NO₂⁻) group in [NiL_{BZ}(NO₂)(ClO₄)]. The conductance value of 0 ohm⁻¹cm²mole⁻¹ of these complexes in chloroform (in which solvent color of the products are as the same as freshly prepared complexes) corresponds to nonelectrolytic nature of the complexes. i.e. the octahedral structure of the complexes. But the molar conductivity values of 154-185 ohm⁻¹cm²mole⁻¹ of their yellow aqueous (Table-3) solutions can be attributed to the formation of square planar species of 1:2 electrolytic nature as discussed earlier [14]. This conversion can be expressed by the following equations 2 & 3.

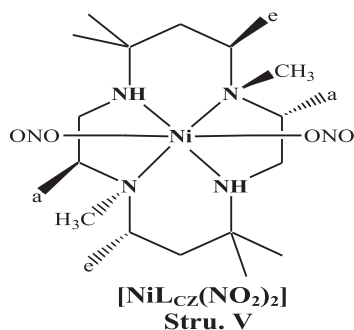
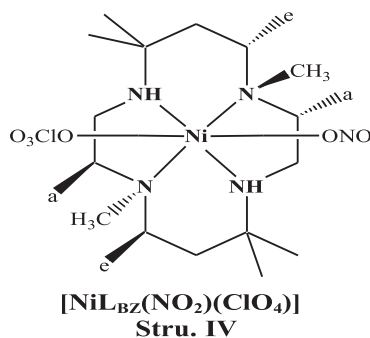


The magnetic moment values (Table-4) of all these complexes correspond to paramagnetic compounds of octahedral structure having two unpaired electrons as expected. The electronic spectral data of these complexes (Table-4) show the d-d bands in chloroform (where color remained unchanged) at 884 nm and 772 nm

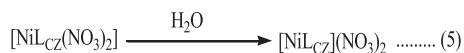
and lower extinction co-efficients (ϵ_{\max} =3 and 6). This observation is the good agreement with the octahedral structure of these complexes. As per above discussion the following structures, Str.-IV and Str.-V are proposed for [NiL_{BZ}(NO₂)(ClO₄)] and [NiL_{CZ}(NO₂)₂] respectively.

3.5 Nitratonickel (II) complexes

Interaction of [NiL_{BZ}](ClO₄)₂ and [NiL_{CZ}](ClO₄)₂ with KNO₃ in the ratio of 1:2 produced solid mass, which on extraction with chloroform gave violet [NiL_{BZ}(NO₃)(ClO₄)] and pink-violet [NiL_{CZ}(NO₃)₂] respectively. The infrared spectra (Table-2) of these complexes show bands due to $\nu_{\text{N-H}}$, $\nu_{\text{C-C}}$, $\nu_{\text{C-H}}$, and ν_{CH_3} , in the proper regions. The spectra of them further exhibit bands at 1440 cm⁻¹ & 1325 cm⁻¹ for [NiL_{BZ}(NO₃)(ClO₄)] and 1445 cm⁻¹ & 1330 cm⁻¹ for [NiL_{CZ}(NO₃)₂] respectively due to coordinated NO₃⁻ groups. Position of these bands and their separation values (near 115 cm⁻¹) correspond to unidentate [21] mode of coordination. But absence of any band at around 1100 cm⁻¹ and 620 cm⁻¹ in case of [NiL_{CZ}(NO₃)₂] demonstrates that all the perchlorates are completely replaced by NO₃⁻ groups. However infrared spectrum (Table-2) of [NiL_{BZ}(NO₃)(ClO₄)] additionally exhibits strong bands at around 1100 cm⁻¹ (splitted) and 620 cm⁻¹ demonstrating the coordination of ClO₄⁻ group. i.e. all the ClO₄⁻ ions were not replaced by the NO₃⁻ groups. This sort of



different behaviour of $[\text{NiL}_{\text{BZ}}](\text{ClO}_4)_2$ towards addition reactions is not well understood. However the stereochemistry of L_{BZ} in $[\text{NiL}_{\text{BZ}}](\text{ClO}_4)_2$ may be responsible for coordination of ClO_4^- ion. The molar conductivity value of $0 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ (Table-3) of the complexes in CHCl_3 in which solvent color of the complexes remained violet and pink-violet indicate that the complexes are non-electrolytic in nature, i.e. anions are in the coordination sphere as expected for six coordinate octahedral nickel (II) complexes. Similar observation was also noted for corresponding copper(II) and nickel(II) complexes [23] of the L_{B} and L_{C} ligands. The molar conductivity values of $185\text{-}207 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ of yellow aqueous solutions of these complexes corresponding to 1:2 electrolytes demonstrate that water forces anions to come out of the coordination sphere to convert octahedral complexes to square planar complexes as happened in corresponding perchlorato and nitro complexes. This conversion can be expressed by the following equations 4 & 5.



These complexes were found to readily convert into yellowish square planar complexes on exposure to open air i.e. in presence of moisture. All the expected d-d bands at $763\text{-}908\text{nm}$ corresponding to octahedral nickel(II) complexes (Table-4) have been recorded for these complexes in chloroform. However the electronic spectra of yellow aqueous solutions of these complexes are corresponding to square planar nickel(II) complexes. The bands around $246\text{-}269 \text{ nm}$ are attributed to the charge transfer transitions. The magnetic moment values of pure violet

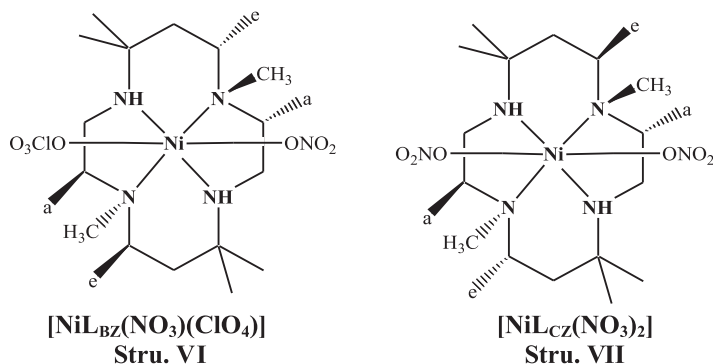
and pink violet products could not be obtained since on contact with moisture they partially convert into yellow square planar species as observed for analogous nickel(II) complexes [14]. Thus magnetic moment values of $0.85\text{-}1.05 \text{ BM}$ for these yellowish complexes (Table-4) also indicate that the octahedral nickel(II) complexes are readily converted into square planar complexes. On the basis of above discussion following octahedral structures Str. VI and Str. VII are proposed for the complexes $[\text{NiL}_{\text{BZ}}(\text{NO}_3)(\text{ClO}_4)]$ and $[\text{NiL}_{\text{CZ}}(\text{NO}_3)_2]$ respectively.

3.6 Antibacterial activities

Antibacterial activities of macrocycles and their complexes have not been studied extensively except few cases [23-26]. So it is noteworthy to examine whether these ligands and complexes show any such activity or not. For the purpose, investigation on the antibacterial activities of concerned ligands, their nickel(II) complexes, solvent DMSO and standard antibiotic 'Ampicilin' have been carried out against some important selected bacteria, *Salmonella typhi*, *Shigella dysenteriae*, *Escherichia coli* and *Bacillus cereus* which cause different fatal diseases. The results (Table-5) show that the ligands and their concerned Ni(II) complexes show different antibacterial activities to a measurable extent but some complexes do not show any such activity.

3.7 Antifungal activities

Studies on antifungal activities of macrocycles, and their complexes have also not been carried out extensively except some reports [26-28]. So it appeared interesting to see whether the compounds involved in this study exhibit any such activity or not. Thus the

**Table-5:** Antibacterial activities of macrocyclic compounds

Compounds	Diameter of zone of inhibition in mm after 24 hours			
	Gram negative		Gram Positive	
	<i>Salmonell typhi</i>	<i>Shigella dysenteriae</i>	<i>Escherichia coli</i>	<i>Bacillus cereus</i>
L _{BZ}	0	0	0	0
L _{CZ}	0	0	0	0
[NiL _{BZ} (ClO ₄) ₂]	6	6	9	10
[NiL _{BZ} (NO ₂)(ClO ₄)]	7	8	0	10
[NiL _{CZ} (NO ₂) ₂]	12	06	11	20
[NiL _{BZ} (NO ₃)(ClO ₄)]	5	02	5	0
[NiL _{CZ} (NO ₃) ₂]	6	06	09	22
Ni(CH ₃ COO) ₂	3	2	3	0
DMSO	0	0	0	0
Ampicillin**	22	19	26	24

** Standard Antibiotic

antifungal activities of present isomeric N-pendent macrocycles, their nickel(II) complexes, solvent DMSO and standard antibiotic 'Gryseofulvin' have been studied against the five selective phytopathogenic fungi such as *Macrophomina phaseolina*, *Alternaria alternata*, *Fusarium equiseti*, *Colletotrichums corcolei*, and *Botrgodiplodia theobromae*. It is evident from the results (Table-6) that the macrocycles and their complexes under investigation show some antifungal activities. The activities of ligands were found to decrease upon coordination to nickel(II) in most of the cases. A minute comparison of the activities of the present ligands and complexes shows that the present compounds have varied amount of effects on the inhibition of mycelial growth. It has been noted that the N-substituted ligands have higher rate of inhibition on mycelial growth [20] and this rate is highest in case of N-

methyl substituted ligands L_{BZ} and L_{CZ}. Further (in most of cases) though the ligands are found to show higher inhibition on the growth of *Macrophomina phaseolina* in comparison with other fungi, but in most cases complexes exhibit better activities against *Fusarium equiseti*, *Colletotrichums corcolei* and *Botrgodiplodia theobromae* compared to other two fungi. It is also observed that for a particular type of complexes, e. g. nitro and nitrate complexes of these N-substituted pendent ligands have different effects on these organisms. Moreover these complexes exhibit higher activities in comparison to corresponding cobalt(III) complexes of their isomeric ligands [29]. From the above discussion it can be concluded that nature of ligands, metals and type of axial ligands play a significant role on the inhibition of mycelial growth. However, reduction of activity on

Table-6: Antifungal activities of macrocyclic compounds

Compounds	% Inhibition of mycelial growth				
	<i>Macrophomina phaseolina</i>	<i>Alternaria alternata</i>	<i>Fusarium equiseti</i>	<i>Colletotrichums corcolei</i>	<i>Botrgodiplodia theobromae</i>
L _{BZ}	52.00	36.00	38.68	39.69	47.58
L _{CZ}	62.65	36.80	38.80	49.62	43.03
[NiL _{BZ} (ClO ₄) ₂]	16.51	8.36	13.13	14.96	31.00
[NiL _{BZ} (NO ₂)(ClO ₄)]	11.23	3.78	2.69	31.63	27.88
[NiL _{CZ} (NO ₂) ₂]	11.00	3.00	31.66	31.33	19.98
[NiL _{BZ} (NO ₃)(ClO ₄)]	2.35	2.38	31.31	26.30	36.35
[NiL _{CZ} (NO ₃) ₂]	10.00	2.58	33.30	31.66	22.23
Ni(OOCCH ₃) ₂	44	20	45	39	38
DMSO	0	0	0	0	0
Griseofulvin	64	68	57	60	52

** Standard Griseofulvin

coordination was found to be low in compared with that of complexes of sulphur containing Schiff bases [30].

Having a look on these results, one cannot make any gradation on the rate of inhibition power of the complexes on a particular bacterial growth. Unlikely their behavior toward antifungal activities, some of the complexes are found to exhibit higher antibacterial activities than their corresponding ligands, whereas these complexes generally show lower antifungal activities than their corresponding ligands. The results of the antimicrobial screening studies of the synthesized compounds presented herein showed that the ligands and their complexes are very effective toward phytopathogens than those of bacteria. By the chelation theory [27], the increased activity of the complexes can be explained. The disturbance of the respiration process of the cell and blockage the synthesis of protein, may restrict further growth of the organism [32] which can also be responsible for the antibacterial activity. However for a clear understanding of the functions responsible for antibacterial activities of macrocycles and their complexes, more studies are needed to be performed with a series of analogous ligands and their complexes against a series of bacteria and fungi.

4. Conclusion

The N-pendent, N, N' dimethyl derivative ligands L_{BZ} and L_{CZ} of isomeric ligands L_B and L_C (isomers of Me₈[14]ane) respectively produced square planar diperchlorate nickel(II) complexes [NiL_{BZ}](ClO₄)₂ and [NiL_{CZ}](ClO₄)₂ when reacted with nickel(II) acetate followed by subsequent addition of NaClO₄.6H₂O. These square planar complexes underwent axial addition reactions with NO₂⁻ and NO₃⁻ to form corresponding octahedral complexes, [NiL_{BZ}(NO₂)(ClO₄)] & [NiL_{CZ}(NO₂)₂] and [NiL_{BZ}(NO₃)(ClO₄)] & [NiL_{CZ}(NO₃)₂] respectively. Moreover [NiL_{BZ}](ClO₄)₂ underwent self axial addition reaction while extracted with CHCl₃. It has been noted that, the complex [NiL_{BZ}](ClO₄)₂ has a fascination to incorporate always a ClO₄⁻ ion in its axial position. This phenomenon may be due to the stereochemical difference between L_{BZ} and L_{CZ}. All the complexes are found to remain intact in geometry in chloroform; however in H₂O, they change their geometry from octahedral to square planar. Though the ligands are inactive as antibacterial agents but all the complexes are found to be active against concerned bacteria. Regarding antifungal activity, the activities are found to decrease on coordination.

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