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Synthesis, Characterization and Biomedical Studies of Cadmium(II) Complexes of an *N*-Pendent Polyazamacrocyclic Ligand

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Abstract

An isomeric octamethyl-substituted tetraazamacrocycle, L_B (a C-chiral isomer of 3,10-C-meso-Me_8[14]ane), was reacted with methyl iodide in a 1:4 molar ratio under reflux in methanol to yield a white N-pendent derivative ligand, L_{BZ}. Complexation of L_{BZ} with cadmium(II) perchlorate produced a six-coordinate diperchlorato octahedral complex, $[CdL_{BZ}(ClO_4)_2]$, and a five-coordinate square-pyramidal complex, $[CdL_{BZ}(ClO_4)]$.

The diperchlorato complex underwent axial substitution reactions with NCS^-, NO_3^-, NO_2^-, Cl^-, Br^- and I^-, forming a series of six-coordinate octahedral complexes: $[CdL_{BZ}(NCS)_2]$, $[CdL_{BZ}(NO_3)(ClO_4)]$, $[CdL_{BZ}(NO_2)(ClO_4)]$, $[CdL_{BZ}Cl(ClO_4)]$, $[CdL_{BZ}Br_2]$ and $[CdL_{BZ}I_2]$. All newly synthesized compounds were characterized using elemental analysis, IR, UV–visible and ^{1}H-NMR spectroscopy, molar conductivity and magnetic susceptibility measurements.

The antibacterial activities of L_{BZ} and its cadmium(II) complexes were evaluated against selected phytopathogenic bacteria. While the free ligands were inactive, most cadmium(II) complexes exhibited significant antibacterial activity, particularly against *Bacillus cereus*.

Keywords: *Macrocyclic ligands; N-pendent derivative; Cadmium(II) complexes; Spectroscopic characterization; Antibacterial activity.*

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সারমর্ম: একটি প্রতিস্থাপিত টেট্রাঅ্যাজা অক্টামিথাইল আইসোমেরিক ম্যাক্রোসাইকেল, L_B (3,10-C-meso-Me_8[14]ane এর একটি C-chiral আইসোমার) মিথানলিক দ্রবণে CH_3I এর সাথে 1:4 অনুপাতে রিফ্লাক্স করার ফলে N-CH_3 বাহু যুক্ত খইত দ্বারা চিহ্নিত একটি সাদা পণ্য তৈরি হয়। L_{BZ} ক্যাডমিয়াম (II) লবণের সাথে বিক্রিয়ার মধ্য দিয়ে ছয় সন্নিবেশ বন্ধন বিশিষ্ট অষ্টতলকীয় এবং পাঁচ সন্নিবেশ বন্ধন বিশিষ্ট বর্গাকার পিরামিডাল সাদা জটিলযৌগ, যথাক্রমে $[CdL_{BZ}(ClO_4)_2]$ এবং $[CdL_{BZ}(ClO_4)](ClO_4)$ তৈরি করে। $[CdL_{BZ}(ClO_4)_2]$ এর উপর NCS^-, NO_3^-, NO_2^-, Cl^-, Br^- এবং I^- এর সাথে অক্ষীয় প্রতিস্থাপন বিক্রিয়াগুলি সাদা রঙের ছয় সন্নিবেশ বন্ধন বিশিষ্ট অষ্টতলীয় প্রতিস্থাপিত পণ্য, যথাক্রমে $[CdL_{BZ}(NCS)_2]$,

$[CdL_{BZ}(NO_3)(ClO_4)]$, $[CdL_{BZ}(NO_2)(ClO_4)]$ $[CdL_{BZ}Cl(ClO_4)]$, $[CdL_{BZ}Br_2]$ এবং $[CdL_{BZ}I_2]$ তৈরি করেছে। জটিলযৌগগুলিকে বিভিন্ন বিশ্লেষণাত্মক পরামিতির ভিত্তিতে চরিত্রায়ন করা হয়েছিল। লিগ্যান্ড L_{BZ} এবং এর জটিলযৌগগুলির বিভিন্ন ফাইটোপ্যাথোজেনিক ব্যাকটেরিয়ার প্রতি অ্যান্টিব্যাকটেরিয়াল সক্রিয়তা পরীক্ষা করা হয়েছিল। জটিলযৌগগুলি প্রায় সকল ব্যাকটেরিয়ার প্রতি উল্লেখ করার মতো অ্যান্টিব্যাকটেরিয়াল সক্রিয়তা দেখিয়েছে।

1. Introduction

Macrocyclic ligands and their metal complexes have achieved engrossing position due to their role in different sectors of science [1-2]. However the macrocyclic compounds are also playing important roles in pharmacological [3] and medicinal sectors because of their antibacterial [4], antifungal [5], anticancer [6] and therapeutic criteria [7]. 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 [14]. Therefore, it was our interest to bring some new cadmium(II) complexes of L_{BZ} and their axial substitution reaction products which are expected to have biological activities. In this connection, the ligand salt, $L.2HClO_4$ and three isomeric ligands, L_A, L_B & L_C of its reduced form (Scheme-1) [16-18] as well as N-pendent derivative L_{BZ} [14] with N, N′-dimethyl groups of the isomeric ligands L_B have been prepared as per literature. The ligand L_{BZ} on interaction with cadmium(II) perchlorate salt produced two complexes, $[CdL_{BZ}(ClO_4)_2]$ and $[CdL_{BZ}(ClO_4)](ClO_4)$. Moreover $[CdL_{BZ}(ClO_4)_2]$ underwent axial substitution reactions to produce a variety of axial substitution derivatives. Herein we report studies on two new cadmium(II) complexes $[CdL_{BZ}(ClO_4)_2]$ and $[CdL_{BZ}(ClO_4)](ClO_4)$ of concerned N-pendent macrocyclic ligand L_{BZ} and axial substitution reaction products of $[CdL_{BZ}(ClO_4)_2]$.

2. Experimental

2.1 Materials 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 and L_C)

Synthesis of the parent ligand, 3,10-C-meso-Me_8[14]dienedihydroperchlorate (L. $2HClO_4$), reduction of this diene and resolution of isomeric Me_8[14]anes, (L_A, L_B & L_C) were carried out as per our earlier studies [15-17].

2.2.2 Syntheses of N, N′-dimethyl pendent ligands L_{BZ}

Synthesis of the N-pendent derivative, L_{BZ} of the isomeric ligand L_B was carried out as per our earlier studies [15].

2.3 Metal complexes

2.3.1 Syntheses of cadmium(II) complexes of the ligand L_{BZ}

2.3.1.1 Syntheses of diperchloratocadmium(II) complex, $[CdL_{BZ}(ClO_4)_2]$ and monoperchloratocadmium(II) perchlorate complex, $[CdL_{BZ}(ClO_4)](ClO_4)$

Cadmium(II) perchlorate (0.3104 g, 1.0 mmol) and L_{BZ} (0.34 g, 1.0 mmol) were separately dissolved in 50 mL methanol and mixed together. The solution was heated on a water bath for 1 hour and allowed to dry. The product was treated with chloroform and filtered. The residue was solid product, $[CdL_{BZ}(ClO_4)](ClO_4)$ and chloroform solution was evaporated to dryness to yield solid product, $[CdL_{BZ}(ClO_4)_2]$. These products were stored in a desiccator over silica gel.

N.B: Melting point of these products could not be measured because of explosive nature of perchlorate ions.

Anal. Calcd. for $[CdL_{BZ}(ClO_4)](ClO_4)$ (%): C, 36.84; H, 6.75; N, 8.59. Found: C, 36.88; H, 6.71; N, 8. 53.

Anal. Calcd. for $[CdL_{BZ}(ClO_4)](ClO_4)$ (%): C, 36.84; H, 6.75; N, 8.59. Found: C, 36.81; H, 6.78; N, 8.55.

2.3.1.2 Syntheses of axial substitution products of diperchloratocadmium(II) complex, $[CdL_{BZ}(ClO_4)_2]$

2.3.1.2.1 $[CdL_{BZ}(NCS)]$

$[CdL_{BZ}(ClO_4)_2]$ (0.65 g, 1.0 mmol) of and KCNS (0.20 g, 2.0 mmol) were separately suspended and dissolved respectively in a 50 mL methanol and mixed together. The suspension was heated on a water bath for 1 hour and allowed to dry. The product was extracted with chloroform and chloroform extract was evaporated to dryness to give solid product, $[CdL_{BZ}(NCS)_2]$. The product was stored in a desiccator over silica gel.

Anal. Calcd. for $[CdL_{BZ}(NCS)_2]$ (%): C, 46.45; H, 7.74; N, 14.78. Found: C, 46.41; H, 7.62; N, 14.66.

2.3.1.2.2 $[CdL_{BZ}Br_2]$, $[CdL_{BZ}I_2]$, $[CdL_{BZ}Cl(ClO_4)]$, $[CdL_{BZ}(NO_3)(ClO_4)]$ and $[CdL_{BZ}(NO_2)(ClO_4)]$

The complexes $[CdL_{BZ}Br_2]$, $[CdL_{BZ}I_2]$, $[CdL_{BZ}Cl(ClO_4)]$, $[CdL_{BZ}(NO_3)(ClO_4)]$ and $[CdL_{BZ}(NO_2)(ClO_4)]$ have been prepared by following the above procedure except adding solution/suspension of KBr, KI, KCl, KNO_3 and $NaNO_2$ respectively instead of KSCN.

Anal. Calcd. for [$CdL_{BZ}(Br)_2$] (%): C, 39.21; H, 7.19; N, 9.15. Found: C, 39.18; H, 7.13; N, 9.05.

Anal. Calcd. for [$CdL_{BZ}(I)_2$] (%): C, 33.98; H, 6.23; N, 7.93. Found: C, 33.95; H, 6.17; N, 7.88.

Anal. Calcd. for [$CdL_{BZ}Cl(ClO_4)$]. (%): C, 40.86; H, 7.49; N, 9.53. Found: C, 40.79; H, 7.38; N, 9.42.

Anal. Calcd. for [$CdL_{BZ}(NO_3)(ClO_4)$] (%): C, 39.11; H, 7.17; N, 11.41. Found: C, 39.08; H, 7.21; N, 11.34.

Anal. Calcd. for [$CdL_{BZ}(NO_2)(ClO_4)$] (%): C, 40.01; H, 7.34; N, 11.67. Found: C, 39.98; H, 7.31; N, 11.63.

2.3.2 Instrumentations

Infrared spectra were taken as KBr discs in the range 4000-400 cm^{-1} on a Perkin-Elmer-883 infrared spectrophotometer or on a IR Prestige-21 Shimadzu spectrophotometer. Electronic spectra of the samples were recorded on a Shimadzu UV-visible spectrophotometer (UV-1800). Conductance measurements of the metal complexes were done in water, DMF and chloroform solutions at 10^{-3}M using a HANNA instrument with HI 8820N conductivity cell. The magnetic measurements have been carried out by Sherwood scientific magnetic susceptibility balance. Microanalysis of C, H, N of the complexes have been carried out on a C, H, N and S analyzer at the Institut der Anorganische and Angewandte Chemie, Hamburg Universitaet, Germany.

2.3.3 Antibacterial activities

Antibacterial activities of the ligands L_B & L_{BZ} and complexes of L_{BZ} 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 ºC). After solidification of NA, the test organisms (suspension in sterilized water) were spread uniformly over the NA with sterilized glass rod separately. The paper discs after soaking with test chemicals (1 mg per 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 4h at low temperature (4 ºC), and the test chemicals diffused from disc to the surrounding medium by this time. The plates were then incubated at (35±2) ºC for growth of test organisms and were observed at 24 and 48 h intervals. The activity was expressed in terms of the zone of inhibition in mm. The results for all prepared compounds have been reported after subtracting values for solvent DMSO itself. Tests were performed in triplicates for statistical analysis.

3. Results and Discussion

All the prepared cadmium(II) complexes are white as expected. All these complexes have been characterized by using IR, UV-visible, ^{1}H-nmr spectroscopy, as well as by solubility, analytical, magnetochemical and conductance measurements which have been described as follows. Since ^{1}H-nmr spectra of all the complexes could not be run due to lack of facility, the stereochemistry of them have been determined, on the basis that axial addition and substitution takes place without change of configuration and conformation of ligand of the original complexes [11-13]. The UV-visible spectra of these complexes do not provide any d-d band except charge transfer bands as expected for d^{10} system. Thus these spectra do not give any worthwhile information about geometry. The magnotochemical studies of these complexes correspond to diamagnetic species as expected for d^{10} system of Cd(II) complexes.

3.1 N-pendent Ligand L_{BZ}

Characterization of the N-pendent derivative, L_{BZ} of the isomeric ligand L_B has been carried out by the procedure adopted in the literature [14]. The structure of L_{BZ} (Fig-1) has been confirmed by X-ray crystallography [14].

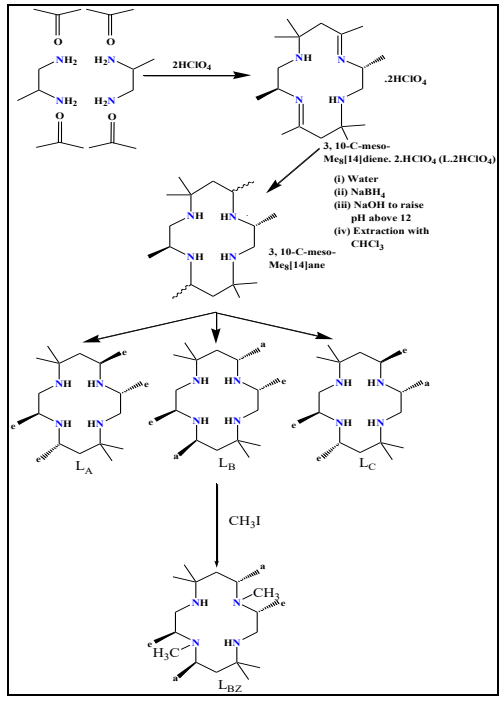


Figure 1. Schematic diagram of the syntheses of diene ligand salt, isomeric ligands, and N-pendent derivative L_{BZ}

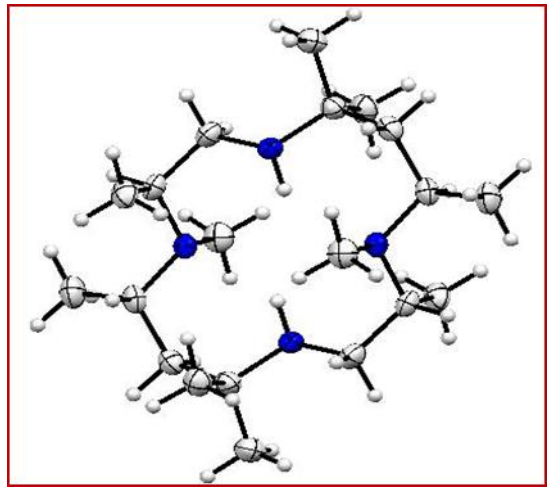


Figure 2. Molecular structure of L_{BZ}

3.2 Cadmium(II) complexes of N-pendent derivative L_{BZ}

All the complexes are white and diamagnetic in nature as expected for the d^{10} system of cadmium(II) complexes.

3.2.1 Cadmium(II) complexes $[CdL_{BZ}(ClO_4)_2]$ and $[CdL_{BZ}(ClO_4)](ClO_4)$ prepared by the direct interaction of L_{BZ} with the cadmium(II) salt

Interaction of the ligand, L_{BZ} with cadmium(II) perchlorate produced white products $[CdL_{BZ}(ClO_4)_2]$ and $[CdL_{BZ}(ClO_4)](ClO_4)$. Solubility data**,** analytical data**,** IR spectral data (Table-1), molar conductivity data (Table-2), ^{1}H-nmr spectra data (Table-3), molar conductivity data, magnotochemical properties support the molecular formula to be $[CdL_{BZ}(ClO_4)_2]$ and $[CdL_{BZ}(ClO_4)](ClO_4)$. The infrared spectra of these complexes exhibit all characteristic bands due to $\nu_{N\text{-}H}$, $\nu_{C\text{-}C}$, $\nu_{Cd\text{-}N}$ and $\nu_{C\text{-}H}$ bands at 3245-3252 cm^{-1}, 1169-1175 cm^{-1}, 515-520 cm^{-1} and 2963-2965 cm^{-1} (Table 1) respectively. The spectra further display perchlorate bands at around 1100 cm^{-1} and 620 cm^{-1} (Table 1). The splitting of a band at 1100 cm^{-1} is an indication of coordination of ClO_4^-. Moreover presence of νCd-O band at 417-448 cm^{-1} is an indication of coordination of Cd with O of ClO_4. The molar conductivity values of these complexes are presented in Table 2. The conductance value of 0 $ohm^{-1}cm^2mole^{-1}$ for the complex, $[CdL_{BZ}(ClO_4)_2]$ in $CHCl_3$ supports the nonelectrolytic nature of the complex i.e. two perchlorate ions (ClO_4^-) are coordinated to cadmium(II) ion. However the molar conductivity value of 70 $ohm^{-1}cm^2$ $mole^{-1}$ (Table-2) in DMSO solution of $[CdL_{BZ}(ClO_4)_2]$ demonstrate that the complex is 1:1 electrolyte in this

solvent [18]. This indicates that the solvent DMSO converts octahedral species into square pyramidal species as indicated by the following expression.

$$[CdL_{BZ}(ClO_4)_2] \underset{}{\overset{DMSO}{\rightleftharpoons}} [CdL_{BZ}(ClO_4)](ClO_4)$$

On the other hand, $[CdL_{BZ}(ClO_4)](ClO_4)$ was insoluble in $CHCl_3$ indicating the electrolytic nature of the complex. However the conductance value of 65 $ohm^{-1}cm^2mole^{-1}$ for this complex in DMSO supports the complex is 1:1 electrolyte in nature [18] as expected for the formula assigned, which means that one perchlorate ion is out of the coordination sphere. But the molar conductivity value of 163 $ohm^{-1}cm^2\ mole^{-1}$ in its aqueous solution demonstrates that this complex is 1:2 electrolyte in this solvent, which is an indication that water converts square pyramidal species into diaqua octahedral species as indicated by the following expression.

$$[CdL_{BZ}(ClO_4)](ClO_4) \xrightarrow{Water} [CdL_{BZ}(H_2O)_2](ClO_4)_2$$

The ^{1}H-nmr spectrum (Table-3) of $[CdL_{BZ}(ClO_4)_2]$ displays three doublets, one overlapped signal resolved into one singlet and one doublet. The doublets at 0.981, 1.034 and 1.141 ppm each corresponding to 3H can be assigned to equatorially oriented methyl groups on three chiral carbons. The overlapped signal at 1.119 ppm corresponding to 9H can be accounted for a singlet integrating to 6H responsible for equatorial components of gem-dimethyl group and a doublet with a integration of 3H responsible for an equatorial methyl protons on one chiral carbon. However the singlets at 1.297 and 1.431 ppm each corresponding to 6H are accountable for axial components of gem-dimethyl groups and methyl protons on N-atoms, respectively. Thus, all equatorial orientation of chiral methyls can be assigned to this complex. Further the spectrum exhibits multiplets at 1.728, 1.939, 2.693 and 3.129 ppm due to CH_2 and CH protons. However the signal at 8.297 ppm can be assigned to NH protons. Based on all these analyses, **Str.-1** and **Str.-2** can be assigned to $[CdL_{BZ}(ClO_4)_2]$ and $[CdL_{BZ}(ClO_4)](ClO_4)$ respectively.

3.3 Axial substitution products of diperchloratocadmium(II) complex, $[CdL_{BZ}(ClO_4)_2]$

The infrared spectra of axial substitution products of $[CdL_{BZ}(ClO_4)_2]$ show all characteristic $\nu_{N\text{-}H}$, $\nu_{C\text{-}C}$, $\nu_{Cd\text{-}N}$ and $\nu_{C\text{-}H}$ bands at 3140-3250 cm^{-1}, 1165-1181 cm^{-1}, 541-552 cm^{-1} and 2962-2971 cm^{-1} (Table 2) respectively. The bands at 2850-2875 cm^{-1} indicate the presence of methyl groups on N-atoms. Moreover, absence of ClO_4^- bands around 1100 cm^{-1} and 620 cm^{-1} in the complexes, $[CdL_{BZ}(NCS)_2]$, $[CdL_{BZ}Br_2]$ and $[CdL_{BZ}I_2]$ indicates that, both the ClO_4^- ions are completely replaced by NCS^-, Br^- and I^-, respectively. On the other hand, The spectra of $[CdL_{BZ}(Cl)(ClO_4)]$,

$[CdL_{BZ}(NO_3)(ClO_4)]$ and $[CdL_{BZ}(NO_2)(ClO_4)]$ further exhibit bands at around 1065 cm^{-1} and 624 cm^{-1} due to the presence of ClO_4^-. The splitting of the band at 1065 cm^{-1} is an indication of the presence of unidentate coordination of perchlorate. These information demand that only one perchlorate ion is replaced by the concerned ions. Moreover, for $[CdL_{BZ}(NCS)_2]$, appearance of sharp ν_{CN} band in the region of 2020 cm^{-1} is a good indication of N-bonded thiocyanate group. This complex also displays $\upsilon_{(CS)}$ band at 850 cm^{-1} and $\delta_{(NCS)}$ at 485 cm^{-1} which do not correspond to ligand in this region and is therefore assigned for a fully N-bonded thiocyanate group [19, 20]. Therefore, this complex can be identified as isothiocyanato complex. However IR spectrum (Table 1) of $[CdL_{BZ}(NO_3)(ClO_4)]$ exhibits a band at 1383 cm^{-1} which supports the presence of CH_3 group overlapped with the bands of NO_3^-. In this complex, appearances of bands at 1330 cm^{-1} and 1445 cm^{-1} are attributed to coordinated NO_3^- group. The separation of the bands by 115 cm^{-1} is accounted for unidentate mode of coordination. Moreover, the nitro complex, $[CdL_{BZ}(NO_2)(ClO_4)]$ exhibits the $\upsilon_{sym(NO2)}$ band at 1340 overlapped with 1383 cm^{-1} for ν_{CH3} and $\upsilon_{asym(NO2)}$ band at 1459 cm^{-1}. Appearance of band at 851 cm^{-1} can be attributed to δ_{NO2} frequency. Further presence of υ_{Cd-N} band at 550 cm^{-1} and other bands in the proper region support the complex to be N-bonded nitro complex. Since IR spectrum could not be run below 400 cm^{-1}, so Cd-Br/Cl/I band could not be detected.

The molar conductivity values of 0 and 31-42 $ohm^{-1}cm^2mol^{-1}$ (Table 2) of these complexes, in chloroform and DMSO, respectively support the non-electrolytic nature of these complexes, i.e. all the anions are in the coordination sphere as expected for the octahedral structure assigned for the prepared complexes. The ^{1}H-nmr spectrum of $[CdL_{BZ}(NCS)_2]$ displays four doublets and four singlets. The singlets (Table-3) at 1.192 and 1.435 ppm each corresponding to 6H can be accounted for equatorial and axial components of gem-dimethyl protons respectively. However the doublets at 0.815, 1.121, 1,215 and 1.252 ppm each corresponding to 3H can be assigned to four equatorial methyls on four chiral carbons. Thus all equatorial orientation of all methyls on four chiral carbons can be accounted for this derivative complex as assigned for the mother complex $[CdL_{BZ}(ClO_4)_2]$. This proves that axial substitution takes place without change of configuration and conformation of the ligand of original complex [11-13]. In addition the singlets at 1.532 and 2.201 ppm each corresponding to 3H can be assigned to two methyl protons on two N-atoms. Appearance of separate singlets for each chiral methyl (all equatorial) and N-methyl protons can be accounted for non symmetry in the molecule. Further the spectrum exhibits multiplets at 1.337, 2.241, 2.896, 3.138, 3.469, 3.582, 4.287 ppm etc due to CH_2 and CH protons. However the signal at 7.250 ppm can be assigned to NH protons.

On the basis of the above discussion the following structures **Str.-3, Str.-4, Str.-5, Str.-6, Str.-7 and Str.-8** can be assigned to $[CdL_{BZ}(NCS)_2]$, $[CdL_{BZ}Br_2]$, $[CdL_{BZ}I_2]$, $[CdL_{BZ}Cl(ClO_4)]$, $[CdL_{BZ}(NO_3)(ClO_4)]$ and $[CdL_{BZ}(NO_3)(ClO_4)]$ respectively.

Table-1: IR spectral data

Complexes	Assignment (cm^{-1})						
	υ_{N-H}	ν_{N-CH3}	υ_{C-H}	υ_{CH3}	υ_{C-C}	υ_{Cd-N}	**Other Bands**
$[CdL_{BZ}(ClO_4)_2]$	3258m	2855s	2963w	1394w	1175w	520m	623 s,1103 vs(υ_{ClO4}); 417 w (υ_{Cd-O})
$[CdL_{BZ}(ClO_4)](ClO_4)$	3245w	2880s	2965w	1392w	1169w	515m	624 s,1099 vs(υ_{ClO4}); 448 w (υ_{Cd-O})
$[CdL_{BZ}(NCS)_2]$	3166 w	2850 m	2962 m	1383s	1175 s	545w	2020(υ_{C-N}) vs, 850 s(ν_{CS}), 485 (δ_{NCS})
$[CdL_{BZ}Br_2]$	3249 m	2855 w	2964 s	1383s	1175vs	552m	----
$[CdL_{BZ}I_2]$	3151 s	2875 s	2965s	138 vs	1174vs	550w	----
$[CdL_{BZ}Cl(ClO_4)]$	3140s	2850 w	2965s	1374 s	1181s	541w	624vs, 1085w (υ_{ClO4})
$[CdL_{BZ}(NO_3)(ClO_4)]$	3170 w	2850 w	2968s	1383 s	1175 vs	550m	624vs, 1086m (υ_{ClO4}), 1330m, 1445m (υ_{NO3})
$[CdL_{BZ}(NO_2)(ClO_4)]$	3150 w	2850 m	2971 s	1383s	1165s	547w	1340s 1459w (υ_{NO2}), 624s, 1103w (υ_{ClO4})

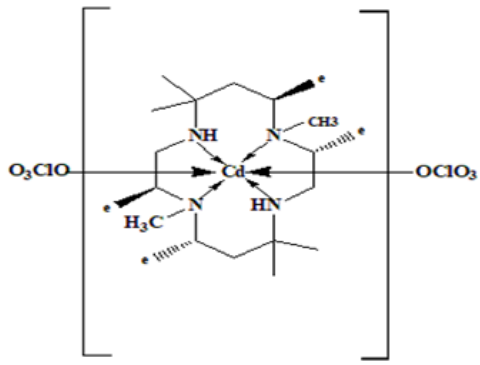
Table-2: Molar conductivity data

Complexes	**Conductance ($ohm^{-1}cm^2mol^{-1}$)**		
	DMSO	**$CHCl_3$**	**H_2O**
$[CdL_{BZ}(ClO_4)_2]$	70	0	--
$[CdL_{BZ}(ClO_4)](ClO_4)$	65	--	163
$[CdL_{BZ}(NCS)_2]$	42	0	--
$[CdL_{BZ}Br_2]$	33	0	--
$[CdL_{BZ}I_2]$	39	0	--
$[CdL_{BZ}Cl(ClO_4)]$	31	0	--
$[CdL_{BZ}(NO_3)(ClO_4)]$	40	0	--
$[CdL_{BZ}(NO_2)(ClO_4)]$	36	0	--

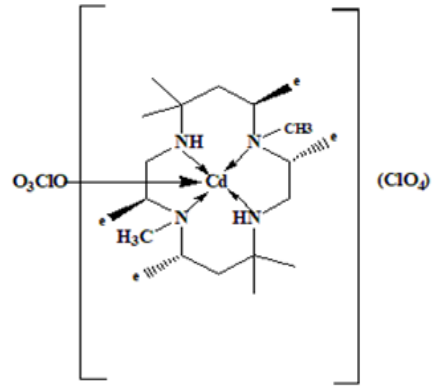
'--' means insoluble.

Table-3: ^{1}H-NMR spectral data

Complex	**Types of protons**				
	Geminal dimethyl δ(ppm)*	Methyl on chiral carbon δ(ppm)*	Methyl on N-atoms δ(ppm)*	CH_2 and CH δ(ppm)*	NH protons δ(ppm)*
$[CdL_{BZ}(ClO_4)_2]$	1.119 ^{ov} (s, 6H, e), 1.297(s,6H,a)	0.981 (d, 3H, e) 1.034 (d, 3H, e) 1.119^{ov}(d, 3H, e) 1.141 (d, 3H, e)	1.431(s, 6H)	1.728(m), 1.939 (m), 2.693 (m), 3.129(m)	8.297
$[CdL_{BZ}(NCS)_2]$	1.192 (s, 6H, e), 1.439 (s, 6H, a)	0.815 (d, 3H, e) 1.121 (d, 3H, e) 1.215(d, 3H, e) 1.252 (s, 3H, e)	1.532 (s, 3H) 2.201 (s, 3H)	1.337 (m), 2.641 (m), 2.896 (m) 3.138 (m) 3.469 (m) 3.582 (m) 4.287 (m)	7.250



Str. 1



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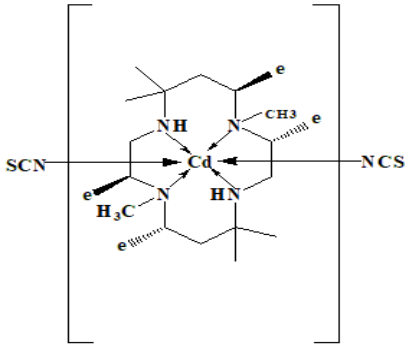

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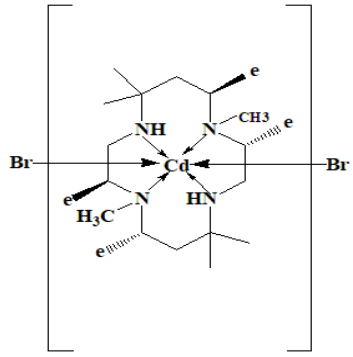

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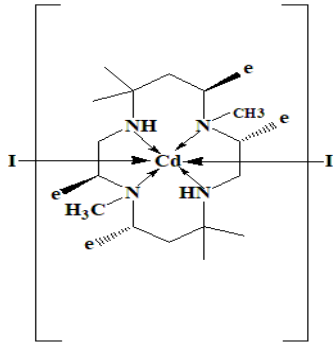

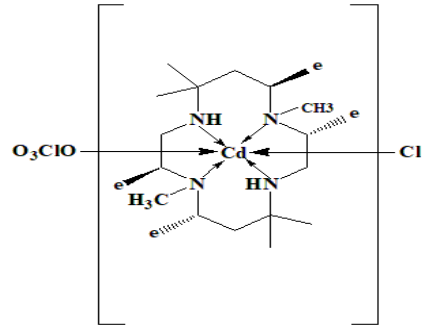

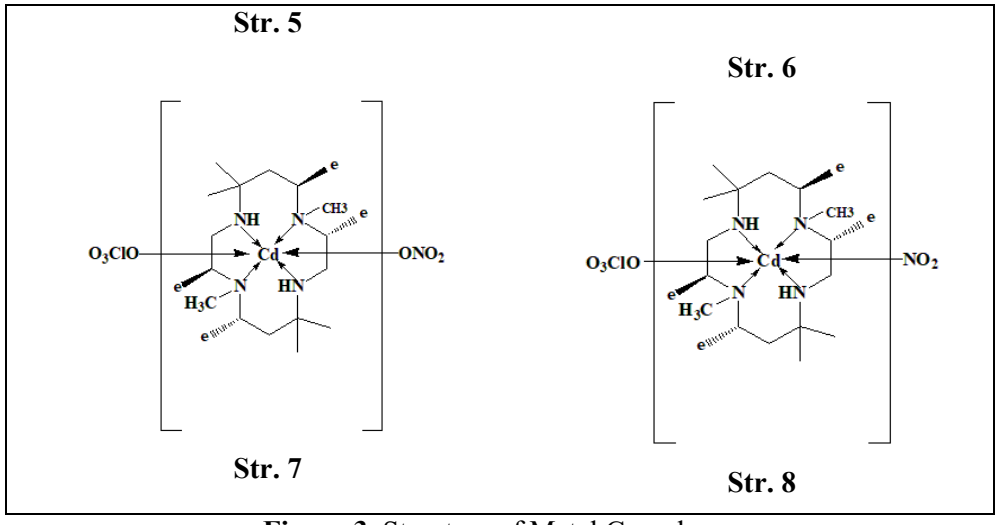

Figure 3. Structure of Metal Complexes

3.4 Antibacterial activities

Antibacterial activities of macrocycles and their complexes have been studied to some extent [11-14]. Therefore, it is noteworthy to examine whether the concerned ligand and complexes show any such activity or not. For the purpose, investigation on the antibacterial activities of the isomeric macrocycle L_B, its N-pendent derivative ligand L_{BZ} and Cd(II) complexes of L_{BZ} have been carried out against two important gram-positive and two gram-negative bacteria which cause different fatal diseases. From the result (Table-4) it is evident that the present macrocycle L_B and its N-pendent ligand L_{BZ} did not show any activity against the tested bacteria as observed in our earlier studies, [3-5, 9] but Cd(II) complexes of L_{BZ} showed significant activity against all bacteria except $[CdL_{BZ}(ClO_4)](ClO_4)$ and $[CdL_{BZ}(NO_3)](ClO_4)$ which were ineffective against *E.coli*. However all the concerned Cd(II) complexes are found to act as the most potent antibacterial against *B.cereus*.

Table-4: Antibacterial Activities

Sample no.	Ligands and their complexes	Zone of inhibition in diameter (mm)			
		Gram posative bacteria		Gram negative bacteria	
		Bacillus cereus	*Staphylococcus aureus*	*Escheri chiacoli*	*Shigella dysenteriae*
L_1	L_B	0	0	0	0
L_2	L_{BZ}	0	0	0	0
C_1	$[CdL_{BZ}(ClO_4)_2]$	17.5	11	9	11.5
C_2	$[CdL_{BZ}(ClO_4)](ClO_4)$	20.5	12	0	16.5
C_3	$[CdL_{BZ}(NCS)_2]$	17.5	12.5	12.5	12
C_4	$[CdL_{BZ}Br_2]$	19	10	8	12.5
C_5	$[CdL_{BZ}I_2]$	24	14	13	12.5
C_6	$[CdL_{BZ}Cl(ClO_4)]$	18.5	11	10	13
C_7	$[CdL_{BZ}(NO_3)(ClO_4)]$	17	12	0	14
C_8	$[CdL_{BZ}(NO_2)(ClO_4)]$	19.5	12.5	12	11.5

4. Conclusions

This research comes out with the fact that N-pendent ligand $L_{BZ,}$ a derivative of L_B undergoes facile complexation when reacts with cadmium(II) perchlorate salt to produce six coordinated octahedral $[CdL_{BZ}(ClO_4)_2]$ and five coordinated square pyramidal $[CdL_{BZ}(ClO_4)](ClO_4)$. The present work also reveals that diperchloratocadmium(II) complex, $[CdL_{BZ}(ClO_4)_2]$ undergoes axial substitution reactions with NCS^-, Br^-, I^-, Cl^-, NO_3^- and NO_2^- to produce octahedral diisothiocyanato, dibromido, diidido, monochloridoperchlorato, mononitratoperchlorato and mononitroperchlorato complexes respectively. Most of the six coordinated octahedral complexes are found to be nonelectrolyte in both $CHCl_3$ and DMSO as expected. These newly produced complexes exhibit high potentiality as antibacterial agents.

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