



# Synthesis, characterization and antimicrobial studies of cadmium(II) complexes with a tetraazamacrocyclic ( $L_B$ ) and its cyanoethyl N-pendent derivative ( $L_{BX}$ )

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**Abstract.** An isomeric ligand,  $L_B$  of 3,10-C-meso-Me<sub>8</sub>[14]ane on alkylation reaction with excess acrylonitrile resulted in a stereoselective product trans-(3S,5S,10R,12R)-N1,N8-bis(2-cyanoethyl)-C-meso-derivative,  $L_{BX}$ . Reaction of  $L_B$  with Cd(ClO<sub>4</sub>)<sub>2</sub> · 4H<sub>2</sub>O in methanol gave the octahedral complex, [Cd( $L_B$ )(ClO<sub>4</sub>)<sub>2</sub>] whereas interaction of the ligand  $L_{BX}$  with Cd(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O in methanol yielded a square pyramidal mononitratocadmium(II) nitrate complex, [Cd( $L_{BX}$ )(NO<sub>3</sub>)](NO<sub>3</sub>) and an octahedral dinitratocadmium(II) complex, [Cd( $L_{BX}$ )(NO<sub>3</sub>)<sub>2</sub>]. The complexes, [Cd( $L_B$ )(ClO<sub>4</sub>)<sub>2</sub>] and [Cd( $L_{BX}$ )(NO<sub>3</sub>)<sub>2</sub>] underwent axial substitution reactions with KCNS and KBr to produce octahedral diisothiocyanatocadmium(II) complexes, [Cd( $L_B$ )(NCS)<sub>2</sub>] and [Cd( $L_{BX}$ )(NCS)<sub>2</sub>] and octahedral dibromidocadmium(II) complexes, [Cd( $L_B$ )(Br)<sub>2</sub>] and [Cd( $L_{BX}$ )(Br)<sub>2</sub>], respectively; whereas, [Cd( $L_{BX}$ )(NO<sub>3</sub>)](NO<sub>3</sub>) underwent axial addition with KCl, simultaneous axial substitution and anion exchange with KCNS and simultaneous axial addition, substitution and anion exchange with NaClO<sub>4</sub> · 6H<sub>2</sub>O to produce octahedral [Cd( $L_{BX}$ )(NO<sub>3</sub>Cl)], square planar octahedral [Cd( $L_{BX}$ )(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, respectively. The newly prepared compounds have been characterized by different analytical and spectroscopic methods. The antibacterial activities of the ligands, metal salts and complexes have been tested against two selected gram positive bacteria and two gram negative bacteria.

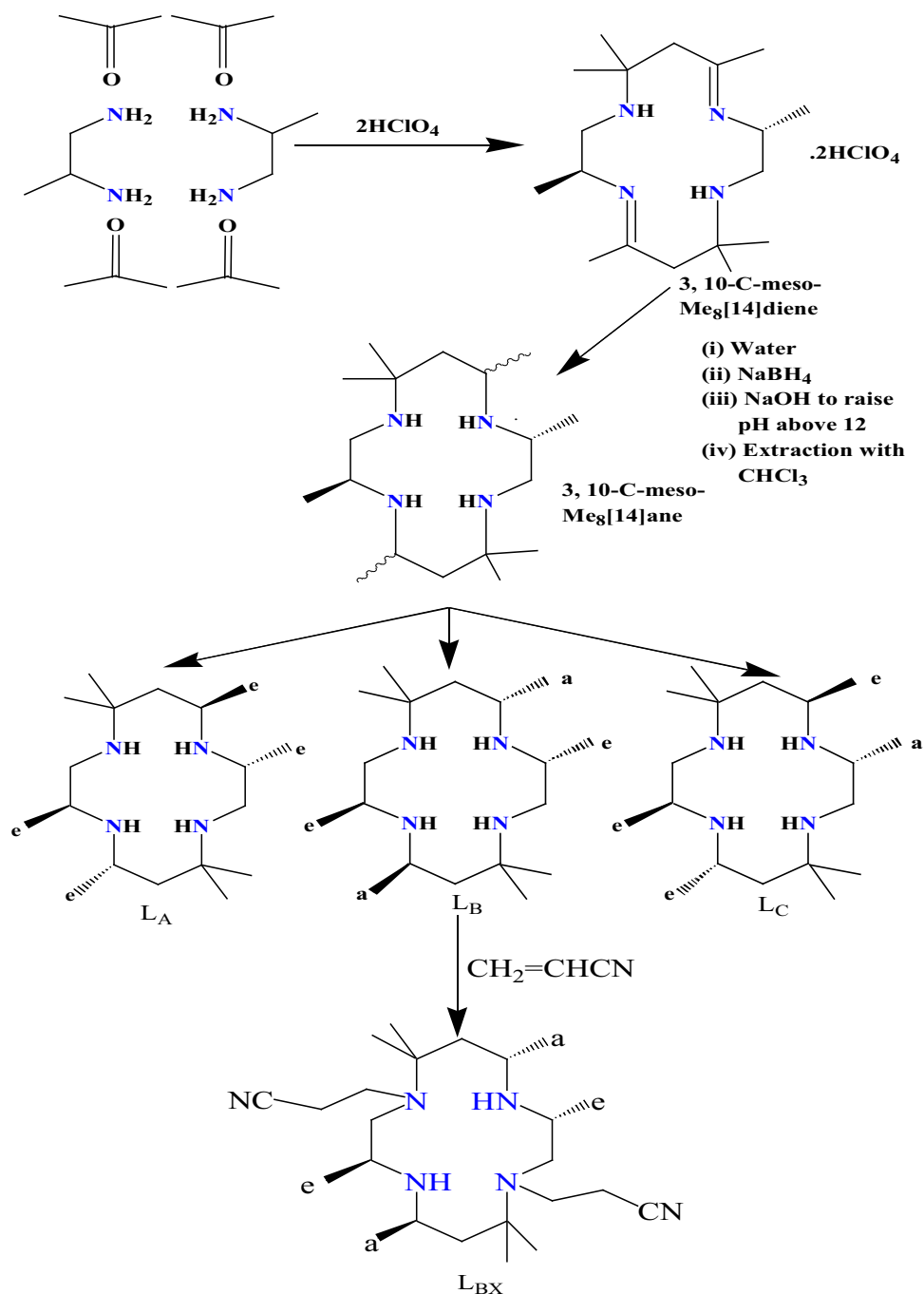
**Keywords.** Macrocyclic ligands; N-pendent derivative; cadmium(II) complex; spectroscopic studies; antibacterial studies.

## 1. Introduction

The importance of synthetic macrocyclic ligands, especially tetraaza N-donors and their complexes have drawn remarkable attraction owing to their structural resemblance to naturally occurring macrocyclic compounds such as porphyrins (hemoglobin) and porphyrin-related molecules (vitamin B12), and the like. On the other hand, metal derivatives thereof have also found wide applications as antitumor,<sup>1</sup> anticancer,<sup>1,2</sup> antibacterial<sup>3</sup> and antifungal<sup>4</sup> agents. Macrocyclic natural products evolved to fulfill numerous biochemical functions, and their profound pharmacological properties have led to their development as pharmaceuticals. Moreover,

the various biological roles played by natural counterparts can be mainly determined by the nature of the metal ions and their confinement in the enclosed cavity of natural macrocycles. In this connection, a number of studies are reported on the syntheses, characterization and biological activity of copper(II), cobalt(III), zinc(II), nickel(II) and cadmium(II) complexes of different macrocyclic ligands as well as their N-pendent derivatives in the literature.<sup>5-9</sup> Some complexes of the isomeric ligand,  $L_B$ <sup>7,9</sup> of 3,10-C-meso-Me<sub>8</sub>[14]ane and its N-pendent derivatives<sup>10-12</sup> have been reported in which structure of the N-pendent ligand  $L_{BX}$  (Bis cyanoethyl derivative of  $L_B$ ) has been studied by X-ray crystallography.<sup>13</sup> Though work on cadmium(II) complexes with different macrocycles are notable<sup>9,14,15</sup> complexes but with N-pendent ligands

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**Scheme 1.** Synthesis of  $\text{L}\cdot 2\text{HClO}_4$ ,  $\text{L}_A$ ,  $\text{L}_B$ ,  $\text{L}_C$  and  $\text{L}_{\text{BX}}$ .

are rare. So it is interesting to synthesize and characterize new cadmium(II) complexes of an isomeric ligand  $\text{L}_B$  and its N-pendent derivative,  $\text{L}_{\text{BX}}$ . With this point of view successful preparation of the ligand salt, octamethyl-tetraazacyclotetradecadiene dihydroperchlorate ( $\text{L}\cdot 2\text{HClO}_4$ ), its reduced isomeric ligands,  $\text{L}_A$ ,  $\text{L}_B$  and  $\text{L}_C$  (Scheme 1) have been prepared as per literature.<sup>16,17</sup> And bis(cyanoethyl) N-pendent derivative,  $\text{L}_{\text{BX}}$  (Scheme 1) of the isomeric ligand ( $\text{L}_B$ ) was

synthesized by using proper alkalyting agent and preparation of cadmium(II) complexes of  $\text{L}_B$  and  $\text{L}_{\text{BX}}$  and their axial addition, substitution and anion exchange products as well as biological activity were carried out. The synthesized ligand  $\text{L}_{\text{BX}}$  and cadmium(II) complexes have been characterized on the basis of different analytical and spectroscopic methods and antibacterial activities have been studied. The results of these studies are reported herein.

## 2. Experimental

### 2.1 Materials and equipments

All the 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 procedures. Equipments used were standard ones.

### 2.2 Syntheses of ligands

**2.2a Ligands, L·2HClO<sub>4</sub>, L<sub>A</sub>, L<sub>B</sub> and L<sub>C</sub>:** The parent ligand salt, L·2HClO<sub>4</sub> was prepared by the method described in literature.<sup>16</sup> The reduction of ligand L·2HClO<sub>4</sub> yielded three isomers L<sub>A</sub>, L<sub>B</sub> and L<sub>C</sub>. The separation and isolation of L<sub>A</sub>, L<sub>B</sub> and L<sub>C</sub> have been carried out as procedure adopted in literature.<sup>17</sup>

**2.2b N-pendent derivative ligand L<sub>BX</sub>:** 0.312 g (1.0 mmol) of L<sub>B</sub> was suspended in 50 mL of vinyl cyanide taken in a round bottom flask and the mixture was refluxed for 12 h on a water bath. After cooling at room temperature, white crystals were observed. The crystals were separated by filtration, washed with dry ethanol and recrystallised from chloroform-methylcyanide mixture, which are dried in vacuum desiccators over silica gel and labeled as L<sub>BX</sub>.

L<sub>BX</sub>: Color, white. Anal: Found: C, 68.94; H, 10.99; N, 20.05% Calc.: C, 68.89; H, 11.00; N, 20.09%. IR (cm<sup>-1</sup>): ν<sub>N-H</sub>, 3180s, ν<sub>C-H</sub> 2950s, ν<sub>CH<sub>3</sub></sub> 1365s, ν<sub>C-C</sub>1180s, ν<sub>C≡N</sub> 2245s; <sup>1</sup>H NMR (δ, ppm in DMSO-d<sub>6</sub>): For CH<sub>3</sub> (Germinal dimethyl), δ = 1.29 (s, equatorial, 6H); 1.43 (s, axial, 6H); For Gem dimethyl proton 0.88 (s, e, 6H); 1.24 (s, e, 6H); For CH<sub>3</sub> (Axial-equatorial) 0.92 (d, e, 6H); 1.02 (d, a, 6H); For CH<sub>2</sub> & CH, δ = 3.2(b), 3.34(b). <sup>13</sup>C NMR (ppm in DMSO) (S2), Peripheral Carbon, 17.91, 19.85, 20.07, 21.78; Macrocyclic ring Carbon, 44.59, 45.58, 46.29, 46.77, 27.07; Methylene Carbon of cyanoethyl groups, 55.96, 57.49; Cyano carbon, 120. Mass spectra (S3) Molecular ion peak, 418; Base peak, 210; Fragment peak, 403, 312,157,126, 85, 73, 53.

### 2.3 Syntheses of cadmium(II) complexes of the ligands, L<sub>B</sub> and L<sub>BX</sub> by different ways

#### 2.3a Direct reactions:

**2.3.1a [Cd(L<sub>B</sub>)(ClO<sub>4</sub>)<sub>2</sub>]** 0.3114 g (1.0 mmol) of cadmium(II) perchlorate and 0.312 g (1.0 mmol) of L<sub>B</sub> were separately dissolved in 50 mL methanol and mixed together. The solution was heated on a water bath for 1 h and allowed to dry. The product was extracted with chloroform and the solution was evaporated to dryness to give solid product, [CdL<sub>B</sub>(ClO<sub>4</sub>)<sub>2</sub>]. The product was stored in a desiccator over silica gel. Color: white. Anal. Found: C, 34.62; H, 6.42; N, 8.96% Calc.: C, 34.66; H,6.46; N, 8.98. IR (cm<sup>-1</sup>): ν<sub>N-H</sub>, 3260m, ν<sub>C-H</sub> 2963m, ν<sub>CH<sub>3</sub></sub> 1373m, ν<sub>C-C</sub> 1177w, ν<sub>N-Cd</sub> 517w, ν<sub>ClO<sub>4</sub></sub> 624s, 1026w, ν<sub>(Cd-O)</sub> 459w. Molar conductivity

(Λ<sub>o</sub>, ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) in DMSO, 31; in Acetonitrile, 126; in H<sub>2</sub>O, 35. Magnetic moment μ<sub>eff</sub> (BM): diamagnetic. <sup>1</sup>H-NMR (δ in ppm in DMSO-d<sub>6</sub>): For CH<sub>3</sub>, d = 1.17e (s, 6H, e), 1.00 (ov, 18H); For CH<sub>2</sub> and NH, δ = 2.76(s), 3.14(m), 3.59(m), 4.45(m).

**2.3.1b [Cd(L<sub>BX</sub>)(NO<sub>3</sub>)](NO<sub>3</sub>) and [Cd(L<sub>BX</sub>)(NO<sub>3</sub>)<sub>2</sub>]** 0.23 64 g (1.0 mmol) of cadmium(II) nitrate and 0.42 g (1.0 mmol) of L<sub>BX</sub> were separately dissolved in a mixture of 50 mL methanol and 5 mL acrylonitrile and mixed together. The solution was heated on a water bath for 1 h and allowed to dry. The product was dissolved with chloroform and filtered. The residue was solid product, [Cd(L<sub>BX</sub>)NO<sub>3</sub>](NO<sub>3</sub>). The chloroform solution was evaporated to dryness to give solid product, [Cd(L<sub>BX</sub>)(NO<sub>3</sub>)<sub>2</sub>]. The products were stored in a desiccator over silica gel.

For [Cd(L<sub>BX</sub>)(NO<sub>3</sub>)](NO<sub>3</sub>): Color: white. Anal. Found: C, 43.98; H, 7.04; N, 17.13% Calc.: C, 44.00; H, 7.08; N, 17.11%. IR (cm<sup>-1</sup>): ν<sub>N-H</sub>, 3260s, ν<sub>C≡N</sub> 2245vs; ν<sub>C-H</sub> 2974s, ν<sub>CH<sub>3</sub></sub> 1385w, ν<sub>C-C</sub> 1169s, ν<sub>N-Cd</sub> 550w, ν<sub>NO<sub>3</sub></sub> 1384s, 1450m. Molar conductivity (Λ<sub>o</sub>, ohm<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>) in DMSO: 65. Magnetic moment μ<sub>eff</sub> (B.M): diamagnetic. <sup>1</sup>H NMR (δ in ppm in DMSO-d<sub>6</sub>): For CH<sub>3</sub>, 1.28 (s, 6H, e), 1.67 (s, 6H, a), 0.95 (d, 6H, e), 1.38 (d, 6H, a); For CH<sub>2</sub> and NH, δ = 2.47 (m), 3.31 (m).

For [Cd(L<sub>BX</sub>)(NO<sub>3</sub>)<sub>2</sub>]: Color: white. Anal. Found: C, 44.05; H, 7.06; N, 17.10% Calcd.: C, 44.00; H, 7.08; N, 17.11%. IR (cm<sup>-1</sup>): ν<sub>N-H</sub> 3260s, ν<sub>C≡N</sub> 2245vs, ν<sub>C-H</sub> 2970s, ν<sub>CH<sub>3</sub></sub> 1384s, ν<sub>C-C</sub> 1169m, ν<sub>N-Cd</sub> 529w, ν<sub>NO<sub>3</sub></sub> 1384s, 1458m. Molar conductivity (Λ<sub>o</sub>, ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) in DMSO: 79; in CHCl<sub>3</sub>, 0, in acetonitrile: 114. Magnetic moment μ<sub>eff</sub> (BM): diamagnetic. <sup>1</sup>H NMR (δ in ppm in DMSO-d<sub>6</sub>): For CH<sub>3</sub>, 1.26 (s, 6H, e), 1.68 (s, 6H, a), 0.98 (d, 6H, e), 1.37 (d, 6H, a); For CH<sub>2</sub> and NH, δ = 2.39 (m), 3.35 (m).

#### 2.3b Axial addition:

**2.3.2a [Cd(L<sub>BX</sub>)(NO<sub>3</sub>)Cl]** 0.24 g (1.0 mmol) of [Cd(L<sub>BX</sub>)(NO<sub>3</sub>)](NO<sub>3</sub>) and 0.149 g (2.0 mmol) of KCl were separately suspended/dissolved in 50 mL methanol and mixed together and 5 mL acrylonitrile was added to it. The suspension was heated on a water bath for 1 h and allowed to dry. The product was extracted with chloroform and chloroform extract was evaporated to dryness to give solid product, [Cd(L<sub>BX</sub>)(NO<sub>3</sub>)Cl]. The product was stored in a desiccator over silica gel. Color: white. Anal. Found: C, 45.83; H, 7.36; N, 15.58% Calc.: C, 45.86; H, 7.38; N, 15.60. IR (cm<sup>-1</sup>): ν<sub>N-H</sub>, 3248m, ν<sub>C≡N</sub> 2245vs; ν<sub>C-H</sub> 2970s; ν<sub>CH<sub>3</sub></sub> 1385s, ν<sub>C-C</sub> 1169m, ν<sub>C-Cd</sub> 559w, ν<sub>NO<sub>3</sub></sub> 1338, 1485. Molar conductivity (Λ<sub>o</sub>, ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>) in DMSO: 26; in CHCl<sub>3</sub>: 0; in acetonitrile: 77. Magnetic moment μ<sub>eff</sub>(B.M): diamagnetic.

#### 2.3c Axial substitution:

**2.3.3a [Cd(L<sub>B</sub>)(SCN)<sub>2</sub>] and [Cd(L<sub>B</sub>)(NO<sub>3</sub>)](NO<sub>3</sub>)** Diisothiocyanatocadmium(II) complex of L<sub>B</sub> [Cd(L<sub>B</sub>)(SCN)<sub>2</sub>] and dibromidocadmium(II) complex of L<sub>B</sub>, [Cd(L<sub>B</sub>)Br<sub>2</sub>] were

prepared as per literature,<sup>9</sup> except carrying out substitution reaction on  $[\text{Cd}(\text{L}_\text{B})(\text{ClO}_4)_2]$  instead of  $[\text{Cd}(\text{L}_\text{B})(\text{NO}_3)](\text{NO}_3)$ .

**2.3.3b**  $[\text{Cd}(\text{L}_\text{BX})(\text{X})_2]$  ( $\text{X} = \text{NCS}$  or  $\text{Br}$ ) 0.24 g (1.0 mmol) of  $[\text{Cd}(\text{L}_\text{BX})(\text{NO}_3)_2]$  was dissolved in methanol (100 mL) containing  $\text{KX}$  ( $\text{X} = \text{SCN}$  or  $\text{Br}$ ) with proper weight, i.e. in the molar ratio of 1:2 and then 5 mL acrylonitrile was added to it. The solution was heated on a water bath for 1 h and allowed to dry. The product was extracted with chloroform and chloroform extract was evaporated to dryness to give brown solid product,  $[\text{Cd}(\text{L}_\text{BX})(\text{X})_2]$ . The product was stored in a desiccator over silica gel. Melting point was above 250 °C.

$[\text{Cd}(\text{L}_\text{BX})(\text{NCS})_2]$ : Color: white. Anal. Found: C, 48.24; H, 7.14; N, 17.30% Calc.: C, 48.25; H, 7.16; N, 17.31%. IR ( $\text{cm}^{-1}$ ):  $\nu_{\text{N-H}}$ , 3198w,  $\nu_{\text{C}\equiv\text{N}}$  2245vs,  $\nu_{\text{C-H}}$  2970m,  $\nu_{\text{CH}_3}$  1377s,  $\nu_{\text{C-C}}$  1173s,  $\nu_{\text{N-Cd}}$  552s,  $\nu_{\text{CN}}$  2045,  $\nu_{\text{CS}}$  783,  $\delta_{\text{NCS}}$ , 486. Molar conductivity ( $\Lambda_0$ ,  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ) in DMSO: 56, in  $\text{CHCl}_3$ : 0; Magnetic moment  $\mu_{\text{eff}}$  (B.M): diamagnetic.  $^1\text{H-NMR}$  ( $\delta$  in ppm in DMSO-d6): For  $\text{CH}_3$ , 1.21 (s, 6H,e), 1.33 (s, 6H,a), 1.01 (d, 6H,e), 1.08 (d, 6H,a); 1.47 (d, 6H,e); For  $\text{CH}_2$  and  $\text{NH}$ ,  $\delta = 1.70$  (s, 4H); 2.82 (m); 3.18 (m).  $[\text{Cd}(\text{L}_\text{BX})(\text{Br})_2]$ : Color: white. Anal. Found: C, 41.70; H, 6.70; N, 12.15% Calc.: C, 41.72; H, 6.71; N, 12.16% IR ( $\text{cm}^{-1}$ ):  $\nu_{\text{N-H}}$ , 3264w,  $\nu_{\text{C}\equiv\text{N}}$  2245vs;  $\nu_{\text{C-H}}$  2970s,  $\nu_{\text{CH}_3}$  1381s,  $\nu_{\text{C-C}}$  1169m,  $\nu_{\text{N-Cd}}$  550w; Molar conductivity ( $\Lambda_0$ ,  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ) in DMSO: 38, in  $\text{CHCl}_3$ : 0; Magnetic moment  $\mu_{\text{eff}}$  (B.M): diamagnetic.

**2.3d** *Simultaneous axial substitution and anion exchange:*

**2.3.4a**  $[\text{Cd}(\text{L}_\text{BX})(\text{SCN})](\text{SCN})$  0.24 g (1.0 mmol) of  $[\text{Cd}(\text{L}_\text{BX})(\text{NO}_3)](\text{NO}_3)$  and 0.20 g (2.0 mmol) of  $\text{KSCN}$  were separately suspended/dissolved in 50 mL methanol and mixed together and 5 mL acrylonitrile was added to it. The suspension was heated on a water bath for 1 h and allowed to dry. The product was extracted with chloroform and chloroform extract was evaporated to dryness to give solid product,  $[\text{Cd}(\text{L}_\text{BX})(\text{SCN})](\text{SCN})$ . The product was stored in a desiccator over silica gel. Color: white. Anal. Found: C, 48.23; H, 7.15; N, 17.29% Calc.: C, 48.25; H, 7.16; N, 17.31%. IR ( $\text{cm}^{-1}$ ):  $\nu_{\text{N-H}}$ , 3260s,  $\nu_{\text{C}\equiv\text{N}}$  2245vs,  $\nu_{\text{C-H}}$  2967s;  $\nu_{\text{CH}_3}$  1373m,  $\nu_{\text{C-C}}$  1181w,  $\nu_{\text{N-Cd}}$  525w,  $\nu_{\text{CN}}$  2064,  $\nu_{\text{CS}}$  780,  $\delta_{\text{NCS}}$  474. Molar conductivity ( $\Lambda_0$ ,  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ): in DMSO: 68. Magnetic moment  $\mu_{\text{eff}}$  (B.M.): Diamagnetic.

**2.3e** *Simultaneous axial addition, substitution and anion exchange:*

**2.3.5a**  $[\text{Cd}(\text{L}_\text{BX})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  The complex  $[\text{Cd}(\text{L}_\text{BX})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  was prepared from  $[\text{Cd}(\text{L}_\text{BX})(\text{NO}_3)](\text{NO}_3)$  by the method described in section 2.3.4a by adding  $\text{NaClO}_4 \cdot 6\text{HClO}_4$  instead of  $\text{KSCN}$ . Color: white. Anal. Found: C, 37.60; H, 6.56; N, 10.95% Calc.: C, 37.63; H, 6.58; N, 10.97%. IR ( $\text{cm}^{-1}$ ):  $\nu_{\text{N-H}}$ , 3248m,  $\nu_{\text{C}\equiv\text{N}}$  2245vs,  $\nu_{\text{C-H}}$  2974s,  $\nu_{\text{CH}_3}$  1385w,  $\nu_{\text{C-C}}$  1169m,  $\nu_{\text{N-Cd}}$  559w,  $\nu_{\text{ClO}_4}$  624s, 1026w,  $\nu_{\text{H}_2\text{O}}$  3433w. Molar conductivity ( $\Lambda_0$ ,  $\text{ohm}^{-1}\text{cm}^2$

$\text{mol}^{-1}$ ) in DMSO: 45, in acetonitrile: 259; Magnetic moment  $\mu_{\text{eff}}$  (B.M): diamagnetic.

## 2.4 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 and INQUIMAE, University of Buenos Aires, Argentina. UV-Visible spectra in DMSO were recorded on a Shimadzu UV-Visible spectrophotometer. Conductance measurements were carried out on a conductivity bridge Hanna instrument HI-8820 in DMSO. Magnetic measurements were performed on Gouy Balance which was calibrated using  $\text{Hg}[\text{Co}(\text{NCS})_4]$ . IR spectra were recorded on a Shimadzu IR 20 spectrophotometer as KBr disks.  $^1\text{H-NMR}$  spectra were recorded in DMSO with a 400 MHz Bruker DPX-400 spectrometer using TMS as internal standard and  $^{13}\text{C-NMR}$  spectra were recorded at the BCSIR Laboratory, Dhaka, Bangladesh.

## 2.5 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 mg/mL 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 h and 48 h intervals. 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.

## 3. Results and Discussion

All synthesized compounds were white and the complexes were diamagnetic as expected for  $d^{10}$  system of  $\text{Cd}^{2+}$ . The stereochemistry of the ligands of these complexes have been assigned on the basis that axial addition and substitution takes place without change of configuration and conformation of the ligand of the original complexes.<sup>6,9,18</sup>



### 3.1 Ligands $L_A$ , $L_B$ and $L_C$

Condensation of 1,2-diaminopropane with acetone in presence of quantitative amount of  $\text{HClO}_4$  resulted a macrocyclic diene ligand, 3,10-C-meso- $\text{Me}_8[14]\text{diene}^{16}$  which on reduction produced three C-chiral isomer ligand designated by  $L_A$ ,  $L_B$  and  $L_C$  (Scheme 1).<sup>17</sup>  $L_B$  on alkylation reaction with vinyl cyanide yielded bis cyanoethyl-N-pendent derivative  $L_{\text{BX}}$  (Scheme 1).

### 3.2 Ligand $L_{\text{BX}}$

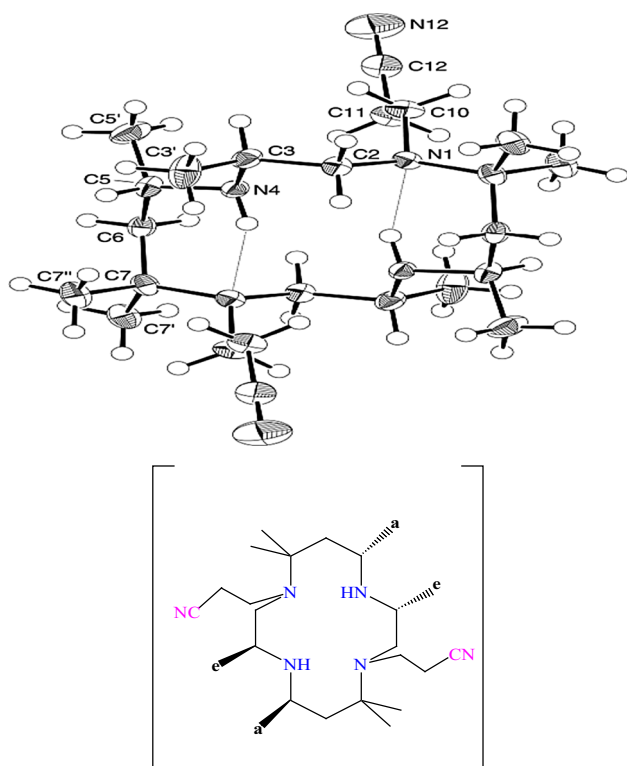
The infrared spectrum of  $L_{\text{BX}}$  displays  $\nu_{\text{NH}}$  bands at  $3180\text{ cm}^{-1}$ ,  $\nu_{\text{C-H}}$  band at  $2950\text{ cm}^{-1}$ ,  $\nu_{\text{CH}_3}$  band at  $1365\text{ cm}^{-1}$  and  $\nu_{\text{C-C}}$  stretching band at  $1180\text{ cm}^{-1}$  in proper positions. Further, the spectrum exhibits  $\nu_{\text{C}\equiv\text{N}}$  band for cyanoethyl group at  $2245\text{ cm}^{-1}$ . The mass spectra of the N-pendent functional group bearing tetraazamacrocyclic ligands are more complicated than their parent tetraazamacrocycles due to more possibilities of cleavage arising out of additional N functional groups. Thus, the mass spectrum of the ligand  $L_{\text{BX}}$  is a complicated one (Scheme S2a and S2b in Supplementary Information) as compared to its original ligand  $L_B$ . The spectrum shows a peak at  $m/z$  418 of low intensity corresponding to molecular ion  $[\text{C}_{24}\text{N}_6\text{H}_{46}]^+$ . The base peak occurs at  $m/z$  210 by the double cleavage of two C – C bonds: C2–C3 bond adjacent to N1 and N4 atoms and C9 – C10 bond adjacent to N8 and N11 atoms ( $\alpha$ -cleavage),<sup>19</sup> followed by transference of one H-atom from the other part of the molecular ion (path – A and A'). The molecular ion can also lose a methyl radical either from the more crowded  $\alpha$ -carbon atom C7 ( $\alpha$ - relative to N8) or C14 ( $\alpha$ - relative to N1) to result in an ion at  $m/z$  403. The molecular ion can further undergo fragmentation to give another big fragment ion at  $m/z$  312 by double cleavage at C15–N1 and C17–N8 bonds, with elimination of two molecules of vinyl cyanide,<sup>19</sup> followed by rearrangement of  $\beta$ -hydrogen on N1 and N8, respectively. Removal of vinyl cyanide from the ion at  $m/z$  210 by rupture of C11–N8 bond or C15–N1 followed by rearrangement of  $\beta$ -hydrogen to nitrogen provides ion at  $m/z$  157. Fragmentation of fragment ion corresponding to base peak at  $m/z = 210$  can be represented by the cleavage of C6–C7 bond to result in fragment at 126 and 85 with transference of one hydrogen atom from other part and without transference of hydrogen atom (homolytic fission), respectively.

In fact, there are two possibilities for this sort of cleavage, one at C5–C6 ( $\alpha$ -cleavage relative to N4) and the second one at C6–C7 bond ( $\alpha$ -cleavage relative to N8). The cleavage at more branched carbon atom C7 is more

likely, the one at C6–C7 is more favorable. The fragment at  $m/z$  126 can further undergo fragmentation to provide fragment ion at  $m/z$  53 by C15–N1 bond rupture and transference of H to N1. The  $^1\text{H-NMR}$  spectrum of this ligand shows two singlets at 0.88 ppm and 1.24 ppm corresponding to six protons each. These singlet signals are assigned to C7 and C14 gem-dimethyl groups having equatorial and axial orientations. The two doublets at 0.92 ppm and 1.02 ppm corresponding to six protons each, can be assigned to a pair to equatorial and axial methyls. Symmetrically, this requires the two methyls at C3, C10 and C5, C12 to be pair-wise equivalent. The downfield spectrum of this ligand is not will resolved but it is possible to identify two broad signals at 2.20 ppm and 2.28 ppm assignable to the four  $\beta$ - and  $\alpha$ -protons, respectively. Two broad peaks at 3.28 ppm and 3.34 ppm can be assigned to methylene protons of N-substituted cyanoethyl groups. It has been noted that diaxial-diequatorial orientation is retained in this N-pendent derivative. The  $^{13}\text{C-NMR}$  spectrum of  $L_{\text{BX}}$  also gives additional evidence on the structure assigned on the basis of  $^1\text{H-NMR}$  spectrum analysis. The spectrum exhibits twelve signals which is just half of the total numbers of the carbons. This observation is in support of the symmetrical diaxial-diequatorial arrangement as has already been assigned on the basis of its  $^1\text{H-NMR}$  spectrum. The first four peaks 15–30 ppm can be assigned to the eight pair-wise equivalent carbons of peripheral methyl groups, fifth peak at 27.5 ppm is for the C6 and C13 carbons which are comparatively more shielded than those of other ring carbons. Next four peaks at 40–50 ppm are due to the ring carbons C2, C3, C5, C7, C9, C10, C11 and C14 where these eight carbons are pairwise equivalent. Another two peaks at 56 ppm and 58 ppm are due to the two methylene carbons of cyanoethyl branch. However, the peak at 120 ppm can be assigned to cyano carbon which is expected to be highly deshielded. Depending on the above studies and the X-ray crystallographic study (Figure 1),<sup>13</sup> the structure has been assigned for the N-pendent ligand  $L_{\text{BX}}$ .

### 3.3 Cadmium(II) complexes

3.3a  $[\text{Cd}(L_B)(\text{ClO}_4)_2]$ ,  $[\text{Cd}(L_{\text{BX}})(\text{NO}_3)](\text{NO}_3)$  and  $[\text{Cd}(L_{\text{BX}})(\text{NO}_3)_2]$ : Octahedral diperchlorato cadmium(II) complex,  $[\text{Cd}(L_B)(\text{ClO}_4)_2]$  has been prepared by the interaction of cadmium(II) perchlorate salt with  $L_B$  whereas square pyramidal mononitrocadmium(II) complex  $[\text{Cd}(L_{\text{BX}})(\text{NO}_3)]\text{NO}_3$  and octahedral dinitrocadmium(II) complex  $[\text{Cd}(L_{\text{BX}})(\text{NO}_3)_2]$  were prepared from the interaction of cadmium(II) nitrate and ligand  $L_{\text{BX}}$ . The infrared spectrum of these complexes exhibit band  $3260\text{ cm}^{-1}$  for  $\nu_{\text{N-H}}$ ,  $1169\text{--}1177\text{ cm}^{-1}$  for  $\nu_{\text{C-C}}$ ,



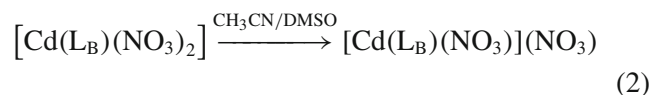
**Figure 1.** X-ray structure (top) and molecular structure (bottom) of N-pendent ligand  $L_{BX}$ .

2963–2974  $\text{cm}^{-1}$  for  $\nu_{\text{C-H}}$ , 517–550  $\text{cm}^{-1}$  for  $\nu_{\text{Cd-N}}$  and 1373–1385  $\text{cm}^{-1}$  for  $\nu_{\text{CH}_3}$  stretching frequencies at the proper regions. The diperchlorato cadmium(II) complex of  $L_B$  exhibits perchlorate bands at 1026  $\text{cm}^{-1}$  and 624  $\text{cm}^{-1}$ . An infrared band at 2245  $\text{cm}^{-1}$  indicates the presence of cyano ( $-\text{C} \equiv \text{N}$ ) group for the nitrate complexes of cadmium(II) with  $L_B$ . On the other hand, nitrate complexes display bands at 1450  $\text{cm}^{-1}$  and 1336  $\text{cm}^{-1}$  attributed to coordinated  $\text{NO}_3^-$  group. The separation of these bands by about 115  $\text{cm}^{-1}$  is accounted for unidentate mode of coordination. The molar conductance values of  $[\text{Cd}(L_B)(\text{ClO}_4)_2]$  is 0  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in  $\text{CHCl}_3$ , 31  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in DMSO and 35  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in  $\text{H}_2\text{O}$ , which strongly support the nonelectrolytic nature<sup>20</sup> of this complex; i.e. two perchlorate ions ( $\text{ClO}_4^-$ ) are coordinated to cadmium(II) ion. However, the molar conductivity value of 126  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in acetonitrile solution of  $[\text{Cd}(L_B)(\text{ClO}_4)_2]$  demonstrate that the complex is 1:1 electrolyte in nature. This indicates that the solvent  $\text{CH}_3\text{CN}$  converts of octahedral species into square pyramidal species as indicated by the following equation.

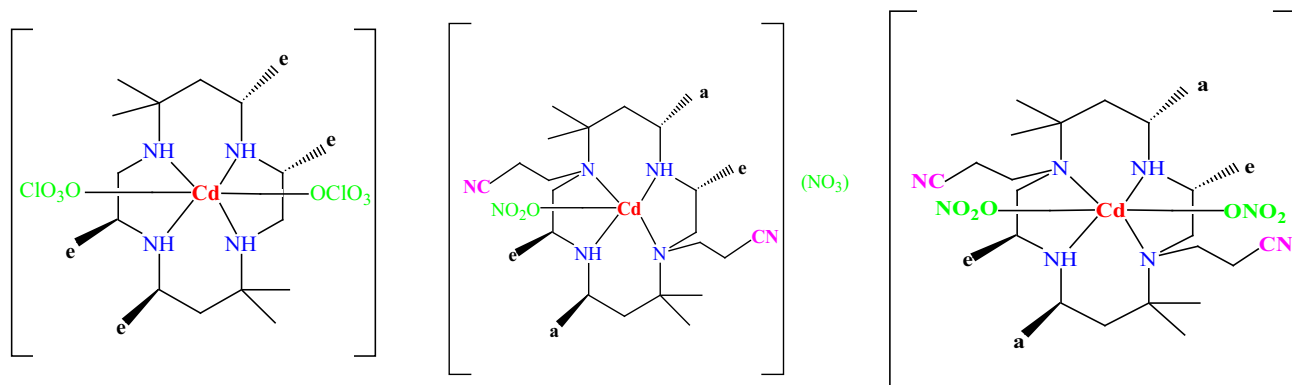


Again, the molar conductivity value of  $[\text{Cd}(L_{BX})(\text{NO}_3)](\text{NO}_3)$  is 65  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in DMSO solution

of this complex indicates that this complex is 1:1 electrolytic in nature; i.e., one  $\text{NO}_3^-$  ion is in coordination sphere and other ion is out of coordination sphere as expected for five coordinated square pyramidal complex corresponding to the formula assigned. On the other hand, molar conductance value of  $[\text{Cd}(L_{BX})(\text{NO}_3)_2]$  is 0  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in  $\text{CHCl}_3$  which strongly supports the nonelectrolytic nature of this complex i.e., two nitrate ions ( $\text{NO}_3^-$ ) are coordinated to cadmium(II) ion. However, the molar conductivity value of 79  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in DMSO solution as well as 114  $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in  $\text{CH}_3\text{CN}$  of  $[\text{Cd}(L_{BX})(\text{NO}_3)_2]$  indicating that the complex is 1:1 electrolyte in these solvents indicating the conversion of octahedral species into square pyramidal species as indicated by the following equation.



The  $^1\text{H-NMR}$  spectrum of  $[\text{Cd}(L_B)(\text{ClO}_4)_2]$  shows sharp methyl singlet at 1.17 ppm which can be assigned to equatorial methyls of the gem-dimethyl group. The other axial methyls of the gemdimethyl which are expected to appear at downfield in comparison overlap with doublets arising out of methyls at C3, C5, C10 and C12 positions. This overlapped multiple appeared at 1.33 ppm. This type of pattern is suggestive of a C-meso structure in which C3, C5, C10, and C12 are equatorial. The methylene and methine protons appear as multiplets at 2.76, 3.14, 3.59 and 4.45 ppm. Thus, this complex is, therefore, assigned a structure as shown in Figure 2 where all the four chiral methyls are equatorial. On the other hand,  $^1\text{H-NMR}$  spectrum of  $[\text{Cd}(L_{BX})(\text{NO}_3)](\text{NO}_3)$  shows two singlet signals at 1.28 ppm and 1.67 ppm corresponding to 6H each and are assigned to equatorial and axial components of two gem-dimethyl pairs. The spectrum further shows two doublets at 0.95 and 1.38 ppm corresponding each to 6H which may arise out of two equatorial and two axial methyl groups respectively which are pair-wise equivalent. So,  $[\text{Cd}(L_{BX})(\text{NO}_3)](\text{NO}_3)$  should therefore have two equatorially oriented methyl groups and two axially oriented methyl groups. The downfield signals of this complex are not well resolved but appearance of two broad signals at 2.47 ppm and 3.31 ppm may be due to methylene, methine and NH-protons. The octahedral  $[\text{Cd}(L_{BX})(\text{NO}_3)_2]$  also exhibits the similar spectral pattern like that of square pyramidal  $[\text{Cd}(L_{BX})(\text{NO}_3)](\text{NO}_3)$ , so a similar diaxial-diequatorial assignment has also been made for this complex. From the above discussion, the structure of  $[\text{Cd}(L_B)(\text{ClO}_4)_2]$   $[\text{Cd}(L_{BX})(\text{NO}_3)](\text{NO}_3)$



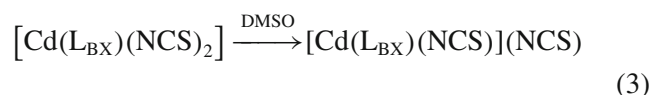
**Figure 2.** Structures of  $[\text{Cd}(\text{L}_\text{B})(\text{ClO}_4)_2]$  (left),  $[\text{Cd}(\text{L}_\text{BX})(\text{NO}_3)](\text{NO}_3)$  (middle) and  $[\text{Cd}(\text{L}_\text{BX})(\text{NO}_3)_2]$ .

and  $[\text{Cd}(\text{L}_\text{BX})(\text{NO}_3)_2]$  complex can be assigned as shown in Figure 2.

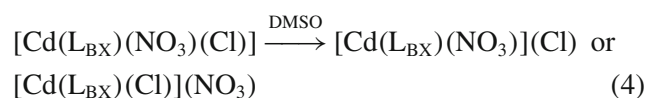
**3.3b**  $[\text{Cd}(\text{L}_\text{B})(\text{NCS})_2]$  and  $[\text{Cd}(\text{L}_\text{B})(\text{Br})_2]$ : Diisothiocyanato cadmium(II) complex  $[\text{Cd}(\text{L}_\text{B})(\text{SCN})_2]$  and dibromido cadmium(II) complex of  $\text{L}_\text{B}$ ,  $[\text{Cd}(\text{L}_\text{B})\text{Br}_2]$  of  $\text{L}_\text{B}$  have been synthesized by the axial substitution reactions of  $[\text{Cd}(\text{L}_\text{B})(\text{ClO}_4)_2]$  with KSCN and KBr, respectively. All the characterization data prove that these complexes are same as the complexes prepared<sup>9</sup> by axial substitution of  $[\text{Cd}(\text{L}_\text{B})(\text{NO}_3)_2]$  with KSCN and KBr, respectively.

**3.3c**  $[\text{Cd}(\text{L}_\text{BX})(\text{NO}_3)\text{Cl}]$ ,  $[\text{Cd}(\text{L}_\text{BX})(\text{SCN})_2]$  and  $[\text{Cd}(\text{L}_\text{BX})(\text{Br})_2]$ :  $[\text{Cd}(\text{L}_\text{BX})(\text{NO}_3)](\text{NO}_3)$  underwent axial addition reaction with KCl to produce an octahedral complex  $[\text{Cd}(\text{L}_\text{BX})(\text{NO}_3)\text{Cl}]$  whereas the axial substitution reaction on the octahedral complexes  $[\text{Cd}(\text{L}_\text{BX})(\text{NO}_3)_2]$  with KSCN and KBr produced octahedral complex  $[\text{Cd}(\text{L}_\text{B})(\text{NCS})_2]$  and  $[\text{Cd}(\text{L}_\text{B})(\text{NO}_3)_2]$ , respectively. The infrared spectrum of this complex exhibits all characteristic bands due to  $\nu_{\text{N-H}}$ ,  $\nu_{\text{C-C}}$ ,  $\nu_{\text{C-H}}$ ,  $\nu_{\text{Cd-N}}$  and  $\nu_{\text{CH}_3}$  stretching bands in the proper positions. An infrared band at  $2245\text{ cm}^{-1}$  indicates the presence of cyano ( $-\text{C} \equiv \text{N}$ ) group found for these complexes of  $\text{L}_\text{BX}$ . In the case of thiocyanato complex, the  $\nu_{\text{NCS}}$  band and  $\nu_{\text{CN}}$  band at  $2025\text{ cm}^{-1}$  and  $2064\text{ cm}^{-1}$  and absence of  $\nu_{\text{NO}_3}$  at  $1336\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$  demonstrate that the  $\text{NO}_3^-$  groups are substituted by  $\text{NCS}^-$  groups. Evidence in favour of co-ordination of  $\text{NCS}^-$  through N-atoms comes from the infrared spectrum of this complex. Appearance of sharp  $\nu_{\text{CN}}$  band in the region of  $2025\text{--}2064\text{ cm}^{-1}$  in the present complexes is a good indication of N-bonded thiocyanate group. The present complexes display  $\nu_{\text{CS}}$  band at  $780\text{--}783\text{ cm}^{-1}$ ,  $\nu_{\text{NCS}}$  band at  $474\text{--}486\text{ cm}^{-1}$  which do not correspond to ligand in this region and is therefore assigned

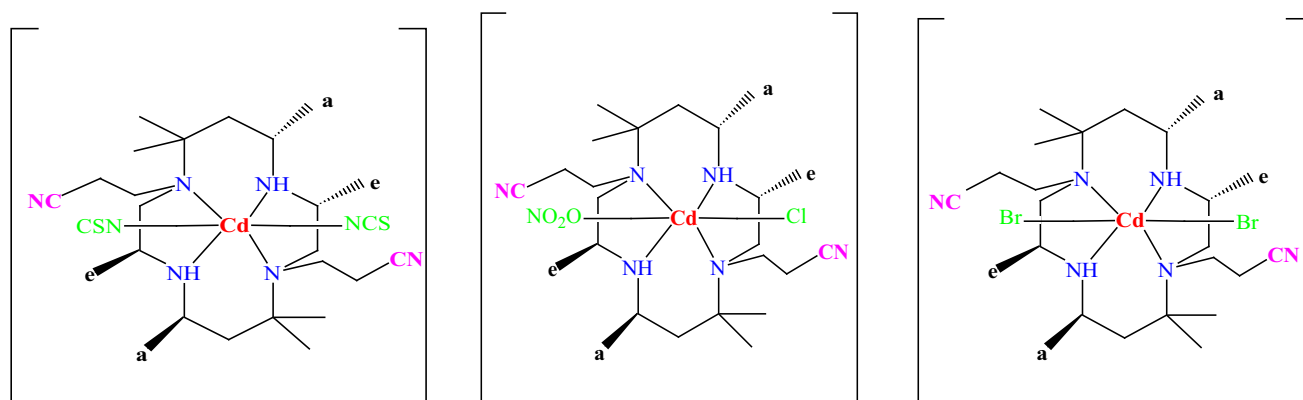
for fully N-bonded thiocyanate group.<sup>21–23</sup> Therefore, the complex can be identified as isothiocyanato complexes. Again, the absence of  $\text{NO}_3^-$  bands around  $1384\text{ cm}^{-1}$  of  $[\text{Cd}(\text{L}_\text{BX})(\text{Br})_2]$  indicates that both the  $\text{NO}_3^-$  ions are completely replaced by  $\text{Br}^-$  ions. Since IR spectrum could not be run below  $400\text{ cm}^{-1}$ , so Cd-Br band could not be detected. The molar conductivity value  $0\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  of  $[\text{Cd}(\text{L}_\text{BX})(\text{NCS})_2]$  in chloroform supports the nonelectrolytic nature of this complex whereas the value of  $56\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  in DMSO indicates that the complex is 1:1 electrolyte in these solvents indicating the conversion of octahedral species into square pyramidal species as indicated by the following equation.



The molar conductivity value  $0\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  of  $[\text{Cd}(\text{L}_\text{BX})(\text{NO}_3)(\text{Cl})]$  in  $\text{CHCl}_3$  and  $26\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  in DMSO solution of this complex shows the nonelectrolytic nature of this complex as expected by the assigned molecular formula. However, the conductance value  $77\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  in acetonitrile corresponding almost to 1:1 electrolyte indicates the conversion of octahedral to square pyramidal complex as indicated by following equation.

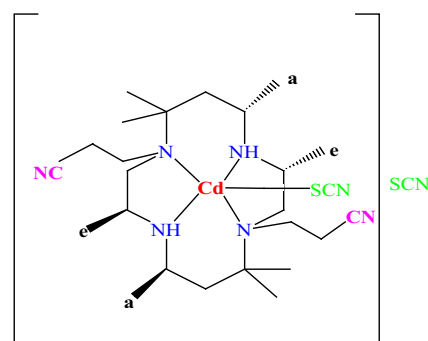


The conductance value of  $0\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  in  $\text{CHCl}_3$  and  $38\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  in DMSO (showing a little ionization) for the complex,  $[\text{Cd}(\text{L}_\text{BX})(\text{Br})_2]$  support the nonelectrolytic nature of his complex. i.e., two bromide ( $\text{Br}^-$ ) ions are coordinated to cadmium(II) ion. The  $^1\text{H-NMR}$  spectrum of the diisothiocyanato cadmium(II) complex of  $\text{L}_\text{BX}$ ,  $[\text{Cd}(\text{L}_\text{BX})(\text{NO}_3)_2]$  displays



**Figure 3.** Structures of  $[\text{Cd}(\text{L}_{\text{BX}})(\text{NCS})_2]$  (left),  $[\text{Cd}(\text{L}_{\text{BX}})(\text{NO}_3)(\text{Cl})]$  (middle) and  $[\text{Cd}(\text{L}_{\text{BX}})(\text{Br})_2]$ .

similar spectral pattern like that of parent complex  $[\text{Cd}(\text{L}_{\text{BX}})(\text{NCS})_2]$  which reveals two singlets. The singlets at 1.21 ppm and 1.33 ppm each corresponding to six protons can be assigned to equatorial and axial components of the gem-dimethyl groups, respectively. The spectrum further reveals two doublets at 1.013 ppm and 1.084 ppm each corresponding to 6H, which can be assigned to equatorially oriented two methyl protons and axially oriented two methyls protons respectively on equivalent chiral carbons. The spectrum further shows some downfield multiplets at 1.47, 1.70, 2.82 and 3.18 ppm due to  $\text{CH}_2$ ,  $\text{CH}$  and  $\text{NH}$  protons. So, the same diaxial-diequatorial assignment is made for this complex as assigned for the parent complex,  $[\text{Cd}(\text{L}_{\text{BX}})(\text{NO}_3)_2]$ . This observation again proves that axial substitution takes place without change of conformation and configuration of the ligand of the original complex. From the above and earlier discussion, the structures for  $[\text{Cd}(\text{L}_{\text{BX}})(\text{NCS})_2]$ ,  $[\text{Cd}(\text{L}_{\text{BX}})(\text{NO}_3)(\text{Cl})]$  and  $[\text{Cd}(\text{L}_{\text{BX}})(\text{Br})_2]$  can be assigned as shown in Figure 3.



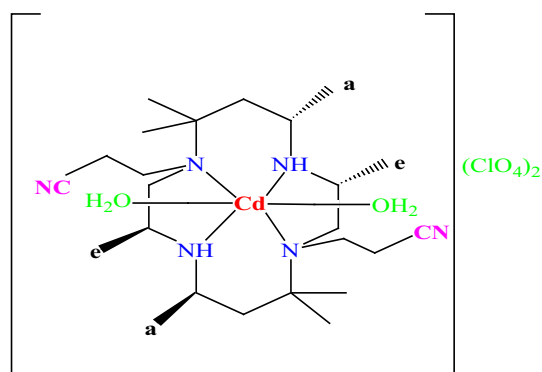
**Figure 4.** Structure of  $[\text{Cd}(\text{L}_{\text{BX}})(\text{SCN})](\text{SCN})$ .

in DMSO of the complex  $[\text{Cd}(\text{L}_{\text{BX}})(\text{NCS})](\text{SCN})$  corresponds to 1:1 electrolyte as expected for the molecular formula assigned. As this complex is found to be insoluble in other solvents like  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{CN}$  and  $\text{H}_2\text{O}$ , so molar conductivity of the complex in these solvents could not be measured. Since the axial substitution and addition takes place without change of conformation and configuration<sup>6,9,18</sup> of the ligand in original complex, the structure of complex  $[\text{Cd}(\text{L}_{\text{BX}})(\text{SCN})](\text{SCN})$  can be assigned by Figure 4.

**3.3d  $[\text{Cd}(\text{L}_{\text{BX}})(\text{SCN})](\text{SCN})$ :** A simultaneous axial substitution and anion exchange reaction on  $[\text{Cd}(\text{L}_{\text{BX}})(\text{NO}_3)](\text{NO}_3)$  by  $\text{KSCN}$  produced a square pyramidal complex  $[\text{Cd}(\text{L}_{\text{BX}})(\text{SCN})](\text{SCN})$ . The infrared spectrum of this isothiocyanato complex shows all characteristic  $\nu_{\text{N-H}}$ ,  $\nu_{\text{C-C}}$  and  $\nu_{\text{C-H}}$  bands in the expected regions. Presence of  $\nu_{\text{NCS}}$  band and  $\nu_{\text{CN}}$  band demonstrate that the  $\text{NO}_3^-$  groups are substituted by  $\text{NCS}$  groups. In the case of complex  $[\text{Cd}(\text{L}_{\text{BX}})(\text{NCS})_2]$  and  $[\text{Cd}(\text{L}_{\text{BX}})(\text{NCS})](\text{SCN})$  an infrared band at  $2245\text{ cm}^{-1}$  indicates the presence of cyano ( $-\text{C} \equiv \text{N}$ ) group whereas a band at  $552\text{ cm}^{-1}$  demonstrates the presence of  $\nu_{\text{C-Cd}}$  band. Evidence in favour of coordination of  $\text{NCS}^-$  ion have been discussed elaborately in the earlier section. The molar conductivity value of  $68\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$

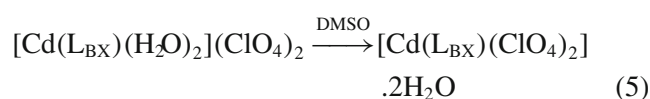
**3.3e  $[\text{Cd}(\text{L}_{\text{BX}})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ :** Square pyramidal  $[\text{Cd}(\text{L}_{\text{BX}})(\text{NO}_3)](\text{NO}_3)$  underwent simultaneous axial addition, substitution and anion exchange reaction with  $\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$  to yield an octahedral complex,  $[\text{Cd}(\text{L}_{\text{BX}})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ . The infrared spectrum of this complex exhibits all characteristic bands due to  $\nu_{\text{N-H}}$ ,  $\nu_{\text{C-C}}$ ,  $\nu_{\text{C-H}}$ ,  $\nu_{\text{Cd-N}}$ , and  $\nu_{\text{CH}_3}$  stretching frequencies at the proper regions. Infrared spectrum further exhibits the perchlorate bands at  $1026\text{ cm}^{-1}$  and  $624\text{ cm}^{-1}$  and  $\nu_{\text{H}_2\text{O}}$  band at  $3433\text{ cm}^{-1}$ . A band at  $2245\text{ cm}^{-1}$  indicates the presence of cyano ( $-\text{C} \equiv \text{N}$ ) group. The conductance value  $259\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  in acetonitrile corresponding to 1:2 electrolyte, coinciding with the assigned molecular formula  $[\text{Cd}(\text{L}_{\text{BX}})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ . However, the conductance of  $45\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  in





**Figure 5.** Structure of  $[\text{Cd}(\text{L}_{\text{BX}})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ .

DMSO solution of this complex shows the nonelectrolytic nature which demonstrates solvent DMSO forces anions to go inside the coordination sphere indicated by the following equation.



From the above and earlier discussion the probable structure of  $[\text{Cd}(\text{L}_{\text{BX}})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  complex can be assigned by Figure 5.

### 3.4 Antibacterial activities

Except for a few cases,<sup>11,24,25</sup> antibacterial activities of the concerned macrocyclic ligands and their metal complexes have not been studied extensively. So it is

noteworthy to examine whether these ligands and complexes show any such activity or not. For this purpose, investigation on the antibacterial activities of isomeric ligand  $\text{L}_{\text{B}}$  and its N-pendent derivative,  $\text{L}_{\text{BX}}$  as well as their Cd(II) complexes have been carried out against two important selected gram-positive and two gram-negative bacteria which cause different diseases, viz., *Bacillus cereus* which causes gastroenteritis, *Salmonella typhi* and *Staphylococcus aureus* which cause diarrhea, vomiting and abdominal pain. *Pseudomonas aeruginosa* causes osteomyelitis, endocarditic, respiratory tract infection and urinary tract infection. The results of overnight observations on concerned bacteria are summarized in Table 1, which show that, while the ligands are ineffective in all cases, several of their complexes exhibit some antibacterial activity. This is in accord with observations on similar systems.<sup>11,24,25</sup> As seen from Table 1, all complexes are highly effective against all bacteria. The antibacterial activity of non coordinated metal salts and DMSO (control) were also investigated for making the comparison. However, no definite trend can be derived from the observations at this stage, but the positive results suggest further studies are warranted. Though cadmium salt also exhibit antibacterial activity in the range of complexes, but cadmium(II) salts are very toxic for human beings. The increased activity in complex is also not due to any ionized  $\text{Cd}^{2+}$  moiety because the complexes are highly stable. The increased activity of the complexes in a few cases compared to ligands can be explained by chelation theory;<sup>26</sup> i.e., the possible mechanism is that the complexes disturb the respiration process of the cell and thus block the synthesis of protein, which restricts further growth of the organism.<sup>27</sup> In

**Table 1.** Antibacterial activities of ligands and their cadmium(II) complexes against some human pathogenic bacteria.

Ligands and their complexes	Zone of inhibition diameter in mm			
	Gram-positive bacteria		Gram-negative bacteria	
	<i>Bacillus cereus</i>	<i>Staphylococcus aureus</i>	<i>Salmonella typhi</i>	<i>Pseudomonas aeruginosa</i>
$\text{L}_{\text{B}}$	0	0	0	0
$\text{L}_{\text{BX}}$	0	0	0	0
$[\text{Cd}(\text{L}_{\text{B}})(\text{ClO}_4)_2]$	17	13	16	14
$[\text{Cd}(\text{L}_{\text{BX}}\text{NO}_3)](\text{NO}_3)$	18	19	20	16
$[\text{Cd}(\text{L}_{\text{BX}})(\text{NO}_3)_2]$	15	16	17	15
$[\text{Cd}(\text{L}_{\text{BX}})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	17	16	17	15
$[\text{Cd}(\text{L}_{\text{BX}}\text{NO}_3)(\text{Cl})]$	18	12	20	17
$[\text{Cd}(\text{L}_{\text{BX}})(\text{SCN})](\text{SCN})$	16	16	13	14
$[\text{Cd}(\text{L}_{\text{BX}})(\text{NCS})_2]$	16	15	16	17
$[\text{Cd}(\text{L}_{\text{BX}})(\text{Br})_2]$	20	19	16	25
Cadmium(II) perchlorate	10	8	8	7

the disc diffusion method, inhibition zone of the complexes is related to susceptibility of the isolate and to diffusion rate of drug through agar medium.<sup>28</sup>

#### 4. Conclusions

This study reveals that the isomeric ligand  $L_B$  of 3,10-C-meso-Me<sub>8</sub>[14]ane and its N-pendent derivative,  $L_{BX}$  undergo facile complexation with cadmium(II) perchlorate salt and cadmium(II) nitrate salt, respectively. The reaction of  $L_B$  with cadmium(II) perchlorate produced octahedral,  $[Cd(L_B)(ClO_4)_2]$  whereas reaction of  $L_{BX}$  with cadmium(II) nitrate produced square pyramidal,  $[Cd(L_{BX})(NO_3)](NO_3)$  and octahedral  $[Cd(L_{BX})(NO_3)_2]$ . The complexes  $[Cd(L_B)(ClO_4)_2]$  and  $[Cd(L_{BX})(NO_3)_2]$  were found to be nonelectrolytes in  $CHCl_3$  as expected for six coordinated octahedral species. However, conductance value of  $[Cd(L_{BX})(NO_3)_2]$  in DMSO and  $CH_3CN$  correspond to 1:1 electrolyte indicating ionization, i.e., conversion of octahedral to square pyramidal species in these solvents. But the complex  $[Cd(L_{BX})(NO_3)](NO_3)$  is 1:1 electrolyte in the only soluble solvent DMSO, as expected. On the other hand, diperchlorato complex of  $L_B$ ,  $[Cd(L_B)(ClO_4)_2]$  and dinitrato complex of  $L_{BX}$ ,  $[Cd(L_{BX})(NO_3)_2]$  undergo axial substitution reactions with  $NCS^-$  and  $Br^-$  to produce the corresponding octahedral substituted complexes, diisothiocyanato and dibromido derivatives, respectively. These complexes were found to be nonelectrolytes in  $CHCl_3$ , as expected for six coordinated octahedral species. However, conductance values in DMSO and  $CH_3CN$  correspond to 1:1 electrolytes which indicate the conversion of octahedral to square pyramidal species in these solvents. Similarly  $[Cd(L_{BX})(NO_3)](NO_3)$  of  $L_{BX}$  undergoes simultaneous axial addition, axial substitution and anion exchange reactions with  $NaClO_4 \cdot 6H_2O$  to produce diaquacadmium(II) diperchlorate; axial addition with  $KCl$  to yield mononitratochlorido cadmium(II) and simultaneous axial substitution and anion exchange reaction with  $KCNS$  to yield monoisothiocyanato cadmium(II) thiocyanate complex. The ligands did not show any activity against the bacteria but the cadmium(II) complexes of these ligands exhibited remarkable activities against the tested bacteria.

#### Supplementary Information (SI)

<sup>1</sup>H-NMR, <sup>13</sup>C-NMR and Mass spectra for the newly synthesized ligand are shown in Figures S1-S3, respectively. The synthesis of  $L$ ,  $2HClO_4$ ,  $L_A$ ,  $L_B$ ,  $L_C$  and  $L_{BX}$  and fragmentation pattern of ligand  $L_{BX}$  have been

shown in Schemes S1, S2a and S2b, respectively. <sup>1</sup>H-NMR spectra for  $[Cd(L_B)(ClO_4)_2]$ ,  $[Cd(L_B)(NO_3)](NO_3)$  and  $[Cd(L_{BX})(NCS)_2]$  are shown in Figures S4–S6, respectively. X-ray structure of ligand  $L_{BX}$ , two dimensional structure of ligand  $L_{BX}$  and structures of cadmium(II) complexes are shown. The results on antibacterial activities of the new compounds have been included in Table S1. Supplementary Information is available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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