

# Synthesis, Characterization And Electrolytic Behavior Of Cadmium(II) Complexes Of 5,7,7,12,14,14-Hexamethyl-1,4,8,11-Tetraazacyclotetradeca-4,11-Diene And Isomers Of Its Saturated Analogue

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## Abstract

Condensation of ethylenediamine with acetone in the presence of quantitative amount of perchloric acid, yielded the ligand 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate (denoted by L.2HClO<sub>4</sub>). The ligand L.2HClO<sub>4</sub> on reduction with NaBH<sub>4</sub>, yielded an isomeric mixture of saturated macrocycles, the Me<sub>6</sub>[14]anes, which were resolved into two distinct C-chiral isomers (denoted by ‘tet-a’ and ‘tet-b’). Interaction of ligands L.2HClO<sub>4</sub>, ‘tet-a’ and ‘tet-b’ with salts CdI<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O, CdCl<sub>2</sub>.2H<sub>2</sub>O and Cd(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O produced different five coordinated square pyramidal and six coordinated octahedral cadmium(II) complexes. Among them the complexes, *cis*-[Cd(tet-a)(NO<sub>3</sub>)](NO<sub>3</sub>) and *cis*-[Cd(tet-b)(NO<sub>3</sub>)](NO<sub>3</sub>) underwent axial ligand substitution reaction with KCNS; whereas complex [Cd(tet-a)I<sub>2</sub>] underwent axial ligand substitution reaction and complex [CdLI](ClO<sub>4</sub>) underwent simultaneous ligand substitution and addition reaction with NaNO<sub>2</sub>. Characterization of all the complexes were carried out on the basis of elemental analysis; FT-IR, UV-Vis. and <sup>1</sup>H-NMR spectroscopy; melting point determination as well as by magnetic moment and conductivity measurements. Molar conductivity measurement of the complexes revealed that they show different electrolytic behavior in different solvents.

**Keywords:** Cadmium(II); Azamacrocyclic ligands; Square pyramidal complexes; Octahedral complexes; Electrolytic behaviour

## Introduction

Great interest in the study of metal complexes with azamacrocyclic ligands is because of their importance in Supramolecular Chemistry, Material Chemistry and Biochemistry (Goher, et al., 1992; Boss, 1984; Escur, et al., 1996; Chandra and Kumar, 2004). The metal complexes containing synthetic tetraazamacrocyclic ligands have attracted a great deal of attention because they can be used as models for more intricate biological systems: metalloporphyrins (hemoglobin, myoglobin, cytochromes and chlorophylls), corrins (vitamin B<sub>12</sub>) and antibiotics (valinomycin, nonactin) (Radecka-Paryzek, et al., 2005; Alborés, et al., 2006; Mohapatra, et al., 2012; Ghachtouli, et al., 2006; Notni, et al., 2006; Suh, et al., 2006). Their (tetraazamacrocyclic ligands) specific complexation behavior is clearly of interest in many areas such as the design of complexes to act as medical imaging agents (Lauffer, 1987), act as effective antibacterial and antifungal agents (Biswas, et al., 2014; Sheikh, et al., 2010) and for the treatment of heavy metal intoxication in the case of metal poisoning (Hancock, et al., 1989; Hancock, et al., 1988).

In earlier study, Roy et al. (1999) prepared six-coordinate copper(II) complexes of octamethyltetraazacyclotetradecadiene of general formula  $[\text{Cu}(\text{Me}_8[14]\text{diene})(\text{ClO}_4)_m\text{X}_n]$ , where  $\text{X} = \text{NCS}^-$ ,  $\text{Cl}^-$  or  $\text{NO}_3^-$ ;  $m = 0$  or  $1$  and  $n = 1$  or  $2$ . In another study, Roy and coworkers (Roy, et al., 2007) prepared octahedral *cis*- and *trans*- cadmium(II) complexes with ligand, 3,10-C-meso-Me<sub>8</sub>[14]ane. The structure of compound *cis*-[CdL<sub>c</sub>(NO<sub>3</sub>)](NO<sub>3</sub>) (where L<sub>c</sub> is one isomeric ligand of Me<sub>8</sub>[14]ane) has been confirmed by X-ray crystallography (Roy, et al., 2010). Roy et al. (2011) reported synthesized a six-coordinate cobalt(III) complex of parent diene ligand (Me<sub>6</sub>[14]diene) of formula  $[\text{Co}(\text{NO}_2)_2(\text{C}_{16}\text{H}_{32}\text{N}_4)]$  and has been confirmed by X-ray crystallography. Recently Yasmin et al. (2013) synthesized and characterized the complexes:  $[\text{Cu}(\text{Me}_6[14]\text{ane})(\text{ClO}_4)_2]$ ,  $[\text{Zn}(\text{Me}_6[14]\text{ane})(\text{NO}_3)_2]$  and  $[\text{Cu}(\text{Me}_6[14]\text{ane})(\text{H}_2\text{O})]\text{Cl}$  X-ray crystallography.

Detailed studies on cadmium(II) complexes of hexamethyltetraazacyclotetradecadiene (L.2HClO<sub>4</sub>) and isomers of its saturated analogues ('teta' and 'tetb') were not reported so far. In our present study, new octahedral and square pyramidal cadmium(II) complexes of ligands L, 'tet-a' and 'tet-b' have been synthesized. Among them, four complexes also give their axial ligand substitution and addition products. Herein, synthesis, characterization and electrolytic behavior of the new cadmium(II) complexes have been reported. These complexes were found as

very much effective antibacterial and antifungal agents as reported recently by our research group (Biswas, et al., 2014).

## Experimental section

### Materials

Ethylenediamine, absolute methanol (99.50%, v/v), dimethyl sulfoxide (DMSO) and sodium borohydride were purchased from Merck, Germany. Perchloric acid (70%, v/v), chloroform, xylene and metal salts ( $\text{CdI}_2$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{KCNS}$  and  $\text{NaNO}_2$ ) were purchased from Sigma-Aldrich, Munich, Germany.  $\text{KBr}$  was purchased from Flucka AG, Switzerland. The solvents were dried using standard literature procedures.

### Measurements

Microanalysis (C, H, N, S analysis) of the complexes have been carried out on a C, H, N, S-analyzer at the Institut der Anorganische und Angewandte Chemie, Hamburg Universitaet, Germany. FT-IR spectra were taken as  $\text{KBr}$  discs in the range  $4000\text{-}400\text{ cm}^{-1}$  on a Perkin-Elmer infrared spectrophotometer, Department of Chemistry, University of Chittagong, Bangladesh. Electronic absorption spectra were recorded on a Shimadzu UV-Visible 265 spectrophotometer.  $^1\text{H-NMR}$  spectra were measured in  $\text{CDCl}_3$  and DMSO solution on a 400 MHz NMR instrument at Bangladesh Council of Scientific and Industrial Research (BCSIR) laboratory, Dhaka, Bangladesh. Chemical shifts are given in ppm relative to tetramethylsilane as an internal reference. Conductance measurements of the metal complexes were done in chloroform, DMSO and water at  $10^{-3}\text{ M}$  using a HANNA instrument equipped with a HI 8820N conductivity cell. Magnetic measurements were carried out with a Gouy balance, calibrated against  $\text{Hg}[\text{Co}(\text{NCS})_4]$ ; susceptibilities were corrected for diamagnetic increments. Melting points of the complexes were measured on a Stuart SMP10 melting point (range: upto  $300^\circ\text{C}$ ) apparatus. For the determination of cadmium in complexes accurately weighed amounts of complexes were heated with a mixture of conc.  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HClO}_4$  to convert cadmium complexes into cadmium(II) salts and then extracted into water. The solution was then titrated with a standard solution of  $\text{Na}_2\text{EDTA}$  using Xylenol orange as indicator.

### Synthesis

**Preparation of macrocycles:** Synthesis of the ligand 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate ( $\text{L} \cdot 2\text{HClO}_4$ ) and isolation of isomers of its saturated analogue ('tet-a' and

'tet-b') were carried out according to the procedure adopted in literature (Busch, et al., 1971; Bembi, et al., 1984).

### Preparation of new cadmium(II) complexes by direct reaction of ligands (L.2HClO<sub>4</sub>, 'tet-a' and 'tet-b') with different cadmium(II) salts

Proper weight (1.0 mmol) of Cadmium(II) salts (CdI<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O, CdCl<sub>2</sub>.2H<sub>2</sub>O or Cd(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O) and ligands (1.0 mmol) (L.2HClO<sub>4</sub>, 'tet-a' or 'tet-b') were suspended/dissolved separately in 25 mL of hot methanol. The ligand solution/suspension was added as soon as possible to the salt solution while hot. The solution mixture was heated on a water bath and the volume of the solution reduced to 15 mL. The solution was allowed to cool for one hour and the white solid product of cadmium(II) complex was filtered off, washed with methanol followed by diethyl ether and dried in a vacuum desiccator over silica gel.

**[CdLI](ClO<sub>4</sub>) (1):** Yield: <85%. m.p.: >300°C. Found: C, 31.11; H, 5.15; N, 9.02; Cd, 18.05. Calcd for C<sub>16</sub>H<sub>32</sub>N<sub>4</sub>CdClO<sub>4</sub>: C, 31.03; H, 5.17; N, 9.05; Cd, 18.17%.

**trans-[Cd(tet-a)I<sub>2</sub>] (2):** Yield: <80%. m.p.: >300°C. Found: C, 30.01; H, 5.51; N, 8.56; Cd, 17.29. Calcd for C<sub>16</sub>H<sub>36</sub>N<sub>4</sub> CdI<sub>2</sub>: C, 29.53; H, 5.54; N, 8.61; Cd, 17.29%.

**trans-[Cd(tet-b)I<sub>2</sub>] (3):** Yield: <78%. m.p.: >300°C. Found: C, 29.98; H, 5.49; N, 8.57; Cd, 17.27. Calcd for C<sub>16</sub>H<sub>36</sub>N<sub>4</sub>CdI<sub>2</sub>: C, 29.53; H, 5.54; N, 8.61; Cd, 17.29%.

**cis-[Cd(tet-a)(NO<sub>3</sub>)](NO<sub>3</sub>) (4)** Yield: <70%. m.p.: >300°C. Found: C, 36.78; H, 6.90; N, 16.12; Cd, 21.63. Calcd for C<sub>16</sub>H<sub>36</sub>N<sub>6</sub>CdO<sub>6</sub>: C, 36.89; H, 6.92; N, 16.14; Cd, 21.59%.

**cis-[Cd(tet-b)(NO<sub>3</sub>)](NO<sub>3</sub>) (5):** Yield: <75%. m.p.: >300°C. Found: C, 36.82; H, 6.89; N, 16.12; Cd, 21.61. Calcd for C<sub>16</sub>H<sub>36</sub>N<sub>6</sub>CdO<sub>6</sub>: C, 36.89; H, 6.92; N, 16.14; Cd, 21.59%.

**[CdLCl]Cl (6):** Yield: <80%. m.p.: >300°C. Found: C, 31.11; H, 5.15; N, 9.02; Cd, 18.05. Calcd for C<sub>16</sub>H<sub>32</sub>N<sub>4</sub>CdCl<sub>2</sub>: C, 31.03; H, 5.17; N, 9.05; Cd, 18.17%.

**trans-[Cd(tet-a)Cl<sub>2</sub>] (7):** Yield: <80%. m.p.: >300°C. Found: C, 41.05; H, 7.71; N, 11.92; Cd, 24.15. Calcd for C<sub>16</sub>H<sub>36</sub>N<sub>4</sub>CdCl<sub>2</sub>: C, 41.08; H, 7.70; N, 11.98; Cd, 24.05%.

**trans-[Cd(tet-b)Cl<sub>2</sub>] (8):** Yield: <75%. m.p.: >300°C. Found: C, 41.04; H, 7.69; N, 11.95; Cd, 24.17. Calcd for C<sub>16</sub>H<sub>36</sub>N<sub>4</sub>CdCl<sub>2</sub>: C, 41.08; H, 7.70; N, 11.98; Cd, 24.05%.

**[CdL(ClO<sub>4</sub>)](ClO<sub>4</sub>) (9):** Yield: <80%. m.p.: >300°C. Found: C, 32.43; H, 5.39; N, 9.44; Cd, 19.12. Calcd for C<sub>16</sub>H<sub>32</sub>N<sub>4</sub>CdCl<sub>2</sub>O<sub>8</sub>: C, 32.47; H, 5.41; N, 9.47; Cd, 19.01%.

**[Cd(tet-a)(ClO<sub>4</sub>)<sub>2</sub>] (10):** Yield: <80%. m.p.: >300°C. Found: C, 32.20; H, 6.05; N, 9.38; Cd, 18.92. Calcd for C<sub>16</sub>H<sub>36</sub>N<sub>4</sub> CdCl<sub>2</sub>O<sub>8</sub>: C, 32.25; H, 6.04; N, 9.41; Cd, 18.88%.

**[Cd(tet-b)(ClO<sub>4</sub>)<sub>2</sub>] (11):** Yield: <85%. m.p.: >300°C. Found: C, 32.21; H, 6.07; N, 9.40; Cd, 18.95. Calcd for C<sub>16</sub>H<sub>36</sub>N<sub>4</sub> CdCl<sub>2</sub>O<sub>8</sub>: C, 32.25; H, 6.04; N, 9.41; Cd, 18.88%.

### **Preparation of axial ligand substitution, axial substitution with anion exchange or simultaneous addition & substitution products of some cadmium(II) complexes**

Proper weight (1.0 mmol) of selected cadmium(II) complexes (*cis*-[Cd(tet-a)(NO<sub>3</sub>)(NO<sub>3</sub>)], *cis*-[Cd(tet-b)(NO<sub>3</sub>)(NO<sub>3</sub>)], *cis*-[CdLI]ClO<sub>4</sub> or *trans*-[Cd(tet-a)I<sub>2</sub>]) and concerned salts (2.0 mmol) (KCNS or NaNO<sub>2</sub>) were suspended/dissolved separately in 25 mL of hot methanol. The solution mixture was heated in a water bath and the volume of the solution reduced to 10 mL. The solution was allowed to cool for three hours and the white solid product of cadmium(II) was filtered off, washed with methanol followed by diethyl ether and dried in a vacuum desiccator over silica gel.

**[Cd(teta)(SCN)](SCN) (12):** Yield: <70%. m.p.: >300°C. Found: C, 42.13; H, 7.04; N, 10.88; S, 12.48; Cd, 21.98. Calcd for C<sub>18</sub>H<sub>36</sub>N<sub>6</sub>CdS<sub>2</sub>: C, 42.15; H, 7.03; N, 10.93; S, 12.49; Cd, 21.94%.

**[Cd(tetb)(SCN)](SCN) (13):** Yield: <70%. m.p.: >300°C. Found: C, 42.12; H, 7.03; N, 10.91; S, 12.49; Cd, 22.01. Calcd for C<sub>18</sub>H<sub>36</sub>N<sub>6</sub>CdS<sub>2</sub>: C, 42.15; H, 7.03; N, 10.93; S, 12.49; Cd, 21.94%.

***trans*-[CdL(NO<sub>2</sub>)<sub>2</sub>] (14):** Yield: <75%. m.p.: >300°C. Found: C, 39.62; H, 6.58; N, 17.33; Cd, 23.26. Calcd for C<sub>16</sub>H<sub>32</sub>N<sub>6</sub>CdO<sub>4</sub>: C, 39.64; H, 6.61; N, 17.34; Cd, 23.20%.

***trans*-[Cd(tet-a)(NO<sub>2</sub>)<sub>2</sub>] (15):** Yield: <75%. m.p.: >300°C. Found: C, 39.28; H, 6.73; N, 17.18; Cd, 23.09. Calcd for C<sub>16</sub>H<sub>36</sub>N<sub>6</sub>CdO<sub>4</sub>: C, 39.31; H, 7.37; N, 17.20; Cd, 23.01%.

## **Results and discussion**

### **Syntheses**

The structures of L.2HClO<sub>4</sub>, ‘tet-a’ and ‘tet-b’ (Figure 1) were established as per literature (Busch, et al., 1971; Bembi, et al., 1984).

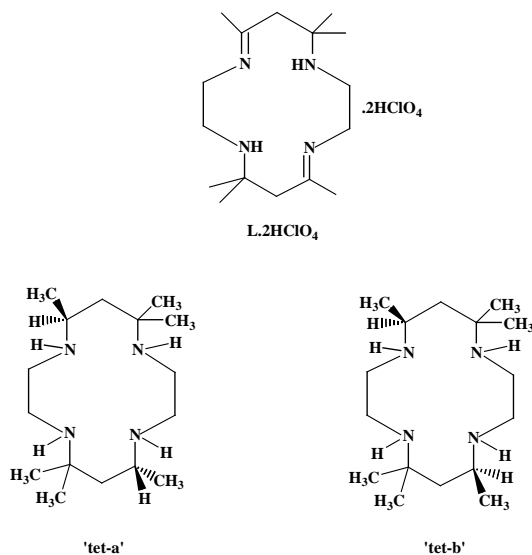


Figure 1. Chemical structure of macrocyclic ligands L.2HClO<sub>4</sub>, 'tet-a' and 'tet-b'.

Macrocyclic ligands L.2HClO<sub>4</sub>, 'tet-a' and 'tet-b' interact with salts CdI<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, CdCl<sub>2</sub>·2H<sub>2</sub>O or Cd(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in methanolic solution to produce six coordinated cis or trans cadmium(II) complexes and five coordinated square pyramidal complexes. The complexes *cis*-[Cd(tet-a)(NO<sub>3</sub>)](NO<sub>3</sub>) and *cis*-[Cd(tet-b)(NO<sub>3</sub>)](NO<sub>3</sub>) underwent axial ligand substitution and anion exchange reaction with KCNS to produce [Cd(tet-a)(SCN)](SCN) and [Cd(tet-b)(SCN)](SCN) respectively. The square pyramidal complex [CdLI](ClO<sub>4</sub>) underwent ligand substitution and addition reaction simultaneously with NaNO<sub>2</sub> to produce *trans*-[CdL(NO<sub>2</sub>)<sub>2</sub>] and the complex *trans*-[Cd(tet-a)I<sub>2</sub>] underwent only axial ligand substitution reaction with NaNO<sub>2</sub> to produce *trans*-[Cd(tet-a)(NO<sub>2</sub>)<sub>2</sub>].

The compounds were characterized by elemental analysis, melting point determination, FT-IR (Table 1), UV-Vis. and <sup>1</sup>H-NMR (Table 2) spectroscopy as well as by magnetochemical and conductivity measurement (Table 3).

The cadmium(II) compounds were found to be diamagnetic as expected for their d<sup>10</sup> electronic configuration. The electronic spectra of these compounds do not exhibit d-d bands, again as expected for d<sup>10</sup> systems. Since infrared spectra of these compounds could not be run at wave numbers lower than 400 cm<sup>-1</sup>, IR bands due to same metal-ligand (axial) stretches could not be recorded. Conductance values of 0 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup> in chloroform and 9-26 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup> in DMSO of some complexes supported the formation of non-electrolytic compounds. Molar conductivity values of 64-92 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup> of some complexes in DMSO indicate that the complexes are 1:1 electrolyte in nature. Figure 2 and Figure 3 represent the

IR spectra of complex  $[\text{CdLCl}]\text{Cl}$  and  $^1\text{H-NMR}$  spectra of complex  $[\text{CdLI}](\text{ClO}_4)$  respectively.

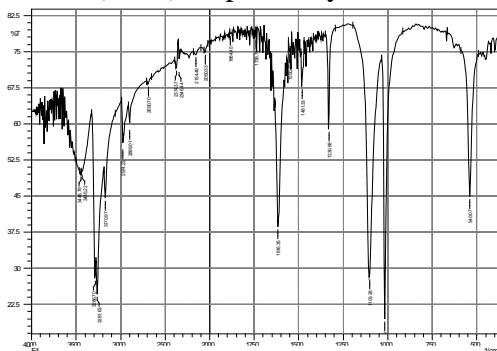


Figure 2. IR spectra of complex  $[\text{CdLCl}]\text{Cl}$

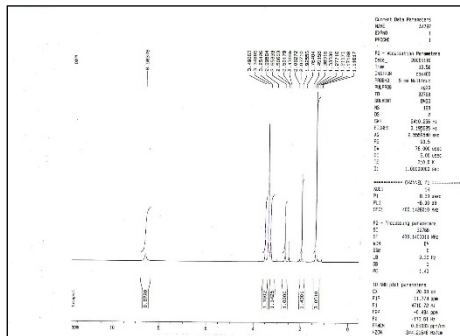


Figure 3.  $^1\text{H-NMR}$  spectra of complex *cis*- $[\text{CdLI}](\text{ClO}_4)$

### Compounds produced by direct reaction of ligands (L.2HClO<sub>4</sub>, ‘tet-a’ and ‘tet-b’) with cadmium(II) salts

All the cadmium(II) complexes are white as expected. The infrared spectra of these compounds exhibit  $\nu\text{N-H}$  bands at around  $3180\text{-}3263\text{ cm}^{-1}$ , and other characteristic  $\nu\text{C-H}$ ,  $\nu\text{CH}_3$ ,  $\nu\text{C-C}$ ,  $\nu\text{Cd-N}$ ,  $\nu\text{C=N}$  bands in the expected regions (Table 1). The complex  $[\text{CdLI}](\text{ClO}_4)$  shows the perchlorate bands around  $1107$  and  $613\text{ cm}^{-1}$  (Table 1). The perchlorate group is ionic in the complex, since there is no splitting of the perchlorate band (Roy and Bembi, 2005) around  $1100\text{ cm}^{-1}$ . The IR spectrum for the complex  $[\text{CdL}(\text{ClO}_4)](\text{ClO}_4)$  exhibits bands at  $1130$ ,  $1070$ ,  $1024$  and  $621\text{ cm}^{-1}$ ; the complexes  $[\text{Cd}(\text{tet-a})(\text{ClO}_4)_2]$  and  $[\text{Cd}(\text{tet-b})(\text{ClO}_4)_2]$  exhibit bands at  $1125$ ,  $1070\text{-}1080$ ,  $1037\text{-}1051$  and  $624\text{ cm}^{-1}$ ; due to the perchlorate group. The splitting of the perchlorate at  $1100\text{ cm}^{-1}$  is an indication of presence of coordinated  $\text{ClO}_4^-$  (Roy, et al., 1999). The IR spectrum of the complexes *cis*- $[\text{Cd}(\text{tet-a})(\text{NO}_3)](\text{NO}_3)$  and *cis*- $[\text{Cd}(\text{tet-b})(\text{NO}_3)](\text{NO}_3)$  display bands attributed to the coordinated  $\text{NO}_3^-$  group (Table 1). Thus, the pattern centered at  $1374\text{-}1375\text{ cm}^{-1}$  of *cis*- $[\text{Cd}(\text{tet-a})(\text{NO}_3)](\text{NO}_3)$  and *cis*- $[\text{Cd}(\text{tet-b})(\text{NO}_3)](\text{NO}_3)$  are splitted into bands at  $1278\text{-}1284$  and  $1458\text{-}1466\text{ cm}^{-1}$ ; the pattern with the separation of these bands by  $180\text{-}182\text{ cm}^{-1}$  respectively being consistent with a bidentate mode of coordination (Roy, et al., 2010). The bands at  $720\text{-}738$  and  $808\text{-}823\text{ cm}^{-1}$  of these complexes support the presence of an ionic nitrate (Hazari, et al., 1997). Since IR spectra of these compounds could not be run at a range lower than  $400\text{ cm}^{-1}$ , Cd-I, Cd-Cl bands could not be recorded.

Table 1. IR spectral data\* ( $\text{cm}^{-1}$ ) for complexes.

Complex No.	$\nu\text{N-H}$	$\nu\text{C-H}$	$\nu\text{CH}_3$	$\nu\text{C-C}$	$\nu\text{Cd-N}$	$\nu\text{C=N}$	Other bands
1	3250 s	2937 m	1360 vw	1170 vw	470 w	1583 m	1107 vs, 613 s, $\nu\text{ClO}_4$
2	3219 m	2978 s	1375 vw	1163 w	545 vw	-	-
3	3219 m	2980 s	1376 vw	1163 w	550 vw	-	-
4	3226 s	2964 vs	1380 vs	1176 s	532 vw	-	738 m, 823 m, 1284 vs, 1375 vs, 1466 s, $\nu\text{NO}_3$
5	3240 m	2964 m	1375 vs	1165 m	561 vw	-	720 w, 808 w, 1278 s, 1374 vs, 1458 m, $\nu\text{NO}_3$
6	3261 m	2974 w	1370 vw	1170 vw	540 w	1616 m	-
7	3255 s	2966 m	1372 w	1166 m	563 vw	-	-
8	3250 m	2966 m	1373 w	1166 m	560 vw	-	-
9	3151 s	2945 m	1373 s	1174 m	536 vw	1666 vs	1100 vs, 621 s, $\nu\text{ClO}_4$
10	3190 m	2980 m	1386 s	1197 m	532 vw	-	1110 vs, 624 s, $\nu\text{ClO}_4$
11	3263 s	2972 m	1373 w	1180 s	520 w	-	1110 vs, 624 s, $\nu\text{ClO}_4$
12	3211 m	2962 m	1380 s	1166 w	550 vw	-	$\nu\text{CN}$ 2071 s, $\nu\text{CS}$ 750 vw, $\delta\text{NCS}$ 425 vw
13	3203 vs	2960 s	1363 m	1165 s	532 vw	-	$\nu\text{CN}$ 2071 vs, $\nu\text{CS}$ 767 w, $\delta\text{NCS}$ 420 vw
14	3196 m	2970 s	1370 w	1180 w	549 m, 432 m	1616 s	vasym 1465 m, vsym 1335 vs, $\delta\text{NO}_2$ 835 m
15	3180 m	2968 s	1375 w	1184 w	540 m, 432 m	-	vasym 1460 m, vsym 1332 vs, $\delta\text{NO}_2$ 835 m

“-”, no band. \*vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

Though  $^1\text{H-NMR}$  spectra of some of these diamagnetic complexes could not be measured, the stereochemistry of these complexes have been assigned as corresponding dichloridocobalt(III) (Roy, et al., 2011) and corresponding zinc(II) (Yasmin, et al., 2013) complexes. This assignment is quite reasonable, because the  $^1\text{H-NMR}$  spectrum of our complexes (Table 2) showed the similar spectral pattern like that of corresponding dichloridocobalt(III) and corresponding zinc(II) complexes of our earlier studies.

$^1\text{H-NMR}$  spectra of complexes  $[\text{CdLI}](\text{ClO}_4)$  and  $[\text{CdLCl}]\text{Cl}$  display three  $\text{CH}_3$  singlets (Table 2). The singlet at 1.33-1.35 ppm, 1.67-1.93 ppm



and 2.54-2.65 ppm can be assigned to methyl protons of equatorial components of gem-dimethyl groups, methyl protons of axial components of gem-dimethyl groups and protons of CH<sub>3</sub> groups on sp<sup>2</sup> carbon (C<sub>5</sub> & C<sub>12</sub>). Both the complexes display singlet at 2.31-2.50 ppm attributable to 4H of two CH<sub>2</sub> groups on C<sub>6</sub> and C<sub>13</sub>. They also display multiplet at 3.49-3.60 ppm due to other CH<sub>2</sub> and singlet at 7.74-8.58 ppm for NH groups (Table 2).

<sup>1</sup>H-NMR spectra of all three complexes of ligand ‘tet-a’ trans-[Cd(tet-a)I<sub>2</sub>], cis-[Cd(tet-a)(NO<sub>3</sub>)] and [Cd(tet-a)(ClO<sub>4</sub>)] show a sharp methyl singlet at 1.21-1.25 ppm corresponding to the methyl protons of axial components of gem-dimethyl groups. The multiplet at 1.15-1.20 ppm corresponding to 12H can be assigned to a singlet (6H) arising out of equatorial components of gem-dimethyl group overlapped with the doublet (6H) arising out of equatorially oriented methyl protons on C<sub>5</sub> and C<sub>12</sub> chiral carbons. Similarly the complexes cis-[Cd(tet-b)(NO<sub>3</sub>)](NO<sub>3</sub>) and [Cd(tet-b)(ClO<sub>4</sub>)<sub>2</sub>] displays two methyl singlets corresponding to 6H of equatorial methyl, two singlet corresponding to 6H of axial methyl of gem-dimethyl group, and one doublet corresponding to equatorial methyls at two chiral carbons. Except cis-[Cd(tet-a)(NO<sub>3</sub>)](NO<sub>3</sub>) and cis-[Cd(tet-b)(NO<sub>3</sub>)](NO<sub>3</sub>) all the complexes of ‘teta’ and ‘tetb’ show a multiplet corresponding to 4H of CH<sub>2</sub> groups on C<sub>6</sub> and C<sub>13</sub> position. In case of complexes cis-[Cd(tet-a)(NO<sub>3</sub>)](NO<sub>3</sub>) and cis-[Cd(tet-b)(NO<sub>3</sub>)](NO<sub>3</sub>) two doublets at 2.56-2.91 ppm and 2.97-3.18 ppm each corresponding to two protons can be assigned to two CH<sub>2</sub> protons on two equivalent carbons on C<sub>6</sub> and C<sub>13</sub>. Distorsion i.e. two doublets for two equivalent CH<sub>2</sub> groups support the cis-configuration. All the complexes show different multiplets (Table 2) corresponding to other CH<sub>2</sub> and a more downfield singlet at 7.21-7.50 ppm has been assigned to NH protons.

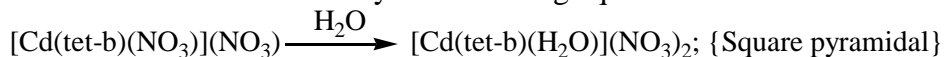
Table 2. <sup>1</sup>H-NMR chemical shifts data (ppm) for the complexes

Complex No.	CH <sub>3</sub> signals δ ppm	Signals for CH <sub>2</sub> on C <sub>6</sub> and C <sub>13</sub> position δ ppm	Other CH <sub>2</sub> and NH signals δ ppm
1	1.33 <sup>c</sup> (s, 6H) 1.93 <sup>a</sup> (s, 6H) 2.65 <sup>e</sup> (s, 6H)	2.50 (s, 4H)	3.49 (m), 8.58 (s, 2H)
2	1.21 <sup>a</sup> (s, 6H) 1.20 (m, 12H)	2.54 (m, 4H)	1.49 (m), 2.20 (m) 7.48 (s, 2H)
4	1.25 <sup>a</sup> (s, 6H) 1.18 (m, 12H)	2.56 (d, 2H) 2.97 (d, 2H)	1.51 (m), 2.17 (m) 3.06 (m), 7.50 (s, 2H)
5	1.14 <sup>e</sup> (s, 6H) 1.28 <sup>a</sup> (s, 6H) 1.22 <sup>e</sup> (s, 6H)	2.91 (d, 2H) 3.18 (d, 2H)	1.96 (m), 2.36 (m) 3.05 (m), 7.25 (s, 2H)
6	1.35 <sup>e</sup> (s, 6H) 1.67 <sup>a</sup> (s, 6H)	2.31 (s, 4H)	3.60 (m), 7.74 (s, 2H)

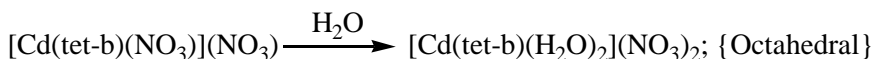
10	2.54 <sup>e</sup> (s, 6H) 1.24 <sup>a</sup> (s, 6H) 1.15 (m, 12H)	2.58 (m, 4H)	1.53 (m), 2.21 (m) 7.30 (s, 2H)
11	1.29 <sup>e</sup> (s, 6H) 1.48 <sup>a</sup> (s, 6H) 1.51 <sup>e</sup> (s, 6H)	2.30 (m, 4H)	1.92 (m), 2.04 (m) 7.21 (s, 2H)
13	1.30 <sup>a</sup> (s, 6H) 1.25 (m, 12H)	2.61 (m, 4H)	1.59 (m), 2.25 (m) 7.41 (s, 2H)
14	1.28 <sup>e</sup> (s, 6H) 1.53 <sup>a</sup> (s, 6H) 2.60 <sup>e</sup> (s, 6H)	2.42 (s, 4H)	3.05 (m), 7.25 (s, 2H)

Multiplicity is given as s, singlet; d, doublet; m, multiplet. a = axial; e = equatorial.

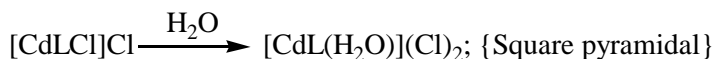
The six coordinated octahedral trans-complexes, trans-[Cd(tet-a)L<sub>2</sub>], [Cd(tet-b)L<sub>2</sub>], [Cd(tet-a)Cl<sub>2</sub>], [Cd(tet-b)Cl<sub>2</sub>], [Cd(tet-a)(ClO<sub>4</sub>)<sub>2</sub>] and [Cd(tet-b)(ClO<sub>4</sub>)<sub>2</sub>] show molar conductivity values (Table 3) of 0 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup> in chloroform and 9-26 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup> in DMSO indicating that the complexes are non-electrolyte in nature, i.e. the anions are coordinated as expected for six-coordinated octahedral cadmium(II) compounds. All the cadmium(II) complexes of diene ligand (L): [CdL](ClO<sub>4</sub>), [CdLCl]Cl, [CdL(ClO<sub>4</sub>)](ClO<sub>4</sub>), and the mononitratocadmium(II) nitrate complexes, *cis*-[Cd(tet-a)(NO<sub>3</sub>)](NO<sub>3</sub>), *cis*-[Cd(tet-b)(NO<sub>3</sub>)](NO<sub>3</sub>) show conductance values (Table 3) of 64-92 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup> in DMSO indicating that the complexes are 1:1 electrolytes as expected for the formulae assigned. The molar conductivity values of 196 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup> and 168 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup> in aqueous solution (Table 3) found for *cis*-[Cd(tet-b)(NO<sub>3</sub>)](NO<sub>3</sub>) and [CdLCl]Cl respectively corresponding to 1:2 electrolytes are probably due to replacement of the coordinated nitrate or chloride ions by one or two molecules of water as shown by the following equations:



Or



Or



Or



Similarly the conductance value of  $214 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  of complex  $[\text{Cd}(\text{tet-b})\text{Cl}_2]$  in aqueous solution corresponding to an 1:2 electrolyte which may be due to the replacement of two chloride ions by two  $\text{H}_2\text{O}$  molecules. This replacement reaction can be expressed by the following equation:

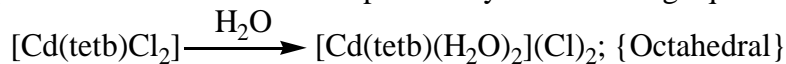


Table 3. Molar conductivity data\* for complexes.

Complex No.	Conductance ( $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ ) in different solvents		
	$\text{CHCl}_3$	DMSO	$\text{H}_2\text{O}$
1	-	64	-
2	0	09	-
3	0	26	-
4	-	66	-
5	-	73	196
6	-	69	168
7	0	18	-
8	0	17	214
9	-	75	-
10	0	21	-
11	0	27	-
12	-	90	-
13	-	86	-
14	0	20	-
15	0	11	-

“-”, not soluble. \* Quoted values are mentioned after subtraction of conductance values of pure solvents.

### Axial ligand substitution, axial substitution with anion exchange or simultaneous addition & substitution products

The concerned octahedral nitratocadmium(II) nitrate complexes, *cis*- $[\text{Cd}(\text{tet-a})(\text{NO}_3)](\text{NO}_3)$  and *cis*- $[\text{Cd}(\text{tet-b})(\text{NO}_3)](\text{NO}_3)$  underwent axial ligand substitution reactions with subsequent anion exchange reactions with the KCNS to yield five coordinate square pyramidal complexes  $[\text{Cd}(\text{tet-a})(\text{SCN})](\text{SCN})$  and  $[\text{Cd}(\text{tet-b})(\text{SCN})](\text{SCN})$  respectively.

The complex *trans*- $[\text{Cd}(\text{tet-a})\text{I}_2]$  underwent axial ligand substitution and the complex  $[\text{CdLI}](\text{ClO}_4)$  underwent simultaneously axial ligand substitution and addition reactions with the  $\text{NaNO}_2$  to yield  $[\text{Cd}(\text{tet-a})(\text{NO}_2)_2]$  and  $[\text{CdL}(\text{NO}_2)_2]$  respectively. These cadmium(II) ligand substitution and addition products are found to be diamagnetic as expected for the presence of paired electron in their  $d^{10}$  system. The electronic spectra of these complexes also do not show d-d bands due to the  $d^{10}$  cadmium(II) but display charge transfer bands at 230 and 340 nm.

The IR spectra of all the four complexes exhibit  $\nu_{\text{N-H}}$  bands at around  $3180\text{-}3211\text{cm}^{-1}$ , and other characteristic  $\nu_{\text{C-H}}$ ,  $\nu_{\text{CH}_3}$ ,  $\nu_{\text{C-C}}$ ,  $\nu_{\text{Cd-N}}$  and  $\nu_{\text{C=N}}$  bands in the expected regions (Table 1). In case of square pyramidal

complexes  $\text{trans-[Cd(tet-a)(SCN)](SCN)}$  and  $\text{trans-[Cd(tet-b)(SCN)](SCN)}$  appearance of sharp  $\nu\text{CN}$  bands in the region of  $2071\text{--}2080\text{ cm}^{-1}$  is a good indication of S-bonded thiocyanate group (Farago and James, 1965). The two complexes display  $\nu\text{C-S}$  bands at  $750\text{--}767\text{ cm}^{-1}$   $\delta\text{NCS}$  bands at  $420\text{--}425\text{ cm}^{-1}$  which do not correspond to ligands in this region and are therefore assigned for fully S-bonded thiocyanate group (Farago and James, 1965; Bembi, et al., 1991). Infrared spectra of the trans complexes  $\text{trans-[CdL(NO}_2)_2]$  and  $\text{trans-[Cd(tet-a)(NO}_2)_2]$  (Table 1) exhibit the  $\nu\text{asym (NO}_2)$  and  $\nu\text{sym (NO}_2)$  bands at  $1465$  &  $1460\text{ cm}^{-1}$  and  $1335$  &  $1332\text{ cm}^{-1}$  respectively. Appearance of a band at around  $835\text{ cm}^{-1}$  can be attributed to  $\delta\text{NO}_2$  frequency and support the complexes to be N-bonded nitro complexes.

The  $^1\text{H-NMR}$  spectrum of complex  $[\text{Cd(tet-a)(SCN)](SCN)}$  shows a methyl singlet at  $1.30\text{ ppm}$  corresponding to the methyl protons of axial components of gem-dimethyl groups. The multiplet at  $1.25\text{ ppm}$  corresponding to  $12\text{H}$  can be assigned to a singlet ( $6\text{H}$ ) arising out of equatorial components of gem-dimethyl group overlapped with the doublet ( $6\text{H}$ ) arising out of equatorially oriented methyl protons on  $\text{C}_5$  and  $\text{C}_{12}$  chiral carbons. Similarly the complex  $\text{trans-[CdL(NO}_2)_2]$  displays three  $\text{CH}_3$  singlets (Table 2), one assignable to methyl protons of equatorial components of gem-dimethyl groups, other to methyl protons of axial components of gem-dimethyl groups and the 3rd one to protons of  $\text{CH}_3$  groups on  $\text{sp}^2$  carbon ( $\text{C}_5$  &  $\text{C}_{12}$ ). Both the complexes display signals corresponding to  $\text{CH}_2$  and  $\text{NH}$  groups as expected (Table 2).

Molar conductivity values of  $90$  and  $86\text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  for complexes  $[\text{Cd(tet-a)(SCN)](SCN)}$  and  $[\text{Cd(tet-b)(SCN)](SCN)}$  respectively in DMSO indicate (Table 3) that these complexes are 1:1 electrolytes as expected for the formulae assigned. On the other hand molar conductivity values of  $20$  and  $11\text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  for complexes  $[\text{CdL(NO}_2)_2]$  and  $[\text{Cd(tet-a)(NO}_2)_2]$  in DMSO solution indicate (Table 3) that these complexes are non electrolyte as expected for the formula assigned.

### Conclusion:

This study reveals that the concerned ligands undergo facile complexation with cadmium(II) to produce square pyramidal, *trans* and *cis* octahedral complexes when react with different cadmium(II) salts. In these cases, though both of  $\text{ClO}_4^-$  and  $\text{NO}_3^-$  could have acted as bidentate ligands, only  $\text{NO}_3^-$  acted as bidentate ligand to produce *cis* complexes,  $\text{ClO}_4^-$  acted as monodentate ligand to produce *trans* products. In one case one  $\text{ClO}_4^-$  did not coordinate at all. This study also shows that though  $\text{Cl}^-$  could replace both  $\text{ClO}_4^-$  ions from ligand salt,  $\text{L}_2\text{HClO}_4$ ,  $\text{I}^-$  could replace only one  $\text{ClO}_4^-$  group in one case, showing more ligating ability of  $\text{Cl}^-$  compared to  $\text{I}^-$ . Though

SCN<sup>-</sup> is a linear and stronger ligand compared to NO<sub>3</sub><sup>-</sup> group, only one SCN<sup>-</sup> group has been incorporated into the coordination sphere.

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