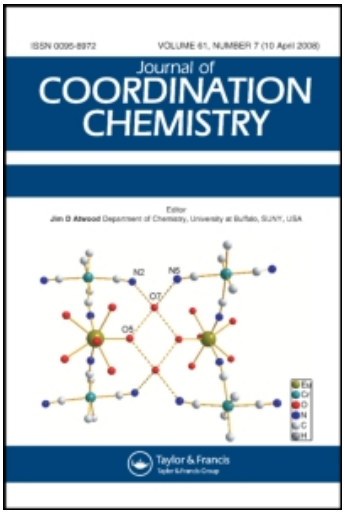

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Synthesis, electrolytic behaviour and antimicrobial activities of cadmium complexes of isomers of 3,10-C-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane

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Synthesis, electrolytic behaviour and antimicrobial activities of cadmium complexes of isomers of 3,10-C-*meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane

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Reactions of two diastereoisomers of 3,10-C-*meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecanes, Me_8[14]ane (L_A and L_B) with $Cd(NO_3)_2$ in methanol produced *trans*-$[CdL(NO_3)_2]$ ($L = L_A$ or L_B). However, the third diastereoisomer, Me_8[14]ane (L_C) did not react with $Cd(NO_3)_2$. *Trans*-$[CdL_B(NO_3)_2]$ undergoes axial ligand substitution reactions with KSCN, KNO_2, KCl, KBr and KI, in the ratio of 1 : 2 to yield white solid products corresponding to molecular formula $[CdL_BX_2]$ where $X = NCS^-$, NO_2^-, Cl^-, Br^- or I^-. Characterization has been carried out on the basis of elemental analysis, IR, UV-visible and ^{1}H-, ^{13}C- and ^{113}Cd-NMR spectroscopy, as well as by magnetic moment and conductivity measurement. These complexes show different electrolytic behaviours in different solvents. In chloroform, they are noneletrolytic indicating that both anions coordinate to cadmium(II) with retention of original molecular formula $[CdL_BX_2]$; their 1 : 2 electrolytic nature in water reveals the formation of diaquo complexes $[CdL_B(H_2O)_2]X_2$. On the other hand, conductance values corresponding to 1 : 2 electrolyte in DMF indicate the formation of square pyramidal complexes $[CdL_B(DMF)]X_2$. The antimicrobial activities of these ligands and their complexes have been tested against some selected fungi and bacteria.

Keywords: Tetraazamacrocycles; Octahedral cadmium complexes; Axial substitutions; Spectral and electrolytic properties; Antimicrobial activities

1. Introduction

Fourteen-membered tetraaza macrocyclic ligands hold the four nitrogen donors in a pre-oriented configuration which is favourable for coordination. So the cavities of these macrocycles with a 5,6,5,6 chelate ring sequence are considered as the best fit cavities for metal ions. One such ligand 3,10-C-*meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene is produced as its perchlorate salt, Me_8[14]diene · $2HClO_4$ by condensation of 1,2-propanediamine with acetone in the

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presence of a quantitative amount of $HClO_4$ [1]. Reduction of this diene generated three C-chiral isomers designated as L_A, L_B and L_C [2, 3].

In earlier studies [4, 5], a number of square planar nickel(II) and copper(II) complexes of general formula $[ML^1](ClO_4)_2$, (M = Cu or Ni, $L^1 = L_A$, L_B or L_C) have been prepared. Due to steric hindrance of eight methyl groups of these ligands and non-coordinating tendency of perchlorate anion, it was expected that preparation of five and six coordinated complexes might be difficult for these metal ions. However, Bembi and coworkers were successful in preparing six coordinate *trans*-dichlorocobalt(III) complexes of general formula $[CoL^1Cl_2](ClO_4)$ [6]. Later some axial substitution products, $[CoL^1X_2](ClO_4)_n$ ($X = NCS^-$, NO_2^-, H_2O or OH^-; $n = 1$ or 3) of these *trans*-dichlorocobalt(III) complexes were prepared [7]. X-ray structure of one dinitrito substitution product $[CoL_{A\alpha}(NO_2)_2](ClO_4)$ has been reported [8]. Hazari and coworkers [9] prepared some new four- and six-coordinate copper(II) complexes of general formula $[CuL^1X_n(H_2O)_x]X_y \cdot (H_2O)_z$, ($X = Cl^-$, Br^- or NO_3^-; n, x, y and $z = 0$, 1 or 2). In another study, Tapashi and coworkers [10, 11] prepared a six-coordinate copper(II) complex of the parent diene ligand of formula $[CuL^2(ClO_4)_2] \cdot 2H_2O$ ($L^2 = Me_8$[14]diene) and its axial ligand substitution products of general formula $[CuL^2(ClO_4)_mX_n]$, where $X = NCS^-$, Cl^-, or NO_3^-, $m = 0$ or 1 and $n = 1$ or 2. The structures of two such compounds $[CuL_B(H_2O)_2](NO_3)_2$ and $[CuL_{C\alpha}(H_2O)_2](ClO_4)_2$ have been confirmed by X-ray analysis [9, 12]. Recently six-coordinate zinc(II) complexes of general formula $[ZnL^1X_2]Y_n$ ($X = NO_3^-$, H_2O or Cl^-, $Y = SO_4^{2-}$ or Cl^-, $n = 0$, 1 or 2), a diaquo perchlorate complex with L_B, $[ZnL_B(H_2O)_2](ClO_4)_2$ and its axial substitution reaction products have been synthesized; where water molecules are substituted by other ligands like NCS^-, ClO_4^-, NO_2^- and NO_3^- [13]. So it appeared interesting to investigate cadmium(II) complexes of these isomeric ligands since reports on Cd(II) complexes of this type of macrocyclic ligand are rare, though reports are available for other macrocyclic ligands [e.g. 14–16]. In this article we report the synthesis and characterization of hexa-coordinate *trans*-dinitratocadmium(II) complexes of L_A and L_B and axial substitution products of one dinitrato complex. Unfortunately, in spite of many efforts, we failed to get single crystals of such cadmium(II) complexes for their structural analyses. The other aim of this study is to investigate the antimicrobial activities of two ligands (L_A and L_B) and their cadmium(II) complexes.

2. Experimental section

2.1. *Measurements*

Infrared spectra were taken as KBr discs in the range 4000–400 cm^{-1} on a Perkin-Elmer-883 infrared spectrophotometer or on a Schimadzu Metared spectrophotomer. Electronic spectra of the samples were recorded on a Schimadzu UV-visible spectrophotometer. ^{1}H- and ^{13}C-NMR spectra of the samples were recorded on a 250 MHz Varian instrument at the Department of Chemistry, University of Southern California, Los Angels, USA and on a 200 MHz Gemini instrument at the Institut der Anorganische und Angewandte Chemie, Hamburg Universitaet, Germany. ^{113}Cd-NMR spectrum of a sample was recorded on a 400 MHz Schimadzu instrument

at the Institut der Anorganische und Angewandte Chemie, Hamburg Universitaet, Germany. 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. Microanalyses of C, H, N of the complexes have been carried out on a C, H, N-analyzer at the Institut der Anorganische und Angewandte Chemie, Hamburg Universitaet, Germany. For the determination of cadmium in complexes accurately weighed amounts of complexes were heated with a mixture of conc. H_2SO_4, HNO_3 and $HClO_4$ to convert cadmium complexes into cadmium(II) and extraction into water. The solution was then titrated with a standard solution of Na_2EDTA using Xylenol orange as indicator.

2.2. *Synthesis*

***trans*-[$CdL_A(NO_3)_2$].** The macrocyclic ligand L_A was prepared as described previously [3]. L_A (0.31 g, 1.0 mmol) and cadmium(II) nitrate hexahydrate (0.34 g, 1.0 mmol) were dissolved separately in hot methanol (15 mL) and mixed while hot. A white product separated out after heating for 30 min. The reaction mixture was heated for another 30 min on a steam bath to ensure completion of the reaction and then allowed to cool. After 1 h the white product was filtered off, washed with methanol followed by diethylether and dried in a desiccator over silica gel. Yield: <55%. m.p.: 273°C (decomposed). Found: C, 39.70; H, 7.09; N, 15.27; Cd, 20.37. Calcd for $C_{18}H_{40}N_6O_6Cd$: C, 39.38; H, 7.34; N, 15.31; Cd 20.48%. IR: 3178 (νN−H), 2975 (νC−H), 1375 (νCH_3), 1160 (νC−C), 535 (νCd−N), 1440 and 1325 cm^{-1}(νNO_3).

***trans*-[$CdL_B(NO_3)_2$].** The macrocyclic ligand L_B was prepared by the literature method [3]. The white compound was prepared from a mixure of ligand L_B and cadmium(II) nitrate hexahydrate according to the procedure described above. Yield: <50%. m.p.: 266°C (decomposed). Found: C, 39.73; H, 7.01; N, 15.22; Cd, 20.45. Calcd for $C_{18}H_{40}N_6O_6Cd$: C, 39.38; H, 7.34; N, 15.31; Cd 20.48%. IR: 3240 (νN−H), 2980 (νC−H), 1380 (νCH_3), 1175 (νC−C), 560 (νCd−N), 1460 and 1335 cm^{-1} (νNO_3). ^{1}H-NMR ($CDCl_3$): δ 1.25 (s, Me), 1.60 (m, Me) ppm.

***trans*-[$CdL_B(NCS)_2$].** The complex *trans*-[$CdL_B(NO_3)_2$] (0.55 g, 1.0 mmol) and KCNS (0.10 g, 2.0 mmol) were taken separately in hot absolute methanol (20 mL) and mixed while hot. The clear and colourless solution was heated on a water bath till completely dry. The product was extracted with chloroform and colourless chloroform extract was evaporated to dryness to give a white solid product. The product was stored in a desiccator over silica gel. Yield: <82%. m.p.: 290°C (decomposed). Found: C, 44.39; H, 7.38; N, 15.34; Cd, 20.59. Calcd for $C_{20}H_{40}N_6S_2Cd$: C, 44.39; H, 7.45; N, 15.53; Cd, 20.77%. IR: 3120 (νN−H), 2980 (νC−H), 1370 (νCH_3), 1180 (νC−C), 550 (νCd−N), 2015 (νCN), 840 (νCS), and 480 cm^{-1} (νNCS). ^{1}H-NMR ($CDCl_3$): δ 1.20 (s, Me), 1.45 (s, Me), 1.15 (d, Me), 1.55 (d, Me) ppm. ^{13}C-NMR ($CDCl_3$): δ 14.84 (Me), 15.45 (Me), 16.41 (Me), 19.85 (Me), 28.47 (Me), 30.18 (Me), 30.74 (Me), 31.35 (Me), 40.65, 42.11, 46.70, 46.87, 47.57, 48.16, 49.48, 50.16, 55.67, 57.6 and 133.87 (NCS) ppm. ^{113}Cd-NMR ($CDCl_3$): δ 420.54 ppm.

***trans*-[CdL$_B$Y$_2$] (Y = NO$_2$, Cl, Br or I).** The white complexes, *trans*-[CdL$_B$(NO$_2$)], *trans*-[CdL$_B$Cl$_2$], *trans*-[CdL$_B$Br$_2$] and *trans*-[CdL$_B$I$_2$] were synthesized from reactions of *trans*-[CdL$_B$(NO$_3$)$_2$] with KNO$_2$, KCl, KBr and KI, respectively, by adopting the procedure similar to that for *trans*-[CdL$_B$(NCS)$_2$]. ***trans*-[CdL$_B$(NO$_2$)$_2$]:** Yield: 60%. m.p.: 285°C (decomposed). Found: C, 40.88; H, 7.38; N, 16.18; Cd, 21.56. Calcd for $C_{18}H_{40}N_6O_4Cd$: C, 41.82; H, 7.80; N, 16.26; Cd, 21.74%. IR: 3210 (νN−H), 2980 (νC−H), 1380 (νCH$_3$), 1180 (νC−C), 550 and 430 (νCd−N), 1460, 1325 and 835 (νNO$_2$) cm^{-1}. ***trans*-[CdL$_B$Cl$_2$]:** Yield: 68% m.p.: 265°C (decomposed). Found: C, 42.95; H, 7.94; N, 11.15; Cd, 22.54; Calcd for $C_{18}H_{40}N_4Cl_2Cd$: C, 43.60; H, 8.13; N, 11.30; Cd, 22.67%. IR: 3148 (νN−H), 2990 (νC−H), 1370 (νCH$_3$), 1160 (νC−C) and 570 (νCd−N) cm^{-1}. ***trans*-[CdL$_B$Br$_2$]:** Yield: <63%. m.p.: 280°C (decomposed). Found: C, 36.83; H, 6.08; N, 9.33; Cd, 19.10; Calcd for $C_{18}H_{40}N_4Br_2Cd$: C, 36.97; H, 6.89; N, 9.58; Cd, 19.22%. IR: 3180 (νN−H), 2980 (νC−H), 1380 (νCH$_3$), 1180 (νC−C) and 535 (νCd−N) cm^{-1}. ***trans*-[CdL$_B$I$_2$]:** Yield: <59%. m.p.: 260°C (decomposed). Found: C, 31.80; H, 5.63; N, 8.15; Cd, 16.49. Calcd for $C_{18}H_{40}N_4I_2Cd$: C, 31.85; H, 5.94; N, 8.25; Cd, 16.56%. IR: 3175 (νN−H), 2975 (νC−H), 1365 (νCH$_3$), 1170 (νC−C), 540 (νCd−N) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.51 (s, Me), 1.60 (s, Me), 1.16 (d, Me), 1.27 (d, Me), 1.285 (d, Me), and 1.40 (d, Me) ppm. ^{13}C-NMR ($CDCl_3$): δ 15.14 (Me), 15.31 (Me), 18.17 (Me), 19.98 (Me), 29.84 (Me), 30.64(Me), 31.30 (Me), 32.05 (Me), 40.63, 42.12, 47.10, 47.31, 47.92, 48.73, 49.95, 51.34, 56.35 and 57.10 ppm.

2.3. *Antimicrobial activity*

The antifungal activities of the complexes (*in vitro*) against some selected phytopathogenic fungi were assessed by the poisoned food technique. Potato Dextrose Agar (PDA) was used as a growth medium. Chloroform was initially used to prepare solutions of the ligands and their complexes as solvent, similarly DMSO was used for preparing the solutions of cadmium salts. The solutions were then mixed with the sterilized PDA to maintain the concentration of the compounds at 0.01%; 20 mL portion of these mixtures were poured into a petri dish. After the medium had solidified, a 5 mm mycelial disc for each fungus was placed in the centre of each assay plate against the control. Linear growth of the fungus was measured in mm after 5 days of incubation at 25 ± 2°C.

The antibacterial activities of the test materials were detected by disc-diffusion method. Standard Nutrient Agar (NA) medium was used throughout the study. It was prepared by dissolving 3 g beef extract, 5 g peptane, 15 g agar, 0.5 g sodium chloride in 1000 mL distilled water. Paper disc (ϕ = 6 mm) and petri plate (ϕ = 70 mm) were used throughout the experiment. Pour plates were made with sterilized melted NA (45°C) and after solidification of pour plates, the test organisms (suspension) were spread uniformly over the pour plate with a sterilized glass rod. The article discs after soaking with test chemicals (1% of ligands and complexes in $CHCl_3$ and 1% of cadmium salts in DMSO) were placed at the center of the inoculated pour plate. A control plate was also maintained in each case with $CHCl_3$ and DMSO, respectively. Firstly, the plates were kept for 4 h at low temperature (4°C) in order to allow the test chemicals to diffuse from disc to the surrounding medium. The plates were then incubated at 35 ± 2°C for growth of test organisms and checked at 24-h intervals. The antimicrobial activity

is expressed in terms of diameter of zone of inhibition in mm. Each experiment was repeated three times.

3. Results and discussion

***trans*-Dinitrato complexes, *trans*-[CdL(NO$_3$)$_2$] (L = L$_A$ or L$_B$).** Reactions of L$_A$ and L$_B$ with Cd(NO$_3$)$_2$ in methanolic solution produced white solid products, consistent with the molecular formula, [CdL(NO$_3$)$_2$] where L = L$_A$ or L$_B$. However, L$_C$ did not react with Cd(NO$_3$)$_2$.

$$Cd(NO_3)_2 + L \xrightarrow[\Delta]{\text{Methanol}} [CdL(NO_3)_2] \quad L = L_A \text{ or } L_B$$

The compounds were characterized by elemental analysis, IR-, UV-visible (table 1) and ^{1}H-NMR spectra as well as by magnetic moment (table 1) and conductivity measurement (table 2).

The infrared spectra of these complexes exhibit ν_{NH} bands around 3180 cm^{-1} and other characteristic ν_{C-C}, ν_{C-H}, ν_{Cd-N} bands in the expected region. The spectra further display bands at 1440–1460 cm^{-1} and 1325–1345 cm^{-1} attributed to coordinated NO_3^-. The separation of these bands by 115 cm^{-1} indicates unidentate mode of coordination [9, 11, 17]. Though NO_3^- can also coordinate as a bidentate ligand [18], this is not possible in this case, because the macrocycle needs to be folded which is difficult due to steric hindrance of eight peripheral methyl groups present. Folding of a 14-membered macrocycle is possible only along a fold axis passing through diagonally opposite nitrogen atoms having their hydrogens lying on the same side [19].

These cadmium(II) complexes are a d^{10} system, and do not show any d–d bands in the visible region in their solid electronic spectra. However, the bands at 248–340 nm in the ultraviolet region (table 1) can be assigned to charge transfer transitions and do not give any information related to the geometry of these complexes.

The 250 MHz ^{1}H-NMR spectrum of *trans*-[CdL$_B$(NO$_3$)$_2$] shows a sharp methyl singlet at 1.25 ppm and an unresolved multiplet at 1.60 ppm. Singlet at 1.25 ppm can be assigned to equatorial methyl of the *gem*-dimethyl group (table 2). The downfield unresolved multiplet at 1.60 ppm can be assigned to other axial methyls of the *gem*-dimethyl which are expected to appear downfield, overlapped with doublets arising from methyls at C$_3$, C$_5$, C$_{10}$ and C$_{12}$ positions. This type of pattern

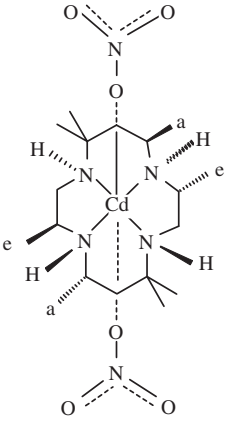
Table 1. Electronic spectral data of the complexes.

Complexes	State	λ_{max} (nm)
[CdL$_A$(NO$_3$)$_2$]	Solid	299, 270, 262
[CdL$_B$(NO$_3$)$_2$]	Solid	340, 299, 248
[CdL$_B$(NCS)$_2$]	Solid	341, 299, 237
[CdL$_B$(NO$_2$)$_2$]	Solid	340, 245, 299
[CdL$_B$Cl$_2$]	Solid	366, 340, 257
[CdL$_B$Br$_2$]	Solid	360, 339, 299,
[CdL$_B$I$_2$]	Solid	364, 340, 299, 255

Table 2. Molar conductivity data* for complexes.

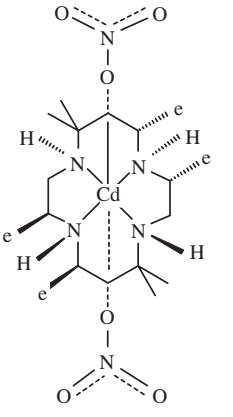
Complexes	In chloroform Conductance ($ohm^{-1}\,cm^2\,M^{-1}$)	*n* water Conductance ($ohm^{-1}\,cm^2\,M^{-1}$)	*n* DMF Conductance ($ohm^{-1}\,cm^2\,M^{-1}$)
$[CdL_A(NO_3)_2]$	0	153	188
$[CdL_B(NO_3)_2]$	0	198	201
$[CdL_B(NCS)_2]$	0	156	188
$[CdL_B(NO_2)_2]$	0	151	178
$[CdL_BCl_2]$	0	154	–
$[CdL_BBr_2]$	0	168	–
$[CdL_BI_2]$	0	192	–

*Data quoted are values after subtraction of conductance values of pure solvents.



$\left[CdL_A(NO_3)_2 \right]$

(I)



$\left[CdL_B(NO_3)_2 \right]$

(II)

Structures I and II.

is suggestive of a C-*meso* structure in which C_3, C_5, C_{10}, and C_{12} are equatorial. The methylene and methine protons appear as multiplets at 2.19 and 2.23 ppm. Thus this complex is assigned a structure where the four chiral methyls are equatorial. Similar assignment has been made for L_A [3] and for analogous $[Ni(teta)](ClO_4)_2$ complex [20]. The same structure has also been assigned to corresponding six-coordinate $[CoL_{B\alpha}Cl_2]^+$ and $[ZnL_B(NO_3)_2]$ [6, 13]. Though the ^{1}H-NMR spectrum of *trans*-$[CdL_A(NO_3)_2]$ could not be taken, structure I below [6] has been assigned as $[CoL_{A\alpha}Cl_2]^+$.

Molar conductivity values (table 2) in chloroform indicated that the complexes are nonelectrolytic in nature, i.e. the anions are in the coordination sphere as expected for six-coordinate octahedral dinitratocadmium(II) complexes.

On the other hand in DMF solution their conductivity values correspond to 1 : 2 electrolytes which indicates replacement of two nitrate ions (NO_3^-) by one DMF molecule.

$$[CdL(NO_3)_2] \xrightarrow{DMF} [CdL(DMF)](NO_3)_2 \quad L = L_A \text{ or } L_B$$

Though 1 : 2 electrolytes can be assigned for square-pyramidal $[CdL(DMF)](NO_3)_2$, tetrahedral $[CdL](NO_3)_2$ or octahedral $[CdL(DMF_2)](NO_3)_2$, square pyramidal is most likely since for formation of tetrahedral geometry, the pre-oriented planar N_4-system has to be disturbed which is almost impossible in these cases. The formation of 1 : 2 electrolytes from the non-electrolyte complexes may also be explained on the basis of formation of an octahedral *bis*-DMF complex,

$$[CdL(NO_3)_2] \xrightarrow{DMF} [CdL(DMF)](NO_3)_2$$

but for octahedral structure, two big DMF molecules should be incorporated into the cavity which is also not favourable. Similar assignment has been made for analogous zinc(II) complexes [21, 22]. X-ray crystallography of square pyramidal zinc(II) complexes of analogous ligands has been reported [22].

Conductance values of their aqueous solutions corresponding to 1 : 2 electrolytes provide evidence that diaquo complexes are formed by replacement of NO_3^- groups by H_2O molecules in aqueous solution.

$$[CdL(NO_3)_2] \xrightarrow{H_2O} [CdL(H_2O)](NO_3)_2 \quad L = L_A \text{ or } L_B$$

Similar observations were also noted for analogous copper(II) complexes [9, 11, 23].

Axial ligand substitution reaction products of *trans*-$[CdL_B(NO_3)_2]$. Axial ligand substitution reactions of *trans*-dichlorocobalt(III) complexes of these isomeric ligands [7] and those of *trans*-diperchlorato copper(II) complexes of parent diene ligands[11] have already been carried out. Moreover some substitution reactions of zinc(II) complexes of analogous azamacrocyclic ligands have also been reported [13, 21, 22] and recently reactions on *trans*-diaquozinc(II) perchlorate complex of L_B, $[ZnL_B(H_2O)_2](ClO_4)_2$ have been carried out successfully [13]. So to see whether the present analogous dinitratocadmium(II) complexes, $[CdL_A(NO_3)_2]$ and $[CdL_B(NO_3)_2]$ undergo axial substitution reactions, the reactions of these complexes with KSCN, KNO_2, KCl, KBr and KI have been carried out. The complex, *trans*-$[CdL_B(NO_3)_2]$ undergoes axial substitution reactions with SCN^-, NO_2^-, Cl^-, Br^- and I^- to form *trans*-diisothiocyanato, -dinitro, -dichloro, -dibromo and –diiodo derivatives. However, *trans*-$[CdL_A(NO_3)_2]$ did not do so. The equitorial arrangement of chiral methyl groups in *trans*-$[CdL_B(NO_3)_2]$ might facilitate axial substitution, whereas diaxial-diequitorial arrangement of the same in *trans*-$[CdL_A(NO_3)_2]$ might hinder axial substitution.

The electronic spectra of these complexes do not show d–d bands due to the d^{10} cadmium(II) but display charge transfer bands at 230 and 340 nm (table 1).

The molar conductivity value of $0\,Ohm^{-1}\,cm^2\,M^{-1}$ of all these complexes in chloroform solution strongly supports the nonelectrolytic nature of these complexes, i.e., both the anions are coordinated to cadmium(II).

On the other hand these complexes are 1 : 2 electrolytes in aqueous solutions and in DMF solutions. These observations can be attributed to the formation of octahedral

diaquo complexes $[CdL_B(H_2O)_2]X_2$ and square pyramidal $[CdL_B(DMF)]X_2$ in aqueous and DMF solutions, respectively, as explained earlier.

$$[CdL_BX_2] \xrightarrow{H_2O} [CdL_B(H_2O)_2]X_2$$

$$[CdL_BX_2] \xrightarrow{DMF} [CdL_B(DMF)]X_2$$

***trans*-Diisothiocyanato complex, *trans*-$[CdL_B(NCS)_2]$.** The infrared spectrum of this complex shows ν_{N-H}, ν_{C-H}, ν_{CH3} and ν_{C-C} stretching bands at 3120, 2980, 1370 and 1180 cm^{-1} respectively. The absence of ν_{NO3} stretching bands at 1460 and 1345 cm^{-1} and the presence of ν_{NCS} and ν_{CN} bands demonstrate that the NO_3^- are substituted completely by NCS^- groups. This complex exhibits ν_{CN} at 2015 cm^{-1}, ν_{CS} band at 840 cm^{-1} and δ_{NCS} band at 480 cm^{-1}. So from these peak positions [11,17, 24–26] it is concluded that the present complex is N-bonded and called isothiocyanato complex. This conclusion is also supported by ^{113}Cd-NMR of the complex which shows a singlet at 420.54 ppm. If NCS^- be coordinated through S-atom then the peak position must be shifted towards higher field [27].

The ^{1}H-NMR spectrum of $[CdL_B(NCS)_2]$ shows singlets at 1.20 ppm and 1.45 ppm corresponding to six protons each that can be assigned to the *gem*-dimethyl groups. The spectrum also shows two doublets at 1.15 and 1.55 ppm, each corresponding to six protons. These data require that C_3, C_{10} and C_5, C_{12} should be in a pairwise equivalent configuration. The upfield doublet can be assigned to equatorial methyls and downfield doublet to axial methyls. Thus a diaxial-diequatorial structure can be assigned to this complex, as assigned to the dinitrato complex. This observation demonstrates that axial substitution takes place without change of conformation and configuration. Similar conclusion has also been drawn in the literature [11]. The other methylene, methine and N–H protons appear as multiplets at 2.25, 2.85 and 3.50 ppm, respectively.

The ^{13}C-NMR spectrum of this complex shows nineteen peaks. Usually the range of chemical shifts assigned for the peripheral methyl carbons are 15–30 ppm and for the ring carbons 40–65 ppm; the first eight peaks at 14–35 ppm are for pheripheral methyl carbons and the next ten at 40–60 ppm are due to ring carbons. The peak at 134 ppm has been assigned for two carbons of two equivalent NCS groups. Observation of eighteen peaks for pheripheral and ring carbons of the pairwise equivalent configuration may be accounted for by distortion in the structure due to different axial ligands.

***trans*-Dinitro complex, *trans*-$[CdL_B(NO_2)_2]$.** The elemental analysis of this compound is fully consistent with the above formula. The infrared spectrum of this complex shows ν_{N-H}, ν_{C-H}, ν_{CH3}, ν_{C-C} and ν_{Cd-N} stretching bands at the expected regions. Moreover the complex exhibits the $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$ bands at 1440 and 1325 cm^{-1}, respectively. Appearance of a band at 835 cm^{-1} can be attributed to δ_{NO2} frequency. Presence of ν_{Cd-N} band at 430 cm^{-1} and the other bands in the proper region strongly support the complex to be N-bonded nitro. Though NO_2^- can also behave as a bidentate ligand, it is difficult in this case as discussed earlier.

According to above evidence and earlier discussion, an octahedral structure with the two nitro groups trans to each other is assigned for *trans*-$[CdL_B(NO_2)_2]$.

***trans*-Dihalo complexes, *trans*-[CdL_BX_2] (X = Cl, Br or I).** The analytical data for these complexes support the molecular formula [CdL_BX_2] (X = Cl, Br or I). The infrared spectra show ν_{N-H}, ν_{C-H}, ν_{CH3}, ν_{C-C} and ν_{Cd-N} stretching bands at the expected regions. The IR-spectra could not be run at a range lower than 400 cm^{-1} preventing observation of bands around 250 cm^{-1} due to Cd–X stretch for [CdL_BX_2].

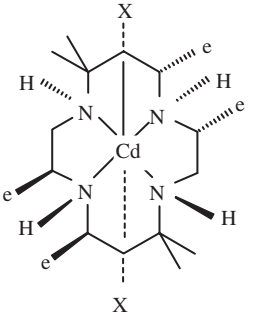
The ^{1}H-NMR spectrum of *trans*-[CdL_BI_2] shows two sharp singlets at 1.51 ppm and 1.60 ppm corresponding to 6H each, assigned to the C_7 and C_{14} *gem*-dimethyl groups having equatorial and axial orientation. The spectrum also shows four doublets at 1.16, 1.27, 1.29 and 1.40 ppm each corresponding to 3H of each chiral methyl. The peak positions of these closely spaced resonances can be attributed to all equatorial arrangement as for its parent dinitrato complex. Other multiplets at 2.55, 2.80, 3.00 and 4.60 ppm are for the methylene, methyl and NH protons.

The ^{13}C-NMR spectrum of [CdL_BI_2] gives additional structural evidence showing eighteen peaks. The first eight peaks are assigned to eight non-equivalent peripheral methyl carbons within the range of 15–32 ppm and the other ten peaks within the range of 40–58 ppm are assigned to ten nonequivalent carbons of the macrocyclic ring.

On the basis of above evidence a common structure III can be assigned to all axial ligand substitution products, where conformation and configuration of ligand of original dinitrato complex, *trans*-[$CdL_B(NO_3)_2$] is retained.

3.1. *Antimicrobial activity*

Very few reports on antifungal activities of macrocycles and their complexes exist [9, 11, 23], so we investigated the antifungal activities of the present cadmium complexes of isomeric macrocyclic ligands including [$Cd(NO_3)_2$,($Cd(NCS)_2$ and $CdCl_2$] against five selective phytopathogenic fungi. It is evident from the results (table 3) that the macrocycles and their complexes under investigation show some antifungal activities. The activities of ligands were generally found to decrease upon coordination to cadmium(II) though the cadmium salts themselves showed very high antimicrobial activities. However the activities of these complexes against *Macrophomina phaseolina* are less than those against the other four fungi and the results are reverse in case of



[CdL_BX_2]

(III)

Structure III (X = Cl, Br, I).

Table 3. *In-vitro* antifungal activities of some cadmium salts, ligands and their cadmium complexes.

Cadmium salts, ligands and cadmium complexes	% Inhibition of mycelial growth				
	M. phaseolina	*Alternaria alternata*	*Fusarium equiseti*	*Colletotrichum corcolei*	*Botryodiplodia theobromae*
$Cd(NO_3)_2$	71.38	50.00	79.38	48.90	65.84
L_A	14.60	27.80	25.02	24.50	21.39
$[CdL_A(NO_3)_2]$	13.38	17.80	9.80	21.62	20.00
L_B	13.50	25.90	21.38	20.63	36.8
$[CdL_B(NO_3)_2]$	10.50	18.50	17.90	22.00	15.00
$Cd(NCS)_2$	93.11	76.49	79.40	72.78	88.12
$[CdL_B(NCS)_2]$	13.50	16.00	12.08	11.69	24.75
$CdCl_2$	89.82	46.47	54.14	66.67	89.60
$[CdL_BCl_2]$	6.34	10.00	20.00	6.00	7.88
$[CdL_BBr_2]$	5.56	8.00	5.00	17.00	19.90
$[CdL_BI_2]$	12.50	23.00	17.00	9.09	11.17
$[CdL_B(NO_2)_2]$	8.28	14.00	18.32	17.56	13.50

Table 4. Antibacterial activities of some cadmium salts, ligands and their cadmium complexes.

Cadmium salts, ligands and cadmium complexes	Diameter of zone of inhibition in mm after 24 h			
	Salmonella typhi	*Shigella dysenteriae*	*Escherichia coli*	*Bacillus cerelus*
$Cd(NO_3)_2$	40	31	20	29
L_A	13	11	4	17
$[CdL_A(NO_3)_2]$	8	0	14	9
L_B	14	16	21	23
$[CdL_B(NO_3)_2]$	0	0	16	20
$Cd(NCS)_2$	45	32	23	32
$[CdL_B(NCS)_2]$	8	13	19	10
$[CdL_B(NO_2)_2]$	10	12	20	0
$CdCl_2$	42	34	25	35
$[CdL_BCl_2]$	0	0	0	8
$[CdL_BBr_2]$	11	0	0	8
$[CdL_BI_2]$	12	15	7	5

cadmium salts. A comparison of activities of these nitrogen containing ligands and their complexes with that of sulphur-containing Schiff bases and their complexes [28, 29] shows that in most cases the activities are lower in the present ligands and complexes. A comparison of the activities of the present ligands and complexes shows that the compounds have varied effects on the inhibition of mycelial growth. Since the cadmium salts exhibit very high activities, the complexes are expected to show higher activities compared to free ligands. But the lower activity values of the these complexes may be attributable to lack of influence of Cd(II) ion on these complexes, which may be due to high stability of the complexes.

Since only a few reports [23] on antibacterial activities of macrocycles and their complexes are available, investigations on antibacterial activities of three cadmium salts [$Cd(NO_3)_2$, ($Cd(NCS)_2$ and $CdCl_2$] have been carried out against some important selected bacteria, which cause different fatal diseases. The results (table 4) show that the ligands and some complexes show different antibacterial activities but some complexes do not show any such activity. However, cadmium salts always exhibit higher

antibacterial activity compared to ligands and complexes. Lack of influence of Cd(II) ion on the antibacterial activities of these complexes may be explained as earlier in case of antifungal activities. One cannot make any prediction on the rate of inhibition power of the complexes on a particular bacterial growth. Unlike their behaviour towards antifungal activities, some of the complexes are found to exhibit higher antibacterial activities than their corresponding ligands. However for a clear understanding of the functions responsible for antibacterial activities of macrocycles and their complexes, more studies are needed to be performed with similar complexes.

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