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Research article

Cadmium(II) compounds of the bis-cyanoethyl derivative (L_{CX}) of Me_8[14]aneC (L_C): characterization and antibacterial studies

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ABSTRACT

The isomeric ligand L_C, a saturated analogue of 2,9-C-meso-Me_8[14]diene, on reflux with excess acrylonitrile afforded 1,8-N-pendant cyanoethyl derivative L_{CX}. Interaction of L_{CX} with cadmium(II) perchlorate, nitrate, acetate, and chloride salts produced six coordinated octahedral compounds, $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$, $[Cd(L_{CX})(NO_3)_2]$, $[Cd(L_{CX})(CH_3COO)_2]$, and $[Cd(L_{CX})Cl_2]$, respectively. Further, axial substitution reactions between $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$ and KI, KBr, KCl, KSCN, and $NaNO_2$ in a 1:2 ratio yielded six coordinated octahedral compounds, $[Cd(L_{CX})I_2]\bullet H_2O$, $[Cd(L_{CX})Br_2]\bullet 2H_2O$, $[Cd(L_{CX})Cl(ClO_4)]\bullet 2H_2O$, $[Cd(L_{CX})(NCS)_2]\bullet H_2O$, and $[Cd(L_{CX})(NO_2)(ClO_4)]\bullet 2H_2O$, respectively. All of the newly prepared compounds have been characterized by analytical, spectroscopic, molar conductivity, and magnetochemical data. The crystal structure of the ligand L_{CX} was determined by x-ray crystallography which showed the 14-membered ring to adopt an extended chair conformation. Antibacterial activities of the newly formed cadmium(II) complexes against selected bacteria showed these to exhibit moderate and selective activity with **1-4** and **8** exhibiting greatest potency against the gram negative bacterium *Salmonella typhi*, and **5**, **6**, and **7** against the gram positive bacterium *Bacillus wiedmannii*.

1. Introduction

Synthetic polyazamacrocycles and their metal complexes have fostered a considerable research field at the interface between chemistry and biology due to their diverse biomedical [1, 2, 3, 4, 5, 6, 7, 8], analytical [9], and industrial [10] applications. These physical, analytical, spectral, electrochemical, structural, and biological investigations attract attention owing to the elevated thermodynamic stability, kinetic inertness, and significant biological activities of the resultant species. The latter includes antibacterial [1], antifungal [1], antioxidant [2], anti-inflammatory [3], antidiabetic [4], and antiproliferative [5] activities. The superiority of synthetic macrocyclic complexes as antitumor [6], anticancer [7], and anti-HIV [8] agents is well documented. The biological role of macrocyclic complexes is dependent on the nature of metal ions and their encapsulation/confinement patterns within the cavity defined by the specific macrocycle. In light of the above, it is reasonable to synthesize new tetraazamacrocyclic complexes and investigate their antibacterial activities.

Due to the multifarious applications [1, 2, 3, 4, 5, 6, 7, 8, 9, 10] of macrocyclic ligands, including differential behavior exhibited by their isomeric forms and their metal complexes in a wide variety of contexts, researchers continue to be fascinated by their chemistry and various applications, including in the development of metal-based drugs and as imaging agents. Relevant to the present study are recent reports describing the antibacterial activities of cadmium compounds [11, 12, 13, 14]. These follow earlier studies, whereby cadmium(II) macrocyclic compounds were reported to exhibit potent antibacterial potential [13, 14]. In addition, we have also reported x-ray crystallographic studies of cadmium(II) compounds with other macrocycles [14, 15]. Though copper(II), nickel(II), and cobalt(III), and chromium(III) complexes of macrocyclic ligands described herein have been reported [16, 17], related studies on cadmium(II) have yet to be reported. So, it was thought of interest to prepare and characterize some new cadmium(II) macrocyclic compounds as well to study their antibacterial activities. In acknowledgement of the above, in this study the newly prepared cadmium macrocycles have been characterized and evaluated for their

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antibacterial potential against selected bacteria. Such studies are motivated by the life-threatening nature of such microbes especially in the context of their ability to develop drug resistance to commonly employed antibiotics. Thus, it is anticipated this study will contribute to the universal challenge faced by researchers in this field: to develop specialized drugs to combat the studied bacteria for the betterment of the human population.

A significant number of metal complexes of different macrocycles [18, 19, 20], including, those relevant to the present investigation, 14-membered octamethyl tetraazamacrocyclic diene ligand (Me_8 [14] diene), isomeric ligands (L_A, L_B, and L_C) and their N-pendent derivative ligands, are available in the literature [21, 22, 23, 24, 25, 26]. In this context, copper(II) and nickel(II) complexes with bis-hydroxyethyl (L_{BY} and L_{CY}) and dimethyl (L_{BZ} and L_{CZ}) derivatives of the isomeric ligands L_B and L_C have been studied [23, 24]. Moreover, some copper(II), nickel(II), and cobalt(III) complexes of bis-cyanoethyl derivative (L_{CX}) of isomeric ligand L_C have been reported recently by our group [17]. In continuation of these studies, 2,9-C-meso-Me_8 [14]diene dihydroperchlorate (L•2$HClO_4$) [27], the isomeric ligand (L_C) [22] of its reduced analogue, and the 1,8-N-pendant bis-cyanoethyl derivative (L_{CX}) [17] of L_C, have been successfully prepared as per the literature; see Scheme 1 for chemical diagrams. Thereafter, cadmium(II) compounds of the ligand L_{CX} have been prepared by direct interaction with cadmium(II) salts as well as by axial ligand substitution reactions on the precursor compounds. The synthesized compounds have been characterized by different analytical, spectroscopic methods and antibacterial activities conducted. Herein, the results of these investigations are described.

2. Experimental

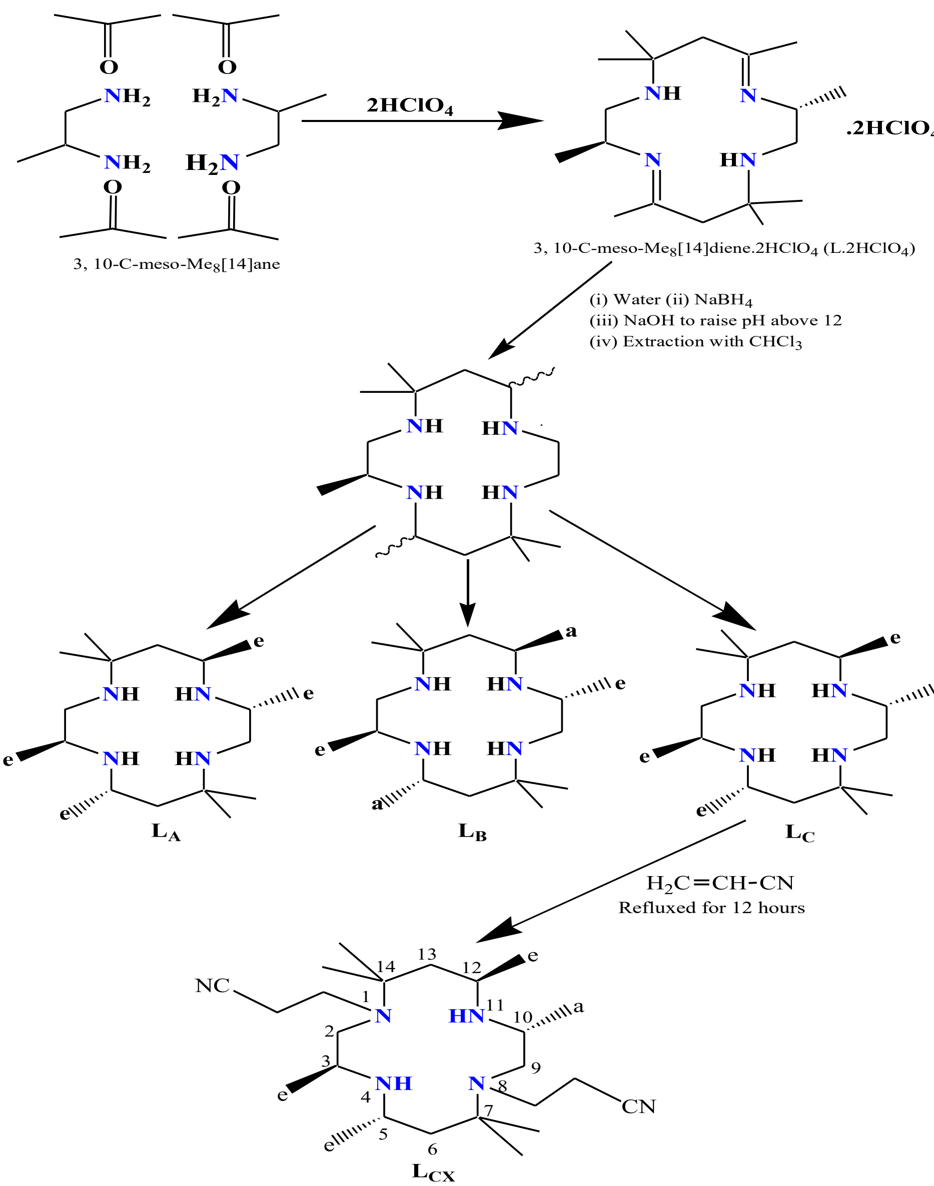
2.1. Chemicals

Chemicals (Analytical grade, Sigma-Aldrich) were used without further purification.

Precaution: *At elevated temperature, perchlorates are explosive in nature.*

2.2. Physical measurements

Microanalysis (CHNS) were determined on a CHNS-932 elemental analyzer; melting point determinations were made on a electrothermal



Scheme 1. Preparation of ligands.

melting point apparatus; IR spectra as KBr disks on a Shimadzu IR 20 spectrophotometer; conductance on a Hanna instrument HI-8820 in $CHCl_3$, DMSO, and CH_3CN solutions; UV-visible spectra were recorded on a Shimadzu UV-visible spectrophotometer in $CHCl_3$ and DMSO solutions; magnetic measurements were made on a Gouy Balance, calibrated with $Hg[Co(NCS)_4]$ and the ^1H NMR & ^{13}C NMR spectra of the compounds were recorded in $CDCl_3$ solution on a 400 MHz Bruker DPX-400 spectrometer using TMS as the internal standard.

2.3. Syntheses of ligands

2.3.1. L·2HClO4, L_C, and L_{CX}

The parent octamethyl substituted ligand salt, $L{\cdot}2HClO_4$, and three isomers L_A, L_B, and L_C of its reduced analogue were prepared as per literature methods [15, 21]. Moreover, the 1,8-N-pendant derivative ligand, L_{CX}, from L_C, has been synthesized (Scheme 1) as recently reported by our group [17].

2.4. Syntheses of cadmium(II) compounds of L_{CX}

2.4.1. Syntheses of cadmium(II) compounds produced by the direct interactions of L_{CX} with cadmium(II) salts (1–4)

L_{CX} (0.418 g, 1.0 mmol) and 1.0 mmol of each of $Cd(ClO_4)_2{\bullet}6H_2O$, $Cd(NO_3)_2{\bullet}4H_2O$, $Cd(CH_3COO)_2{\bullet}3H_2O$, and $CdCl_2{\bullet}H_2O$ were separately dissolved in hot methanol (30 mL) and to each of the salt solutions was added an acrylonitrile solution (5 mL) of L_{CX}. The mixtures were heated on a water bath for 1 h and allowed to dry. The products were extracted with chloroform and the extracts were evaporated to dryness to give white solid products, i.e., $[Cd(L_{CX})(ClO_4)_2]{\bullet}2H_2O$, $[Cd(L_{CX})(NO_3)_2]$, $[Cd(L_{CX})(CH_3COO)_2]$, and $[Cd(L_{CX})Cl_2]$, respectively. The products were then washed with ethanol followed by diethyl ether and stored in a desiccator over silica gel.

$[Cd(L_{CX})(ClO_4)_2]{\bullet}2H_2O$ (**1**): Color: white. Melting Point: 132 °C. M. W.: 765.98. Anal. Found: C, 37.52; H, 6.49; N, 10.88%. Calc. for $C_{24}H_{50}CdCl_2N_6O_{10}$: C, 37.60; H, 6.58; N, 10.97%. IR (cm^{-1}) (Fig. S1(a), Supplementary Materials): ν_{H2O} 3433w, 1658s, $\nu_{N\text{–}H}$ 3255m; $\nu_{C\text{–}H}$ 2974m; $\nu_{C\equiv N}$ 2251m; ν_{CH3} 1395m; $\nu_{C\text{–}C}$ 1173w; ν_{ClO4}, 1111s, 1095s, 1062s, 622s; $\nu_{Cd\text{–}N}$ 461w. Molar conductivity (Λ_o, $ohm^{-1}cm^2mol^{-1}$) in CH_3Cl, 0; DMSO, 69; CH_3CN, 291. Magnetic moment μ_{eff} (BM): diamagnetic. ^1H NMR (δ, ppm in $CDCl_3$; os = overlapped singlet, od = overlapped doublet) (Fig. S2, Supplementary Materials): For CH_3 (gem dimethyl), δ = 1.255 (os, e, 6H), 1.312 (os, a, 6H); for methyl protons on chiral carbon, δ = 1.148 (od, e, 3H), 1.215 (od, e, 3H), 1.303 (od, a, 6H); for CH_2, CH, NH, and H_2O protons, δ = 2.621 (m), 3.428 (m), 3.665 (m), 4.026 (m), 5.355 (m), 7.285 (m). ^{13}C NMR (δ, ppm in $CDCl_3$) (Fig. S3, Supplementary Materials): peripheral methyl carbons, δ = 18.731, 29.955, 30.185, 34.842; macrocyclic ring carbon, δ = 51.711, 51.821, 53.424, 58.777, 58.954; cyanoethyl carbon, δ = 66.232, 67.051, 67.965.

$[Cd(L_{CX})(NO_3)_2]$ (**2**): Color: white. Melting Point: 147 °C. M. W.: 655.083. Anal. Found: C, 43.92; H, 7.13; N, 17.09%. Calc. for $C_{24}H_{46}CdN_8O_6$: C, 44.00; H, 7.08; N, 17.11%. IR (cm^{-1}) (Fig. S1(b), Supplementary Materials): $\nu_{N\text{–}H}$ 3214w; $\nu_{C\text{–}H}$ 2971m; $\nu_{C\equiv N}$ 2246w; ν_{NO3} 1445m, 1383vs, 1329s; ν_{CH3} 1383vs; $\nu_{C\text{–}C}$ 1173s; $\nu_{Cd\text{–}N}$ 461w. Molar conductivity (Λ_o, $ohm^{-1}cm^2mol^{-1}$) in CH_3Cl, 0; DMSO, 64; CH_3CN, 175. Magnetic moment μ_{eff} (BM): diamagnetic. ^1H NMR (δ, ppm in $CDCl_3$) (Fig. S4, Supplementary Materials): For CH_3 (gem dimethyl), δ = 1.277 (os, e, 6H), 1.304 (os, a, 6H); methyl protons on chiral carbon, δ = 1.107 (od, e, 6H), 1.554 (od, a, 6H); for CH_2, CH, and NH protons, δ = 2.070, 2.287, 2.888, 3.426, 3.786, 7.285.

$[Cd(L_{CX})(CH_3COO)_2]$ (**3**): Color: white. Melting Point: 135 °C. M. W.: 649.18. Anal. Found: C, 51.81; H, 8.06; N, 12.91%. Calc. for $C_{28}H_{52}CdN_6O_4$: C, 51.76; H, 8.07; N, 12.95%. IR (cm^{-1}) (Fig. S1(c), Supplementary Materials): $\nu_{N\text{–}H}$ 3216w; $\nu_{C\text{–}H}$ 2969m; $\nu_{C\equiv N}$ 2248m; ν_{CH3COO} 1571s, 1416s; ν_{CH3} 1390m; $\nu_{C\text{–}C}$ 1174m; $\nu_{Cd\text{–}N}$ 461w. Molar conductivity (Λ_o, $ohm^{-1}cm^2mol^{-1}$) in CH_3Cl, 0; DMSO, 8; CH_3CN, 76. Magnetic moment μ_{eff} (BM): diamagnetic.

$[Cd(L_{CX})Cl_2]$ (**4**): Color: white. Melting Point: 152 °C. M. W.: 601.98. Anal. Found: C, 47.95; H, 7.73; N, 13.98%. Calc. for $C_{24}H_{46}CdCl_2N_6$: C, 47.84; H, 7.70; N, 13.96%. IR (cm^{-1}) (Fig. S1(d), Supplementary Materials): $\nu_{N\text{–}H}$ 3217m; $\nu_{C\text{–}H}$ 2970s; $\nu_{C\equiv N}$ 2249m; ν_{CH3} 1383s; $\nu_{C\text{–}C}$ 1174s; $\nu_{Cd\text{–}N}$ 476w. Molar conductivity (Λ_o, $ohm^{-1}cm^2mol^{-1}$) in CH_3Cl, 0; DMSO, 28; CH_3CN, 110. Magnetic moment μ_{eff} (BM): diamagnetic.

2.4.2. Syntheses of axial ligand substitution products of $[Cd(L_{CX})(ClO_4)_2]{\bullet}2H_2O$ (5–9)

$[Cd(L_{CX})(ClO_4)_2]{\bullet}2H_2O$ (0.766 g, 1.0 mmol), KX (X = I, Br, Cl, and SCN), and $NaNO_2$ (2.0 mmol) were dissolved/suspended separately in hot absolute methanol (30 mL) and mixed while hot. The mixtures were concentrated to 5 mL by heating on a water bath. On cooling, the mixtures were filtered off and the filtrates evaporated to dryness. The products were then extracted with $CHCl_3$. On evaporation of the chloroform extracts, the solid white products $[Cd(L_{CX})I_2]{\bullet}H_2O$, $[Cd(L_{CX})Br_2]{\bullet}2H_2O$, $[Cd(L_{CX})Cl(ClO_4)]{\bullet}2H_2O$, $[Cd(L_{CX})(NCS)_2]{\bullet}H_2O$, and $[Cd(L_{CX})(NO_2)(ClO_4)]{\bullet}2H_2O$ were obtained, respectively, and dried in a desiccator over silica gel.

$[Cd(L_{CX})I_2]{\bullet}H_2O$ (**5**): Color: white. Melting Point: 122 °C. M. W.: 802.88. Anal. Found: C, 35.88; H, 6.11; N, 10.55%. Calc. for $C_{24}H_{48}CdI_2N_6O$: C, 35.87; H, 6.03; N, 10.47%. IR (cm^{-1}) (Fig. S1(e), Supplementary Materials):: ν_{H2O} 3401w, 1684m; $\nu_{N\text{–}H}$ 3241w; $\nu_{C\text{–}H}$ 2965m; $\nu_{C\equiv N}$ 2245m; ν_{CH3} 1375s; $\nu_{C\text{–}C}$ 1176s; $\nu_{Cd\text{–}N}$ 476w. Molar conductivity (Λ_o, $ohm^{-1}cm^2mol^{-1}$) in CH_3Cl, 0; DMSO, 30; CH_3CN, 127. Magnetic moment μ_{eff} (BM): diamagnetic. ^1H NMR (δ, ppm in $CDCl_3$) (Fig. S5, Supplementary Materials): For CH_3 (gem dimethyl), δ = 1.339 (os, e, 6H), 1.541 (os, a, 3H), 1.563 (os, a, 3H), for methyl protons on chiral carbon, δ = 1.210 (od, e, 3H), 1.312 (od, e, 3H), 1.392 (od, a, 3H), 1.508 (od, a, 3H); for CH_2, CH, and NH protons, δ = 2.875(m), 3.269 (m), 3.547 (m), 4.706(m), 5.320(m), 7.285(m).

$[Cd(L_{CX})Br_2]{\bullet}2H_2O$ (**6**): Color: white. Melting Point: 143 °C. M. W.: 726.88. Anal. Found: C, 39.73; H, 6.99; N, 11.48%. Calc. for $C_{24}H_{50}Br_2CdN_6O_2$: C, 39.62; H, 6.93; N, 11.56%. IR (cm^{-1}) (Fig. S1(f), Supplementary Materials): $\nu_{N\text{–}H}$ 3191w; $\nu_{C\text{–}H}$ 2966m; ν_{CH3} 1375s; $\nu_{C\text{–}C}$ 1175s; $\nu_{Cd\text{–}N}$ 472w; $\nu_{C\equiv N}$ 2249s; ν_{H2O} 3434w, 1668s. Molar conductivity (Λ_o, $ohm^{-1}cm^2mol^{-1}$) in CH_3Cl, 0; DMSO, 26; CH_3CN, 112. Magnetic moment μ_{eff} (BM): diamagnetic.

$[Cd(L_{CX})Cl(ClO_4)]{\bullet}2H_2O$ (**7**): Color: white. Melting Point: 129 °C. M. W.: 701.98. Anal. Found: C, 41.19; H, 7.15; N, 11.91%. Calc. for $C_{24}H_{50}CdCl_2N_6O_6$: C, 41.03; H, 7.18; N, 11.97%. IR (cm^{-1}) (Fig. S1(g), Supplementary Materials): ν_{H2O} 3445w, 1668s; $\nu_{N\text{–}H}$ 3201w; $\nu_{C\text{–}H}$ 2967m; $\nu_{C\equiv N}$ 2249s; ν_{CH3} 1377s; $\nu_{C\text{–}C}$ 1176m; ν_{ClO4} 1090s, 624s; $\nu_{Cd\text{–}N}$ 470w. Molar conductivity (Λ_o, $ohm^{-1}cm^2mol^{-1}$) in CH_3Cl, 0; DMSO, 26; CH_3CN, 112. Magnetic moment μ_{eff} (BM): diamagnetic.

$[Cd(L_{CX})(NCS)_2]{\bullet}H_2O$ (**8**): Color: white. Melting Point: 136 °C. M. W.: 665.26. Anal. Found: C, 46.81; H, 7.33; N, 16.79; S, 9.59%. Calc. for $C_{26}H_{48}CdN_8OS_2$: C, 46.90; H, 7.27; N, 16.84; S, 9.64%. IR (cm^{-1}) (Fig. S1(h), Supplementary Materials): ν_{H2O} 3459w, 1668m; $\nu_{N\text{–}H}$ 3213w; $\nu_{C\text{–}H}$ 2970m; $\nu_{C\equiv N}$ 2247m; ν_{CN} 2053vs; ν_{CH3} 1377m; $\nu_{C\text{–}C}$ 1176m; ν_{CS} 803w; δ_{NCS} 472; $\nu_{Cd\text{–}N}$ 449w. Molar conductivity (Λ_o, $ohm^{-1}cm^2mol^{-1}$) in CH_3Cl, 0; DMSO, 68; CH_3CN, 124. Magnetic moment μ_{eff} (BM): diamagnetic.

$[Cd(L_{CX})(NO_2)(ClO_4)]{\bullet}2H_2O$ (**9**): Color: white. Melting Point: 117 °C. M. W.: 712.53. Anal. Found: C, 40.33; H, 7.15; N, 13.82%. Calc. for $C_{24}H_{50}CdClN_7O_8$: C, 40.42; H, 7.07; N, 13.76%. IR (cm^{-1}) (Fig. S1(i), Supplementary Materials): ν_{H2O} 3412w, 1668s; $\nu_{N\text{–}H}$ 3192w; $\nu_{C\text{–}H}$ 2967m; $\nu_{C\equiv N}$ 2248m; $\nu_{asym(NO2)}$ 1456m; ν_{CH3} 1375m; $\nu_{sym(NO2)}$ 1320w; $\nu_{C\text{–}C}$ 1176w; ν_{ClO4} 1081m, 624m, δ_{NO2} 806w; $\nu_{Cd\text{–}N}$ 468w. Molar conductivity (Λ_o, $ohm^{-1}cm^2mol^{-1}$) in CH_3Cl, 0; DMSO, 39; CH_3CN, 201. Magnetic moment μ_{eff} (BM): diamagnetic.

2.5. Antibacterial studies

Antibacterial studies of the relevant macrocycles and their cadmium(II) compounds were carried out by the disc diffusion method against two gram-positive i.e., *Bacillus wiedmannii* and *Bacillus aerius*, and three gram-negative bacteria, i.e., *Escherichia coli, Shigella flexneri* and *Salmonella typhi* by using the method described in our recent report [17]. For comparison, the activity of non-coordinated metal salt $Cd(ClO_4)_2$•$6H_2O$ was also tested against all bacteria. Tests were repeated thrice for statistical analysis and finally, the antibacterial activities of the tested compounds are reported by subtracting the values for solvent (negative control).

2.6. Crystal structure determination

The colorless crystals of L_{CX} were isolated from the slow evaporation of its acrylonitrile solution. Intensity data for a colorless crystal of L_{CX} (0.12 × 0.15 × 0.17 mm) were measured at 298 K on a Rigaku/Oxford Diffraction XtaLAB Synergy diffractometer (Dualflex, AtlasS2) fitted with CuKα radiation (λ = 1.54178 Å) so that θ_{max} was 67.1° for 100% completeness. Data processing and gaussian absorption corrections were accomplished with CrysAlisPro [28]. The structure was solved by direct methods [29] and the refinement was by full-matrix least squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms [30]. The C-bound hydrogen atoms were placed on stereochemical grounds and refined with fixed geometries. The unique N-bound hydrogen atom was located from a difference map and refined with N–H = 0.86 ± 0.01 Å. A weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.061\ P)^2 + 0.232P]$, where $P = (F_o^2 + 2F_c^2)/3$, was introduced in the refinement. Owing to poor agreement, one reflection, i.e., (2 1 1), was omitted from the final cycles of refinement. The programs WinGX [31], ORTEP-3 for Windows [31], PLATON [32], and DIAMOND [33] were also used in the study. Crystal data and refinement details are given in Table 1.

CCDC 2113786 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033).

3. Results and discussion

All of the newly prepared cadmium(II) compounds were isolated, as expected, as white powders. Analytical and spectroscopic data are given in the experimental section. While connectivity of the various ligands in the cadmium compounds have been established, regrettably, single crystals of the cadmium compounds could not be prepared for x-ray analysis for the determination of fine details of the molecular structures and supramolecular association. Since IR spectra were not recorded below 400 cm^{-1}, the bands for Cd–Cl, Cd–I, and Cd–Br, expected at around 260 cm^{-1} in the spectra of $[Cd(L_{CX})Cl_2]$, $[Cd(L_{CX})Cl(ClO_4)]$•$2H_2O$, $[Cd(L_{CX})I_2]$•H_2O, and $[Cd(L_{CX})Br_2]$•$2H_2O$, were not detected. Magnetochemical studies indicate all compounds are diamagnetic species. The UV-visible spectra did not exhibit any d-d bands but displayed charge transfer bands as expected for d^{10} system. Consistent with previous work, the stereochemistry of the compounds does not change during axial substitution reactions [19], so the stereochemistry of axial ligand substitution products of $[Cd(L_{CX})\ (ClO_4)_2]$•$2H_2O$ were assigned by comparison with the ^{1}H-NMR data of $[Cd(L_{CX})\ (ClO_4)_2]$•$2H_2O$.

Table 1. Crystal and refinement data for L_{CX}.

Molecular formula	$C_{24}H_{46}N_6$
Molecular weight	418.67
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.0044(1)
b/Å	17.8006(3)
c/Å	9.0697(1)
β/°	98.928(1)
V/Å^3	1276.62(3)
Z	2
D_x/g cm^{-3}	1.089
F (000)	464
μ/mm^{-1}	0.505
No. reflections measured	15376
No. independent reflections	2292
No. reflections with $I \geq 2\ \sigma\ (I)$	2072
R (obs. data)	0.042
$wR2$ (all data)	0.117

3.1. L•2HClO$_4$, L_C, and L_{CX}

Ligands, L•$2HClO_4$ [22,27], L_C [22, 27], and L_{CX} [17] have been characterized as per the indicated literature.

3.1.1. Crystal and molecular structures of L_{CX}

Crystals of L_{CX} were obtained and subjected to an x-ray crystallographic study. The molecular structure of the centrosymmetric molecule is shown in Figure 1. The 14-membered ring has an extended chair conformation and is stabilized by intramolecular amine-N–H…N(tertiary amine) hydrogen bonds [N1–H1n…N2^i = 2.257(11) Å, N1…N2^i = 2.9550(13) Å with angle at H1n = 138.3(11)° for symmetry operation (i) 1-x, 1-y, 1-z]. The chirality at each of the C1 and C5 atoms is *S* and, being a centrosymmetric molecule, the chirality at each of the C1^i and C5^i atoms is *R*. The amine-N2 atom carries a cyanoethyl substituent with the N2–C3–C4–C7 torsion angle of 175.66(12)° being indicative of an + anti-periplanar (+ap) configuration.

In the absence of conventional hydrogen bonding, the supramolecular association in the crystal of L_{CX} is largely devoid of directional interactions. Indeed, the only identifiable contacts within the standard distance criteria of PLATON [32] are methyl-C-H…N(cyano) contacts. From symmetry, each molecule forms four such contacts which extend laterally to form a square grid, these stack in an …AAA… fashion in the crystal; relevant diagrams and data are given in Fig. S6, Supplementary Materials.

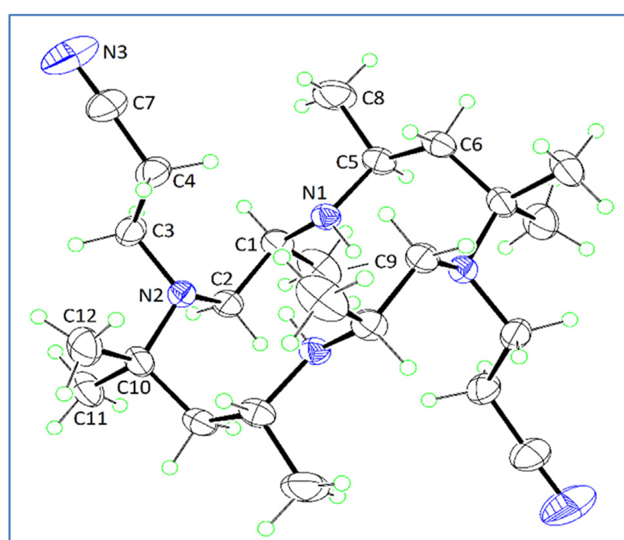


Figure 1. The molecular structure of L_{CX}, showing the atom-labelling scheme and displacement ellipsoids at the 35% probability level. The molecule is disposed about an inversion center with unlabeled atoms related by the symmetry operation 1-x, 1-y, 1-z.

3.2. Cadmium(II) compounds of L_{CX}

3.2.1. Cadmium(II) compounds (1–4) produced by the direct interaction of L_{CX} with cadmium(II) salts

Six coordinated octahedral $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$, $[Cd(L_{CX})(NO_3)_2]$, $[Cd(L_{CX})(CH_3COO)_2]$, and $[Cd(L_{CX})Cl_2]$ compounds were prepared by the direct interaction of L_{CX} with each of $Cd(ClO_4)_2\bullet 6H_2O$, $Cd(NO_3)_2\bullet 4H_2O$, $Cd(CH_3COO)_2\bullet 3H_2O$, and $CdCl_2\bullet H_2O$, respectively. The infrared spectra [Fig. S1(a)-S1(d), Supplementary Materials] exhibit bands in the ranges 3214-3255 cm^{-1} for ν_{N-H}, 2969-2974 cm^{-1} for ν_{C-H}, 1383-1395 cm^{-1} for ν_{CH3}, 1173-1174 cm^{-1} for ν_{C-C}, and 461-476 cm^{-1} for ν_{Cd-N} stretching frequencies. Further, all compounds display bands due to $\nu_{C\equiv N}$ in the range 2246–2251 cm^{-1} which compares with 2245 cm^{-1} in the spectrum of L_{CX} [17]. This agreement thus provides strong evidence for the presence of N-pendant cyanoethyl branches in the ligand which are non-coordinating. The appearance of bands at 3433 cm^{-1} and 1658 cm^{-1} can be accounted for by the presence of water molecules of crystallization in the products [34, 35]. The infrared spectrum of $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$ displays perchlorate bands at around 1111, 1095, 1062 and 622 cm^{-1}, where the splitting of the band at 1095 cm^{-1} into two medium bands at 1111 and 1062 cm^{-1} is attributed to coordinated perchlorate [36]. The spectrum of $[Cd(L_{CX})(NO_3)_2]$ showed a band at 1383 cm^{-1} split into two medium bands at 1329 and 1445 cm^{-1} which can be attributed to a coordinated NO_3^- group. The separation of the bands by 116 cm^{-1} is consistent with a unidentate mode of coordination [37]. The spectrum of $[Cd(L_{CX})(CH_3COO)_2]$ also exhibits strong bands at 1571 and 1416 cm^{-1} with the separation of 155 cm^{-1} giving evidence in favor of a unidentate mode of coordination by the CH_3COO^- ion [38]. The molar conductance values for all four compounds in chloroform and for $[Cd(L_{CX})(CH_3COO)_2]$ and $[Cd(L_{CX})Cl_2]$ in DMSO were found in the range of 0–28 $\Omega^{-1}cm^2mole^{-1}$, which support their non-electrolytic nature [39] of these compounds, indicating the anions (ClO_4^-, NO_3^-, CH_3COO^-, and Cl^-) are coordinated to cadmium(II). By contrast, the molar conductance values (64-110 $\Omega^{-1}cm^2mole^{-1}$) for $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$ and $[Cd(L_{CX})(NO_3)_2]$ in DMSO, and $[Cd(L_{CX})(CH_3COO)_2]$ and $[Cd(L_{CX})Cl_2]$ in CH_3CN support 1:1 electrolytic character [40]. This is due to the conversion of the original octahedral geometry to square pyramidal as indicated by expression (1). Crystal structure determinations are available for an analog for the nitrate derivative in expression (1), namely $[Cd(L_C)(NO_3)](NO_3)$ [14] and $[Cd(L_B)(NO_3)](NO_3).0.5H_2O$ [15]. Here, one nitrate is weakly coordinated above the N_4 plane and one nitrate is non-coordinating thereby providing indirect evidence for the formulation of the products in expression (1). Further, the values in the range 175–291 $\Omega^{-1}cm^2mole^{-1}$ measured for $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$ and $[Cd(L_{CX})(NO_3)_2]$ in CH_3CN demonstrate the 1:2 electrolytic nature [40] of these two compounds in this solvent due to the conversion of octahedral dianionic (ClO_4^- and NO_3^-) species into octahedral diaqua species as revealed by expression (2).

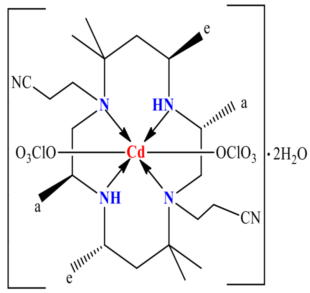
$$[Cd(L_{CX})(X)_2]nH_2O \xrightarrow{DMSO/CH_3CN} [Cd(L_{CX})(X)](X)nH_2O \quad \text{[(X=ClO}_4\text{,NO}_3\text{,CH}_3\text{COO,or Cl) and (n=0 or 2)]} \tag{1}$$

$$[Cd(L_{CX})(Y)_2]nH_2O \xrightarrow{CH_3CN} [Cd(L_{CX})(H_2O)_2](Y)_2 \quad \text{[(Y=ClO}_4\text{ or NO}_3\text{) and (n=2 or 0)]} \tag{2}$$

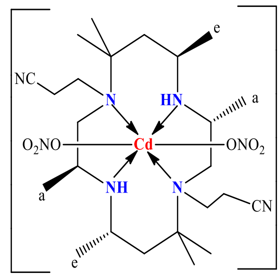
The ^{1}H-NMR spectrum (Fig. S2, Supplementary Materials) of the diperchloratocadmium(II) dihydrate compound $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$ exhibits overlapped signals corresponding to 24H. However, resolution of this multiplet shows that this signal is composed of two singlets and three doublets. The singlets at 1.255 and 1.312 ppm, each corresponding to 6H, can be assigned to equatorial and axial components of gem-dimethyl protons, respectively, whereas the doublets at 1.148, 1.215, and 1.303 ppm in the ratio of 1:1:2 corresponds to 3H, 3H, and 6H, respectively. The two doublets at 1.148 and 1.215 ppm can be assigned to two equatorial methyl protons on two chiral carbons and the doublet at 1.303 ppm to the axial methyl protons on the other two equivalent chiral carbons. Thus, a diaxial-diequatorial orientation, as revealed by the x-ray analysis (Chart 1) can be assigned to this compound. The spectrum further exhibits multiplets at 2.621, 3.428, and 3.665 ppm due to CH_2, and at 4.026, 5.350, and 7.285 ppm due to CH, H_2O, and NH protons, respectively. The ^{13}C NMR spectrum (Fig. S3, Supplementary Materials) exhibits only 12 resonances (half the number of total number of carbon atoms), which can be accounted for pairwise equivalency of carbon atoms. This observation is in support of the symmetric diaxial-diequatorial orientation as has already been assigned on the basis of the ^{1}H NMR spectrum. The four resonances in the region 18–35 ppm can be assigned to the eight carbon atoms of eight peripheral methyl carbons. The five resonances in the region 51–59 ppm can be accounted for by the 10 ring carbons and the three downfield resonances in the range of 66–68 ppm are attributed to pairwise equivalent six carbons in the two cyanoethyl branches ($-CH_2-CH_2-CN$). Further, the ^{1}H NMR spectrum (Fig. S4, Supplementary Materials) of $[Cd(L_{CX})(NO_3)_2]$ revealed two singlets at 1.277 and 1.304 ppm with these being ascribed to the equatorial and axial methyl groups of two gem-dimethyl pairs. The spectrum further shows two doublets at 1.107 and 1.554 ppm, corresponding to 6H each, which arise due to two equatorial and two axial methyl groups, respectively, which are pairwise equivalent. So, $[Cd(L_{CX})(NO_3)_2]$ should therefore, have two equatorially oriented and two axially oriented methyl groups on chiral carbons. However, the signals are not well resolved but are overlapped. The downfield signals (most are multiplets) at 2.070, 2.287, and 2.888 ppm due to CH_2, and 3.426–3.786, and 7.285 ppm due to CH, and NH-protons. Hence, a similar diaxial-diequatorial structure (Str. 2, Chart 1) can also be assigned to $[Cd(L_{CX})(NO_3)_2]$. On the other hand, though the ligand of the complex $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$ contains 24 carbons, based on the above evidence and earlier discussion, structures Str. 1, 2, 3, and 4 (Chart 1) can be assigned to $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$, $[Cd(L_{CX})(NO_3)_2]$, $[Cd(L_{CX})(CH_3COO)_2]$, and $[Cd(L_{CX})Cl_2]$, respectively.

3.2.2. Axial ligand substitution products derived from $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$ (5–9)

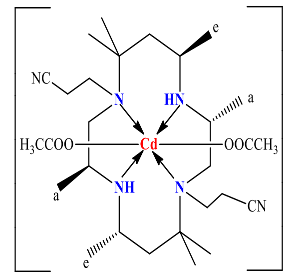
$[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$ was subjected to axial substitution reactions with KX (X = I, Br, Cl, and SCN) and $NaNO_2$ in a 1:2 ratio to afford the six coordinated octahedral compounds $[Cd(L_{CX})I_2]\bullet H_2O$, $[Cd(L_{CX})Br_2]\bullet 2H_2O$, $[Cd(L_{CX})Cl(ClO_4)]\bullet 2H_2O$, $[Cd(L_{CX})(NCS)_2]\bullet H_2O$, and $[Cd(L_{CX})(NO_2)(ClO_4)]\bullet 2H_2O$, respectively. The infrared spectra [Fig. S1(e)–(i), Supplementary Materials] of these compounds exhibit bands at 3191-3241 cm^{-1} for ν_{N-H}, 2965-2970 cm^{-1} for ν_{C-H}, 1375-1377 cm^{-1} for ν_{CH3}, 1175-1176 cm^{-1} for ν_{C-C}, 449-476 cm^{-1} for ν_{Cd-N}, and 2245-2249 cm^{-1} for $\nu_{C\equiv N}$ stretching frequencies, i.e., in the anticipated regions. The presence of bands at 624 cm^{-1} and 1081-1090 cm^{-1} in the IR spectra of $[Cd(L_{CX})Cl(ClO_4)]\bullet 2H_2O$ and $[Cd(L_{CX})(NO_2)(ClO_4)]\bullet 2H_2O$ indicate that only one perchlorate ion from the coordination sphere of $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$ was substituted by Cl^- and NO_2^- ions, respectively; the other perchlorate remained coordinated. However, the absence of such bands in the spectra of other compounds indicate that both of perchlorate ions of $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$ were completely replaced by $I^-/Br^-/SCN^-$ ions. The appearance of bands at 3401–3459 and 1668-1684 cm^{-1} in the IR spectra of all of these five compounds are accounted for by the presence of water of crystallization [35, 36]. In addition, the IR spectrum of $[Cd(L_{CX})(NCS)_2]\bullet H_2O$ exhibits bands at 2053 cm^{-1} for ν_{CN}, 803 cm^{-1} for ν_{CS}, and 472 cm^{-1} for δ_{NCS} which can be assigned to the N-bonded thiocyanate group [41, 42, 43]. The IR spectrum of $[Cd(L_{CX})(NO_2)(ClO_4)]\bullet 2H_2O$ exhibits bands at 1456 cm^{-1} ascribed to $\nu_{asym(NO2)}$, 1320 cm^{-1} for $\nu_{sym(NO2)}$ overlapped with 1375 cm^{-1} for ν_{CH3}, and 806 cm^{-1} for δ_{NO2} which can be attributed to a N-bonded nitro complex [44]. The molar conductivity values 0-39 $\Omega^{-1}cm^2mole^{-1}$ for **5**–**9** in chloroform and for all four compounds except $[Cd(L_{CX})(NCS)_2]\bullet H_2O$ in DMSO indicate the non-electrolytic nature [39] i.e., all the anions are in the coordination sphere, which supports the octahedral structures. However, the molar conductivity values for $[Cd(L_{CX})(NCS)_2]\bullet H_2O$ in DMSO and four of the five compounds, except $[Cd(L_{CX})(NO_2)(ClO_4)]\bullet 2H_2O$, in CH_3CN in the range of 68–127



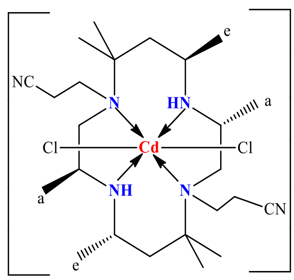
[Cd(L$_{CX}$)(ClO$_4$)$_2$]·2H$_2$O (**1**)



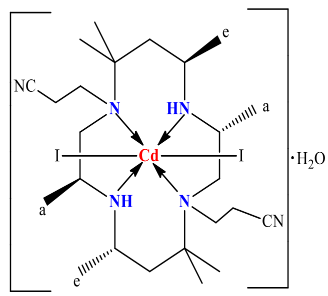
[Cd(L$_{CX}$)(NO$_3$)$_2$] (**2**)



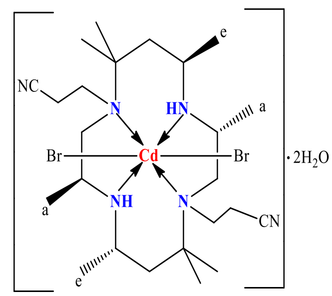
[Cd(L$_{CX}$)(CH$_3$COO)$_2$] (**3**)



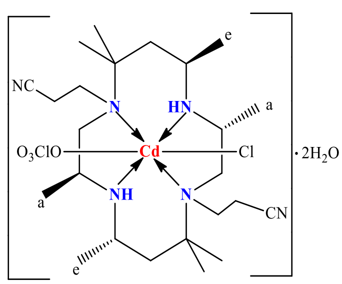
[Cd(L$_{CX}$)Cl$_2$] (**4**)



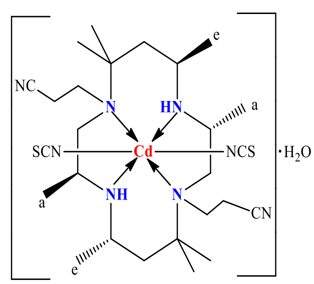
[Cd(L$_{CX}$)I$_2$]·H$_2$O (**5**)



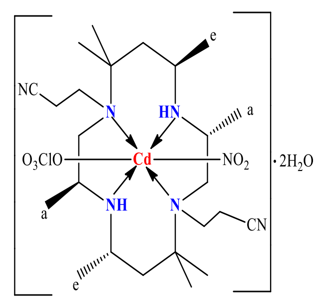
[Cd(L$_{CX}$)Br$_2$]·2H$_2$O (**6**)



[Cd(L$_{CX}$)Cl(ClO$_4$)]·2H$_2$O (**7**)



[Cd(L$_{CX}$)(NCS)$_2$]·H$_2$O (**8**)



[Cd(L$_{CX}$)(NO$_2$)(ClO$_4$)]·2H$_2$O (**9**)

Chart 1. Cadmium(II) compounds of L$_{CX}$.

Ω^{-1}cm^{2}mole^{-1} are indicative of 1:1 electrolytes [40] owing to the conversion of octahedral species into square pyramidal species as indicated by expressions (3), (4a), and (4b). On the other hand, the value 201 Ω^{-1}cm^{2}mole^{-1} for [Cd(L$_{CX}$) (NO$_2$) (ClO$_4$)]•2H$_2$O in CH$_3$CN gives evidence in favor of 1:2 electrolytic behavior [40] in this solvent due to conversion of the original octahedral mononitroperchlorato species into octahedral diaqua species as shown by expression (5).

$$[Cd(L_{CX})(Z)_2]nH_2O \xrightarrow[\text{[Z=NCS,I or Br; n=1 or 2]}]{DMSO/CH_3CN} [Cd(L_{CX})(Z)](Z)nH_2O \quad (3)$$

$$[Cd(L_{CX})Cl(ClO_4)]2H_2O \xrightarrow[\text{Or}]{CH_3CN} [Cd(L_{CX})Cl(ClO_4)]2H_2O \quad (4a)$$

$$[Cd(L_{CX})Cl(ClO_4)]2H_2O \xrightarrow{CH_3CN} [Cd(L_{CX})(ClO_4)]Cl\ 2H_2O \quad (4b)$$

$$[Cd(L_{CX})(NO_2)(ClO_4)]2H_2O \xrightarrow{CH_3CN} [Cd(L_{CX})(H_2O)_2](NO_2)(ClO_4) \quad (5)$$

The ^{1}H NMR spectrum (Fig. S5, Supplementary Materials) of [Cd(L$_{CX}$) I$_2$]•H$_2$O, an axial substitution product of [Cd(L$_{CX}$) (ClO$_4$)$_2$]•2H$_2$O, exhibits an overlapped pattern for the peripheral methyl groups which can be resolved into two parts. One part (region 1.2–1.4 ppm) contains a singlet at 1.339 ppm corresponding to 6H and two doublets at 1.210 and 1.312 ppm, each integrating to 3H. These resonances can be attributed to the equatorial components of gem-dimethyl groups and two equatorial methyl protons on two chiral carbons, respectively. Other resonances include two singlets at 1.541 and 1.563 ppm, and two doublets at 1.392 and 1.508 ppm which are attributed to axial components of gem-dimethyl pairs and two axially oriented methyl protons on two equivalent chiral carbons, respectively. Thus, the diaxial-diequatorial orientation (Str. 5, Chart 1) assigned to this molecule, as assigned to the parent compound, which requires methyl groups on C$_7$ and C$_{14}$ to be equatorially (Scheme 1) and those on C$_2$ and C$_9$ axially oriented or vice versa and similar observation was noted in related studies [23, 45, 46]. Separate signals for equivalent methyl groups indicate the distortion in the substitution product. The spectrum further displays downfield multiplets at 2.875, 3.269 ppm, and 3.547 due to CH$_2$, and 4.706, 5.320, and 7.285 ppm, which are accounted for by CH, H$_2$O, and NH proton. Based on the above evidence and earlier discussion, the structures Str. 5, 6, 7, 8, and 9 (Chart 1) can be assigned to [Cd(L$_{CX}$)I$_2$]•H$_2$O, [Cd(L$_{CX}$)Br$_2$]•2H$_2$O, [Cd(L$_{CX}$)Cl(ClO$_4$)]•2H$_2$O, [Cd(L$_{CX}$) (NCS)$_2$]•H$_2$O, and [Cd(L$_{CX}$) (NO$_2$) (ClO$_4$)]•2H$_2$O, respectively.

Table 2. Antibacterial activities of L_{CX} and cadmium(II) compounds.

Sample No.	Compounds	Zone of inhibition in diameter (mm)				
		Gram-positive bacteria		Gram-negative bacteria		
		B. wiedmannii 24 h	*B. aerius* 24 h	*E. coli* 24 h	*S. flexneri* 24 h	S. typhi 24 h
	L_{CX}	0	0	0	0	0
(1)	$[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$	13	14	10	12	19
(2)	$[Cd(L_{CX})(NO_3)_2]$	9	12	9	11	17
(3)	$[Cd(L_{CX})(CH_3COO)_2]$	12	14	13	15	18
(4)	$[Cd(L_{CX})Cl_2]$	11	14	12	14	15
(5)	$[Cd(L_{CX})I_2]\bullet H_2O$	20	13	11	10	9
(6)	$[Cd(L_{CX})Br_2]\bullet 2H_2O$	19	15	14	11	12
(7)	$[Cd(L_{CX})Cl(ClO_4)]\bullet 2H_2O$	19	14	14	15	15
(8)	$[Cd(L_{CX})(NCS)_2]\bullet H_2O$	8	10	11	12	14
(9)	$[Cd(L_{CX})(NO_2)(ClO_4)]\bullet 2H_2O$	12	12	11	10	13
	$Cd(ClO_4)_2\bullet 6H_2O$	22	16	15	15	19
	Chloramphenicol	26	20	30	30	36
	DMSO	0	0	0	0	0

3.3. Antibacterial studies

Antibacterial activities of L_{CX} and cadmium(II) complexes were investigated against two gram-positive (*Bacillus wiedmannii*, which causes foodborne illness, and *Bacillus aerius*, the causative agent of infectious diseases like burn infections, ear infections, etc.) and three gram-negative (*Escherichia coli* which causes cholangitis, urinary tract infections, etc.; *Shigella flexneri*, which causes diarrhea; and *Salmonella typhi*, responsible for high fever, diarrhea, and vomiting) bacteria. These bacteria are responsible a variety of diseases and there is an urgent need to develop effective drugs for treatment. Thus, in this context, we carried out antibacterial studies on the new cadmium(II) compounds to investigate their activities against these microbes. The evaluation of the MIC (minimum inhibitory concentration) of the test samples were determined and shown to be 5 mg/mL. Therefore, all of the test samples including controls and a non-coordinated cadmium(II) salt were studied at a concentration of 5 mg/mL. The macrocycle L_{CX} was ineffective against all the tested bacteria as observed previously [23, 24, 47, 48]. The results are summarized in Table 2 and Supplementary Materials Fig. S7(a)–(e), and reveal that all of the cadmium(II) compounds of L_{CX} exhibit remarkable antibacterial activity. Further, the data indicate distinctive activities against the studied bacteria. Thus, the diperchloratocadmium(II) (**1**), dinitratocadmium(II) (**2**), diacetatocadmium(II) (**3**), dichloridocadmium(II) (**4**), diisothiocyanatocadmium(II) (**8**), and mononitroperchloratocadmium(II) (**9**) derivatives exhibit maximum activity against *Salmonella typhi.* By contrast, the diiodidocadmium(II) (**5**), dibromidocadmium(II) (**6**), and monochloridoperchloratocadmium(II) (**7**) derivatives are most potent against *Bacillus wiedmannii*. Against *Bacillus aerius*, the most active compound was the dibromidocadmium(II) species (**6**), against *E. coli*, and the monochloridoperchloratocadmium(II) (**7**) derivative were most potent, and against *S. flexneri*, (**7**) was most effective. The present cadmium(II) compounds revealed comparable activities to other reported cadmium(II) macrocyclic compounds [13, 14]. By contrast to the negative control (DMSO), which was totally ineffective against all evaluated bacteria, the free salt $[Cd(ClO_4)_2\bullet 6H_2O]$ as well as the positive control (chloramphenicol) were highly potent. As the compounds are very stable, there is little possibility of dissociation of the compounds to release metal ion [47]. Elevated activities of the cadmium(II) complexes compared to L_{CX} can be explained by the chelation theory [49]}.

4. Conclusions

This study reveals the 1,8-N-pendent derivative ligand, L_{CX}, underwent facile complexation with cadmium(II) perchlorate, nitrate, acetate, and cadmium(II) chloride salts to afford six coordinated octahedral compounds, $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$, $[Cd(L_{CX})(NO_3)_2]$, $[Cd(L_{CX})(CH_3COO)_2]$, and $[Cd(L_{CX})Cl_2]$, respectively. The compound $[Cd(L_{CX})(ClO_4)_2]\bullet 2H_2O$ underwent axial substitutions with KX (X = I, Br, Cl, and SCN) and $NaNO_2$ to furnish six coordinated octahedral substituted compounds $[Cd(L_{CX})I_2]\bullet H_2O$, $[Cd(L_{CX})Br_2]\bullet 2H_2O$, $[Cd(L_{CX})Cl(ClO_4)]\bullet 2H_2O$, $[Cd(L_{CX})(NCS)_2]\bullet H_2O$, and $[Cd(L_{CX})(NO_2)(ClO_4)]\bullet 2H_2O$, respectively. All compounds were found to be non-electrolytes in $CHCl_3$ as expected for octahedral geometries. The molar conductivity values of the compounds in DMSO and CH_3CN is an indication of changes of geometry/ionization of these compounds in these solvents. Though the ligand L_{CX} was found to be ineffective against all the bacteria tested, the cadmium(II) compounds of this ligand showed remarkably elevated activities against all the tested bacteria.

Declarations

Author contribution statement

Avijit Chakraborty: Performed the experiments; Wrote the Paper.

Saswata Rabi: Conceived and designed the experiments; Wrote the Paper.

Lucky Dey: Performed the experiments; Analyzed and interpreted the data.

Debashis Palit, Benu Kumar Dey: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Edward R.T. Tiekink: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Tapashi Ghosh Roy: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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