

Zinc(II) complexes of 3,10-*C-meso*-2,5,5,7,9,12,12,14-octamethyl-1,8-diaza-4,11-diazoniacyclotetradecane as its bis(acetate) trihydrate, $[L_BH_2][CH_3COO]_2 \cdot 3H_2O$: Synthesis, Characterization and antimicrobial studies

Foni B. Biswas, MS

Department of Chemistry, University of Chittagong, Chittagong, Bangladesh

Saswata Rabi, MS

Department of Chemistry, Chittagong University of Engineering and Technology, Chittagong, Bangladesh

Kanak Barua, PhD

Department of Chemistry, Chittagong College, Chittagong, Bangladesh

Tapashi G. Roy, PhD

Debashis Palit, PhD

Benu K. Dey, MSc

Department of Chemistry, University of Chittagong, Chittagong, Bangladesh

Doi: 10.19044/esj.2018.v14n24p330 [URL:http://dx.doi.org/10.19044/esj.2018.v14n24p330](http://dx.doi.org/10.19044/esj.2018.v14n24p330)

Abstract

One isomeric ligand, L_B among three isomers (L_A , L_B and L_C) of 2,9-*C-meso*-2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecanes, differing in the orientation of methyl groups on the chiral carbon atoms) on interaction with vinyl acetate produces 2,9-*C-meso*-2,5,5,7,9,12,12,14-octamethyl-1,8-diaza-4,11-diazoniacyclotetradecane as its bis(acetate) trihydrate, $[L_BH_2][OOCCH_3]_2 \cdot 3H_2O$. This ligand salt trihydrate reacts with $Zn(CH_3COO)_2 \cdot 2H_2O$ to produce square pyramidal monoacetatozinc(II) acetate complex $[ZnL_B(CH_3COO)](CH_3COO)$, which undergoes anion exchange reaction with $NaClO_4 \cdot 6H_2O$ to produce monoacetatozinc(II) perchlorate complex, $[ZnL_B(CH_3COO)](ClO_4)$. The complex, $[ZnL_B(CH_3COO)](ClO_4)$ undergoes axial substitution reactions with $KSCN$, $NaNO_2$ and KNO_3 to form the substitution products, $[ZnL_B(NCS)](NCS)$, $[ZnL_B(NO_2)](ClO_4)$ and $[ZnL_B(NO_3)](ClO_4)$ respectively where CH_3COO^- is replaced by NCS^- , NO_3^- and NO_2^- . All these complexes have been characterized on the basis of analytical, spectroscopic, conductometric and magnetochemical data. The antifungal and antibacterial activities of these compounds have been studied against some phytopathogenic fungi and bacteria.

Keywords: Azamacrocyclic ligand; Zinc(II) complexes; Analytical and spectroscopic studies; Square pyramidal; Antimicrobial activities

Introduction

The research interest about the field of macrocyclic chemistry is growing prominently due to its application in the multifarious sections of the present-time science. The macrocyclic ligands and their different metal complexes are playing a vital role not only in the field of industrial (Hitoshi, 2002) and analytical (Kolthoff, 1979) but also in the field of pharmacology by working as antibacterial (Shankarwar, et al., 2015), antifungal (Gull, et al., 2016), antitumor (Rzuezek, et al., 2010) and MRI (Hermann, et al, 2008) agents. Moreover, some naturally occurring macrocycles such as vitamin B₁₂, haemoglobin, chlorophyll, etc. are also participating in a large extent in the development of the biological system of the environment. Considering the all above motif it is reasonable to assemble some new macrocyclic compounds and perform their biological investigations. Different metal complexes of macrocyclic ligands as well as their N-pendent derivatives are available in the literature (Nath, et al., 2013; Roy, et al., 2006; 2007; 2011; Alam, et al., 2018). So it appeared interesting to see whether a similar type of an N-pendent ligand could be prepared by the interaction of L_B (one isomer of Me₈[14]ane) with vinyl acetate. Thus the ligand salt (L_B·2HClO₄) and isomeric ligands, L_A, L_B & L_C (Scheme 1) of its reduced form have been prepared according to the literature method (Curtis, et. al, 1969; Bembi et.al, 1989). But reaction product (Scheme 2) obtained by the reaction of L_B with vinyl acetate has been analyzed as tri-hydrate acetate salt of L_B, [L_BH₂](CH₃COO)₂·3H₂O instead of expected N-pendent ligand [L_B-2H](-CH₂-CH₂-OOC-CH₃)₂. Similar observation was also noted during the preparation of another N-pendent derivative of L_B with dibromoxylene (Babul, et. al, 2018) However the same isomeric ligand L_B, underwent alkylation reaction with acrylonitrile to produce cyanoethyl (Alam, et. al, 2018), methyl iodide to produce dimethyl (Roy, et. al, 2014) and ethylene oxide to produce hydroxyl ethyl (Roy, et. al., 2004) derivatives. The concerned ligand salt, [L_BH₂](CH₃COO)₂·3H₂O, produced some new zinc(II) complexes. All the compounds have been characterized on the basis of various analytical and spectroscopic methods. Confirmation of molecular structures of concerned ligand salt, [L_BH₂](CH₃COO)₂·3H₂O (Hazari, et. al, 2008) and one zinc(II) complex, [ZnL_B(CH₃COO)](ClO₄) (Roy, et. al, 2011) by X-ray crystallography have been reported in our earlier reports. Antibacterial & antifungal activities of the concerned ligand salt and its zinc(II) complexes have been studied against different bacteria and fungi. Herein we report these studies.

Experimental

Materials and equipment

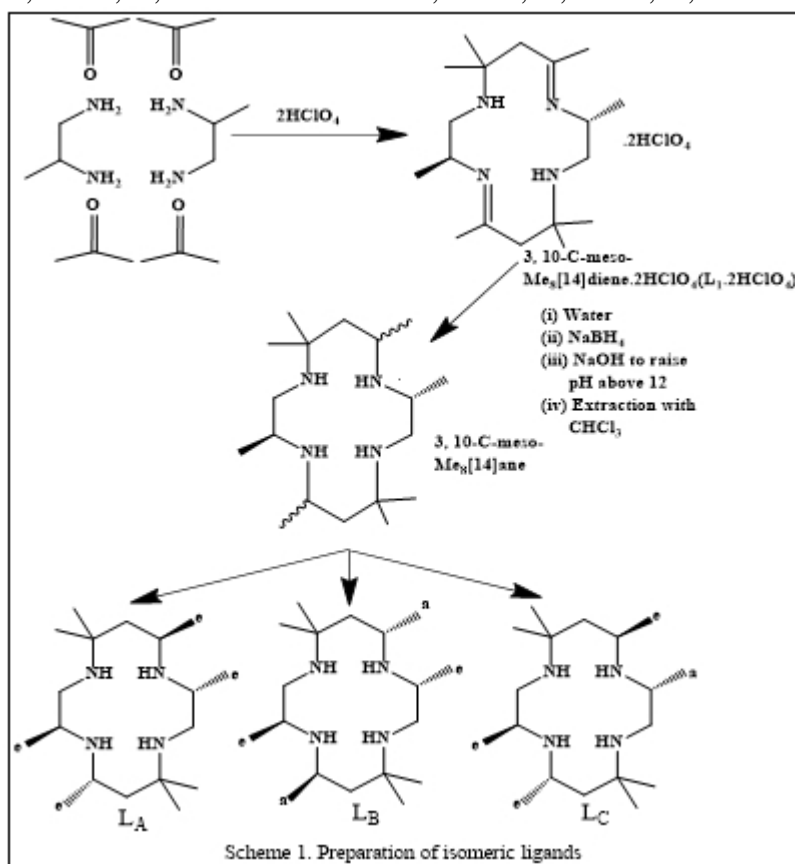
All the chemicals used were of analytical reagent grade. These were used without further purification. Equipments used were of standard ones.

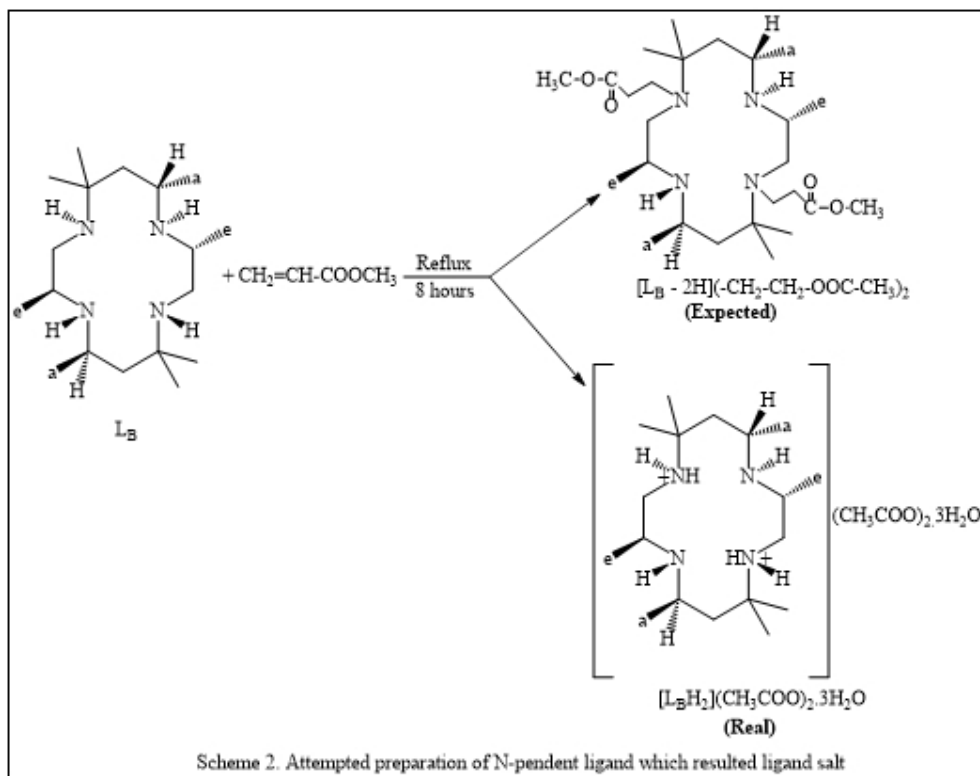
Synthesis

$[L_B H_2](CH_3COO)_2 \cdot 3H_2O$

0.624 g (2.0 mmol) of L_B was suspended in 20 ml of vinyl acetate taken in a round bottomed flask. The mixture was refluxed for 8 hours on a heating mantle until a clear solution was obtained. The reaction mixture was filtered and kept at room temperature. On standing for 24 hours at room temperature, the solution gave colourless crystals which were filtered off, washed with vinyl acetate followed by diethylether and finally dried over silicagel in a desiccator and labeled as $[L_B H_2][(CH_3COO)_2 \cdot 3H_2O]$.

$[L_B H_2](CH_3COO)_2 \cdot 3H_2O$, Yield: 65%. m.p.: >300 °C. Found: C, 54.30; H, 11.08; N, 11.56. Calcd for : C, 54.32; H, 11.11; N, 11.52%.





$[ZnL_B(CH_3COO)](CH_3COO)$

0.450 g (1.0 mmol) of $[L_BH_2](CH_3COO)_2 \cdot 3H_2O$ and 0.297 g (1.0 mmol) of zinc(II) acetate were dissolved separately in 30 ml of hot methanol. The reaction mixture was heated on a water bath for one hour when a white solid product, $[ZnL_B(CH_3COO)](CH_3COO)$ started to separate out. After cooling at room temperature for one hour, the white product was filtered off, washed with methanol followed by diethylether and dried in desiccator over silicagel.

$[ZnL_B(CH_3COO)](CH_3COO)$, Yield: 35%. m.p.: >300 °C. Found: C, 53.30; H, 8.50; N, 10.27; Zn, 13.25. Calcd: C, 53.28; H, 8.47; N, 11.30; Zn, 13.20%.

$[ZnL_B(CH_3COO)](ClO_4)$

0.495 g (1.0 mmol) of $[ZnL_B(CH_3COO)](CH_3COO)$ was dissolved in 40 ml of hot methanol and 0.460 g (2.0 mmol) of sodium perchlorate hexahydrate were added to it. The reaction mixture was heated for 15 minutes. During heating a white product separated out immediately. After cooling at room temperature for half an hour the white product, $[ZnL_B(CH_3COO)](ClO_4)$ was filtered off, washed with methanol followed by diethylether and dried in desiccator over silicagel.

$[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$, Yield: 40%. m.p.: $>300\text{ }^\circ\text{C}$. Found: C, 44.82; H, 7.41; N, 10.44; Zn, 18.05. Calcd: C, 44.78; H, 7.46; N, 10.45; Zn, 18.06%.

Axial substitution products of acetatozinc(II) perchlorate complex, $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$

$[\text{ZnL}_B(\text{NCS})](\text{NCS})$

0.518 g (1.0 mmol) of $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$ and 0.194 g (2.0 mmol) of KSCN were taken separately in 20 ml hot absolute methanol and mixed while hot. A white product appeared immediately. The white product was removed at this stage. The filtrate was heated on a water bath till the volume reduced to 5 ml. After cooling at room temperature, the solid product $[\text{ZnL}_B(\text{NCS})](\text{NCS})$ was filtered off, washed with methanol followed by diethylether and dried in a desiccator over silicagel.

$[\text{ZnL}_B(\text{NCS})](\text{NCS})$, Yield: 33%. m.p.: $>300\text{ }^\circ\text{C}$. Found: C, 52.04; H, 8.62; N, 18.25; Zn, 14.18. Calcd: C, 52.01; H, 8.66; N, 18.20; Zn, 14.17%.

$[\text{ZnL}_B(\text{NO}_2)](\text{ClO}_4)$

The mononitrozinc(II) perchlorate complex, $[\text{ZnL}_B(\text{NO}_2)](\text{ClO}_4)$ was prepared by the same method described for $[\text{ZnL}_B(\text{NCS})](\text{NCS})$ by using NaNO_2 instead of KSCN.

$[\text{ZnL}_B(\text{NO}_2)](\text{ClO}_4)$, Yield: 35%. m.p.: $>300\text{ }^\circ\text{C}$. Found: C, 41.27; H, 7.68; N, 13.40; Zn, 12.48. Calcd: C, 41.30; H, 7.65; N, 13.38; Zn, 12.51%.

$[\text{ZnL}_B(\text{NO}_3)](\text{ClO}_4)$

The monoacetatozinc(II) perchlorate complex, $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$ was prepared by the same method described for $[\text{ZnL}_B(\text{NCS})](\text{NCS})$ by using KNO_3 instead of KSCN.

$[\text{ZnL}_B(\text{NO}_3)](\text{ClO}_4)$, Yield: 27%. m.p.: $>300\text{ }^\circ\text{C}$. Found: C, 40.06; H, 7.39; N, 13.01; Zn, 12.27. Calcd: C, 40.08; H, 7.42; N, 12.98; Zn, 12.31%.

Physical measurements

Microanalysis (C, H, N analysis) of the complexes have been carried out on a C, H, N analyzer at the Inorganic Research Laboratory of the Institut der Anorganische und Angewandte Chemie, Hamburg Universitaet, Germany and at Department of Chemistry, Kyungpook National University, Daegu, South Korea and INQUIMAE, University of Buenos Aires, Argentina. IR spectra were recorded on a Shimadzu IR 20 spectrophotometer as KBr disks. UV-visible spectra were recorded on a Shimadzu UV-visible spectrophotometer in DMSO. Conductance measurements were carried out on a conductivity bridge Hanna instrument HI-8820 in DMSO, CHCl_3 , H_2O , CH_3CN , and DMF. Magnetic measurements were performed on Gouy Balance

which was calibrated using $\text{Hg}[\text{Co}(\text{NCS})_4]$. Mass spectra were recorded in Friedrich Schiller University, Jena, Germany. ^1H -NMR and ^{13}C -NMR spectra were recorded in DMSO with a 400 MHz Bruker DPX-400 spectrometer using TMS as internal standard at Friedrich Schiller University, Jena, Germany. Metal estimation has been performed by complexometric method.

Antibacterial activities

Antibacterial activities of the ligands and their complexes against selected gram-positive and gram-negative bacteria were investigated by the disc diffusion method. Paper disc (6 mm in diameter) and Petri plates (70 mm in diameter) were used throughout the experiment. Pour plates were made with sterilized melted nutrient agar NA (45°C) and after solidification of pour plates, the test organisms (suspension in sterilized water) were spread uniformly over the pour plates with sterilized glass rod separately. The paper discs after soaking with test chemicals (1 mg/1mL in DMSO) were placed at the center of the inoculated pour plates. A control plate was also maintained in each case with DMSO. At first the plates were left for four hours at low temperature (4°C) and the test chemicals diffused from disc to the surrounding medium by this time. The plates were then incubated at $(35\pm 2)^\circ\text{C}$ for growth of test organisms and were observed at 24-hours and 48 hours interval. The activity was expressed in terms of zone of inhibition in mm. The results for all concerned compounds have been reported after subtracting values for solvent DMSO itself. Tests were repeated thrice for statistical analysis.

Antifungal activities

The *in vitro* antifungal activities of the complexes against selected phytopathogenic fungi were assessed by the poisoned food technique. Potato Dextros Agar (PDA) was used as a growth medium. Dimethylsulphoxide was used as the solvent to prepare solutions of the tested compounds. The solutions were then mixed with the sterilized PDA so as to maintain concentrations of the compounds of 0.1% (ca. $3\mu\text{L}$). 20 mL of these solutions were each poured into a petri dish. After the medium had solidified, a 5 mm micelial disc of each fungus was placed in the center of each assay plate, along with a control. Linear growth of the fungus was measured in mm after five days of incubation at $25 \pm 2^\circ\text{C}$.

Results and Discussion

The ligand salt, Li_2HClO_4 was synthesized and isomeric ligands of its reduced form, L_A , L_B & L_C were isolated as per procedure adopted in the literature (Curtis, et. al., 1969; Bembi, et. al., 1989) (Scheme 1). Attempt to prepare N,N'-aceatoethyl derivative, $[\text{L}_\text{B}-2\text{H}][-\text{CH}_2-\text{CH}_2-\text{COOCH}_3]_2$ by interaction of L_B with vinyl acetate resulted ligand salt trihydrate

$[L_BH_2][OOCCH_3]_2 \cdot 3H_2O$. This ligand salt produced square pyramidal complex $[ZnL_B(CH_3COO)](CH_3COO)$ by the reaction with $Zn(CH_3COO)_2 \cdot 2H_2O$. However $ZnL_B(CH_3COO)(ClO_4)$ was prepared by the anion exchange reaction on $[ZnL_B(CH_3COO)](CH_3COO)$ with $NaClO_4 \cdot 6H_2O$. Moreover axial substitution reactions on $[ZnL_B(CH_3COO)](ClO_4)$ with $KSCN$, $NaNO_2$ and KNO_3 produced $[ZnL_B(NCS)](NCS)$, $[ZnL_B(NO_2)](ClO_4)$ and $[ZnL_B(NO_3)](ClO_4)$ respectively. Due to the presence of paired electrons in their d^{10} system, all these zinc(II) complexes were found to be diamagnetic as expected. The electronic spectra of these complexes did not show any d-d band as expected for their d^{10} system but the spectra display Zn-N charge transfer bands. Since 1H -NMR spectra of two axial substitution products have not been measured, so the stereochemistry of them has been assigned on the basis that, axial substitution takes place without change of conformation and configuration of the ligand of original complex (Roy, et. al., 2006, 2007, 2011). The characterization of the concerned ligand salt and its zinc(II) complexes have been described as follows.

Ligand salt $[L_BH_2](CH_3COO)_2 \cdot 3H_2O$

The reaction of vinylacetate ($CH_2=CH-COOCH_3$) with L_B produced white mass of molecular formula $C_{22}H_{54}N_4O_7$ corresponding to $[L_BH_2](CH_3COO)_2 \cdot 3H_2O$ which is a hydrated acetate salt of L_B instead of replacing NH-protons by $-CH_2-CH_2-COOCH_3$ to form bis(acetatoethyl) derivative, $[L_B-2H][(CH_2-CH_2-COOCH_3)_2]$. The infrared spectrum (Table 1) of this ligand salt displays ν_{N-H} , ν_{C-H} , ν_{CH_3} and ν_{C-C} bands in the expected region. Bands at 1567 cm^{-1} indicate the presence of acetate ion. This ligand salt also shows ν_{OH} band at around 3397 cm^{-1} and δ_{H_2O} at 1630 cm^{-1} for the presence of water of crystallization. Further the spectrum exhibits band at 1650 cm^{-1} for $\nu_{NH_2^+}$. The mass spectrum of this acetate salt of ligand does not show any m/z value corresponding to molecular ion peak. However highest m/z value at 312 corresponding to molecular ion peak of parent ligand L_B has been observed. All other m/z values corresponding to base peaks as well as to other fragment peaks revealed by the spectrum are same as those shown by L_B (Bembi, et. al, 1989; Roy, et. al., 2002) This observation may be accounted for the decomposition of ligand salts into free ligand during measuring mass spectrum. However the formula and molecular structure has been confirmed by its X-ray analysis [Figure 1] (Hazari, et. al., 2008) The 1H -NMR spectrum (Table 2) of this acetate salt of ligand L_B exhibits similar pattern of peaks as observed for free ligand L_B (Bembi, et. al, 1989). An extra triplet corresponding to four protons at 2.62 ppm appeared due to NH_2^+ protons on N_4 and N_{11} nitrogens. Moreover appearance of a prominent extra singlet at 1.68 ppm corresponding to 6H can be assigned for six CH_3 protons of CH_3COO^- groups. Expected singlet corresponding to $3H_2O$ molecules of this

ligand coincide with the singlet arising from water of solvent at 3.40 ppm. The positions of signals arising from chiral methyls on chiral carbons indicate that the diaxial-diequatorial configuration of L_B is retained in this ligand salt too. The ^{13}C -NMR spectrum (Table 3) of this ligand salt displays eleven peaks for twenty two carbons. The first four peaks out of five peaks in the region of 16-28 ppm can be assigned for eight peripheral methyl carbons and the 5th peak of that region for two carbons of CH_3 on two CH_3COO^- groups. The next 5 peaks in the region of 43-54 ppm may be assigned for 10 ring carbons. However the most upfield peak at 173.90 ppm can be assigned for two carbons of COO portion of two CH_3COO^- groups. Thus this spectral analysis gives an additional evidence for the formulation of this ligand salt. Moreover appearance of eleven peaks i.e., half the number of total carbon atoms is also an indication of pairwise equivalency of the structure which means that this analysis also support the symmetrical diaxial-diequatorial arrangement of the structure of L_B in its acetate salt as assigned from its ^1H -NMR spectrum. The structure of this ligand salt has been presented in Scheme 2.

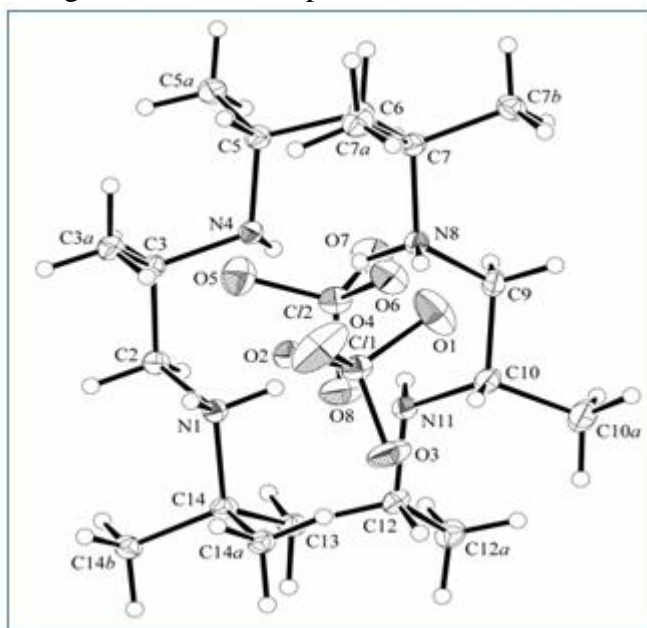


Figure 1. Molecular structure of $[\text{L}_B\text{H}_2](\text{CH}_3\text{COO})_2$

Table 1. IR spectral data* (cm^{-1}) for ligand salt and complexes.

Ligand salt & complexes	$\nu\text{N-H}$	$\nu\text{C-H}$	νCH_3	$\nu\text{C-C}$	$\nu\text{Zn-N}$	Other bands
$[\text{L}_B\text{H}_2](\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$	3224 s	2982 s	1383 w	1162 w	-	1567 m, νCOO ; 3397 s, νOH ; 1630 s, δHOH ; 1650 m, νNH_2^+
$[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})$	3180 m	2972 s	1392 vw	1184 vw	550 vw	1405 m, 1577 m, νCOO

[ZnL _B (CH ₃ COO)](ClO ₄)	3227s	2975 m	1392 w	1186 m	552 vw	1599 m, vCOO; 1129 vs, 624 s, vClO ₄
[ZnL _B (NCS)](NCS)	3136 m	2970 s	1393 s	1174 s	532 vw	vCN; 2050 s, vCS; 888 vw, δNCS; 481 vw
[ZnL _B (NO ₂)](ClO ₄)	3182 s	2981 s	1383 vs	1176 m	561 vw	1132 vs, 623 s, vClO ₄ ; 1410 m, vasm(NO ₂); 1295 vs, vsym(NO ₂); 835 m, δNO ₂
[ZnL _B (NO ₃)](ClO ₄)	3219 m	2972 m	1380 vw	1170 w	540 w	1138 vs, 625 s, vClO ₄ ; 1430 w, 1310 w, vNO ₃

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

Table 2. ¹H-NMR chemical shift data (ppm) for the ligand salt and complexes

Ligand salt & complexes	Types of protons		
	Geminal dimethyl δ(ppm)	Methyl on chiral carbon δ(ppm)	CH ₂ , CH & NH multiplets and others δ(ppm)
[L _B H ₂](CH ₃ COO) ₂ .3H ₂ O	1.05 (s, 6H, e) 1.13 (s, 6H, a)	0.93 (d, 6H, e) 1.00 (d, 6H, a)	3.09 (m), 3.60 (m), 3.51 (m); 2.62 (t, 4H) (NH ₂ ⁺ protons); 1.68 (s, 6H) (CH ₃ protons of CH ₃ COO ⁻ group)
[ZnL _B (CH ₃ COO)](ClO ₄)	1.12 (s, 3H, e) 1.14 (s, 3H, e) 1.23 (s, 3H, a)	1.07 (d, 3H, e) 1.13 (d, 3H, e) 1.20 (d, 3H, a)	2.66 (m), 2.78 (m), 3.31 (m); 1.50 (s, 3H) (CH ₃ protons of CH ₃ COO ⁻ group)
[ZnL _B (NCS)](NCS)	1.32(s, 3H, a) 1.20 (s, 6H, e) 1.24 (s, 6H, a)	1.25 (d, 3H, a) 1.01 (d, 3H, e) 1.04 (d, 3H, e) 1.08 (d, 6H, a)	3.59 (m), 3.62 (m), 2.85 (m)

Multiplicity is given as s, singlet; d, doublet; t, triplet; a = axial; e = equatorial

Table 3. ¹³C-NMR spectral data (ppm) for the ligand salt and complex

Compound	No of peaks	Types of carbons		
		Peripheral δ(ppm)	Ring δ(ppm)	Others δ(ppm)
[L _B H ₂](CH ₃ COO) ₂ .3H ₂ O	11 (5+5+1)	16.11, 19.08, 24.23, 25.16	43.03, 45.51, 46.38, 46.81, 53.82	27.60 (Carbon of CH ₃ in CH ₃ COO ⁻ group), 173.90 (Carbon of COO ⁻ group)
[ZnL _B (CH ₃ COO)](ClO ₄)	20[(8+1)+10+1]	14.13, 14.97, 17.28, 18.46, 19.83, 24.23, 24.83, 27.17	40.12, 40.49, 44.97, 45.66, 45.86, 46.93, 47.29, 48.87, 53.53, 58.17	28.52 (Carbon of methyl in acetate), 130.60 (Carbon of COO ⁻ in CH ₃ COO ⁻)

Table 4. Molar conductivity data* for complexes.

Complexes	Conductance (ohm ⁻¹ cm ² mole ⁻¹) in different solvents				
	CHCl ₃	DMSO	H ₂ O	CH ₃ CN	DMF

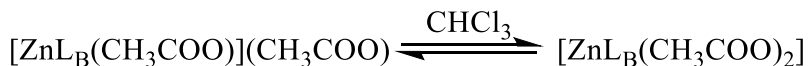
$[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})$	0	34	-	-	-
$[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$	-	-	227	245	-
$[\text{ZnL}_B(\text{NCS})](\text{NCS})$	-	87	280	-	124
$[\text{ZnL}_B(\text{NO}_2)](\text{ClO}_4)$	-	95	272	-	-
$[\text{ZnL}_B(\text{NO}_3)](\text{ClO}_4)$	-	92	260	-	-

* “-”, not soluble. *Data quoted are values after subtraction of conductance values of pure solvents.

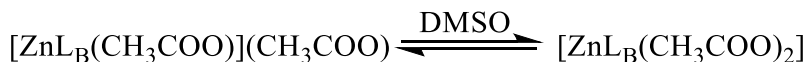
Zinc(II) complexes

$[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$ and $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})$

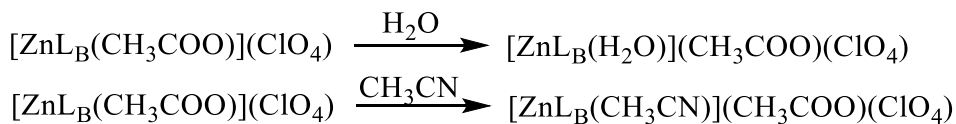
Interaction of $[\text{L}_B\text{H}_2](\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ with zinc(II) acetate produced white solid product, $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})$ which undergoes anion exchange reaction with $\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ to produce $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$. The infrared spectra of these complexes (Table 1) exhibit ν_{NH} bands at 3101-3227 cm^{-1} and other characteristic $\nu_{\text{C-H}}$, ν_{CH_3} , $\nu_{\text{C-C}}$ and $\nu_{\text{Ni-N}}$ bands at the expected region. The spectra further show bands at 1577-1599 cm^{-1} due to the presence of coordinated CH_3COO^- group. In addition the spectrum of $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})$ exhibit band at 1405 cm^{-1} due to ionic CH_3COO^- . Further the spectrum of $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$ further shows bands at 1129 cm^{-1} and 624 cm^{-1} which support the presence of ClO_4^- ion. Molar conductivity value (Table 4) of 0 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ of $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})$ in chloroform supports the nonelectrolytic nature of this complex i.e, chloroform forces the anion to take axial position in the coordination sphere.



But the conductance value of 34 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ of its DMSO solution corresponding almost to 1:1 electrolyte provide evidence that this complex may exist in a equilibrium between square pyramidal $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})$ and octahedral $[\text{ZnL}_B(\text{CH}_3\text{COO})_2]$.

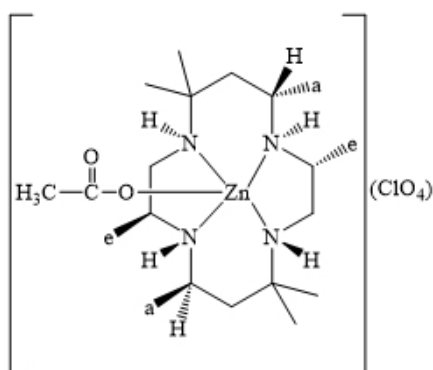
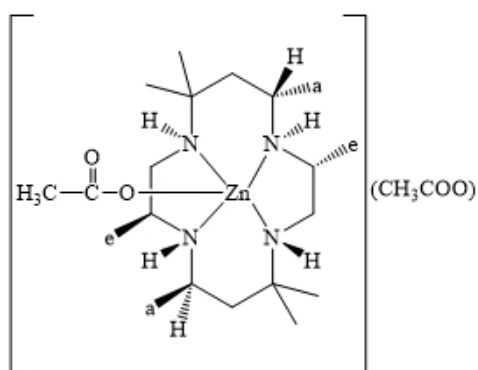


However molar conductivity value (Table 4) of 227 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ in H_2O and 245 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ in methylcyanide in case of $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$ corresponding to 1:2 electrolyte is probably due to the replacement of acetate ion by one H_2O molecule and one CH_3CN from the coordination sphere respectively. These replacement reactions can be expressed by the following expressions.



The $^1\text{H-NMR}$ spectrum of $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$ (Table 2) is not well resolved. However in the region of 1.07-1.32 ppm, four singlets and four

doublets each corresponding to three protons are observed for eight peripheral methyl groups. The upfield two singlets at 1.12 ppm and 1.14 ppm can be assigned to two equatorial components and the downfield two singlets at 1.23 ppm and 1.32 ppm for axial components of dimethyl groups. Similarly two upfield doublets at 1.07 ppm and 1.13 ppm can be assigned for two equatorial methyls on chiral carbons and the two downfield doublets at 1.20 ppm and 1.25 ppm to two axial methyl protons on chiral carbons. The spectrum further exhibits one more singlet at 1.50 ppm corresponding to three protons, which can be assigned to three protons of CH_3COO^- group, Thus a diaxial-diequatorial arrangement can be assigned for this complex. However separate signal for each peripheral methyl protons demonstrates the high distortion in this complex. This distortion may be due to presence of one acetate group in one axial position on a square pyramidal structure. The other multiplets at downfield can be assigned for NH, CH_2 and CH protons. The ^{13}C -NMR spectrum of $[\text{ZnL}_\text{B}(\text{CH}_3\text{COO})](\text{ClO}_4)$ (Table 3) displays twenty peaks for twenty carbons. The first eight peaks out of nine peaks in the region of 14-29 ppm can be assigned for eight peripheral methyl carbons and the 9th peak of that region for one CH_3 carbon of CH_3COO^- group. The next ten peaks in the region of 40-59 ppm may be assigned for ten ring carbons. However the most downfield peak at 130.60 ppm can be assigned for one carbon of COO portion of CH_3COO^- group. Appearance of twenty peaks for twenty carbons in this complex gives evidence that all carbons are nonequivalent. The ^1H -NMR of this complex also reveals non symmetry in the molecule. On the basis of above discussion square pyramidal structures 1 & 2 can be assigned for $[\text{ZnL}_\text{B}(\text{CH}_3\text{COO})](\text{ClO}_4)$ and $[\text{ZnL}_\text{B}(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})$. The structure of $[\text{ZnL}_\text{B}(\text{CH}_3\text{COO})](\text{ClO}_4)$ (Figure 2) has also been confirmed by X-ray analysis as our earlier report (Roy, et. al., 2011).

Structure 1. $[\text{ZnL}_\text{B}(\text{CH}_3\text{COO})](\text{ClO}_4)$ Structure 2. $[\text{ZnL}_\text{B}(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})$

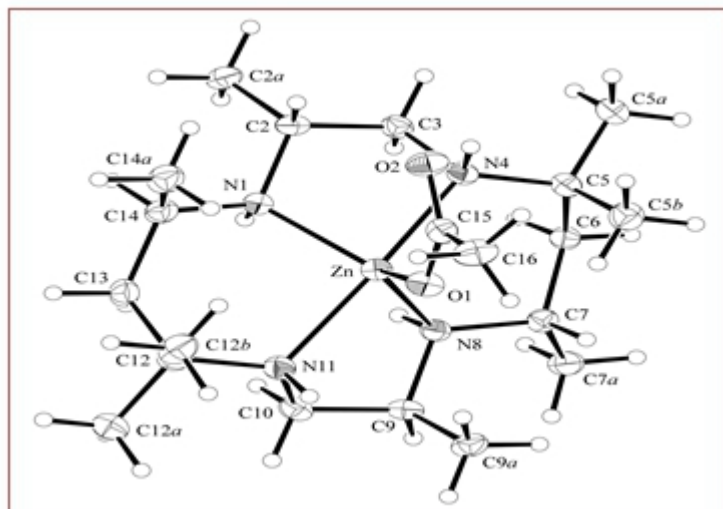
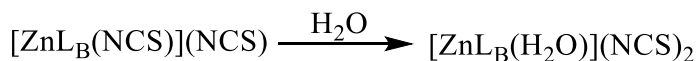


Figure 2. Molecular structure of $[\text{ZnL}_B(\text{CH}_3\text{COO})]^+$

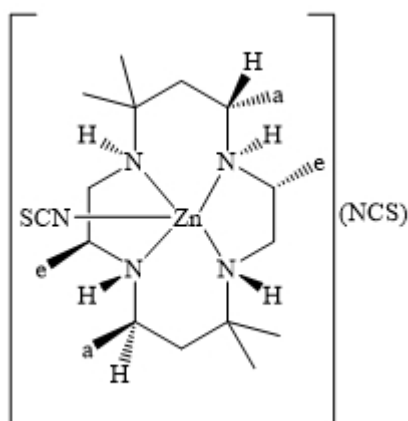
Axial ligand substitution products of $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$ $[\text{ZnL}_B(\text{NCS})](\text{NCS})$

The interaction of $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$ with KSCN in the ratio of 1:2 yielded white substituted solid product, $[\text{ZnL}_B(\text{NCS})](\text{NCS})$. The infrared spectrum (Table 1) of the complex $[\text{ZnL}_B(\text{NCS})](\text{NCS})$ exhibits ν_{NH} band at around 3136 cm^{-1} and other characteristic $\nu_{\text{C-H}}$, ν_{CH_3} and $\nu_{\text{C-C}}$ bands at the expected region. Absence of ν_{COO} and ν_{ClO_4} stretching bands in this complex, but presence of ν_{CN} , ν_{CS} and δ_{NCS} bands at 2050 cm^{-1} , 481 cm^{-1} and 888 cm^{-1} respectively demonstrates that CH_3COO^- and ClO_4^- ions from $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$ are substituted completely by NCS^- groups. An additional band at 2040 cm^{-1} can be accounted for ionic SCN^- . The positions of bands indicate it to be of N-bonded thiocyanate complex (Alam et. al., 2018) i.e., an isothiocyanato complex. The molar conductivity values of $87\text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ (Table 4) in DMSO and $124\text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ in DMF of this complex correspond to 1:1 electrolyte. This observation can be accounted for square pyramidal structure of the complex. On the other hand, molar conductivity value of $280\text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ of this complex in aqueous solution corresponds to 1:2 electrolytes (Table 4), i.e., the NCS^- ion comes out of the coordination sphere in water to form aqua complex.



The $^1\text{H-NMR}$ spectrum (Table 2) of this complex reveals two singlets at 1.20 ppm and 1.24 ppm each corresponding to six protons. These singlets can be assigned to a pair of equatorial methyls and axial methyls of gem-dimethyl groups respectively. An overlapped complex pattern is also observed in the region of 1.01-1.08 ppm which can be resolved into three doublets at

1.01 ppm, 1.04 ppm and 1.08 ppm. The upfield two doublets each corresponding to three protons can be attributed to two equatorial methyls on two chiral carbons and the downfield doublet at 1.08 ppm to a pair of axial methyl proton on other two chiral carbons. This assignment requires C2, C9 and C7, C14 to be pairwise equivalent. Thus a diaxial-diequatorial arrangement has been assigned for this complex as like as parent complex $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$ as explained earlier. Since two doublets are observed for two equatorial methyls on two chiral carbons, so distortion is expected for this complex too. However since four singlets for four gem-methyls and four doublets for four methyls on two chiral carbons are observed for parent $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$ (as discussed earlier), so this substituted structure complex is more symmetrical than the parent one (Structure 2). On the basis of above discussion the following structure 3 can be assigned for the complex $[\text{ZnL}_B(\text{NCS})](\text{NCS})$.

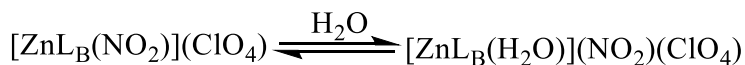


Structure 3. $[\text{ZnL}_B(\text{NCS})](\text{NCS})$

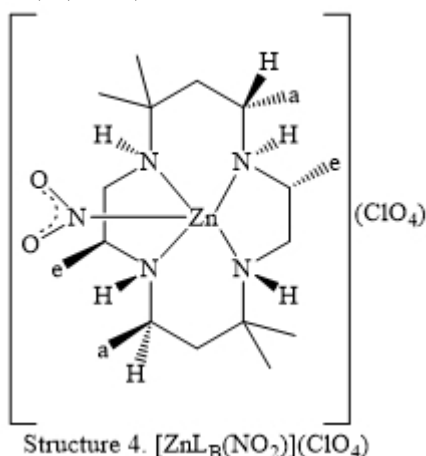
$[\text{ZnL}_B(\text{NO}_2)](\text{ClO}_4)$

Reaction of $[\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$ with NaNO_2 in methanolic solution resulted to a substituted white mass, $[\text{ZnL}_B(\text{NO}_2)](\text{ClO}_4)$. The infrared spectrum (Table 1) of this complex exhibits ν_{NH} , $\nu_{\text{C-H}}$, ν_{CH_3} , $\nu_{\text{C-C}}$ and $\nu_{\text{Zn-N}}$ stretching bands in the expected region. Moreover the complex exhibits the $\nu_{\text{asym}}(\text{NO}_2)$ and $\nu_{\text{sym}}(\text{NO}_2)$ bands at 1410 cm^{-1} and 1295 cm^{-1} respectively. Appearance of a band at 835 cm^{-1} can be attributed to δ_{NO_2} frequency. Presence of $\nu_{\text{Zn-N}}$ band at 430 cm^{-1} and other bands in the proper region strongly support the complex to be N-bonded nitro complex. Though NO_2^- group can also behave as bidentate ligand, it is difficult in this case due to steric effect of the ligand. The spectrum further shows bands at 1119 cm^{-1} and 625 cm^{-1} due to perchlorate group. No splitting around 1100 cm^{-1} supports that ClO_4^- ion is out of coordination sphere. The molar conductivity (Table 4) value of $95 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ in DMSO solution of this complex corresponding to 1:1 electrolyte

supports the square pyramidal structure of the formula assigned for this complex. However molar conductivity value $272 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ of aqueous solution of this complex corresponding to 1:2 electrolyte demonstrates that H_2O molecule forces the anion to come out of the coordination sphere to form aqua complex. This phenomenon can be expressed by the following reaction.

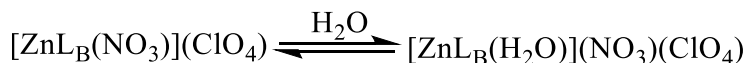


On the basis of above discussion the following structure 4 can be assigned for the complex, $[\text{ZnL}_B(\text{NO}_2)](\text{ClO}_4)$.

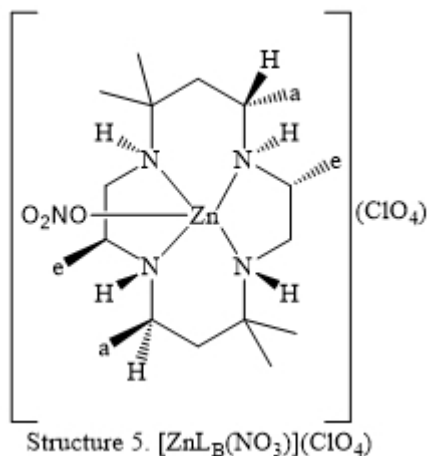


$[\text{ZnL}_B(\text{NO}_3)](\text{ClO}_4)$

$\text{ZnL}_B(\text{CH}_3\text{COO})](\text{ClO}_4)$ underwent axial substitution reaction with KNO_3 in the ratio of 1:2 to produce white product $[\text{ZnL}_B(\text{NO}_3)](\text{ClO}_4)$ in methanolic solution. The infrared spectrum (Table 1) of this complex exhibits characteristic ν_{NH} , $\nu_{\text{C-H}}$, ν_{CH_3} , $\nu_{\text{C-C}}$ and $\nu_{\text{Zn-N}}$ bands in the expected region. The spectrum further displays bands at 1138 cm^{-1} and 625 cm^{-1} . No splitting of the band around 1100 cm^{-1} indicates that ClO_4^- is out of coordination sphere. However appearance of a band at 1310 cm^{-1} and 1430 cm^{-1} can be attributed to coordinate NO_3^- group. The separation of these bands by 120 cm^{-1} is accounted for unidentate mode of coordination (Roy, et. al, 2006). The molar conductivity (Table 4) value of $92 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ in DMSO solution of this complex corresponds to 1:1 electrolyte. This phenomenon can be accounted for square pyramidal structure of the complex. On the other hand, the molar conductivity value $260 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$ of aqueous solution of this complex corresponding to 1:2 electrolyte demonstrates that H_2O molecules forces the anion to come out of the coordination sphere to form aqua complex. The phenomenon can be expressed by the following reaction.



On the basis of above discussion the following structure 5 can be assigned for the complex $[\text{ZnL}_\text{B}(\text{NO}_3)](\text{ClO}_4)$.



Antifungal activities

The results of percent inhibition of mycellial growth of all test synthesized compounds in mm have been shown in Table 5. The overall results indicated that *Alternaria alternata* toward $[\text{ZnL}_\text{B}(\text{CH}_3\text{COO})](\text{ClO}_4)$ and $[\text{ZnL}_\text{B}(\text{NO}_3)](\text{ClO}_4)$, *Fusarium equiseti* toward $[\text{L}_\text{B}\text{H}_2](\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and *Curvularia lunata* toward $[\text{ZnL}_\text{B}(\text{CH}_3\text{COO})](\text{ClO}_4)$ and $[\text{ZnL}_\text{B}(\text{NCS})](\text{NCS})$ are more sensitive than those of other test organism. However $[\text{ZnL}_\text{B}(\text{NCS})](\text{NCS})$ against *Curvularia lunata* and $[\text{L}_\text{B}\text{H}_2](\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ against *Fusarium equiseti* show high inhibition compared to standard antibiotic Nystatin. All the compounds were found to be ineffective toward *Colletotrichum corchori*. It is quite interesting to observe that $[\text{ZnL}_\text{B}(\text{CH}_3\text{COO})](\text{ClO}_4)$ showed stimulation rather than inhibition against the *Fusarium equiseti*.

Table 5. In vitro antifungal activities of ligand salt and complexes

Ligand salt and its zinc(II) complexes	Percent (%) inhibition of mycellial growth				
	<i>M. phaseolina</i>	<i>C. lunata</i>	<i>F. equiseti</i>	<i>C. corchori</i>	<i>A. alternata</i>
$[\text{L}_\text{B}\text{H}_2](\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$	9.09	36.36	49.10	0	7.69
$[\text{ZnL}_\text{B}(\text{CH}_3\text{COO})](\text{CH}_3\text{COO})$	27.27	9.09	10.94	0	23.07
$[\text{ZnL}_\text{B}(\text{CH}_3\text{COO})](\text{ClO}_4)$	45.45	54.54	+27.22	0	53.84
$[\text{ZnL}_\text{B}(\text{NCS})](\text{NCS})$	18.18	70.90	23.66	0	23.07
$[\text{ZnL}_\text{B}(\text{NO}_2)](\text{ClO}_4)$	10.15	20.22	21.25	0	18.76
$[\text{ZnL}_\text{B}(\text{NO}_3)](\text{ClO}_4)$	9.09	18.18	23.66	0	53.84
** Nystatin (100 µg/mL)	76.00	70.00	45.00	41.00	51.00

“***”: Standard antifungal; “0”: No inhibition; “+”: Stimulation

Antibacterial activities

Except for a few cases, (Roy, et al., 2006; 2007; 2011; Alam, et. al., 2018) anti-bacterial activity of macrocycles and their complexes have not been studied extensively. The results of antibacterial activity studies of the compounds against gram-positive and gram-negative bacteria have been shown in Table 6 and Table 7 respectively. From these Tables it is noted that, except *B. Cereus*, *B. Subtilis*, *S. typhi* and *S. Paratyphi*, the ligand salt was ineffective against all other gram positive and gram negative bacteria. However most the complexes were effective against any one or more bacteria. From Tables 6 & 7 it is observed that, $[ZnL_B(NCS)](NCS)$, $[ZnL_B(NO_3)](ClO_4)$ and $[ZnL_B(NO_3)](ClO_4)$ are comparatively more effective than other complexes. A note worthy observation from the experimental data presented in Table 6 and Table 7 is that, except $[ZnL_B(NO_2)](ClO_4)$. all the complexes and ligand salt are not effective against *Shigella dysenteriae*. Again except $[ZnL_B(NCS)](NCS)$ and $[ZnL_B(NO_3)](ClO_4)$ all compounds are ineffective against *S. aureus*.

The results of the antimicrobial screening studies of the synthesized compounds presented herein showed that the ligand salt and its complexes are very effective toward phytopathogens than those of bacteria. By the chelation theory (Salahi, et. al., 2015), the increased activity of the complexes can be explained. The disturbance of the respiration process of the cell and blockage the synthesis of protein, may restrict further growth of the organism (Dhrmaraj, et. al., 2001) which can also be responsible for the antibacterial activity.

Table 6. In vitro antibacterial activities of ligand salt and complexes against gram positive bacteria

Ligand salt and its zinc(II) complexes	Zone of inhibition in mm							
	<i>B. cereus</i>		<i>B. subtilis</i>		<i>S. aureus</i>		<i>B. magaterium</i>	
	24 hrs	48 hrs	24 hrs	48 hrs	24 hrs	48 hrs	24 hrs	48 hrs
$[L_BH_2](CH_3COO)_2 \cdot 3H_2O$	0	7	5	5	0	0	0	0
$[ZnL_B(CH_3COO)](CH_3COO)$	0	10	0	0	0	0	0	0
$[ZnL_B(CH_3COO)](ClO_4)$	0	6	5	5	0	0	0	5
$[ZnL_B(NCS)](NCS)$	0	5	5	5	8	8	0	0
$[ZnL_B(NO_2)](ClO_4)$	0	5	6	6	7	7	0	0
$[ZnL_B(NO_3)](ClO_4)$	0	8	5	5	0	0	0	5
Ampicillin*	16	-	25	-	24	-	19	-

*Standard antibiotic; "0": No inhibition; "-": Not done

Table 7. In vitro antibacterial activities of ligand salt and complexes against gram negative bacteria

Ligand salt and its zinc(II) complexes	Zone of inhibition in mm												
	<i>E. coli</i>		<i>V. cholerae</i>		<i>S. typhi</i>		<i>S. paratyphi</i>		<i>P. species</i>		<i>S. dysentery</i>		
	24 hrs	48 hrs	24 hrs	48 hrs	24 hrs	48 hrs	24 hrs	48 hrs	24 hrs	48 hrs	24 hrs	48 hrs	
[L _B H ₂](CH ₃ COO) ₂ .3H ₂ O	0	5	0	0	0	5	5	5	5	0	0	0	0
[ZnL _B (CH ₃ COO)](CH ₃ COO)	0	8	10	10	0	5	0	0	0	10	0	0	0
[ZnL _B (CH ₃ COO)](ClO ₄)	8	15	0	0	0	0	0	5	0	0	0	0	0
[ZnL _B (NCS)](NCS)	6	15	0	0	0	0	5	5	0	10	0	0	0
[ZnL _B (NO ₂)](ClO ₄)	9	12	0	5	0	0	8	10	11	12	8	8	8
[ZnL _B (NO ₃)](ClO ₄)	6	15	0	0	0	0	5	5	0	10	0	0	0
Ampicillin*	30	-	32	-	25	-	28	-	35	-	35	-	-

*Standard antibiotic; “0”: No inhibition; “-”: Not done

Conclusion

This study reveals that attempt to prepare N-pendent derivative of isomeric ligand L_B (an isomer of Me₈[14]ane) by the alkylation reaction with vinyl acetate was not successful, rather a ligand salt [H₂L_B](CH₃COO)₂.3H₂O resulted. This ligand salt underwent faciale complexation with zinc(II) acetate dehydrate to form a square pyramidal complex [ZnL_B(CH₃COO)](CH₃COO). This acetatozinc(II) acetate complex underwent anion exchange reaction with NaClO₄.6H₂O to produce [ZnL_B(CH₃COO)](ClO₄) which in turn underwent simultaneous axial substitution and anion exchange reactions with KSCN to form [ZnL_B(NCS)](SCN). However the same complex underwent only axial substitution reactions with NaNO₂ and KNO₃ to result mononitro- and mononitratozinc(II) complexes, [ZnL_B(NO₂)](ClO₄) and [ZnL_B(NO₃)](ClO₄) respectively. It is interesting to note that almost all complexes except [ZnL_B(CH₃COO)](CH₃COO) were found to have fascination for water molecules to form aqua complexes. It is interesting to note that the concerned ligand salt and its complexes are highly effective toward phytopathogens than those of bacteria. A few compounds against some pathogens show very high inhibition even more than standard antibiotic Nystatin.

Acknowledgement

We are grateful to the Ministry of Science and Technology, People’s Republic of Bangladesh for awarding a research grand to Professor Tapashi Ghosh Roy and Professor Debashis Palit, Department of Chemistry, University of Chittagong, Bangladesh.

References:

1. Alam, S., Rabi, S., Rahman, M., Baidya, A., Debi, M. & Roy, T. G. (2018). Synthesis, characterization and antimicrobial studies of

- cadmium(II) complexes with tetraazamacrocyclic (L_B) and its cyanoethyl N-pendent derivative (L_{BX}). *J. Chem. Sci.*, 130:35.
2. Bembi, R., Sondhi, S. M., Singh, A. K., Jhanjii, A. K., Roy, T. G., Lown, J. W. & Ball, R. G. (1989). Polyazamacrocyclic V. Structure of isomeric 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecanes. *Bull. Chem. Soc. Jpn.*, 62, 3701.
 3. Curtis, N. F., Swann, S. A., Waters, T. N. & Maxwell, I. E. (1969). Isomerism of some octamethyl-1,5,8,12-tetraazacyclotetradecadiene complexes of nickel(II) and copper(II). *J. Am. Chem. Soc.*, 91, 4588.
 4. Dharmaraj, N., Viswanathamurthi & Nataranjan, K. (2001). Ruthenium(II) complexes containing bidentate Schiff bases and their antifungal activity. *Trans. Met. Chem.*, 26, 105.
 5. Gull, P., Dar, O. A., Malik, M. A. & Hashmi, A. A. (2016). Design, synthesis, characterization and antimicrobial/antioxidant activities of 1, 4-dicarbonyl-phenyl dihydrazide based macrocyclic ligand and its Cu(II), Co(II) and Ni(II) complexes. *Microb. Pathog.*, 237.
 6. Hazari, S. K. S., Roy, T. G., Barua, K. K. & Tiekink, E. R. T. (2008). Supramolecular association in the structure of 2,9-C-meso-2,5,5,7,9,12,12,14-octamethyl-1,8-diaza-4,11-diazoniacyclotetradecane as its bis(nitrate) and bis(acetate) trihydrate. *J. Chem. Cryst.*, 38, 1.
 7. Hermann, P., Kotek J., Kubíček V. & Lukeš I. (2008). Gadolinium(III) complexes as MRI contrast agents: ligand design and properties of the complexes. *Dalton Trans.*, 23, 3027.
 8. Hitoshi, H. (2002). Present Status of Industrial Application of Cyclodextrins in Japan, *J. Incl. Phenom. Macrocycl. Chem.*, 44(1–4), 57.
 9. Kolthoff, I. M. (1979). Application of macrocyclic compounds in chemical analysis. *Anal. Chem.*, 51(5), 1.
 10. Nath, B. C., Rabi, S., Hazari, S. K. S., Roy, T. G., Olbrich, F. & Rehder, D. (2018). A new macrocyclic ligand salt, 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane dihydrobromide dehydrate [H₂L_{Bc}]Br₂·2H₂O and some of its metal complexes-Synthesis, characterization and antimicrobial studies. *Inorg. Chim. Acta*, 479, 203.
 11. Nath, B. C., Suarez, S., Doctorovich, F., Roy, T. G. & Baggio, R. (2013). Two solvatomorphic forms of a copper complex formulated as Cu(L)(ClO₄)₂·2(H₂O)(I) and Cu(L)(ClO₄)₂(II), where L is 3,10-C-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane, C₁₈H₄₀N₄. *Acta Cryst.*, C69, 689.
 12. Rzuzek, S. G., Pilch, D. S., Liu, A., Liu, L., LaVoie, E. J. & Rice J E. (2010) Macrocyclic Pyridyl Polyoxazoles: Selective RNA and DNA

- G-Quadruplex Ligands as Antitumor Agents. *J. Med. Chem.*, 53(9), 3632.
13. Roy T. G., Hazari, S. K. S., Miah, H. A., Gupta, S. K. D., Roy, P. G., Behrens U. & Rehder, D. (2014). Synthesis and antimicrobial activities of copper(II) complexes of N(4),N(11)-dimethyl (L_{BZ} & L_{CZ}) and N(4)-monomethyl (L_{CZ1})-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane. Crystal and molecular structure of [CuL_{CZ1}](ClO₄)₂. *Inorg. Chim. Acta*, 415, 124.
 14. Roy, T. G., Hazari, S. K. S., Dey, B. K., Nath, B. C., Dutta, A., Olbrich, F. & Rehder, D. (2011). Syntheses, electrolytic behaviour and antifungal activities of Zn(II) complexes of isomers of 3,10-C-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane (L). Crystal and molecular structure of [ZnL_B(NO₃)]NO₃(L_B= a,e,a,e-L). *Inorg. Chim. Acta*, 371, 63.
 15. Roy, T. G., Hazari, S. K. S., Barua, K. K. & Tiekink, E. R. T. (2011). (Acetato-κO)(2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane-κ⁴N,N',N'',N''')zinc perchlorate. *Acta. Cryst.*, E67, m1659-m1660.
 16. Roy, T. G., Hazari, S. K. S., Dey, B. K., Meah, H. A., Rahman, M. S., Kim, D. I. & Park, Y. C. (2007). 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. *J. Coord. Chem.*, 40, 1567.
 17. Roy, T. G., Hazari, S. K. S., Dey, B. K., Nath, A., Kim, D. I. & Park, Y. C. (2007). Synthesis of some octahedral nickel(II) complexes of one isomer of isomeric Me₈[14]anes: X-ray structure of diisothiocyanato (3,10-C-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane, L_C) nickel(II), [NiL_C(NCS)₂]. *J. Incl. Phen. Mac. Chem.*, 58, 249.
 18. Roy, T. G., Hazari, S. K. S., Dey, B. K., Miah, H. A., Olbrich, F. & Rehder, D. (2007). Syntheses and antimicrobial activities of isomers of N(4), N(11)-dimethyl-3,10-C-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane and their nickel(II) complexes. *Inorg. Chem.*, 46, 5372.
 19. Roy, T. G., Hazari, S. K. S., Dey, B. K., Sutradhar, R., Dey, L., Anowar, N. and Tiekink, E. R. T. (2006). Axial ligand substitution in diastereoisomeric trans-[Co(Me₈[14]ane)Cl₂]⁺ complexes and their antifungal activities *J. Coord. Chem.*, 59(3) 351.
 20. Roy, T. G., Hazari, S. K. S., Dutta, S., Monsur, M. A. & Tiekink, E. R. T., (2006). Axial addition in diastereoisomeric [Cu(Me₈[14]ane)](ClO₄)₂ complexes: Anti-fungal and anti- bacterial activities. *J. Coord. Chem.*, 59(15), 1757.

21. Roy, T. G., Hazari, S. K. S., Dey, B. K., Sutradhar, R, Dey, L., Anowar, N. & Tiekink, E. R. T. (2006). Axial ligand substitution in diastereoisomeric trans-[Co(Me₈[14]ane)Cl₂]⁺Complexes and their antifungal activities *J. Coord. Chem.*, 59(3), 351.
22. Roy, T. G., Hazari, S. K. S., Dey, B. K, Meah, H. A., Bader, C. & Rehder, D. (2004). Copper(II) and nickel(II) complexes of N,N-bis(2-hydroxyethyl)-octamethyl-1,4,8,11-tetraaza-cyclotetradecane. *Eur. J. Inorg. Chem.*, 4115.
23. Roy, T. G. & Bembi, R. (2002). Mass spectral studies of isomeric 3,5,7,7,10,12,14,14-octamethyl-tetraazacyclotetradecane. *J. Bang. Chem. Soc.*, 15(1), 23.
24. Salehi, M. & Hasanzadeh, M. (2015). Characterization, crystal structures, electrochemical and antibacterial studies of four new binuclear cobalt(III) complexes derived from o-aminobenzyl alcohol. *Inorg. Chim. Acta*, 426, 6.
25. Shankarwar, S. G., Nagolkar, B. B., Shelke, V. A. & Chondhekar, T. K. (2015). Synthesis, spectral, thermal and antimicrobial studies of transition metal complexes of 14-membered tetraaza[N4] macrocyclic ligand. *Spectrochim. Acta A*, 145, 188.