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Research Article

Zinc(II) Complexes with One Isomer of Tetraazamacrocyclic Ligand and its N-Pendent Bis-cyanoethyl Derivative: Synthesis, Characterization and Antibacterial Studies

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Abstract

Isomeric ligand, tet-b was produced by the reduction of hexamethyl tetraazacyclotetradecadiene diperchlorate salt, Me_6[14] diene.$2HClO_4$ and N–pendent bis-cyanoethyl derivative tet-bx, of this isomeric ligand was obtained by refluxing tet-b with excess of acrylonitrile. Reactions of tet-b and tet-bx with zinc(II) perchlorate and zinc(II) chloride yielded octahedral diperchloratozinc(II) complex, $[Zn(tet\text{-}b)(ClO_4)_2]$ and square pyramidal monochloridozinc(II) chloride complex, [Zn(tet-bx)Cl]Cl respectively. The complex, $[Zn(tet\text{-}b)(ClO_4)_2]$ underwent partial axial substitution reactions with KNO_3 and $NaNO_2$ to yield square pyramidal complexes, mononitratozinc(II) perchlorate, $[Zn(tet\text{-}b)(NO_3)](ClO_4)$ and mononitrozinc(II) perchlorate, $[Zn(tet\text{-}b)(NO_2)](ClO_4)$ respectively. Moreover, the complex [Zn(tet-bx)Cl]Cl produced square pyramidal monoisothiocyanatozinc(II) thiocyanate [Zn(tet-bx)(NCS)](NCS) and octahedral diisothiocyanatozinc(II) $[Zn(tet\text{-}bx)(NCS)_2]$ complex by undergoing simultaneous axial substitution and anion exchange and axial addition and substitution with KSCN respectively. However, the same complex underwent axial substitution and anion exchange reactions with KNO_3, $NaNO_2$, KI and KBr to yield square pyramidal complexes, $[Zn(tet\text{-}bx)(NO_3)](NO_3)$, $[Zn(tet\text{-}bx)(NO_2)](NO_2)$, [Zn(tet-bx)I]I and [Zn(tet-bx)Br]Br respectively. The complexes have been characterized on the basis of analytical and spectroscopic data. The antibacterial activities of the ligands and their new zinc(II) complexes have been investigated against some selected bacteria.

Keywords: N-pendent derivative; Zinc(II) complexes; Characterization; Addition and substitution reactions; Antibacterial

Introduction

Macrocyclic ligands and their different metal complexes have taken a remarkable position in medicinal chemistry due to their potential activity as pharmacological agents [1-7]. Macrocycles are capable to change dynamically their conformation due to their increased number of H-bond donors and acceptors, often polar backbone and therefore can become more drug-like than expected based on their physicochemical and pharma-cokinetic properties [8]. Thus scientists are continuously reporting their different [1-8] findings on macrocyclic compounds. Different metal complexes with the isomeric ligand tet-b (isomer of Me_6[14]ane) have been reported in the literature [9-13]. Moreover copper(II), nickel(II) and cobalt(III) complexes of cyanoethyl derivative tet-bx of the isomeric ligand tet-b have also been reported [14-16] but zinc(II) complexes of the same have not been reported so far. So it is reasonable to prepare some new zinc(II) complexes of tet-bx and characterize them to establish their structures. In this connection, we have synthesized some zinc(II) complexes of tet-bx by the direct reactions with metal salts as well as by axial substitution and addition reactions. Moreover, though some zinc(II) complexes of the isomeric ligand tet-b by different reactions have been reported [11,12] by our research group but in this research, we successfully prepared some new zinc(II) complexes of tet-b with different geometry and synthetic procedure. Thus this research study contains

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an exhaustive studies of some zinc(II) complexes with one isomer of tetraazamacrocyclic ligand tet-b and its N- pendent bis-cyanoethyl derivative tet-bx.

Syntheses

Ligands

The isomeric ligand, tet-b and its N-pendent cyanoethyl derivative tet-bx [15] have been synthesized and characterized as per literature [15,17].

Zinc(II) complexes of tet-b and tet-bx

Zinc(II) complexes by the direct reactions of the ligands with zinc(II) salts

[Zn(tet-b)(ClO_4)$_2$]

Isomeric ligand tet-b (0.298 g, 1.0 mmol) and zinc(II) perchlorate hexahydrate (0.372 g, 1.0 mmol) were dissolved separately in 20 mL of hot methanol and mixed while hot. The solution was concentrated to 10 mL by heating on a water bath, and then allowed to cool while the white product, [Zn(tet-b)(ClO_4)$_2$] crystallized out which was filtered off, washed with methanol followed by diethylether, and dried in a desiccator over silica gel.

[Zn(tet-b)(ClO_4)$_2$]

($C_{16}H_{36}N_4Cl_2O_8Zn$): Color: White. Anal. Calcd. (%): C, 35.02; H, 6.61; N, 10.21. Found (%): C, 35.00; H, 6.67; N, 10.25. IR (KBr disc, cm^{-1}): ν_{N-H}, 3248m; ν_{C-H}, 2974m; ν_{CH3}, 1368m; ν_{C-C}, 1166w; ν_{N-Zn}, 565w; ν_{ClO4}, 624s, 1026vs. Conductance ($ohm^{-1}cm^2mole^{-1}$): in DMSO 65; in Chloroform 0; in H_2O 160.

[Zn(tet-bx)Cl]Cl

Isomeric ligand tet-bx (0.390 g, 1.0 mmol) and zinc(II) chloride (0.136 g, 1.0 mmol) were dissolved separately in 20 mL of hot methanol and mixed while hot. The solution was heated on a steam bath till the volume of the solution reduced and an oily product was formed. The oily product was allowed to cool overnight while this product tuned into sticky product, this sticky product was collected by decanting of the mother liquor which was titurated with cold methanol while white product, [Zn(tet-bx)Cl]Cl crystallized out which was filtered off, washed with methanol followed by diethylether and dried in a vacuum desiccator over silica gel.

[Zn(tet-bx)Cl]Cl

($C_{22}H_{42}N_6Cl_2Zn$): Color: White. Melting point: Above 250^0C. Anal. Calcd. (%): C, 50.15; H, 8.03; N, 15.95. Found (%): C, 50.10; H, 8.08; N, 15.94. IR (KBr disc, cm^{-1}): ν_{N-H}, 3264s; $\nu_{C\equiv N,}$ 2248vs; ν_{C-H}, 2968s; ν_{CH3}, 1374w; ν_{C-C}, 1172s; ν_{N-Zn}, 599w. Conductance ($ohm^{-1}cm^2mole^{-1}$): in DMSO 61; in H_2O 265. ^{1}H NMR (δ, ppm): For Geminal dimethyl $(CH_3)_2$, δ = 1.039 (s, equatorial, 6 H), 1.213 (os, axial, 6 H); For methyl on chiral carbon CH_3, δ = 0.883 (d, equatorial, 3 H), 1.213 (od, axial, 3 H); For CH_2, CH and NH, δ = 1.339 (m), 1.881 (m), 2.864 (m).

Partial axial substitution products of [Zn(tet-b)(ClO_4)$_2$]

[Zn(tet-b)(NO_3)](ClO_4) and [Zn(tet-b)(NO_2)](ClO_4)

KNO_3 and $NaNO_2$ were separately dissolved in hot methanol (20 mL) by their proper weights(2.0 mmol) and then added separately to a hot methanolic suspension (20 mL) of the complex, [Zn(tet-b)(ClO_4)$_2$] in the molar ratio of 2:1. The solutions were reduced to 5 mL by heating on a water bath, and then allowed to cool while the white product, [Zn(tet-b)(NO_3)](ClO_4) and [Zn(tet-b)(NO_2)](ClO_4) crystallized out which were filtered off, washed with little water, methanol followed by diethylether and dried in a desiccator over silica gel.

[Zn(tet-b)(NO_3)](ClO_4) ($C_{16}H_{36}N_5O_7ClZn$)

Color: White. Anal. Calcd. (%): C, 37.58; H, 7.10; N, 13.70. Found (%): C, 37.57; H, 7.08; N, 13.68. IR (KBr disc, cm^{-1}): ν_{N-H}, 3257m; ν_{C-H}, 2970m; ν_{CH3}, 1373w; ν_{C-C}, 1181w; ν_{N-Zn}, 565w; ν_{ClO4}, 626s, 1041w; $\nu_{NO3,}$ 1435s, 1324s. Conductance ($ohm^{-1}cm^2mole^{-1}$): in DMSO 107; in H_2O 214. ^{1}H NMR (δ, ppm): For geminal dimethyl $(CH_3)_2$, δ = 1.308 (s, equatorial, 6 H), 1.230 (s, axial, 6 H); For methyl on chiral carbon CH_3, δ = 1.130 (d, equatorial, 3 H), 1.162 (d, equatorial, 3 H); For CH_2, CH and NH, δ = 1.611 (m), 2.239 (m), 2.557 (m), 3.092(m).

[Zn(tet-b)(NO_2)](ClO_4) ($C_{16}H_{36}N_5O_6ClZn$)

Color: White. Anal. Calcd. (%): C, 38.80; H, 7.33; N, 14.14. Found (%): C, 38.76; H, 7.38; N, 14.09. IR (KBr disc, cm^{-1}): ν_{N-H}, 3268s; ν_{C-H}, 2972s; ν_{CH3}, 1367m; ν_{C-C}, 1168w; ν_{N-Zn}, 565w; ν_{ClO4}, 624s, 1050w; $\nu_{NO2(asym)}$, 1463s; $\nu_{NO2(sym)}$,1341m. Conductance ($ohm^{-1}cm^2mole^{-1}$): in DMSO 60; in Chloroform 0; in H_2O 209.

Axial addition and substitution and anion exchange reaction products of [Zn(tet-bx)Cl]Cl

[Zn(tet-bx)(NCS)](SCN) and [Zn(tet-bx)(NCS)$_2$]

[Zn(tet-bx)Cl]Cl (0.52 g, 1.0 mmol) and KSCN (0.20 g, 2.0 mmol) were dissolved separately in 20 mL hot absolute methanol and mixed while hot. The colorless solution thus obtained was heated on a steam bath and completely dried. The dry product was treated with chloroform and filtered. The residue solid complex, [Zn(tet-bx)(NCS)](NCS) was collected after washing with water, methanol followed by diethylether and chloroform solution was evaporated to dryness to give solid [Zn(tet-bx)(NCS)$_2$]. The products were stored in a desiccator over silica gel.

[Zn(tet-bx)(NCS)](SCN)

($C_{24}H_{42}N_8S_2Zn$): Color: White. Anal. Calcd. (%): C, 50.38; H, 7.40; N, 19.58. Found (%): C, 50.35; H, 7.45; N, 19.51. IR (KBr disc, cm^{-1}): $\nu_{N\text{-}H}$, 3176s; $\nu_{C\equiv N}$, 2252w; $\nu_{C\text{-}H}$, 2972s; ν_{CH3}, 1375m; $\nu_{C\text{-}C}$, 1168s; $\nu_{N\text{-}Zn}$, 597w; 2067vs(ν_{CN}), 819m(ν_{CS}), 480s (δ_{NCS}); Conductance (ohm^{-1}cm^{2}mole^{-1}): in DMSO 95. ^{1}H NMR (δ, ppm): For geminal dimethyl $(CH_3)_2$, δ = 1.045 (s, equatorial, 6 H), 1.194 (os, axial, 6 H); For methyl on chiral carbon CH_3, δ = 0.891 (d, equatorial, 3 H), 1.194 (od, axial, 3 H); For CH_2, CH and NH, δ = 1.853 (m), 2.032 (m), 2.261 (m).

[Zn(tet-bx)(NCS)$_2$]

($C_{24}H_{42}N_8S_2Zn$): Color: White. Anal. Calcd. (%): C, 50.38; H, 7.40; N, 19.58. Found (%): C, 50.32; H, 7.48; N, 19.56. IR (KBr disc, cm^{-1}): $\nu_{N\text{-}H}$, 3178w; $\nu_{C\equiv N}$, 2252w; $\nu_{C\text{-}H}$, 2974m; ν_{CH3}, 1375w; $\nu_{C\text{-}C}$, 1168s; $\nu_{N\text{-}Zn}$, 597w; 2067vs(ν_{CN}), 821m(ν_{CS}), 480s (δ_{NCS}); Conductance (ohm^{-1}cm^{2}mole^{-1}): in DMSO 92; in H_2O 258, in chloroform 0.

[Zn(tet-bx)(NO$_3$)](NO$_3$), [Zn(tet-bx)(NO$_2$)](NO$_2$), [Zn(tet-bx)Br]Br and [Zn(tet-bx)I]I

The complexes were prepared by following the above mentioned procedure adopted for preparation of zinc(II) isothiocyanato complexes by using KNO_3, $NaNO_2$, KI and KBr instead of KSCN in the proper ratio.

[Zn(tet-bx)(NO$_3$)](NO$_3$)

($C_{22}H_{42}N_8O_6Zn$): Color: White. Anal. Calcd. (%): C, 45.56; H, 7.30; N, 19.32. Found (%): C, 45.52; H, 7.36; N, 19.32. IR (KBr disc, cm^{-1}): $\nu_{N\text{-}H}$, 3263m; $\nu_{C\equiv N}$, 2250w; $\nu_{C\text{-}H}$, 2970s; ν_{CH3}, 1376w; $\nu_{C\text{-}C}$, 1173m; $\nu_{N\text{-}Zn}$, 607w; 1451s(ν_{NO3}), 1325s(ν_{NO3}); Conductance (ohm^{-1}cm^{2}mole^{-1}): in DMSO 104; in H_2O 218.

[Zn(tet-bx)(NO$_2$)](NO$_2$)

($C_{22}H_{42}N_8O_4Zn$): Color: White. Anal. Calcd. (%): C, 48.22; H, 7.72; N, 20.45. Found (%): C, 48.18; H, 7.76; N, 20.47. IR (KBr disc, cm^{-1}): $\nu_{N\text{-}H}$, 3264W; $\nu_{C\equiv N}$, 2252w; $\nu_{C\text{-}H}$, 2973s; ν_{CH3}, 1375w; $\nu_{C\text{-}C}$, 1172m; $\nu_{N\text{-}Zn}$, 566w; 1462s(ν_{asym}), 1335w(ν_{sym}); Conductance (ohm^{-1}cm^{2}mole^{-1}): in DMSO 66; in H_2O 238.

[Zn(tet-bx)I]I

($C_{22}H_{42}N_6I_2Zn$): Color: White. Anal. Calcd. (%): C, 37.13; H, 5.96; N, 11.84. Found (%): C, 37.22; H, 6.01; N, 11.79. IR (KBr disc, cm^{-1}): $\nu_{N\text{-}H}$, 3266s; $\nu_{C\equiv N}$, 2250w; $\nu_{C\text{-}H}$, 2965m; ν_{CH3}, 1375m; $\nu_{C\text{-}C}$, 1170s; $\nu_{N\text{-}Zn}$, 597w; $\nu_{I\text{-}Zn}$(IR spectrum has not been carried out below 400 cm^{-1}, the band for I-Zn could not be detected) Conductance (ohm^{-1}cm^{2}mole^{-1}): in DMSO 95; in H_2O 244.

[Zn(tet-bx)Br]Br

($C_{22}H_{42}N_6Br_2Zn$): Color: White. Anal. Calcd. (%): C, 42.91; H, 6.87; N, 13.65. Found (%): C, 42.87; H, 6.90; N, 13.61. IR (KBr disc, cm^{-1}): $\nu_{N\text{-}H}$, 3264s; $\nu_{C\equiv N}$, 2254w; $\nu_{C\text{-}H}$, 2966w; ν_{CH3}, 1375m; $\nu_{C\text{-}C}$, 1172s; $\nu_{N\text{-}Zn}$, 599m; $\nu_{Br\text{-}Zn}$(IR spectrum has not been carried out below 400 cm^{-1}, the band for Zn-Br could not be detected) Conductance (ohm^{-1}cm^{2}mole^{-1}): in DMSO 60; in H_2O 248.

Physical measurement

Analytical reagent grade (Sigma Aldrich, USA) chemicals were used for the preparation of the complexes. Microanalysis have been carried out on C, H, N, and S analyzer at the Department of Chemistry, Friedrich Schiller University, Jena, Germany. The infrared spectra were taken as KBr disc in the range 4000-400 cm^{-1} on a Shimadzu IR 20 spectrophotometer at the Department of Chemistry, University of Chittagong, Chattogram, Bangladesh. Conductance measurements were done using HANNA instrument with HI 8820N conductivity cell. ^{1}H-NMR spectra were recorded in DMSO with a 400 MHz Bruker DPX-400 spectrometer using TMS as internal standard at the WMSRC Jahangirnagar University, Savar, Dhaka, Bangladesh.

Antibacterial activities

The antibacterial activity of these compounds were investigated against selected gram-positive and gram-negative bacteria, by using standard method described in the literature [14-16].

Results and Discussion

Ligands

The isomeric ligand (tet-b) and its N-pendent derivative (tet-bx) were prepared and characterized as per literature [15,17].

Zinc(II) complexes of tet-b

[Zn(tet-b)(ClO$_4$)$_2$]

Interaction of the ligand, tet-b with zinc(II) perchlorate hexahydrate in methanol produced white product., [Zn(tet-b)(ClO$_4$)$_2$].

The IR spectrum of this complex exhibits intense C-H band at 2974 cm^{-1}, C-C at 1166 cm^{-1} and Zn-N at 565 cm^{-1}, N-H band at 3248 cm^{-1}, CH$_3$ at 1368 cm^{-1}. The other bands appearing at 624 cm^{-1} and 1026 cm^{-1} are attributed to perchlorate whereas ν_{N-H} stretching frequencies appear at 3248 cm^{-1}. The splitting at 1026 cm^{-1} can be accounted for the coordination of ClO_4^-. The molar conductivity value of 0 ohm^{-1}cm^{2}mole^{-1} for this complex in CHCl$_3$ indicates that the complex is nonelectrolyte as expected for formula assigned. However the value of 65 ohm^{-1}cm^{2}mole^{-1} in DMSO solution demonstrates that the complex is 1:1 electrolyte in this solvent [18], which can be attributed to the conversion of [Zn(tet-b)(ClO$_4$)$_2$] to [Zn(tet-b)(ClO$_4$)](ClO$_4$). Again the conductance value is 160 ohm^{-1}cm^{2}mole^{-1} for this complex in H$_2$O reveals that the complex is 1:2 electrolyte as shown in the expression-1. Thus based on these evidences, structure-I (Chart-1) can be assigned for [Zn(tet-b)(ClO$_4$)$_2$] complex.

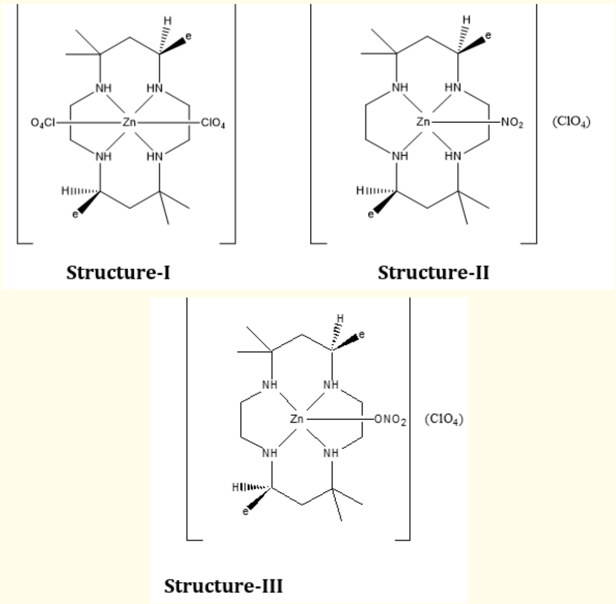
$$[\mathrm{Zn(tet\text{-}b)(ClO_4)_2}] \xrightarrow{\mathrm{H_2O}} [\mathrm{Zn(tet\text{-}b)(H_2O)_2](ClO_4)_2} \text{---------(1)}$$

[Zn(tet-b)(NO$_3$)](ClO$_4$) and [Zn(tet-b)(NO$_2$)](ClO$_4$)

[Zn(tet-b)(ClO$_4$)$_2$] underwent partial axial substitution with KNO$_3$ and NaNO$_2$ with proper ratio in methanol to produce five coordinated square pyramidal white products, [Zn(tet-b)(NO$_3$)](ClO$_4$) and [Zn(tet-b)(NO$_2$)](ClO$_4$) respectively. The infrared spectra of these complexes exhibit all characteristic bands due to ν_{N-H}, ν_{C-C}, ν_{C-H}, ν_{ClO4-}, ν_{Zn-N} and ν_{CH3} stretching frequencies at the proper regions. The non-splitting of the band at 1050 cm^{-1} can be accounted for the non-coordination of ClO_4^-. Moreover NO_3^- band around 1384 cm^{-1} splitted to 1324 cm^{-1} ^{and} 1435 cm^{-1} with a separation of 111 cm^{-1} of the complex, [Zn(tet-b)(NO$_3$)](ClO$_4$) indicating the unidentate coordination of NO_3^- ion [19]. Again [Zn(tet-b)(NO$_2$)](ClO$_4$) exhibits the $\nu_{asym(NO2)}$ and $\nu_{sym(NO2)}$ bands at 1463 cm^{-1} and 1341 cm^{-1} respectively indicating the complex to be N-bonded nitro complex and appearance of a band at 858 cm^{-1} can be attributed to δ_{NO2} frequency. The conductance values of 60-107 ohm^{-1}cm^{2}mole^{-1} for these complexes in DMSO indicate the 1:1 electrolytic behavior [18] as expected for formulae assigned. However the value of 209-214 ohm^{-1}cm^{2}mole^{-1} in H$_2$O of both complexes demonstrate that these complexes convert to 1:2 electrolytes as expressed by the following conversion-2. However that of 0 ohm^{-1}cm^{2}mole^{-1} in CHCl$_3$ for complex [Zn(tet-b)(NO$_2$)](ClO$_4$) is an indication of nonelectrolytic nature as expressed by the following expression-3. The ^{1}H-nmr spectrum of [Zn(tet-b)(NO$_3$)](ClO$_4$) shows two sharp methyl singlets at 1.308 ppm and 1.230 ppm corresponding to 6H each which can be assigned to equatorial and axial methyls of the gem-dimethyl groups. Appearance of two closely spaced doublets at 1.130 ppm and 1.162 ppm each corresponding to (3H) can be assigned to two equatorially oriented methyls on each chiral carbon. This type of pattern is suggestive of a diequatorial orientation of methyls on chiral carbons. The methylene, methane and NH protons appear as multiplets at 1.611, 2.239, 2.557, 3.092, 3.690, 5.347 and 8.347 ppm. Thus the complex [Zn(tet-b)(NO$_3$)](ClO$_4$) is, therefore, assigned a structure by Structure-II where both the chiral methyls are equatorial. So based on these evidences, the structure-II and structure-III (Chart-1) can be assigned for [Zn(tet-b)(NO$_3$)](ClO$_4$) and [Zn(tet-b)(NO$_2$)](ClO$_4$) respectively.

$$[\mathrm{Zn(tet\text{-}b)(X)]\ (ClO_4)} \xrightarrow[\mathrm{(X\,=\,NO_3\ or\ NO_2)}]{\mathrm{H_2O}} [\mathrm{Zn(tet\text{-}b)(H_2O)](ClO_4)(X)}\text{----(2)}$$

$$[\mathrm{Zn(tet\text{-}b)(NO_2)](ClO_4)} \xrightarrow{\mathrm{CHCl_3}} [\mathrm{Zn(tet\text{-}b)(NO_2)(ClO_4)}]\text{---------(3)}$$



Structure-I

Structure-II

Structure-III

Chart 1: Zinc(II) complexes of tet-b.

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Zinc(II) complexes of tet-bx

[Zn(tet-bx)Cl]Cl

Interaction of the ligand, tet-bx with zinc(II) chloride produced sticky product, which on tituration with cold methanol furnished white monochloridozinc(II) chloride complex [Zn(tet-bx)Cl]Cl of tet-bx,. Infrared spectrum of this complex shows a $\nu_{N\text{-}H}$ band at 3264 cm^{-1}. An infrared band at 2248 cm^{-1} indicates the presence of cyano (-C≡N) group [14-16] whereas a band at 599 cm^{-1} demonstrates the presence of $\nu_{Zn\text{-}N}$ band. Other than these bands, the infrared spectrum of this complex also displays bands for $\nu_{C\text{-}H,}$ ν_{CH3} and $\nu_{C\text{-}C}$ at 2968 cm^{-1}, 1374 cm^{-1} and 1172 cm^{-1} respectively. Since the IR spectrum has not been carried out below 400 cm^{-1}, the band for Zn-Cl could not be detected. The molar conductivity value of 61 $ohm^{-1}cm^2mole^{-1}$ in DMSO solution of this complex indicates that this complex is 1:1 electrolytic in nature [18], i.e. one Cl^- ion is in coordination sphere and the other ion is out of coordination sphere as expected for five coordinated square pyramidal complex corresponding to the formula assigned. Again the conductance value of 265 $ohm^{-1}cm^2mole^{-1}$ for this complex in H_2O is an indication of the complex to be 1:2 electrolyte as expressed by the following expression-4. The ^{1}H-nmr spectrum of this complex displays one singlet at 1.039 ppm, a doublet at 0.883 ppm and a overlapped doublet with a singlet at 1.213 ppm. The singlet at 1.039 ppm corresponding to six protons can be assigned to equatorial components of the gem-dimethyl groups and the doublet at 0.883 ppm corresponding to (3H) can be assigned to equatorially oriented one methyl protons on one chiral carbon. However, the overlapped signal corresponding to 9H can be assigned to one singlet arising out of axial components (6H) of gem-dimethyl groups and a doublet corresponding to axially oriented one methyl protons (3H) on other chiral carbon. The spectrum further shows some downfield multiplets at 1.339, 1.881, 2.86, 2.97, 8.57 ppm due to $CH_{2,}$ CH and NH protons. So, axial-equatorial assignment is made for this complex. Thus the structure-IV (Chart-2) can be assigned for [Zn(tet-bx)Cl]Cl complex.

$$[\mathrm{Zn(tet\text{-}bx)Cl}]\mathrm{Cl} \xrightarrow{\mathrm{H_2O}} [\mathrm{Zn(tet\text{-}bx)(H_2O)}]\mathrm{Cl_2}\text{--------(4)}$$

[Zn(tet-bx)(NCS)$_2$], [Zn(tet-bx)(NCS)](SCN) and [Zn(tet-bx)X′] X′ (Where X′=NO$_3$, NO$_2$, Br or I)

[Zn(tet-bx)Cl]Cl underwent simultaneous axial substitution and anion exchange reaction with KX″ (Where X″= NO_3, Br or I) and $NaNO_2$ to produce [Zn(tet-bx)X′′]X′′ and [Zn(tet-bx)(NO_2)](NO_2) respectively whereas [Zn(tet-bx)$(NCS)_2$] was resulted by the simultaneous axial addition and substitution of [Zn(tet-bx)Cl]Cl by KSCN, at the same time [Zn(tet-bx)(NCS)](SCN) was also resulted by the simultaneous axial substitution and anion exchange reaction with the KSCN. The infrared spectra of the complexes show characteristic bands at proper region. Presence of $\delta_{(NCS)}$ band and ν_{CN} band demonstrate that the Cl^- groups are substituted by NCS^- groups and appearance of sharp ν_{CN} band in the region of 2025-2080 cm^{-1} is a good indication of N-bonded thiocyanate [20] group in both zinc(II) isothiocyanato complexes of tet-bx. These complexes display $\delta_{(NCS)}$ band at 480 cm^{-1} and ν_{CS} band at 819-821 cm^{-1} which do not correspond to ligand in this region and are therefore assigned for fully N-bonded thiocyanate groups [20,21]. Therefore these complexes can be identified as isothiocyanato complexes. For the complex [Zn(tet-bx)(NO_3)](NO_3) a band at 1384 cm^{-1} demonstrates the presence of υ_{NO3} which was splitted into 1325 cm^{-1} and 1451 cm^{-1} with a separation of 126 cm^{-1} indicating the unidentate mode of coordination of NO_3^- ion [22]. Moreover the complex [Zn(tet-bx)(NO_2)](NO_2) exhibits the $\nu_{asym(NO2)}$ and $\nu_{sym(NO2)}$ bands at 1462 cm^{-1} and 1335 cm^{-1} respectively indicating the formation of N-bonded nitro complex. All the complexes exhibit $\nu_{Zn\text{–}N}$ band at 566-599 cm^{-1}. The molar conductivity of 0 $ohm^{-1}cm^2mol^{-1}$ of [Zn(tet-bx)$(NCS)_2$] in chloroform support the nonelectolytic nature of this complex whereas the value of 92 $ohm^{-1}cm^2mole^{-1}$ in DMSO indicates that the complex is 1:1 electrolyte in this solvent revealing the conversion of octahedral species into square pyramidal species as indicated by the expression-5. Moreover the conductance value of 258 $ohm^{-1}cm^2mol^{-1}$ of the same complex in H_2O corresponding to 1:2 electrolyte [18] can be expressed by the conversion-6. However the molar conductivity value of 60-104 $ohm^{-1}cm^2mole^{-1}$ in DMSO of all complexes except [Zn(tet-bx)$(NCS)_2$] corresponds to 1:1 electrolyte as expected for the molecular formulae assigned whereas the conductance value of 218-248 $ohm^{-1}cm^2mole^{-1}$ in H_2O corresponding to 1:2 electrolyte can be expressed by the expression-7.

$$[\mathrm{Zn(tet\text{-}bx)(NCS)_2}] \xrightarrow{\mathrm{DMSO}} [\mathrm{Zn(tet\text{-}bx)(DMSO)(NCS)}]\mathrm{(NCS)}\text{---(5)}$$

$$[\mathrm{Zn(tet\text{-}bx)(NCS)_2}] \xrightarrow{\mathrm{DMSO}} [\mathrm{Zn(tet\text{-}bx)(H_2O)_2}]\mathrm{(NCS)_2}\text{-----------(6)}$$

$$[\mathrm{Zn(tet\text{-}bx)(X''']}\mathrm{(X''')} \xrightarrow{\mathrm{DMSO}} [\mathrm{Zn(tet\text{-}bx)(H_2O)}]\mathrm{(X''')_2}\text{------(7)}$$

$$(\mathrm{X'''} = \mathrm{NCS, NO_3, NO_2, Br\ or\ I})$$

The ^{1}H-NMR spectrum of [Zn(tet-bx)(NCS)](NCS) shows similar spectral pattern like that of parent complex, [Zn(tet-bx)Cl]Cl revealing one doublet at 0.891 ppm, one singlet at 1.045 ppm and an overlapped doublet with a singlet at 1.194 ppm. The singlet at 1.045 ppm corresponding to (6H) can be assigned to equatorial components of two gem-dimethyl pairs and the doublet corresponding to (3H) at 0.891 ppm is assigned to one equatorial methyl group on one chiral carbon. The overlapped doublet with a singlet at 1.194 ppm corresponding to (9H) can be assigned to a singlet (6H) corresponding to axial components of gem-dimethyl groups and a doublet (3H) to one methyl protons on other chiral carbon. So, [Zn(tet-bx)(NCS)](NCS) should have one equatorially oriented methyl group and one axially oriented methyl. Therefore a same axial-equatorial assignment has been made for this complex as assigned for its parent complex [Zn(tet-bx)Cl]Cl. This observation proves that axial substitution takes place without change of conformation and configuration of the ligand of the original complex [10,11]. The downfield signals of this complex at 1.853, 2.032, 2.261, 2.853, 3.92, 8.15, 8.320 ppm etc. may be due to methylene, methine, and NH protons. Based on the above evidences the following structures-V to X (Chart 2) can be assigned for these zinc(II) complexes of tet-bx.

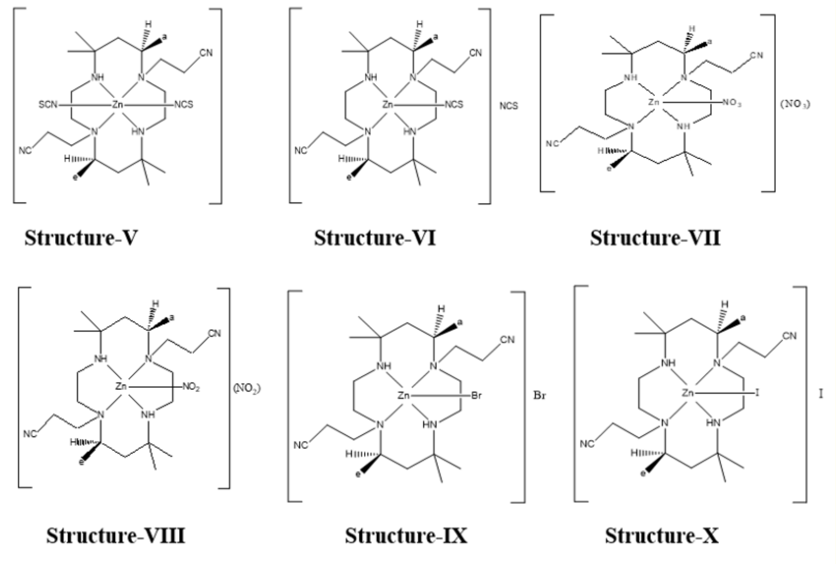

Chart 2: Zinc(II) complexes of tet-bx.

Antibacterial activities

Zinc(II) complexes showed various activity against the different types of bacteria (Table 1). Nitratozinc(II) complex of tet-bx showed ineffectiveness against all the bacteria except *Klebsiella Pneumoniae*, but nitratozinc(II) complex of tet-b was ineffective against two gram positive but effective against the gram negaive bacteria. However monochlorido zinc(II) complex of tet-bx, diperchlorato zinc(II) complex of tet-b against *Shigella sonnei* and mononitro zinc(II) complex of tet-b against *Klebsiella Pneumoniae* showed remarkable activity as antibacterial agent. On the other hand, thiocyanato and iodido complex of tet-bx for *Shigella sonnei* and diperchlorato complex of tet-b for *Klebsiella Pneumoniae* showed stimulation which means the complexes enhanced the growth of concerned bacteria. However by depending on the positive results of this investigation it can be concluded that further studies are warranted in this area with analogous ligands and complexes. The mechanism of the antibacterial activity can be explained by the chelation theory and blocking of the protein synthesis system to protect the growth of the bacteria [23,24]. However it is surprising to note that, though the ligand tet-b was ineffective but its N-pendent derivative tet-bx exhibits measurable amount of activity.

	Zone of inhibition in diameter			
Ligands and their complexes	**Gram-positive Bacteria**		**Gram-negative Bacteria**	
	Bacillus cereus	***Staphylococcus aureus***	***Shigella sonnei***	***Klebsiella pneumoniae***
tet-bx	5	7	6	7
[Zn(tet-bx)Cl]Cl	0	0	15	10
[Zn(tet-bx)(NCS)](NCS)	0	0	+	10
[Zn(tet-bx)$(NCS)_2$]	0	0	13	0
[Zn(tet-bx)(NO_3)](NO_3)	0	0	0	12
[Zn(tet-bx)(NO_2)](NO_2)	8	8	9	6
[Zn(tet-bx)Br]Br	7	9	10	10
[Zn(tet-bx)I]I	9	9	11	+
tet-b	0	0	0	0
[Zn(tet-b)$(ClO_4)_2$]	0	0	14	+
[Zn(tet-b)(NO_3)](ClO_4)	0	0	10	10
[Zn(tet-b)(NO_2)](ClO_4)	0	0	11	14
Zinc(II)chloride	2	4	3	3
Ampicillin	24	21	26	23
Control (DMSO)	0	0	0	0

Table 1: Antibacterial activities of ligands and their metal complexes.

Conclusion

This study reveals that, interaction of tet-b and tet-bx with zinc(II) perchlorate and zinc(II) chloride respectively gave the octahedral complex, [Zn(tet-b)$(ClO_4)_2$] and square pyramidal complex, [Zn(tet-bx)Cl]Cl respectively. Moreover these complexes underwent simultaneous axial substitution and anion exchange reactions with KNO_3, $NaNO_2$, KI and KBr while [Zn(tet-bx)Cl]Cl underwent simultaneous axial addition and substitution with KSCN also. Antibacterial studies of the ligand tet-bx and its Zinc(II) complexes explored that, both the ligand and complexes were very fruitful against most of the bacteria but few of the complexes and the ligand tet-b were ineffective against some of the bacteria.

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Conflict of Interest

The authors declare that they have no personal relationships or known competing financial interests that could have appeared to influence the work reported in this research work.

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