



Copper(II) Complexes of an N-pendent Cyanoethyl Derivative of a Tetraazamacrocyclic Ligand: Synthesis, Characterization and Antibacterial Studies

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Abstract

One of the isomers of the ligand Me₆[14]ane, 'tet-b' upon reflux with acrylonitrile produced N-pendent derivative 'tet-bx' in which two cyano-ethyl groups were attached on less crowded two *trans*-N atoms. The reaction of copper(II) perchlorate hexahydrate with 'tet-bx' yielded six coordinated octahedral reddish-purple [Cu(tet-bx)(ClO₄)₂]. The axial substitution reactions of [Cu(tet-bx)(ClO₄)₂] with KX (X= SCN, NO₃, Cl, Br or I) and NaNO₂ afforded six coordinated blue [Cu(tet-bx)(NCS)(ClO₄)] and [Cu(tet-bx)(NO₂)(H₂O)]ClO₄; red [Cu(tet-bx)(NO₃)(H₂O)]ClO₄ and [Cu(tet-bx)Cl(H₂O)]ClO₄ and purple [Cu(tet-bx)Br(H₂O)]ClO₄ and [Cu(tet-bx)I(H₂O)]ClO₄. The complexes were characterized on the basis of elemental, spectroscopic, magnetochemical and conductometric analysis. The antibacterial activities of the concerned ligand and its copper(II) complexes have been tested against four selected bacteria.

Keywords: N-pendant Tetraazamacrocyclic Ligand; Copper (II) Complexes; Spectroscopic Studies; Antibacterial Activities

Introduction

The research interest on macrocyclic transition metal complexes have considerably increased due to their variety of applications in the field of Coordination and Medicinal Chemistry [1-18]. The structural design of macrocyclic complexes is very similar to naturally occurring macrocycles, like porphyrins, chlorin and corrins [9]. The electronic properties and reactivity of the macrocycles and their complexes promoted great fascination to prepare these types of complexes. In the area of pharmaceutical sector, the implication of macrocyclic complexes as antibacterial [10], antifungal [11], antioxidizing [12], antiproliferative [13], antidiabetic [14], antitumor [15] and anticancer [16] drugs has drawn great attention. Moreover, the significant use as MRI contrast agents [17], therapeutic reagents [18], chemical sensor,

ion transporter and as catalysts as [19] well in crystal engineering [20] have motivated the researchers to expand the research on these complexes. A comprehensive literature survey [21-26] have been carried out on copper(II) complexes with different macrocycles. In our previous study, metal complexes of hexamethyl-tetraazacyclotetradecadiene, Me₆[14]diene and isomers (tet-a and tet-b) of its reduced analogue have been reported [25-29]. Moreover, syntheses and characterization of the concerned N-pendent derivative (tet-bx) of an isomeric ligand, 'tet-b' and its one diperchloratocopper(II) complex [Cu(tet-bx)(ClO₄)₂] and some nickel(II) complexes have also been reported [25]. But the axial substitution reactions on the prepared diperchloratocopper(II) complex [Cu(tet-bx)(ClO₄)₂] has not been carried out yet. So, due to the great importance of the macrocyclic complexes as pointed

out above, it was interesting to observe the behavior of axial substitution products of the copper(II) complexes. Thus in this study, axial substitution products of six coordinated octahedral diperchloratocopper(II) complex, $[\text{Cu}(\text{tet-bx})(\text{ClO}_4)_2]$ of tet-bx and their antibacterial activities against different bacteria have been reported.

Experimental

Materials and Methods

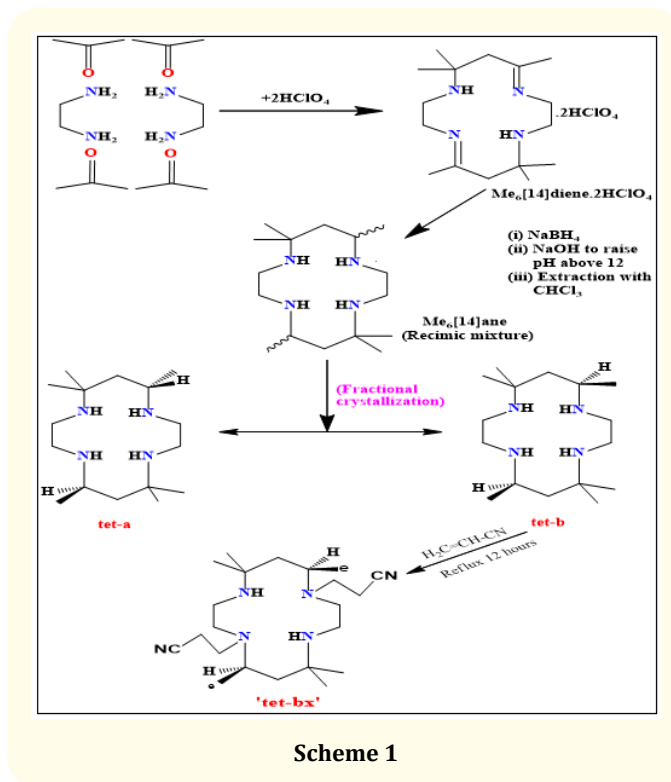
The chemicals were of analytical reagent grade (Sigma Aldrich, USA) which were used without further purification. Microanalysis of C, H, N and S of the compounds have been carried out on a CHNS analyzer at the Department of Chemistry, Friedrich Schiller University, Jena, Germany. Melting points of the complexes were obtained with an electrothermal melting point apparatus at the Inorganic Research Laboratory of Chittagong University. Conductance measurements of the metal complexes were done in CHCl_3 , DMSO, H_2O and CH_3CN solutions using HANNA instrument with HI 8820N conductivity cell at the University of Chittagong. The infrared spectra of the complexes were taken as KBr discs in the range $4000\text{-}400\text{ cm}^{-1}$ at the Department of Chemistry, University of Chittagong, Chattogram, Bangladesh. Electronic spectra of the samples were recorded on a Shimadzu UV-visible spectrophotometer. All the magnetic measurements have been carried out by SHERWOOD SCIENTIFIC magnetic susceptibility balance. All measurements on antibacterial activities against four bacteria have been carried out at the Department of Microbiology, University of Chittagong as described in experimental section.

Ligand

The ligand salt, hexamethyl-tetraazacyclotetradecadiene dihydroperchlorate ($\text{L}\cdot 2\text{HClO}_4$), its reduced isomeric ligands, 'tet-a' and 'tet-b' [30] and N-pendent cyanoethyl derivative 'tet-bx' of 'tet-b', (Scheme 1) have been prepared as per literature [25].

Copper complexes

The diperchloratocopper(II) complex $[\text{Cu}(\text{tet-bx})(\text{ClO}_4)_2]$ of tet-bx has been synthesized as per literature [25].



Axial substitution products of $[\text{Cu}(\text{tet-bx})(\text{ClO}_4)_2]$

$[\text{Cu}(\text{tet-bx})(\text{X}_1)(\text{H}_2\text{O})_m(\text{ClO}_4)_n](\text{ClO}_4)_x$ ($\text{X}_1 = \text{NCS}, \text{NO}_3, \text{NO}_2, \text{Cl}, \text{Br}$ or I) and ($m=1$ or 0 , $n=0$ or 1 and $x=1$ or 0)

The complex $[\text{Cu}(\text{tet-bx})(\text{ClO}_4)_2]$ (0.163 g; 0.25 mmol) and KX/NaNO_2 ($\text{X} = \text{SCN}, \text{NO}_3, \text{Cl}, \text{Br}$ or I) (0.5 mmol) were dissolved/suspended separately in 25 mL hot acetonitrile and methanol respectively, and mixed while hot. The variant colored solutions like green, violet and blue solutions were resulted when heated on water bath to complete the reaction, meanwhile some white precipitates were formed which were removed by filtration. On reducing the filtrate to about 10 mL on water bath, blue $[\text{Cu}(\text{tet-bx})(\text{NCS})(\text{ClO}_4)]$, red $[\text{Cu}(\text{tet-bx})(\text{NO}_3)(\text{H}_2\text{O})](\text{ClO}_4)$, orange red $[\text{Cu}(\text{tet-bx})\text{Cl}(\text{H}_2\text{O})](\text{ClO}_4)$, purple $[\text{Cu}(\text{tet-bx})\text{Br}(\text{H}_2\text{O})](\text{ClO}_4)$, red $[\text{Cu}(\text{tet-bx})\text{I}(\text{H}_2\text{O})](\text{ClO}_4)$ and blue $[\text{Cu}(\text{tet-bx})(\text{NO}_2)(\text{H}_2\text{O})](\text{ClO}_4)$ were produced. After cooling the mixtures at room temperature, the products were separated by filtration and washed with methanol followed by diethylether and finally stored in a vacuum desiccator over silica gel.

For [Cu(tet-bx)(NCS)(ClO₄)]: Anal. calcd. %: C 45.16, H 6.92, N 16.03. Found (%): C 45.10, H 6.63, N 16.08. IR (ν, cm⁻¹): 3232m v(N-H), 2973s v(C-H), 1383m v(CH₃), 1173s v(C-C), 586w v(N-Cu), 2252s v(C≡N), 624vs, 1072s, 1107m, 1053sh v(ClO₄⁻), 2052vs v(CN), 852 v(CS), 482 δ(NCS). Conductance (ohm⁻¹cm²mol⁻¹): in CHCl₃ 0, in DMSO, 70; in H₂O, 269; in acetonitrile, 251. UV vis [λ_{max} in nm (ε_{max})]: in DMSO 560(149), 347(4000), 326(4000), 297(4000), 281(4000), 257(4000), 236(2545), 223(364); in H₂O 553(189), 308(4000); in acetonitrile, 632(280), 357(4000), 347(4000), 332(4000), 323(4000), 316(4000), 305(4000), 293(4000), 284(4000), 279(4000), 227(4000). Magnetic Moment μ_{eff} (B.M): 1.76.

For [Cu(tet-bx)(NO₃)(H₂O)](ClO₄): Anal. calcd. %: C 42.79, H 7.01, N 15.50. Found (%): C 41.80, H 6.98, N 15.42. IR (ν, cm⁻¹): 3185vs v(N-H), 2975w v(C-H), 1383m v(CH₃), 1176m v(C-C), 542vw v(N-Cu), 2253m v(C≡N), 624vs, 1081vs v(ClO₄⁻), 1455m, 1330sh v(NO₃), 430w v(Cu-O), 3433b v(OH). Conductance (ohm⁻¹cm²mol⁻¹): in DMSO, 79; in H₂O, 272; in acetonitrile, 263. UV vis [λ_{max} in nm (ε_{max})]: in DMSO 548(168), 318(4000); in H₂O 536(147), 352(4000), 329(4000), 307(4000), 301(4000), 216(4000); in acetonitrile, 547(180), 355(4000), 350(4000), 341(4000), 326(4000), 317(4000), 302(4000). Magnetic Moment μ_{eff} (B.M): 1.84.

For [Cu(tet-bx)Cl(H₂O)]ClO₄: Anal. calcd. %: C 45.53, H 7.31, N 13.84. Found (%): C 45.48, H 7.35, N 13.79. IR (ν, cm⁻¹): 3221m v(N-H), 2978s v(C-H), 1383s v(CH₃), 1175s v(C-C), 532w v(N-Cu), 2252s v(C≡N), 624vs, 1088s v(ClO₄⁻), 435m v(Cu-O), 3487bs v(OH). Conductance (ohm⁻¹cm²mol⁻¹): in DMSO, 60; in H₂O, 176; in acetonitrile, 186. UV vis [λ_{max} in nm (ε_{max})]: in DMSO 547(196), 355(4000), 345(4000), 326(4000), 312(4000), 297(4000), 279(4000), 273(4000), 256(4000), 244(2545); in H₂O 536(155)317(4000); in acetonitrile, 547(151), 355(4000), 347(4000), 341(4000), 329(4000), 313(4000). Magnetic Moment μ_{eff} (B.M): 1.81.

For [Cu(tet-bx)Br(H₂O)](ClO₄): Anal. calcd. %: C 40.51, H 6.75, N 12.89. Found (%): C 40.56; H 6.78, N 12.85. IR (ν, cm⁻¹): 3220s v(N-H), 2970w v(C-H), 1383s v(CH₃), 1174s v(C-C), 561w v(N-Cu), 2250s v(C≡N), 636vs, 1087m v(ClO₄⁻), 437m v(Cu-O), 3443s v(OH). Conductance (ohm⁻¹cm²mol⁻¹): in DMSO, 75; in H₂O, 220; in acetonitrile, 210. UV vis [λ_{max} in nm (ε_{max})]: in DMSO 554(242),

320(4000), 264(4000); in H₂O 540(213), 347(4000), 323(4000); in acetonitrile, 554(262), 354(4000), 342(4000), 331(4000), 318(4000), 308(4000). Magnetic Moment μ_{eff} (B.M): 1.73.

For [Cu(tet-bx)I(H₂O)](ClO₄): Anal. calcd. %: C 37.79, H 6.29, N 12.02. Found (%): C 37.82, H 6.25, N 11.98. IR (ν, cm⁻¹): 3226m v(N-H), 2986m v(C-H), 1383m v(CH₃), 1173s v(C-C), 545w v(N-Cu), 2245s v(C≡N), 636s, 1082w v(ClO₄⁻), 437w v(Cu-O), 3441bs v(OH). Conductance (ohm⁻¹cm²mol⁻¹): in DMSO, 93; in H₂O, 243; in acetonitrile, 204. UV vis [λ_{max} in nm (ε_{max})]: in DMSO 543(132), 339(4000), 327(4000), 316(4000), 301(4000), 287(4000), 257(4000), 241(1818); in H₂O 540(120), 314(4000); in acetonitrile, 540(69), 306(3967), 262(4000), 232(4000). Magnetic Moment μ_{eff} (B.M): 1.83.

For [Cu(tet-bx)(NO₂)(H₂O)]ClO₄: Anal. calcd. %: C 42.78, H 7.18, N 15.87. Found (%): C 42.70, H 7.24, N 15.80. IR (ν, cm⁻¹): 3228m v(N-H), 2975m v(C-H), 1383w v(CH₃), 1137w v(C-C), 551vw, 430w v(N-Cu), 2257s v(C≡N), 625vs, 1088s v(ClO₄⁻), 1464s v_{asym}(NO₂), 1338m v_{sym}(NO₂), 844s δ(NO₂), 435vw v(Cu-O), 3437bs v(OH). Conductance (ohm⁻¹cm²mol⁻¹): in DMSO, 62; in H₂O, 178; in acetonitrile, 224. UV vis [λ_{max} in nm (ε_{max})]: in DMSO 594(234), 309(4000); in H₂O 567(164), 311(4000); in acetonitrile, 595(209), 342(4000), 333(4000), 319(4000), 303(4000). Magnetic Moment μ_{eff} (B.M): 1.79.

Antibacterial activities

The antibacterial activities of the concerned copper salt, N-pendent macrocyclic ligand, tet-bx and its copper(II) complexes were carried out by the disc diffusion method against two important gram-positive and two gram-negative bacteria which cause different fatal diseases. Paper disc of 4 mm in diameter and the petriplate of 90 mm in diameter were used throughout the experiment. Solutions of the test samples were made by dissolving measured amount (10 mg) of the samples in definite volume (1 mL) of the solvent. Paper discs were sterilized in an autoclave and dried at 100°C in an oven. About 1 mL of bacterial suspension was taken in a sterilized petridish and then approximately 20 mL of sterilized melted nutrient agar (45°C) was poured into the plate followed by mixing thoroughly with the direction of clockwise and anticlockwise. After solidification of the seeded nutrient agar medium, paper disc (4 mm in diameter) after soaking with test

chemicals (1% in DMSO) were placed on the agar of the center of the pour plate. A control plate was also maintained in each case with DMSO. These plates were then kept at low temperature (4 °C) for 2-4 hours for allowing maximum diffusion. During this time dried discs absorbed water from the surrounding media and then the test materials were dissolved and diffused out of the media. Thereafter the plates were incubated at 37 °C for 48 hours for allowing maximum growth of the organisms at inverted position. The activity was expressed in terms of zone of inhibition in mm. The experiment was repeated thrice for statistical analysis.

Results and Discussion

Ligand

The N-pendent cyanoethyl derivative <tet-bx> of isomeric ligand of 'tet-b', (Scheme 1) has been prepared and characterized as per our previous study [25].

Copper(II) complexes of 'tet-bx'

The complex [Cu(tet-bx)(ClO₄)₂] (I) has been prepared and characterized as per literature [25].

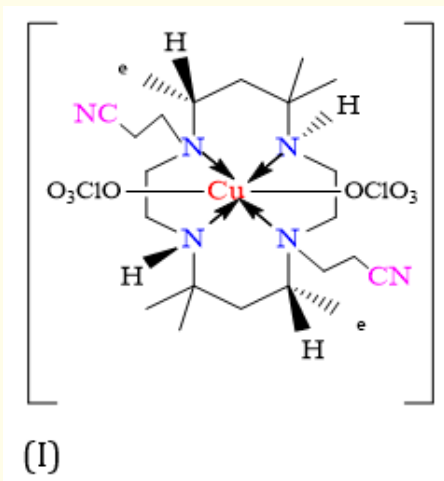


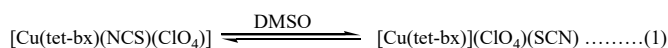
Figure 1

Axial ligand substitution products of [Cu(tet-bx)(ClO₄)₂]

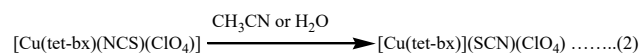
[Cu(tet-bx)(NCS)(ClO₄)]

Interaction between [Cu(tet-bx)(ClO₄)₂] and KSCN in a molar ratio of 1:2 produced six coordinated octahedral axial substitution product [Cu(tet-bx)(NCS)(ClO₄)]. The infrared spectrum of this

complex displays $\nu(\text{N-H})$, $\nu(\text{C-H})$, $\nu(\text{CH}_3)$, $\nu(\text{C-C})$, $\nu(\text{N-Cu})$ and $\nu(\text{C}\equiv\text{N})$ bands at 3232 cm⁻¹, 2973 cm⁻¹, 1383 cm⁻¹, 1173 cm⁻¹, 586 cm⁻¹ and 2252 cm⁻¹ respectively. Presence of sharp $\nu(\text{ClO}_4^-)$ bands at 1107 cm⁻¹ and 624 cm⁻¹ in this complex reveals that the ClO₄⁻ ions are not fully replaced by NCS⁻ ion. The splitting of band at around 1100 cm⁻¹, to 1072 cm⁻¹ and 1053 cm⁻¹ supports the unidentate coordination of ClO₄⁻ ion in [Cu(tet-bx)(NCS)(ClO₄)] [31]. Appearance of $\nu(\text{CN})$ band at 2052 cm⁻¹, $\nu(\text{CS})$ at 852 cm⁻¹ and δ_{NCS} at 482 cm⁻¹ in the present complex is a good indication of N-bonded thiocyanate group [31-34]. So from these peak positions, it is concluded that the present complex is N-bonded isothiocyanatoperchlorato complex [32-34]. The conductance value of 0 ohm⁻¹cm²mol⁻¹ for this complex in CHCl₃ (Color remains intact in CHCl₃) supports the nonelectrolytic nature of this complex i.e. the anions are in the coordination sphere as expected for six coordinated octahedral complexes. But the molar conductivity value 70 ohm⁻¹cm²mol⁻¹ in DMSO corresponding to 1:1 electrolyte [35] may be due to equilibrium between octahedral and square planar species as shown below by the expression-1.

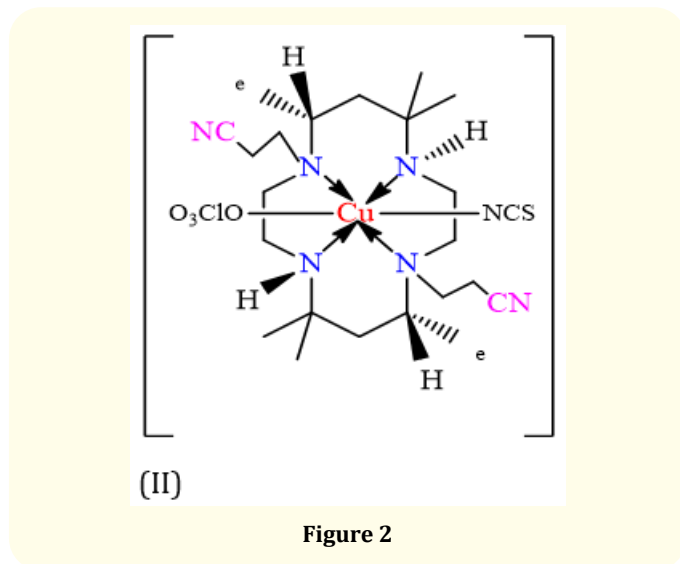


Again molar conductivity values of 251 ohm⁻¹cm²mol⁻¹ in acetonitrile and 269 ohm⁻¹cm²mol⁻¹ in H₂O indicate that the complex is 1:2 electrolyte which can be accounted for the expulsion of both anions i.e.(NCS⁻) and (ClO₄⁻) from coordination sphere to form square planar complex [Cu(tet-bx)](SCN)(ClO₄) as expressed by the expression-2.



The electronic spectra of this complex show d-d bands in the region of 553-632 nm. Appearance of d-d bands in this region can be attributed to the square planar or tetragonally distorted octahedral geometry [34]. However other experimental studies are in support of octahedral geometry. The spectra also display bands at around 223-357 nm in different solvents due to Cu-N charge transfer. The magnetic moment value (1.76 B.M) of this complex can be accounted for a paramagnetic complex corresponding to one unpaired electron as expected for copper(II) complex of d⁹ system. As per our earlier study [25], a diequatorial assignment has been

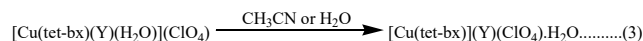
made for the mother complex $[\text{Cu}(\text{tet-bx})(\text{ClO}_4)_2]$ (I). Based on the above evidences as well as on the basis that, axial substitution takes place without change of configuration and conformation of the ligand of the original complexes [36,37], the structure (II) can be assigned to $[\text{Cu}(\text{tet-bx})(\text{NCS})(\text{ClO}_4)]$.



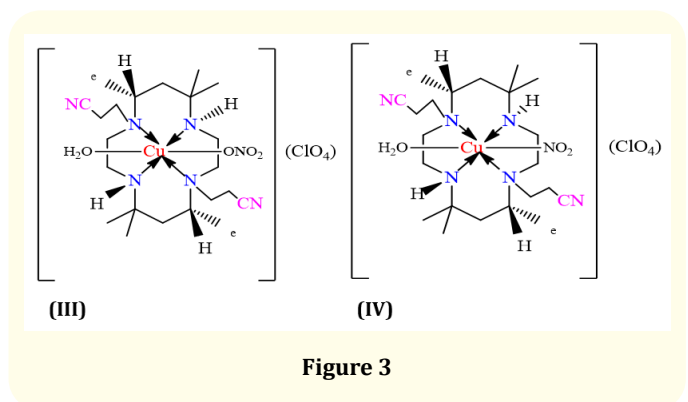
$[\text{Cu}(\text{tet-bx})(\text{Y})(\text{H}_2\text{O})](\text{ClO}_4)$ ($\text{Y}=\text{NO}_3$ or NO_2)

Interaction of $[\text{Cu}(\text{tet-bx})(\text{ClO}_4)_2]$ with KNO_3 or NaNO_2 in a molar ratio of 1:2 afforded six coordinated octahedral axial substitution products $[\text{Cu}(\text{tet-bx})(\text{NO}_3)(\text{H}_2\text{O})](\text{ClO}_4)$ and $[\text{Cu}(\text{tet-bx})(\text{NO}_2)(\text{H}_2\text{O})](\text{ClO}_4)$ respectively. Infrared spectra of these complexes show $\nu(\text{N-H})$, $\nu(\text{C-H})$, $\nu(\text{CH}_3)$, $\nu(\text{C-C})$, $\nu(\text{C}^\alpha\text{N})$ and $\nu(\text{N-Cu})$ stretching bands at the expected regions. The complexes, $[\text{Cu}(\text{tet-bx})(\text{Y})(\text{H}_2\text{O})](\text{ClO}_4)$ display bands at 3433 cm^{-1} and 3437 cm^{-1} due to ν_{OH} which can be accounted for coordinated water molecule and bands at $430\text{-}435 \text{ cm}^{-1}$ can be safely assigned for Cu-O stretching band for these aqua complexes [34]. The additional bands at $1081\text{-}1088 \text{ cm}^{-1}$ and $624\text{-}625 \text{ cm}^{-1}$ demonstrate the presence of ClO_4^- group in these complexes. Further the complex $[\text{Cu}(\text{tet-bx})(\text{NO}_3)(\text{H}_2\text{O})](\text{ClO}_4)$ displays a overlapped band at 1383 cm^{-1} due to presence of CH_3 group and NO_3^- group. Moreover, splitting of this band to 1330 cm^{-1} and 1455 cm^{-1} are attributed to coordinated NO_3^- group. The separation of the bands by 125 cm^{-1} is accounted for unidentate mode of coordination [38]. The band at around 450 cm^{-1} due to Cu-O assignable for bond of Cu with 'O' of ONO_2 group [38]. Additionally the complex $[\text{Cu}(\text{tet-bx})(\text{NO}_2)(\text{H}_2\text{O})](\text{ClO}_4)$ exhibits the $\nu_{\text{asym}}(\text{NO}_2)$,

$\nu_{\text{sym}}(\text{NO}_2)$ and $\delta(\text{NO}_2)$ bands at 1464 cm^{-1} , 1338 cm^{-1} and 844 cm^{-1} respectively. The positions of these bands and absence of $\nu(\text{M-O})$ are in support of N-bonded nitro complex [39]. For both complexes the molar conductivity values of 79 and $62 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in DMSO (color remaining intact) demonstrate that these complexes are 1:1 electrolytes as expected for the formulae assigned [35]. However molar conductivity values corresponding to 1:2 electrolyte in H_2O and acetonitrile can be expressed by the expression-3.



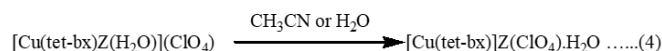
The magnetochemical measurements of these six coordinate octahedral complexes exhibit paramagnetism corresponding to one unpaired electron. The electronic spectra of these complexes explore d-d bands at $536\text{-}595 \text{ nm}$ and charge transfer bands at $216\text{-}355 \text{ nm}$ in different solvents which support the octahedral structure of these complexes [34]. From the above discussion the structures (III) and (IV) can be assigned to $[\text{Cu}(\text{tet-bx})(\text{NO}_3)(\text{H}_2\text{O})](\text{ClO}_4)$ and $[\text{Cu}(\text{tet-bx})(\text{NO}_2)(\text{H}_2\text{O})](\text{ClO}_4)$ respectively.



$[\text{Cu}(\text{tet-bx})\text{Z}(\text{H}_2\text{O})](\text{ClO}_4)$ ($\text{Z}=\text{Cl, Br or I}$)

The complex $[\text{Cu}(\text{tet-bx})(\text{ClO}_4)_2]$ underwent axial substitution reactions with KZ ($\text{Z}=\text{Cl, Br or I}$) in a molar ratio of 1:2 furnished six coordinated octahedral axial substitution products $[\text{Cu}(\text{tet-bx})\text{Z}(\text{H}_2\text{O})](\text{ClO}_4)$. Infrared spectra of these complexes show $\nu(\text{N-H})$, $\nu(\text{C-H})$, $\nu(\text{CH}_3)$, $\nu(\text{C}^\alpha\text{N})$ and $\nu(\text{C-C})$ stretching bands at the expected regions. Appearance of bands at $1082\text{-}1091 \text{ cm}^{-1}$ and $624\text{-}636 \text{ cm}^{-1}$ are attributed to ClO_4^- . Further appearance of bands at $3441\text{-}3487 \text{ cm}^{-1}$ due to $\nu(\text{OH})$ and at $435\text{-}437 \text{ cm}^{-1}$ due to $\nu(\text{M-O})$ can be accounted for coordination of H_2O to form aqua complex [34]. The bands for Cu-Z, ($\text{Z}=\text{Cl, Br or I}$) expected at around 260

cm⁻¹ could not be detected as the spectra could not be run below 400 cm⁻¹. The molar conductivity values of 60-93 ohm⁻¹cm²mol⁻¹ for these complexes in DMSO corresponding to 1:1 electrolyte are as expected for the assigned formulae, [Cu(tet-bx)Z(H₂O)](ClO₄) (Z= Cl, Br or I). Again molar conductivity values of 186-210 ohm⁻¹cm²mol⁻¹ in acetonitrile and 176-243 ohm⁻¹cm²mol⁻¹ in H₂O of these complexes demonstrate the formation of 1:2 electrolytes [35] as expressed by the following conversion in acetonitrile and H₂O.



The magnetic moment values of these complexes show paramagnetism corresponding to one unpaired electron as expected. The d-d bands in electronic spectra of these complexes are in good agreement with six-coordinated octahedral copper(II) complexes [34]. Based on the above evidences, the structures V, VI and VII can be assigned to [Cu(tet-bx)Cl(H₂O)](ClO₄), [Cu(tet-bx)Br(H₂O)](ClO₄) and [Cu(tet-bx)I(H₂O)](ClO₄) respectively.

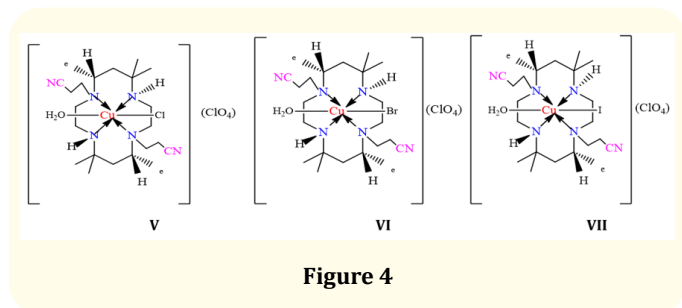


Figure 4

Antibacterial activities

Antibacterial activities of macrocycles and their complexes have been studied to some extent [23-30]. So it is noteworthy to examine whether the concerned N-pendent derivative ligand and its copper(II) complexes show any such activity or not. As per our earlier studies [24] N-pendent ligands did not show any activity against the tested bacteria. Similarly the concerned N-pendent ligand also did the same but some of its copper(II) complexes explored activity. As for example, isothiocyanatoperchlorato (S-1) and aquaiodido complex (S-6) showed activities against gram negative bacteria *Shigella dysenteriae*. Similarly aquanitro (S-3), aquanitro (S-2) and aquaiodido (S-6) complexes explored their potentiality against gram negative bacteria *Escherichia coli* remarkably. Antibacterial activity of the complex [Cu(tet-bx)(ClO₄)₂] has been studied earlier [25]. However it is surprising to note that all these complexes did not show any activity against two selected gram positive bacteria *Bacillus Cereus* and *Staphylococcus aureus* (Table 1). Antibacterial activities of the concerned non coordinated metal salt Cu(ClO₄)₂·6H₂O, solvent DMSO (as control) and ampicillin (Standard) were also performed for the comparison. It is notable to mention that, for the first time some copper(II) complexes of the concerned ligand did not show any potentiality against most of the concerned bacteria. However no definite trend can be made from the observations at this stage, but the positive result suggest further studies with more samples are necessary.

Sample no.	Ligand and its complexes	Zone of inhibition in diameter (mm)			
		Gram positive bacteria		Gram negative bacteria	
		<i>S. aureus</i>	<i>B. cereus</i>	<i>E. coli</i>	<i>S. dysenteriae</i>
L	tet-bx	0	0	0	0
S-1	[Cu(tet-bx)(NCS)(ClO ₄)]	0	0	0	10
S-2	[Cu(tet-bx)(NO ₃)(H ₂ O)](ClO ₄)	0	0	12	0
S-3	[Cu(tet-bx)(NO ₂)(H ₂ O)](ClO ₄)	0	0	10	0
S-4	[Cu(tet-bx)Br(H ₂ O)](ClO ₄)	0	0	0	0
S-5	[Cu(tet-bx)Cl(H ₂ O)](ClO ₄)	0	0	0	0
S-6	[Cu(tet-bx)I(H ₂ O)](ClO ₄)	0	0	11	10
	DMSO	0	0	0	0
	Cu(ClO ₄) ₂ ·6H ₂ O	5	5	4	7
	Ampicillin (Standard)	22	24	34	25

Table 1: Antibacterial activities of Copper(II) complexes.

Conclusion

Reactions of 'tet-bx' with copper(II) perchlorate hexahydrate in methanol produced the octahedral diperchloratocopper(II) complex $[\text{Cu}(\text{tet-bx})(\text{ClO}_4)_2]$. This complex underwent axial substitution reactions with SCN^- , NO_3^- , NO_2^- , Cl^- , Br^- and I^- to produce corresponding octahedral substituted complexes. All these complexes are found to be paramagnetic as expected. However, conductance values of all the complexes in acetonitrile and H_2O corresponding to 1:2 electrolytes indicate the conversion of octahedral to square planar species in these solvents. In antibacterial test, some of the complexes are found to be potential as antibacterial agents, while the most of them are ineffective against almost all bacteria.

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