Asian Journal of Chemistry; Vol. 37, No. 11 (2025), 2697-2702
ASIAN JOURNAL OF CHEMISTRY
https://doi.org/10.14233/ajchem.2025.34504

Studies on Vanadate(V) Complexes of an N-Pendent Cyanoethyl Derivative of Octamethyl-Tetraaza Macrocyclic Chelator

MANISHA RANI ROY[1], SASWATA RABI[2], PRADIP PAUL[1], FONI BUSHON BISWAS[1], DEBASHIS PALIT[1], ISMAIL RAHMAN[3] and TAPASHI GHOSH ROY[1,*]

[1]Department of Chemistry, University of Chittagong, Chattogram-4331, Bangladesh
[2]Department of Chemistry, Chittagong University of Engineering & Technology, Chattogram-4349, Bangladesh
[3]Institute of Environmental Radioactivity, Fukushima University, 1 Kanayagawa, Fukushima City, Fukushima 960-1296, Japan

*Corresponding author: E-mail: tapashir57@cu.ac.bd

Received: 21 July 2025 *Accepted*: 10 September 2025 *Published online*: 27 October 2025 AJC-22156

Dihydroperchlorate salt of a 14-membered tetraazamacrocycle, Me_8[14]diene·2$HClO_4$ (L·2$HClO_4$) was synthesized by the condensation of 1,2-diaminopropane with acetone in the presence of a stoichiometric amount of perchloric acid. L_B, one of the three isomers (L_A, L_B and L_C: isolated from the reduced product of the ligand salt (L·2$HClO_4$), on reflux with excess amount of acrylonitrile produced corresponding white solid product, L_{BX} (*trans*-N_4,N_{11}-*bis*(2-cyanoethyl) 2,9-C-*meso*-3,5,7,7,10,12,14,14-tetraazacyclotetradecane). The reactions of L_{BX} with vanadyl acetylacetonate followed by addition of few drops of vinyl cyanide yielded the pale green product, [VO(L_{BX})(acac)](ClO_4)$_2$. The axial substitution reactions on [VO(L_{BX})(acac)](ClO_4)$_2$ with NCS^-, NO_3^-, NO_2^-, Cl^-, Br^- and I^- furnished different coloured axial substitution products with different geometries. The structural features of the complexes were confirmed using IR, NMR and UV-Vis spectroscopy, revealing their octahedral geometry. Antibacterial studies showed selective activities against Gram-positive and Gram-negative bacteria, suggesting potential biomedical applications.

Keywords: Tetraazamacrocycle, Vanadium(V) complexes, Antibacterial activity.

INTRODUCTION

Macrocyclic compounds have gained significant importance in the current research world due to the various pharmaceutical applications. Moreover, studies on macrocyclic complexes also prove their unique properties on other aspects [1-7]. In this connection, different metal complexes of the macrocyclic ligands have been reported in sliterature [8-10]. Vanadium complexes, in particular, exhibit promising catalytic and antimicrobial properties, making them valuable in biomedical and environmental applications [4-7]. However, syntheses and characterization of various complexes of the concerned ligands [11,12] including some vanadium complexes with other macrocyclic ligands [13-17] are available in the literature. But the vanadium complexes with the concerned ligand have not been reported so far. Therefore, it was of interest to investigate whether complexes of the concerned ligand could be prepared using vanadium as metal template. This study explores the synthesis and characterization of vanadate(V) complexes and N-pendent cyanoethyl derivative of an octamethyl tetraaza-macrocyclic chelator (L_{BX}), evaluating their structural and biological properties to uncover potential applications.

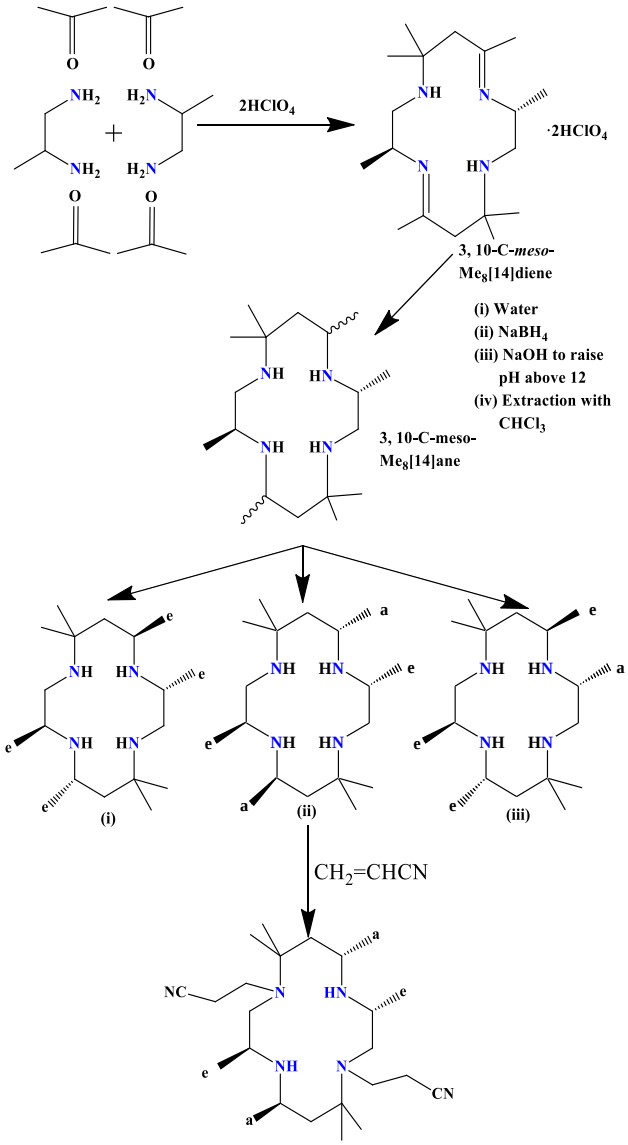
EXPERIMENTAL

All chemical compounds and solvents used were purchased from Sigma Aldrich and Fluka and were used without further purification.

Physical measurements: Elemental analyses (CHN) were performed on a LECO CHNS-932 elemental analyzer (LECO Corporation, USA). IR spectra were recorded on a Shimadzu IR 20 spectrophotometer (Shimadzu, Japan) as KBr disks. ^{1}H NMR measurement was carried out on a Bruker AVANCE 400 spectrometer (Bruker AG, Karlsruhe, Germany). Conductance measurements were conducted on a conductivity bridge HI-8820 (Hanna Instruments, Italy).

Ligands: Ligand salt, Me_8[14]diene·2$HClO_4$ (L·2$HClO_4$), was synthesized following a literature method [18]. Three

isomers L_A, L_B and L_C of the reduced form of mother ligand $L{\cdot}2HClO_4$, were isolated and the N-pendent ligand L_{BX} was also synthesized by adopting literature (**Scheme-I**) [11,19].



Scheme-I: Synthesis of N-pendent ligand L_{BX}

Ligand salt, $L_{BX}{\cdot}2HClO_4$: N-pendent ligand L_{BX} (0.418 g, 1.0 mmol) was suspended in 20 mL of ethanol in a round bottom flask and a few drops of vinyl cyanide were added. The reaction mixture was then refluxed for 30 min. Further excess of 70% $HClO_4$ (3 mmol) was added dropwise into the solution until pH was 7. The reaction mixture was heated over water bath for 10 min and kept at room temperature. After 24 h, a white crystalline product $L_{BX}{\cdot}2HClO_4$ was observed. The crystals were separated by filtration, washed with ethanol followed by ether.

Vanadium complexes

$[VO(L_{BX})(acac)](ClO_4)_2$: The complex was prepared by direct interaction of ligand salt $L_{BX}{\cdot}2HClO_4$ with vanadyl salt. In brief, a suspension of 0.619 g (1.0 mmol) of ligand $L_{BX}{\cdot}2HClO_4$ in 20 mL ethanol was added to 20 mL ethanolic solution of 0.265 g (1.0 mmol) vanadyl acetylacetonate followed by few drops of vinyl cyanide. While the mixture was refluxed for 5 h, a pale green product was resulted. After cooling at room temperature for 1 h, the pale green product, $[VO(L_{BX})(acac)](ClO_4)_2$ was filtered off, washed with ethanol followed by diethyl ether and dried in a desiccator over silica gel. Colour: Pale green, m.p.: 240 ºC; Anal. calcd. (found) %: C, 44.44 (44.40); H, 6.77 (6.73); N, 10.72 (10.64). IR (KBr, cm^{-1}): $\nu_{N\text{-}H}$, 3209s; $\nu_{C\equiv N}$, 2253vs; $\nu_{C\text{-}H}$, 2981s; ν_{CH_3}, 1394w; $\nu_{C\text{-}C}$, 1177s; ν_{ClO_4}, 1041s, 624m; $\nu_{V=O}$, 983m; $\nu_{V\text{-}N}$, 522w. Conductance ($ohm^{-1}\ cm^2\ mol^{-1}$): 160 (in DMSO); 260 (in H_2O), 320 (in acetonitrile); ^1H NMR (δ ppm): For geminal dimethyl, 1.009 (s, equatorial, 6 H), 1.278 (s, axial, 6H); For methyl on chiral carbon 1.111 (d, equatorial, 6H), 1.350 (d, axial, 6H); methyl of acetylacetonate ions, 2.677 (s, 3H), 2.808 (s, 3H), For CH_2, CH & NH, 2.509 (s), 2.251 (m), 2.951 (m), 7.296 (m), 8.318 (m), 8.564 (m). ^{13}C NMR (δ, ppm): Peripheral carbons, 15.464, 16.963, 18.180, 19.027, 19.798, 23.192, 24.488, 24.673, 25.259, 25.302, 25.631, 26.352, ring carbons, 42.262, 43.195, 43.828, 45.493, 46.343, 47.292, 48.535, 49.052, 49.593, 49.838, methylene carbons of N-cyanoethyl groups, 56.492, 58.276, 58.792, 60.145, carbons of cyano group, 120.021, 120.720. UV-visible [λ_{max} in nm (ε_{max})]: In DMSO, 268, 247; in water, 343, 268; in acetonitrile: 261. μ_{eff} (B.M.): diamagnetic.

$[VO(L_{BX})(SCN)](ClO_4)_2$: This complex was synthesized by the axial substitution reaction on $[VO(L_{BX})(acac)](ClO_4)_2$. In brief, $[VO(L_{BX})(acac)](ClO_4)_2$ (0.7829 g, 1.0 mmol) and KSCN (1.94 g, 20.0 mmol) were taken separately in 20 mL ethanol and mixed in a round bottom flask. Then few drops of acrylonitrile were also added. The mixture was refluxed for 4 h and pinkish green precipitate was observed at the bottom. After cooling, the reaction mixture was filtered off and then the pinkish green precipitate was washed with a little ethanol followed by little ether and finally stored in a desiccator over silica gel. Colour: Pinkish green. m.p.: 240 ºC: 210 ºC. Anal. calcd. (found) %: C, 40.44 (40.46); H, 6.19 (6.21); N, 13.21 (13.24); IR (KBr disc, cm^{-1}): $\nu_{N\text{-}H}$, 3093m; $\nu_{C\equiv N}$, 2247s; $\nu_{C\text{-}H}$, 2976m; ν_{CH_3}, 1387s; $\nu_{C\text{-}C}$, 1193m; ν_{ClO_4}, 1040m, 626vs, $\nu_{V=O}$, 983vs, $\nu_{V\text{-}N}$, 474s. Conductance ($ohm^{-1}\ cm^2\ mol^{-1}$): 165 (in DMSO), 340 (in acetonitrile); ^1H NMR (δ, ppm): For geminal dimethyl, 1.151 (s, equatorial, 6 H), 1.343 (s, equatorial, 6H); for methyl on chiral carbon. 938 (d, equatorial, 6H), 1.216-1.343 (d, axial, 6H); For methylene, methene and NH protons 2.312(m), 2.776(m), 6.707(m), 7.283(m) and 8.367 (m). UV-visible [λ_{max} in nm (ε_{max})]: In DMSO, 268, 247; in water, 343, 268; in acetonitrile: 261. μ_{eff} (B.M.): Diamagnetic.

$[VO(L_{BX})(NO_3)](ClO_4)_2$: $[VO(L_{BX})(acac)](ClO_4)_2$ (0.7829 g, 1.0 mmol) was refluxed with KNO_3 (0.4044 g, 4.0 mmol) in 40 mL ethanol in presence of acrylonitrile for 4 h. The mixture was filtered off after cooling to remove the residue. The filtrate was then heated on a water bath till completely dried up. The dry light green coloured product $[VO(L_{BX})(NO_3)](ClO_4)_2$ was washed with a little ethanol followed by little ether and finally stored in a desiccator over silica gel. Colour: Light green. m.p.: 260 ºC; Anal. calcd. (found) %: C, 38.61 (38.60); H, 6.17 (6.16); N, 13.14 (13.13). IR (KBr disc, cm^{-1}): $\nu_{N\text{-}H}$, 3244w; $\nu_{C\equiv N}$, 2241s; $\nu_{C\text{-}H}$, 2973w; ν_{CH_3}, 1384w; $\nu_{C\text{-}C}$, 1162m;

ν_{ClO_4}, 1046w, 625vs, $\nu_{V=O}$, 984s, ν_{V-N}, 488w. Conductance (ohm^{-1} cm^2 mol^{-1}): 181 (in DMSO), 275 (in H_2O). UV-visible [λ_{max} in nm (ε_{max})]: In DMSO, 306. μ_{eff} (B.M): Diamagnetic.

[VO(L$_{BX}$)(Cl)](ClO$_4$)$_2$: [VO(L$_{BX}$)(acac)](ClO$_4$)$_2$ (0.7829 g, 1.0 mmol) and KCl (0.8935 g, 12.0 mmol) were taken separately in 20 mL ethanol and mixed, followed by addition of few drops of acrylonitrile. The mixture was refluxed for 2 h. After cooling, the mixture was filtered off and washed with ethanol. The filtrate was then heated on a water bath till completely dried up. The dry light green coloured product [VOL$_{BX}$(Cl)](ClO$_4$)$_2$ was washed with a little ethanol followed by little ether and finally stored in a desiccator over silica gel. Colour: Light green, m.p.: 200 ºC; Anal. calcd. (found) %: C, 40.03 (40.07); H, 6.39 (6.43); N, 11.67 (11.69). IR (KBr disc, cm^{-1}): ν_{N-H}, 3018w; $\nu_{C\equiv N}$, 2241s; ν_{C-H}, 2992w; ν_{CH_3}, 1386vs; ν_{C-C}, 1180s; ν_{ClO_4}, 1103s, 624s, $\nu_{V=O}$, 987vs, ν_{V-N}, 513s. Conductance (ohm^{-1} cm^2 mol^{-1}): 151 (in DMSO), 270 (in H_2O). UV-visible [λ_{max} in nm (ε_{max})]: 327 (in DMSO); 318 (in water). μ_{eff} (B.M): Diamagnetic.

[VO(L$_{BX}$)(NO$_2$)](ClO$_4$)$_2$, [VO(L$_{BX}$)(Br)](ClO$_4$)$_2$ and [VO(L$_{BX}$)(I)](ClO$_4$)$_2$: The axial substitution complexes such as [VO(L$_{BX}$)(NO$_2$)](ClO$_4$)$_2$, [VO(L$_{BX}$)(Br)](ClO$_4$)$_2$ and [VO(L$_{BX}$)-(I)](ClO$_4$)$_2$ were synthesized by following the above procedure by using required amount of $NaNO_2$, KBr and KI respectively instead of KCl.

[VO(L$_{BX}$)(NO$_2$)](ClO$_4$)$_2$: Colour: Brown, m.p.: 210 ºC; Anal. calcd. (found) %: C, 39.46 (39.43); H, 6.30 (6.27); N, 13.43 (13.42). IR (KBr disc, cm^{-1}): ν_{N-H}, 3279w; $\nu_{C\equiv N}$, 2246s; ν_{C-H}, 2974m; ν_{CH_3}, 1383s; ν_{C-C}, 1174w; ν_{ClO_4}, 1088w, 624vs, $\nu_{V=O}$, 979s, ν_{V-N}, 492w. Conductance (ohm^{-1} cm^2 mol^{-1}): 199 (in DMSO). UV-visible [λ_{max} in nm (ε_{max})]: In DMSO, 363. μ_{eff} (B.M): Diamagnetic.

[VO(L$_{BX}$)(Br)](ClO$_4$)$_2$: Colour: Deep green, m.p.: 220 ºC; Anal. calcd. (found) %: C, 37.70 (37.66); H, 6.02 (6.00); N, 10.99 (10.95). IR (KBr disc, cm^{-1}): ν_{N-H}, 3181w; $\nu_{C\equiv N}$, 2242m; ν_{C-H}, 2976w; ν_{CH_3}, 1383m; ν_{C-C}, 1177m; ν_{ClO_4}, 1046m, 626s, $\nu_{V=O}$, 983s, ν_{V-N}, 498w. Conductance (ohm^{-1} cm^2 mol^{-1}): 196 (in DMSO), 287 (in H_2O). UV-visible [λ_{max} in nm (ε_{max})]: 246 (in DMSO); 325 (in water). μ_{eff} (B.M): Diamagnetic.

[VO(L$_{BX}$)(I)](ClO$_4$)$_2$: Colour: Yellow, m.p.: 230 ºC; Anal. calcd. (found) %: C, 35.52 (35.50); H, 5.67 (5.65); N, 10.36 (10.35). IR (KBr disc, cm^{-1}): ν_{N-H}, 3151w; $\nu_{C\equiv N}$, 2246s; ν_{C-H}, 2972w; ν_{CH_3}, 1382vs; ν_{C-C}, 1175m; ν_{ClO_4}, 1045m, 626s, $\nu_{V=O}$, 976m, ν_{V-N}, 459m. Conductance (ohm^{-1} cm^2 mol^{-1}): 170 (in DMSO), 252 (in H_2O), 330 (in acetonitrile). UV-visible [λ_{max} in nm (ε_{max})]: 367 (in DMSO), 296; 297 (in water); 359, 291 (in acetonitrile). μ_{eff} (B.M): Diamagnetic.

Antibacterial studies: Antibacterial activities of the N-pendent derivative L$_{BX}$ and its vanadate(V) complexes were investigated against selected bacteria as per standard methods described in our published report [11].

RESULTS AND DISCUSSION

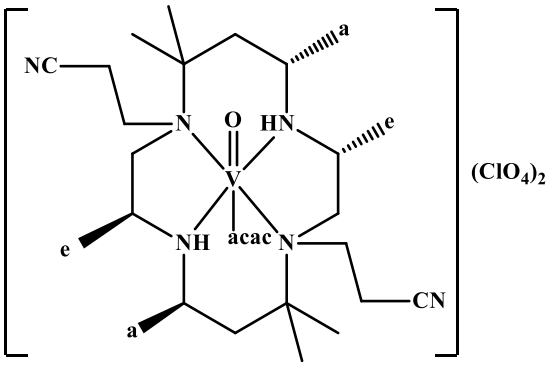
Isomeric ligand L$_B$ [18] and its N-pendent derivative L$_{BX}$ [11] (**Scheme-I**) were synthesized and characterized according to our previous study. The molecular structure of N-pendent ligand L$_{BX}$ was also confirmed as per earlier report [12].

[VO(L$_{BX}$)(acac)](ClO$_4$)$_2$: The ligand salt L$_{BX}$·2HClO$_4$ produced a pale green solid product [VO(L$_{BX}$)(acac)](ClO$_4$)$_2$ by the reaction with oxovanadyl(IV) acetylacetonate in ethanol where vanadium was in its +V oxidation state, though in starting salt vanadium was in its +IV oxidation state. It is to be noted that the ligand L$_{BX}$ does not undergo complexation with vanadyl salt in its free state other than salt form. The IR spectrum of the complex exhibits ν_{N-H}, ν_{C-H}, ν_{CH_3}, ν_{C-C} and $\nu_{V=O}$ stretching bands at 3209 cm^{-1}, 2981 cm^{-1}, 1394 cm^{-1}, 1177 cm^{-1} and 983 cm^{-1} respectively, which are at the expected regions. Moreover, the complex exhibits additional stretching frequencies at 1041 cm^{-1} and 624 cm^{-1} which demonstrates the presence of ClO_4 group in ionic state. Appearance of the band at 2253 cm^{-1} is an indication of the presence of C≡N group of cyanoethyl group [20]. The molar conductivity value of the complex, 160 ohm^{-1} cm^2 mol^{-1} in DMSO and 260 ohm^{-1} cm^2 mol^{-1} in water indicates that the complex is 1:2 electrolyte as expected for the assigned formula [21]. The colour remained intact in these solvents. However, the molar conductance value of 320 ohm^{-1} cm^2 mol^{-1} in acetonitrile of the complex corresponding to 1:3 electrolytes explores that CH_3CN might force acac$^-$ ion out of coordination sphere as per eqn. 1:

$$[VO(L_{BX})(acac)](ClO_4)_2 \xrightarrow{CH_3CN} [VO(L_{BX})(CH_3CN)](acac)(ClO_4)_2 \quad (1)$$

The electronic spectrum of acetylacetonato oxovanadate(V) diperchlorate complex did not display any *d-d* band as expected for d^0 system. However, the bands at 247-343 nm can be assigned to charge transfer bands. ^{1}H NMR spectrum of [VO(L$_{BX}$)(acac)](ClO$_4$)$_2$ shows two singlets at 1.009 ppm and 1.278 ppm each corresponding to 6H and are assigned to equatorial and axial components of two *gem*-dimethyl pairs. The spectrum further exhibits two doublets at 1.111 ppm and 1.350 ppm each corresponding to 6H, which may arise out of two equatorial and two axial methyl groups respectively which are pairwise equivalent. So, [VO(L$_{BX}$)(acac)](ClO$_4$)$_2$ should therefore have two equatorially oriented methyl groups and two axially oriented chiral methyl groups. However, appearance of two singlets at 2.677 and 2.208 ppm each corresponding to 3H and one singlet at 2.509 ppm corresponding to 1H can be accounted for two methyl protons and one CH proton of one acetylacetonate ion respectively. The spectrum further exhibits some downfield multiplets at 2.251, 2.951, 7.296, 8.318 and 8.564 ppm *etc.* due to CH_2, CH and NH protons. So, a diequatorial-diaxial assignment is made for this complex as its corresponding ligand L$_{BX}$. The ^{13}C NMR spectrum of [VO(L$_{BX}$)(acac)](ClO$_4$)$_2$ displays 24 signals, which is just the same as the total numbers of the carbons. Though the symmetrical diaxial-diequatorial arrangement has already been assigned on the basis of its ^{1}H NMR spectrum, but appearance of 24 signals for 24 carbons can be accounted for distortion in the molecule. The first eight peaks at 15-26 ppm can be assigned to the eight carbons of peripheral methyl groups. Next 10 peaks at 42-50 ppm are due to the ring carbons C_2, C_3, C_5, C_6 C_7, C_9, C_{10}, C_{12}, C_{13} and C_{14}. Another four peaks at 56-61 ppm can be accounted for the four-methylene carbons of cyanoethyl branches. However, the peak at 120.021 ppm

and 120.720 ppm can be assigned to cyano carbons which are expected to be highly deshielded. Complex $[VO(L_{BX})(acac)](ClO_4)_2$ was found to be diamagnetic as expected for octahedral vanadate(V) complexes having d^0 system. Thus, based on the above evidences, the structure of $[VO(L_{BX})(acac)](ClO_4)_2$ can be assigned to as follows:



$[VO(L_{BX})(acac)](ClO_4)_2$

Axial substitution products of $[VO(L_{BX})(acac)](ClO_4)_2$: The axial substitution products $[VO(L_{BX})(NCS)](ClO_4)_2$ $[VO(L_{BX})(NO_3)](ClO_4)_2$ $[VO(L_{BX})(Cl)](ClO_4)_2$, $[VO(L_{BX})(NO_2)](ClO_4)_2$; $[VO(L_{BX})(Br)](ClO_4)_2$ and $[VO(L_{BX})(I)](ClO_4)_2$ were synthesized by the interaction of $[VO(L_{BX})(acac)](ClO_4)_2$ with KSCN, KNO_3, $NaNO_2$, KCl, KBr and KI respectively. Infrared spectra of these complexes show ν_{N-H}, ν_{C-H}, ν_{CH_3}, ν_{C-C}, $\nu_{V=O}$ and ν_{ClO_4} stretching bands at the expected regions. These complexes therefore exhibit $\nu_{C\equiv N}$ band at 2250-2247 cm^{-1} for -C≡N moiety of cyano-ethyl group. Again in case of $[VO(L_{BX})(NCS)](ClO_4)_2$ appearance of sharp ν_{CN} band at 2045 cm^{-1} is a good indication of N-bonded thiocyanate group [22]. The concerned complex displays ν_{CS} band at 766 cm^{-1} and $\delta_{(NCS)}$ band at 504 cm^{-1} which do not correspond to the ligand in this region and are therefore assigned for fully N-bonded thiocyanate group [22,23]. Therefore, this complex can be identified as isothiocyanato complex. However, the complex $[VO(L_{BX})(NO_2)](ClO_4)_2$ exhibits the $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$ bands at 1458 cm^{-1} and 1383 cm^{-1} respectively indicating that the complex to be a N- bonded nitro complex [24]. Appearance of band at 827 cm^{-1} can be attributed to δ_{NO_2} frequency. In addition, $[VO(L_{BX})(NO_3)](ClO_4)_2$ reveals a band at 1384 cm^{-1} which demonstrates the presence of ν_{NO_3} band and splitting of this band into two bands at 1458 and 1334 cm^{-1} with a separation of 124 cm^{-1} of this complex, explores the unidentate mode of coordination of NO_3^- ion [25]. Since IR spectra of these halo complexes, $[VO(L_{BX})(X)](ClO_4)_2$ (X= Cl/Br/I^-) could not be run below 400 cm^{-1} so the IR stretch due to $\nu_{M-Cl/Br/I}$ which is supposed to appear around 260 cm^{-1}, that could not be detected. Absence of ν_{acac} bands in the region 1517-1500 cm^{-1} demonstrate that the acac group is substituted completely by Cl/Br/I^- group.

Molar conductivity values, 151-199 ohm^{-1} cm^2 mol^{-1} in DMSO solution of these complexes indicate that the complex to be of 1:2 electrolyte as expected for the formulae assigned. The molar conductivity values 330-340 ohm^{-1} cm^2 mol^{-1} in acetonitrile of $[VO(L_{BX})(NCS)](ClO_4)_2$ and $[VO(L_{BX})(I)](ClO_4)_2$ demonstrate that these complexes are 1:3 electrolytes which explores that CH_3CN might force NCS^-/I ion out of coordination sphere as per the following equations:

$$[VO(L_{BX})(NCS)](ClO_4)_2 \xrightarrow{CH_3CN} [VO(L_{BX})(CH_3CN)](SCN)(ClO_4)_2$$

$$[VO(L_{BX})(I)](ClO_4)_2 \xrightarrow{CH_3CN} [VO(L_{BX})(CH_3CN)](I)(ClO_4)_2$$

Moreover, the molar conductivity values 270-287 ohm^{-1} cm^2 mol^{-1} in water of $[VO(L_{BX})(Br)](ClO_4)_2$ and $[VO(L_{BX})(I)](ClO_4)_2$ also correspond to 1:3 electrolyte which explores that H_2O might force Br^-/I^- ion out of coordination sphere as per the following equation:

$$[VO(L_{BX})(Br/I)](ClO_4)_2 \xrightarrow{H_2O} [VO(L_{BX})(H_2O](Br/I)(ClO_4)_2$$

The vanadate(V) complexes are diamagnetic as expected for d^0 configuration. Thus, these diamagnetic vanadate(V) complexes do not show any *d-d* bands and their spectra are dominated only by charge transfer bands. Such as, in these complexes the charge transfer bands are observed at 246-367 nm in DMSO, 297-325 nm in water and 291-359 nm in acetonitrile [21].

The ^{1}H NMR spectrum of $[VO(L_{BX})(NCS)](ClO_4)_2$ displays one doublet at 0.938 ppm and an overlapped signal at 1.151-1.343 ppm with an integration of 18 protons. The doublet at 0.938 ppm corresponding to six protons can be assigned to two equatorial methyl protons on two chiral carbons, while the overlapped signal of 18H at 1.151-1.343 ppm can be resolved into two singlets at 1.151 and 1.343 ppm each of 6H and a doublet of 6H at about 1.216-1.343 ppm. The singlets at 1.151 and 1.343 ppm can be accounted for equatorial and axial components of *gem*-dimethyl groups whereas the overlapped doublet of 6H can be assigned to two axially oriented methyl protons on two chiral carbons. Symmetrically, this requires the four methyls on four chiral carbons to be pairwise equivalent. The downfield multiplets at 2.312, 2.776, 6.707, 7.283 and 8.367 ppm can be accounted for methylene, methene and NH protons. Thus, a diequatorial-diaxial orientation of the chiral methyls can be assigned as assigned for its parent complex $[VO(L_{BX})(acac)](ClO_4)_2$. This gives evidence that the axial substitution takes place without change of conformation and configuration of the ligand of the mother complex [11]. So based on these evidences, the structures, Str. 2 to Str. 7 (Fig. 1) can be assigned for the axial substitution products of $[VO(L_{BX})(acac)](ClO_4)_2$.

Antibacterial activities: The antibacterial activities of N-pendent ligand L_{BX} and its vanadate(v) complexes were carried out against some selected Gram-positive and Gram-negative bacteria. Table-1 shows that the ligands are ineffective in all cases as similar to previous study [11], but most of the vanadate(V) complexes of L_{BX} exhibit remarkable antibacterial activity except few of them with no activity against some bacteria such as $[VO(L_{BX})(acac)](ClO_4)_2$ against *E. coli and S. typhi*; $[VO(L_{BX})(Cl)](ClO_4)_2$ against *S. aureus* and *M. luteus etc*. while compared with positive control. However, $[VO(L_{BX})(Cl)](ClO_4)_2$ against *B. cereus* and $[VO(L_{BX})(NCS)](ClO_4)_2$ against *M. luteus* & *S. typhi* and $[VO(L_{BX})-(I)]$-

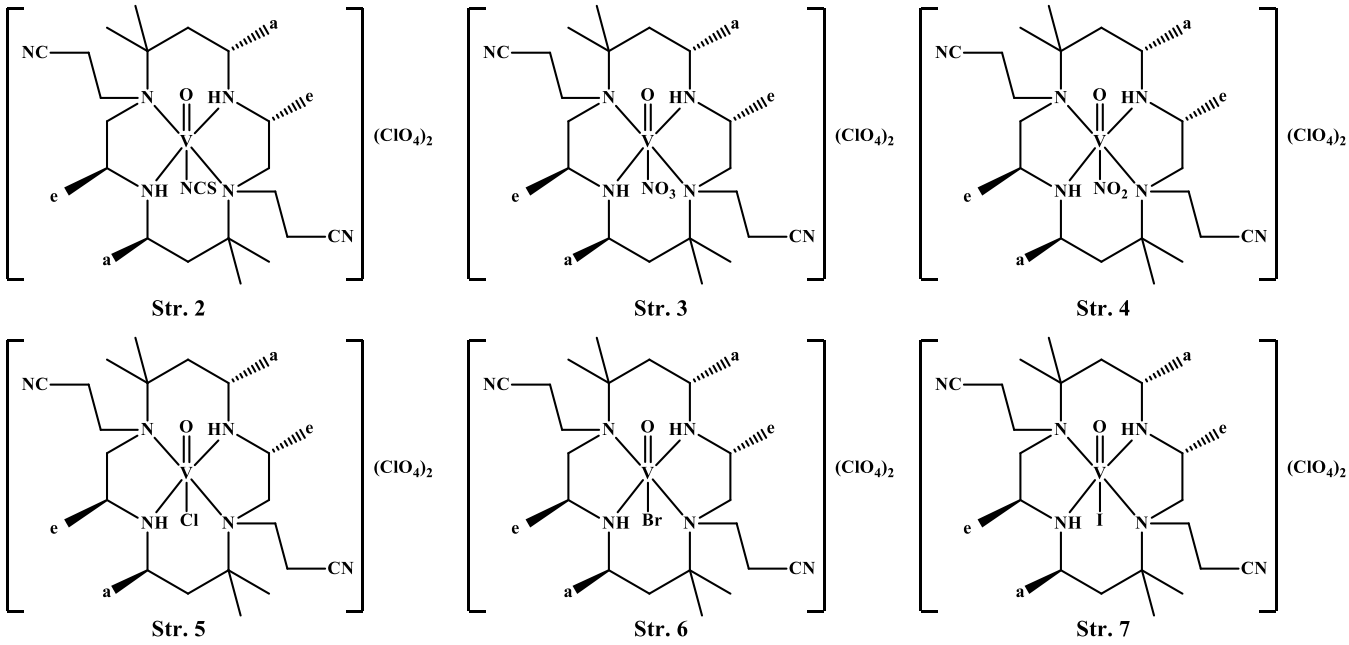


Fig. 1. Axial substitution products of $[VO(L_{BX})(acac)](ClO_4)_2$

TABLE-1
ANTIBACTERIAL ACTIVITIES OF VANADATE(V) COMPLEXES

Sample No.	Compounds	Inhibition zones in diameter (mm)				
		Gram-positive bacteria			Gram-negative bacteria	
		B. cereus	*S. aureus*	*M. luteus*	*E. coli*	*S. typhi*
Ligand	L_{BX}	0	0	0	0	0
1	$[VO(L_{BX})(acac)](ClO_4)_2$	17	8	14	0	0
2	$[VO(L_{BX})(NCS)](ClO_4)_2$	0	6	24	14	29
3	$[VO(L_{BX})(Cl)](ClO_4)_2$	21	0	0	6	16
4	$[VO(L_{BX})(Br)](ClO_4)_2$	15	7	0	13	14
5	$[VO(L_{BX})(I)](ClO_4)_2$	24	18	14	0	0
6	$[VO(L_{BX})(NO_2)](ClO_4)_2$	0	0	9	20	0
7	$[VO(L_{BX})(NO_3)](ClO_4)_2$	0	17	0	0	12
PC	Chloramphenicol	25	25	26	24	30
NC	DMSO	0	0	0	0	0

$(ClO_4)_2$ *B. cereus* against exhibit mentionable antibacterial activities. As seen from the results (Table-1), the synthesized complexes show different activities against different bacteria. However, no definite trend can be made at this stage. So, more studies are warranted. It is observed that antibacterial activities of solvent DMSO as negative control, chloramphenicol (standard antibiotic) as positive control and non-coordinated metal salt were also done for the comparison. The result reveals that DMSO (negative control) was inactive against all bacteria, whereas chloramphenicol (positive control) were highly active against all bacteria. It has been observed that the metal salt shows some activities against all bacteria, but the activities shown by the complexes are not due to the metal ions. As the complexes are very much stable, there is no possibility of dissociation of complexes to release metal ions [26]. As a whole, the antibacterial activity patterns suggest that the nature of axial ligands modulates the biological interactions of vanadium complexes. Further investigation into these interactions and their mechanisms is warranted to optimize their potential applications.

Conclusion

This study reveals that the N-pendent ligand L_{BX} undergoes facile complexation when reacts with vanadyl(IV) acetylacetonate salt to produce octahedral complex, $[VO(L_{BX})(acac)](ClO_4)_2$. In this complex, vanadium is in +5 oxidation state. Though, in our previous studies with different ligands except one other N-pendent ligand (which gave vanadate(V) complex) vanadyl(IV) complexes have been synthesized with the same salt and same procedure, but in this case, vanadate(V) complexes were synthesized in the open air which gives inference that though tetraaza macrocyclic ligands without N-pendent groups afford vanadyl(IV) complexes with vanadyl(IV) salts, but N-pendent ligands produce the vanadate(V) complexes with the same salt and same experimental condition. Moreover acetylacetonatooxovanadate(V) diperchlorate complex, $[VO(L_{BX})(acac)](ClO_4)_2$ of the cyanoethyl derivative ligand, L_{BX} undergoes axial substitution reactions with NCS^-, I^-, Br^-, Cl^-, NO_3^- and NO_2^- in the ratio of 1:4-1:24 to form octahedral monoisothiocyanato, monoiodido, monobromido, monochlorido,

mononitro, mononitrato derivatives. The stereochemistry of the synthesized derivatives was determined on ^{1}H NMR spectra as well as on the basis that axial substitution products retain the same stereochemistry (*i.e.* axial and equatorial conformation of the CH_3 groups on the chiral carbons of the ligands of the mother complex remains the same in their derivatives). Another important observation is that although only one axial ligand is ultimately incorporated in these reactions, the reactions do not proceed unless an excess typically 4 to 24 equivalents of the axial ligand is present. This study demonstrates the potential of vanadate(V) complexes with macrocyclic ligands for antimicrobial applications. The findings highlight the influence of axial ligands on biological activity and open avenues for further research into their catalytic and therapeutic properties.

ACKNOWLEDGEMENTS

This work was supported by grants from Environmental Radioactivity Research Network Center, Japan (ERAN: I-23-17) awarded by Dr. Foni Bushon Biswas.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. T. Aiyelabola, J. Jordaan, D. Otto and E. Akinkunmi, *Adv. Bio. Chem.*, **11**, 79 (2021); https://doi.org/10.4236/abc.2021.113007
2. Subhash, A. Chaudhary and Mamta, *Chem. Pap*., **77**, 5059 (2023); https://doi.org/10.1007/s11696-023-02843-y
3. M. Tosun, A. Uysal, A.N. Kursunlu and E Guler, *Tetrahedron*, **151**, 133812 (2024); https://doi.org/10.1016/j.tet.2023.133812
4. Subhash, A. Chaudhary and Jyoti, *J. Chem. Sci.*, **134**, 113 (2022); https://doi.org/10.1007/s12039-022-02109-2
5. F. Liu and X. Min, *Tetrahedron Lett.*, **169**, 155760 (2025); https://doi.org/10.1016/j.tetlet.2025.155760
6. M. Sutradhar, L.M.D.R.S. Martins, M.F.C. Guedes da Silva and A.J.L. Pombeiro, *Coord. Chem. Rev*., **301-302**, 200 (2015); https://doi.org/10.1016/j.ccr.2015.01.020
7. R.R. Langeslay, D.M. Kaphan, C.L. Marshall, P.C. Stair, A.P. Sattelberger and M. Delferro, *Chem. Rev*., **119**, 2128 (2019); https://doi.org/10.1021/acs.chemrev.8b00245
8. S.G. Shankarwar, B.B. Nagolkar, V.A. Shelke and T.K. Chondhekar, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **145**, 188 (2015); https://doi.org/10.1016/j.saa.2015.02.006
9. N. Fahmi, M. Upadhyay, N. Sharma and S. Belwal, *J. Chem. Res.*, **44**, 336 (2020); https://doi.org/10.1177/1747519819893885
10. K.R. Chaudhari, A. Kunwar, N. Bhuvanesh and S. Dey, *New J. Chem.*, **44**, 7329 (2020); https://doi.org/10.1039/C9NJ06052A
11. M.S. Alam, S. Rabi, M.M. Rahman, A. Baidya, M. Debi and T.G. Roy, *J. Chem. Sci.*, **130**, 35 (2018); https://doi.org/10.1007/s12039-018-1438-z
12. T.G. Roy, S.K.S. Hazari, B.K. Dey, H.A. Miah and E.R.T. Tiekink, *Acta Crystallogr. Sect. E Struct. Rep. Online*, **57**, 524 (2001); https://doi.org/10.1107/S160053680100784X
13. C. Lap-Yan, E.C. Constable, M.S. Khan and J. Lewis, *Inorg. Chim. Acta*, **185**, 93 (1991); https://doi.org/10.1016/S0020-1693(00)81681-3
14. V. Pawar, S. Joshi and V. Uma, *Biokemistri*, **23**, 21 (2011).
15. S. Singh, H.S. Yadav, A.K. Yadava and D.P. Rao, *J. Chem.*, **2013**, 947325 (2013); https://doi.org/10.1155/2013/947325
16. S.N. Thakur, K.S. Yadav, N.P. Singh and H.S. Yadav, *J. Iran. Chem. Soc.*, **5**, 328 (2008); https://doi.org/10.1007/BF03246126
17. N. Raman, J.D. Raja and A. Sakthivel, *J. Chil. Chem. Soc.*, **53**, 1568 (2008).
18. N.F. Curtis, S.A. Swann, T.N. Waters and I.E. Maxwell, *J. Am. Chem. Soc.*, **91**, 4588 (1969); https://doi.org/10.1021/ja01044a068
19. R. Bembi, S. M. Sondhi, A. K. Singh, A. K. Jhanji, T. G. Roy, J.W. Lown and R.G. Ball, *Bull. Chem. Soc. Jpn.*, **62**, 3701 (1989); https://doi.org/10.1246/bcsj.62.3701
20. B.M. Sarhan, R.M. Rumez and H.A. Hassan, *J. Pure Appl. Sci.*, **26**, 178 (2013).
21. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971); https://doi.org/10.1016/S0010-8545(00)80009-0
22. M.E. Farago and J.M. James, *Inorg. Chem.*, **4**, 1706 (1965); https://doi.org/10.1021/ic50034a007
23. A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965); https://doi.org/10.1021/ic50029a007
24. A.V. Iogansen and G.D. Litovchenko, *J. Appl. Spectrosc.*, **2**, 159 (1965); https://doi.org/10.1007/BF00655122
25. A.B.P. Lever, E. Mantovani and B.S. Ramaswamy, *Can. J. Chem.*, **49**, 1957 (1971); https://doi.org/10.1139/v71-315
26. F.B. Biswas, S. Saha and M.K. Ali, *Asian Pac. J. Trop. Biomed.*, **4(Suppl. 2)**, 792 (2014); https://doi.org/10.12980/APJTB.4.2014C1298